Studies on Halogenated Methane Sulphonates and Polysulphonated Methane Derivatives

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Für meine Familie

Don't judge each day by the harvest you reap but by the seeds that you plant.

Robert Louis Stevenson

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Abstract

Derivatives of methanesulphonic acid are assembled by formal substitution of the hydrogen atoms at the methyl function on CH₃SO₃H. Substitution of H with halogens such as Cl and Br deliver the halogenated methanesulphonic acids Cl₃CSO₃H and Br₃CSO₃H. Trichloromethanesulphonate "trichlate" and tribromomethanesulphonate "tribrate" salts are characterised by X-ray diffraction for structure determination. Experimentally trichlate compounds are obtained in a three-step reaction mechanism starting from relatively cheap starting materials CS2 and chlorine gas. Comparable to triflate salts, the trichlate compounds are prone to build layered structures due to the amphiphilic character of the anion. Additionally, the crystal structures frequently entail water, which has a high share in the saturation of the coordination sphere of the respective cation. Thus, the weak coordinating character of [Cl₃CSO₃]⁻ results in the structures $[Fe(DMSO)_6][Cl_3CSO_3]_3$ and $[Co(H_2O)_6][Cl_3CSO_3]_2$, where the coordination sphere around the cation is entirely built by solvent molecules. The trichlate anion is stable up to temperatures of roughly 600 K. Bromination reaction of aromatic methanesulphonates, such as phenyl methanesulphonate with a freshly prepared hypobromite solution followed by cleavage of the aromatic ring generates tribrate compounds. Crystal structures of lithium and potassium tribrates show similar characteristics as their smaller siblings. The tribrate anion has a staggered conformation, crystal structures contain layers and crystal water, that has a high impact on the coordination sphere of the respective cation.

Formal substitution of H with SO₃H unities at the methyl group in CH₃SO₃H delivers polysulphonic acids. Analysis of solid state structures of lithium, caesium and potassium methanedisulphonate show an isotypy to lithium and potassium disulphate. Salts displaying the $[CH(SO_3)_3]^{3-}$ anion show a diversity in their crystal structures, that does not reveal clear trends or isostructural relations.

List of Abbreviations

MSA	Methanesulphonic Acid
MDA	Methanedisulphonic Acid
MTA	Methanetrisulphonic Acid
OTf	Triflate/triflic
W	weak
VW	very weak
sh	shoulder
br	broad
S	strong
VS	very strong
m	medium
DFT	Density Functional Theory
DMF	<i>N</i> , <i>N</i> -Dimethylformamide
DMSO	Dimethylsulfoxide
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
TGA	Thermogravimetric Analysis
TG	Thermogravimetry
IR	Infrared
NMR	Nuclear Magnetic Resonance
XRD	X-ray Diffraction
OHCD	Optical Heating Crystallisation Device
LASER	Light Amplification by Stimulated Emission of Radiation
PXRD	Powder X-ray Diffraction
HT	High Temperature
LT	Low Temperature

Motivation and Experimental Aim

Experimental aim of this work is the preparation and characterisation of derivatives of methanesulphonic acid (MSA). Special focus is laid on the structural determination of newly synthesised compounds. Targeted are polysulphonate derivatives of MSA and trihalomethanesulphonates. Therefore, new assemblies are created by formal substitution at the carbon atom of the MSA backbone (Figure 1). Since trifluoromethanesulphonates are common entities, this work focuses on the preparation and characterisation of its larger siblings trichloro- and tribromomethanesulphonates.



Figure 1: Experimental Aim: Sulphonation of the carbon atom leading to polysulphonic acid derivatives of methanesulphonic acid and halogenation of the methyl function to obtain $[X_3CSO_3]^-$ compounds.

1. State of Knowledge

1.1. Methanesulphonic Acid (MSA)

Methanesulphonic acid (MSA) is the smallest combination of an alkyl side chain with a sulphonic acid functional group. With a pKa value of -1.9, the clear, colourless acid classifies as a strong acid and thus almost completely protolyses in 0.1 M aqueous solutions.^[1] MSA has a low melting point around 293 K and thus is liquid at room temperature. Comparable to organic sulphonic acids with longer alkyl chains, it has a high boiling point and cannot be distilled at ambient pressure without decomposition.^[2] Its application field is wide due to the numerous positive physical and chemical properties. Main advantages of MSA are the high saturation metal salt solubility, high conductivity and low relative toxicity.^[3] At 0.1 N MSA has an electrolyte conductivity of $372.74 \text{ S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$.^[4] While other acid electrolytes might be superior in their conductivity, another advantage of MSA lies in the relative high stability of metal solutions regarding the oxidation state of metal cations with accessible higher valency. In contrast to well established compounds such as sulphuric or nitric acid, MSA is less oxidising. Today, MSA is a commercial standard electrolyte for electroplating and especially gaining esteem in the electroplating of Sn/Pb solder and lead surfaces in general, where it is widely replacing fluoroboric acid (HBF₄).^[4] Furthermore, MSA is often referred to as a green chemical, as it is considered to be readily biodegradable as a part of the sulphur cycle.^[5] When protolysed, the anion exhibits a negative charge that is delocalised around the oxygen atoms of the SO₃-unit. This delocalisation stabilises the anion and thus contributes to the strong acidity of its acid. Furthermore, it manifests the classification as a relatively soft ligand with regard to HSAB principle. The methanesulphonate anion has therefore weakly coordinating abilities, which is applied in for instance catalysis.^[6]

MSA was first synthesised by *Proell* in the 1940's via a NO_x catalysed air oxidation of methyl mercaptan.^[7] *Proell* also patented several applications of MSA, clearly anticipating its potential for the usage as catalyst and as electroplating electrolyte.^[2,8,9]

$$2 CH_3 SH + 3 O_2 \xrightarrow{NO_x} 2 CH_3 SO_3 H$$
 Equation 1

While the concept of air oxidation is advantageous with regard to cheap starting materials, it is lacking in convenience and potentially hazardous as it can lead to explosions. In 1967,

the *Pennwalt Corporation* first used a chlorine oxidation in aqueous emulsion of an alkyl mercaptan or a dialkyl disulphide:

RSH +
$$3 \text{ Cl}_2$$
 + $3 \text{ H}_2\text{O} \xrightarrow{\text{conc. HCl}} \text{RSO}_3\text{H}$ + $6 \text{ HCl} \qquad Equation 2$
RSSR + 5 Cl_2 + $6 \text{ H}_2\text{O} \xrightarrow{\text{conc. HCl}} 2 \text{ RSO}_3\text{H}$ + $10 \text{ HCl} \qquad Equation 3$

RSSR' + 5 Cl₂ + 6 H₂O
$$\xrightarrow{\text{conc. HCl}}$$
 RSO₃H + R'SO₃H + 10 HCl Equation 4

This method, applying chlorine as oxidising agent is still used in the industry, predominantly by *Arkema SA* (France), one of the two major distributor of MSA.^[10] Contrary, *BASF SE* (Germany), the second global player on the MSA market, practices a variation of the oxygen oxidation process as first described by *Proell*. Oxidation with chlorine leads to a high emission of hydrochloric acid as unwanted by-product. Therefore, BASF developed a synthesis, where methanol, hydrogen and sulphur are introduced as starting materials, converting to dimethyldisulphide, followed by the catalytic air oxidation.^[11]

$$2 CH_3OH + H_2 + 2 S \longrightarrow S_2(CH_3)_2 + 2 H_2O \qquad Equation 5$$

$$S_2(CH_3)_2 + 5/2 O_2 + H_2O \longrightarrow 2 CH_3SO_3H \qquad Equation 6$$

While these two synthetic routes are applied on a wide scale process, meeting economic needs, the most efficient and elegant synthesis of MSA would be an adoption of the synthesis of sulphuric acid, starting from methane and sulphur trioxide. In fact, this idea has been tested and was first published by *Sen et al.* in 1996 using fuming sulphuric acid (oleum) as SO₃ source and potassium peroxodisulphate as initiator in a radical-initiated reaction.^[12] This method was further improved by *Bell* and co-workers in 2001.^[13,14] Here, $K_2S_2O_8$ is the radical initiator, decomposing to two potassium sulphate radicals upon treatment at elevated temperature. The initiation process is complete, when the radical is transferred to the methyl group, producing potassium hydrogen sulphate as by-product. Following is the chain reaction in which the methyl radical reacts with SO₃ to build a methanesulphonyl radical, which delivers the desired MSA after the reaction with another methane unit:

 $K_{2}S_{2}O_{8} \longrightarrow 2 KSO_{4}^{\bullet} \qquad Equation 7$ $KSO_{4}^{\bullet} + CH_{4} \longrightarrow KHSO_{4} + CH_{3}^{\bullet} \qquad Equation 8$

$$CH_3^{\bullet} + SO_3 \longrightarrow CH_3SO_3^{\bullet}$$
 Equation 9
 $CH_3SO_3^{\bullet} + CH_4 \longrightarrow CH_3SO_3H + CH_3^{\bullet}$ Equation 10

An industrial application of this synthetic route was adapted by *Grillo-Werke* AG (Germany) in 2016 and advertised as the *Grillo-Methane Sulphonation* (GMS) process.^[10,11,15] In this case, the electrophilic initiator is a sulphonyl peroxide derivative.

With vastly extending usage of MSA, an increasing production in the future is expected. Already the approximate yearly global production exceeds 50,000 t and thus underlines the importance of this chemical for appliances ranging from catalysis over pharmaceutical to electrochemical functions.^[4,16–19]

The reaction of MSA with metals leads to highly soluble metal sulphonates which is one major advantage opposed to, for instance, their sulphates. A wide range of compounds with a methanesulphonate unit have been structurally elucidated by X-ray diffraction.^{[20–} ^{26]} Upon crystallization from aqueous solutions, oftentimes water implements in the crystal structure. Crystal structures [Al(H₂O)₆][H₃CSO₃]₃, Mg[H₃CSO₃]₂ · 12 H₂O, and $Zn[H_3CSO_3] \cdot 12 H_2O$ are examples, where the cation is completely saturated with water molecules and the methanesulphonate anion merely functions as counter charge.^[25–27] Na[H₃CSO₃] and Cs[H₃CSO₃] are examples for solvent-free crystal structures, the latter being the very first crystal structure published in 1966.^[28] Exemplary, the build-up of Na[H₃CSO₃] will be discussed in the following. As represented in Figure 2 (p. 5), the methanesulphonate anion has a staggered conformation with all substituents to the C-S centre fragment aiming at minimal sterical hindrance. This leads to torsion angles (O-S-C-H) close to 60°. The sodium salt crystallises in the orthorhombic space group *Pbma* (No. 57) with Z = 20. Cell parameters are a = 1707.13(6) pm, b = 2202.17(6) pm, c = 560.58(3) pm and V = 2107.4(2) Å³. The asymmetric unit consists of three unique methanesulphonate anions and three sodium cations. One sodium cation and one anion have special site symmetry, as they are located on a twofold rotational axis (Na3) or a mirror plane (Wyckoff description 4d, 4c). A look at the cross section of the crystal structure along the (0 0 1) plane reveals a layered packing of anions and cations. Atoms positioned on special sites of the space group are recognised in this overview. One sodium cation occupies the 4c position on the edges of the unit cell, as well as two positions along the middle. The three crystallographically distinguishable anions are oriented differently. Two anions are stacked almost parallel, while one anion is oriented with the C-S bond normal to the *b*-axis. The atoms C3, S3, O8 and H7, belonging to this anion, are occupying the Wyckoff position *4d* (mirror plane). Bond lengths within the three unique anions are narrowly distributed, S-O distances range from 144.60(1) pm (S3-O8) to 146.16(0) pm (S2-O4), C-S bonds from 175.2(0) pm (C1-S1) to 175.57(1) pm (C3-S3). Bond lengths of the methyl group show the largest deviations, which can be attributed to the method of X-ray diffraction and the low electron density within the C-H bonds. O-S-O bond angles range from 110.302(1)° to 113.140(1)°, O-S-C angles from 105.890(1)° to 107.915(2)°.



Figure 2: Crystal structure of Na[H₃CSO₃]; Anion in Newman-projection, asymmetric unit and cross-section of the crystal structure.^[23]

The coordination number of Na1 and Na3 is six and the resulting polyhedrons are distorted octahedrons (Figure 3, p. 6). Na2 is coordinated by seven oxygen atoms. Two anions (around S1 and S2) have a higher share in the coordination sphere of Na as opposed to the anion around S3. Comparing the shortest and longest S-O bond lengths to the coordination spheres of Na1, Na2 and Na3, a correlation becomes evident. O8 does not coordinate, thus the S3-O8 bond is not weakened by further coordination, whilst O4 shows high participation in the coordination sphere of Na1, Na2 and Na3.



Figure 3: Coordination polyhedrons of Na1, Na2 and Na3 in Na[H₃CSO₃].

1.2. Halogenated Methanesulphonic Acids

As mentioned above, MSA has a wide range of possible applications and its consumer demand is in a steady upwards trend. It is only natural, that chemists focus on a further modification of MSA to gain substances with new or strengthened positive properties. One way to modify MSA is by substitution of hydrogen with a halogen. Following our chemical intuition, these substances should have a higher acidity and exhibit a weaker coordination ability. The following chapters focus on X_3CSO_3 -compounds.

Triflic Acid and Triflate Salts

Trifluoromethanesulphonic acid, also referred to as triflic acid, was first synthesised in 1954 by *Haszeldine* and *Kidd* from bis(trifluoromethylthio)mercury, $(F_3CS)_2Hg$, by oxidation with aqueous hydrogen peroxide.^[29] To obtain $(F_3CS)_2Hg$, irradiation of bistrifluoromethyl disulphide (CF₃SSCF₃) in the presence of mercury is required. A reaction scheme, starting from a reaction of CS₂ with IF₅ or CF₃I and sulphur to yield CF₃SSCF₃ is depicted below:



The synthesis step in Equation 11 (p. 6) has later been modified to a direct synthesis of $(F_3CS)_2Hg$ from CS_2 and HgF_2 with HgS as by-product.^[30] Alternate routes include the formation of CF_3SCl from F_3CSSCF_3 with chlorine. The former is then oxidised to F_3CSO_2Cl . This oxidation from CF_3SCl to the corresponding F_3CSO_2Cl , followed by treatment of alkali aqueous solutions is likewise applied in the synthesis of trichloromethanesulphonates.^{[31,32][33]}

$$F_{3}CSSCF_{3} \xrightarrow{Cl_{2}} F_{3}CSCI \xrightarrow{Cl_{2}} F_{3}CSO_{2}CI \qquad Equation 14$$

$$F_{3}CSO_{2}CI \xrightarrow{15\% \text{ NaOH}} F_{3}CSO_{3}\text{Na} \qquad Equation 15$$

Pure F_3CSO_3H is a colourless liquid with a relatively low boiling point of 435 K (at ambient pressure), when compared to H_3CSO_3H , which boils at 435 K under reduced pressure (0.11 bar).^[34] When in contact with air, the acid builds hydrates, better described as hydronium hydrates. (H₃O)[F₃CSO₃] is stable at room temperature and crystallises in the monoclinic space group $P2_1/c$.^[35] Other hydroxonium triflates that have been structurally characterised are (H₅O₂)[F₃CSO₃], (H₉O₄)[F₃CSO₃] and (H₁₁O₅)[F₃CSO₃].^[36–38]

Conductivity studies on dilution series of several strong acids in anhydrous acetic acid revealed a higher acidity from F₃CSO₃H with regard to perchloric acid and FSO₃H.^[39] This manifests the classification of triflic acid as *super acid*. The strength in acidity for common strong acids is reported as follows: $F_3CSO_3H > HClO_4 > HBr >$ $HI > FSO_3H > H_2SO_4 > HCl.$ ^[39]

Triflic acid and its salts are readily soluble in organic solvents such as DMF, DMSO, CH₃CN, as well as alcohols, esters, ethers and ketones. Unlike H₂SO₄, CH₃SO₃H and F₃CCOOH, triflic acid is completely soluble in DMSO.^[40] Comparable to the outstanding solubility of methanesulphonic acid and its salts, the high solubility of triflate species is vital for the wide range use of this chemical. The sheer number of appliances in the field of organic synthesis is astounding. For example, acyl triflates are powerful acylating agents in *Friedel-Crafts* reactions:^[40]





Furthermore, triflic acid is a catalyst for the homo- and co-polymerisation of cyclic acetals.^[40] Also, the acid is used to remove amino protecting groups.^[41] In inorganic chemistry the high solubility of rare earth triflates benefits the extraction of these metals from ores, such as bastnasite.^[42,43]

Structurally, the anion is well characterised with a variety of counter cations, ranging from large organic compounds to inorganic salts.^[44–50] In the following, the crystal structure of Na[F₃CSO₃] is the exemplary to show properties of a triflate anion in the bulk, solid material.^[51] The sodium triflate crystallises in the triclinic space group $P\bar{I}$ with $a = 965.9(1) \text{ pm}, b = 1117.5(1) \text{ pm}, c = 1127.7(1) \text{ pm}, a = 101.878(2)^{\circ}, \beta = 105.292(2)^{\circ}, \beta = 105.292(2)^{\circ},$ $\gamma = 110.501(3)^{\circ}$, V = 1038.2(2) Å³ and Z = 8. The asymmetric unit consists of four crystallographically distinguishable triflate anions and five unique sodium cations (Figure 4, p. 9). Comparable to the [H₃CSO₃]⁻ anion, the triflate anion has a staggered conformation. One sodium cation has special site symmetry, as it occupies the inversion centre at 0, $\frac{1}{2}$, $\frac{1}{2}$ (Wyckoff letter 1g). The C-F bond lengths range from 129.9(5) pm to 132.1(3) pm and the C-S bonds from 180.5(3) pm to 181.4(2) pm. The shortest S-O bond is 142.3(2) pm long, while the longest conducts 144.6(1) pm. F-C-F and F-C-S bond angles are narrowly distributed and lie between 108.2(3)° and 109.6(3)° (F-C-F), as well as 109.4(1)° and 111.0(2)° (F-C-S). All O-S-O bond angles are larger and deviate between 112.3(1)° and 115.8(1)°. The crystal structure consists of layers, so that F₃C-groups are facing each other, while the SO₃-groups are pointing in the opposite direction, oriented towards each other as well, leaving room for the sodium cations in between. Slightly enlarged thermal ellipsoids of the fluorine atom hint at an increased movement of the F₃C-group.



Figure 4: Crystal Structure of Na[F_3 CSO₃]: Extended asymmetric unit and anion in Newman projection at the top (thermal ellipsoids are set to 70%), cross section of the crystal structure along the (0 1 0) and (1 0 0) plane at the bottom.^[51]

All sodium cations are coordinated by oxygen atoms of the SO_3 -groups. The coordination number varies between five and six, resulting in distorted tetragonal pyramidal and distorted octahedral coordination. Maximum Na-O distance is 277.0(2) pm and minimum Na-O distance portrays 226.9(2) pm. One sodium cation (Na5) has a split occupancy of 0.5.

Triflate salts are prone to build crystal structures, which incorporate solvent, in particular, water molecules. The water-free Na[F₃CSO₃] could only be obtained after extraction of the crystal water from Na[F₃CSO₃] · H₂O via an exhaustive drying process over a long period of time.^[51] Solvent-free alkali triflate salts are of special interest due to their promising electrochemical properties.^[52–61] Ion conductivity roots in the presence of defects throughout the crystal lattice and is enhanced through energetically convenient diffusion pathways, small ionic radii and low charge of the mobile ions. Thus, research mainly focuses on Li[F₃CSO₃] and Na[F₃CSO₃]. Structurally, triflate salts provide easy pathways for ion current due to their crystal layers. Furthermore, the anion itself can act as a promoter of ion conductivity via rotation (*paddle-wheel-mechanism*), after phase transition at elevated temperature to its HT-modification.^[61,62] Hence, the specific ion conductivity increases in Cs[F₃CSO₃] from $1.06 \cdot 10^{-8} \text{ S} \cdot \text{cm}^{-1}$ (393 K) to $5.18 \cdot 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ (519 K), after transition from the α -(RT)-modification to the

 β -(HT)-modification at 380 K.^[54] For Li[F₃CSO₃] the specific ion conductivity rises from 4.03 \cdot 10⁻⁹ S \cdot cm⁻¹ (422 K) to 1.10 \cdot 10⁻⁵ S \cdot cm⁻¹ (633 K). The lithium salt undergoes phase transition at 430 K from its β - to the HT γ -modification.^[63] In fact, the high disorder and thus mobility of the ions in this modification results in the inability to locate the cations by X-ray diffraction.^[64] Li[F₃CSO₃] plays an important role in lithium ion batteries (LIBs), where it benefits as electrolyte.^[65,66] Sodium ion conductivity in Na[F₃CSO₃] increases from 1.75 \cdot 10⁻⁸ S \cdot cm⁻¹ (413 K) to 8.78 \cdot 10⁻⁶ S \cdot cm⁻¹ (633 K). Na[F₃CSO₃] shows a phase transition to a HT-modification at 525 K \pm 3 K, shortly before the melting point at 532 K. At 673 K the salt decomposes, which leads to the detection of S₂O₄F, SO₂F, SOF₂, CF₃ and CO₂F fragments.^[51,53,67]

To conclude, triflate salts and triflic acid have a wide range of application in inorganic, organic, pharmaceutical and electrochemical chemistry. Today, the production relies on electrofluorination. Fluorinated alkanesulphonic acids are prepared by the *Simons* process, where organic molecules are dissolved in anhydrous HF and fluorinated at the anode, which usually consists of nickel.^[34,68,69] Conversion leads to compounds with perfluorinated alkyl chains.

Anode:
$$C_mH_n + nHF \longrightarrow C_mF_n + 2nH^+ + 2ne^-$$
 Equation 18
Cathode: $2nH^+ + 2ne^- \longrightarrow nH_2$ Equation 19

Perfluorinated sulfonyl fluoride is obtained through electrofluorination and hydrolysis then generates trflic acid. While the electrofluorination is a method delivering good yields, it is a costly process.

Trichlic Acid and Trichlate Salts

Kolbe first synthesised trichloromethanesulphonic acid and their corresponding trichlate salts in 1845, thus roughly 100 years before *Haszeldine* and *Kidd* introduced triflate-compounds to the world.^[33] Nevertheless, research on trichlate compounds is rather subdued: A literature survey on the database *Scifinder* for references referring to the word *'trichlate'* delivered five hits (called upon 15th September 2023), while 21694 references were found for the feed *'triflate'*. A three-step synthesis is required to obtain trichlate salts, which left traces in chemical literature going through three centuries. First step is the synthesis of trichloromethanesulphonyl chloride (Cl₃CSO₂Cl) from which the trichlate species can be generated.

Kolbe was the first to analyse the reaction of CS₂ with chlorine by adding CS₂ with HCl and MgO₂ in 1845. In his studies he identified the red liquid formed as an adduct of CS_2 and CCl₄ ('gepaarte Verbindung'), which today, we know to be thiophosgene. This product, when treated with water containing chlorine gas or nitric acid delivered a formula CCl_2SO_2 compound which Kolbe gave the ('schwefligsaures Kohlensuperchlorid') described as a white, volatile solid with a strong odour that sublimates on glass surfaces as transparent, rhombic tablets. Furthermore, the solid has a melting point of 408 K and its boiling point is 443 K. With this compound Kolbe synthesised the potassium, sodium, barium and silver trichlates for the first time.^[33] It is astounding, how accurate the interpretation of these reactions were at a time with far more restricted means of characterisation and a quiet different understanding of chemical reactions. In 1873 Rathke investigated the reaction of chlorine with CS₂ in further detail.^[70] His primary objective was the synthesis of thiophosgene, which at that time was known by its correct formula CSCl₂. Similar to the approach by *Kolbe*, MgO₂ and HCl were given to CS₂, while this time a small amount of iodine was added. The reaction mixture was, under occasional shaking, kept in a glass vessel for weeks. After a steam distillation, it was fractional distilled and three products were separated. The desired CSCl₂ was merely found in small amounts, while the majority consisted of CS₂, CCl₄ and a mixture of a new compound, collected at 418-423 K. This compound was a mixture of a yellow liquid and a colourless solid, identified as Cl₃CSCl and Cl₃CSO₂Cl. Rathke modified his synthesis in order to produce Cl₃CSCl, which he found to be the main product of the synthesis as described by *Kolbe*, in a quicker manner. He directly reacted chlorine gas with dry CS₂ under the presence of a small amount of iodine. Rathke named the new product perchloromethyl mercaptan, as he interpreted it as a methyl mercaptan, whose hydrogen is entirely substituted by chlorine. Klason gave more insights on this reaction, especially the purification processes after the reaction, in 1887.^[71] Helfrich and *Reid* postulated the first reaction equation and an even more straight forward process towards Cl₃CSCl in 1921.^[72] While the general reaction procedure coincides with Rathke's method, the purification via fractional distillation under reduced pressure is a crucial aspect to obtain a pure product and higher yields, as the product decomposes easily at temperatures above 418 K. Thus, Helfrich and Reid claimed to have achieved a yield of up to 65%.^[72]

 $2 CS_2 + 5 CI_2 \longrightarrow 2 CI_3 CSCI + S_2 CI_2$ Equation 20

Emanating from Cl₃CSCl, concerted oxidation delivers Cl₃CSO₂Cl. *Schechter* and *Haller* synthesised Cl₃CSO₂Cl from Cl₃CSCl and fuming nitric acid in glacial acetic acid with a yield of 50%.^[73] They stated a melting point of 413 K, which is close to initial findings by *Kolbe* in 1845 (408 K). Twenty years later (1961), *Sosnovsky* investigated the oxidation of Cl₃CSCl in acetic acid via hydrogen peroxide, peracetic acid and urea-hydrogen peroxide.^[74] Utilising 30% aqueous hydrogen peroxide solution, the yield was, with 78%, the highest:

$$CI_3CSCI + 2H_2O_2 \longrightarrow CI_3CSO_2CI + 2H_2O$$
 Equation 21

Lastly, a conversion of Cl₃CSO₂Cl with a metal hydroxide delivers the respective metal trichlate. The first trichlate, which has been structurally elucidated, was published in 2006, by two unaffiliated research groups.^[75,76] The Na[Cl₃CSO₃] · H₂O crystallises in the monoclinic space group $P2_1/c$ with a = 1255.8(5) pm, b = 581.4(3) pm, and $Z = 4.^{[76]}$ $\beta = 103.76(3)^{\circ}$ c = 1067.9(5) pm,The crystal contains one crystallographically distinguishable trichlate anion, one Na cation and one water molecule (Figure 5, p. 13). In accordance with the sodium triflate, the crystal consists of layers, constructed by the arrangement of the trichlate anion in order to achieve reagents of mutual polarity for the non-polar CCl₃-groups and polar SO₃-functions. Counter sodium cations and the water molecules, which co-crystallise in the structure, fill the polar layers. A staggered conformation of the substituents accentuates the anticipated $C_{3\nu}$ symmetry of the trichlate anion. S-O distances range from 143.0(6) pm to 145.6(6) pm, and 144.4(3) pm to 145.5(2) pm, respectively.^[75,76] The C-Cl bonds range from 143(1) pm, to 147(1) pm (175.7(4) pm to 177.7(3) pm).^[75,76] In both documented structures, one C-Cl bond is slightly enlarged, due to the proximity of that respective chlorine atom to the sodium cation. Five oxygen atoms coordinate to Na in a range from 235.5(6) pm to 239.6(7) pm (235.8(3) pm to 241.7(3) pm) in a square-pyramidal environment. The distance from Na to Cl is 333.9(5) pm (337.0(4) pm). Including this bond between Na and Cl, the coordination sphere around the cation builds a distorted octahedron. Na binds to three separate trichlate anions and two oxygen atoms of water molecules. The C-S bond is 186(1) pm (184.7(4) pm) long and thus significantly longer than those obtained for Na[F₃CSO₃]. It is noteworthy, however, that both structures obtained for Na[Cl₃CSO₃] · H₂O are from datasets obtained at room temperature, while the sodium triflate was measured at 100 K.



Figure 5: Crystal structure of Na[Cl₃CSO₃] ·H₂O: Upper left corner shows the asymmetric unit in an ellipsoidal plot with 70% probability level, upper right corner depicts the coordination sphere of sodium, the bottom depicts cross-sections of the crystal portraying the layered structure.^[75]

Ben Atlabef et al. further contributed vibrational spectroscopy data and quantum chemical calculations (DFT) on the sodium trichlate monohydrate. Prior to these investigations, *Miles et al.*, *Edwards et al.* and *Bürger et al.* performed vibrational studies on the trichlate anion.^[77–79] There are 18 vibrational modes expected, classified as $5A_1 + A_2 + 6E$, assuming an ideally isolated trichlate anion with $C_{3\nu}$ symmetry. The A₂ torsion is inactive in *Raman* and IR spectroscopy, leaving eleven predicted vibrational modes. While this is true for all investigations, the assignments on the measured bands varies. Correct assignment and interpretation of the measured spectra is deterred by a decay of degenerated states in the bulk material. Within the crystal structure of Na[Cl₃CSO₃] · H₂O, the anion has C_1 site symmetry, thus encounters higher asymmetry, which will split vibrational modes in the spectrum.

1.3. Methanepolysulphonic Acids

Starting from MSA, formal substitution of hydrogen by sulphonyl groups will lead to methanepolysulphonic acids and their respective salts. These acids are categorised into methanedisulphonc acids (MDA), methanetrisulphonic acids (MTA) and methanetetrasulphonic acids (MTeA). In this fashion, the single proton donator MSA transforms into a diprotic, triprotic and potentially tetraprotic acid. In contrast to halogenated MSA, no amphiphilic compounds are created, instead the polarity and hydrophilicity of methanepolysulphonic acids should increase. Furthermore, addition of sulphonyl groups at the carbon centre will render the remaining hydrogen atoms, bonding to said carbon atom, more acidic.

Methanedisulphonic Acid (MDA)

In 1833, methanedisulphonic acid was first produced, unknowingly, as a decomposition product of ethanedisulphonic acid (Weinschwefelsäure), synthesised from diethyl ether (or ethanol) and anhydrous sulphuric acid by Magnus.^[80] Historically, the foundation of this and the following studies was devoted to the targeted production of ether from alcohol and strong anhydrous acids. *Liebig* gives clearer overview in his elaborate recapitulation "Thatsachen zur Geschichte des Aethers", on the various collected sulphonic acids obtained from synthesis of alcohols with concentrated, dry sulphuric acid.^[81] Furthermore, Liebig introduced the name ethionic acid as a better description for what was previously assumed and named Weinschwefelsäure, for the first time.^[81] Redtenbacher analysed the barium salt of MDA, and is the first to implement the name methionic acid, following the previous description by *Liebig* for ethanedisulphonic acid.^[82] Even today, the term methionic acid is still sometimes used for CH₂(SO₃H)₂. In 1856 Strecker was the first to analyse various salts of methionic acid. His synthetic procedure was in accordance with previously mentioned techniques, using ether and anhydrous sulphuric acid. In this case, higher yields were obtained, by conversion of ether with anhydrous sulphuric acid and trapping the evolving gases within the reaction flask (graduated cylinder) to achieve maximum conversion.^[83] In this fashion, Strecker obtained two phases, which both obtained amounts of methionic acid. In the same year, Buckton and Hofmann synthesised the acid from reaction of acetonitrile or acetamide with fuming sulphuric acid.^[84] Another synthetic procedure was introduced in 1897 by Schroeter, who reacted acetylene with fuming sulphuric acid to obtain acetaldehyde disulphonic acids, which decompose to methionic acid upon boiling in alkaline medium.^[85] A drawback of all these synthetic routes lies in the presence of various byproducts. A somewhat more direct synthesis with higher yields was introduced by Backer in 1929, reacting dichloromethane (CH₂Cl₂) and potassium sulphite under hydrothermal conditions.[86]

$$CH_2CI_2 + K_2SO_3 \xrightarrow{234 \text{ K}} K_2[CH_2(SO_3)_2] + 2 \text{ HCI} \qquad Equation 22$$

According to Equation 22, the potassium salt of MDA was obtained as a crystalline solid and could be produced in an 85% yield after recrystallisation from hot water. Further formation of the barium salt by conversion with barium chloride solution and subsequent treatment with sulphuric acid delivered the desired MDA. With this new approach towards MDA, *Backer* continued the work of *Schröter*, analysing various salts of MDA in more detail.^[85,87] Thus, crystals of Li to Cs-, Ag-, Ca-, Ba-, Cu-, Co-, Ni-, La-, Pb-, and ammonium methanedisulphonates were analysed by the available means of that time. Composition and crystal system according to *Backer* is given in Table 1 (p. 16). The formation of hydrates is relatively common. In case of the silver salt, *Backer* states that there are three different hydrates formed. For Barium, two different crystals are obtained, depending on the cooling rate upon crystallisation. These results are, of course, vague interpretations of true crystal structure, due to limited characterisation methods of that time. Roughly 30 years later, the first single crystal structure was published, characterised by X-ray diffraction. The potassium salt portrays indeed the monoclinic crystal system, and no water is found in its structure, as postulated by *Backer*.^[88] _

Composition	Crystal Properties
Li ₂ [CH ₂ (SO ₃) ₂]	crystalline powder
Na ₂ [CH ₂ (SO ₃) ₂] · 2.5 H ₂ O	triclinic
$K_2[CH_2(SO_3)_2]$	monoclinic
$Rb_2[CH_2(SO_3)_2]$	monoclinic
$Cs_2[CH_2(SO_3)_2]$	rhombohedral
$Ag_2[CH_2(SO_3)_2] \cdot 2 H_2O$	clear, monoclinic
Ag ₂ [CH ₂ (SO ₃) ₂] · 0.5 H ₂ O	elongated crystals, triclinic
$Ag_2[CH_2(SO_3)_2]$	agglomerated plates, rhombohedral
$Tl_2[CH_2(SO_3)_2]$	monoclinic
$Ca[CH_2(SO_3)_2] \cdot 3 H_2O$	monoclinic
$Sr[CH_2(SO_3)_2] \cdot 2 H_2O$	rhombohedral
$Ba[CH_2(SO_3)_2] \cdot 2 H_2O I$	thin plates, rhombohedral
$Ba[CH_2(SO_3)_2] \cdot 2 H_2O II$	elongated needles, rhombohedral
$Cu[CH_2(SO_3)_2] \cdot 5 H_2O$	blue plates, monoclinic
$Cu[CH_2(SO_3)_2]\cdot 7 H_2O$	blue prisms, triclinic
$Pb[CH_2(SO_3)_2] \cdot 2 H_2O$	plates, rhombohedral
$Fe[CH_2(SO_3)_2] \cdot 5 H_2O$	green solution, anhydrous: Colourless solid
$Co[CH_2(SO_3)_2] \cdot 5 H_2O$	red/brown, rhombohedral
Ni[CH ₂ (SO ₃) ₂] · 5 H ₂ O	green solution, anhydrous: Colourless solid
La ₂ [CH ₂ (SO ₃) ₂] ₃ · 6 H ₂ O	triclinic, high solubility
$(NH_4)_2[CH_2(SO_3)_2]$	monoclinic

Table 1: Results of Studies on Solid State Structures of Methanedisulphonate Salts, performed in 1929^[87].

K₂[CH₂(SO₃)₂] crystallises in the space group *C*2/*c*, with four formula units and the cell parameters a = 1255.6 pm, b = 777.3 pm, c = 725.3 pm and $\beta = 90.30^{\circ}$. The extended asymmetric unit consists of one anion and one cation. The carbon atom lies on a two-fold rotational axis, occupying special site location *4e*. Thus, crystallographically, only one unique SO₃-group is evident (Figure 6, p. 17). Due to the age of the dataset, no thermal ellipsoids can be given. S-O bond lengths lie between 144.9 pm and 145.9 pm and are therefore in accordance with S-O bond lengths found for Na[H₃CSO₃] (144.6-146.2 pm). With 176.3 pm, the C-S distance is agreeable to that found for the sodium methanesulphonate (175.2-175.6 pm). While the O-S-O angles are narrowly distributed around 113°, the C-S-O angles vary significantly. The C1-S1-O2 angle is smaller

(102.5°), than the angles found between C1-S1-O1 (107.5°) and C1-S1-O3 (106.4°). Overall, layers build the crystal structure. Along the (0 1 0) plane these layers consist of the anions, stacked in a parallel fashion with the CH₂-moity in the middle and the potassium cations located at the outer SO₃-groups. Not many salts of MDA have been elucidated structurally. To this day not many more than a handful crystals have been analysed, including the free acid and its hydrate, the Na-, Ca-, Cd-, and the Ag-salt of MDA.^[89–93]



Figure 6: Crystal structure of $K_2[CH_2(SO_3)_2]$. Top: Asymmetric unit and cross section of the crystal along the c/a-plane, bottom: Structure along c-viewing direction and coordination sphere of K1.

Today, MDA is produced by hydrolysing methanebisdisulphonyl chloride. The disulphonyl chloride can be prepared after *Fild* and *Rieck*:^[94]

$$2 \text{ CISO}_3\text{H} + \text{CH}_3\text{COOH} \xrightarrow{P_4\text{O}_{10}} \text{CH}_2(\text{SO}_2\text{CI})_2 + \text{CO}_2 + 2 \text{H}_2\text{O}$$
 Equation 23

MDA has a melting point of 369-373 K and an acidity close to that of sulphuric acid.^[95] In 1996, *Jüschke* and *Sartori* investigated the acidity of alkanepolysulphonic acids by NMR-spectroscopy.^[96] Therefore, ²⁹Si-NMR spectra of trimethylsilyl esters of strong acids with known pK_a values were measured. The corresponding shift in the NMR spectra was correlated to the pK_a values (solely first deprotonation), and the obtained fitted linear

function used for estimation of pK_a values of polysulphonic acids. According to the ²⁹Si-NMR spectrum of CH₂(SO₃-SiMe₃)₂, MDA has an estimated pK_a of -2.1(5) for the first deprotonation step. While the melting points of MDA and MSA (~370 K vs. 293 K) differ greatly, their strength in acidity and high solubility is similar. Nevertheless, a widespread industrial importance of MDA is not evident.

Methanetrisulphonic Acids (MTA)

Methanetrisulphonic acid (MTA) was first synthesised in 1868 by *Theilkuhl*, reacting calcium methylsulphate with anhydrous sulphuric acid.^[97] In 1899, *Bagnall* synthesised MTA as well as the silver(I), copper, calcium, barium, ammonium, sodium and potassium salt. He brought dichlorodiazetylbenzidine, diacetylbenzidine, acetyl- α -naphtylamine, acetanilide and propanilide to reaction with fuming sulphuric acid (70% free SO₃) and obtained the acid from all procedures in varying yields. *Bagnall* further stated, that the acid is gathered as the hydrate from aqueous solution. He suggested the formula CH(SO₃H)₃ · 4 H₂O. Due to the high deliquescence of the acid, it was unknown at that point, whether the acid obtains crystal water or simply absorbs water from the atmosphere. Furthermore, it was found, that the highest yield was obtained for acetyl- α -naphtylamine.

$$\begin{array}{c} O \\ H \\ H \end{array} + H_2 SO_4/SO_3 \xrightarrow{403 \text{ K}, 3 \text{ h}} CH(SO_3H)_3 + CO_2 + H_2 \\ \hline H \\ \hline H \\ \hline \end{array} Equation 24$$

In 1930, *Backer* conducted further investigations based on these findings.^[98] Essentially, his procedure is similar to that of *Bagnall*, using fuming sulphuric acid as sulphonation agent and various reactants. Interestingly, next to anilide derivatives, he also sulphonated methionic acid (MDA) and nitromethionic acid (NO₂CH(SO₃H)₂) with potassium sulphite, potassium diazomethionate (N₂C(SO₃K)₂) with potassium bisulfite and he converted mercaptomethanetrisulphonic acid (HSC(SO₃H)₃) to K₃[CH(SO₃)₃] by reaction with potassium carbonate in chlorine atmosphere. The simplest reaction between MDA and oleum delivered only 10% of MTA. In agreement with *Backer*, the reaction of acetanilide with oleum yielded 57%, the highest amount of MTA. *Sartori* and *Jüschke* provided a facile preparation of MTA, with fewer side products, more than 60 years later.^[99] Using acetone instead of acetanilide as reactant for the sulphonation, not only prevents unwanted by-products, but also increases the yield of the reaction up to 30%.

Therefore, at temperatures below 278 K, acetone is slowly added to a 65% solution of oleum and subsequently gradually heated to 358 K. After neutralisation with potassium hydroxide, the potassium methanetrisulphonate is obtained next to potassium sulphate:

$$\begin{array}{c} 0 \\ \hline \\ -CO_2 \end{array} \xrightarrow{\mathsf{H}_2 \mathrm{SO}_4/\mathrm{SO}_3} 2 \mathrm{CH}(\mathrm{SO}_3 \mathrm{H})_3 \xrightarrow{\mathsf{KOH}} 2 \mathrm{K}_3[\mathrm{CH}(\mathrm{SO}_3)_3] \cdot \mathrm{H}_2 \mathrm{O} \quad Equation \ 25 \mathrm{CH}(\mathrm{SO}_3)_3] \cdot \mathrm{H}_2 \mathrm{O} \quad Equation \ 25 \mathrm{CH}(\mathrm{SO}_3)_3 \xrightarrow{\mathsf{KOH}} 2 \mathrm$$

 $K_3[CH(SO_3)_3] \cdot H_2O$, was the first methanetrisulphonate salt subjected to single crystal diffraction, in 1980.^[100] It crystallises in the orthorhombic, acentric space group $P2_12_12_1$ with four formula units and a = 935.33(2) pm, b = 936.72(2) pm and c = 1225.22(2) pm. Interestingly, the cell parameters are not far from the tetragonal lattice, with the *a* and *b* axis so similar. The asymmetric unit consists of one anion, three cations needed for charge equilibrium and one water molecule. All atoms are located on general position of the unit cell.



Figure 7: Crystal structure of $K_3[CH(SO_3)_3] \cdot H_2O$.^[100] Top: Asymmetric unit with thermal ellipsoids set to 70% probability level and cross section of the cell along a-viewing direction with CSO₃-polyhedrons in yellow. Bottom: Coordination sphere of the three distinguished potassium cations.

The demonstrated cross section of the unit cell shows an alternating arrangement of $[CH(SO_3)_3]^{3-}$ anions and the potassium cations. For a clearer overview, the SO₃-moities 19

are depicted as tetrahedrons (CSO₃). Three bonded oxygen atoms and the carbon atom span the tetrahedrons around the sulphur atoms. Oxygen atoms of all three SO₃-groups of the anion and the oxygen atom of the water molecule coordinate to each potassium cation. The coordination number varies between eight (K1, K3) and nine (K2). The K-O distances range from 265.6(3) pm (K1-O9) to 329.1(3) pm (K2-O8). S-O bonds within the anion are narrowly distributed between 145.1(3) pm (S1-O1) and 145.9(3) pm (S1-O2, S2-O6) and thus similar to those of K₂[CH₂(SO₃)₂]. However, comparing the C-S bonds of K₂[CH₂(SO₃)₂] and K₃[CH(SO₃)₃] \cdot H₂O a slight increase towards the trisulphonate is detected. While the C-S bond in K₂[CH₂(SO₃)₂] is 176.3 pm long, it obtains between 181.5(4) pm (S1-C1) and 182.1(4) pm (S2-C1) in the trisulphonate.

With the aid of *Sartori* and *Jüschke's* straightforward synthetic approach towards MTA, Oelkers and co-workers synthesised a variety of different metal salts of MTA by simple acid-base reactions.^[101] Products of these syntheses were crystalline and single crystal elucidation was conducted by X-ray diffraction. Hence, crystal structures of Li- to Cs-, Ca-, Ba-, Ag-, Tl-, Cu-, La-, Pb-, Cr-, Ni-, and Zn-MTS as well as the ammonium salt and the acid are now known. Similar to compounds of MSA, MDA and the trihalomethanesulphonates, an inclination towards the formation of hydrates is observed. For some compositions, no coordination of the methanetrisulphonate anion to the metal cation is detected ($[Cr(H_2O)_6][CH(SO_3)_3] \cdot 4 H_2O$). The variety of different hydrates impede the distinction and comparison of the structures. Solely the compounds $[Ni(H_2O)_6][Ni(H_2O)_4(CH(SO_3)_3]_2$ and $[Zn(H_2O)_6][Zn(H_2O)_4(CH(SO_3)_3]_2$ are isotypic. Even with the same cation, different compositions can be formed, which was shown for (NH₄)₃[CH(SO₃)₃] and (NH₄)₆[CH(SO₃)₃]₂ · H₂O. Next to transition metal, alkali and other metal salts, Oelkers and co-workers also published the structure of MTA. The acid crystallises with three water molecules in the hexagonal space group $P6_3$. Astonishingly, the crystal system and the axis ratio coincide with those postulated by Backer and Terpestra.^[102] Bagnall already stated the melting point of MTA to be at 423-426 K, and a decomposition at 453 K, without prior loss of crystal water. Backer and Terpestra corrected the melting point to 435 K. The high resistance towards water loss is expected for strong acids, more so with the aid of the crystallographic data, revealing, that the acid is in fact built by methanetrisulphonate anions and hydroxonium cations. Based on the ²⁹Si-NMR investigations on the trimethylsilylester of MTA, a pK_a value around -3.7(5)is estimated, which would categorize MTA as a super acid.^[96] An application for the acid is found in organic chemistry, where MTA poses as a favourable catalyst for *Wagner-Meerwein* rearrangement, *Friedel-Crafts* alkylation and acylation reactions.^[103]

2. Main Part

2.1. Methanesulphonic Acid (MSA) and Methanesulphonic Salts

Methanesulphonic Acid (MSA)

Taking into account the industrial importance of a compound such as MSA, it is astounding, that no crystallographic data on the free acid has been provided until now. To gain more insight on the structural properties and obtain more information on the molecule, which can be described as "point zero" of this work on all its highly acidic derivatives, investigations via X-ray diffraction were undertaken. The acid was purchased in its free form, with a chemical purity of at least 99% from *Sigma Aldrich* and stored under argon atmosphere in a glovebox. MSA is liquid at room temperature, which impedes crystallisation by convenient methods. Therefore, the acid was crystallised *in situ* on the diffractometer with the aid of an OHCD (*optical heating crystallisation device*) LASER under steady cooling nitrogen flow.





Capillary, prior to OHCD treatment, filled with liquid MSA, small red dot indicates the focus of the LASER.

Capillary cooled under N₂flow: Solid MSA, red light indicates the focus of the LASER.



Capillary cooled under N₂flow: Solid MSA with a droplet of liquid MSA, red light indicates the focus of the LASER.

Figure 8: Various stages of MSA within the capillary during OHCD treatment.

Practically, MSA was transferred into a quartz capillary, sealed and the capillary was cooled down on the diffractometer. Subsequently the CO₂ LASER is used to heat the shock frozen acid in the capillary in order to provoke zone melting and crystallite formation. With the aid of a visible red LASER, the correct focus is achieved. MSA crystallises in the monoclinic space group $P2_1/c$ with four formula units and the cell parameters a = 842.07(4) pm, b = 582.20(3) pm, c = 820.38(4) pm, $\beta = 106.459(2)^{\circ}$ and

V = 385.71(3) Å³. See crystallographic tables in the appendix (p. 147 and following) for more details and crystal data refinement.



Figure 9: Transformation of the diffraction pattern from mostly polycrystalline (left) to a single dominant crystalline domain during treatment with a CO₂ LASER at 191 K.

The asymmetric unit consists of only one molecule MSA, with all atoms on general positions. The hydrogen atom at the SO₃-group could be freely refined. Unlike some highly acidic acids introduced in the first chapter of this work, MSA does not crystallise as a hydroxonium salt. The acid molecules are arranged in two different orientations within the unit cell (Figure 10). Bond lengths between S1-O11 (144.15(7) pm) and S1-O13 (142.57(8) pm) are significantly shorter, than S1-O12 (154.28(7) pm). The C-S bond lengths is 173.8(1) pm and thus slightly shorter than what was found for Na[H₃CSO₃] (~175 pm). Bond angles vary immensely due to the elongated bond between S1-O12 with respect to the other S-O bonds. The angle between O11-S1-O13 is the largest with 117.41(5)°, while O12-S1-O13 is the average 110.30(5)° and O11-S1-O12 is slightly compressed to 104.98(5)°. Nevertheless, a look along the C-S bond in Newman projection shows a staggered arrangement of the substituents along this bond.



Figure 10: Crystal structure of CH_3SO_3H : Asymmetric unit with thermal ellipsoids set to 70% and cross section through the crystal in viewing direction of the b-axis.

Rubidium Methanesulphonate Monohydrate

Literature provides crystallographic data on all alkali metal methanesulphonates, with the exception of the rubidium salt.^[23,28,104] Therefore, through acid base reaction a sample of Rb[H₃CSO₃] was prepared and analysed via X-ray diffraction. The analysed crystal of rubidium methanesulphonate contains water, resulting in the composition Rb₂[H₃CSO₃]₂ · H₂O. The salt crystallises in the monoclinic space group $P2_1/c$ with a = 606.22(4) pm, b = 1969.1(1) pm, c = 890.08(6) pm, $\beta = 91.558(2)^\circ$, V = 1062.1(1) Å³ and Z = 4. Detailed crystallographic tables can be found in the appendix (p. 157 and following).



Figure 11: Asymmetric unit of Rb₂[H₃CSO₃]₂ · H₂O and light microscope picture of the crystals. Thermal ellipsoids are set to 70% probability.

The asymmetric unit holds two distinct anions, two Rb cations and one water molecule. Bond lengths and angles of the two crystallographically distinguishable anions are very similar. S-O bonds range from 145.13(9) pm (S1-O22) to 146.85(9) pm (S2-O23). The C1-S1 bond is 176.5(1) pm long, and the C2-S2 bond obtains 176.2(1) pm. Bond lengths within the methyl group are less distinct, as can be expected by structural elucidation with X-ray diffraction at electron density. All C-H bonds are shorter than 100 pm. Bond angles within the SO₃-group lie between 111° (smallest: O21-S2-O23 111.21(6)°) and 113° (largest: O12-S1-O13 112.59(6)°). Bond angles spanned over C-S-O are just as narrowly distributed and lie between 105.49(6)° (C2-S2-O23) and 107.48(6)° (C1-S1-O13). A cross section of the crystal shows no obvious preference of orientation for the anion. The coordination sphere of rubidium was investigated with the aid of the program *Chardi2015*.^[105,106] The rubidium cation is coordinated by oxygen from the sulphonate anions and water alike. Rb1 has the coordination number eight. The shortest Rb1-O distance lies between Rb1-O23 with 282.63(9) pm and the longest between Rb1-O13 with 350.7(1) pm. For Rb2 the coordination number is nine. Here, the shortest bond is found between Rb2-O22 with 290.42(9) pm and the longest between Rb2-O1 with 324.5(1) pm.



Figure 12: Cross section of the crystal structure of $Rb_2[H_3CSO_3]_2 \cdot H_2O$ and coordination polyhedrons around Rb1 and Rb2.

Table 2 (p. 26) contains selected parameters of all published crystal structures of methanesulphonate salts with alkali metals. A comparison of the bond lengths found in the literature with those measured in this work for $Rb_2[H_3CSO_3]_2 \cdot H_2O$ shows a good agreement. The medium S-O bond length within the rubidium salt is 145.9(2) pm and is thus the same average as found for Li[H_3CSO_3]. Generally, the S-O bonds of all compositions are very similar. For the C-S bonds, a similar result is found. With roughly 176 pm, the C-S bond lengths within the rubidium salt fits the literature findings. The information provided for the caesium methanesulphonate delivers the highest uncertainties, which can be ascribed to the date of data publication. With higher ionic radii, the coordination number of the cation increases and so does the average distance between metal centre and oxygen ligand. Starting from a tetrahedral coordination of lithium with Li-O distances below 200 pm, coordination number and radius of coordination sphere increase up to Cs-O distances well over 300 pm and coordination

number nine. Thus, the data obtained for $Rb_2[H_3CSO_3]_2 \cdot H_2O$ fits perfectly into the knowledge gap between K[H_3CSO_3] and Cs[H_3CSO_3].

Compound	$Li[H_3CSO_3]^{[104]}$	Na[H ₃ CSO ₃] ^[23]	$K[H_3CSO_3]^{[104]}$	$Cs[H_3CSO_3]^{[28]}$
Crystal system	monoclinic	orthorhombic	tetragonal	orthorhombic
Space group	C2/m	Pbma	I4/m	Pnma
Year	2020	1980	2020	1966
T [K]	150(2)	297	299(4)	295
Radiation	Μοκα	$Cu_{K\alpha}$	Μοκα	Μοκα
dø S-O [pm]	146.2(1)	145.4(3)	145.2(5)	144.8(2)
dø C-S [pm]	175.3(2)	175.4(5)	175.1(3)	180.4(1)
CN _{Cation}	4	6-7	6-9	9
d _{O-Cat.} max	197.9(2)	283.39(1)	306.23(4)	335.5(2)
d _{O-Cat.} min	191.5(2)	227.58(1)	264.6(2)	312.0(1)

Table 2: Selected Parameters of Alkali Methanesulphonate Crystal Structures found inLiterature.

Peculiar however, is the fact, that the measured rubidium methanesulphonate is the first hydrate salt obtained in the row of alkali salts. The presence of hydrogen bridges was investigated based on regulations provided by *Steiner*.^[107] Figure 13 depicts the hydrogen bonds formed. Solely O23 and O21 participate in hydrogen bonding, probably due to the relatively low amount of water in the crystal structure. The O_D-H···O_A distances are 283.7(1) pm (O1-H···O23) and 279.1(1) pm (O1-H···O21) and the angles O_D-H-O_A conduct 176(2)° (O1-H1A-O21) and 169(3)° (O1-H1B-O23).



Figure 13: H-Bonding within $Rb_2[H_3CSO_3]_2 \cdot H_2O$.

Rubidium methanesulphonate is highly hygroscopic; therefore, powder X-ray diffraction (PXRD) experiments were conducted on a flat sample holder, as grinding of the sample led to a pulp like habitus. Comparison of the measured powder diffraction pattern with the simulated data from the single crystal of Rb₂[H₃CSO₃]₂ · H₂O was facilitated by a *Rietveld* plot. While the difference curve of the *Rietveld* refinement shows one distinct peak at 13.5°, the overall diffractogram does not hint at a second crystalline phase. The deviation between measured and simulated pattern lies in the intensity of the reflection and not the angle of diffraction. This could mainly be caused by a general poor crystallinity, which is evident in the noise of both measured diffractogram and the difference curve. As expected the refined cell parameters are larger at room temperature, most affected is the *b*-axis. Table 3 on page 28 lists the refined cell parameters and obtained quality factors. Furthermore, the atom positions for both rubidium cations were refined.



Figure 14: X-ray powder diffraction pattern of $Rb_2[H_3CSO_3]_2 \cdot H_2O$ (black, cross) and Rietveld fit in red. The difference curve is given in the bottom in blue. The sample was measured as a flat preparation with Mo_{Kal} -radiation.

Parameters	Rietveld Refinement	Single Crystal	
<i>a</i> [pm]	614.99(4)	606.22(4)	
<i>b</i> [pm]	1989.0(2)	1969.1(1)	
<i>c</i> [pm]	893.6(1)	890.08(6)	
V [Å ³]	1092.9(2)	1062.1(1)	
T [K]	293	100	
Rwp	3.162		
Rexp	3.802		
Rp	2.523		
gof	0.832		

Table 3: Results of the Rietveld Refinement for $Rb_2[H_3CSO_3]_2 \cdot H_2O$.

Thermogravimetric investigations on the obtained rubidium methanesulphonate reveals a thermal stability up to 700 K. At roughly 340 K the first drop in the TG curve commences (Onset: 386 K). At 420 K the drastic mass loss is completed and only a slight decrease in mass is observed until 700 K. The first drop can be assigned to the loss of crystal water and is accompanied by a broad endothermic signal in the DSC curve.



Figure 15: DSC/TG measurement of a sample of Rb₂[H₃CSO₃]₂ · H₂O, heated at 5 K/min under steady argon gas flow to a maximum temperature of 1259 K.

Prior to the loss of water another endothermic peak is observed at 350 K. The first drop encompasses 7% of the initial sample mass, concluding that either, the sample contains more water than expected from X-ray analysis (~ $1.5 \times H_2O$), or, during transport to the DSC instrument additional water adhered to the compound. At 613 K an endothermic
peak appears in the DSC curve, most likely caused by the melting of the water-free rubidium methanesulphonate. The subsequent drop in the TG curve, displaying the decomposition of the methanesulphonate unit, is characterised by a very strong exothermic peak, declaring the obtained water-free rubidium methanesulphonate as *meta*-stable.

Table 4: Overview of the DSC/TG-MS Measurement of $Rb_2[H_3CSO_3]_2 \cdot H_2O$.

T _{Onset} [K]	T _{Offset} [K]	Mass loss [%]	Possible fragments	Remaining compound
386	420	6.9	H ₂ O/OH	Rb ₂ [H ₃ CSO ₃] ₂
697	711	29.1	CO ₂ , SO, SO ₂	Rb_2SO_4

Interestingly, the decomposition is sudden and completed in a very narrow temperature frame and followed by a significant increase of weight afterwards. This peculiar occurrence is compound specific, could be reproduced and is also evident for K[H₃CSO₃] (Appendix, Figure 111, p. 244). Taking the slight increase in mass into account, the second drop includes roughly 29% of the initial sample mass. This approximately correlates to the expected mass loss of the [H₃CSO₃]⁻ fragment. However, a large amount of substance remains after heating above 1200 K. The remaining compound (62% of initial mass) was analysed by X-ray powder diffraction and Rb₂SO₄ was identified as the only crystalline phase in the remaining sample (appendix, Figure 101, p. 237).

Silver Methanesulphonate

In alignment with the preparation of the rubidium salt, a silver methanesulphonate salt was synthesised by simple acid base reaction with methanesulphonic acid and silver nitrate. Based on a single crystal diffraction experiment, the obtained compound crystallises as Ag[H₃CSO₃], without additional crystal water in the monoclinic space group $P2_1/c$ with a = 869.1(1) pm, b = 574.18(6) pm, c = 823.4(1) pm, $\beta = 100.322(6)^\circ$, V = 404.23(9) Å³ and Z = 4. All crystal data can be found in the appendix (p. 152 and following). The asymmetric unit consists of only one anion and cation, with all atoms on general site positions. In viewing direction of the *b*-axis, a layered structure can be found, with all [H₃CSO₃]⁻ anions in a parallel arrangement (Figure 16, p. 30). The SO₃-units are 29 pointing towards each other, with the silver cations functioning as separators. Bond lengths and angles agree with those previously discussed (d_{C-S}: 175.2(4) pm, S1-O11: 146.1(3) pm, S1-O12: 146.1(3) pm, S1-O13: 148.3(3) pm). The S1-O13 bond length is slightly increased, probably due to the higher participation in the coordination sphere of Ag. Ag-O distances range from 234.8(3) pm (Ag1-O12) to 292.1(4) pm (Ag1-O11). All bond lengths are in the same range as those found for silver sulphate (min. d_{Ag-O} : 239.7(2) pm, max. d_{Ag-O} : 266.5(3) pm), with the exception of the extraordinarily long bond between Ag1 and O11.^[108] The interaction between Ag1 and O11 was confirmed with the software *Chardi2015*.^[105,106] A powder diffraction pattern of the product was measured and phase purity was validated by *Rietveld* refinement. The diffraction data and *Rietveld* fit can be found in the appendix (Figure 100, p. 236).



Figure 16: Crystal structure of Ag[H₃CSO₃]. Top: Asymmetric unit of the measured single crystal (thermal ellipsoids are set to 70%) and picture of the obtained crystals. Bottom: Cross section of the unit cell portraying the (0 1 0) plane and coordination sphere of silver.

As mentioned above, the thermal decomposition of methanesulphonates of rubidium and potassium takes place around 700 K and the identified decomposition product was the respective sulphates. Thermal treatment of silver methanesulphonate delivers a different TG curve (Figure 17, p. 31). At 532 K an endothermic peak accompanies a small drop in the TG curve of roughly 3%. Starting at 578 K a bigger drop in mass loss is observed,

presumably correlating to the decomposition of the methanesulphonate fragment. At 657 K the sample mass has reduced to 53% and no further change is detected for the measurement up to 1272 K. Hence, the silver salt has a higher thermal liability and most likely decomposes in two steps. The remains after heating could not be analysed via PXRD, since the very hygroscopic compound liquefied within seconds, when in contact with air.



Figure 17: DTA/TG curve for Ag[H₃CSO₃], heated with 5 K/min under steady nitrogen gas flow to a maximum temperature of 1272 K.

2.2. Methanedisulphonic Acid and Methanedisulphonate Salts Methanedisulphonic Acid (MDA) Dihydrate

MDA can be synthesised via two different routes. One relies on the hydrothermal reaction of CH₂Cl₂ with potassium sulphite to gather the potassium salt of MDA, introduced by *Backer* in 1929 (Equation 22, p. 15).^[86] Historically, the acid was synthesised after conversion of the respective potassium salt to the less soluble barium salt and finally treatment with sulphuric acid. In this work, however, the acid was obtained by running an aqueous solution of K₂[CH₂(SO₃)₂] through an ion exchange column with a strongly acidic stationary phase. Notwithstanding the facile and fast preparation of the potassium (or sodium) methanedisulphonate salt, higher yields of MDA are accessible by hydrolysing methanebisdisulphonyl chloride which is gained from chlorosulphonic acid and acetic acid under the presence of phosphoryl chloride or phosphorous pentoxide (Equation 23, p. 17). In both ways the acid was gained as its hydroxonium salt (H₃O)₂[CH₂(SO₃)₂]. The acid crystallises in elongated partially agglomerated needles.



Figure 18: Light microscope picture of the colourless, needle shaped, large crystals, obtained from solution after hydrolysis of CH₂(SO₂Cl)₂.

The generated acid was characterised by X-ray diffraction. Due to the high hygroscopy and mechanical habitus of the acid, a preparation in a capillary was not applicable. Even after weeks in the inert glovebox environment, the acid still obtained too much water and maintained its slushy appearance. Therefore, flat preparations were considered using conventional scotch tape and *Kapton* foil to prohibit further water contaminations. A series of several 30 min measurements with regular scotch tape showed that after the first measurement the sample only contained an amorphous noise background, suggesting a relatively quick contamination with water. The first measurement of this series is given in the appendix (Figure 102 p. 237) and clearly shows a good overlay with the simulated pattern from single crystal data for $(H_3O)_2[CH_2(SO_3)_2]$. Due to the poor crystallinity another set of measurements were conducted, this time using *Kapton* foil and the sample was prepared on a *Rigaku* X-ray diffractometer, operating in *Bragg-Brentano* geometry. The diffraction pattern is more distinct, of higher crystallinity and constant over a span of 6 h. While the diffractogram clearly states that the compound is identified as $(H_3O)_2[CH_2(SO_3)_2]$, a discrepancy in intensities between the measured and simulated patterns is evident. The reflections at 14.5° (1 1 0) and 16.6° (1 1 –1) are lower in intensity, while the reflections at 28.6° (4 0 0) and 59.3°(6 0 0) are more intense in the measured pattern. This peculiarity is abrogated in the measurement collected at the *Stoe* diffractometer, operating in *Debye-Scherrer* geometry.



Figure 19: X-ray powder diffraction pattern of MSA in black with simulated pattern from $(H_3O)_2[CH_2(SO_3)_2]$ from Sartori in blue.^[109] The sample was measured as a flat preparation with Kapton foil for inert conditions and with Cu_{Kal} radiation in Bragg-Brentano geometry. An empty measurement of the Kapton foil was used for background substraction.

Looking at the crystal build-up, the preferred orientation is rooted in the layered structure of the single crystal. The acid crystallises in the space group C2/c with four formula units. The asymmetric unit consists of one crystallographically distinguishable SO₃-unit and one C-H moiety. The carbon atom possesses special site symmetry and occupies the two-fold rotational axis 4e. All SO₃-units point towards each other, resulting in a parallel alignment of $[CH_2(SO_3)_2]^-$ anions (Figure 20, p. 34). The hydroxonium cations are located in close proximity to the charged SO₃-functions. The acid was thoroughly dried

under reduced pressure and stored under argon atmosphere before investigations in its thermal stability were conducted via DSC-TG/MS (Figure 21).



Figure 20: Extended asymmetric unit and cross section of a measured single crystal of $(H_3O)_2[CH_2(SO_3)_2]$. Crystal structure is identical to literature known data delivered by Sartori et al.^[109]



Figure 21: DSC-TG/MS measurement of a sample of $(H_3O)_2[CH_2(SO_3)_2]$, heated with 5 K/min to a maximum temperature of 1260 K. Bottom shows the detected masses $(m/z = 15 \ (CH_3), m/z = 18 \ (H_2O), m/z = 44 \ (CO_2), m/z = 48 \ (SO), m/z = 64 \ (SO_2), m/z = 80 \ (SO_3)).$

Before the acid decomposes at 529 K (Onset) an initial loss of water takes place starting at approximately 350 K. The broad, slow loss of mass is affiliated with an equally broad signal in the mass spectrum for m/z = 18 (bottom, red curve). A rather continuous drop in sample mass is observed, where a clear distinction between loss of water and decomposition is not found. Roughly, the removal of water leads to an absolute mass loss of 19%, agreeing with the assumption, that the acid is indeed phase pure and only in its hydrated form as hydroxonium salt. As expected, the acid presumably decomposes to the fragments CH₃, SO₃, SO, and SO₂. At 570 K the acid has entirely decomposed. At roughly

750 K the DSC curve shows a small endothermic peak and the masses m/z = 64 (SO₂) and m/z = 48 (SO) are detected. Table 5 summarises the calculated mass losses and interprets the decomposition of the acid.

T _{Onset} [K]	T _{Offset} [K]	Mass loss [%]	Possible fragments	Remaining compound
347	469	19	H ₂ O/OH	$CH_2(SO_3H)_2$
529	556	70	CH ₃ , SO ₃ , SO, SO ₂	-

Table 5: Overview of the DSC/TG-MS Measurement of $(H_3O)_2[CH_2(SO_3)_2]$.

Lithium Methanedisulphonate

A reaction between LiOH and MDA at ambient conditions delivered crystalline material of lithium methanedisulphonate. The salt crystallises as Li₂[CH₂(SO₃)₂] in the orthorhombic space group *Pnma* with four formula units. The extended asymmetric unit is depicted in Figure 22 and consists of one crystallographically unique carbon atom, two unique sulphur atoms, one hydrogen and four unique oxygen atoms. The anion is located on a mirror plane, specifically the atoms O12, S1, C1, S2 and O22 occupy special 4c Wyckoff position. This leads to the symmetrical reproduction of O11, H1 and O21. $Li_2[CH_2(SO_3)_2]$ crystallises isotypically to lithium disulphate ($Li_2[S_2O_7]$), merely the central oxygen atom of the disulphate anion is replaced by carbon in the methanedisulphonate.^[110] Figure 22 on p. 36 depicts the asymmetric units and cross sections of the two crystal structures. A comparison of the cell parameters is given in Table 6, p. 36. The overall cell volume and the *c*-axis of the two unit cells are quite similar. The *a*-axis is roughly 34 pm longer in the disulphonate. A look at the cross section of the unit cell, exhibits the anions in parallel arrangement along the *a*-axis. Hence, probable cause for the elongated a-axis in the methanedisulphonate is the longer C-S distance as opposed to the S-O bond of the bridging oxygen atom in the disulphate.



Figure 22: Crystal structure of $Li_2[CH_2(SO_3)_2]$ (top). Extended asymmetric unit (thermal ellipsoids set to 70%) and cross section of the crystal, portraying the mirror plane along (0 1 0) (fractioned line, abbreviated with m). Structure of $Li_2[CH_2(SO_3)_2]$ is isotypic to $Li_2[S_2O_7]$ (bottom).^[110]

The S1-C1 bond is 178.1(2) pm long and the S2-C1 bond conducts of 177.2(2) pm. For comparison, the S1-O3 bond within $\text{Li}_2[S_2O_7]$ is 166.7(1) pm and the S2-O3 bond is 161.0(1) pm long. The *b*-axis is approximately 18 pm longer in the disulphate and is mostly influenced by the (terminal) SO₃-units. There is no significant difference in the SO bond lengths between the disulphate and methanedisulphonate (with the exception of S1-O3, S2-O3). The medium S-O bond length in $\text{Li}_2[CH_2(SO_3)_2]$ is 145.7(3) pm long and thus in the same range as found in the previously described methanesulphonates and the literature published methanedisulphonates Na₂[CH₂(SO₃)₂] and K₂[CH₂(SO₃)₂].^[93,111] Comparing the C-S bonds of lithium methanedisulphonate to those found for alkali methanesulphonates, a very small increase is observed.

Compound	$Li_2[CH_2(SO_3)_2]$	$Li_2[S_2O_7]^{[110]}$
<i>a</i> [pm]	1352.00(8)	1317.7(2)
<i>b</i> [pm]	806.87(6)	825.16(7)
<i>c</i> [pm]	489.87(3)	485.47(4)
V [Å ³]	534.39(6)	527.9(1)

Table 6: Comparison of Selected Cell Parameters of Li₂[CH₂(SO₃)₂] and Li₂[S₂O₇].

Lithium is coordinated by four oxygen atoms in the shape of a distorted tetragonal prism. The shortest Li-O distances lies between Li1-O11 with 195.3(3) pm and the longest between Li1-O21 with 213.2(3) pm. One anion coordinates as a two dentate ligand over O11 and O21, while the other oxygen atoms (O22, O12 and another O21) coordinate only terminaly. The same is evident for the lithium disulphate, where O21 equals O4, O11 equals O1, O22 equals O5 and O12 is replaced by O2. For comparison, in the disulphate the Li-O distances range from 194.8(4) pm (Li1-O1) to 213.3(4) pm (Li1-O4) and are therefore almost identical to those found in the methanedisulphonate.



Figure 23: Coordination sphere of Li in Li₂[CH₂(SO₃)₂] (left) and for comparison coordination sphere of Li in Li₂[S₂O₇].^[110]

Li₂[CH₂(SO₃)₂] is hygroscopic and thus best handled under inert, or water-free environment. After several days in the inert atmosphere of an argon glovebox, the compound still shows typical characteristics for hygroscopic chemicals. A strong adhesion to glass and other substrates and agglomeration of material is evident. For this reason phase purity was investigated with PXRD via a flat preparation of the material on a glass substrate. *Rietveld* refinement of the measured and simulated diffraction pattern indicates no further crystalline phases (Figure 24, p. 38). For the *Rietveld* refinement the cell parameters a, b, c and V were refined. Additionally the atom coordinates for the atoms O, C and S were refined and a preferred orientation along (1 0 0) was observed. Refinement of the preferred orientation along (1 0 0) yielded the parameter 0.742(2). A possible explanation for this directory might lie in the matching orientation of the shortest Li-O bonds (Li1-O11). Due to the difference in temperature during measurement, the refined cell parameters from the powder diffraction pattern are somewhat smaller.



Figure 24: X-ray powder diffraction pattern (black, cross) measured as a flat preparation with Cu_{Kal} radiation in Bragg-Brentano geometry, with Rietveld refinement (red) and difference curve (blue).

Parameters	Rietveld Refinement	Single Crystal
<i>a</i> [pm]	1358.03(3)	1352.00(8)
<i>b</i> [pm]	811.58(4)	806.87(6)
<i>c</i> [pm]	491.77(2)	489.87(3)
V [Å ³]	542.15(4)	534.39(6)
T [K]	293	100
Rwp	3.139	
Rexp	1.845	
Rp	2.438	
gof	1.701	

Table 7: Results of the Rietveld Refinement for Li₂[CH₂(SO₃)₂].

Rubidium and Caesium Methanedisulphonate

Conversion of the hydroxonium salt of methanedisulphonic acid with rubidium and caesium hydroxide led to the respective alkali methanedisulphonates. Rubidium and caesium methanedisulphonate crystallise isotypically in the monoclinic space group C2/c with four formula units. Furthermore, the obtained crystal structures are isotypic to the published crystal structure of K₂[CH₂(SO₃)₂] by *Truter*.^[111] As the provided data set is from 1962 and lacks in certain information, such as anisotropic displacement of the atoms, a single crystal of K₂[CH₂(SO₃)₂] was measured and compared to the rubidium and 38

caesium salts. More detailed data on the structure solutions and refinements can be found in the crystallographic tables for all three compounds (appendix p. 157 and following). Table 8 summarises and correlates selected cell parameters and bond lengths of the obtained crystal structures. As expected, $Cs_2[CH_2(SO_3)_2]$ exhibits slightly longer cell edges, as it incorporates the largest cation. The cell volume increases from $Rb_2[CH_2(SO_3)_2]$ to $Cs_2[CH_2(SO_3)_2]$ by roughly 12% and from $K_2[CH_2(SO_3)_2]$ to $Rb_2[CH_2(SO_3)_2]$ by roughly 8%. Bond lengths between the sulphur and oxygen atoms are very narrowly distributed and conduct of 145.7(5) pm in average (all structures), and the medium C-S bond is 178.4(2) pm. These findings agree with previously discussed bond lengths for the $[CH_2(SO_3)_2]^{2-}$ anion.

Table 8: Comparison of Selected Parameters of the Isotypic Structures of Potassium,Rubidium and Caesium Methanedisulphonate.

Compound	$K_2[CH_2(SO_3)_2]$	$Rb_2[CH_2(SO_3)_2]$	$Cs_2[CH_2(SO_3)_2]$
<i>a</i> [pm]	1239.0(2)	1282.05(6)	1331.45(7)
<i>b</i> [pm]	771.7(1)	771.93(4)	798.52(4)
<i>c</i> [pm]	724.2(1)	756.62(3)	786.61(4)
β[°]	90.149(7)	91.310(2)	91.791(2)
V [Å ³]	692.4(2)	748.60(6)	835.91(7)
density [g/cm ³]	2.421	3.062	3.496
d _{s1-C1} [pm]	178.1(1)	178.3(1)	178.8(2)
d _{S1-O11} [pm]	145.9(1)	146.4(1)	145.6(2)
ds1-012 [pm]	145.8(1)	145.8(1)	145.5(2)
ds1-013 [pm]	145.4(1)	145.8(2)	145.3(2)

The carbon atom is located on a twofold rotational axis (*Wyckoff* position 4e). Hence, Figure 25 on p. 40 depicts the extended asymmetric unit, displaying the entire methanedisulphonate anion, while crystallographically there is only one distinguishable SO₃-unit. The special site symmetry of the carbon atom is well recognised in the cross section pictures of the unit cell, where C1 is occupying positions on the cell edges and along the middle of the unit cell. In all three cases, the obtained compounds are hygroscopic, but crystallisation from aqueous solutions delivered no structures with incorporated crystal water. The structures consist of layers, formed by the difference in polarity of the anion. The CH₂-moities of the anions are facing each other and the counter cations surround the SO₃-units.



Figure 25: Crystal structure of Rb₂[CH₂(SO₃)₂] (left) and Cs₂[CH₂(SO₃)₂] (right). From top to bottom: Light microscope picture of the single crystals, extended asymmetric unit of the structure (70% probability level of thermal ellipsoids), cross sections of the unit cells.

While the lithium methanedisulphonate is isotypic to its disulphate, for rubidium and caesium this analogy cannot be proven. A literature survey offered no crystal structure for the respective rubidium disulphate, while $Cs_2[S_2O_7]$ crystallises in a triclinic unit cell.^[112] However, $K_2[CH_2(SO_3)_2]$ and $K_2[S_2O_7]$ show the same isotypy.^[113] Hence, all three methanedisulphonate structures from potassium to caesium are isotypic to $K_2[S_2O_7]$.

In all three isotypic compounds, the coordination number of the cation is nine. The coordination sphere is built by coordination of three O11, three O12 and three atoms of O13. As expected, shortest distances between the respective cation and oxygen are found for $K_2[CH_2(SO_3)_2]$ and distance between central cation and oxygen within the coordination sphere increases with cationic radii. The smallest distance lies between K1 and O12 and conducts 270.2(1) pm, while the longest distance is 334.0(1) pm (K1-O13⁶). For Rb and Cs, the longest distance lies between the cation and O13¹ (322.7(2) pm, 337.8(2) pm). For Rb the shortest interaction is between Rb1 and O12 with 285.3(1) pm and for Cs between Cs1 and O12² with 302.2(2) pm. While the distances between the respective cation and the coordinating oxygen are average in all compounds, the constant coordination number of nine is unexpected. A higher coordination number with larger cation, as found for the respective methanesulphonates (see Table 2, p. 26) is not evident. The coordination sphere of the individual cations was established with the software *Chardi2015*.^[105,106]



Figure 26: Coordination polyhedrons around K1, Rb1 and Cs1 in their respective methanedisulphonates.

Phase purity was proven by PXRD and *Rietveld* refinement of the measured pattern and the simulated data from the single crystal for Rb₂[CH₂(SO₃)₂]. The diffraction pattern and a table with the refined unit cell parameters and quality factors is given in the appendix (p. 238). After the assessment of phase purity, a DSC/TG-MS experiment was undertaken to compare the thermal decomposition of Rb₂[H₃CSO₃]₂ · H₂O with Rb₂[CH₂(SO₃)₂]. Figure 27 (p. 42) depicts the collected data. Between 300 and 400 K a slight drop in sample mass is detected in the red TG curve. Two broad signals are correlating to this mass loss, belonging to m/z = 17 (OH) and m/z = 18 (H₂O). From X-ray diffraction experiments, the incorporation of crystal water in form of hydrates has been ruled out. The hygroscopicity of the sample however, suggests a strong adhesion of water. Thus, the mass loss of 3.4% most likely stems from adhered water. Around 600 K a second drop in the TG curve occurs, while the expected masses for CO, CO₂, CH₃, CH₄, SO, SO₂ and

SO₃ were not detected. This mass loss of roughly 6% remains unsolved. Around 700 K the largest drop in the TG curve takes place and it is accompanied with the detection of the masses m/z = 44 (CO₂), m/z = 48 (SO) and m/z = 64 (SO₂). An overview on the detected mass loss and possible fragmentation is given in Table 9. Comparable to the decomposition of Rb₂[H₃CSO₃]₂ · H₂O, a sharp exothermic signal describes the decomposition of the anion, suggesting a *meta*-stable phase. After the decomposition step, 68.5% of the initial mass remain. Via PXRD the resulting compound was identified as Rb₂SO₄ (see appendix, p. 239), identical to the decomposition process of Rb₂[H₃CSO₃]₂ · H₂O. With 24.4 mg of starting material, and the assumption, that 3.5% of that sample consists of adhered water, the presumed absolute mass of Rb₂[CH₂(SO₃)₂] consists of 23.5 mg (0.068 mmol). With a remaining mass of 68.5% (16.7 mg) and under the assumption, that the persisting compound solely consist of the sulphate, 0.063 mmol of Rb₂SO₄ are generated.



Figure 27: DSC/TG-MS curve of a sample of $Rb_2[CH_2(SO_3)_2]$, measured with 5 K/min to a maximum temperature of 961 K. Bottom shows the detected masses $(m/z = 17 \text{ (OH)}, m/z = 18 \text{ (H}_2O), m/z = 44 \text{ (CO}_2), m/z = 48 \text{ (SO)}, m/z = 64 \text{ (SO}_2)).$

Table 9: Overview of the DSC/TG-MS Measurement of Rb₂[CH₂(SO₃)₂].

T _{Onset} [K]	T _{Offset} [K]	Mass loss [%]	Possible fragments	Remaining compound
297	377	3.4	H ₂ O/OH	$Rb_2[CH_2(SO_3)_2]$
453	606	6.2	unknown	unknown
708	713	18.0	CO_2 , SO , SO_2	Rb_2SO_4

IR measurements of all synthesized alkali MDS salts from lithium to caesium exhibit very similar datasets. The obtained spectra are depicted in the appendix and additionally an excerpt of the measured data is depicted from 450 cm^{-1} to 1700 cm^{-1} (p. 245). As a representative only the spectrum of Rb₂[CH₂(SO₃)₂] is shown below. A geometry optimisation for the anion [CH₂(SO₃)₂]²⁻ within density functional theory (DFT) was conducted using the *PBE0* exchange-correlation functional and a *cc-pVTZ* basis set for all elements.^[114] The results of the theoretical vibrational modes with assignment are compared with all measured bands in Table 10, p. 44.



Figure 28: Measured IR-spectrum for $Rb_2[CH_2(SO_3)_2]$ in black with calculated bands for the $[CH_2(SO_3)_2]^{2-}$ anion in olive green.

For the lithium, sodium and caesium salt, strong and broad additional bands are detected around 3000 and 1700 cm⁻¹, which can be assigned to the stretching vibration (above 3000 cm^{-1}) and the deformation vibration of H₂O (around 1700 cm⁻¹). Below 600 cm⁻¹ five different deformation vibrations are present, in which almost all atoms of the molecule are participating. For the calculated bands, the deformation vibration at 579 cm⁻¹ is the only one with moderate intensity. This is not the case for the measured bands. The difference can be gathered from the table below by the descriptions assigned to the intensity of the observed peak. At 623 cm⁻¹ the anion exhibits a deformation vibration of the CS₂-fragment, closer described by a scissoring movement. This rather weak vibration is distinct in all measured spectra.

LiMDS	NaMDS	KMDS	RbMDS	CsMDS	Theory	Assignment
465 s		459 w				
475 s						
498 s	504 sh	480 sh		479 <i>s</i>	493 w	δ -SO ₃
518 s	512 m	514 s	513 s	502 s	509 w	δ -CH ₂ SO ₂
537 s	538 m	533 m	533 m	527 m	522 w	δ -SO ₂
556 s					525 vw	δ -SO ₂
570 s	577 m	586 m	583 s	567 s	579 m	δ -SO ₃
601 sh	638 m	636 w	635 w	629 w	623vw	δ -CS ₂
650 m				637 w		
714 sh	739 m	735 w	770 m	770 m	741 w	v _{sym} -CS ₂
791 s	778 m	773 w	808 s	795 s	783 m	vasym-CS ₂
	792 m					
	822 w	811 m	827 sh	883 br	828 vw	δ -CH ₂
861 m	855 w					
995 br,s	1033 s	1021 m	1018 s	991 br	1022 s	v _{sym} -SO ₃
1028 sh	1068 m					
	1087 m	1060 w	1064 sh	1047 sh	1066 vw	v _{sym} -SO ₃
1093 s	1104 m	1076 sh	1074 w	1064 w		
1130 sh	1129 m	1128 sh	1096 vw	1116 sh	1107 vw	δ -CH ₂
1172 vs	1174 sh	1140 sh	1132 w	1147 br	1180 vw	δ -CH ₂
1213 vs	1194 s	1204 s	1200 s	1225 br	1234 vs	v_{asym} -SO ₃
1232 s	1204 s	1219 s	1214 s			
1245 sh	1241 m	1272 m	1228 s	1243 sh	1275 vs	vasym-SO3
	1286 vw		1266 m	1290 sh		
1371 w	1364 w	1379 vw	1383 w	1384 vw	1393 vw	δ -CH ₂
	1381 vw					
	1402 vw					
1696 br	1637 m			1692 br		δ -H ₂ O [*]
~3000 br	3430 br			~3000 br		$v-H_2O^*$
2955 m	2966 w	2972 w	2958 w	2939 w	3085 w	v _{sym} -CH ₂
3017 m	3022 m	3027 w	3015 w	3000 w	3155 w	vasym-CH2

Table 10: Measured IR-Bands for all Alkali Methanedisulphonate Salts and Theoretical Bands Based on DFT Calculations with Assignment.

*Assignment not based on Calculations.

At 741 cm⁻¹ and 783 cm⁻¹ the symmetric and asymmetric stretching vibration of the CS₂unit are represented by two peaks, which differ in their intensity. The symmetric stretching vibration has a weaker signal than the asymmetric stretching vibration. This is also true for the spectrum of Rb₂[CH₂(SO₃)₂]. The symmetric stretching vibration of the SO₃-groups is located around 1022 cm⁻¹ and 1066 cm⁻¹. The measured bands reveal a suspension of degeneracy, as at least one vibration is split into two individual bands. The same is evident for the bands assigned to the asymmetric stretching vibrations of the SO₃units around 1234 cm⁻¹ and 1275 cm⁻¹. A sort of "fingerprint" of the MDA salts are the very small but distinct vibrations around 3000 cm⁻¹ and 3020 cm⁻¹. These bands are always located at lower energy, when compared to the calculated data set (3085 cm⁻¹ and 3155 cm⁻¹) and are evident in all measured samples. These bands can be assigned to the symmetric and asymmetric stretching vibrations of the CH₂-group in the anion.

Barium Potassium Methanedisulphonate

According to the reaction as introduced by Backer, dichloromethane and potassium sulphite were converted hydrothermally in a sealed glass ampoule to $K_2[CH_2(SO_3)_2]$. An attempt at a salt metathesis, exchanging potassium with barium by reaction with BaCl₂, led to a peculiar single crystal of $BaK_2[CH_2(SO_3)_2]_2$. The obtained single crystal is the first bi-cationic compound, which is structurally elucidated. Obviously, the exchange of the cations was only partially successful. This most likely is due to the high driving force towards BaSO₄, which was identified as the main product of this synthesis by PXRD (appendix, Figure 105, p. 239). BaK₂[CH₂(SO₃)₂]₂ crystallises in the orthorhombic space group *Pbca* with eight formula units. The cell parameters are a = 957.54(5) pm, b = 1419.70(7) pm, c = 1969.6(1) and V = 2677.5(2) Å³. For more detailed data on the crystal structure and its refinement see crystallographic tables in the appendix (p. 164 and following). All atoms are located on general positions of the unit cell and the asymmetric unit consists of two crystallographically differentiated potassium cations, K1 and K2, and one unique barium cation, Ba1. As required for equalisation of charge, two methanedisulphonate anions counter the three cations. Bond lengths and angles of the two crystallographically distinguishable anions are very similar. The SO bond lengths lie between 145.13(6) pm (S22-O222) and 146.67(7) pm (S11-O112), hence show hardly any significance of deviation with the range of the stated error. The medium S-O bond is 145.7(2) pm long and correlates well with previously discussed S-O bonds of alkali methanedisulphonates. The medium C-S bond length is 178.5(2), which coincides well with the data provided for all alkali methanedisulphonates. A somewhat higher discrepancy is evident for the bond angles of the anion. The O-S-O angles range from $110.39(4)^{\circ}$ (O223-S22-O221) to $114.14(4)^{\circ}$ (O221-S22-O222). The same is found for the O-S-C angles, which lie between $102.22(4)^{\circ}$ (O222-S21-C2) and $108.34(4)^{\circ}$ (O121-S12-C1).

K2 🗟



Figure 29: Asymmetric unit of BaK₂[CH₂(SO₃)₂]₂ and cross section through the unit cell. Thermal ellipsoids are set at 70% probability level.

The structure has a layered build-up alternating in three different layers, reminding of a cubic close packing (*ccp*) made by the layers *A*, *B* and *C*. In this case, one layer incorporates all the cations, while the other two layers are formed by the anions, oriented in different fashions (Figure 30, p. 47). In one layer (*A*), the anions are stacked in two different orientations (180°) diagonal in the (0 0 1) plane. The next layer holds all cations, four potassium cations, in a *zig-zag* pattern along the *b*-axis and two barium cations. The last layer (*C*) portrays the anions stretched along the *b*-axis and arranged in a parallel

fashion along a, with alternating orientations, switching from one direction to the other in a 180° flip.



Figure 30: Illustration of the three layers found in $BaK_2[CH_2(SO_3)_2]_2$.

K1 and K2 are coordinated by seven oxygen atoms each, for Ba1 the coordination number is nine. All oxygen atoms participate in the coordination spheres of the cations. While O223 donates to K1, K2 and Ba1, O211 and O222 only participate in one coordination to Ba1, respectively. As stated above, the degree of participation to the cationic coordination spheres has no significant influence on the S-O bonds. For K1 the K-O distances range from 265.32(7) pm (K1-O113) to 316.43(8) pm (K1-O123). For K2 the shortest distance to oxygen lies between K2-O121 with 261.57(7) pm and the longest between K2-O111 with 299.34(8) pm. This coincides well with the average coordination of oxygen to potassium and agrees with the data mentioned beforehand. For Ba1, the shortest distance lies between Ba1-O212 with 268.52(7) pm and the longest between Ba1-O223 with 303.49(7) pm. These Ba-O distances are in the same range as those found for BaSO₄ (baryt).^[115]



Figure 31: Coordination polyhedrons within of BaK₂[CH₂(SO₃)₂]₂.

Four new crystal structures with the anion $[CH_2(SO_3)_2]^{2-}$ could be synthesised and characterised by single crystal X-ray diffraction. Through acid-base reactions of $(H_3O)_2[CH_2(SO_3)_2]$ with alkali salts the compounds $Li_2[CH_2(SO_3)_2]$, $Rb_2[CH_2(SO_3)_2]$ and $Cs_2[CH_2(SO_3)_2]$ were prepared in crystalline form. $Li_2[CH_2(SO_3)_2]$ is isotypic to Li₂[S₂O₇], while Rb₂[CH₂(SO₃)₂] and Cs₂[CH₂(SO₃)₂] are isotypic to K₂[CH₂(SO₃)₂] and $K_2[S_2O_7]$ Within the characterised structures, $[CH_2(SO_3)_2]^{2-}$ exhibits slightly longer C-S bonds (~2.5 pm) than [H₃CSO₃]⁻. Bond angles and lengths within the SO₃ unit(s) within $[H_3CSO_3]^-$ and $[CH_2(SO_3)_2]^{2-}$ are almost identical. Next to diffraction experiments on both single crystals and powders, the alkali salts of MDA were analysed by IRspectroscopy. The obtained vibrational bands for all compounds are very similar, showing an annulment of degeneracy for the asymmetric stretching vibrations of the SO₃-groups, unlike the calculated data by DFT for the isolated anion. A DSC/TG-MS measurement on Rb₂[CH₂(SO₃)₂] shows a decomposition of the compound around 700 K. Hence, thermal stability of MDA-salts is similar to MSA-salts. In both cases the decomposition of the alkali methane(di)sulphonate follows a first drop in the TG curve, suggesting an initial loss of water. The assumed water-free compounds then decompose with an exothermal signal in the DSC curves.

2.3. Methanetrisulphonic Acid (MTA) and Methanetrisulphonate Salts

Synthesis and Characterisation of K₃[CH(SO₃)₃] · H₂O

According to the facile preparation, introduced by Sartori and Jüschke, potassium methanetrisulfonate monohydrate was synthesized from oleum and acetone (Equation 25, p. 19).^[99] A survey applying several solutions of fuming sulphuric acid with varying SO₃ contents in the proposed reaction with dry acetone was conducted. Therefore, concentrated sulphuric acid was enriched with free SO₃ leading to oleum of 43%, 56%, 64% and 69%. Additionally, the commercially available acids with 20% and 65% SO₃ amount were utilised. The prepared solutions revealed different behaviour regarding their freezing points, which poorly influences the succession of the reaction, as cooling and stirring are the vital aspects of this synthesis.^[99,116,117] With the exception of the commercially obtained 65% (free SO₃) oleum solution, all attempts to synthesise $K_3[CH(SO_3)_3] \cdot H_2O$ starting from the prepared solutions, even with higher SO₃ content, failed. In those attempts, only K₂SO₄ was identified as product of the reaction. Thus, for all further syntheses dry acetone and purchased oleum (65% free SO₃) were combined dropwise at roughly 268 K under close observation. A slight brownish/cognac colouring of the reaction mixture is anticipated, but a darker brownish/black colouring of the mixture indicates the instantaneous decomposition of acetone and a failure of the synthesis, leading to only amorphous carbon residues and K₂SO₄. The temperature of the reaction mixture has to be meticulously kept above 263 K and below 273 K. Is the temperature to low, freezing of the solution will lead to an inhomogeneous concertation of starting material, as the magnetic stirring bar will be stuck, while the reaction mixture turns immediately black, when the temperature is too high. The same will happen in a miniscule region, when too much acetone is added at once and the exothermic reaction leads to a regional temperature increase. Once all the acetone is added (1:6 eq. with regard to amount of SO₃), a slow and stepwise heating of the reaction mixture is undertaken. After completion of the reaction (roughly 3 h) the reaction mixture is poured onto ice water and neutralised with KOH. This will inevitably generate large portions of K₂SO₄ next to the desired product. Several recrystallisation steps are required to ensure a product free of residual potassium sulphate. After recrystallisation, $K_3[CH(SO_3)_3] \cdot H_2O$ is obtained as colourless, large (~cm), needle shaped crystals. Phase purity was analysed by PXRD with *Rietveld* refinement. Figure 32 (p. 50) depicts the measured diffractogram with *Rietveld* fit and difference curve. The cell parameters *a*, *b*, *c* and *V*, as well as the atom coordinates for K1, K2, K3 and all sulphur and oxygen atoms were refined. Table 11 lists the processed cell parameters of the powder and quality factors for the fit. The cell parameters prior and after *Rietveld* refinement are close to a tetragonal lattice.



Figure 32: X-ray powder diffraction pattern (black, cross) measured in an 0.3 mm capillary with M_{OKal} radiation, with Rietveld Refinement (red) and difference curve (blue). The reference was taken from a measured single crystal of $K_3[CH(SO_3)_3] \cdot H_2O$.

Parameters	Rietveld Refinement	Single Crystal
<i>a</i> [pm]	941.60(6)	934.90(2)
<i>b</i> [pm]	940.82(5)	934.90(2)
<i>c</i> [pm]	1233.62(6)	1228.01(3)
V [Å ³]	1092.8(1)	1073.33(4)
T [K]	293	293(2)
Rwp	10.097	
Rexp	11.064	
Rp	7.697	
gof	0.913	

Table 11: Results of the Rietveld Refinement for $K_3[CH(SO_3)_3] \cdot H_2O$.

K₃[CH(SO₃)₃] · H₂O loses its crystal water between 400-420 K (Figure 33, p. 51). The measured DSC/TG-MS data shows a drop in the TG curve of roughly 6%, which is only slightly more than the calculated mass loss for the monohydrate (4.7%). At the same temperature window a detection of the masses m/z = 17 (OH) and m/z = 18 (H₂O) is

observed. The methanetrisulphonate is stable up to 650 K and decomposes below 700 K with a strong exothermic peak and the presumable fragmentation into SO, SO₂ and CO₂. A mass loss of 52.5% takes place and that leaves approximately 46% of initial mass after this decomposition step. The remaining sample was submitted to PXRD and identified as K_2SO_4 (see appendix, Figure 106, p. 240). Overall, with the gathered intel on the thermal decomposition of $Rb_2[H_3CSO_3]_2 \cdot H_2O$, $Rb_2[CH_2(SO_3)_2]$ and $K_3[CH(SO_3)_3] \cdot H_2O$, it can be stated, that no clear trend towards higher or lower thermal stability is observed for alkali methane- and polysulphonate salts. Table 12 summarises the observed TG-data with possible fragmentation based on the detected masses.



Figure 33: DSC/TG-MS measurement of $K_3[CH(SO_3)_3] \cdot H_2O$, heated with 7 K/min to a maximum temperature of 823 K. The detected masses are depicted in the bottom: m/z = 17, m/z = 18, m/z = 44, m/z = 48, m/z = 64.

Table 12: Overview of the DSC/TG-MS Measurement of K₃[CH(SO₃)₃].

T _{Onset} [K]	T _{Offset} [K]	Mass loss [%]	Possible fragments	Remaining compound
347	445	6.5	H ₂ O/OH	K ₃ [CH(SO ₃) ₃]
683	688	52.2	CO ₂ , SO, SO ₂	K_2SO_4

Methanetrisulphonic Acid Trihydrate

Starting from the potassium salt, the acid is easily accessible with the aid of an ion exchange column with a strong acidic stationary phase. The exchange of potassium cations with protons takes place in aqueous solution, wherefore the acid is yielded highly diluted in water. Large amounts of water can be reduced by rotary evaporation, followed by a more thorough drying procedure at the Schlenk line with lower pressure (~0.001 mbar). Afterwards the product consists of needle shaped colourless crystals within a slightly rose coloured liquid of high viscosity. At this point the yield of the crude product is roughly 148%, thus a high amount of water is still present. So far no method of characterisation (NMR, IR or XRD) could hint at the reason for the slight colouring of the sample, since both methanetrisulphonic acid and the starting material $(K_3[CH(SO_3)_3] \cdot H_2O)$ are colourless. Most likely, the colouring derives from some part of the composition of the exchange resin. This suggestion however, is purely based on speculation due to the orange/reddish colour of the resin. The acid hydrate is stored under inert atmosphere in an argon-filled glovebox. Within time (~months) more crystals grow from the liquid. The crystals were submitted to single crystal diffraction and the compound was characterised as the hydroxonium salt of methanetrisulphonic acid trihydrate. Interestingly, the solved crystal structure is not identical to the one provided by Oelkers et al.^[101] The found crystal structure has been previously mentioned in a science lab course within this research group (Oldenburg, 2011), but has not been published on any database. The following data was obtained within the scope of this dissertation. $(H_3O)_3[CH(SO_3)_3]$ can crystallise in the hexagonal space group $P6_3$ or in the trigonal space group R3c. Cell parameters are of the same magnitude, as Table 13 shows.

Cell Parameters	$(H_3O)_3[CH(SO_3)_3]^{[101]}$	(H ₃ O) ₃ [CH(SO ₃) ₃]
Crystal system	hexagonal	trigonal
Space group	<i>P</i> 6 ₃	R3c
<i>a</i> [pm]	1365.48(2)	1322.13(4)
<i>b</i> [pm]	1365.48(2)	1322.13(4)
<i>c</i> [pm]	931.93(1)	977.40(5)
V [Å ³]	1504.82(5)	1479.6(1)
T [K]	150	99

Table 13: Comparison of the Two Modifications Found for (H₃O)₃[CH(SO₃)₃].

Within the trigonal crystal structure, the asymmetric unit is made up by one anion, and one differentiated hydroxonium cation. The carbon atom C1 and its attached hydrogen atom H1 are situated on a threefold screw axis (31, *Wyckoff* position *6a*). Thus, Figure 34 (top) depicts the extended asymmetric unit, showing all crystallographically identical SO₃-functions on the carbon atom. The hexagonal structure is similar, but of slightly less symmetry. Here, the asymmetric unit consists of three unique carbon atoms, their attached hydrogen atoms and one SO₃ function, respectively (see Figure 34, bottom). C2, H2, C3 and H3 are located on a three-fold rotaional axis (*Wyckoff* position *2b*) which generates the crystallographically identical SO₃-groups around each carbon atom. C1 and H1 are located on the cell edges on a six-fold screw axis (*6*₃, *Wyckoff* position *2a*). The cross section of the two unit cells, clearly shows the small differences in the two structures. In the hexagonal structure, the anions located fully within the unit cell are not superimposed, as the rotational axis which C2, C3 and H1, H2 occupy does not include the translation which generates the perfect allignement in the trigonal space group.



Figure 34: Top: Crystal structure and extended asymmetric unit of $(H_3O)_3[CH(SO_3)_3]$ in the trigonal space group R3c. Bottom: Crystal structure and asymmetric unit of $(H_3O)_3[CH(SO_3)_3]$ in the hexagonal space group P6₃.

Both structures give similar bond lengths and angles for the $[CH(SO_3)]^{3-}$ anion. The S-O bond lengths range from 143.3(1) pm to 147.2(1) pm and the medium S-O bond length for both structures is 145.6(6). For comparison, within K₃[CH(SO₃)₃] · H₂O, the shortest S-O bond is at 144.3(2) pm and the longest conducts of 145.9(2) pm, with an arithmetic mean of 145.1(6) pm. Differences in the S-O bond lengths within one structure could be

a result of different participation in hydrogen bonding of the oxygen atoms at the SO₃-groups. For the acid, crystallising in *R*3*c* for instance, the shortest S-O bond lies between S1-O11 while the longest lies between S1-O13. O11 does not contribute to H-bonding, while O13 participates in two hydrogen bridges (appendix, Table 95). The C-S bonds within the acid range from 181.4(1) pm to 182.4(1) pm. In the potassium salt, the C-S bond lengths are of the same magnitude with values between 180.8(2) pm and 182.0(2) pm. Obviously, the C-S bond is highly affected when an additional SO₃-unit is inserted. Table 14 compares the three analysed acids and their observed bond lengths. The S-O bonds are not influenced by the amount of SO₃-functions at the carbon centre, as can be seen when comparing MDA with MTA. For MSA, the medium S-O bond differs, as it is the only "naked" acid with the hydrogen atom attached to an oxygen atom at the SO₃-unit. This of course, weakens the S-O bond, which is why the S1-O12 bond is elongated and a medium bond length for S-O within MSA is less informative. The C-S bond lengths increase with each substitution of hydrogen with SO₃.

Table 14: Comparison of the Medium Bond Lengths within (Poly)sulphonic Acids of Methane.



Both modifications for $(H_3O)_3[CH(SO_3)_3]$ can be obtained from the synthesis as stated above. Frequently, the hexagonal structure was encountered directly after the synthesis in the crude product, while the trigonal structure was usually found after recrystallisation and thermal treatment. The two modifications could be gathered separately (PXRD with Rietveld refinement in the appendix, p. 240 and following) or as a mixed phase. Figure *35* (p. 55) depicts the *Rietveld* refinement of a sample with both modifications present. After refinement of cell parameters and under liberalisation of the atom position of the carbon atoms and the free oxygen atoms of the hydroxonium cations, a mixture of 8.64% to 91.36% (*R*3*c* : *P*6₃) was identified. Cell parameters and quality factors of the *Rietveld* refinement are stated in Table 15.



Figure 35: X-ray diffraction pattern of a sample of $(H_3O)_3[CH(SO_3)_3]$ with both modification present, measured with M_{OKal} radiation in a 0.3 mm capillary. Rietveld refinement for both modifications (P6₃, R3c) is added in red with the difference curve in blue.

Parameters	R3c	<i>Rietveld</i> Refinement	<i>P</i> 6 ₃	<i>Rietveld</i> Refinement
<i>a</i> [pm]	1322.13(4)	1328.4(6)	1365.48(2)	1391.75(8)
<i>b</i> [pm]	1322.13(4)	1328.4(6)	1365.48(2)	1391.75(8)
<i>c</i> [pm]	977.40(5)	981.4(3)	931.93(1)	942.17(6)
V [Å ³]	1479.6(1)	1496(10)	1504.82(5)	1581.2(6)
T [K]	99	293	150	293
[%]		8.64		91.36
Rwp		13.114		13.114
Rexp		12.035		12.035
Rp		10.209		10.209
gof		1.090		1.090

Table 15: Rietveld Refinement of $(H_3O)_3[CH(SO_3)_3]$ for a sample with both crystal structures present.

Thermal analysis of the acid was conducted in sealed quartz glass ampoules in the hope to better understand the transition between the two phases. Figure 36 on p. 56 depicts the two measured cycles in a temperature range from room temperature to 473 K. The acid has a melting point of roughly 440 K and freezes around 356 K. There is no indication of another phase transition. The exo- and endothermic signals of the melting and recrystallisation process are similar in both cycles. The powder diffraction pattern of the

sample after the DSC measurement is given in the appendix (p. 240) and it solely shows reflections of the trigonal crystal structure.



Figure 36: DSC measurement ($[\mu V/mg]$) of (H₃O)₃[CH(SO₃)₃] in a sealed glass ampoule, measured with 2 K/min to a maximum temperature of 473 K.

Lithium Methanetrisulphonate Tetrahydrate

After a hydrothermal reaction between LiOH and MTA in a sealed glass ampoule, colourless crystals of Li₃[CH(SO₃)₃] · 4 H₂O were yielded and could be solved by X-ray diffraction. The analysed crystal portrays the lithium salt in the monoclinic space group $P2_1/c$. Macroscopically, the crystals are thin, elongated plates, which adhere to one another.



Figure 37: Light microscope picture of the Li₃[CH(SO₃)₃] · 4 H₂O crystals

Lithium methanetrisulphonate tetrahydrate crystallises with four formula units with the cell parameters a = 747.90(4) pm, b = 1006.63(5) pm, c = 1545.32(7) pm, $\beta = 100.274(2)^{\circ}$ and V = 1144.8(1) Å³. All atoms possess general site symmetry 4e and thus the asymmetric unit consists of three unique lithium cations, one methanetrisulphonate anion and four water molecules (Figure 38). Similar to the sodium, potassium and caesium methanetrisulphonate, the lithium salt is a hydrate. However, the load of water within the crystal structure is the highest for Li₃[CH(SO₃)₃] · 4 H₂O.



Figure 38: Crystal structure of Li₃[CH(SO₃)₃] · 4 H₂O: Asymmetric unit with atom labels (thermal ellipsoids are set to 70% probability) and cross sections of the unit cell. Bottom: Additional polyhedrons around the sulphur atoms.

While the potassium salt crystallises in the orthorhombic space group, the other alkali methanetrisulphonate salts all crystallise in space group No. 14. While the observed structures show some similarities, no structures are isotypic. Figure 38 depicts the asymmetric unit and cross section of the unit cell. Additionally, cross sections of the unit cell are portrayed with polyhedrons around the sulphur atoms for more overview. These distorted tetrahedrons are spanned between the carbon atom of the anion and the three oxygen atoms of the respective SO₃-unit. Akin to $K_3[CH(SO_3)_3] \cdot H_2O$, the lithium salt builds layers. One layer consists of the anions and one set of lithium cations (Li2) while

all water molecules, Li1 and Li3 make up the other layer. There are three different coordination spheres for Li. With the aid of the program *Polynator* polyhedrons can be further analysed and classified regarding their closest fit towards a perfect polyhedron.^[118] The deviation from the perfect geometrical polyhedron is given in form of a distortion parameter (δ), which goes against zero for a perfect alignment and is higher, the more the polyhedron is distorted. Li1 has the coordination number six and the octahedron formed is a twisted trigonal prism ($\delta = 3.196$).^[118] Li2 and Li3 are coordinated by five oxygen atoms and build a highly distorted polyhedron. All oxygen atoms of the SO₃-groups and the water molecules participate in the bond to lithium. The shortest Li-O bond lies between Li1-O1 with 189.7(3) pm and the longest between Li1-O12 with 227.9(3) pm. The coordination radius is therefore quite similar to that found for lithium methanedisulphonate. Solely the Li1-O12 bond is rather elongated, when compared to typical Li-O distances. The coordination sphere around the lithium cation was identified using the software *Chardi2015*.^[105,106]



Figure 39: Coordination around Li1, Li2 and Li3 in $Li_3[CH(SO_3)_3] \cdot 4 H_2O$

Hydrogen bridging occurs between the water molecules and the oxygen atoms of the SO₃-groups. Criteria for H-bonding is a relatively close distance between donor and acceptor oxygen (below 300 pm) and a O_D-H-O_A angle close to 180° (between 110- 250°).^[107] O11 builds two H-bonds to H1B and H2A with distances below 300 pm and angles above 160° (for more detail, see appendix, crystallographic tables p. 170 and following). O13, O23, O31 and O33 are participating in one hydrogen bond each while O12, O21, O22 and O32 do not engage in intermolecular bonds. Figure 40 on p. 59 depicts the discussed hydrogen bridges within Li₃[CH(SO₃)₃] · 4 H₂O.



Figure 40: Hydrogen bridging within $Li_3[CH(SO_3)_3] \cdot 4 H_2O$

S-O bond lengths within the anion are in agreement with those found for other methane(poly)sulphonate salts and are distributed between 144.4(1) pm (S2-O22, S3-O32) and 146.3(1) pm (S1-O11). The degree of participation in the hydrogen bridges possibly has an influence in the small nuances between the various S-O bond lengths. The longest S-O bond is found for O11, which contributes to two hydrogen bonds, while the shortest S-O bonds are found for O32 and O22, which are not weakened by intermolecular forces. One C-S bond is slightly shorter than the other two. The S1-C1 bond obtains 180.8(2) pm, while C1-S2 is 182.4(2) pm and C1-S3 is 182.2(2) pm long. A possible explanation for the slightly elongated C1-S1 bond might be the high participation from O12 to the coordination sphere of Li1 and Li3, as well as the high participation in H-bridging by O11.

Li₃[CH(SO₃)₃] \cdot 4 H₂O crystallises phase pure, which shows in the respective powder Xray diffraction pattern. Regardless of the preparation method, whether yielded from hydrothermal synthesis at elevated temperatures, or at ambient conditions from aqueous solutions, the diffractogram of the ground powders concurs well with those simulated for Li₃[CH(SO₃)₃] \cdot 4 H₂O (Figure 41, p 60).



Figure 41: Powder X-ray diffraction pattern (black) and Rietveld refinement (red) for $Li_3[CH(SO_3)_3] \cdot 4 H_2O$. The sample was measured with Mo_{Kal} radiation in a 0.3 mm capillary. The difference curve is added in blue.

Table 16 lists the refined cell parameters and quality factors from the *Rietveld* fit. Due to the difference in temperature between the measured powder X-ray diffraction (RT) and single crystal X-ray diffraction (101 K) experiments, the cell parameters of the *Rietveld* refinement are slightly increased. Additionally, atom positions of all sulphur and oxygen atoms were refined.

Parameters	Rietveld Refinement	Single Crystal
<i>a</i> [pm]	751.72(4)	747.90(4)
<i>b</i> [pm]	1011.96(4)	1006.63(5)
<i>c</i> [pm]	1559.34(6)	1545.32(7)
β [°]	100.679(3)	100.274(2)
V [Å ³]	765.3(3)	748.60(6)
T [K]	293	101
Rwp	6.466	
Rexp	5.779	
Rp	4.989	
gof	1.119	

Table 16: Rietveld Refinement for $Li_3[CH(SO_3)_3] \cdot 4 H_2O$.

Rubidium Methanetrisulphonate Monohydrate

With the preparation and analysis of a single crystal of $Rb_3[CH(SO_3)_3] \cdot H_2O$, the series of alkali methanetrisulphonates started by *Oelkers* and co-workers is completed.^[101] Equal to the respective potassium salt, the rubidium methanetrisulphonate crystallises as a monohydrate in the same space group $P2_12_12_1$ with similar cell parameters. The rubidium salt is solved as an inversion twin. While the two structures are very similar, they are not isotypic, as the atom positions cannot be brought in alignment, even considering switching of the axes, shifting the origin or inverting the structure obtained for $Rb_3[CH(SO_3)_3] \cdot H_2O$.

Compound	$K_3[CH(SO_3)_3] \cdot H_2O$	$Rb_3[CH(SO_3)_3] \cdot H_2O$
<i>a</i> [pm]	934.90(2)	963.94(5)
<i>b</i> [pm]	934.90(2)	966.25(5)
<i>c</i> [pm]	1228.01(3)	1250.87(6)
V [Å ³]	1073.33(5)	1165.1(1)
density [g/cm ³]	2.404	3.008
Flack	-0.01(1)	0.027(5)

Table 17: Comparison of Cell Parameters for the Two Similar Structures $Rb_3[CH(SO_3)_3] \cdot H_2O$ and $K_3[CH(SO_3)_3] \cdot H_2O$.

Macroscopically, there are two sets of crystals obtained, which both resulted in the same cell, when analysed on the diffractometer. Figure 42 (p. 62) depicts the light microscope pictures of the synthesised crystals. Thin needles, which are very long in the magnitude of ~1 cm grow in a star-like appearance, sharing one origin and stretching outwards in a 360° radius. These needles optically appear as one phase, when analysed under the polarised light. Next to the longer, but significantly thinner needles, block-type crystals were obtained, shaped in a trapezium form. When analysed under the polarised light of the microscope, the crystals appear as multi-domain solids and are thus most likely built by adhered smaller crystallites. For the X-ray experiments, the crystals were broken down, or rather cut for suitable data collection.



Figure 42: Single Crystals obtained in a crystallisation dish after evaporation of solvent from an aqueous solution of Rb₃[CH(SO₃)₃].

All atoms possess general site symmetry and therefore, the asymmetric unit is built by one water molecule, one methanetrisulphonate anion and three individual rubidium cations. Again, a tendency towards layered structures is observed:



Figure 43: Crystal structure of $Rb_3[CH(SO_3)_3] \cdot H_2O$. Top: Asymmetric unit with thermal ellipsoids (set to 70%) and two different cross sections through the cell. The bottom right corner depicts a multi-cell view of the (0 1 0) plane.

These layers are not as easily defined as for $Li_3[CH(SO_3)_3] \cdot 4 H_2O$ but are well recognised in the multi-cell description (Figure 43, bottom right). The formed layers can

be descibed as rubidium rich and rubidium poor. Within one layer more rubidium cations and the water molecules are located, whereas the other layer is mostly made up by the anions. For a better overview, the picture shows the anions with polyhedrons around the sulphur atoms. These tetrahedrons are distorted, as the O-S-O angles are larger than the ideal tetrahedral angle of 109.5°, while the O-S-C angles are smaller. The C-S bond lengths are 182.6(3) pm for S1-C1, 182.1(3) pm for S2-C2 and 182.0(3) pm for S3-C3. The S-O bond lengths are almost identical, ranging from 145.1(2) pm (S3-O31) to 145.9(2) pm (S1-O11). These bond lengths are therefore, close to what was determined for the lithium salt. The structure was investigated on potential H-bonds between the crystal water and the SO₃-units of the anions. Two are found, one bridging from O21 over H1B to O1 and one from O11 over H1B to O1. The distances between donor and acceptor oxygen are below 300 pm and the angles are $144(6)^{\circ}$ (O1-H1B-O11) and $134(6)^{\circ}$ (O1-H1BO21). Another, but weaker interaction, lies between O11-H1A-O1. Here the distance between donor and acceptor lie slightly above 300 pm and the O11-H1A-O1 angle obtains $148(5)^{\circ}$.



Figure 44: H-Bonds in $Rb_3[CH(SO_3)_3] \cdot H_2O$.

The coordination polyhedrons for Rb1, Rb2 and Rb3 resemble those found for K1, K2 and K3 in K₃[CH(SO₃)₃] \cdot H₂O. Only the atom labels and distances between central cation and coordinating atoms vary (Figure 45, p. 64). For Rb1 the coordination number is eleven, for Rb2 it is eight and for Rb3 it is nine. For Rb1 the shortest distance lies between Rb1-O33 with 287.3(2) pm and the longest between Rb1-O12 with 367.2(2) pm. For comparison, the isostructural K3 cation has the closest oxygen within a proximity of 273.10(2) pm and the furthest away at 361.51(3) pm. The shortest Rb2-O bond lies between Rb2-O31 with 277.2(2) pm and the longest between Rb2-O32 with 315.0(2) pm. Within the equal potassium cation, the shortest bond obtains 266.18(2) pm and the longest 301.48(2) pm.



Figure 45: Coordination of Rb1, Rb2 and Rb3 in $Rb_3[CH(SO_3)_3] \cdot H_2O$. For comparison the coordination polyhedrons around K1, K2 and K3 from the similar compound $K_3[CH(SO_3)_3] \cdot H_2O$ are given without atom labels.

Lastly, for Rb3 the distances range from 279.5(2) pm (Rb3-O33) to 333.8(2) pm (Rb3-O32). For the respective potassium cations the distances range from 267.57(2) pm to 326.92(3) pm. Therefore, the coordination bonds are of the same magnitude, with those for the similar structure $K_3[CH(SO_3)_3] \cdot H_2O$ only roughly 5-10 pm shorter, due to the
smaller cationic radius. All oxygen atoms coordinate to Rb, with the highest participation coming from O1, the oxygen atom of the water molecule. All oxygen atoms bonded to sulphur coordinate to all three unique cations, with the exception of O11, O13 and O21, which only coordinate to two rubidium cations, respectively.

Powder diffraction measurements show the crystallographic purity of the yielded compound. A *Rietveld* refinement of the experimentally obtained diffractogram is given in Figure 46. The blue difference curve reveals small discrepancies for the reflections with highest intensities. Due to the difference in temperature during the single crystal and powder diffraction, all cell parameters were refined. Also, the atom positions of all rubidium cations, sulphur atoms and O1 were refined. Additionally, a preferred orientation along (0 1 1) was refined and yielded the parameter 1.190(5), indicating an underrepresentation of this direction. The Rb cations are positioned along the (0 1 1) plane (see Figure 43, p. 62). Table 18 on page 66 lists the refined cell parameters and quality factors of the *Rietveld* fit.



Figure 46: Powder diffraction pattern and Rietveld refinement for $Rb_3[CH(SO_3)_3] \cdot H_2O$. The sample was measured as a flat preparation with $Cu_{K\alpha l}$ radiation in Bragg-Brentano geometry.

Rietveld Refinement	Single Crystal
969.64(2)	693.94(5)
973.76(2)	966.25(5)
1261.74(2)	1250.87(6)
1191.34(4)	1165.1(1)
293	100
3.178	
0.446	
2.226	
7.131	
	Rietveld Refinement 969.64(2) 973.76(2) 1261.74(2) 1191.34(4) 293 3.178 0.446 2.226 7.131

Table 18: Rietveld Refinement for $Rb_3[CH(SO_3)_3] \cdot H_2O$.

Silver Methanetrisulphonate Monohydrate

A single crystal of silver methanetrisulphonate monohydrate was analysed via X-ray diffraction after the successful hydrothermal reaction between silver(I)carbonate and MTA in a sealed glass ampoule. The salt was first synthesised and characterised by *Bagnall* in 1899.^[119] *Bagnall* obtained the silver salt by neutralisation of pure MTA with a freshly prepared solution of Ag₂CO₃. After evaporation of solvent (water), crystals were collected, which contained one equivalent of water. According to Bagnall, the crystal lattice for silver methanetrisulphonate is orthorhombic. While the silver salt does crystallise as a monohydrate, the observed crystal lattice for the measured single crystal is monoclinic. The measured crystal of $Ag[CH(SO_3)_3] \cdot H_2O$ crystallises in the space group $P2_1/n$ with four formula units and the cell parameters a = 682.42(5), b = 983.89(7) pm, c = 1439.9(1) pm, $\beta = 98.194(3)^{\circ}$ and V = 956.9(1) Å³. Interestingly, these results differ from unpublished data obtained in this research group for Ag[CH(SO₃)₃] \cdot H₂O. In 2011 during a practical lab course at the university in Oldenburg, a single crystal of Ag[CH(SO₃)₃] \cdot H₂O was solved in the monoclinic space group $P2_1/c$ a = 756.0(1), b = 2167.5(4) pm, c = 5.960(1) pm, $\beta = 97.58(3)^{\circ}$ with and V = 968.0(3) Å³. Due to the similar cell volumes, a high and low temperature modification is unlikely. This, unpublished data could be reproduced in another synthesis and the yielded crystals were submitted to single crystal diffraction in order to compare the two datasets. The second, precedent structure was solved as a two domain twin. In the following, the newly obtained structure for Ag[CH(SO₃)₃] \cdot H₂O in the space group $P2_1/n$ will be discussed (*Structure A*) and compared to the measured single crystal, with the precedent solution in $P2_1/c$ (*Structure B*). Details of the diffraction experiments and refinements are listed in the crystallographic tables.

In both crystal structures, all atoms are located on general positions of the unit cell and the asymmetric unit entails three unique silver cations, one methanetrisulphonate anion and one molecule of water. Cross sections through the unit cell show a varying parallel stacking of the anions, resulting in a layered structure of the compound. For *Structure A* (Figure 47) neighbouring anions within one layer are positioned in alternating, differing by 180° , orientations. This is represented best in the cross section depicting the (0 1 0) plane. Thus, the hydrogen atom at the central carbon atom protrude out of the layer in two directions, which deviate by 180° . Furthermore, this arrangement allows an orientation of hydrogen atoms towards each other (C-H···H-C).



Figure 47: Crystal structure of $Ag_3[CH(SO_3)_3] \cdot H_2O$ in Structure A. Top: Asymmetric unit with thermal ellipsoids (set to 70%) and two different cross sections through the cell.

For *Structure B* (Figure 48) there are also two different orientations for the anions available, which are interchangeable by a 180° rotation. The cross section showing the

(100) plane depicts four layers of two anions respectively, which share the same orientation and are thus arranged in a parallel fashion. Next to the rotation by 180°, the anion is also tilted in two different directions. Along viewing direction of the *c*-axis the inversion centre of the unit cell becomes prominent. There are clear areas of high amount of water and silver, and layers of stacked anions. These layers do not continue throughout the lengths of the unit cell and instead two sets of the same layers are obtained, shifted with regard to one another by $\frac{1}{2}a$.



Figure 48: Crystal structure of $Ag_3[CH(SO_3)_3] \cdot H_2O$ in Structure B. Top: Asymmetric unit with thermal ellipsoids (set to 70%) and two different cross sections through the cell.

Comparing *Structure A* with *Structure B* it becomes evident, that the main difference lies in the orientation and stacking of the methanetrisulphonate anions.

Bond lengths for the anion within $Ag_3[CH(SO_3)_3] \cdot H_2O$ are almost identical with those previously described for $Rb_3[CH(SO_3)_3] \cdot H_2O$. S-O bonds lie between 145.2(2) pm (S1-O11) and 146.8(2) pm (S3-O31) (for *Structure A*) and 144.7(3) pm (S1-O11) and 146.5(3) pm (S2-O21) (for *Structure B*) and C-S bonds are 181.6(3) pm, 181.8(3) pm and 181.3(3) pm (*Structure A*) and 183.0(4) pm, 181.7(4) pm and 182.0(4) pm (*Structure B*). The depicted tetrahedrons around the sulphur atoms are distorted, as the O-S-O angled

deviate from the C-S-O angles. While the O-S-O angles are larger than what would be the ideal tetrahedral angle, the C-S-O angles are smaller. Exemplary for *Structure A*, values of the O-S-O angles range from $111.6(1)^{\circ}$ (O21-S2-O23, O31-S3-O32) to $114.3(1)^{\circ}$ (O33-S3-O31). The C-S-O angles on the other hand range from $103.7(1)^{\circ}$ (O33-S3-C1) to $107.3(1)^{\circ}$ (O31-S3-C1).

The coordination number for silver varies between five and seven. For *Structure A* The shortest Ag-O distance lies between Ag3-O1 and conducts 225.8(2) pm. The longest Ag-O bond is between Ag1-O32 with 301.3(2) pm. For comparison, within Ag[H₃CSO₃] the Ag-O distances lie in between 234.8(3) pm and 292.1(4) pm. The coordination from O32 can be considered rather weak, as the distance is relatively long, when compared to other Ag-O bond lengths.^[120-122] O21 and O31 show the highest participation in coordination, as they coordinate to all three unique Ag cations. Oll and Ol3 only coordinate to one cation, respectively. Unlike the coordination as found in the rubidium salt, the oxygen atom of the water molecule (O1) only coordinates to Ag3 and thus has the lowest impact on the coordination sphere of silver. While the S-O bond lengths are quite narrow, small deviations root in the different degree of participation in coordination from the respective oxygen atoms. As mentioned above, for Structure A, the shortest S-O bond lies between S1-O11 and the longest between S3-O31. Similar results are found for Structure B. Here, the shortest Ag-O distance lies between Ag1-O1 with 229.8(3) pm and the longest between Ag1-O13 with 315.4(3) pm. Highest participation in coordination bonds to silver comes from O13 and O22, lowest from O33, which does not coordinate to any silver cation.



Figure 49: Coordination polyhedrons for Ag1, Ag2 and Ag3 within $Ag_3[CH(SO_3)_3] \cdot H_2O$ in both obtained structures.

While O11 and O13 within *Structure A* have a small influence on the coordination of the cations, they build hydrogen bridges to the water molecule within the structure. O11 bonds over H1A to O1, while O13 bridges towards H1B to O1. The distances between donor and acceptor oxygen are 287.4(3) pm (O1-H1A…O11) and 277.7(3) pm (O1-H1B…O13) and the angles are $168(5)^{\circ}$ (O1-H1A-O11) and $156(6)^{\circ}$ (O1-H1B-O13). Within *Structure B*, H-bridges are found between O33 to H1B and H1A, from O11 to H1A and from O23 to H1A. Further details can be found in the crystallographic tables for both structures (appendix, p. 178 and following).



Figure 50: H-Bridging within $Ag_3[CH(SO_3)_3] \cdot H_2O$.

Synthesis between silver(I)-carbonate (or silver(I)acetate) with MTA delivers single crystals of $Ag_3[CH(SO_3)_3] \cdot H_2O$. Apparently, the synthetic procedure influences the modification of the gathered solid. *Structure A* was obtained in a solvothermal process, using Ag_2CO_3 and MTA in a 1:1.5 ratio with a small amount of water. The maximum temperature was relatively moderate with 373 K. A slow cooling rate of 0.8 K/h was applied. In 2011 *Structure B* was obtained from an aqueous solution of a reaction mixture of Ag_2CO_3 and MTA. This mixture was heated to its boiling point and afterwards poured onto a crystallisation dish, where slow evaporation of the solvent led to single crystals. Thus, synthesis proceeded in an open system. In this work, *Structure B* was the solution

of a single crystal yielded at ambient conditions: For the synthesis, the reactants silver(I)carbonate (or silver(I)acetate) and MTA were ground in a mortar and the colourless solid was gathered in minimum amount of water needed for the dissolution. After evaporation of water at room temperature, thin, elongated crystals were obtained.



Figure 51: Pictures of $Ag_3[CH(SO_3)_3] \cdot H_2O$ under the light microscope.

The crystals were ground and submitted to X-ray powder diffraction. The received diffraction pattern is depicted in Figure 52 (p. 72) and equals the simulated pattern for *Structure B*. To represent the phase purity a *Rietveld* refinement was conducted, refining the cell parameters for *Structure B* and atom positions of all silver atoms and O1 (water). The blue difference curve shows minor peaks, which all coincide in their diffraction angle with reflections assigned to the analysed phase. Merely the intensities vary. Table 19 (p. 72) lists the refined cell parameters and quality factors of the *Rietveld* fit.

Additionally a powder diffraction pattern of a sample, collected after the hydrothermal process in a sealed glass ampoule was measured. While the obtained diffraction pattern resembles the simulated pattern for *Structure A* for the most part, additional reflections are visible. Therefore a *Rietveld* refinement on the measured diffraction data was undertaken, fitting both structures (Figure 53, p. 73). With the exception of two predominant signals in the blue difference curve, the *Rietveld* plot describes the measured sample very well.



Figure 52: Measured X-Ray powder diffraction pattern of a sample of $Ag_3[CH(SO_3)_3] \cdot H_2O$, synthesized under ambient conditions in black. Sample was measured in a 0.3 mm capillary with Mo_{Kal} radiation. Rietveld Refinement with crystallographic data from $Ag_3[CH(SO_3)_3] \cdot H_2O$, solved in $P2_1/c$ (Structure B) is added in red and difference curve is blue.

Parameters	Rietveld Refinement	Single Crystal
<i>a</i> [pm]	756.06(1)	753.26(7)
<i>b</i> [pm]	2167.64(4)	2154.2(2)
<i>c</i> [pm]	596.03(1)	592.84(5)
V [Å ³]	968.28(3)	953.6(1)
T [K]	293	100
Rwp	7.155	
Rexp	4.959	
Rp	5.622	
gof	1.443	

Table 19: Rietveld Refinement of $Ag_3[CH(SO_3)_3] \cdot H_2O$ after synthesis at ambient condition with crystal data from Structure B ($P2_1/c$)



Figure 53: Measured X-ray powder diffraction pattern of a sample of $Ag_3[CH(SO_3)_3] \cdot H_2O$, synthesized under hydrothermal conditions. Sample was measured in a 0.3 mm capillary with $Mo_{K\alpha l}$ radiation. Rietveld Refinement with crystallographic data from both structures for $Ag_3[CH(SO_3)_3] \cdot H_2O$, solved in $P2_1/n$ (Structure A) and $P2_1/c$ (Structure B) is added in red and difference curve is given in blue.

The excerpt in Figure 54 gives a clearer overview on the found discrepancies between 12° and $16^{\circ} 2\theta$. Obviously, there is an additional reflection at 12.8° , which belongs to neither of the two crystal structures refined. This reflection could belong to an impurity or another phase.



Figure 54: Excerpt of Figure 53, Powder diffraction pattern of $Ag_3[CH(SO_3)_3] \cdot H_2O$ with Rietveld refinement for both structure types.

The other strong inconsistency is the signal at 14.2° . This could be either an additional reflection of an unidentified species, or a poor fit of the simulated pattern for the reflection at slightly higher diffraction angles. Table 20 comprises the refined cell parameters and quality factors of the *Rietveld* refinement. The solid obtained from the hydrothermal process at $T_{max} = 373$ K has a composition in its crystalline phase of 78.1% *Structure A* and 21.9% *Structure B*.

Parameters	P2 ₁ /n Structure A	<i>Rietveld</i> Refinement	P2 ₁ /c Structure B	<i>Rietveld</i> Refinement
<i>a</i> [pm]	682.42(5)	687.40(6)	753.26(7)	757.6(2)
<i>b</i> [pm]	983.89(7)	987.37(8)	2154.2(2)	2171.7(5)
<i>c</i> [pm]	1439.9(1)	1450.1(2)	592.84(5)	596.4(2)
V [Å ³]	956.9(1)	973.3(2)	953.6(1)	974.0(5)
T [K]	100	293	100	293
[%]		78.1		21.9
Rwp		13.428		13.428
Rexp		4.966		4.966
Rp		9.724		9.724
gof		2.704		2.704

Table 20: Rietveld Refinement of $Ag_3[CH(SO_3)_3] \cdot H_2O$ for a Sample after Hydrothermal Synthesis with Both Crystal Structures Present.

IR-spectra of all synthesized MTS-salts are depicted in Figure 55 (p. 75) and a detailed description of the measured bands with assignment is given in Table 21 (p. 86). A geometry optimization for the anion $[CH(SO_3)_3]^{3-}$ within density functional theory (DFT) was conducted using the *PBEO* exchange-correlation functional and a *cc-pVTZ* basis set for all elements.^[114] Assignment of the measured bands is based on calculations of the isolated anion. All measured spectra show bands at the same wavenumber with similar shape in asymmetry. Below 700 cm⁻¹ deformation vibrations of the CSO₃-fragment are observed. Around 500 cm⁻¹ six deformation vibrations occur, where the SO₃-groups show *scissoring* motions of two oxygen atoms towards each other, while the C-S bond follows this motion and vibrates in tandem.



Figure 55: Measured IR-spectra of LiMTS, KMTS, RbMTS, and AgMTS with calculated data in black at the top. Spectra are normed and an offset is applied for clearer portrayal.

Between 600 cm⁻¹ and 700 cm⁻¹ the same atoms join in a deformation vibration, but the definition is rather an *umbrella*-type vibration, where all three oxygen atoms of the SO₃-group vibrate towards each other, while the C-S bond is pushed out of plane for a larger radius. These nine individual deformation vibrations are energetically in close proximity, thus the theoretical IR spectrum (black) reveals only three bands, two around 500 cm^{-1} (499 cm⁻¹, 515 cm⁻¹) and one peak with higher intensity at 603 cm⁻¹. For the first set of deformation vibrations (scissoring) all measured spectra show more bands than the calculated data. Thus, the different deformation vibrations are not equal in energy, which is anticipated for salts where the SO₃-groups immensely participate in bonds to the respective cations. The band around 600 cm⁻¹ is more distinct, but shows an asymmetry towards higher wavenumbers, suggesting a cancellation of degeneracy, as well. Table 21 counts these peaks with the abbreviation sh for shoulder. At 721 cm⁻¹ a deformation of the C-S bonds leads to a peak of very low intensity. This vibration is somewhat higher in intensity in the measured IR spectra, usually observed as a relatively weak and broad signal at slightly higher wave numbers. At 773 cm^{-1} and 774 cm^{-1} two asymmetric stretching vibrations of the CS₂ fragment are combined in one peak for the calculated spectrum. This one peak splits in two separate peaks in the measured datasets, and is shifted to higher wave numbers. The same is true for the symmetric stretching vibrations observed at 1020 cm⁻¹ in the theoretical spectrum. Generally, the asymmetric stretching vibrations of the SO₃-group around 1250 cm⁻¹ are broader in the measured spectra. In addition, they are at slightly lower energies, especially in the case of silver methanetrisulphonate. Comparable to the IR-data collected for the MDA-salts, two characteristic small peaks are observed around 3500 cm^{-1} . For the methanetrisulphonate anion the C-H stretching vibration is calculated at 3136 cm^{-1} . As there is only one hydrogen atom at the central carbon atom, there should be only one peak for this type of vibration. Most likely, the C-H stretching correlates to the small peak at roughly 2900 cm⁻¹. Interaction between the anion and the water molecules within the crystal structure at room temperature could be a cause of these additional vibrations at 3500 cm⁻¹. The IR spectra depicted in Figure 55 are from compounds yielded from aqueous solutions. Another spectrum of Rb₃[CH(SO₃)₃] of a sample synthesised from the solid compounds (H₃O)₃[CH(SO₃)₃] and RbOH in the argon atmosphere of a glovebox by mechanical treatment in a mortar, and an excerpt of Figure 55, is given in the appendix (p. 246).

LiMTS	KMTS	RbMDS	AgMTS	Theory	Assignment
			457 m	499	δ -CSO ₃
506 s	509 s	506 s	504 s	514	δ -CSO ₃
522 sh	524 sh	523 m	521 s	515	δ -CSO ₃
		529 m	532 sh	517	δ -CSO ₃
	531 m			531	δ -CSO ₃
573 m	547 m	545 w	549 m	535	δ -CSO ₃
603 m	609 s	605 s	585 s	602	δ -CSO ₃
630 sh	653 m	617 sh	598 s	604	δ -CSO ₃
	665 sh	653 br	658 br	664	δ -CSO ₃
	680 w	673 w	675 w		
730 br	743 w	754 w	710 br	721	δ -CS ₃
771 w	758 w		751 m	773	v_{asym} -CS ₂
807 m	820 m	813 m	803 s	774	v_{asym} -CS ₂
819 sh	834 sh	831 w	816 m		
	1024 s	1022 s	1008 s	1020	v _{sym} -SO ₃
1031 s	1036 m	1034 m		1021	v _{sym} -SO ₃
	1050 w	1089 w	1076 s	1075	v_{sym} -SO ₃
1096 m	1091 w			1127	δ -CH
1139 w	1126 br	1154 vw	1129 m	1131	δ -CH
	1177 w	1170 w	1148 sh		

Table 21: Measured IR-bands for Methanetrisulphonate Salts of Silver, Potassium,Rubidium and Lithium with Theoretical Bands and Assignment.

1204 sh	1203 sh	1198 sh	1169 s	1200	vasym-SO3
1218 s	1224 <i>s</i>	1219 s	1197 s	1231	vasym-SO3
1231 sh		1236 sh	1217 m	1232	vasym-SO3
1267 s	1261 m	1253 m	1227 m	1255	vasym-SO3
	1302 w	1264 sh	1237 sh	1255	vasym-SO3
	1329 w			1258	vasym-SO3
1627 w	1642 w	1646 w	1621 w		
1648 w	1711 w				
2935 vw	2938 w	2950 vw	2927 w	3136	v-CH
2956 w					
3415 w			3237 br		
3471 br	3489 w		3342 w		
3504 sh	3561 w	3478 w	3472 w		
3548 m		3559 w			

Rubidium Silver Methanetrisulphonate

A heteroleptic methanetrisulphonate salt was synthesised from Rb₂CO₃, Ag₂CO₃ and MTA. The hydrothermal process delivered single crystals, suitable for X-ray diffraction. From this synthesis, two different crystal structures could be solved. The targeted compound of a methanetrisulphonate with a 2:1 ratio of rubidium to silver however, was not produced. Instead, the first crystal analysed was identified as the silver deprived structure $Rb_5Ag[CH(SO_3)_3]_2 \cdot 2 H_2O$. The salt crystallises in the acentric tetragonal space group $P4_{1}2_{1}2$ with four formula units. With a = 735.32(2) pm and c = 4166.3(2) pm, the cell is elongated in one favoured direction. The asymmetric unit consists of one unique anion, one water molecule, one silver cation and three unique rubidium cations (Figure 56, p. 78). Ag1 and Rb3 are located on the special position 4a, a two-fold rotational axis along the face diagonal of the *c*-plane. For $P4_12_12$ this is the only special site symmetry accessible. Unlike for other discussed structures, there are no typical layers observed. All components are arranged in a circular motif parallel to the c-axis. A view on the (0 0 1) plane of the cell reveals a small cavity in the middle of the unit cell (Figure 56, p. 78). In accordance with previous depictions, the CSO₃-fragments are shown as yellow tetrahedrons for a better overview.



Figure 56: Crystal structure of $Rb_5Ag[CH(SO_3)_3]_2 \cdot 2H_2O$. Top left corner shows the asymmetric unit in ellipsoidal representation (thermal ellipsoids set to 70%). Cross sections through the unit cell show the long c-axis.

Figure 57 shows the unit cell in a 2D perspective in viewing direction of the face diagonal of the c-plane (1 1 0). The cell is only filled with Ag1 and Rb3 to demonstrate the rotational axis, which the two individual cations occupy.



Figure 57: Cations Rb3 and Ag1, situated on a two-fold rotational axis.

The coordination number of the respective cations varies between six for Ag1, ten for Rb1, nine for Rb2 and eight for Rb3. Due to the special symmetry found for Ag1 and Rb3, the surrounding of the respective cation is made-up by three unique oxygen atoms in the case of silver and four unique oxygen atoms for Rb3. For Ag1 the coordination

sphere can be described as a 4+2 type of coordination, with the atoms O23 and O33 in closer proximity, than O31, which is situated further away. Between Ag1-O23 lie 240.4(3) pm, between Ag1-O33 237.0(3) pm, while distance between Ag1-O31 conducts 311.6(3) pm. For Rb1 the largest distance from coordinating oxygen is 350.1(3) pm and lies between Rb1-O22. The strongest interaction can be assumed between Rb1-O13, with a bond length of 289.3(3) pm. The longest distance lies between Rb1-O22 with 350.1(3) pm (Rb2-O32). Lastly, Rb3 is coordinated by the atoms O1, O32, O33 and O22. For Rb3 the distances to all surrounding oxygen atoms are narrowly distributed. The longest distance lies between Rb3-O1 with 292.2(4) pm and the shortest between Rb3-O22 with 280.2(3) pm.



Figure 58: Coordination to Ag1, Rb1, R2 and Rb3.

All oxygen atoms coordinate to the cations within the crystal structure, with the highest participation coming from O33, followed by O32, O22, O31 and O23. The atoms O11, O13 and O21 show the smallest share in the coordination to the cations. This has slight influences on the obtained bond lengths between sulphur and the respective oxygen. The medium bond lengths for S-O is 145.5(9) pm. For S3-O33 the longest bond length of 147.0(3) pm is observed. However, overall the S-O bonds are narrowly distributed around

145 pm, which is in accordance to previous findings. The C-S bond length is 182.3(4) pm for S1-C1, 183.6(5) pm for S2-C1 and 182.9(4) pm for S3-C1. These values are marginally smaller than those for the homoleptic silver and rubidium methane-trisulphonate salts. The bond angles within the anion are similar to those previously discussed. For more crystallographic detail, see appendix p. 185 and the following.

In agreement with previous crystal structures, the crystal water at hand does not play a domineering role in the surrounding of the cationic species, as is oftentimes evident, when combined with weakly coordinating anions. The structure was investigated for possible H-bridging and suitable bonds were found between O11…H1A-O1 and O21…H1B-O1. The distance between donor and acceptor oxygen atoms is 284.9(5) pm (O1-O11) and 293.1(6) pm (O1-O21).



Figure 59: H-Bridging within $Rb_5Ag[CH(SO_3)_3]_2 \cdot 2H_2O$.

The second crystal yielded and analysed from the synthesis of Rb₂CO₃, Ag₂CO₃ and MTA was identified as a heteroleptic salt of methanetrisulphonic acid without additional crystal water and a stoichiometry of silver to rubidium of 1:1. The characterised compound crystallises as Rb₃Ag₃[CH(SO₃)₃]₂ in the triclinic space group $P\bar{1}$ with one formula unit and the cell parameters a = 750.17(5) pm, b = 754.08(5) pm, c = 973.20(6) pm, $\alpha = 89.447(2)^{\circ}$, $\beta = 76.43(6)^{\circ}$ and $\gamma = 62.861(2)^{\circ}$. Ag2 and Rb2 are situated on inversion centres of the unit cell. Ag2 occupies *Wyckoff* position *1c*, the inversion centre at 0 ½ 0 and Rb2 possess position *1f*, the inversion centre with the coordinates ½ 0 ½. The atoms are surely identified in the cross section of the unit cell, as they are located at the middle of the respective cell edge (Figure 60, p. 81). A view at the (0 1 0) and (1 0 0) plane reveals a layered structure. The layers are built in an A, B, C arrangement with one layer consisting of one set of cations (silver), the next contains the anions and the third layer

encompasses the other set of cations (rubidium). The anions are equally arranged in each layer, while those of the next layer are facing in the opposite direction. C-S bond lengths range from 181.9(2) pm for S3-C1, over 182.1(2) pm for S2-C1, to 183.0(2) pm for S1-C1. The similarity to prior discussed crystal structures of MTA salts is also evident for the respective S-O bond lengths and all bond angles (for more detail, see crystallographic tables, p. 189 and following). The medium S-O bond length is 145.6(3) pm, which is almost identical to that found for Rb₅Ag[CH(SO₃)₃]₂ · 2 H₂O.



Figure 60: Crystal structure of Rb₃Ag₃[CH(SO₃)₃]₂. Top left corner shows the asymmetric unit in ellipsoidal representation (thermal ellipsoids set to 70 %). Cross sections through the unit cell show a layered arrangement.

Figure 61 depicts the four coordination polyhedrons of the respective cations. As expected, for Ag2 and Rb2 a high symmetry of the coordination sphere leads to an ordered polyhedron. With the aid of the program *Polynator* the polyhedrons were further analysed and classified regarding their closest fit towards a perfect polyhedron for their respective coordination number.^[118] Ag2 has the coordination number six. For Ag2 the resulting octahedron is best described as a trigonal antiprism with the relatively low distortion value of $\delta = 4.612$. For Rb2 the coordination number is twelve and best description of the observed polyhedron is the shape of a cuboctahedron with the distortion value for that

model being $\delta = 6.402$. For Ag1 the coordination number is seven and for Rb1 the coordination number is eleven. The Ag1-O distances are narrowly distributed between 242.8(1) pm and 247.4(1) pm. For Ag2 more deviations are found. The shortest Ag-O distance lies between Ag2-O12 with 237.7(1) pm and the longest Ag-O interaction is evident between Ag1-O23 with 282.4(1) pm. These distances are in the same range as those found for Ag₃[CH(SO₃)₃] · H₂O (225.8(2) pm – 301.3(2) pm). All Rb-O bonds range from 289.3(1) pm (Rb1-O21) to 353.0(2) pm (Rb2-O31). Generally, the Rb2-O distances are larger, than those observed for Rb1-O. The surrounding of the cations was calculated with the program *Chardi2015*.^[105,106]



Figure 61: Coordination polyhedrons of Ag1, Ag2, Rb1 and Rb2 within Rb₃Ag₃[CH(SO₃)₃]₂.

The synthesis of Rb₂CO₃, Ag₂CO₃ and MTA in a hydrothermal process proved, that heteroleptic compounds, such as the two analysed single crystals are accessible. These results also show that a tuning of different stoichiometry of the respective cations should be possible. The problem of a lack of phase purity could be overcome by a different method of preparation, as the sealed ampoule hinders the homogeneity that could be achieved by simple aid of, for instance, a magnetic stirring bar, rendering a better miscibility of reactants possible.

To recapitulate, this chapter included the unprecedented crystal structures of lithium and rubidium methanetrisulphonate as well as a successful reproduction of the compounds $K_3[CH(SO_3)_3] \cdot H_2O$ and $(H_3O)_3[CH(SO_3)_3]$. For $Ag_3[CH(SO_3)_3] \cdot H_2O$ two modification were discussed, one of which has been previously documented in unpublished data within this research group (Oldenburg, 2011). Similar to the silver salt, methanetrisulphonic acid also appears in two modifications. In both compounds, a clear definition of a HT and LT modification seems inadequate, as cell volumes and densities are similar. Through PXRD analysis with *Rietveld* refinement it was shown, that both compounds can exist phase pure, or as a mixture of both accessible modifications. Generally, the trend of a slightly increasing C-S bond with further substitution of H-atoms with SO₃-units is continued from $[CH_2(SO_3)_2]^{2-}$ to $[CH(SO_3)_3]^{3-}$.

2.4. Silver Methanetetrasulphonate

A reaction targeting the previously discussed silver methanetrisulphonate let to the production of a silver salt with the unprecedented $[C(SO_3)_4]^{4-}$ anion. The herein reported crystal structure delivers the proof, that exhaustive sulphonation at the carbon central atom leads to the newly found anion, which exhibits sufficient stability for X-ray analysis. This fascinating anion shows an isotropy with four equal substituents and a high negative charge. Furthermore, it completes the row of methanepolysulphonates. This new, small, inorganic anion has the potential to play a fundamental role in future textbooks.

The reactants Ag_2CO_3 and $(H_3O)_3[CH(SO_3)_3]_{(aq)}$ were brought to reaction in a sealed glass ampoule with a small amount of water (1 mL). The stoichiometry was roughly 1.9 eq silver salt to 1.0 eq of acid and the maximum temperature was 413 K. After synthesis, the ampoule is filled with an aqueous suspension with a grey, solid compound. Only a handful of small, rod-shaped colourless crystals were detected under the light microscope.



Figure 62: Picture of the crystals under a light microscope.

The analysed crystal was solved as $Ag_{9}[C(SO_{3})_{4}]_{2}Cl \cdot 4 H_{2}O$, crystallising in the space group $P\overline{I}$. The investigated single crystal suffers from an unsolved multi-domain problem. The selected single crystal was measured at three different temperatures and a phase transition below 250 K, while heating from 100 K to room temperature, towards a smaller cell was observed. Furthermore, additional diffraction data was collected at room temperature, which also resulted in the smaller triclinic cell. The crystal structure was solved for all three datasets, but unfortunately the presence of at least one overlapping domain results in solutions with a high amount of residual electron density. At 100 K, $Ag_{9}[C(SO_{3})_{4}]_{2}Cl \cdot 4 H_{2}O$ crystallises with four formula units and the cell parameters b = 1381.66(9) pm, c = 1604.7(1) pm,a = 1361.27(8) pm, $\alpha = 100.752(2)^{\circ}$, $\beta = 90.052(2)^{\circ}$, $\gamma = 111.167(2)^{\circ}$ and V = 2755.5(3) Å³. The asymmetric unit is built-up by 18 unique silver cations, three unique chloride anions, four crystallographically distinguishable $[C(SO_3)_4]^{4-}$ anions and eight oxygen atoms (Figure 63). Presumably, the eight oxygen atoms belong to crystal water, the respective hydrogen atoms could not be refined. Ag7 is split into 88.4% Ag7A and 11.6% Ag7B. Cl1 and Cl2 are located on inversion centres of the triclinic unit cell. Cl1 occupies the Wyckoff position *1b*, at the edges of the unit cell with the coordinates 0 0 ½. Cl2 occupies the *Wyckoff* position *1a*, at the corners of the unit cell with the coordinates 0 0 0. While chlorine is not incorporated in the chosen reactants, it is most likely a residue from the regeneration process of the ion exchange column. After each ion exchange, the stationary phase is regenerated with a 3 M solution of HCl. Thus, a plausible source of the chloride anions are traces of said HCl in the starting material of methanetrisulphonic acid. Figure 63 depicts the asymmetric unit without atom labels for the [C(SO₃)]^{4–} anions for a better overview.



Figure 63: Asymmetric unit of the crystal structure $Ag_9[C(SO_3)_4]_2Cl \cdot 4H_2O$ measured at 100 K. Thermal ellipsoids are set to 70% probability. Due to the high amount of atoms, labels for the $[C(SO_3)]^{4-}$ anions are neglected.

Figure 64 (p. 86) portrays the novel polysulphonate anion in its *ORTEP* plot and pictured with tetrahedrons around the sulphur atoms. Bond angles and lengths are discussed exemplary for the anion around C1. More data is listed in the crystallographic tables in the appendix (p. 192 and following). The atoms S11, S12, S13 and S14 are bonded to the central carbon atom in an almost perfect tetrahedral environment. The S-C-S bond angles range from 108.5(2)° to 110.2(2)°. The C-S bond is very long, ranging from 185.0(4) pm

(C1-S12) to 186.3(4) pm (C1-S13). Considering all four unique anions, the longest C-S bond conducts of 186.4(5) pm and the average C-S bond is 186(2) pm long. This is a significant increase with respect to the C-S bond lengths found for $[CH(SO_3)_3]^{3-}$ and $[CH_2(SO_3)_2]^{2-}$. Table 22 compares the average bond lengths for all methane(poly)-sulphonate anions. References are taken from $Rb_2[H_3CSO_3]_2 \cdot H_2O$, $Rb_2[CH_2(SO_3)_2]$, $Rb_5Ag[CH(SO_3)_3] \cdot H_2O$ and $Ag_9[C(SO_3)_4]_2C1 \cdot 4 H_2O$. For the latter only the average bond lengths on the depicted anion around C2 is given, to ensure the same degree of uncertainty. The data reinforces the previous statement, that a higher count of SO₃-groups at the methyl group does not influence the S-O bonds. On the contrary, the C-S bond increases with each addition of an SO₃-moiety.



Figure 64:.Depicture of the $[C(SO_3)_4]^{4-}$ anion with labels (left) and with polyhedrons (right) around the centre carbon atom and the sulphur atoms.

Table 22: Comparison of the Average Bond Lengths within the Anions $[H_3CSO_3]^ [CH_2(SO_3)_2]^{2-}$, $[CH(SO_3)_3]^{3-}$ and $[C(SO_3)_4]^{4-}$.



Figure 65 on page 87 depicts cross sections of the unit cell. $Ag_9[C(SO_3)_4]_2Cl \cdot 4 H_2O$ crystallises in layers. The polysulphonate anions are arranged in rows, parallel towards each other along the *a*- and *c*-axis. These anions are embedded between a layer of Cl and Ag, and a layer of Ag and water. Notwithstanding the isotropic property of the $[C(SO_3)_4]^{4-}$ anion, obvious layers are visible in the crystal structure.



Figure 65: Cross sections through the crystal structure of $Ag_9[C(SO_3)_4]_2Cl \cdot 4H_2O$.

An interesting feature of the crystal structure are the [Ag₆Cl]-octahedrons. All chloride atoms are surrounded by six silver cations, leading to perfectly shaped trigonal antiprisms with $\delta = 0.759$. The Ag-Cl distances range from 286.0(1) pm to 273.83(4) pm. For comparison, within AgCl, which has a rock salt structure type, the Ag-Cl distances are 277.3 pm long.^[123]



Figure 66: Coordination polyhedrons around Cl1, Cl2 and Cl3.

The incorporation of the trigonal antiprisms around the chloride anions in the cross section of the crystal structure brings out the layered structure even more (Figure 67). Following the distribution of silver cations within the two separated layers, the exclusion from the [Ag₆Cl]-polyhedrons leaves the atoms Ag4, Ag5, Ag6, Ag7A, Ag7B, Ag8 and Ag9 in the "water" layer. These atoms are not coordinated by chlorine, while the silver atoms depicted above are not coordinated by water. The coordination number for silver varies between seven and nine. One chlorine atom and six oxygen atoms, respectively saturate Ag10, Ag14, Ag11, Ag15 and Ag3. For Ag17, Ag16, Ag2, Ag18, Ag1, Ag12 and Ag13 the coordination sphere consists of seven oxygen atoms and one chloride anion, each. The atoms Ag4, Ag5, Ag6, Ag7A, Ag7B, Ag8 and Ag9 are solely surrounded by oxygen with coordination numbers seven (Ag8), eight (Ag4, Ag5, Ag9, Ag7A) and nine (Ag7B, Ag6). These atoms are coordinated by the [C(SO₃)₄]⁴⁻ anion, as well as the free oxygen atoms from the assumed water molecules. The longest Ag-O distance lies

between Ag5-O323 and conducts of 347.4(4) pm. The shortest Ag-O distance lies between Ag8-O6 with 234.6(3) pm, neglecting the shortest distances found for Ag7B (Ag7B-O441: 213.4(7) pm, Ag7B-O432: 224.3(7) pm).



Figure 67: Multi-cell representation of the (1 0 0) plane with polyhedrons around the chloride anions and the sulphur atoms.

As already mentioned above, the measured crystal shows a phase transition to a smaller, triclinic cell below 250 K. Another dataset was collected at room temperature in the hope to overcome the disorder and high residual electron density. Unfortunately, still a residual electron density of 3.10 and $-2.78 \text{ e} \cdot \text{Å}^{-3}$ is evident in the solved structure at room temperature. The smaller cell has the cell parameters a = 792.3(2) pm, b = 796.5(2) pm, c = 1287.7(3) pm, $\alpha = 86.099(9)^{\circ}$, $\beta = 80.049(8)^{\circ}$, $\gamma = 61.073(7)^{\circ}$ and V = 700.5(3) Å³. In this modification $Ag_{9}[C(SO_{3})_{4}]_{2}Cl \cdot 4 H_{2}O$ crystallises with one formula unit in the space group $P\overline{I}$. The asymmetric unit and cross sections through the unit cell are depicted in Figure 68 (p. 89). There are five differentiated silver cations, two oxygen atoms, presumably belonging to crystal water, one polysulphonate anion and one chloride anion within the asymmetric unit. Cl1 and Ag2 have an occupancy of 50%. The oxygen atoms O1 and O2 show large thermal ellipsoids. Comparable to the low temperature measurement, Cl1 is located on an inversion centre of the unit cell, occupying the Wyckoff position lf which has the cell coordinates $\frac{1}{2}0\frac{1}{2}$. Furthermore, the perfectly shaped [Ag₆Cl]-polyhedrons as well as the building of layers are reoccurring features in this modification. While Ag3, Ag5 and Ag1 are in close proximity to the chloride anion, Ag4 and Ag2 remain in close proximity to O1 and O2.



Figure 68: Crystal structure of $Ag_9[C(SO_3)_4]_2Cl \cdot 4H_2O$, measured at room temperature. Thermal ellipsoids are set to 70% probability level.

The polyhedron around Cl1 is best described by a trigonal-antiprism, with a very low distortion value of $\delta = 0.996$. The Cl-Ag bond lengths are 270.6(2) pm, 271.4(2) pm and 271.8(1) pm long. These lie directly in the middle of the obtained values for the Cl-Ag distances from the low temperature measurement. Bond lengths within the $[C(SO_3)_4]^{4-}$ anion suffer from a relatively high uncertainty, hence, a meaningful comparison to the low temperature measurement is not possible. The C-S bonds lie between 185(1) pm and 187(2) pm, The S-O bonds between 143(1) pm and 146(1) pm. The S-C-S bond angles are close to a perfect tetrahedral angle and lie between 108.8(7)° and 109.8(7)°.

Figure 69 depicts all polyhedrons, built around the silver cations. The upper three polyhedrons are those for Ag1, Ag3 and Ag5, incorporating chlorine within the coordination sphere. The bottom depicts the silver cations Ag2 and Ag4, which can be found in the "water" layer and are surrounded by oxygen atoms from the presumed water molecules and the SO₃-groups alike. The coordination number varies between seven and

eight. Shortest Ag-O distance lies between Ag1 and O11 with 239(1) pm and the longest between Ag3-O32 and Ag4-O33 with 316(1) pm.



Figure 69: Coordination polyhedrons around all silver cations in $Ag_9[C(SO_3)_4]_2Cl \cdot 4H_2O$, measured at room temperature.

While this crystal of a methanetetrasulphonate salt is structurally phenomenal and interesting, as it is the first of its class, it is a random occurrence, which could not be reproduced. The bulk, powder material gained from the synthesis was analysed by PXRD and identified as mostly Ag_2SO_4 . Thus, the fascinating structure with the elusive $[C(SO_3)_4]^{4-}$ anion is most likely a decomposition product of $Ag_3[CH(SO_3)_3]$, caused by high temperature. The powder diffractogram is depicted in the appendix, p. 242.

2.5. Trichlic Acid and Trichlate Salts

Incorporation of three chlorine atoms at a methanesulphonate building block leads to the so-called trichlate anion. This specific anion was synthesised in a three-step reaction route. First synthesis was conducted according to Rathke's approach followed by the work-up introduced by *Helfrich* and *Reid*.^[70,72] Thus, in line with Equation 20 (p. 11), CS₂ was reacted with chlorine gas under the presence of 0.4 w% I₂. The reaction is carried out, until the initial volume of CS₂ has doubled. The work-up of the synthesised Cl₃CSCl includes a distillation up to 373 °K to rid the crude product of CCl₄ and unreacted CS₂. Afterwards a steam distillation is conducted. Through the hot water steam, sulphur chlorides are decomposed and cast out as gaseous compounds, witnessed as yellow evolving gases. Furthermore, the steam distillation carries the product into the distillate, presumably under the formation of an azeotrope. Lastly, the gathered distillate is subjected to fractional distillation, which allows to purely obtain Cl₃CSCl with a minimum loss due to thermal decomposition. The yield of 65%, as stated by Helfrich and Reid was never achieved in the course of this work. Mostly a yield around 20% was reached. The synthesised Cl₃CSCl was oxidized according to Sosnovsky's method, Equation 21 (p. 12).^[74] Hence, concentrated hydrogen peroxide was used to oxidise Cl₃CSCl to Cl₃CSO₂Cl in glacial acetic acid. The yield of this reaction is approximately 70%. Lastly, the final step of synthesising trichlate species in alignment with Kolbe entails the combination of Cl₃CSO₂Cl with metal hydroxides in aqueous solution.^[33]

Potassium Trichlate Monohydrate

A reaction of Cl_3CSO_2Cl with an excess of KOH in aqueous solution at 323 K brought thin, colourless crystals, which adhered to one another. The selected single crystal was solved as K[Cl_3CSO_3] · H_2O.



Figure 70: Light microscope picture of the crystalline material yielded for *K*[*Cl*₃*CSO*₃].

Similar to the respective sodium salt, the obtained potassium trichlate is yielded as a monohydrate.^[75] The potassium trichlate crystallises in the triclinic space group $P\overline{I}$ with four formula units. The cell parameters are a = 656.67(7) pm, b = 1094.0(1) pm, c = 1241.1(1) pm, $\alpha = 73.416(4)^{\circ}$, $\beta = 85.008(5)^{\circ}$, $\gamma = 89.921(5)^{\circ}$ and V = 851.02 Å³. All atoms are located at general site positions. The asymmetric unit consists of two crystallographically unique anions, cations and water molecules.



Figure 71: Asymmetric unit of $K[Cl_3CSO_3] \cdot H_2O$ (left) and water molecules with Hbonds (right). Thermal ellipsoids are set to 70% probability.

Hydrogen bonding occurs from the SO₃-units to the two unique water molecules. O12 and O23 build two H-bonds, respectively (Figure 71, right). The distances between donor and acceptor oxygen atom are between 285.8(3) and 293.7(3) pm and the angles between $153(5)^{\circ}$ and $174(4)^{\circ}$. This and more crystallographic data can be found in the crystallographic tables in the appendix (p. 206 and following).

The two crystallographically differentiated trichlate anions are similar regarding their bond lengths and angles. The C-Cl bonds lie between 175.4(3) pm (C1-Cl13) and

176.9(3) pm (C2-Cl21). For comparison, the C-Cl bond in a high pressure form of CCl₄ is 176.6(3) pm long. S-O bonds lie between 144.3(2) pm (S1-O11) and 145.2(2) pm (S1-O13). This is in agreement with those S-O bonds discussed for the methanepolysulphonate salts. The bond between C1 and S1 conducts of 184.0(3) pm and the bond between C2 and S2 of 184.6(2) pm. A comparison with the medium C-S bonds listed in Table 22, p. 86 ranks the C-S bond length of the trichlate anion in between the observed bond lengths for methanetrisulphonate species and the methanetetrasulphonate anion. A comparison with triflate salts delivers similar results, in regard to constant S-O bond lengths and slight changes for the C-S bond. Within K[F₃CSO₃] the medium C-S bond (three unique anions) is 179(1) pm and thus significantly shorter.^[53] The O-S-O bond angles range from 113.2(1)° (O22-S2-O23) to 115.0(1)° (O21-S2-O22). While these are in the same range as those angles discussed for the methanepolysulphonate salts, the O-S-O angles of the trichlate anion are more narrowly distributed. The O-S-C angles are also very similar and vary among the range of the stated error around 104°. Obviously, this angle is smaller than the O-S-C angles obtained for methanetrisulphonate salts, due to a higher sterically demanding environment. However, the O-S-C angles within the trichlate are similar to those found in the MSA salts (Ag[H₃CSO₃] : $106.2(2)^{\circ}$ - $107.7(2)^{\circ}$) and MDA salts (Rb[CH₂(SO₃)₂] : 103.0(1)°- 107.78(7)°). The Cl-C-S angles are narrowly distributed around 108° and the Cl-C-Cl angles are all very close to 110°. An interesting feature of the trichlate anion is represented by the torsion angles. Similar to its smaller triflate sibling, the trichlate anion exhibits a staggered conformation, where all substituents along the C-S bond are oriented to achieve the highest degree of sterical freedom. In a perfect staggered conformation the torsion angles portray 60°. For $K[Cl_3CSO_3] \cdot H_2O$ the torsion angles are very close to 60°, the highest deviation being 1.8°.

Cross sections of the unit cell portraying the crystallographic (1 0 0) and (0 1 0) plane reveal the overall layered structure (Figure 72, p. 94). The potassium cations and the water molecules are embedded between the SO₃-functions, whereas the CCl₃-groups are all pointing towards each other in the opposite direction. This layered build-up is also a common feature among triflate compounds.^[51,53,61,64,124,125] The gap between CCl₃-groups of opposing layers is relatively large, probably caused by weaker *van der Waals* interaction as opposed to *dipol-dipol* interactions in the polar layer. This is a significant difference to the previously discussed methanepolysulphonic salts, which in majority, portrayed layered structures as well. Within the methanepolysulphonic salts all layers were combined by *dipol-dipol* forces and (or) coordination bonds.



Figure 72: Crystal structure along the crystallographic a-axis (left), and along the crystallographic b-axis (right).

K1 and K2 have the coordination number eight and are both coordinated by seven oxygen atoms and one chlorine atom. The oxygen atoms derive from water molecules as well as the trichlate anions. K1 is surrounded by oxygen in a distance range from 270.4(2) pm (K1-O13) to 307.5(2) pm (K1-O23). The bond to Cl21 is 361.7(1) pm long and was confirmed by the software *Chardi2015*.^[105,106] For K2 the K2-O distances range from 269.3(2) pm (K2-O22) to 279.7(2) pm (K2-O1) and the K2-Cl12 distance conducts of 358.3(1) pm.



Figure 73: Coordination sphere of K1 (left) and K2 (right).

A powder diffraction pattern of the product reveals a successful recrystallisation with no more KCl present. However, the measured pattern does not coincide with the simulated pattern from the single crystal, suggesting a phase transition between low temperature single crystal XRD measurements (100 K) and room temperature, or other processes, for

instance the loss of crystal water. The powder diffraction pattern is attached in the appendix, p. 243.

Thermal analysis on the bulk material of the obtained potassium trichlate was conducted by DSC/TG-MS coupled measurement. Figure 74 depicts the collected data. The TGcurve is constant at nearly 100% until 600 K. Hence, the monohydrate of the potassium trichlate most likely lost its crystal water prior to the thermal analysis during the storage under argon atmosphere. The first mass loss of roughly 52% above 600 K is accompanied by the mass detection suiting the fragments SO, SO₂ and CCl₃. Thus, this step can be assigned to the decomposition of the trichlate anion. DSC/TG measurements of K[F₃CSO₃] show the decomposition of the smaller triflate anion above 673 K with a mass loss of approximately 35.2%.^[53] Therefore, trichlates are only slightly thermally less stable than their smaller analogues. The residue after the first mass drop most likely consists of a mixture of potassium chloride and potassium sulphate. The former has been identified by PXRD data. Furthermore, the endothermic peak at 1050 K could be assigned to the melting of potassium chloride.



Figure 74: DSC/TG-MS data for $K[Cl_3CSO_3]$: Top shows the TG curve in red and DSC data in black (dashed line). Bottom depicts the detected masses for m/z: 117 (CCl₃) in green, m/z = 64 (SO₂) in yellow and m/z = 48 (SO) in red.

Rubidium Trichlate

Rubidium trichlate is obtained in a hydrothermal synthesis between Cl₃CSO₂Cl and RbOH in a sealed glass ampoule at 403 K. The yielded crystals have the shape of needles, are thin and adhered to one another. A preferred orientation of growth is immediately recognised under the light microscope, leading to an elongation in one direction (~cm).



Figure 75: Pictures of the needle-shaped crystals obtained for Rb[Cl₃CSO₃].

In accordance with the findings for Cs[Cl₃CSO₃], hydrothermal processing leads to no crystal water within the lattice.^[126] The observed crystal lattice is triclinic and the space group found is $P\overline{1}$. Following chemical intuition, the alkali trichlate salts show a decreasing affinity to include crystal water with growing radii of the respective cation. Three unique rubidium cations and trichlate anions build the asymmetric unit, portrayed in an *ORTEP* plot in Figure 76 (p. 97). With two formula units Rb[Cl₃CSO₃] crystallises with the cell parameters a = 601.32(6) pm, b = 1228.5(1) pm, c = 1578.6(2) pm, $a = 106.241(3)^\circ$, $\beta = 90.832(3)$, $\gamma = 100.862(4)^\circ$ and V = 1096.7(2) Å³. All bond lengths are comparable to those found for K[Cl₃CSO₃]. S-O bonds range from 144.1(3) pm (S1-O12, S3-O33) to 145.3(3) pm (S1-O13), C-S bonds from 184.6(3) pm (S1-C1) to 185.4(4) pm (S3-C3) and C-Cl bonds from 174.8(3) pm (C1-Cl11) to 177.3(3) pm (C1-Cl12). All bond lengths and angles can be found in the crystallographic tables (p. 210 and following).



Figure 76: Asymmetric unit of *Rb*[*Cl*₃*CSO*₃] depicted as thermal ellipsoids with 70% occupation probability.

Agreeable to previous findings the rubidium trichlate crystallises in layers. The cations are surrounded by the SO₃-functions of the trichlate anions. The overall build-up of the trichlate salts reminds of the structure of cell membranes: Each layer consists of two rows of trichlate anions which are separated by the rubidium cations. This is best represented in the multi-cell depiction below. Between the space of these layers, *van der Waals* interactions are present between the CCl₃-groups of neighbouring layers.



Figure 77: Crystal structure of Rb[Cl₃CSO₃]. Left: Cross section of the unit cell portraying the (1 0 0) plane. Right: Layered structure of Rb[Cl₃CSO₃] in a multi-cell arrangement showcasing the (0 0 1) plane.

The coordination sphere of Rb1, Rb2 and Rb3 was determined with *Chardi2015*.^[105,106] The coordination number for Rb1, Rb2 and Rb3 is ten. All three cations are coordinated by both oxygen and chlorine atoms. Figure 78 depicts the coordination spheres for Rb1, Rb2 and Rb3. Compared to the sodium and potassium trichlate, the coordination number for Rb is higher, as is expected for a cation with a larger cationic radius. Also, the

participation from chlorine in the coordination sphere is higher. Rb1 is surrounded by six oxygen atoms, in a range from 286.2(2) pm (Rb1-O11) to 372.4(3) pm (Rb1-O33). The oxygen and chlorine atoms belong to five different trichlate anions but derive from only two crystallographically unique anions (around S1, S3). The distance from Rb1 to chlorine lies between 375.1(1) pm (Rb1-Cl32) and 380.9(1) pm (Rb1-Cl12). For Rb1 the participation of chlorine in the coordination sphere is the highest.

Nine oxygen atoms and one chlorine atom coordinate Rb2. The shortest distance between Rb2 and O lays within Rb2 and O21 with 289.4(3) pm and the longest between Rb2 and O12 with 349.2(3) pm. Solely the trichlate anions around S1 and S2 participate in the coordination to Rb2. In sum, oxygen and chlorine atoms of six trichlate anions build the coordination sphere. One anion delivers three contact points: O12, O13 and Cl13. The distance between Rb2 and Cl13 is 396.4(1) pm, which is overall the longest coordinative bond in Rb[Cl₃CSO₃].

Eight oxygen atoms and two chlorine atoms from five different trichlate anions coordinate Rb3. The Rb3-O distances range from 282.0(2) pm (Rb3-O31) to 363.3(3) pm (Rb3-O32), which is the longest Rb-O bond observed. Rb-Cl distances are 342.62(9) pm (Rb3-Cl32), which is the shortest Rb-Cl bond found, and 362.6(1) pm (Rb4-Cl31).



Figure 78: Coordination sphere of Rb1 (left), Rb2 (right) and Rb3 (bottom).

A powder diffraction pattern of the sample with *Rietveld* refinement shows a relatively good convergence with the simulated data from the single crystal. Due to the difference in temperature during single crystal and powder X-ray diffraction measurements, all cell parameter were refined. Additionally, the atom coordinates for the heaviest atoms, rubidium and chlorine, were refined. The difference curve in Figure 79 reveals small discrepancies around the diffraction angles 7.5° , 30.5° and 51° within the intensities of the observed reflections. Notwithstanding, there is no evident of another crystalline phase. Two preferred orientations were refined along (0 1 0) and (1 1 -3). The yielded low refinement parameters (<0.5) underline the positive favourability of these planes. The (0 1 0) plane converges with the observed layers within the crystal structure. For the (1 1 -3) plane, however, no obvious explanation could be identified.



Figure 79: Powder diffraction pattern and Rietveld refinement of $Rb[Cl_3CSO_3]$. The sample was measured with Cu_{Kal} radiation Bragg-Brentano geometry.

Table 23 on page 100 lists the refined cell parameters of the crystalline powder and quality factors for the refinement. As expected, the refined cell from the powder diffraction data collected at room temperature has larger cell parameters and a higher cell volume.

Parameters	Rietveld Refinement	Single Crystal
<i>a</i> [pm]	607.0(2)	601.32(6)
<i>b</i> [pm]	1243.44(8)	1228.5(1)
<i>c</i> [pm]	1606.2(4)	1578.6(2)
α [°]	106.688(9)	106.241(3)
β [°]	91.17(1)	90.832(3)
γ [°]	100.77(1)	100.862(4)
V [Å ³]	1137.6(4)	1096.7(2)
T [K]	293	100
Rwp	7.855	
Rexp	7.375	
Rp	5.378	
gof	10.651	

Table 23: *Rietveld Refinement for Rb[Cl₃CSO₃]*.

Figure 80 depicts the IR-spectra of all measured alkali trichlates with the calculated bands for the trichlate anion in black and Table 24 (p. 101) lists all measured bands with assignments based on the calculated data.



Figure 80: Measured IR spectra of all alkali trichlate salts from Lithium to Caesium with calculated vibrational bands for the anion $[Cl_3CSO_3]^-$ in black.

A geometry optimisation for the anion $[Cl_3CSO_3]^-$ within DFT was conducted using the *PBEO* exchange-correlation functional and a *cc-pVTZ* basis set for all elements.^[114] The theoretical vibrational modes are compared to the experimental data and assignments of the vibrational bands is based on the theoretical calculations.
Li	Na	K	Rb	Cs	$[Cl_3CSO_3]^-$	Assignment
493 br	541 s	548 s	514 w	511 sh	531	δ -SO ₃ sciss.
	590 m	556 sh	535 sh	533 s	536	δ -SO ₃ sciss
			541 s	549 s		
			546 sh			
			555 m			
		584 sh	572 m	577 sh		
			585 s			
601 br	613 m	610 <i>s</i>	606 s	600 s	607	δ -all
	644 sh		626 m	614 sh		
705 br	752 w	748 w	701 w	707 w	779	vasym-CCl ₃
			749 w	745 w		
800 s	788 m	797 s	789 s	788 s	792	v-CS
	801 m		805 m			
	814 m	809 sh	814 m	812 sh		
	831 w	832 w	831 w	822 vw		
			872 m	854 w		
			884 sh			
			1020 sh	999 sh		
1066 s	1062 m	1060 m	1055 s	1049 s	1063	v _{sym} -SO ₃
1104 sh	1076 sh			1175 w		
1217 s	1233 s	1243 s	1221 s	1245 s	1307	vasym-SO3
1231 sh	1261 m	1270 m	1243 s	1256 sh		
1246 sh			1260 s	1287 vw		
1267 m						
1296 w						
1304 w	1374 vw	1385 br				
1634 w	1583 vw	1616 w				δ -H ₂ O [*]
1658 sh	1623 w	1637 sh				δ -H ₂ O*
	1698 vw	3219 br				δ -H ₂ O*
3393 m	2975 vw					v-H ₂ O*
3459 m	3478 w	3447 vw				v-H ₂ O*

Table 24: Measured IR-bands of $Li[Cl_3CSO_3] \cdot 2 H_2O$, $Na[Cl_3CSO_3] \cdot H_2O$, $K[Cl_3CSO_3] \cdot H_2O$, $Rb[Cl_3CSO_3]$ and $Cs[Cl_3CSO_3]$ with calculated data for $[Cl_3CSO_3]^-$ and Assignments.

3530 w	3545 w	3543 w	v-H ₂ O*
3771 sh		3610 w	v-H ₂ O*

*Assignments are not based on DFT calculations.

All trichlate salts with water within their crystal structure show additional signals above 1500 cm^{-1} which are assigned to the deformation vibrations (~1620 cm⁻¹) or stretching vibrations (above 3000 cm^{-1}) of water. The asymmetric stretching vibrations (~ 1300 cm^{-1}) of the SO₃ units show an annulment of degeneracy by multiple bands, where the calculated spectrum shows only one single peak. Furthermore, the experimental energy of these vibrations is lower, than theory proclaims. With the exception of the water vibrations above 1500 cm^{-1} and the foreign bands at 701 cm⁻¹, 872 cm⁻¹ and 884 cm⁻¹ obtained for the rubidium salt, all experimental data are very similar.

Rubidium Trichlate Chloride

Within my master thesis a bi-anionic potassium trichlate chloride with the formula $K_3[Cl_3CSO_3]_2Cl$ was synthesised and characterised by X-ray diffraction.^[126] The potassium salt was prepared by a solid state reaction between Cl_3CSO_2Cl and an aliquot of KOH in a glass ampoule at 423 K. A slow cooling rate of 1.25 K/h led to crystallisation of colourless, elongated needles.

The isotypic rubidium salt was synthesised in a round bottom flask at mild conditions of 333 K in aqueous solution. The obtained single crystals characterise as a heteroleptic compound with trichlate and chloride anions within the structure. Both compounds crystallise in the monoclinic space group I2/a with eight formula units. A comparison of the cell parameters of both structures is given in Table 25. The cell parameters are of the same magnitude, with the *a*- and *b*-axes enlarged for Rb₃[Cl₃CSO₃]₂Cl, while the *c*-axis is slightly shorter in the rubidium salt. As expected, the cell volume of Rb₃[Cl₃CSO₃]₂Cl is somewhat larger, as it incorporates the larger cation.

Compound	K ₃ [Cl ₃ CSO ₃] ₂ Cl	Rb ₃ [Cl ₃ CSO ₃] ₂ Cl	
<i>a</i> [pm]	2464.3(8)	2554.7(6)	
<i>b</i> [pm]	593.9(2)	613.15(9)	
<i>c</i> [pm]	2352.4(8)	2324.0(4)	
β [°]	102.91(3)	103.343(3)	
V [Å ³]	3356(2)	3542(1)	
density [g/cm ³]	2.176	2.583	
T [K]	150	100	

Table 25: Comparison of the Cell Parameters of the two Isotypic Structures $K_3[Cl_3CSO_3]_2Cl$ and $Rb_3[Cl_3CSO_3]_2Cl$.

The asymmetric units consist of two unique trichlate anions, one chloride anion and four unique potassium or rubidium cations, respectively:



Figure 81: Asymmetric unit of the two isotypic structures of K₃[Cl₃CSO₃]₂Cl (top) and Rb₃[Cl₃CSO₃]₂Cl (bottom).

Bond angles of the two unique trichlate anions within Rb₃[Cl₃CSO₃]₂Cl vary only in the range of the stated error. All bond angles around the sulphur atom exhibit larger 103

deviations from a perfect tetrahedral angle as opposed to bond angles around the carbon atom. Within the potassium salt S-O bond lengths range from 142.7(7) pm to 145.9(8) pm. The shortest S-O distance lies between S2-O23 and the longest S-O distance between S2-O21. Difference of the bond lengths lies in the coordination ability of the individual oxygen atoms. O22 coordinates solely to one potassium cation (K1), O23 to K2 and K3, whereas O21 coordinates to K1, K2 and K3. The C-Cl distances vary between 174(1) pm (C1-Cl11) and 178(1) pm (C1-Cl12, C2-Cl21, C2-Cl22). The respective rubidium salt exhibits the shortest S-O distance in the S1-O11 and S2-O22 bond with 144.0(3) pm. The longest S-O distance can be found in the S1-O12 bond with 144.7(2) pm. The C-Cl bonds are almost identical, ranging from 176.0(3) pm (C1-Cl11, C1-Cl13) to 176.9(3) pm (C2-Cl23). Unlike the potassium salt, the rubidium analogue reveals no significant difference in the S-O and C-Cl bond lengths of the two unique trichlate anions.

Two of the four unique potassium (rubidium) cations are located at special sites of the unit cell. K2 (Rb2) is located on *4a* and K4 (Rb4) on *4e Wyckoff* position (Figure 82). K2 (Rb2) sits on an inversion centre and K4 (Rb4) is located on a two-fold rotational axis. Identical to other trichlate salts, a cross section of the unit cell clearly depicts the layered build-up of the structure. The chloride anions are incorporated within the polar layer, in between the SO₃-functions with all counter potassium cations. That leaves all CCl₃-groups facing each other in the non-polar layer with merely *Van der Waals* interactions.



Figure 82: Cross section of the unit cell, description of the special positions for K2 (Rb2) and K4 (Rb4).

Four distinguishable coordination spheres are found for potassium and rubidium. The coordination number varies between seven (K2) and eight (K1, K3, K4) for potassium and lies between seven (Rb3), eight (Rb2, Rb4) and nine (Rb1) for rubidium. With the exception of Rb1 and K1, the coordination spheres of the specific cations are equal:



Figure 83: Coordination spheres of the cations within $K_3[Cl_3CSO_3]_2Cl$ and $Rb_3[Cl_3CSO_3]_2Cl$.

In the case of Rb1, a similar coordination as observed for K1 is found, with two additional bonds from Cl21 and Cl22, leading to the coordination number nine (Figure 83). The cations of highest symmetry are K2 and Rb2. The respective cation is surrounded by a six-atom ring in chair conformation with further coordination to two equal oxygen atoms normal to the six-atom ring. Rb4 and K4 are positioned on a two-fold rotational axis, as can be easily deduced from the coordination sphere. The potassium oxygen distances range from 265.3(8) pm (K1-O22) to 312.3(8) pm (K4-O12) and the potassium chlorine distances reach from 297.4(4) pm (K3-Cl1) to 364.4(4) pm (K2-Cl23). The Rb-O coordination sphere is limited to a maximum distance of 322.5(2) pm (Rb4-O12), the longest Rb-Cl distance is 384.09(9) pm (Rb1-Cl21). A shorter distance between the cationic species and the free chloride anions (Cl1) is observed due to closer proximity and higher electrostatic interaction. These two crystal structures for the heteroleptic trichlate chlorides show, that the postulated reaction equation according to Kolbe, is not as straight forward as initially hypothesised. Next to the inevitable production of alkali chlorides, which undoubtedly are the driving force of the reaction mechanism, other chloride containing compounds can be gathered, as well. The preparation of both Rb₃[Cl₃CSO₃]₂Cl and K₃[Cl₃CSO₃]₂Cl, produced via different methods, once under ambient conditions (rubidium salt) and once under hydrothermal conditions (potassium salt), show that the synthesis according to Equation 26 is variable.

 $CI_3CSO_2CI + 2 MOH \longrightarrow M[CI_3CSO_3] + MCI + H_2O Equation 26$

These insights, as well as the inconvenient removal of metal chlorides, made the preparation of the free trichlic acid a vital aspect of this work.

Publication 1

Trichlates, an Unattended Class of Compounds: Characterization of Cl₃CSO₂Cl, and (H₅O₂)[Cl₃CSO₃]

Alisha Mertens, David van Gerven, Inka Kunert, Mathias S. Wickleder

Chem. Eur. J. 2023, e2023302128, 4-11.

This paper discusses the synthesis and characterisation of trichloromethanesulphonic acid and its precursor, trichloromethanesulphonyl chloride. The characterisation entails the structural determination by single crystal and OHCD aided X-ray diffraction. Furthermore, the named compounds are analysed regarding their thermal and spectroscopic behaviour and calculated by the aid of DFT. The supplementary information delivers detailed description on the synthesis and additional characterisation methods, such as NMR spectroscopy.

Including the draft of the manuscript, the principal author synthesised all analysed products, conducted the characterisation experiments, when not stated otherwise below, evaluated all collected data and plotted these results for the publication. Dr. David van Gerven provided the DFT calculations and supervised the OHCD enhanced crystal diffraction experiments. Dr. Inka Kunert conducted the low temperature DSC measurements at the TH Dresden. Prof. Dr. Mathias S. Wickleder is the leader of this research group and supervised the entire research topic. Additionally, Prof. Dr. Mathias S. Wickleder is the second author of this paper and contributed by proof reading the manuscript and its revision process.

Publication 2

Synthesis and Characterization of the Trichlates [N(CH₃)₄][Cl₃CSO₃], [NH₄][Cl₃CSO₃], and the Dichlate [NH₄][Cl₂CHSO₃]

Alisha Mertens, David van Gerven, Hyunsong Lee and Mathias S. Wickleder

Eur. J. Inorg. Chem. 2023, e202300535, 1-7.

This publication involves the preparation and characterisation of three compounds, two trichlate salts and an ammonium dichloromethanesulphonate ("dichlate") species. All three salts are structurally elucidated by single crystal X-ray diffraction. Furthermore, DFT calculations and IR spectroscopy is given on the two trichlate salts. These results are discussed and compared. Thermal stability and decomposition of the two trichlate species was investigated by MS-coupled DSC/TG measurements. The ammonium dichlate was randomly prepared in a synthesis, combining the reactants Ba(OH)₂ and (H₅O₂)[Cl₃CSO₃] in the presence of NH₃, aiming at the earth-alkali trichlate Ba[Cl₃CSO₃]₂. Notwithstanding the accidental preparation of [NH₄][Cl₂CHSO₃], the obtained single crystal delivered the first crystal structure of a dihalidomethane-sulphonate.

The principal author synthesised and characterised the trichlate salts $[N(CH_3)_4][Cl_3CSO_3]$ and $[NH_4][Cl_3CSO_3]$, plotted all data for the publication and drafted the manuscript. Dr. David van Gerven performed the DFT calculations on the ions $[N(CH_3)_4]^+$, $[NH_4]^+$ and $[Cl_3CSO_3]^-$. Hyunsong Lee synthesised the ammonium dichlate in the course of her Bachelor degree under the supervision of the research group led by Prof. Dr. Mathias S. Wickleder, who is also the co-author to this manuscript.

Transition Metal Trichlates

While the main focus of this work is dedicated to alkali trichlates, as they might play an important role for electrochemical appliances akin to triflates, a few investigations on trichlate species of metals with higher valency were made. Transition metal trichlate salts of copper and cobalt were yielded in their oxidation state +II. Furthermore a reaction of an iron(III)-salt with trichlic acid in DMSO let to a trichlate salt with a cation in the oxidation state +III.

Tetraaqua-bis-Trichloromethansulphonato-Copper(II)

Exothermic reaction of (H₅O₂)[Cl₃CSO₃] with Cu(NO₃)₂, with small amounts of water present, is instantaneous. Figure 84 depicts the produced crystalline material of copper trichlate. When analysed under the microscope, the compound appears as agglomerated multi-domain crystals. The agglomerated, blue crystalline bulk shows clear edges. These layered, rectangular crystals however, show different colours under the polarised light of the microscope, suggesting further anisotropy of the smooth surfaces. When pried apart, each rectangular crystal falls into several smaller, colourless crystallites, hence delivering thin plates, which are almost undetectable under the microscope.



Figure 84: Pictures of the obtained crystalline material of Cu[Cl₃CSO₃]₂ · 4 H₂O under the light microscope: Left: Product from aqueous solution in a crystallisation dish, Right: Product from hydrothermal reaction in a glass ampoule.

Several synthetic approaches were necessary in order to achieve suitable single crystals for X-ray diffraction measurements. A single crystal from a hydrothermal reaction between $(H_5O_2)[Cl_3CSO_3]$ and $Cu(NO_3)_2$, with 0.2 mL H₂O and a maximum reaction temperature of 353 K, was solved by X-ray diffraction. The measured single crystal has

an unresolved multi-domain problem, which leads to high disorder within the suggested structure refinement. Probable cause of the multi-domain existence are the very thin crystal layers, which are most likely oriented in a random fashion. Initially the crystals were measured at 100 K. In this case, the temperature was risen to 250 K to allow reorientation of the shock-frozen multi-domain (layered) sample. The copper trichlate was solved as a tetrahydrate, crystallising in the monoclinic space group *C*2/*m* with four formula units and the cell parameters a = 747.11(6) pm, b = 988.01(8) pm, c = 2352.7(2) pm, $\beta = 90.415(3)^{\circ}$ and V = 1736.6 Å³. The extended asymmetric unit consists of two unique trichlate anions, two copper cations and two water molecules. The chlorine atoms suffer from severe disorder.



Figure 85: Extended asymmetric unit of $Cu[Cl_3CSO_3]_2 \cdot 4 H_2O$ with disorder of the chlorine atoms (top) and showing only one set of chlorine atoms (bottom). Thermal ellipsoids are set to 70% probability.

Overall, the thermal ellipsoids are large, showing a residual high degree of displacement, that could not be overcome by refinement of the suggested disorder. The atoms S1, S2, O11, O21, Cl1A (Cl1B) and Cl3A (Cl3B) are located on a mirror plane (*Wyckoff* position *4i*). Cu1 and Cu2 possess the cell edges at the coordinates 0 0 0 (*Wyckoff* position *2a*,

Cu2) and $\frac{1}{2}$ 0 $\frac{1}{2}$ (*Wyckoff* position 2*d*, Cu1). Thus, the reduced asymmetric unit consists of two halves of trichlate anions and two quarters of Cu²⁺ cations, resulting in an equalisation of charge.

In accordance to previously discussed crystal structures of alkali trichlates, the crystal structure consists of layers, created by the amphiphilic polarity of the trichlate anion. The CCl₃-groups are facing each other head-on, the SO₃-groups are connected to the copper cation through coordination from O21 or O11. The reoccurring building block is the $[Cu(H_2O)_4(Cl_3CSO_3)_2]$ complex, stacked in rows in a parallel fashion. Hence the copper trichlate does not classify as a typical salt and rather a neutral complex and will therefore from here on out be summarised as $[Cu(H_2O)_4(Cl_3CSO_3)_2]$.



Figure 86: Crystal structure of $[Cu(H_2O)_4(Cl_3CSO_3)_2]$, cross sections of the unit cell depicting the (1 0 0) and (0 1 0) plane.

Six oxygen atoms, two belonging to one set of trichlate anions and the other four deriving from one set of water molecules coordinate Cu1 and Cu2 (Figure 87). Due to the high symmetry of the position Cu1 and Cu2 inhabit (2/m), only two unique oxygen atoms build each coordination sphere. The Cu-O distances lie at 192.2(8) pm for Cu2-O2, 236(1) pm 111

for Cu2-O21, 192.1(8) pm for Cu1-O1 and 237(1) pm for Cu1-O11. These findings concur with those found for Cu[F₃CSO₃]₂: The copper triflate consists of Cu(OTf)₆ octahedrons, and displays Cu-O distances of 228.0(6) pm (axial coordination) and 198.1(7) – 192.8(9) pm (equatorial coordination)^[125]. In accordance to the symmetry of the centre cations, the built octahedrons are best described as parallelogrammic bipyramids, with distortion values of $\delta = 3.455$ (Cu1) and $\delta = 3.435$ (Cu2). Owed to the prior discussed issues of the quality of the crystals and the resulting uncertainties of the modulated solution, a further discussion of bond lengths and angles of the anion will be neglected. All data can be found in the appendix (p. 218 and following).



Figure 87: Coordination around Cu1 and Cu2 within [Cu(H₂O)₄(Cl₃CSO₃)₂].

The measured powder diffraction pattern reveals that the copper trichlate is the only crystalline phase present. This was further established by *Rietveld* refinement (Figure 88).



Figure 88: Measured powder diffraction pattern (black) with Rietveld refinement (red) and difference curve (blue) for $[Cu(H_2O)_4(Cl_3CSO_3)_2]$. The sample was measured with M_{OKal} radiation in a capillary with 0.3 mm diameter.

The blue difference curve shows only mild differences around the diffraction angles 8° and 14° . For the refinement plot, all cell parameters were refined. The resulting data and quality factors are given in Table 26. The refined cell at room temperature has slightly larger cell parameters, however, the cell parameter *a* is almost constant, while *b* and *c* increase. The highest change is evident for the cell parameter *c*. This could hint at a further distancing of the layers along the crystallographic *c*-axis, where the layers are merely held together by *van der Waals* interactions.

Parameters	Rietveld Refinement	Single Crystal	
<i>a</i> [pm]	748.9(1)	747.11(6)	
<i>b</i> [pm]	991.13(9)	988.01(8)	
<i>c</i> [pm]	2364.0(3)	2352.7(2)	
β[°]	90.28(1)	90.415(3)	
V [Å ³]	1754.7(4)	1736.6(3)	
T [K]	293	100	
Rwp	8.084		
Rexp	6.298		
Rp	6.522		
gof	1.284		

Table 26: Rietveld Refinement for $[Cu(H_2O)_4(Cl_3CSO_3)_2]$.

Hexaaqua-Cobalt(II) Trichloromethanesulphonate

Conversion of $Co(NO_3)_2$ with $(H_5O_2)[Cl_3CSO_3]$ in a stoichiometric ration of 1:2, followed by recrystallisation in a sealed glass ampoule with 0.2 mL of H₂O, led to the formation of a pink solution, from which colourless crystalline material grew. Comparable to the copper trichlate the observed single crystals show a rectangular shape and are mostly adhered to one another. Similarly to $[Cu(H_2O)_4(Cl_3CSO_3)_2]$, the adhered crystals reveal very thin plates when pried apart.



Figure 89: Picture of the content of an ampoule, after the conversion of $Co(NO_3)_2$ with trichlic acid under the presence of 0.2 mL H₂O.

The measured single crystal could be solved as $[Co(H_2O)_6][Cl_3CSO_3]_2$, crystallising in the monoclinic space group $P2_1/n$ with a = 661.32(2) pm, b = 648.54(3) pm, c = 2319.9 pm, $\beta = 91.257(2)^\circ$, V = 994.75(7) Å³ and Z = 2. One unique trichlate anion, one cobalt cation and three unique water molecules make up the asymmetric unit. Figure 90 depicts the asymmetric unit, showing rather large thermal ellipsoids within the CCl₃group. Co1 occupies the special site of an inversion centre with the *Wyckoff* description 2*b*.



Figure 90: Asymmetric unit of $[Co(H_2O)_6][Cl_3CSO_3]_2$. Thermal ellipsoids are set to 70%.

Co1 is coordinated by six oxygen atoms, belonging to three unique water molecules. Thus, unlike within the structure of copper trichlate tetrahydrate, no coordination from the trichlate anion to the metal centre is evident. The $[Co(H_2O)_6]^{2+}$ octahedrons are closest to a perfect trigonal antiprism with a low distortion value of $\delta = 1.502$. The Co-O distances vary between 205.5(2) pm (Co1-O2) and 209.0(2) pm (Co1-O3). For comparison, the respective hexaaqua-cobalt(II) sulphate has a similar arrangement, with

 $[Co(H_2O)_6]^{2+}$ octahedrons, where the Co-O distances range from 204.8(5) pm to 211.2(4) pm. A connection from the respective $[Co(H_2O)_6]^{2+}$ polyhedrons to the trichlate anion is present through hydrogen bonding from water molecules to the SO₃-groups of the anions (Figure 91, bottom). Even without actual coordination of the SO₃-functions to the metal cations, the typical layers, where SO₃-groups imbed the counter ions and the incorporated water, is prominent. S-O distances are almost identical, varying only at the first decimal place (144.2(2) pm – 144.6(2) pm). The C-S bond conducts 183.8(3) pm and the C-Cl bonds range from 174.8(4) pm (C1-Cl11) to 176.9(3) pm (C1-Cl13). These bond lengths are in the same range as those of previous structures. All bond lengths and angles are listed in the crystallographic tables, p. 222 and following.



Figure 91: Crystal structure of $[Co(H_2O)_6][Cl_3CSO_3]_2$: Cross sections of the unit cell, coordination around Co1 and hydrogen bonds between the water molecules and the trichlate anions..

Figure 92 (p. 116) depicts the measured powder diffraction pattern of the cobalt trichlate with *Rietveld* refinement and difference curve. While most of the reflections can be brought into convergence with the single crystal data set, larger discrepancies in the intensities of individual reflections are observed. Furthermore, at least two foreign reflections are detected at 7.6° and 8.5° . These reflections cannot be assigned to either modifications for (H₅O₂)[Cl₃CSO₃] nor Co(NO₃)₂ or CoSO₄. For the *Rietveld* fit all cell

parameters were refined, as well as atom positions for the chlorine atoms and the oxygen atoms from the water molecules. Refinement of a preferred orientation along the (0 0 1) plane delivered the parameter 0.23(7), revealing the favoured direction of growth in alignment to the observed layers. Table 27 lists the refined cell parameters with the original data from the single crystal diffraction experiments. Comparable to the results obtained for the *Rietveld* fit for [Cu(H₂O)₄(Cl₃CSO₃)₂], two cell parameters change, while one parameter remains almost identical (*b*). Increase of the *c*-axis might hint at a further separation of the layers.



Figure 92: Measured powder diffraction pattern (black) with Rietveld refinement (red) and difference curve (blue) for $[Co(H_2O)_6][Cl_3CSO_3]_2$ The sample was measured with $Mo_{K\alpha 1}$ radiation in a capillary with 0.3 mm diameter

Parameters	Rietveld Refinement	Single Crystal
<i>a</i> [pm]	665.9(1)	661.32(2)
<i>b</i> [pm]	649.6(1)	648.54(3)
<i>c</i> [pm]	2331.3(5)	2319.9(1)
β [°]	91.07(2)	91.2577(7)
V[Å ³]	1008.3(4)	994.75(7)
T [K]	293	100
Rwp	10.721	
Rexp	6.546	
Rp	8.401	
gof	1.638	

Table 27: Rietveld Refinement for $[Co(H_2O)_6][Cl_3CSO_3]_2$.

Hexakis-Dimethylsulfoxide-Iron(III) Trichloromethanesulphonate

A reaction of iron(III)-acetate with trichlic acid in a stoichiometric ratio of 1:3 at ambient conditions led to an iron(III)-trichlate salt. Various crystallisation attempts in other solvents than water were attempted throughout this work in order to provoke a structure, that ideally does not incorporate crystal water. The yielded iron salt was converted utilising DMSO as solvent, leading to a [Fe(DMSO)₆][Cl₃CSO₃]₃ single crystal. Hence, while the exclusion of water within the structure was successful, the cation is still solvated. The synthesis produced light, yellow crystals with a rectangular shape. Unlike the cobalt and copper trichlates, these crystals were not as agglomerated.



Figure 93: Light microscope picture of the obtained crystals of [Fe(DMSO)₆][Cl₃CSO₃].

The characterised single crystal of $[Fe(DMSO)_6][Cl_3CSO_3]_3$ crystallises with four formula units in the monoclinic space group $P2_1/c$ with the cell parameters a = 1100.25(3) pm, b = 1100.45(3) pm, c = 3565.8(1) pm, $\beta = 90.996(1)^{\circ}$ and V = 4316.7(2) Å³. The elongation of at least one cell parameter can be recognised in the macroscopic appearance of the crystals (Figure 93). All atoms are located on general sites of the unit cell. The asymmetric unit consists of three unique trichlate anions, one iron cation and six solvent molecules, surrounding the metal centre. There is no additional coordination from the trichlate anions to iron, instead the anions are undisturbed in close proximity to the $[Fe(DMSO)_6]^{3+}$ complexes.



Figure 94: Asymmetric unit of [*Fe*(DMSO)₆][*Cl*₃*CSO*₃], thermal ellipsoids are set to 70% probability.

The solvation of iron by DMSO leads to a disruption of the typical layered crystal structure, as observed in other compounds. Comparable to $[N(CH_3)_4][Cl_3CSO_3]$, the outer shell around the cation works as a buffer of positive charge and changes the polarity of the surface of the iron complex. The absence of crystal layers might also be responsible for the more facile preparation and extraction of single crystals, suitable for X-ray diffraction. In viewing direction of the crystallographic *b*-axis, six different orientations of the trichlate anions are shown (Figure 94, p. 118). Each unique anion has two orientations, which are superimposable by a two-fold rotation. The anion around C1 is oriented parallel to the *a*-axis, while the anion around C2 can be found in line with the iron-DMSO polyhedrons. The trichlate anion around C3 shows both orientations next to one another, with its C-S bond on the cell edges and along $\frac{1}{2}$ of c (Figure 95, (010) plane). The Fe-O distances vary between 198.3(2) pm (Fe1-O1/O3) and 202.3(2) pm (Fe1-O4). Those are in the same range as distances found for the cationic complex of [Fe(DMSO)₅Cl][O(FeCl₃)₂], solved from X-ray powder diffraction experiments $(d_{\text{Fe-O}}: 200.3 \text{ pm} - 206.5 \text{ pm}).^{[127]}$ With the aid of the program *polynator*, a further description of the octahedron as *didigonal scalenohedron* ($\overline{4}2m$) with the low distortion value of $\delta = 1.217$ was determined. Bond angles and lengths of the three unique trichlate anions are similar to those found for previously discussed crystal structures. Comparable to the results of the cobalt trichlate, the undisturbed, non-coordinating trichlate anions have very narrowly distributed bond lengths, which also applies to the S-O bonds. The S-O bonds range from 143.8(2) pm (S3-O33, S3-O32) to 144.8(2) pm (S2-O21), the C-S

bonds from 184.7(3) pm (S3-C3) to 185.5(3) pm (S2-C2) and the C-Cl bonds from 176.1(3) pm (C3-Cl32) to 176.9(3) pm (C1-Cl13). A more detailed list of selected bond lengths and angles is attached in the appendix, p. 225 and following.



Figure 95: Cross sections of the unit cell of [*Fe*(DMSO)₆][*Cl*₃*CSO*₃] and coordination to Fe1.

While the utilised reactant trichlic acid is not free of water, the produced iron trichlate salt is free of additional crystal water. Presumably, next to the very low amount of water present, the incorporation of DMSO within the crystal lattice changes the hydrophilicity of the product. Furthermore, the production of a trichlate salt with DMSO as the sole ligand to Fe^{3+} underlines the weak coordination ability of the trichlate anion. A ligand exchange after the solvation of iron acetate in DMSO does not occur.

Decaaqua-Dinitrato-di-µ-Trichloromethanesulphonato-di-Lanthanum(III) *Bis*-Trichloromethanesulphonate Dihydrate

 $La(NO_3)_3$ and $(H_5O_2)[Cl_3CSO_3]$ were solved in the amount of water necessary for dissolution. The solution was poured onto a crystallisation dish and slow evaporation of solvent led to colourless, needle shaped crystals.



Figure 96: Picture of the yielded crystals under the light microscope after a reaction between $La(NO_3)_3$ and $(H_5O_2)[Cl_3CSO_3]$.

A measured single crystal was solved as a lanthanum salt with a dinuclear complex with the composition $[La_2(H_2O)_{10}(NO_3)_2(\mu-Cl_3CSO_3)_2](Cl_3CSO_3)_2 \cdot 2H_2O$. The compound crystallises in the triclinic space group $P\bar{l}$ with one formula unit and the cell parameters $a = 639.17(4) \text{ pm}, b = 1289.39(6) \text{ pm}, c = 6354.2(2) \text{ pm}, a = 63.542(2)^{\circ}, \beta = 88.816(2)^{\circ}, \beta$ $y = 75.698(2)^{\circ}$ and $V = 1028.2(1) \text{ Å}^3$. The asymmetric unit consists of two unique trichlate anions, one nitrate anion, six unique water molecules and one lanthanum cation, all located on general sites. Cross section of the unit cell displaying the (100) plane reveals the typical arrangement of the trichlate anions (Figure 97, p. 121). The CCl₃groups are pointing in one direction, while the SO₃-groups are pointing in the opposite direction, oriented towards the positive charge of La^{3+} . Five of the six unique water molecules are close to the cation, building the coordination sphere and are thus incorporated into what was previously described as the polar layer. Contrary, one water molecule around O9 is located further away from the cationic sphere and relatively close to the CCl₃-groups, previously discussed as non-polar region. Furthermore, the insertion of nitrate anions into the crystal structure hinders the formation of perfect layers, as was observed for most of the alkali trichlate salts. While the nitrate anion is in line, embedded within neighbouring trichlate anions, it does not exhibit the same amphiphilic property and hence breaks the typical layered build-up. The water molecule around O9 is located in close proximity to the nitrate anion.



Figure 97: Asymmetric unit and cross section through the unit cell for $[La_2(H_2O)_{10}(NO_3)_2(\mu-Cl_3CSO_3)_2](Cl_3CSO_3)_2 \cdot 2 H_2O$. Thermal ellipsoids are set to 70%.

Five water molecules, two trichlate anions and one nitrate anion, leading to the coordination number nine, coordinate lanthanum (Figure 98). Only one of the two distinguishable trichlate anions coordinates to the cation over O22 and O23. The nitrate anions have a chelating coordination, bonding with two oxygen atoms (O6, O7).



Figure 98: Coordination around La1 within $[La_2(H_2O)_{10}(NO_3)_2(\mu-Cl_3CSO_3)_2](Cl_3CSO_3)_2 \cdot 2 H_2O.$

The La-O distances lie between 246.1(1) pm (La1-O4) and 264.6(2) pm (La1-O6). With a bond length of 257.5(2) pm for La1-O7, the two bonds from nitrate to lanthanum are very similar to La-O bonds from LaO(NO₃) (La-O: 268.4(7) pm, 257.8(2) pm).^[128] The nitrate anion is nearly planar, with O-N-O angles close to 120° (116.1(2)°, 121.4(2)°, 122.5(2)°). All N-O bond lengths are slightly shorter, than those observed for LaO(NO₃).

This is in particular the case for N1-O8, where the bond lengths conducts 122.1(2) pm. O8 does not coordinate to lanthanum, other than O6 and O7, where the N-O bonds are weakened due to the additional coordination. The bonds N1-O6 (126.4(2) pm) and N1-O7 (127.7(2) pm) are closer to the bond lengths found for LaO(NO₃) (129(1) pm), 128.4(9) pm), where all oxygen atoms of the anion coordinate (two unique oxygens). The trichlate anions coordinate with La1-O bond lengths of 250.7(2) pm (La1-O23) and 257.3(2) pm (La1-O22). A literature survey on the crystallographic database CCDC (January 2024) reveals, that the amount of lanthanum triflates, where lanthanum is coordinated by both, water and triflate anions is limited. The few crystal structures where this applies are also coordinated by large organic ligands, which have multiple binding sites and are sterically demanding. One of those examples is the tetra-aqua-(2,6*bis*((4*S*,5*S*)-4,5-diphenyl-1,3-oxazolin-2-yl)pyridine-*N*,*N*',*N*'')-*bis*(tri-fluoromethanesulphonato-O)-lanthanum(III)trifluoromethanesulphonate monohydrate.^[129] In this case, La^{3+} is coordinated by two triflate anions, four water molecules and one large organic ligand, chelating with three bonds from nitrogen to lanthanum. The La-O distances from the triflate anions obtain 250.6(8) pm and 250.7(6) pm and are therefore in the same range as the La1-O distances found in this trichlate salt. Furthermore, heteroleptic compounds with two different coordinating anions are rather scarce, which renders this particular lanthanum compound even more special. Comparable to [Fe(DMSO)₆][Cl₃CSO₃]₃, these results reveal the weak coordinating ability of trichlate anions with respect to solvents and in this case the nitrate anion.

Even though only one of the two crystallographically distinguishable trichlate anions coordinates to the cation, bond lengths and angles of the two unique anions are almost identical. The S-O distances vary between 144.6(2) pm (S2-O21) and 145.4(2) pm (S2-O23, S1-O13). The C-S bond lengths are 184.1(2) pm and 184.7(2) pm long. The C-Cl bonds range from 175.0(3) pm to 176.3(3) pm. Further information on bond lengths and angles can be found in the crystallographic tables, p. 231 and following.

A powder diffraction pattern of the acquired compound indicates a poor crystallinity due to a high background noise. Unfortunately, the attempt to reach a higher crystallinity after tempering of the sample at 328 K led to a new diffraction pattern, suggesting a phase transition or more likely, decomposition of the product. The initial powder diffraction pattern is given below and suggest that the structure of the analysed single crystal represents the main crystalline phase. However, due to the low quality of the obtained diffraction pattern, additional foreign, crystalline phases cannot be ruled out.



Figure 99: Measured powder diffraction pattern of $La[Cl_3CSO_3]_2NO_3 \cdot 6 H_2O$ (black) with simulated data from the respective single crystal in green. The sample was measured with MO_{Kal} radiation in a capillary with a diameter of 0.3 mm.

2.6. Tribric Acid and Tribrate Salts

The route towards tribromomethanesulphonates, short tribrates, is mainly unchartered territory. As mentioned in previous chapters, Cl₃CSCl is the first step towards trichloromethanesulphonates, using the cheap starting material CS₂ and chlorine gas. A reaction between CS₂ and bromine, however, delivers the carbon disulphotetrabromide (CS_2Br_4) .^[130] Instead, in order to synthesise the corresponding Br₃CSCl, carbon sulphur selenide should be applied as reactant in the reaction with bromine.^[130] Unlike CS₂, CSSe is not commercially available. *Henriksen* introduced the most promising synthesis of CSSe with the cheapest starting materials.^[131] Here, sodium selenide is converted with *N*,*N*-dimethylthiocarbamoyl chloride to sodium *N*,*N*-dimethylthioselenocarbamate. Lastly, reaction with trichloroacetic acid should generate CSSe.

$$N - \begin{pmatrix} S \\ CI \end{pmatrix} + Na_{2}Se \longrightarrow N - \begin{pmatrix} S \\ Se^{-} \end{pmatrix} + NaCI \qquad Equation 27$$

$$N - \begin{pmatrix} S \\ Na^{+} \end{pmatrix} + \begin{pmatrix} CI_{3}CCOOH \\ -NaCI \\ -Me_{2}NH \end{pmatrix} \quad Se \equiv C \equiv S \qquad Equation 28$$

The yield of CSSe, as a starting material for tribrates has been found as too low, and the synthetic effort too high. The synthesis of CSSe relies on several purification techniques, mainly extraction and distillation. A major drawback are the large amounts of side products obtained (CSe₂ and CS₂). A synthetic route towards [Br₃CSO₃]⁻ from CSSe was therefore deemed inefficient. While the tribrate anion has yet to be introduced into the scientific world, (Br₃CSO₂)- and (Br₃CSO₃)- fragments as part of larger, organic molecules are not new to chemists. *Ochal et al.* and *Van Waes et al.* reported the successful bromination of methylsulphones and methanesulphonates with larger organic residues utilising potassium hypobromite:^[132,133]



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A bromination of trichlic acid and methanesulphonic acid using KOBr remained unsuccessful, yielding merely large amounts of KBr and KBrO₃ next to remaining starting material. Hence, the aromatic ring plays a crucial part in the reaction mechanism, which has yet to be understood completely. Therefore, the simplest reactant for the purpose of creating a tribrate compounds with the smallest amount of side products and lowest environmental impact is phenyl methanesulphonate. After bromination with KOBr, the organic phenyl ring has to be cleaved off. This process of cleavage was impossible for phenyl sulfones (see Equation 29) as the carbon sulphur bond is too strong. Separation of tribromomethanesulphonates in alkaline medium however was successful.

Publication 3

Triflate's Bigger Brother: The Unprecedented Tribrate Anion, [Br₃CSO₃]⁻

Alisha Mertens, Katrin Eppers, David van Gerven and Mathias S. Wickleder

Eur. J. Inorg. Chem. 2023, e202303617, 1-7.

This publication focuses on the synthesis and structural analysis of the unprecedented $[Br_3CSO_3]^-$ anion (tribrate). A detailed description of the synthesis is delivered and two crystallographic structures, solved from single crystal X-ray diffraction experiments are discussed. Next to K[Br_3CSO_3] · H₂O, the first tribrate salt published in literature, the crystal structure of the intermediate towards tribrates, prior to the cleavage of the organic ring is given. Main features of the molecular crystal structure of C₆H₅OSO₂CBr₃ (phenyl tribromomethanesulphonate) is described and detailed crystallographic data on both crystal structures are provided in the supplementary information. Spectroscopically the potassium tribrate was analysed by *Raman* spectroscopy and a correlation to theoretical presumptions from DFT calculations is given.

The main author drafted the manuscript, provided all graphics for the publication, solved the crystal structures and synthesised the phenyl tribromomethanesulphonate. Katrin Eppers synthesised the potassium tribrate salt in the course of her practical lab course within the research group of Professor Dr. Mathias S. Wickleder, supervised by the main author. Dr. David van Gerven provided the DFT calculation for the tribrate anion and Professor Dr. Mathias S. Wickleder is the co-author of this manuscript and research group leader.

Publication 4

The Molecular Structures of Lithium Trichlate, Li[Cl₃CSO₃] · 2 H₂O, and Lithium Tribrate, Li[Br₃CSO₃] · 2 H₂O

Alisha Mertens, Katrin Eppers, David van Gerven and Mathias S. Wickleder

Eur. J. Inorg. Chem. 2024, e202400060, 1-6.

This publication discusses the crystal structures obtained for the lithium trihalomethanesulphonates $Li[Cl_3CSO_3] \cdot 2 H_2O$ and $Li[Br_3CSO_3] \cdot 2 H_2O$. Both compounds crystallise in the triclinic space group $P\overline{I}$ with molecular structures featuring $\{Li_2[X_3CSO_3]_{2/1}(H_2O)_{2/2}\}$ -dimers (X = Cl,Br). In the centre of these dimers two edge-sharing $[LiO_4]$ -tetrahedrons are located. The shared edge of the two tetrahedrons possess an inversion centre of the unit cell, resulting in the crystallographic equal duplicate of one monomer of $Li[X_3CSO_3] \cdot 2 H_2O$. With the aid of DFT the molecular dimers for both structures could be calculated and bond lengths and angles could be compared to experimentally deduced properties. Furthermore, measured IR-spectra for both structures could be interpreted by theoretical calculations.

The main author drafted the manuscript with Prof. Mathias S. Wickleder as co-author. Also, the main author contributed by solving and refining of both crystal structures, synthesis of precursors for both lithium compounds and plotting of all accumulated data. Katrin Eppers produced the lithium tribrate salt in the course of her master thesis, supervised by the main author. Dr. David van Gerven provided the DFT calclutaions for both {Li₂[X₃CSO₃]_{2/1}(H₂O)_{2/2}}-dimers. Prof. Dr. Mathias S. Wickleder is the research group leader.

3. Conclusion

Fundament of this work was the preparation and structural analysis of compounds, which can be classified as derivatives of methanesulphonic acid (MSA), or compounds, that have a building block, similar to CH₃SO₃H. Thus, focus lay on two major derivatives of MSA: Halogenated methanesulphonates and methanepolysulphonates. The elucidation of the crystal structure of MSA is necessary, for a better understanding of structural changes, when hydrogen is replaced by either a halogen or another sulphonyl group. With the aid of OHCD, the structure of MSA was successfully solved. The acid crystallises without crystal water in the space group $P2_1/c$. The C-S bond length lies at 173.8(1) pm. The bond between the sulphur atom and the oxygen atom carrying the hydrogen conducts 154.28(7) pm and is approximately 10 pm longer than the other two S-O bonds. The acid has a staggered conformation along the C-S bond. With a solution for the crystal structure of $Rb_2[H_3CSO_3]_2 \cdot H_2O$, the row of structurally analysed alkali methanesulphonates is completed. The respective rubidium salt is the only alkali salt with water in its crystal structure. A thermal analysis shows that the water can be thermally removed. The rubidium and potassium methane sulphonate decompose at 700 K, leaving the respective sulphates as remaining decomposition products. With 175.1(3) pm to 180.4(1) pm the observed C-S bond lengths of the alkali salts are slightly longer than the C-S bond of the acid.

Methanedisulphonic acid (MDA) could be successfully synthesised via two different routes. The preparation from dichloromethane and potassium sulphite delivered potassium methanedisulphonate, which was then converted to the acid with the aid of an ion exchange column. Alternatively, the acid was yielded from hydrolysis of $CH_2(SO_2Cl)_2$, obtained by reaction of chlorosulphonic acid and glacial acetic acid under the presence of phosphoryl chloride. MDA crystallises as its hydroxonium salt. While the water can be thermally removed between 350-500 K, it is followed by the instant decomposition of the remaining acid between 500 K and 570 K. Crystal structures of $Li_2[CH_2(SO_3)_3]$, $Rb_2[CH_2(SO_3)_2]$ and $Cs_2[CH_2(SO_3)_2]$ were solved and an isotypy to disulphates was found. $Li_2[CH_2(SO_3)_3]$ crystallises in the space group *Pnma*, isotypic to $Li_2[S_2O_7]$ with the carbon atom occupying the position, that the bridging oxygen encompasses within the disulphate. The structure exhibits a high symmetry, as the anions are located on a mirror plane. $Rb_2[CH_2(SO_3)_2]$ and $Cs_2[CH_2(SO_3)_2]$ are isotypic to $K_2[CH_2(SO_3)_2]$, crystallising in the monoclinic space group *C2/c* with four formula units.

Furthermore, all three structures are isotypic to $K_2[S_2O_7]$. The carbon atom (sulphur in the disulphate) is located on a two-fold rotational axis. Thermal stability of methanedisulphonate salts was characterised using the rubidium salt as a representative. Decomposition takes place around 600 K, releasing the fragments SO, SO₂ and CO₂. The remaining 68.5% of the initial sample mass was analysed by X-ray powder diffraction and the only crystalline phase observed belongs to Rb₂SO₄.

Methanetrisulphonic acid (MTA) was successfully prepared according to the facilitated method after Jüschke and Sartori.^[99] Crucial for the successful synthesis is the right temperature frame during the combination of the reactants oleum and acetone. The preparation of oleum with several concentrations of SO₃ displayed different behaviour in their changes of aggregate state from their respective commercially procured solutions. This might be founded in the additives, or stabilisers, applied by the industry, which were not further identified. Hence, regardless of the concentration, synthetic approaches with self-made oleum were unsuccessful, producing large amounts of potassium sulphate. Syntheses applying purchased oleum with 65% SO₃ content were prosperous, when the temperature during combination of starting material was kept between 263 K and 273 K. (H₃O)₃[CH(SO₃)₃] crystallises in two modifications, a trigonal and a hexagonal structure. The hexagonal structure is literature-known, while the trigonal structure has been encountered in unpublished, previous work within the research group of Prof. Dr. Wickleder. A DSC analysis showed no additional peak for a phase transition between freezing and melting of the sample. This, as well as the almost identical cell volume and densities of both structures, suggests that both compounds crystallise simultaneously during the process of freezing. X-ray powder diffraction patterns with Rietveld refinement demonstrate that both structures can appear together as well as individually. It has been found, that the hexagonal structure is the main, or only phase right after the synthesis, while altering of the sample or recrystallisation leads to an increased appearance of the trigonal modification. Thermal analysis of MTA-salts was conducted on the potassium salt, displaying a decomposition of the anion between 650 K and 700 K. Hence, thermal stability of methanesulphonates and methane di- and tri-sulphonates exhibit no clear trend towards higher or lower stability. For rubidium methanesulphonate the decomposition is instantaneous at 700 K, for rubidium methanedisulphonate between 700 K and 725 K, while the potassium methanetrisulphonate has a slightly higher thermal lability, having decomposed below 700 K. Solid state structures of lithium, rubidium and silver methanetrisulphonate were solved from single crystal X-ray data and phase purity was confirmed by X-ray powder diffraction with *Rietveld* refinement. Following the literature findings for a variety of methanetrisulphonates of main group and transition metal group elements alike, a diversity of crystal structures was found. All three compounds have water within their crystal structure. While the lithium salt is a tetrahydrate, rubidium and silver methanetrisulphonate crystallise as monohydrates. For the lithium and silver salts space group number 14 was observed, while the rubidium salt crystallises in the asymmetric orthorhombic space group $P2_12_12_1$. The rubidium salt crystallises similarly to the respective potassium methanetrisulphonate monohydrate, displaying the same space group and similar cell parameters.

An attempt towards the heteroleptic compound $Rb_2Ag[CH(SO_3)_3]$, generated two different compositions within the same reaction batch. The reaction led to a silver deprived structure, $Rb_5Ag[CH(SO_3)_3]_2 \cdot 2 H_2O$, and a crystal with mutual amount of silver and rubidium, $Rb_3Ag_3[CH(SO_3)_3]_2$. The crystals were obtained from a reaction in a sealed glass ampoule at elevated temperature. While the results confirm the previously discussed diversity within crystal structures for MTA-salts, a more controlled setting during the reaction might render the targeted production of heteroleptic compounds possible. Higher homogeneity in the distribution of starting material might lead to phase purity.

The unprecedented methanetetrasulphonate anion was structurally investigated embedded in the compound Ag₉[C(SO₃)₄]Cl · 4 H₂O. The characterised single crystal was of poor quality, leaving a high residual electron density after the suggested structure solution and refinement. From lower to higher temperatures, a phase transition was observed, and a smaller cell could be found. While the high remaining electron density leaves the possibility for more disorder, additional solvent or foreign elements within the suggested structure, resolution of the [C(SO₃)₄]^{4–} anions is adequate. The new anion exhibits a medium C-S bond length of 186(2) pm, and S-O bond lengths between 144.5(5) pm and 146.6(4) pm. Interestingly, with a medium S-C-S angle of $110(1)^{\circ}$ the S-C-S angles are only slightly smaller, than those found for methanetrisulphonates. There is, however, a significant difference in the bond angles towards the methanedisulphonates, where the S-C-S angles lie between $113.8(1)^{\circ}$ (Lithium) and $119.8(2)^{\circ}$ (Rubidium). Table 28 depicts one anion of each class of methane(poly)sulphonates with the observed (medium) bond lengths for this particular anion. In summary, the S-O distances are not influenced by substitution at the carbon atom. However, the C-S bonds significantly increase with the introduction of further SO₃-units. From $[H_3CSO_3]^-$ to $[C(SO_3)_4]^{4-}$ the C-S bond lengths elongates by roughly 10 pm.

Table 28: Development of the Bond Lengths from $[H_3CSO_3]^-$ to $[C(SO_3)_4]^{4-}$.



The second half of this thesis focused on the preparation and characterisation of trichloromethanesulphonate (trichlate) and tribromomethanesulphonate (tribrate) compounds. The main precursor for trichlates is trichloromethanesulfonyl chloride (Cl_3CSO_2Cl) , a colourless solid with a strong odour. Cl_3CSO_2Cl was prepared by oxidation of trichloromethanesulfenyl chloride (Cl₃CSCl) a product from the chlorination of carbon disulphide. Upon colder glass surfaces, Cl₃CSO₂Cl resublimes in rhomb-shaped crystals, which appear to be isotopic under the microscope. Indexing of the observed reflections from the powder diffractogram suggests a cubic, body centred cell. Cl₃CSO₂Cl shows a phase transition from a disordered, cubic, high temperature modification to an ordered, triclinic, low temperature, modification. With the help of an OHCD the low temperature modification could be solved and refined. The molecule has a staggered conformation along the C-S bond. The C-S bond is 186.3(1) pm long, the S-Cl bond 199.5(1) pm and the two S-O bonds are almost identical at 141.5(3) pm and 141.1(3) pm. Trichlates were synthesised from either trichloromethanesulphonic (trichlic) acid through Brønsted acid-base reactions or from trichloromethanesulfonyl chloride with metal hydroxides. The latter proved to be particularly successful for alkali hydroxides, leading to the assumption that the production of alkali chlorides as a side product is the main driving force of the reaction. A drawback of this synthesis lies in the additional step of recrystallisation to rid the product of remaining alkali chlorides. This is especially inconvenient due to a similar solubility of trichlate and chloride salts in aqueous solutions. Furthermore, as shown by the obtained crystal structure of Rb₃[Cl₃CSO₃]₂Cl, heteroleptic compounds can be formed.

Trichlic acid is yielded from sodium or potassium trichlate by conversion on an ion exchange column with a strong acidic stationary phase. The acid is obtained as the hydroxonium salt of its dihydrate. Special feature within $(H_5O_2)[Cl_3CSO_3]$ is the *Zundel* cation, build by two water molecules embedding the free proton that fluctuates in between. $(H_5O_2)[Cl_3CSO_3]$ has been yielded in two modifications, which according to powder diffraction measurements, always appear together. Both structure types were solved by single crystal X-ray diffraction. Modification 1 exhibits the space group $P2_1/n$, while the second modification crystallises in the acentric space group Cc. Comparable to the results from methanetrisulphonic acid, a distinction between a low or high temperature modification is impossible. DSC measurements suggest that both structures are almost identical.

Numerous compounds with the $[Cl_3CSO_3]^-$ anion were prepared and structurally investigated. A reoccurring feature within the observed structures are layers. The amphiphilic character of the trichlate anion causes layers that have a similarity to cell membranes. The SO₃-groups are pointing towards each other, with the counter cations in between. If crystal water is present, it also locates within the space contained by SO₃functions. The CCl₃-groups point in the opposite direction, leaving larger distances to the next layers. This interesting arrangement is also encountered within triflates, and led to the investigation of ion conductivity. It is vital to focus on the production of solvent free alkali trichlates, which should then be investigated regarding their electrochemical behaviour.

Comparable to the respective triflate compounds, the CCl_3 -groups show larger thermal displacement, which in some crystal structures led to disorder for the chlorine atoms. This is particularly true for $[Cu(H_2O)_4(Cl_3CSO_3)_2]$. Furthermore, the found disorder could be a result of a multi-domain crystal, formed by displacement of the individual layers with respect to one another. For some compounds, the clear distinction of polar and non-polar regions was disrupted, leading to crystal structures, where no layers are observed. Examples are $[N(CH_4)_4][Cl_3CSO_3]$, due to the shielding of the positive charge by the methyl groups or $[Fe(DMSO)_6][Cl_3CSO_3]_3$ for the same reason.

The investigated trichlate salts are stable up to 550 K-600 K and decompose while liberating the fragments CCl₃, SO, SO₂ and CO₂. Therefore, trichlates have a somewhat

higher thermal lability than triflates (~90 K). The observed decomposition products suggest that the C-S bond is the most fragile component of the complex anion. Elongation of the C-S bond from triflates to trichlates further hints at a weakening of the bond. Table 29 compares the observed C-S bond lengths for both potassium and rubidium trihalomethanesulphonates. An increase of approximately 4-5 pm is evident. While the electron-withdrawing effect of the CX₃-groups should be larger for the CF₃-function, the larger atomic radius of chlorine could lead to higher steric demands, resulting in an expansion of the C-S bond. In addition, the degree of participation from the halogen in the coordination sphere of the cation should not be neglected. Stronger coordination from fluorine or chlorine could lead to a weakening of the C-X bonds and thus diminish the electron withdrawing effect of the CX₃-group.

Table 29: Comparison of the C-S Bonds within Potassium and Rubidium Triflate/Trichlate.

K[F ₃ CSO ₃] ^[53]	K[Cl ₃ CSO ₃] · H ₂ O	β -Rb[F ₃ CSO ₃] ^[124]	Rb[Cl ₃ CSO ₃]
Ød _{C-S} : 179(1) pm	Ød _{C-S} :184.3(4) pm	d _{C-s} : 180.7 pm	Ød _{C-S} : 184.9(6) pm

Lastly, the property of weak coordination ability of $[Cl_3CSO_3]^-$ should be addressed. It has been shown, that solvent free compounds are hard to achieve and usually the cationic coordination sphere is saturated by the addition of solvent molecules and/or foreign anions. In fact, compounds have been synthesised, where no coordination from the trichlate to the centre cation is observed. This is true for $[Co(H_2O)_6][Cl_3CSO_3]_2$ and $[Fe(DMSO)_6][Cl_3CSO_3]_3$. A synthesis utilising La(NO₃)₃ and trichlic acid as reactants led to the preparation of $[La_2(H_2O)_{10}(NO_3)_2(\mu-Cl_3CSO_3)_2](Cl_3CSO_3)_2 \cdot 2 H_2O$. The observed coordination number for lanthanum is nine and next to the coordination from two trichlate anions and five water molecules, $[NO_3]^-$ coordinates to the cation in a bidentate chelating fashion. This shows that the strength of the bond from both ligands to La³⁺ is mutual.

Tribrates were synthesised by bromination of phenyl methanesulphonate, leading to the intermediate phenyl tribromomethanesulphonate. This molecule was structurally investigated and a disorder of the phenyl ring was encountered, while the CBr₃-group upholds a distinct position in the unit cell. Through hydrolysis in alkaline medium the desired [Br₃CSO₃]⁻ anion is liberated. K[Br₃CSO₃] · H₂O crystallises in the monoclinic space group C2/c. Similar to triflate and trichlate salts, the structure is made up by layers. A large amount of remaining electron density for the solved and refined structure is found

around the CBr₃-group, suggesting a similar high displacement of the bromine atoms, as observed for the chlorine atoms within the trichlates. The tribrate anions coordinate to potassium with a small participation from bromine. S-O bond lengths for the trihalomethanesulphonates are not influenced by the specific halogen at the CX₃-group and are constant with minor differences caused by the coordination to the respective cation. The C-S bonds for potassium tribrate are in average 183(1) pm long. Hence, the increase in C-S bond length from triflates to trichlates is not continued. This might be founded in the lower electron-withdrawing capacity of the CBr₃-group. While the bromine atom is larger in its diameter, demanding more space, the C-Br bond has a lower partial charge, drawing less electron density from the C-S bond.

Li[Cl₃CSO₃] · 2 H₂O and Li[Br₃CSO₃] · 2 H₂O crystallise in the space group $P\bar{1}$ with an identical structural motif. The tribrate salt has a larger asymmetric unit, resulting in the larger unit cell. Both structures are build by dimers of {Li₂[X₃CSO₃]_{2/1}(H₂O)_{2/1}(H₂O)_{2/2}} (X = Cl, Br). In the centre of these dimers are the [LiO₄]-tetrahedrons, which share an edge. The shared tetrahedral edge lies on an inversion centre, increasing the symmetry of the structure. Each [LiO₄]-tetrahedron is built by coordination to lithium from two sets of unique water molecules and one [X₃CSO₃]⁻ anion. Overall, layers are formed by parallely stacked {Li₂[X₃CSO₃]_{2/1}(H₂O)_{2/1}(H₂O)_{2/2}} -dimers.

While the synthesis and structural analysis of trihalomethanesulphonates was successful, further investigations are advantageous. For one, the newly found tribrate anion should be further analysed regarding its coordination ability with respect to already well established triflate compounds. Furthermore, tribrates should be analysed regarding possible phase transitions, which are common for triflate salts. The synthetic route towards tribrates arises the question of a more facile preparation for trichlates. It should therefore be investigated, whether a reaction with hypochlorite could lead to phenyl trichloromethanesulphonate and if the cleavage of the ring leaves the [Cl₃CSO₃]-moiety in tact. This synthetic route would spare the production of large amounts of Cl₃CSCl and its side product thiophosgene, both of which are extremely toxic. Furthermore, as stated above, the layered structures of alkali trihalomethanesulphonates deliver good pathways for diffusion and thus possible ion conductivity. Positive electrochemical properties might lead to a replacement of environmentally precarious triflate compounds.

4. Experimental Section

4.1. Synthesis

This Section encompasses all syntheses that led to compounds discussed within this thesis, which are not part of a published scientific article. Each journal article has an experimental section that includes details regarding the preparation of those compounds. Further information is given in the associated supplementary information, which is added to the appendix p. **Fehler! Textmarke nicht definiert.** and following.

General Procedure: Synthesis in Sealed Glass Ampoules

Synthesis and single crystal growth was undertaken concurrently in sealed glass ampoules. The reactants were weighed in and transferred into an ampoule. The load of the ampoule was cooled by liquid nitrogen, while the ampoule was evacuated. Once the pressure had settled and no further changes were observed, the ampoule was torch sealed with a natural gas burner. When the temperature of the content within the ampoule had approximately assimilated to room temperature, it was given into a tube furnace and heated according to a specific temperature profile.

Methanesulphonates

Single crystals of silver and rubidium methanesulphonate were obtained by crystallisation in sealed glass ampoules with slow cooling rates. No additional solvent was used. The reactants were combined in a stoichiometric ratio of 1:1. Methanesulphonic acid was purchased from *Sigma Aldrich Chemie GmbH* with a reagent grade of \geq 99.0%.

Reactants	m [mg]	n [mmol]	7	\rightarrow	7	T _{max} [K]
RbOH	512.3	5.0	1 h	2 h	14 h	272
CH ₃ SO ₃ H	480.5	5.0		Ζ Π	14 11	575
AgNO ₃	849.3	5.0	2 h	2 h	16 h	272
CH ₃ SO ₃ H	480.5	5.0	2 fl	2 n	10 II	5/5

 Table 30: Load of the Ampoules and Temperature Profiles.

In-situ Crystallisation of MSA

Commercially obtained methanesulphonic acid (*Sigma Aldrich*, \geq 99%) was stored under argon atmosphere in a glovebox. A quartz capillary with an outer diameter of 0.3 mm and a glass wall thickness of 0.01 mm was clipped off at the end, to generate a thin glass tube that had two openings, at the top and at the bottom. The open capillary was vertically immersed into the acid. Through capillary forces, the liquid was absorbed into the glass tube. Finally, the capillary was sealed at both ends with picein (*Roth*). The capillary was cooled down to 191 K on the diffractometer. Subsequently the *LASER* was focused on a defined range along the capillary (~1 cm) with the aid of a red *LASER* (650 nm). Then the CO₂ *LASER* was used to heat the pre-defined range with the shock frozen acid in the capillary in order to provoke zone melting and crystallite formation. With a number of still images the diffraction pattern was observed to obtain an understanding of crystallite growth. When sufficient crystallite size was reached, data collection on the diffractometer began.

Methanedisulphonates

Synthesis of Methanedisulphonic Acid (MDA) via CH₂(SO₂Cl)₂

Under the argon atmosphere of the glovebox, 20 g (0.13 mol, 11.9 mL, 2 eq.) POCl₃ were given to a two-necked round bottom flask. At a *Schlenk* line and under argon gas counter flow, the two-necked round bottom flask was united with a prior evacuated and inert gas filled reflux condenser. Under argon gas counter flow 8.7 mL (0.13 mol, 15.15 g, 2 eq.) CISO₃H were added. A dropping funnel with dry glacial acetic acid (3.7 mL, 0.065 mol, 3.9 g) was added to the apparatus. Slowly, the acetic acid was given to the reaction mixture under steady stirring. The brownish reaction mixture was stepwise heated to a maximum temperature of 418 K at which it was stirred for 6 h. The crude product was fractional distilled under reduced pressure. At 88 mbar and 314 °K a small amount of a very volatile compound was gathered. At 20 mbar and 340 K a fuming liquid was collected. The product, a colourless liquid (6.83 g, 49%) obtained at 0.24 mbar and 367 °K, shows small traces of the acid.

CH₂(SO₂Cl)₂:

¹³C-NMR (75 MHz, CDCl₃-d1): δ /ppm = 84.127 (CH₂). (Appendix, Figure 117, p. 248)
¹**H-NMR** (300 MHz, CDCl₃-*d1*): δ/ppm = 5.162 (s, CH₂), 11.67 (s, SO₃H). (Appendix, Figure 118, p. 248)

20 mL of water were added to the light yellowish solution and a gas evolvement and heating was observed. The yellow solution was reduced at a rotary evaporator and further dried under vacuum. Elongated crystalline needles grew from the solution.

(H₃O)₂[CH₂(SO₃)₂]: XRD: *mC*, 14.1, 7.0, 8.1, 90°, 118°, 90°.

Synthesis of Methanedisulphonic Acid (MDA) via K₂[CH₂(SO₃)₂]

Hydrothermal synthesis of K_2SO_3 with CH_2Cl_2 in sealed glass ampoules, applying slow cooling rates led to crystalline material of $K_2[CH_2(SO_3)_2]$. Different stoichiometric ratios and a varying amount of water was applied, while an excess of CH_2Cl_2 was always present. Reactions without crystal water did not lead to the desired product. Table 31 (p. 138) lists the load of the ampoules. Stoichiometry varied from 2 eq of CH_2Cl_2 up to 3.5 eq. $K_2[CH_2(SO_3)_2]$ could be yielded from all syntheses, however single crystals were only obtained for syntheses 1, 2 and 4.

A solution of 1.0 g (3.96 mmol, 1 eq.) $K_2[CH_2(SO_3)_2]$ in as little amount of water needed for dissolution was prepared. The mixture was moderately heated ~323 K, until the remaining solid was dissolved. The solution was poured onto an ion exchange column with a strong acidic stationary phase (*Merck, Ionexchanger V*). The column was rinsed with several volumes of water and the *p*H-value of the collected product was probed sporadically. After indication of a neutral *p*H another 200 mL of water were added onto the column and the collected aqueous solutions were combined and reduced by a rotary evaporator. The obtained colourless droplets (~1.2 g) were further dried at a *Schlenk* line. Colourless, elongated, needle shaped crystals are yielded (362 mg, 1.69 mmol, 43%).

No.	Reactants	m [mg]	n [mmol]	V [ml]	7	\rightarrow	У	T _{max} [K]
	K ₂ SO ₃	500	3.16	-				
1	CH ₂ Cl ₂	665	7.83	0.50	6 h	12 h	24 h	423
	H ₂ O	499	27.7	0.50				
	K ₂ SO ₃	500.0	3.16					
2	CH ₂ Cl ₂	811	9.55	0.61	6 h	12 h	24 h	423
	H_2O	480.5	5.0	0.60				
	K ₂ SO ₃	500.0	3.16	-				
3	CH ₂ Cl ₂	944	11.12	0.71	6 h	12 h	24 h	423
	H ₂ O	699	38.8	0.7				
	K_2SO_3	500.0	3.16	-				
4	CH ₂ Cl ₂	545	6.42	0.41	6 h	12 h	24 h	423
	H ₂ O	499	27.7	0.50				
	K_2SO_3	500.0	3.16					
5	CH ₂ Cl ₂	665	7.83	0.50	6 h	12 h	24 h	423
	H ₂ O	499	27.7	0.50				
	K_2SO_3	500.0	3.16	-				
6	CH ₂ Cl ₂	811	9.55	0.61	6 h	12 h	24 h	423
	H ₂ O	499	27.7	0.50				
	K_2SO_3	500.0	3.16	-				
7	CH ₂ Cl ₂	944	11.12	0.71	6 h	12 h	24 h	423
	H ₂ O	250	13.9	0.25				

Table 31: Hydrothermal Syntheses of K₂[CH₂(SO₃)₂].

Syntheses of Li₂[CH₂(SO₃)₂], Rb₂[CH₂(SO₃)₂] and Cs₂[CH₂(SO₃)₂]

Single crystals of Li₂[CH₂(SO₃)₂], Rb₂[CH₂(SO₃)₂] and Cs₂[CH₂(SO₃)₂] were obtained from reaction of the respective alkali hydroxides with $(H_3O)_2$ [CH₂(SO₃)₂]. Therefore, the reactants were weighed in and combined according to Table 32 (p. 139). The produced aqueous solutions were poured onto crystallisation dishes. Slow evaporation of solvent at ambient conditions led to the formation of colourless crystals.

Reactants	m [mg]	n [mmol]	Eq.	V [ml]
LiOH	24	1.00	2.3	-
MDA^*	95	0.44	1.0	-
H ₂ O	299	16.6	-	0.3
RbOH	50	0.49	2.0	-
MDA^*	52	0.24	1.0	
H_2O	998	55.4	-	1.0
CsOH	50	0.334	2.0	
MDA^*	36	0.168	1.0	
H ₂ O	998	55.4	-	1.0

 Table 32: Syntheses of Methanedisulphonates.

 $^{*}MDA = (H_{3}O)_{2}[CH_{2}(SO_{3})_{2}]$

Synthesis of BaK₂[CH₂(SO₃)₂]

The attempt at a salt metatheses to gather Ba[CH₂(SO₃)₂] from K₂[CH₂(SO₃)₂] led to the production of a single crystal of BaK₂[CH₂(SO₃)₂]₂ instead. In a hydrothermal synthesis, the K₂[CH₂(SO₃)₂] was converted with BaCl₂ according to Table 33.

Table 33: Load of the Ampoule and Temperature Profile.

Reactants	m [mg]	n [mmol]	V [mL]	7	\rightarrow	7	T _{max} [K]
BaCl ₂	209	1.0	-				
$K_2[CH_2(SO_3)_2]$	204	0.8		4 h	8 h	30 h	403
H_2O	699	38.8	0.7				

Methanetrisulphonates

Synthesis of Methanetrisulphonic Acid

$$\underbrace{O}_{+} H_2 SO_4 / SO_3 \xrightarrow{358 \text{ K}, 3 \text{ h}}_{- \text{ CO}_2} CH(SO_3H)_3 \xrightarrow{\text{KOH}} K_3 [CH(SO_3)_3] \cdot H_2 O$$

A three-necked round bottom flask with *Dimroth* condenser was evacuated and flushed with argon inert gas four times, before 25 mL of 65% oleum were added under argon counter flow. The reaction flask was cooled with a mixture of ice and ethanol and the targeted temperature range of 263 K-273 K was meticulously controlled with the aid of a 139

thermometer. During the assembly and evacuation of the reaction apparatus, a syringe with acetone (3.9 mL, 531 mmol, 1 eq) was contained in a freezer. Through a septum, acetone was slowly added to the oleum solution, all the while the temperature was monitored. The viscous reaction mixture turned beige. Once all the acetone was added, and no colour change to black was observed, the ice bath was removed. When the reaction mixture had reached room temperature (~1 h), the temperature was carefully increased to 368 K. After approximately 3 h the oil bath was removed. The reaction mixture was quenched by pouring the acidic reaction mixture onto 200 mL of crushed ice. The solution was neutralised with KOH (~70 g) and the produced suspension was diluted with several amounts of water. The orange solution was seperated from the slightly yellowish solid by filtration. Approximately 30 g of crude product were obtained. The crude product contained large amounts of K₂SO₄. Recrystallisation from hot aqueous solution was undertaken until the X-ray powder diffractogram revealed no remaining pattern belonging to K₂SO₄. Roughly 13 g (33.46 mmol, 63%) of K₃[CH(SO₃)₃] · H₂O were yielded in the form of colourless, needle shaped crystals.

2 g (5.15 mmol, 1 eq.) of K₃[CH(SO₃)₃] · H₂O were solved in a small amount of water (~5-10 mL). The mixture was moderately heated to achieve complete dissolution. The solution was given onto an ion exchange column with a strongly acidic stationary phase (*Merck, Ionexchanger V*). The column was rinsed with several volumes of water and the *p*H-value of the collected product was probed sporadically. After indication of a neutral *p*H, another 200 mL of water were added onto the column and the collected aqueous solutions were combined and reduced by a rotary evaporator. The dried, hygroscopic, colourless solid was kept under inert atmosphere, where it loss further water over time. Roughly 1.44 g (4.64 mmol, 90%) of (H₃O)₃[CH(SO₃)₃] were yielded.

Synthesis of $Li_3[CH(SO_3)_3] \cdot 4 H_2O$, $Rb_3[CH(SO_3)_3] \cdot H_2O$ and $Ag_3[CH(SO_3)_3] \cdot H_2O$,

Single crystals of lithium, rubidium and silver methanetrisulphonate could be obtained from hydrothermal syntheses in sealed glass ampoules. The respective alkali carbonate and $(H_3O)_3[CH(SO_3)_3]$ were converted according to Table 34 (p. 141) in a stoichiometric ratio of one equivalent acid to 1.5 equivalent of alkali salt.

Reactants	m [mg]	n [mmol]	V [mL]	7	\rightarrow	У	T _{max} [K]
Rb ₂ CO ₃	158	0.68	-				
MTA^*	142	0.46	-	8 h	10 h	100 h	373
H_2O	99.8	5.54	0.1				
Ag ₂ CO ₃	188	0.68	-				
MTA^*	142	0.46	-	8 h	10 h	100 h	373
H_2O	99.8	5.54	0.1				
Li ₂ CO ₃	25	0.34	-				
MTA^*	71	0.23	-	8 h	10 h	100 h	373
H_2O	99.8	5.54	0.1				

Table 34: Load of the Ampoules and Temperature Profile.

 $*MTA = (H_3O)_3[CH(SO_3)_3]$

Synthesis of Rb₅Ag[CH(SO₃)₃]₂ · 2 H₂O and Rb₃Ag₃[CH(SO₃)₃]₂

Hydrothermal reaction between Rb_2CO_3 , Ag_2CO_3 and $(H_3O)_3[CH(SO_3)_3]$ according to Table 35, led to two different compounds, identified by single crystal X-ray diffraction.

Table 35: Load of the Ampoule and Temperature Profile.

Reactants	m [mg]	n [mmol]	V [mL]	7	\rightarrow	7	T _{max} [K]
Rb ₂ CO ₃	53	0.23	-				
Ag_2CO_3	31	0.11	-	0 h	10 h	100 h	373
MTA^*	71	0.23	-	8 11	10 II	1 100 11	
H_2O	99.8	5.54	0.1				

 $^{*}\mathrm{MTA} = (\mathrm{H}_{3}\mathrm{O})_{3}[\mathrm{CH}(\mathrm{SO}_{3})_{3}]$

Silver Methanetetrasulphonate

A hydrothermal reaction between Ag_2CO_3 and MTA in a sealed ampoule delivered the analysed single crystal with the novel $[C(SO_3)_4]^{4-}$ anion. Another identified product of this reaction was Ag_2SO_4 . Table 36 (p. 142) summarises the amount of reactants converted and the temperature profile of the hydrothermal process.

Reactants	m [mg]	n [mmol]	V [mL]	7	\rightarrow	7	T _{max} [K]
Ag ₂ CO ₃	209	1.63	-				
MTA^*	260	0.84	-	14 h	5 h	150 h	413
H_2O	998	55.4	1.0				

 Table 36: Load of the Ampoule and Temperature Profile.

 $*MTA = (H_3O)_3[CH(SO_3)_3]$

Trichlates

Tichlates were synthesised from either Cl_3CSO_2Cl or $(H_5O_2)[Cl_3CSO_3]$. The synthetic route towards both compounds is described in detail within the publication *Tichlates, an Unattended Class of Compunds: Characterization of Cl_3CSO_2Cl and (H_5O_2)[Cl_3CSO_3]* (Publication 1, p. 107 and following). Further information is given in the corresponding supporting information, added to the appendix (p. **Fehler! Textmarke nicht definiert.** and following).

Syntheses of Rb₃[Cl₃CSO₃]₂Cl

In a round bottom flask, 748 mg (7.34 mmol, 2 eq.) of RbOH and 801 mg (3.67 mmol, 1 eq.) Cl_3CSO_2Cl were solved in 13 mL of H₂O. The mixture was heated to 333 K for 24 h and the remaining, undissolved solid was filtered of. The solution was reduced by a rotary evaporator and the collected colourless solid was recrystallised from H₂O/EtOH (2 : 1). Colourless, needle-shaped crystals were obtained.

Syntheses of K[Cl₃CSO₃] · H₂O

In a round bottom flask, 8.32 g (148.24 mmol, 4 eq.) of KOH and 8.00 mg (36.7 mmol, 1 eq.) Cl_3CSO_2Cl were solved in 100 mL of H_2O . Therefore, the mixture was heated at 323 K for 24 h and the remaining, undissolved solid was filtered of. The solution was reduced by a rotary evaporator and the collected colourless solid was recrystallised from water. Colourless, thin, plate-shaped crystals were obtained.

Syntheses of $Rb[Cl_3CSO_3] \cdot H_2O$

The discussed single crystal structure stemmed from a hydrothermal reaction between RbOH and Cl₃CSO₂Cl according to Table 37. After the reaction, the ampoule was filled with a colourless liquid and thin, needle-shaped crystals.

Table 37: Load of the Ampoule and Temperature Profile.

Reactants	m [mg]	n [mmol]	V [mL]	7	\rightarrow	7	T _{max} [K]
RbOH	141	1.38	-				
Cl ₃ CSO ₂ Cl	300	1.38	-	10 h	24 h	100 h	403
H ₂ O	199.6	11.08	0.2				

The product could be reproduced by a reaction of $(H_5O_2)[Cl_3CSO_3]$ with RbOH. Therefore, 21.7 mg (0.212 mmol, 1 eq.) RbOH and 50 mg (0.212 mmol, 1 eq.) $(H_5O_2)[Cl_3CSO_3]$ were solved in 0.5 mL H₂O. The solution was poured onto a crystallisation dish and the solvent was evaporated at ambient conditions.

4.2. Analytics

Single Crystal X-Ray Diffraction

Suitable single crystals were selected with the aid of a light microscope. Crystals from solvothermal syntheses were kept within the atmosphere of the sealed ampoule until shortly before the measurement. The gaseous content of the ampoules was cooled by liquid nitrogen and a horizontal line was carved into the ampoule with a glasscutter. With applied pressure on both sides of the cut, the ampoule was broken into two parts. Prior identified crystalline material was carefully scooped up with a spatula coated in inert oil. Single crystal structure determination has been performed on a *Bruker D8 VENTURE KAPPA* diffractometer with a microfocus sealed tube using a multilayer mirror as monochromator and *a Bruker PHOTON III* detector. MoK $_{\alpha}$ radiation (71.073 pm) was used as X-ray source. The crystals were prepared in perfluorinated ether (*Fomblin*[®] *YR-180*) and selected with the aid of a light microscope with a polarisation filter. The crystals were fixed on a micromount with a 150 µm polymer loop and adjusted to the X-ray beam under cooling at 100 K if not stated otherwise (see crystallographic tables). The intensity data were collected and the images processed using *APEX4*.^[134] The integration was done 143

with *SAINT* and a multi-scan absorption correction using *SADABS* was applied.^[135,136] The structure solution was performed in the software *Olex2* by intrinsic phasing (*SHELXT*) and the structural model was refined by least squares methods using *SHELXL*.^[137]

X-Ray Powder Diffraction

For powder diffraction analysis, all samples were prepared by sufficient grinding of product with the aid of a mortar and pistil. The homogenous samples were either prepared inert in glass capillaries or as flat preparations. Two different X-ray sources were used. *Rietveld* refinement were performed using *Topas* in combination with *Jedit* (Version 5.5.0).^[138–140] For graphical depiction of the results *OriginPro 2021b* was used.^[141]

X-Ray Source: Molybdenum

The powders were prepared in borosilicate glass capillaries with an outer diameter of 0.3 mm and glass wall thickness of 0.01 mm. The experimental powder data was measured on a *STOE Stadi P* diffractometer (*STOE & Cie GmbH*, Darmstadt, DE) with $Mo_{K\alpha 1}$ radiation (70.930 pm) in *Debye-Scherrer* geometry at room temperature. The reflections were collected on a silicon-based *Dectris Mythen 1K* detector (*Dectris Ltd.*, Baden-Daettwil, CH). The data was processed with *WinXPOW* (version 3.6.0.1).^[142]

X-Ray Source: Copper

Powders were measured on a *Rigaku Miniflex* with $Cu_{K\alpha}$ radiation and data was collected on a *HyPix-400 MF 2D* hybrid pixel array detector (HPAD) in *Bragg-Brentano* geometry at room temperature. The samples were prepared on glass holders. Data was processed with *SmartLab Studio II*, version 4.4.295.0.^[143]

IR Spectroscopy

The IR spectra were measured on a *PerkinElmer* FTIR-ATR (*UATR TWO*) at room temperature with a maximum resolution of 1 cm⁻¹. Data was processed with the program *Spectrum*, version 10.6.1.942.^[144] For graphical depiction of the results *OriginPro 2021b* was used.^[141]

Thermal Analysis

DSC/TG-MS

Thermogravimetric analyses of the samples were performed on a thermal analyser *STA* 409 (*Netzsch*) coupled with a quadrupole mass spectrometer (*QMS* 421, *BALZERS*). The samples were prepared in Al₂O₃ crucibles under ambient conditions. The measurements were performed under argon flow (80 mL \cdot min⁻¹). Mass analysis was carried out in a scanning mode with predefined *m/z* values. Colleted data was processed by the program *Proteus* version 6.1.^[145]

DSC

DSC measurements were performed in sealed quartz glass ampoules. Prior to torchsealing the quartz glass was sufficiently heated under reduced pressure to free the glass ware of adsorbed water. The ampoules were measured under argon flow (60 mL \cdot min⁻¹) on a *Netzsch DTA 404* and the colleted data was processed by the program *Proteus* version 6.1.^[145]

DTA/TG

Differential thermal analysis was conducted on a *STA6000* from *PerkinElmer* in combination with the software *Pyris* (Version 13.3.2). The thermal analyser *STA6000* is equipped with an auto-sampler. All samples are weighed into a corundum crucible and thermal analysis is coupled with TG.

Theoretical Calculations

A full geometry optimisation for $[H_3CSO_3]^-$, $[CH_2(SO_3)_2]^{2-}$ and $[CH(SO_3)_3]^{3-}$ were performed within DFT calculation utilising the exchange correlation functional *PBEO* and the basis set *cc-pVTZ* for all elements.^[114] Assignment of the IR-bands is based on the theoretical calculations. Throughout the study the Orca 5.0.3 program package was used.^[114]

NMR-Spectroscopy

¹³C-{¹H}-DEPTQ and ¹H-NMR spectra were measured on a *Bruker Avance II 300* spectrometer. The obtained data was processed with the software *TopSpin*.^[146]

5. Appendix

5.1. Crystallographic Data

CH₃SO₃H

Table 38: Crystal Data	and Structure	Refinement for	CH ₃ SO ₃ H.
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Empirical formula	CH ₄ O ₃ S
Formula Weight	96.107 g/mol
Temperature	191 K
Wavelength	71.073 pm (Mo _{Kα})
Crystal system	monoclinic
Space group	$P2_{1}/c$
Unit cell parameters	a = 842.07(4) pm
	<i>b</i> = 582.20(3) pm
	c = 820.38(4)pm
	$\beta = 106.459(2)^{\circ}$
Volume	385.71(3) Å ³
Ζ	4
Density (calculated)	1.655 g/cm ³
Absorption coefficient	0.667 mm ⁻¹
F(000)	200
Crystal size	0.3 x 0.3 x 0.3 mm ³
2θ Range for data collection	$5.044-69.994^{\circ}$
Index range	−13≤h≤13, −9≤k≤9, −13≤l≤13
Reflections collected	114841
Independent reflections	1684 [$R_{\text{int}} = 0.0480, R_{\sigma} = 0.0216$]
Completeness	98.9%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7478/0.4878
Refinement method	Least Squares
Data/Restraints/Parameters	16840/48
Goodness-of-fit on F^2	1.096
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0275, wR_2 = 0.0819$
R Indices (all data)	$R_1 = 0.0284, wR_2 = 0.0828$
Largest diff. peak and hole	$0.43/-0.39 \text{ e} \cdot \text{\AA}^{-3}$

CCDC Deposition Number	2305646
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Table 39: Fractional Atomic Coordinates $(x10^4)$ and Equivalent Isotropic Displacement Parameters (\mathring{A}^2x10^3) for CH₃SO₃H.

Atom	X	у	Z.	U(eq)
S1	7406.7(2)	3816.1(3)	3475.0(2)	22.16(8)
011	6765(1)	4571(1)	4837.9(9)	33.1(2)
012	5885.6(9)	2915(1)	2092(1)	34.4(2)
013	8684(1)	2126(2)	3867(1)	41.3(2)
C1	8029(2)	6232(2)	2572(2)	37.1(2)

Table 40: Anisotropic Displacement Parameters $(Å^2 x 10^3)$ for CH₃SO₃H.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S 1	24.4(1)	23.2(1)	19.9(1)	0.64(5)	7.98(7)	1.29(5)
O11	49.2(4)	31.5(3)	24.0(3)	0.5(2)	19.2(3)	3.9(3)
O12	27.2(3)	40.1(4)	35.9(4)	-14.0(3)	9.3(3)	-6.7(3)
013	39.3(4)	40.0(4)	42.8(4)	3.2(3)	8.9(3)	17.2(3)
C1	39.4(5)	36.5(5)	38.7(5)	6.5(4)	16.1(4)	-9.3(4)

*Table 41: Experimental Bond Lengths for CH*₃*SO*₃*H.*

Bond	Length [pm]	Bond	Length [pm]
S1-O11	144.15(7)	C1-H1A	98
S1-O12	154.28(7)	C1-H1B	98
S1-O13	142.57(8)	C1-H1C	98
S1-C1	173.8(1)		

 Table 42: Experimental Bond Angles for CH₃SO₃H.

				_
Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]	
O11-S1-O12	104.98(5)	O13-S1-C1	110.81(6)	
O12-S1-O13	110.30(5)	H1A-C1-H1B	109.5	
O13-S1-O11	117.41(5)	H1B-C1-H1C	109.5	
O11-S1-C1	107.98(5)	H1C-C1-H1A	109.5	
O12-S1-C1	104.46(6)			

Atom	x	У	Z.	U(eq)
H12	6198.42	2008.7	1447.67	52
H1A	7086.69	7276.5	2167.39	56
H1B	8435.29	5765.89	1614.23	56
H1C	8916.41	7016.32	3425.54	56

Table 43: Hydrogen Atom Coordinates $(\mathring{A} \times 10^4)$ and Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for CH₃SO₃H.

$Rb_2[H_3CSO_3]_2 \cdot H_2O$

Table 44: Crystal Data and Structure Refinement for $Rb_2[H_3CSO_3]_2 \cdot H_2O$.

Empirical formula	$C_2H_8O_7Rb_2S_2$
Formula Weight	379.14 g/mol
Temperature	100 K
Wavelength	71.073 pm (Mo _{Kα})
Crystal system	monoclinic
Space group	$P2_{1}/c$
Unit cell parameters	a = 606.22(4) pm
	<i>b</i> = 1969.1(1) pm
	c = 890.08(6)pm
	$\beta = 91.558(2)^{\circ}$
Volume	$1062.1(1) \text{ Å}^3$
Ζ	4
Density (calculated)	2.371 g/cm ³
Absorption coefficient	9.611 mm ⁻¹
F(000)	728
Crystal size	0.356 x 0.143 x 0.128 mm ³
2θ Range for data collection	$4.136 - 61.998^{\circ}$
Index range	$-8 \le h \le 8, -28 \le k \le 28, -11 \le l \le 12$
Reflections collected	33318
Independent reflections	3377 [$R_{\text{int}} = 0.0475, R_{\sigma} = 0.0203$]
Completeness	99.7%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7474/0.3630

Refinement method	Least Squares
Data/Restraints/Parameters	3377/0/151
Goodness-of-fit on F^2	1.152
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0152, wR_2 = 0.0385$
R Indices (all data)	$R_1 = 0.0155, wR_2 = 0.0387$
Largest diff. peak and hole	$0.57/-0.0387 \ e \cdot \text{\AA}^{-3}$
CCDC Deposition Number	2305648

Table 45: Fractional Atomic Coordinates $(x10^4)$ and Equivalent Isotropic Displacement Parameters (\mathring{A}^2x10^3) for $Rb_2[H_3CSO_3]_2 \cdot H_2O$.

Atom	x	у	Z	U(eq)
Rb1	1699.3(2)	7399.7(2)	7696.0(2)	11.09(4)
Rb2	3548.2(2)	3951.5(2)	4278.7(2)	12.31(4)
S 1	6699.4(4)	7888.6(2)	5035.6(3)	10.08(5)
S2	1492.7(5)	5378.0(2)	7359.4(3)	11.61(6)
011	4680(1)	7501.4(5)	5261(1)	16.0(2)
O12	8655(2)	7452.8(5)	5133(1)	15.3(2)
013	6594(2)	8288.8(5)	3662(1)	22.0(2)
C1	6930(2)	8460.6(6)	6558(1)	17.1(2)
C2	8029(2)	6232(2)	2572(2)	37.1(2)
O21	-710(2)	5085.4(5)	7447(1)	18.1(2)
O22	3100(2)	4934.1(5)	6684(1)	19.7(2)
O23	1429(2)	6048.3(4)	6637(1)	16.3(2)

Table 46: Anisotropic Displacement Parameters $(\mathring{A}^2 x 10^3)$ for $Rb_2[H_3CSO_3]_2 \cdot H_2O$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rb1	12.53(6)	10.88(6)	9.83(5)	-1.57(3)	-0.30(4)	0.40(3)
Rb2	13.22(6)	10.66(6)	13.02(6)	-1.08(3)	0.08(4)	0.42(3)
S 1	11.3(1)	11.0(1)	7.9(1)	0.16(8)	0.11(8)	0.50(8)
S2	15.0(1)	9.0(1)	10.9(1)	-0.14(8)	0.31(8)	-0.80(8)
011	11.3(4)	20.4(4)	16.4(4)	-2.6(3)	0.0(3)	-3.0(3)
O12	12.1(4)	19.0(4)	14.8(4)	-2.6(3)	-0.1(3)	3.8(3)
013	34.1(5)	20.4(4)	11.4(4)	6.0(3)	1.7(3)	3.2(4)
C1	20.5(5)	15.7(5)	15.0(5)	-4.5(4)	-0.9(4)	0.6(4)
C2	27.6(6)	27.7(7)	13.3(5)	-0.3(5)	-1.4(4)	-9.0(5)
O21	16.9(4)	15.1(4)	22.3(4)	1.5(3)	-0.9(3)	-4.8(3)

O22	23.9(4)	14.5(4)	21.1(4)	-0.9(3)	5.0(3)	5.3(3)
O23	22.7(4)	9.1(4)	17.2(4)	1.5(3)	1.2(3)	-0.3(3)

Bond Length [pm] Bond Length [pm] S1-O11 144.15(7) S2-O21 145.81(9) S1-O12 154.28(7) S2-O22 145.13(9) S1-O13 142.57(8) 146.85(9) S2-O23 S1-C1 173.8(1) S2-C2 176.2(1) C1-H1C 94(2) C2-H2A 95(3) C1-H1D 88(2) C2-H2B 94(2) C1-H1E C2-H2C 92(2) 88(2) $Rb1-O1^4$ Rb2-O11⁵ 287.2(1) 307.9(1) Rb1-O11 286.58(9) Rb2-O22 290.42(9) Rb1-O12¹ 290.02(9) Rb2-O22⁵ 312.6(1) Rb1-O13² 335.33(1) Rb2-O1 324.5(1) Rb1-O13¹ Rb2-O23⁶ 350.73(1) 310.4(1) Rb1-O11² Rb2-O23⁵ 287.95(9) 317.3(1) Rb1-O12³ Rb2-O21⁶ 289.71(9) 296.21(9) Rb2-O13⁷ Rb1-O23 282.63(9) 292.43(9)

Table 47: Experimental Bond Lengths for $Rb_2[H_3CSO_3]_2 \cdot H_2O$.

Table 48: Selected Experimental Bond Angles for $Rb_2[H_3CSO_3]_2 \cdot H_2O$.

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]	
O11-S1-O12	111.49(6)	O21-S2-O22	114.23(6)	_
O12-S1-O13	112.59(6)	O22-S2-O23	111.71(6)	
O13-S1-O11	112.37(6)	O23-S2-O21	111.43(6)	
O11-S1-C1	106.06(6)	O21-S2-C2	106.39(6)	
O12-S1-C1	106.36(6)	O22-S2-C2	106.94(7)	
O13-S1-C1	107.48(6)	O23-S2-C2	105.49(6)	
H1C-C1-S1	108(1)	H2A-C2-S2	109(2)	
H1D-C1-S1	110(1)	H2B-C2-S2	106(1)	
H1E-C1-S1	108(1)	H2C-C2-S2	108(1)	
H1C-C1-H1D	110(2)	H2A-C2-H2B	109(2)	
H1D-C1-H1E	110(2)	H2B-C2-H2C	106(2)	

H1E-C1-H1C

H2C-C2-H2A

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117(2)
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Atom-Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom-Atom	Angle [°]
O12-S1-C1-H1C	-58(1)	O22-S2-C2-H2A	-66(2)
H1C-C1-S1-O11	60(1)	H2A-C2-S2-O21	56(2)
O11-S1-C1-H1D	-60(1)	O21-S2-C2-H2B	-61(1)
H1D-C1-S1-O13	60(1)	H2B-C2-S2-O23	57(1)
O13-S1-C1-H1E	-60(2)	O23-S2-C2-H2C	-57(2)
H1E-C1-S1-O12	61(2)	H2C-C2-S2-O22	62(2)

Table 49: Selected Torsion Angles for $Rb_2[H_3CSO_3]_2 \cdot H_2O$.

110(2)

Table 50: Hydrogen Atom Coordinates $(\mathring{A} \times 10^4)$ and Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Rb_2[H_3CSO_3]_2 \cdot H_2O$.

Atom	x	у	Z.	U(eq)
H1A	8270(30)	4156(11)	6800(20)	24(5)
H2A	2360(40)	5113(14)	9780(30)	47(7)
H1C	7020(30)	8209(10)	7450(20)	24(5)
H1B	8240(40)	3845(12)	5650(30)	35(6)
H1D	5780(40)	8734(11)	6560(20)	29(5)
H1E	8200(40)	8709(11)	6450(30)	37(6)
H2B	1420(30)	5836(11)	9630(20)	27(5)
H2C	3690(40)	5735(12)	9200(20)	33(6)

Table 51: Hydrogen Bonding within $Rb_2[H_3CSO_3]_2 \cdot H_2O$.

O _D -H…O _A	d _{D-A} [pm]	$\angle O_D$ -H-O _A [°]
O1-H1A-O21	279.1(1)	176(2)
O1-H1B-O23	283.7(1)	169(3)

Ag[H₃CSO₃]

Table 52: Crystal Data and Structure Refinement for Ag[H₃CSO₃].

Empirical formula	CH ₃ AgO ₃ S
Formula Weight	202.96 g/mol
Temperature	100 K
Wavelength	71.073 рт (Мока)

Crystal system	monoclinic
Space group	$P2_{1}/c$
Unit cell parameters	<i>a</i> = 869.1(1) pm
	<i>b</i> = 574.18(6) pm
	c = 823.4(1) pm
	$\beta = 100.322(6)^{\circ}$
Volume	404.23(9) Å ³
Ζ	4
Density (calculated)	3.335 g/cm ³
Absorption coefficient	5.346 mm ⁻¹
F(000)	384
Crystal size	0.133 x 0.114 x 0.019 mm ³
2θ Range for data collection	$4.764 - 52.958^{\circ}$
Index range	$-10 \le h \le 10, -7 \le k \le 7, -10 \le l \le 10$
Reflections collected	3995
Independent reflections	837 [$R_{int} = 0.0557, R_{\sigma} = 0.0432$]
Completeness	100%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7483 / 0.6435
Refinement method	Least Squares
Data/Restraints/Parameters	837/0/56
Goodness-of-fit on F^2	1.118
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0258, wR_2 = 0.0515$
<i>R</i> Indices (all data)	$R_1 = 0.0301, wR_2 = 0.0536$
Largest diff. peak and hole	$0.60/-0.75 \text{ e} \cdot \text{\AA}^{-3}$
CCDC Deposition Number	2305642

Table 53: Fractional Atomic Coordinates $(x10^4)$ and Equivalent Isotropic Displacement Parameters (\mathring{A}^2x10^3) for $Ag[H_3CSO_3]$.

Atom	X	у	Z.	U(eq)
Ag1	4417.4(4)	6558.0(5)	7874.8(4)	12.5(1)
S 1	2685(1)	3744(2)	4226(1)	9.4(2)
011	2591(4)	5198(5)	2756(4)	17.2(7)
012	2548(4)	5066(5)	5711(4)	16.1(7)
O13	4110(4)	2272(5)	4464(4)	14.7(7)

C1	1094(5)	1822(7)	3890(6)	15(1)
01	10) 1(0)	1022(/)	2070(0)	10(1)

Atom	U_{11}	U_{22}	<i>U</i> 33	U_{23}	U_{13}	U_{12}
Ag1	12.2(2)	12.9(2)	12.2(2)	-1.2(1)	Ag1	12.2(2)
S 1	8.9(6)	9.4(4)	9.9(5)	0.0(4)	S 1	8.9(6)
O11	16(2)	17(1)	18(2)	5(1)	O11	16(2)
O12	14(2)	20(2)	14(2)	-6(1)	O12	14(2)
O13	14(2)	17(2)	14(2)	-2(1)	013	14(2)
C1	9(3)	18(2)	16(2)	-1(2)	C1	9(3)

Table 54: Anisotropic Displacement Parameters $(Å^2 \times 10^3)$ for Ag[H₃CSO₃].

 Table 55: Selected Bond Lengths for Ag[H₃CSO₃].

Bond	Length [pm]	Bond	Length [pm]
S1-O11	146.1(3)	Ag1-O11 ³	243.8(3)
S1-O12	146.1(3)	Ag1-O12	234.8(3)
S1-O13	148.3(3)	Ag1-O13 ⁴	258.5(3)
S1-C1	175.2(4)	Ag1-O13 ²	236.7(3)
C1-H1A	98	Ag1-O13 ⁵	259.7(3)
C1-H1B	98	Ag1-Ag1 ¹	314.21(4)
C1-H1C	98	Ag1-Ag1 ²	314.21(4)

¹1-X,-1/2+Y,3/2-Z; ²1-X,1/2+Y,3/2-Z; ³+X,3/2-Y,1/2+Z; ⁴1-X,1-Y,1-Z; ⁵+X,1/2-Y,1/2+Z

 Table 56: Selected Bond Angles for Ag[H₃CSO₃].

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
O11-S1-O12	113.3(2)	H1A-C1-S1	109.5
O12-S1-O13	112.1(2)	H1B-C1-S1	109.5
O13-S1-O11	110.9(2)	H1C-C1-S1	109.5
O11-S1-C1	107.7(2)	H1A-C1-H1B	109.5
O12-S1-C1	106.2(2)	H1B-C1-H1C	109.5
O13-S1-C1	106.2(2)	H1C-C1-H1A	109.5

 Table 57: Selected Torsion Angles for Ag[H₃CSO₃].

Atom-Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom-Atom	Angle [°]
O11-S1-C1-H1A	-67.8(4)	H1B-C1-S1-O13	53.5(4)
H1A-C1-S1-O12	53.9(4)	O13-S1-C1-H1C	-66.5(4)
O12-S1-C1-H1B	-66.1(4)	H1C-C1-S1-O11	52.3(4)

Table 58: Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement	
Parameters $(Å^2 \times 10^3)$ for Ag[H ₃ CSO ₃].	

Atom	X	у	Z	U(eq)
H1A	121	2698.99	3854	22
H1B	1204.62	682.95	4790.31	22
H2C	1066.39	1008.77	2839.23	22

$Li_2[CH_2(SO_3)_2]$

Table 59: Crystal Data and Structure Refinement for Li₂[CH₂(SO₃)₂].

Empirical formula	$CH_2Li_2O_6S_2$
Formula Weight	188.03 g/mol
Temperature	100 K
Wavelength	71.073 pm (Mo _{Kα})
Crystal system	orthorhombic
Space group	Pnma
Unit cell parameters	a = 1352.00(8) pm
	<i>b</i> = 806.87(6) pm
	c = 489.87(3) pm
Volume	534.39(6) Å ³
Ζ	4
Density (calculated)	2.337 g/cm ³
Absorption coefficient	0.955 mm ⁻¹
F(000)	376
Crystal size	0.163 x 0.113 x 0.069 mm ³
2θ Range for data collection	$6.026 - 63.018^{\circ}$
Index range	$-19 \le h \le 18, -11 \le k \le 11, -7 \le l \le 7$
Reflections collected	9017
Independent reflections	942 [$R_{\text{int}} = 0.0433, R_{\sigma} = 0.0243$]
Completeness	99.6%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7079/0.6746
Refinement method	Least Squares
Data/Restraints/Parameters	942/0/62

Goodness-of-fit on F^2	1.136
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0280, wR_2 = 0.0631$
R Indices (all data)	$R_1 = 0.0355, wR_2 = 0.0661$
Largest diff. peak and hole	$0.42/-0.53 \text{ e} \cdot \text{\AA}^{-3}$
CCDC Deposition Number	2305645

Table 60: Fractional Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for Li₂[CH₂(SO₃)₂].

Atom	x	У	Z	U(eq)
Li1	3961(2)	-716(4)	5998(6)	12.6(6)
S 1	2818.8(4)	2500	7779(1)	7.5(1)
S2	4981.3(4)	2500	8908(1)	7.0(1)
011	2941.2(8)	995(2)	6193(2)	10.5(2)
012	1912.2(12)	2500	9391(3)	9.6(3)
O21	5070.3(8)	995(1)	7273(2)	8.9(2)
O22	5639(1)	2500	11268(3)	9.0(3)
C1	3770(2)	2500	10292(5)	9.0(4)

Table 61: Anisotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Li_2[CH_2(SO_3)_2]$.

Atom	U_{11}	U_{22}	<i>U</i> ₃₃	U_{23}	U_{13}	U_{12}
Li1	14.(1)	10(1)	14(1)	1(1)	-2(1)	2(1)
S 1	7.2(2)	6.9(2)	8.4(2)	0	0.4(2)	0
S 2	7.5(2)	6.4(2)	7.1(2)	0	-0.1(2)	0
011	10.7(5)	8.5(5)	12.3(5)	-2.6(4)	-0.3(4)	1.4(4)
O12	7.8(7)	9.2(7)	11.7(8)	0	2.9(6)	0
O21	10.1(5)	7.5(5)	9.3(5)	-1.7(4)	0.6(4)	-0.1(4)
O22	9.8(7)	8.6(7)	8.5(7)	0	-2.4(6)	0
C1	8.0(9)	10(1)	9.2(9)	0	0.4(8)	0

Table 62: Selected Bond Lengths for Li₂[CH₂(SO₃)₂].

Bond	Length [pm]	Bond	Length [pm]
S1-O11	145.1(1)	C1-H1	97(2)
S1-O12	145.8(2)	Li1-O21	213.2(3)
S1-C1	178.1(2)	Li1-O11	195.3(3)
S2-O21	146.0(1)	Li1-O12	202.1(3)
S2-O22	145.9(2)	Li1-O22	203.9(3)

S2-C1	177.2(2)	Li1-021	208.2(3)
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Table 63:	Selected	Bond An	gles for	Li ₂ [CH	$[2(SO_3)_2].$
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Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
O11-S1-O12	112.69(6)	O21-S2-O22	112.61(6)
O11-S1-O11	113.6(1)	O21-S2-O21	112.6(1)
O11-S1-C1	106.72(6)	O21-S2-C1	106.63(6)
O12-S1-C1	103.5(1)	O22-S2-C1	105.1(1)
S1-C1-H1	107(1)	S2-C1-H1	107(1)
H1-C1-H1	114(3)	S1-C1-S2	113.8(1)

Table 64: Hydrogen Atom Coordinates $(\mathring{A} \times 10^4)$ and Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Li_2[CH_2(SO_3)_2]$.

Atom	x	у	Z.	U(eq)
H1	3700(15)	1490(30)	11340(40)	14(5)

$Rb_2[CH_2(SO_3)_2]$

Table 65: Crystal Data and Structure Refinement for Rb₂[CH₂(SO₃)₂].

Empirical formula	$CH_2O_6Rb_2S_2$
Formula Weight	345.09 g/mol
Temperature	101 K
Wavelength	71.073 pm (Mo _{Kα})
Crystal system	monoclinic
Space group	C2/c
Unit cell parameters	a = 1282.05(6) pm
	<i>b</i> = 771.93(4) pm
	c = 756.62(3) pm
	$\beta = 91.310(2)^{\circ}$
Volume	748.60(6) Å ³
Ζ	4
Density (calculated)	3.062 g/cm ³
Absorption coefficient	13.610 mm ⁻¹
F(000)	648
Crystal size	$0.272 \text{ x } 0.238 \text{ x } 0.153 \text{ mm}^3$

2θ Range for data collection	$6.162 - 54.996^{\circ}$
Index range	-16≤h≤16, -10≤k≤10, -9≤l≤9
Reflections collected	8085
Independent reflections	852 [$R_{int} = 0.0497, R_{\sigma} = 0.0383$]
Completeness	99.6%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7479/0.2898
Refinement method	Least Squares
Refinement method Data/Restraints/Parameters	Least Squares 852/0/56
Refinement method Data/Restraints/Parameters Goodness-of-fit on F^2	Least Squares 852/0/56 1.136
Refinement method Data/Restraints/Parameters Goodness-of-fit on F^2 Final <i>R</i> Indices [I $\ge 2\sigma(I)$]	Least Squares 852/0/56 1.136 $R_1 = 0.0196, wR_2 = 0.0460$
Refinement method Data/Restraints/Parameters Goodness-of-fit on F^2 Final <i>R</i> Indices [I $\ge 2\sigma(I)$] <i>R</i> Indices (all data)	Least Squares 852/0/56 1.136 $R_1 = 0.0196, wR_2 = 0.0460$ $R_1 = 0.0197, wR_2 = 0.0461$
Refinement method Data/Restraints/Parameters Goodness-of-fit on F^2 Final <i>R</i> Indices [I $\geq 2\sigma(I)$] <i>R</i> Indices (all data) Largest diff. peak and hole	Least Squares 852/0/56 1.136 $R_1 = 0.0196, wR_2 = 0.0460$ $R_1 = 0.0197, wR_2 = 0.0461$ $0.75/-0.54 e \cdot Å^{-3}$

Table 66: Fractional Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Rb_2[CH_2(SO_3)_2]$.

Atom	X	у	Z	U(eq)
Rb1	6500.0(2)	8617.4(2)	3552.2(2)	8.6(1)
S 1	6031.4(4)	6825.2(6)	8589.0(6)	6.3(1)
011	5576(1)	7850(2)	10005(2)	9.9(3)
O12	6509(1)	7910(2)	7254(2)	10.0(3)
013	6718(1)	5447(2)	9236(2)	11.9(3)
C1	5000	5667(3)	7500	7.5(5)

Table 67: Anisotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Rb_2[CH_2(SO_3)_2]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rb1	9(1)	10.1(1)	6.8(1)	1.24(5)	1.03(8)	0.48(6)
S 1	6.6(2)	7.3(2)	5.1(2)	0.1(2)	0.9(2)	-0.2(2)
O11	11.3(6)	12.1(7)	6.5(6)	-3.7(5)	1.9(5)	0.8(5)
O12	11.0(6)	11.1(7)	8.0(6)	1.6(5)	2.7(5)	-2.0(5)
O13	10.5(7)	12.5(7)	12.7(7)	1.6(5)	-1.5(5)	2.4(5)
C1	10(1)	6(1)	7(1)	0	0.5(9)	0

Table 68: Selected Bond Lengths for Rb₂[CH₂(SO₃)₂].

Bond	Length [pm]	Bond	Length [pm]

S1-O11	146.4(1)	Rb1-O11 ⁴	296.9(1)
S1-O12	145.8(1)	Rb1-O12	285.3(1)
S1-O13	145.8(2)	Rb1-O12 ¹	288.9(2)
S1-C1	178.3(1)	Rb1-O12 ²	285.5(2)
C1-H1	88(3)	Rb1-O13 ¹	322.7(2)
Rb1-O11 ²	317.9(2)	Rb1-O13 ⁵	319.1(2)
Rb1-O11 ³	296.0(2)	Rb1-O13 ⁶	313.7(1)

¹3/2-X,3/2-Y,1-Z; ²+X,2-Y,-1/2+Z; ³1-X,+Y,3/2-Z; ⁴+X,+Y,-1+Z; ⁵+X,1-Y,-1/2+Z; ⁶3/2-X,1/2+Y,3/2-Z

Table 69: Selected Bond Angles for Rb₂[CH₂(SO₃)₂].

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
O11-S1-O12	112.19(9)	O13-S1-C1	103.0(1)
O12-S1-O13	113.07(9)	S1-C1-S1 ¹	119.8(2)
O13-S1-O11	113.35(9)	S1-C1-H1	105(2)
O11-S1-C1	107.78(7)	H1-C1-H1	104(4)
O12-S1-C1	106.67(7)		

¹1-X,+Y,3/2-Z

Table 70: Hydrogen Atom Coordinates $(\mathring{A} \times 10^4)$ and Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Rb_2[CH_2(SO_3)_2]$.

Atom	x	у	Z.	U(eq)
H1	5250(20)	4970(40)	6700(40)	12(6)

$Cs_2[CH_2(SO_3)_2]$

Table 71: Crystal Data and Structure Refinement for Cs₂[CH₂(SO₃)₂].

Empirical formula	CH ₂ Cs ₂ O ₆ S ₂
Formula Weight	439.97 g/mol
Temperature	101 K
Wavelength	71.073 pm (Mo _{Kα})
Crystal system	monoclinic
Space group	<i>C</i> 2/ <i>c</i>
Unit cell parameters	a = 1331.45(7)pm
	<i>b</i> = 798.52(4) pm
	c = 786.61(4) pm
	$\beta = 91.791(2)^{\circ}$

Volume	835.91(7) Å ³
Ζ	4
Density (calculated)	3.496 g/cm ³
Absorption coefficient	9.203 mm ⁻¹
F(000)	792
Crystal size	0.329 x 0.157 x 0.100 mm ³
2θ Range for data collection	$5.950 - 54.988^{\circ}$
Index range	$-17 \le h \le 17, -10 \le k \le 10, -10 \le l \le 10$
Reflections collected	28440
Independent reflections	963 [$R_{int} = 0.0631, R_{\sigma} = 0.0148$]
Completeness	99.9%
Completeness Absorption correction	99.9% Multi-Scan
Completeness Absorption correction Max./Min. Transmission	99.9% Multi-Scan 0.7461/0.3395
Completeness Absorption correction Max./Min. Transmission Refinement method	99.9% Multi-Scan 0.7461/0.3395 Least Squares
Completeness Absorption correction Max./Min. Transmission Refinement method Data/Restraints/Parameters	99.9% Multi-Scan 0.7461/0.3395 Least Squares 963/0/56
Completeness Absorption correction Max./Min. Transmission Refinement method Data/Restraints/Parameters Goodness-of-fit on F^2	99.9% Multi-Scan 0.7461/0.3395 Least Squares 963/0/56 1.113
Completeness Absorption correction Max./Min. Transmission Refinement method Data/Restraints/Parameters Goodness-of-fit on F^2 Final <i>R</i> Indices [I $\ge 2\sigma(I)$]	99.9% Multi-Scan 0.7461/0.3395 Least Squares 963/0/56 1.113 $R_1 = 0.0134, wR_2 = 0.0351$
Completeness Absorption correction Max./Min. Transmission Refinement method Data/Restraints/Parameters Goodness-of-fit on F^2 Final R Indices [I $\ge 2\sigma(I)$] R Indices (all data)	99.9% Multi-Scan 0.7461/0.3395 Least Squares 963/0/56 1.113 $R_1 = 0.0134, wR_2 = 0.0351$ $R_1 = 0.0152, wR_2 = 0.0356$
Completeness Absorption correction Max./Min. Transmission Refinement method Data/Restraints/Parameters Goodness-of-fit on F^2 Final <i>R</i> Indices [I $\ge 2\sigma$ (I)] <i>R</i> Indices (all data) Largest diff. peak and hole	99.9% Multi-Scan 0.7461/0.3395 Least Squares 963/0/56 1.113 $R_1 = 0.0134, wR_2 = 0.0351$ $R_1 = 0.0152, wR_2 = 0.0356$ 0.61/-0.60 e · Å ⁻³

Table 72: Fractional Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Cs_2[CH_2(SO_3)_2]$.

Atom	X	У	Z	U(eq)
Cs1	3511.1(2)	8633.5(2)	6487.0(2)	10.63(8)
S 1	4001.4(5)	6736.1(7)	1450.9(7)	9.2(1)
011	4437(1)	7713(2)	96(2)	13.3(4)
012	3551(1)	7786(2)	2732(2)	12.7(4)
013	3335(1)	5419(2)	824(2)	14.2(4)
C1	5000	5604(4)	2500	9.8(6)

Table 73: Anisotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Cs_2[CH_2(SO_3)_2]$.

Atom	U_{11}	U_{22}	<i>U</i> 33	U_{23}	U_{13}	U_{12}
Cs1	10.1(1)	11.7(1)	10.1(1)	-1.24(5)	1.46(6)	-0.25(5)
S 1	8.6(3)	10.0(3)	9.1(3)	0.0(2)	1.5(2)	0.5(2)
O11	10.8(9)	17.1(9)	12.2(8)	3.5(7)	2.8(7)	0.2(7)

012	12.8(9)	13.5(8)	12.1(8)	-2.0(7)	3.2(7)	3.3(7)
O13	11.7(9)	14.9(8)	15.8(9)	-2.5(7)	-3.2(7)	-0.7(7)
C1	10(2)	10(1)	10(2)	0	3(1)	0

Table 74: Selected Bond Lengths for Cs₂[CH₂(SO₃)₂].

Bond	Length [pm]	Bond	Length [pm]
S1-O11	145.6(2)	Cs1-O12 ²	302.2(2)
S1-O12	145.5(2)	Cs1-O11 ²	336.4(2)
S1-O13	145.3(2)	Cs1-O11 ³	312.5(2)
S1-C1	178.8(2)	Cs1-O11 ⁴	314.7(2)
C1-H1	100(2)	Cs1-O13 ¹	337.8(2)
Cs1-O12	303.2(2)	Cs1-O13 ⁵	333.1(2)
Cs1-O12 ¹	305.1(2)	Cs1-O13 ⁶	328.5(2)

¹1/2-X,3/2-Y,1-Z; ²+X,2-Y,1/2+Z; ³1-X,+Y,1/2-Z; ⁴+X,+Y,1+Z; ⁵1/2-X,1/2+Y,1/2-Z; ⁶+X,1-Y,1/2+Z

 Table 75: Selected Bond Angles for Cs2[CH2(SO3)2].

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
O11-S1-O12	112.4(1)	O13-S1-C1	103.2(1)
O12-S1-O13	113.1(1)	S1-C1-S1 ¹	119.3(2)
O13-S1-O11	113.1(1)	S1-C1-H1	109(2)
O11-S1-C1	107.52(9)	H1-C1-H1	101(3)
O12-S1-C1	106.76(8)		
11 V + V 1/2 7			

 $^{1}1$ -X,+Y,1/2-Z

Table 76: Hydrogen Atom Coordinates $(\mathring{A} \times 10^4)$ and Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Cs_2[CH_2(SO_3)_2]$.

Atom	x	у	Z.	U(eq)
H1	5290(20)	4810(30)	1670(30)	9(7)

$K_2[CH_2(SO_3)_2]$

The following dataset is a reproduction of already published data by *Truter*.^[111] The following data for the measured single crystal of $K_2[CH_2(SO_3)_2]$ was taken for comparison to the isotypic structures $Cs_2[CH_2(SO_3)_2]$ and $Rb_2[CH_2(SO_3)_2]$.

Empirical formula	$CH_2K_2O_6S_2$
Formula Weight	252.35 g/mol
Temperature	100 K
Wavelength	71.073 pm (Mo _{Kα})
Crystal system	monoclinic
Space group	C2/c
Unit cell parameters	a = 1239.0(2) pm
	b = 771.7(1) pm
	c = 724.2(1)pm
	90.149(7)
Volume	692.4(2) Å ³
Ζ	4
Density (calculated)	2.421 g/cm ³
Absorption coefficient	1.948 mm ⁻¹
F(000)	504
Crystal size	$0.227 \text{ x } 0.212 \text{ x } 0.084 \text{ mm}^3$
2θ Range for data collection	$6.220 - 52.862^{\circ}$
Index range	$-15 \le h \le 15, -8 \le k \le 8, -9 \le l \le 9$
Reflections collected	4589
Independent reflections	710 [$R_{int} = 0.0261, R_{\sigma} = 0.0198$]
Completeness	98.7%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7466/0.5039
Refinement method	Least Squares
Data/Restraints/Parameters	710/0/56
Goodness-of-fit on F^2	1.102
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0166, wR_2 = 0.0431$
R Indices (all data)	$R_1 = 0.0172, wR_2 = 0.0434$
Largest diff. peak and hole	$0.31/-0.37 \text{ e} \cdot \text{\AA}^{-3}$

Table 77: Crystal Data and Structure Refinement for $K_2[CH_2(SO_3)_2]$.

Table 78: Fractional Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $K_2[CH_2(SO_3)_2]$.

Atom	X	у	Z	U(eq)
K1	6515.5(2)	8702.7(4)	3560.3(4)	12.1(1)

S 1	6055.3(3)	6921.7(4)	8623.4(5)	8.9(1)
O11	5571.8(8)	7954(1)	10093(1)	12.1(2)
O12	6563.0(8)	7993(1)	7213(1)	12.1(2)
O13	6758.0(8)	5552.(1)	9301(1)	14.3(2)
C1	5000	5758(3)	7500	10.0(4)

Table 79: Anisotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $K_2[CH_2(SO_3)_2]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K1	10.9(2)	16.2(2)	9.2(2)	1.7(1)	0.6(1)	0.8(1)
S 1	8.4(2)	10.9(2)	7.5(2)	0.5(1)	0.6(1)	0.2(1)
O11	11.7(5)	14.7(5)	9.8(5)	-3.0(4)	0.6(4)	-0.2(4)
O12	12.2(5)	13.9(5)	10.1(5)	1.5(4)	1.6(4)	-2.7(4)
O13	11.8(5)	17.0(5)	14.1(5)	3.0(4)	-0.5(4)	3.6(4)
C1	10.6(9)	10.0(9)	9.3(9)	0	-0.2(7)	0

Table 80: Selected Bond Lengths for K₂[CH₂(SO₃)₂].

Bond	Length [pm]	Bond	Length [pm]
S1-O11	145.9(1)	K1-O11 ⁴	282.7(1)
S1-O12	145.8(1)	K1-O12	270.2(1)
S1-O13	145.4(1)	K1-O12 ¹	277.5(1)
S1-C1	178.1(1)	K1-O12 ²	273.1(1)
C1-H1	93(2)	K1-O13 ¹	303.7(1)
K1-O11 ²	304.4(1)	K1-O13 ⁵	334.0(1)
K1-O11 ³	282.6(1)	K1-O13 ⁶	299.9(1)

 $\overline{{}^{1}3/2\text{-}X,3/2\text{-}Y,1\text{-}Z;}\,{}^{2}\text{+}X,2\text{-}Y,-1/2\text{+}Z;}\,{}^{3}1\text{-}X,+Y,3/2\text{-}Z;}\,{}^{4}\text{+}X,+Y,-1\text{+}Z;}\,{}^{5}\text{+}X,1\text{-}Y,-1/2\text{+}Z;}\,{}^{6}3/2\text{-}X,1/2\text{+}Y,3/2\text{-}Z;}$

Table 81: Selected Bond Angles for $K_2[CH_2(SO_3)_2]$.

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
O11-S1-O12	112.36(6)	O13-S1-C1	103.07(8)
O12-S1-O13	112.93(6)	S1-C1-S1 ¹	119.5(1)
O13-S1-O11	113.39(6)	S1-C1-H1	107(1)
O11-S1-C1	107.82(5)	H1-C1-H1	110(2)
O12-S1-C1	106.45(5)		
¹ 1-X,+Y,3/2-Z			

Table 82: Hydrogen Atom Coordinates $(\mathring{A} \times 10^4)$ and Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $K_2[CH_2(SO_3)_2]$.

Atom	x	у	Z.	U(eq)
H1	4675(15)	5060(20)	8390(20)	12(4)

BaK₂[CH₂(SO₃)₂]₂

Table 83: Crystal Data and Structure Refinement for BaK₂[CH₂(SO₃)₂]₂.

Empirical formula	$C_2H_4BaK_2O_{12}S_4$
Formula Weight	563.83 g/mol
Temperature	100 K
Wavelength	71.073 рт (Мока)
Crystal system	orthorhombic
Space group	Pbca
Unit cell parameters	<i>a</i> = 957.54(5) pm
	<i>b</i> = 1419.70(7) pm
	c = 1969.6(1) pm
Volume	2677.5(2) Å ³
Ζ	8
Density (calculated)	2.797 g/cm ³
Absorption coefficient	4.271 mm ⁻¹
F(000)	2160
Crystal size	0.314 x 0.282 x 0.194 mm ³
2θ Range for data collection	$4.136 - 51.996^{\circ}$
Index range	$-11 \le h \le 11, -17 \le k \le 17, -24 \le l \le 24$
Reflections collected	51233
Independent reflections	2610 [$R_{\text{int}} = 0.0280, R_{\sigma} = 0.0145$]
Completeness	99.4%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7473/0.5008
Refinement method	Least Squares
Data/Restraints/Parameters	2610/0/206
Goodness-of-fit on F^2	1.207
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0151, wR_2 = 0.0373$

R Indices (all data)	$R_1 = 0.0152, wR_2 = 0.0373$
Largest diff. peak and hole	$0.48/-0.68 \ e \cdot \text{\AA}^{-3}$
CCDC Deposition Number	2120002

Table 84: Fractional Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for BaK₂[CH₂(SO₃)₂]₂.

Atom	X	у	Z.	U(eq)
Ba1	7256.6(2)	6880.4(2)	1383.0(2)	4.46(5)
K2	7299.8(5)	1632.2(3)	3603.2(2)	9.0(1)
K1	986.4(5)	1012.7(3)	5661.1(2)	8.8(1)
S21	9859.8(5)	3142.9(3)	2473.5(2)	5.1(1)
S 11	4847.8(5)	1850.0(3)	5284.5(3)	6.2(1)
S22	9953.7(5)	5301.9(3)	2399.8(2)	5.3(1)
S12	7423.4(5)	632.8(3)	5419.5(3)	5.6(1)
O213	10341(2)	2974(1)	1779.5(7)	8.1(3)
0111	5671(2)	2666(1)	5482.5(8)	10.0(3)
O211	10981(2)	3199(1)	2967.2(7)	7.8(3)
O221	10678(2)	5430(1)	3043.7(7)	9.5(3)
0122	8195(2)	1423(1)	5703.2(8)	12.2(3)
0112	4858(2)	1707(1)	4549.5(8)	11.3(3)
O121	7825(2)	-253(1)	5734.9(8)	11.0(3)
O212	8757(2)	2480(1)	2653.2(7)	7.9(3)
O222	10875(2)	5192(1)	1820.5(8)	10.7(3)
0113	3454(2)	1851(1)	5576.6(8)	11.8(3)
O223	8869(2)	6011(1)	2305.4(8)	9.5(3)
O123	7511(2)	574(1)	4683.9(8)	12.0(3)
C1	5647(2)	826(1)	5645(1)	6.0(4)
C2	8961(2)	4244(1)	2474(1)	6.8(4)

Table 85: Anisotro	nic Displacemen	t Parameters ()	$Å^2 \times 10^3$) for	$BaK_2[CH_2(SO_3)_2]_2$

U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
4.52(7)	5.06(7)	3.80(7)	-0.06(4)	-0.05(4)	-0.22(4)
10.6(2)	9.2(2)	7.2(2)	2.0(2)	1.6(2)	1.8(2)
6.8(2)	10.7(2)	8.9(2)	-1.4(2)	0.9(2)	0.6(2)
5.2(2)	7.3(2)	6.1(2)	-0.4(2)	-1.0(2)	0.2(2)
5.5(2)	5.8(2)	5.5(2)	0.1(2)	0.7(2)	0.5(2)
	U_{11} 4.52(7) 10.6(2) 6.8(2) 5.2(2) 5.5(2)	U_{11} U_{22} $4.52(7)$ $5.06(7)$ $10.6(2)$ $9.2(2)$ $6.8(2)$ $10.7(2)$ $5.2(2)$ $7.3(2)$ $5.5(2)$ $5.8(2)$	U_{11} U_{22} U_{33} $4.52(7)$ $5.06(7)$ $3.80(7)$ $10.6(2)$ $9.2(2)$ $7.2(2)$ $6.8(2)$ $10.7(2)$ $8.9(2)$ $5.2(2)$ $7.3(2)$ $6.1(2)$ $5.5(2)$ $5.8(2)$ $5.5(2)$	U_{11} U_{22} U_{33} U_{23} $4.52(7)$ $5.06(7)$ $3.80(7)$ $-0.06(4)$ $10.6(2)$ $9.2(2)$ $7.2(2)$ $2.0(2)$ $6.8(2)$ $10.7(2)$ $8.9(2)$ $-1.4(2)$ $5.2(2)$ $7.3(2)$ $6.1(2)$ $-0.4(2)$ $5.5(2)$ $5.8(2)$ $5.5(2)$ $0.1(2)$	U_{11} U_{22} U_{33} U_{23} U_{13} 4.52(7)5.06(7)3.80(7) $-0.06(4)$ $-0.05(4)$ 10.6(2)9.2(2)7.2(2)2.0(2)1.6(2)6.8(2)10.7(2)8.9(2) $-1.4(2)$ 0.9(2)5.2(2)7.3(2)6.1(2) $-0.4(2)$ $-1.0(2)$ 5.5(2)5.8(2)5.5(2)0.1(2)0.7(2)

S21	5.6(2)	5.1(2)	4.5(2)	-0.2(2)	-0.4(2)	0.3(2)
S22	5.9(2)	4.9(2)	5.1(2)	0.1(2)	-0.9(2)	-0.4(2)
O111	9.5(7)	8.6(7)	11.9(7)	1.5(6)	-4.4(6)	-1.6(6)
O112	12.6(8)	14.8(8)	6.6(7)	-0.4(6)	-2.4(6)	3.0(6)
O113	6.9(7)	12.1(8)	16.5(8)	-0.9(6)	2.4(6)	0.8(6)
O121	10.9(8)	9.3(7)	12.6(7)	4.2(6)	0.5(6)	1.9(6)
O122	6.6(7)	10.0(7)	20.1(8)	-5.6(6)	0.4(6)	-1.0(6)
O123	15.0(8)	14.8(8)	6.1(7)	1.3(6)	2.5(6)	5.3(6)
O211	8.1(7)	8.6(7)	6.8(7)	-1.1(5)	-2.3(6)	0.9(5)
O212	8.0(7)	6.8(6)	8.9(7)	1.0(5)	0.1(6)	-1.2(6)
O213	11.2(7)	8.2(7)	4.8(7)	-1.1(5)	0.8(6)	1.4(6)
O221	11.4(7)	9.4(7)	7.8(7)	0.5(6)	-4.9(6)	-2.9(6)
O222	12.0(7)	10.4(7)	9.8(7)	-0.6(6)	4.4(6)	-3.0(6)
O223	9.8(7)	5.8(7)	12.9(8)	0.5(6)	-2.8(6)	0.8(6)
C1	6.7(9)	7.5(9)	4(1)	0.2(7)	1.4(7)	-0.2(8)
C2	4.7(9)	7.1(9)	9(1)	-0.2(8)	-0.8(8)	-0.6(7)

 Table 86: Selected Bond Lengths for BaK2[CH2(SO3)2]2.

Bond	Length [pm]	Bond	Length [pm]
S11-O111	146.11(7)	Ba1-O122	279.02(7)
S11-O112	145.67(7)	Ba1-O123	269.48(7)
S11-O113	145.27(7)	Ba1-O212	268.52(7)
S12-O121	145.32(7)	Ba1-O211	279.29(6)
S12-O122	145.49(7)	Ba1-O222	282.82(6)
S12-O123	145.62(7)	Ba1-O221	281.58(7)
S11-C1	179.07(8)	Ba1-O223	303.49(7)
S12-C1	178.04(8)	K1-O123	316.43(8)
C1-H1A	91(2)	K1-O121	275.76(7)
C1-H1B	93(2)	K1-O112	294.71(7)
S21-O211	145.79(7)	K1-O122	274.01(7)
S21-O212	145.99(7)	K1-O113	265.32(7)
S21-O213	145.25(7)	K1-O223	270.30(7)
S22-O221	145.92(6)	K1-O213	285.61(7)
S22-O222	145.13(6)	K2-O221	262.81(7)
S22-O223	146.30(6)	K2-O223	278.07(7)

S21-C2	178.48(8)	K2-O212	292.81(8)
S22-C2	178.53(8)	K2-O111	299.34(8)
C2-H2A	93(2)	K2-O121	261.57(7)
C2H2B	93(2)	K2-O213	281.70(7)
Ba1-O111	274.75(7)	K2-O113	291.06(8)
Ba1-O112	273.91(7)		

 Table 87: Selected Bond Angles for BaK2[CH2(SO3)2]2.

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
O111-S11-O112	111.84(4)	H1A-C1-H1B	105(2)
O112-S11-O113	112.91(4)	O211-S21-O212	111.37(4)
O113-S11-O111	113.61(5)	O212-S21-O213	113.94(4)
O121-S12-O122	113.51(5)	O213-S21-O211	114.13(4)
O122-S12-O123	111.67(5)	O221-S22-O222	114.14(4)
O123-S12-O121	111.04(4)	O222-S22-O223	113.84(4)
O111-S11-C1	106.15(4)	O223-S22-O221	110.39(4)
O112-S11-C1	107.94(4)	O211-S21-C2	106.79(4)
O113-S11-C1	103.65(4)	O212-S21-C2	102.22(4)
O121-S12-C1	108.34(4)	O213-S21-C2	107.33(4)
O122-S12-C1	105.60(4)	O221-S22-C2	102.41(4)
O123-S12-C1	106.22(4)	O222-S22-C2	108.00(4)
S11-C1-S12	115.8(1)	O223-S22-C2	107.16(4)
S21-C2-S22	118.7(1)	S21-C2-H2A	105(1)
S11-C1-H1A	107(1)	S21-C2-H2B	108(1)
S11-C1-H1B	109(1)	S22-C2-H2A	108(1)
S12-C1-H1A	108(1)	S22-C2-H2B	106(1)
S12-C1-H1B	111(1)	H2A-C2-H2B	112(2)

Table 88: Hydrogen Atom Coordinates $(\mathring{A} \times 10^4)$ and Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $BaK_2[CH_2(SO_3)_2]_2$.

Atom	x	у	Z	U(eq)
H1A	5590(30)	884(17)	6080(14)	6(6)
H1B	5110(30)	294(18)	5536(12)	3(6)
H2A	8490(30)	4300(20)	2882(16)	19(7)
H2B	8360(30)	4220(20)	2107(15)	18(7)

(H₃O)₃[CH(SO₃)₃]

Empirical formula	$CH_{10}O_{12}S_3$
Formula Weight	310.27 g/mol
Temperature	99 K
Wavelength	71.073 pm (Mo _{Kα})
Crystal system	trigonal
Space group	R3c
Unit cell parameters	a = 1322.13(4) pm
	<i>b</i> = 1322.13(4) pm
	c = 977.40(5) pm
Volume	1479.6(1) Å ³
Ζ	6
Density (calculated)	2.089 g/cm ³
Absorption coefficient	0.813 mm ⁻¹
F(000)	960
Crystal size	$0.297 \text{ x } 0.207 \text{ x } 0.142 \text{ mm}^3$
2θ Range for data collection	$6.164 - 60.966^{\circ}$
Index range	$-18 \le h \le 18, -18 \le k \le 17, -13 \le l \le 13$
Reflections collected	10309
Independent reflections	997 [$R_{int} = 0.0383, R_{\sigma} = 0.0192$]
Completeness	99.8%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7410/0.7376
Refinement method	Least Squares
Data/Restraints/Parameters	997/1/62
Goodness-of-fit on F^2	1.084
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0161, wR_2 = 0.0396$
<i>R</i> Indices (all data)	$R_1 = 0.0173, wR_2 = 0.0401$
Largest diff. peak and hole	$0.24/-0.20 \text{ e} \cdot \text{\AA}^{-3}$
Flack parameter	0.00(3)
CCDC Deposition Number	2310267

Table 89: Crystal Data and Structure Refinement for $(H_3O)_3[CH(SO_3)_3]$.

Table 90: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement
Parameters $(\text{\AA}^2 \times 10^3)$ for $(H_3O)_3[CH(SO_3)_3]$.	

Atom	X	У	Z.	U(eq)
C1	6666.67	3333.33	3933(3)	9.2(4)
S 1	6574.9(3)	4592.5(3)	4506.6(4)	9.4(1)
011	7007(1)	4853(1)	5882(1)	13.8(2)
O12	5339(1)	4240(1)	4344(1)	12.5(2)
013	7279(1)	5510(1)	3505(1)	11.7(2)
01	4134(1)	3820(1)	6507(1)	13.3(2)

Table 91: Anisotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $(H_3O)_3[CH(SO_3)_3]$.

Atom	U_{11}	U_{22}	<i>U</i> 33	U_{23}	U_{13}	U_{12}
C1	8.6(6)	8.6(6)	11(1)	0	0	4.3(3)
S 1	10.3(2)	9.5(2)	8.8(2)	-0.5(1)	-0.2(1)	5.32(2)
011	17.4(6)	15.2(6)	9.5(5)	-2.2(4)	-1.8(4)	8.7(5)
O12	11.4(5)	14.1(5)	13.3(5)	-0.5(4)	0.4(4)	7.3(4)
O13	12.8(5)	10.9(5)	11.1(5)	1.3(4)	0.9(4)	5.8(4)
O1	13.8(6)	13.1(6)	14.3(5)	0.6(4)	1.6(4)	7.5(4)

Table 92: Selected Bond Lengths for $(H_3O)_3[CH(SO_3)_3]$.

Bond	Length [pm]
S1-O11	143.3(12)
S1-O12	146.6(1)
S1-O13	147.2(1)
S1-C1	181.72(9)

Table 93: Selected Bond Angles for $(H_3O)_3[CH(SO_3)_3]$.

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
O11-S1-O12	115.12(7)	O11-S1-C1	107.94(9)
O12-S1-O13	109.55(7)	O12-S1-C1	104.47(5)
O13-S1-O11	114.46(8)	O13-S1-C1	104.21(8)
S1-C1-H1	107.97(1)	S1-C1-S1 ¹	110.94(7)

¹1+Y-X,1-X,+Z; ²1-Y,+X-Y,+Z

Table 94: Hydrogen Atom Coordinates $(\mathring{A} \times 10^4)$ and Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $(H_3O)_3[CH(SO_3)_3]$.

Atom	x	У	Z.	U(eq)
H1	6666.67	3333.33	2910.22	11
H1A	4290(30)	4540(30)	6750(40)	43(9)
H1B	4340(20)	3450(20)	7150(30)	17(6)
H1C	4540(30)	3990(30)	5790(50)	47(9)

Table 95: Hydrogen Bonding within $(H_3O)_3[CH(SO_3)_3]$.

D-H-A	d _{D-A} [pm]	∠ D-H-A [°]
O1-H1A-O13	262.2(2)	163(3)
O1-H1B-O13	261.3(2)	169(3)
O1-H1C-O12	253.5(2)	176(2)

$Li_3[CH(SO_3)_3] \cdot 4 H_2O$

Table 96: Crystal Data and Structure Refinement for $Li_3[CH(SO_3)_3] \cdot 4H_2O$.

Empirical formula	CH ₉ Li ₃ O ₁₃ S ₃
Formula Weight	346.08 g/mol
Temperature	101 K
Wavelength	71.073 pm (Μο _{Kα})
Crystal system	monoclinic
Space group	$P2_{1}/c$
Unit cell parameters	a = 747.90(4) pm
	<i>b</i> = 1006.63(5) pm
	c = 1545.32(7) pm
	$\beta = 100.274(2)^{\circ}$
Volume	1144.8(1) Å ³
Ζ	4
Density (calculated)	2.008 g/cm ³
Absorption coefficient	0.714 mm ⁻¹
F(000)	704
Crystal size	0.156 x 0.130 x 0.114 mm ³
2θ Range for data collection	$4.852 - 52.992^{\circ}$

Index range	$-9 \le h \le 9, -12 \le k \le 12, -19 \le l \le 19$
Reflections collected	33544
Independent reflections	2376 [$R_{\text{int}} = 0.0641, R_{\sigma} = 0.0244$]
Completeness	99.9%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7412/0.7052
Refinement method	Least Squares
Data/Restraints/Parameters	2376/0/218
Goodness-of-fit on F^2	1.050
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0240, wR_2 = 0.0634$
R Indices (all data)	$R_1 = 0.0258, wR_2 = 0.0651$
Largest diff. peak and hole	$0.36/-0.44 \text{ e} \cdot \text{\AA}^{-3}$
CCDC Deposition Number	2305643

Table 97: Fractional Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Li_3[CH(SO_3)_3] \cdot 4 H_2O$.

Atom	X	у	Z.	U(eq)
S 1	2227.1(5)	7555.4(4)	8504.9(2)	7.6(1)
S2	1156.8(5)	7442.0(4)	6542.7(2)	8.2(1)
S 3	3965.3(5)	5541.9(4)	7480.8(2)	8.3(1)
O11	1035(2)	6445(1)	8626.2(7)	10.3(2)
O12	3847(2)	7634(1)	9174.8(7)	10.2(2)
O13	1271(2)	8813(1)	8373.3(7)	10.1(2)
O21	-390(2)	6699(1)	6740.8(7)	11.5(2)
O22	1870(2)	6968(1)	5790.5(7)	12.3(2)
O23	831(2)	8873(1)	6517.2(7)	10.7(2)
O31	2418(2)	4631(1)	7345.9(8)	11.5(2)
O32	4987(2)	5527(1)	6771.2(8)	12.5(2)
O33	5086(2)	5376(1)	8344.3(7)	11.9(2)
C1	2984(2)	7198(2)	7482(1)	7.8(3)
Li1	4402(4)	6231(3)	5471(2)	15.6(6)
Li2	99(4)	10054(3)	7433(2)	14.0(6)
Li3	6103(4)	6531(3)	9473.(2)	14.9(6)
01	7695(2)	5093(1)	9845.4(9)	19.5(3)
O2	7826(2)	7758(1)	9052.0(9)	13.7(3)
O3	3177(2)	4623(1)	4809.3(8)	12.0(2)

O4 5953(2) 7970(1) 5810.1(8) 12.8(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S 1	8.0(2)	7.2(2)	7.5(2)	-0.3(1)	1.2(1)	0.3(1)
S2	9.2(2)	7.5(2)	7.7(2)	0.5(1)	1.0(1)	0.6(1)
S 3	8.9(2)	7.1(2)	8.7(2)	0.1(1)	1.5(1)	1.0(1)
O11	10.8(5)	9.4(5)	10.8(5)	1.0(4)	2.8(4)	-1.8(4)
O12	9.7(6)	11.0(5)	9.1(5)	-1.8(4)	-0.4(4)	1.5(4)
O13	11.8(5)	8.1(5)	10.2(5)	-0.5(4)	1.6(4)	2.6(4)
O21	9.6(5)	11.5(5)	13.0(6)	2.0(4)	0.5(4)	-1.4(4)
O22	14.6(6)	13.7(6)	8.8(5)	-1.6(4)	2.4(4)	2.7(5)
O23	13.2(5)	8.3(5)	10.6(5)	1.5(4)	2.1(4)	2.0(4)
O31	10.7(5)	8.6(5)	15.2(6)	-1.8(4)	2.2(4)	-1.0(4)
O32	13.8(6)	12.6(6)	12.3(6)	0.4(4)	5.6(4)	3.5(4)
O33	12.7(6)	10.9(5)	10.7(6)	0.6(4)	-1.3(4)	1.4(4)
C1	7.7(7)	7.3(7)	8.3(7)	-0.3(6)	1.0(6)	-0.6(6)
Li1	18(1)	14(1)	16(1)	-2(1)	3(1)	-2(1)
Li2	15(1)	14(1)	14(1)	-1(1)	3(1)	3(1)
Li3	15(1)	13(1)	16(1)	2(1)	2(1)	2(1)
01	29.3(7)	19.3(7)	9.0(6)	1.0(5)	1.3(5)	13.2(6)
O2	12.3(6)	13.5(6)	16.4(6)	3.5(5)	5.5(5)	3.0(5)
O3	14.2(6)	10.7(6)	10.7(6)	1.5(5)	1.4(5)	-0.1(5)
O4	14.5(6)	11.3(6)	11.9(6)	-1.0(5)	0.7(5)	0.4(5)

Table 98: Anisotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Li_3[CH(SO_3)_3] \cdot 4 H_2O$.

Table 99: Selected Bond Lengths for $Li_3[CH(SO_3)_3] \cdot 4 H_2O$.

Bond	Length [pm]	Bond	Length [pm]
S1-O11	146.3(1)	O4-H4A	83(3)
S1-O12	144.9(1)	O4-H4B	77(3)
S1-O13	145.0(1)	Li1-O3	204.2(3)
S2-O21	145.6(1)	Li1-O3 ³	211.7(3)
S2-O22	144.4(1)	Li1-O22	217.1(3)
S2-O23	146.1(1)	Li1-O32	210.2(3)
S3-O31	146.2(1)	Li1-O4	211.4(3)
S3-O32	144.4(1)	Li1 ² -O12	227.9(3)
S3-O33	145.3(1)	Li2 ¹ -O11	220.5(3)
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S1-C1	180.8(2)	Li2 ¹ -O21	2.079(3)
S2-C1	182.4(2)	Li2 ¹ -O31	201.8(3)
S3-C1	182.2(2)	Li2-O13	199.7(3)
C1-H1	91(2)	Li2-O23	199.7(3)
O1-H1A	78(3)	Li3-O1	189.7(3)
O1-H1B	81(3)	Li3-O2	197.7(3)
O2-H2A	73(3)	Li3 ⁴ -O4	214.9(3)
O2-H2B	80(3)	Li3-O12	200.3(3)
O3-H3A	81(3)	Li3-O33	212.1(3)
O3-H3B	80(3)		

¹-X,-1/2+Y,3/2-Z; ²+X,3/2-Y,1/2+Z; ³1-X,1-Y,1-Z; ⁴+X,3/2-Y,-1/2+Z; ⁵-X,1/2+Y,3/2-Z.

Table 100: Selected Bond Angles for $Li_3[CH(SO_3)_3] \cdot 4 H_2O$.

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
O11-S1-O12	113.67(7)	O23-S2-C1	104.60(7)
012-\$1-013	112.41(7)	S31-S3-C1	105.40(7)
O13-S1-O11	112.86(7)	S32-S3-C2	106.14(7)
O21-S2-O22	114.91(7)	S33-S3-C3	105.70(7)
022-\$2-023	112.84(7)	S1-C1-S2	111.21(8)
O23-S2-O21	112.19(7)	S2-C1-S3	111.55(8)
O31-S3-O32	113.43(7)	S3-C1-S1	111.82(8)
032-\$3-033	113.55(7)	S1-C1-H1	108(1)
033-\$3-031	111.78(7)	S2-C1-H1	107(1)
O11-S1-C1	104.67(7)	S3-C1-H1	107(1)
O12-S1-C1	106.45(7)	H1A-O1-H1B	107(3)
O13-S1-C1	105.93(7)	H2A-O2-H2B	106(3)
O21-S2-C1	105.94(7)	H3A-O3-H3B	102(3)
O22-S2-C1	105.29(7)	H4A-O4-H4B	108(3)

Table 101: Hydrogen Atom Coordinates $(\mathring{A} \times 10^4)$ and Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for Li₃[CH(SO₃)₃] · 4 H₂O.

Atom	x	у	Z.	U(eq)
H1	3880(30)	7790(20)	7423(12)	10(5)
H1A	8120(40)	4720(30)	9488(18)	33(7)
H1B	8160(40)	4780(30)	10315(19)	37(7)

H2A	8680(40)	7400(30)	9066(17)	29(7)
H2B	7720(40)	8240(30)	8634(19)	43(8)
H3A	2590(40)	4160(30)	5086(18)	32(7)
H3B	2450(40)	4810(30)	4380(20)	47(8)
H4A	5610(40)	8660(30)	6030(17)	35(7)
H4B	6840(40)	7740(30)	6110(19)	38(8)

Table 102: Hydrogen Bonding within $Li_3[CH(SO_3)_3] \cdot 4 H_2O$.

O _D -H···O _A	d _{D-A} [pm]	∠ O _D -H-O _A [°]
O1-H1A-O23	282.6(2)	175(3)
O1-H1B-O11	284.2(2)	165(3)
O2-H2A-O11	291.7(2)	161(3)
O2-H2B-O31	284.8(2)	174(3)
O3-H3A-O2	276.6(2)	156(3)
O3-H3B-O13	288.3(2)	152(3)
O4-H4A-O33	292.3(2)	176(3)

$Rb_3[CH(SO_3)_3] \cdot H_2O$

Table 103: Crystal Data and Structure Refinement for $Rb_3[CH(SO_3)_3] \cdot H_2O$.

Empirical formula	$CH_3Rb_3O_{10}S_3$	
Formula Weight	527.62 g/mol	
Temperature	100 K	
Wavelength	71.073 pm (Mo _{Kα})	
Crystal system	orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell parameters	a = 963.94(5) pm	
	<i>b</i> = 966.25(5) pm	
	c = 1250.87(6) pm	
Volume	1165.1(1) Å ³	
Ζ	4	
Density (calculated)	3.008 g/cm ³	
Absorption coefficient	13.127 mm ⁻¹	
F(000)	992	

Crystal size	0.258 x 0.219 x 0.111 mm ³
2θ Range for data collection	$5.328 - 61.008^{\circ}$
Index range	−13≤h≤13, −13≤k≤13, −17≤l≤17
Reflections collected	34673
Independent reflections	3538 [$R_{int} = 0.0545, R_{\sigma} = 0.0336$]
Completeness	99.8%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7461/0.3823
Refinement method	Least Squares
Data/Restraints/Parameters	3538/0/168
Goodness-of-fit on F^2	1.040
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0163, wR_2 = 0.0356$
R Indices (all data)	$R_1 = 0.0185, wR_2 = 0.0369$
Largest diff. peak and hole	$0.54/-0.81 \text{ e} \cdot \text{\AA}^{-3}$
Flack parameter	0.027(5)
CCDC Deposition Number	2154779

Table 104: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters ($\mathring{A}^2 \times 10^3$) for $Rb_3[CH(SO_3)_3]H_2O$.

Atom	x	у	Z.	U(eq)
Rb1	2090.0(3)	7716.3(3)	7781.3(3)	15.10(7)
Rb2	4891.4(3)	10023.7(3)	5618.4(2)	8.82(6)
Rb3	2458.8(3)	3403.5(3)	6678.9(2)	8.95(6)
C1	5405(3)	5720(3)	5290(2)	7.5(5)
S 1	3808.9(7)	6271.1(7)	4630.2(5)	9.0(1)
S2	5834.8(7)	3923.2(8)	5001.4(5)	7.7(1)
S 3	5436.5(7)	6147.4(7)	6706.8(6)	7.6(1)
011	4266(2)	6537(3)	3537(2)	16.8(5)
012	2835(2)	5131(2)	4724(2)	12.8(4)
013	3356(2)	7522(2)	5174(2)	16.4(5)
O21	5346(2)	3660(2)	3918(2)	13.1(4)
O22	5156(2)	3062(2)	5798(2)	11.9(4)
O23	7342(2)	3862(2)	5078(2)	11.5(4)
O31	5611(2)	7639(2)	6718(2)	10.9(4)
O32	6619(2)	5425(2)	7171(2)	11.4(4)
O33	4118(2)	5695(2)	7153(2)	11.5(4)

01	28(3)	5340(3)	6772(2)	22 2(5)
01	-28(3)	3340(3)	0772(2)	22.2(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rb1	12.4(1)	14.1(1)	18.8(1)	-5.1(1)	-0.4(1)	-0.5(1)
Rb2	8.5(1)	8.5(1)	9.4(1)	0.5(1)	-0.29(9)	0.5(1)
Rb3	7.9(1)	10.3(1)	8.7(1)	-0.3(1)	-0.07(9)	-1.05(9)
C1	6(1)	10(1)	7(1)	2(1)	-0.2(9)	0(1)
S 1	8.4(3)	9.2(3)	9.5(3)	0.7(3)	-2.7(2)	-0.1(2)
S2	7.0(3)	8.2(3)	7.8(3)	-1.0(2)	0.4(2)	0.5(2)
S 3	8.6(3)	7.6(3)	6.5(3)	0.0(3)	-1.2(2)	-0.1(2)
O11	16(1)	25(1)	9.4(9)	6.3(9)	-3.5(7)	-2(1)
O12	9.7(9)	11(1)	17(1)	2.1(9)	-2.4(8)	-2.5(8)
O13	15(1)	12(1)	22(1)	-4.3(9)	-7.9(8)	5.4(8)
O21	15(1)	14(1)	10.4(9)	-4.4(8)	-2.1(8)	2.6(8)
O22	13(1)	8(1)	15(1)	1.0(8)	3.9(8)	-0.3(8)
O23	7.2(9)	12(1)	15.3(9)	-1.2(8)	1.0(7)	1.4(8)
O31	15(1)	8(1)	9.5(9)	-1.6(8)	-2.6(8)	-0.9(8)
O32	12.0(9)	13(1)	9.7(9)	1.0(8)	-2.9(8)	2.5(8)
O33	11(1)	13(1)	10(1)	-1.2(9)	1.7(8)	-1.6(8)
01	29(1)	28.(1)	10(1)	-2(1)	-1(1)	15(1)

Table 105: Anisotropic Displacement Parameters $(Å^2 \times 10^3)$ for $Rb_3[CH(SO_3)_3]H_2O$.

Table 106: Selected Bond Lengths for Rb3[CH(SO3)3]H2O.

Bond	Length [pm]	Bond	Length [pm]
S1-O11	145.9(2)	Rb1-O13	348.7(2)
S1-O12	145.2(2)	Rb1-O22 ⁵	321.2(2)
S1-O13	145.4(2)	Rb1-O31	364.6(2)
S2-O21	145.7(2)	Rb1-O12	367.2(2)
S2-O22	145.4(2)	Rb2-O12 ⁶	287.3(2)
S2-O23	145.7(2)	Rb2-O32 ⁵	314.9(2)
S3-O31	145.1(2)	Rb2-O31	277.2(2)
S3-O32	145.7(2)	Rb2-O23 ⁷	282.1(2)
S3-O33	145.5(2)	Rb2-O13	288.8(2)
S1-C1	182.6(3)	Rb2-O22 ⁴	295.5(2)
S2-C1	182.1(3)	Rb2-O1 ⁶	301.2(2)

S3-C1	182.0(3)	Rb2-O33 ⁵	301.8(2)
C1-H1	87(4)	Rb3-O33	279.5(2)
O1-H1A	84(5)	Rb3-O12	298.3(2)
O1-H1B	72(6)	Rb3-O32 ²	333.9(2)
Rb1-O33	287.3(2)	Rb3-O31 ²	283.4(2)
Rb1-O32 ⁵	289.9(2)	Rb3-O23 ¹	310.4(2)
Rb1-O23 ⁵	294.9(2)	Rb3-O21 ¹	294.6(2)
Rb1-O21 ³	305.0(2)	Rb3-O11 ³	285.9(2)
Rb1-O11 ⁷	326.3(2)	Rb3-O22	284.3(2)
Rb1-O1	332.2(3)	Rb3-O1	304.3(3)
Rb1-O1 ⁸	327.0(3)		

 $\overline{{}^{1}-1/2+X,1/2-Y,1-Z;} \ {}^{2}1-X,-1/2+Y,3/2-Z; \ {}^{3}1/2-X,1-Y,1/2+Z; \ {}^{4}+X,1+Y,+Z; \ {}^{5}1-X,1/2+Y,3/2-Z; \ {}^{6}1/2+X,3/2-Y,1-Z; \ {}^{7}-1/2+X,3/2-Y,1-Z; \ {}^{8}-X,1/2+Y,3/2-Z; \ {}^{6}-1/2+X,3/2-Y,1-Z; \ {}^{6}-1/2+X,3/2-X; \ {}^{6}-1/2+X,3/2-X; \ {}^{6}-1/2+X,3/2-X; \ {}^{6}-1/2+X,3/2-X; \ {}^{6}-1/2+X,3/2-X; \ {}^{6}-1/2+X,3/2-X;$

Table 107:	Selected	Bond	Angles for	Rb ₃ [CH	$[(SO_3)_3]H_2O.$
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Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
O11-S1-O12	113.9(1)	S3-C1-S1	113.5(2)
O12-S1-O13	113.5(1)	O13-S1-C1	106.5(1)
O13-S1-O11	112.5(2)	O21-S2-C1	106.1(1)
O21-S2-O22	113.1(1)	O22-S2-C1	107.9(1)
O22-S2-O23	112.4(1)	O23-S2-C1	104.6(1)
O23-S2-O21	112.1(1)	S31-S3-C1	103.7(1)
O31-S3-O32	112.4(1)	S32-S3-C1	107.0(1)
O32-S3-O33	112.7(1)	S33-S3-C1	106.9(1)
O33-S3-O31	113.3(1)	S1-C1-H1	105(3)
O11-S1-C1	102.7(1)	S2-C1-H1	108(3)
O12-S1-C1	106.7(1)	S3-C1-H1	104(3)
S1-C1-S2	112.1(2)	H1A-O1-H1B	107(5)
S2-C1-S3	112.2(2)		

Table 108: Hydrogen Atom Coordinates $(\mathring{A} \times 10^4)$ and Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Rb_3[CH(SO_3)_3]H_2O$.

Atom	X	У	Z.	U(eq)
H1	6060(40)	6240(40)	5020(30)	21(10)
H1A	-540(60)	6030(60)	6720(40)	45(16)
H1B	-30(60)	5140(60)	7330(50)	52(18)

O _D -H…O _A	d _{D-A} [pm]	$\angle O_D$ -H-O _A [°]
O1-H1A-O11	311.8(4)	148(5)
O1-H1B-O11	295.0(4)	144(6)
O1-H1B-O21	287.0(3)	134(6)

Table 109: Hydrogen Bonding within $Rb_3[CH(SO_3)_3] \cdot H_2O$

$Ag_3[CH(SO_3)_3] \cdot H_2O$

Table 110: Crystal Data and Structure Refinement for $Ag_3[CH(SO_3)_3] \cdot H_2O$ (Structure A).

Empirical formula	$CH_3Ag_3O_{10}S_3$
Formula Weight	594.82 g/mol
Temperature	100 K
Wavelength	71.073 рт (Мока)
Crystal system	monoclinic
Space group	$P2_{1}/n$
Unit cell parameters	a = 682.42(5) pm
	<i>b</i> = 983.89(7) pm
	c = 1439.9(1) pm
	$\beta = 98.194(2)^{\circ}$
Volume	956.9(1) Å ³
Ζ	4
Density (calculated)	4.129 g/cm ³
Absorption coefficient	6.778 mm ⁻¹
F(000)	1112
Crystal size	0.236 x 0.155 x 0.082 mm ³
2θ Range for data collection	$5.03 - 57.39^{\circ}$
Index range	–9≤h≤9, –13≤k≤13, –19≤l≤19
Reflections collected	17230
Independent reflections	2471 [$R_{int} = 0.0420, R_{\sigma} = 0.0258$]
Completeness	100%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7458/0.6402
Refinement method	Least Squares

Data/Restraints/Parameters	2471/0/167
Goodness-of-fit on F^2	1.138
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0196, wR_2 = 0.0415$
R Indices (all data)	$R_1 = 0.0216, wR_2 = 0.0420$
Largest diff. peak and hole	$1.09/-0.59 \text{ e} \cdot \text{\AA}^{-3}$
CCDC Deposition Number	2154778

Table 111: Fractional Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Ag_3[CH(SO_3)_3]H_2O$ (Structure A).

Atom	X	у	Z.	U(eq)
Ag1	-1267.7(3)	4579.7(2)	6219.8(2)	11.93(6)
Ag2	-950.0(3)	10337.9(2)	6532.0(2)	11.92(6)
Ag3	10953.8(4)	7209.6(2)	7803.1(2)	14.74(7)
C1	4229(4)	7045(3)	5920(2)	8.2(5)
S 1	2075(1)	8103.8(7)	5558.2(5)	8.9(1)
S2	3537(1)	5313.6(7)	6172.3(5)	8.4(1)
S 3	5918(1)	7784.2(7)	6872.2(5)	8.9(1)
011	640(3)	7221(2)	5014.(2)	12.5(4)
012	1450(3)	8615(2)	6421(1)	11.8(4)
013	2766(3)	9179(2)	4990(2)	12.7(4)
O21	5314(3)	4689(2)	66859(2)	11.5(4)
O22	2922(3)	4685(2)	5266(2)	12.0(4)
O23	1959(3)	5422(2)	6753(2)	11.9(4)
O31	5126(3)	7489(2)	7746(2)	12.3(4)
O32	5940(3)	9234(2)	6685(2)	13.4(4)
O33	7782(3)	7099(2)	6812(2)	13.9(4)
01	11703(4)	6829(2)	9360(2)	13.9(4)

Table 112: Anisotropic Displacement Parameters $(Å^2 \times 10^3)$ for $Ag_3[CH(SO_3)_3]H_2O$ (Structure A).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag1	10.6(1)	13.9(1)	10.6(1)	0.24(8)	-0.87(8)	0.89(8)
Ag2	13.1(1)	11.6(1)	10.4(1)	-0.26(8)	-0.59(8)	0.13(8)
Ag3	16.5(1)	17.0(1)	10.0(1)	-1.36(9)	-0.61(8)	2.56(9)
C1	8(1)	9.0(12)	8(1)	-0.6(11)	0.2(10)	-1(1)
S 1	8.9(3)	8.2(3)	8.8(3)	0.0(3)	-1.1(3)	0.4(2)

S2	8.8(3)	7.5(3)	8.5(3)	0.2(3)	-0.3(3)	-0.5(2)
S 3	8.2(3)	8.9(3)	9.0(3)	-0.6(3)	-1.2(2)	-1.0(3)
O11	10(1)	11.2(9)	15(1)	-2.3(9)	-2.8(8)	-0.4(8)
O12	13(1)	12.1(9)	10.3(9)	-2.2(8)	2.2(8)	1.8(8)
O13	15(1)	10.1(9)	13(1)	2.8(8)	0.9(8)	0.5(8)
O21	11(1)	9.3(9)	14(1)	2.2(8)	-0.4(8)	1.7(8)
O22	14(1)	11.1(9)	10(1)	-1.2(8)	-1.1(8)	-0.6(8)
O23	12(1)	11.0(9)	13(1)	0.8(8)	2.6(8)	-1.8(8)
O31	15(1)	13(1)	9(1)	-1.0(8)	0.7(8)	1.1(8)
O32	15(1)	9.4(9)	15(1)	0.8(8)	0.0(9)	-3.3(8)
O33	10(1)	16(1)	16(1)	-2.3(9)	-1.8(8)	1.2(8)
O1	15(1)	11(1)	16(1)	0.7(9)	-1.4(9)	-2.4(9)

Table 113: Selected Bond Lengths for $Ag_3[CH(SO_3)_3] \cdot H_2O$ (Structure A).

Bond	Length [pm]	Bond	Length [pm]
S1-O11	145.2(2)	Ag1-O23	237.6(2)
S1-O12	146.0(2)	Ag1-O22	238.4(2)
S1-O13	145.7(2)	Ag1-O32	301.3(2)
S2-O21	146.2(2)	Ag1-O33	272.9(3)
S2-O22	145.2(2)	Ag1-O11	258.8(2)
S2-O23	145.9(2)	Ag2-O12	237.8(2)
S3-O31	146.8(2)	Ag2-O21	262.1(2)
S3-O32	145.2(2)	Ag2-O31	238.9(2)
S3-O33	145.3(2)	Ag2-O13	240.6(2)
S1-C1	181.6(3)	Ag2-O32	242.2(2)
S2-C1	181.8(3)	Ag3-O1	225.8(2)
S3-C1	181.3(3)	Ag3-O23	247.9(2)
C1-H1	87(4)	Ag3-O33	241.9(2)
O1-H1A	73(5)	Ag3-O21	272.5(2)
O1-H1B	74(6)	Ag3-O31	287.3(2)
Ag1-O21	252.0(2)	Ag3-O12	248.6(2)
Ag1-O31	259.3(2)		

Table 114: Selected Bond Angles for $Ag_3[CH(SO_3)_3] \cdot H_2O$ (Structure A).

Atom-AtomAngle [°]Atom-Atom-AtomAngle [°]	Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
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O11-S1-O12	114.1(1)	S3-C1-S1	112.8(2)
O12-S1-O13	112.7(1)	O13-S1-C1	105.3(1)
O13-S1-O11	112.2(1)	O21-S2-C1	105.9(1)
O21-S2-O22	112.8(1)	O22-S2-C1	105.6(1)
O22-S2-O23	113.9(1)	O23-S2-C1	106.2(1)
O23-S2-O21	111.6(1)	S31-S3-C1	107.3(1)
O31-S3-O32	111.6(1)	S32-S3-C1	106.0(1)
032-\$3-033	114.3(1)	S33-S3-C1	103.7(1)
O33-S3-O31	113.1(1)	S1-C1-H1	105(3)
O11-S1-C1	105.5(1)	S2-C1-H1	107(3)
O12-S1-C1	106.0(1)	S3-C1-H1	108(3)
S1-C1-S2	111.9(2)	H1A-O1-H1B	115(6)
S2-C1-S3	112.3(2)		

Table 115: Hydrogen Atom Coordinates $(\mathring{A} \times 10^4)$ and Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Ag_3[CH(SO_3)_3] \cdot H_2O$ (Structure A).

Atom	X	у	Z.	U(eq)
H1	4840(60)	7000(40)	5430(30)	15(9)
H1A	12640(70)	7120(40)	9590(30)	17(11)
H1B	11600(80)	6090(60)	9410(40)	55(17)

Table 116: Hydrogen Bonding within $Ag_3[CH(SO_3)_3] \cdot H_2O$ (Structure A).

O _D -H…O _A	d _{D-A} [pm]	$\angle O_D$ -H-O _A [°]
O1-H1A-O11	287.4(3)	168(5)
O1-H1B-O13	277.7(3)	156(6)

The following dataset gives the crystallographic information on a reproduced, solved and refined crystal structure on $Ag_3[CH(SO_3)_3] \cdot H_2O$.

Table 117: Crystal Data and Structure Refinement for $Ag_3[CH(SO_3)_3] \cdot H_2O$ (Structure B).

Empirical formula	$CH_3Ag_3O_{10}S_3$
Formula Weight	594.82 g/mol
Temperature	100 K
Wavelength	71.073 pm (Mo _{Kα})
Crystal system	monoclinic

Space group	$P2_{1}/c$
Unit cell parameters	a = 753.42(5) pm
	<i>b</i> = 2154.2(2) pm
	c = 592.84(5) pm
	$\beta = 97.556(3)^{\circ}$
Volume	953.6(1) Å ³
Ζ	4
Density (calculated)	4.143 g/cm ³
Absorption coefficient	6.801 mm ⁻¹
F(000)	1112
Crystal size	0.23 x 0.16 x 0.03 mm ³
2θ Range for data collection	$5.456 - 57.998^{\circ}$
Index range	0≤h≤10, -29≤k≤0, -8≤l≤8
Reflections collected	2511
Independent reflections	2511 [$R_{\sigma} = 0.0279$]
Completeness	99.5%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7465/0.34869
Refinement method	Least Squares
Data/Restraints/Parameters	2511/0/164
Goodness-of-fit on F^2	1.289
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0242, wR_2 = 0.0619$
R Indices (all data)	$R_1 = 0.0243, wR_2 = 0.0620$
Largest diff. peak and hole	$1.00/-1.64 \mathrm{e} \cdot \mathrm{\AA}^{-3}$
BASF	0.219(1)
CCDC Deposition Number	2330301

Table 118: Fractional Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Ag_3[CH(SO_3)_3]H_2O$ (Structure B).

Atom	X	у	Z.	U(eq)
Ag1	5800.0(4)	7096.9(2)	7834.9(5)	11.18(9)
Ag2	9052.6(4)	5862.5(2)	6449.2(5)	9.63(9)
Ag3	6080.4(4)	4631.4(2)	2713.6(5)	11.15(9)
C1	2807(5)	6342(2)	2234(6)	6.7(6)
S 1	1430(1)	5640.3(4)	1911(2)	7.0(2)
S2	5196(1)	6181.1(4)	2626(2)	6.4(2)

S 3	2141(1)	6850.2(4)	4429(2)	6.8(2)
O11	-307(4)	5826(1)	2465(5)	10.3(5)
O12	1415(4)	5470(1)	-467(5)	10.3(5)
O13	2323(4)	5180(1)	3476(5)	10.3(5)
O21	5413(4)	5655(1)	1139(5)	10.4(5)
O22	5699(4)	6038(1)	5041(5)	9.6(5)
O23	6045(4)	6742(1)	1927(5)	10.0(5)
O31	2053(4)	6456(1)	6410(5)	10.2(5)
O32	3558(4)	7317(1)	4841(5)	9.1(5)
O33	445(4)	7113(1)	3427(5)	12.0(5)
01	8709(4)	6776(1)	8804(5)	10.8(5)

Table 119: Anisotropic Displacement Parameters $(Å^2 \times 10^3)$ for $Ag_3[CH(SO_3)_3]H_2O$ (Structure B).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag1	9.4(1)	13.2(1)	10.5(1)	0.2(1)	-0.2(1)	3.27(9)
Ag2	8.1(1)	9.7(1)	11.0(1)	0.1(1)	0.8(1)	-1.27(9)
Ag3	14.7(2)	10.8(1)	8.0(1)	1.2(1)	1.8(1)	1.73(9)
C1	7(1)	6(1)	8(2)	-1(1)	2(1)	1(1)
S 1	7.3(4)	5.9(3)	7.6(4)	0.2(3)	0.6(3)	-1.3(3)
S2	5.2(4)	6.3(3)	7.7(4)	0.7(3)	0.4(3)	0.1(3)
S 3	6.9(4)	6.4(4)	7.1(4)	-0.1(3)	0.7(3)	0.0(3)
O11	4(1)	15(1)	14(1)	-2(1)	5(1)	-0.9(9)
O12	13(1)	10(1)	9(1)	0.1(9)	2(1)	-2(1)
O13	13(1)	8(1)	9(1)	3(1)	-4(1)	-2.3(9)
O21	10(1)	9(1)	12(1)	-2(1)	0(1)	2.8(9)
O22	9(1)	11(1)	9(1)	1.3(9)	0(1)	1(1)
O23	8(1)	8(1)	14(1)	2(1)	2(1)	-2.0(9)
O31	11(1)	12(1)	9(1)	1(1)	3(1)	-1(1)
O32	10(1)	8(1)	10(1)	-1.5(9)	0(1)	-2.4(9)
O33	9(1)	13(1)	14(1)	-3(1)	0(1)	3(1)
01	10(1)	13(1)	10(1)	1(1)	1(1)	-1(1)

Table 120: Selected Bond Lengths for $Ag_3[CH(SO_3)_3] \cdot H_2O$ (Structure B).

Bond	Length [pm]	Bond	Length [pm]
S1-O11	144.7(3)	Ag1-O32	2.332(3)

S1-O12	145.5(3)	Ag1-O23 ⁵	2.527(3)
S1-O13	146.0(3)	Ag1-O32 ⁶	2.527(3)
S2-O21	145.7(3)	Ag1-O23 ⁶	2.570(3)
S2-O22	146.5(3)	Ag2-O1	2.446(3)
S2-O23	145.3(3)	Ag2-O12	2.523(3)
S3-O31	145.8(3)	Ag2-O31	2.599(3)
S3-O32	146.4(3)	Ag2-O13 ²	2.477(3)
S3-O33	145.1(3)	Ag2-O11 ¹	2.473(3)
S1-C1	183.0(4)	Ag2-O22	2.582(3)
S2-C1	181.7(4)	Ag3-O13 ²	244.9(3)
S3-C1	182.0(4)	Ag3-O22	247.4(3)
C1-H1	100.0(4)	Ag3-O31	274.6(3)
O1-H1A	71(8)	Ag3-O12 ⁴	245.8(3)
O1-H1B	80(10)	Ag3-O21 ⁴	248.8(3)
Ag1-O1	229.8(3)	Ag3-O21	242.2(3)
Ag1-O22 ²	247.3(3)	Ag3-O13	315.4(3)

¹1+X,+Y,+Z; ²1-X,1-Y,1-Z; ³1+X,+Y,1+Z; ⁴1-X,1-Y,-Z; ⁵+X,+Y,1+Z; ⁶+X,3/2-Y,1/2+Z.

Table 121: Selected Bond Angles for $Ag_3[CH(SO_3)_3] \cdot H_2O$ (Structure B).

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
O11-S1-O12	113.4(2)	S3-C1-S1	111.5(2)
O12-S1-O13	112.9(2)	O13-S1-C1	106.7(2)
O13-S1-O11	113.5(2)	O21-S2-C1	105.0(2)
O21-S2-O22	113.1(2)	O22-S2-C1	106.8(2)
O22-S2-O23	112.7(2)	O23-S2-C1	105.7(2)
O23-S2-O21	112.6(2)	S31-S3-C1	105.8(2)
O31-S3-O32	112.0(2)	S32-S3-C1	105.6(2)
O32-S3-O33	112.6(2)	S33-S3-C1	104.7(2)
O33-S3-O31	115.2(2)	S1-C1-H1	106(3)
O11-S1-C1	105.4(2)	S2-C1-H1	106(3)
O12-S1-C1	104.0(2)	S3-C1-H1	106(3)
S1-C1-S2	113.2(2)	H1A-O1-H1B	124(10)
S2-C1-S3	112.7(2)		

Table 122: Hydrogen Atom Coordinates $(\mathring{A} \times 10^4)$ and Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Ag_3[CH(SO_3)_3] \cdot H_2O$ (Structure B).

Atom	x	у	Z.	U(eq)
H1	2551.41	6574.73	767.5	8
H1A	8760(100)	6640(30)	9900(140)	31(19)
H1B	9290(140)	7070(50)	8510(190)	70(30)

Table 123: Hydrogen Bonding within $Ag_3[CH(SO_3)_3] \cdot H_2O$ (Structure B).

O _D -H···O _A	d _{D-A} [pm]	$\angle O_D$ -H-O _A [°]
O1-H1A-O11	300.4(4)	150(8)
O1-H1A-O23	290.5(5)	117(7)
O1-H1A-O33	296.8(4)	124(8)
O1-H1B-O33	275.5(4)	166(11)

Rb5Ag[CH(SO3)3]2 · 2 H2O

Table 124: Crystal Data and Structure Refinement for $Rb_5Ag[CH(SO_3)_3]_2 \cdot 2H_2O$.

Empirical formula	$Rb_5Ag[CH(SO_3)_3]_2 \cdot 2 H_2O$
Formula Weight	1077.65 g/mol
Temperature	100 K
Wavelength	71.073 pm (Mo _{Kα})
Crystal system	tetragonal
Space group	P41212
Unit cell parameters	a = 735.32(2) pm
	c = 4166.3(1) pm
Volume	2252.7(2) Å ³
Ζ	4
Density (calculated)	3.177 g/cm ³
Absorption coefficient	12.275 mm ⁻¹
F(000)	2024
Crystal size	$0.186 \ge 0.185 \ge 0.056 \text{ mm}^3$
2θ Range for data collection	$3.91 - 51.948^{\circ}$
Index range	$-9 \le h \le 9, -8 \le k \le 9, -51 \le l \le 51$
Reflections collected	27796

Independent reflections	2208 [$R_{\text{int}} = 0.0592, R_{\sigma} = 0.0287$]
Completeness	100%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7466/0.5547
Refinement method	Least Squares
Data/Restraints/Parameters	2208/0/168
Goodness-of-fit on F^2	1.041
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0177, wR_2 = 0.0367$
R Indices (all data)	$R_1 = 0.0188, wR_2 = 0.0372$
Largest diff. peak and hole	$0.49/-0.37 \text{ e} \cdot \text{\AA}^{-3}$
Flack parameter	0.057(8)
CCDC Deposition Number	2310268

Table 125: Fractional Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Rb_5Ag[CH(SO_3)_3]_2 \cdot 2H_2O$.

Atom	x	у	Z.	U(eq)
Rb1	2421.6(6)	-567.0(6)	3727.0(2)	10.1(1)
Rb2	5120.9(6)	7642.1(6)	2851.3(2)	11.1(1)
Rb3	-2695.6(6)	2695.6(6)	2500	10.8(1)
Ag1	607.8(5)	9392.2(5)	2500	12.3(1)
C1	1288(6)	4050(6)	3221(1)	6.9(9)
S 1	2747(2)	4718(2)	3554.7(2)	8.8(2)
S2	129(2)	6007(2)	3039.1(3)	8.4(2)
S 3	2442(2)	2642(1)	2921.9(2)	8.4(2)
011	1463(4)	5336(5)	3797.2(7)	11.6(7)
O12	3918(4)	6164(4)	3434.2(7)	10.2(7)
O13	3757(4)	3107(4)	3648.4(7)	11.9(7)
O21	29(4)	7410(4)	3284.7(7)	11.6(7)
O22	-1646(4)	5324(5)	2950.2(8)	15.4(8)
O23	1244(5)	6557(4)	2764.6(7)	13.1(7)
O31	2827(5)	919(4)	3077.2(7)	13.8(7)
O32	4027(4)	3651(4)	2819.0(7)	12.8(7)
O33	1095(4)	2441(4)	2663.5(7)	11.2(7)
01	7790(7)	10491(6)	3077.1(9)	25.6(9)

Atom	U_{11}	U_{22}	<i>U</i> 33	U_{23}	U_{13}	U_{12}
Rb1	9.7(2)	9.4(2)	11.3(2)	-0.2(2)	-0.2(2)	-0.3(2)
Rb2	9.6(2)	12.2(2)	11.4(2)	2.3(2)	1.1(2)	-0.1(2)
Rb3	9.2(2)	9.2(2)	14.1(3)	-2.2(2)	-2.2(2)	1.1(3)
Ag1	9.2(2)	9.2(2)	18.5(2)	-1.0(2)	-1.0(2)	0.5(2)
C1	4(2)	11(3)	6(2)	1(2)	1(2)	-1(2)
S 1	9.4(6)	8.2(6)	8.9(5)	0.4(4)	-1.8(4)	-0.7(5)
S 2	8.3(6)	8.1(6)	8.8(5)	-0.2(4)	-0.2(4)	1.1(4)
S 3	9.1(5)	7.2(5)	8.9(5)	-0.4(4)	0.4(4)	0.8(5)
011	12(2)	15(2)	8(2)	-1(1)	1(1)	-1(1)
O12	8(2)	12(2)	11(2)	0(1)	0(1)	-2(1)
O13	11(2)	12(2)	13(2)	2(1)	-3(1)	0.1)
O21	15(2)	9(2)	11(2)	-3(1)	-2(1)	3(1)
O22	9(2)	13(2)	24(2)	-2(2)	-4(1)	0(1)
O23	16(2)	13(2)	11(2)	4(1)	2(1)	3(2)
O31	20(2)	9(2)	12(2)	-1(1)	2(1)	3.(2)
O32	9(2)	15(2)	14(2)	-2(1)	5(1)	-1(1)
O33	10(2)	12(2)	12(2)	-1(1)	-1(1)	2(2)
01	35(3)	28(2)	13(2)	1.(2)	2(2)	-2(2)

Table 126: Anisotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Rb_5Ag[CH(SO_3)_3]_2 \cdot 2 H_2O$.

Table 127: Selected Bond Lengths for $Rb_5Ag[CH(SO_3)_3]_2 \cdot 2 H_2O$.

Bond	Length [pm]	Bond	Length [pm]
S1-O11	145.5(3)	Rb1-O11 ⁶	297.8(3)
S1-O12	145.7(3)	Rb1-O21 ⁴	295.1(3)
S1-O13	145.2(3)	Rb1-O31	293.5(3)
S2-O21	145.5(3)	Rb1-O12 ⁴	291.1(3)
S2-O22	144.6(3)	Rb1-O11 ⁴	310.8(3)
S2-O23	146.4(3)	Rb1-O13 ⁵	328.7(3)
S3-O31	145.1(3)	Rb1-O21 ⁶	310.7(3)
S3-O32	144.7(3)	Rb2-O1	302.1(4)
S 3-O33	147.0(3)	Rb2-O31 ¹	308.8(3)
S1-C1	182.3(5)	Rb2-O12	280.4(3)
S2-C1	183.7(5)	Rb2-O23 ²	296.3(3)

S3-C1	182.9(5)	Rb2-O32	304.6(3)
C1-H1	86(5)	Rb2-O23	298.2(3)
O1-H1A	79(7)	Rb2-O32 ²	318.1(3)
O1-H1B	76(1)	Rb2-O33 ²	294.6(3)
Ag1-O23	240.4(3)	Rb2-O22 ¹⁰	295.4(3)
Ag1-O31	311.6(3)	Rb3-O1	292.2(4)
Ag1-O33	237.0(3)	Rb3-O22	280.2(3)
Rb1-O22 ⁶	350.1(3)	Rb3-O32	284.0(3)
Rb1-O12 ⁵	297.0(3)	Rb3-O33	287.6(3)
Rb1-O13	289.3(3)		

 $\overline{{}^{1}+X,1+Y,+Z;} \, {}^{2}1-Y,1-X,1/2-Z; \, {}^{3}-Y,1-X,1/2-Z; \, {}^{4}+X,-1+Y,+Z; \, {}^{5}-1/2+X,1/2-Y,3/4-Z; \, {}^{6}1/2+X,1/2-Y,3/4-Z; \, {}^{7}-Y,-X,1/2-Z; \, {}^{8}-1+X,+Y,+Z; \, {}^{9}-1+X,-1+Y,+Z; \, {}^{10}1+X,+Y,+Z; \, {}^{10}1+X,+Y,+Z; \, {}^{10}1+X,+Y,+Z; \, {}^{10}1+X,-1+Y,+Z; \, {}^{10}1+X,-1+Y,-Z; \, {}^{10}1+X,-Y,-Z; \,$

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
O11-S1-O12	113.3(2)	S3-C1-S1	113.5(2)
O12-S1-O13	112.7(2)	O13-S1-C1	106.6(2)
O13-S1-O11	113.6(2)	O21-S2-C1	106.8(2)
O21-S2-O22	112.4(2)	O22-S2-C1	104.6(2)
O22-S2-O23	113.6(2)	O23-S2-C1	106.2(2)
O23-S2-O21	112.4(2)	S31-S3-C1	106.3(2)
O31-S3-O32	115.0(2)	S32-S3-C1	106.6(2)
O32-S3-O33	112.2(2)	S33-S3-C1	104.1(2)
O33-S3-O31	111.7(2)	S1-C1-H1	103(3)
O11-S1-C1	103.4(2)	S2-C1-H1	110(3)
O12-S1-C1	106.4(2)	S3-C1-H1	105(3)
S1-C1-S2	112.1(2)	H1A-O1-H1B	109(10)
S2-C1-S3	112.2(2)		

Table 128: Selected Bond Angles for $Rb_5Ag[CH(SO_3)_3]_2 \cdot 2H_2O$.

Table 129: Hydrogen Atom Coordinates $(\mathring{A} \times 10^4)$ and Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Rb_5Ag[CH(SO_3)_3]_2 \cdot 2 H_2O$.

Atom	X	у	Z.	U(eq)
H1	500(70)	3350(70)	3311(10)	7(13)
H1A	7130(90)	10970(90)	3201(15)	40(20)
H1B	8520(180)	9980(190)	3170(30)	220(80)

O_D -H···O _A	d _{D-A} [pm]	$\angle O_D$ -H-O _A [°]
O1-H1A-O11	284.9(5)	122(6)
O1-H1B-O21	293.1(5)	151(13)

Table 130: Hydrogen Bonding within $Rb_5Ag[CH(SO_3)_3]_2 \cdot 2 H_2O$.

$Rb_3Ag_3[CH(SO_3)_3]_2$

Table 131: Crystal Data and Structure Refinement for Rb₃Ag₃[CH(SO₃)₃]₂.

Empirical formula	$C_2H_2Ag_3O_{18}Rb_3S_6$
Formula Weight	1086.42 g/mol
Temperature	100 K
Wavelength	71.073 pm (Mo _{Kα})
Crystal system	triclinic
Space group	PĪ
Unit cell parameters	a = 750.17(5) pm
	<i>b</i> = 754.08(5) pm
	c = 973.20(6) pm
	$\alpha = 89.447(2)^{\circ}$
	$\beta = 98.194(2)^{\circ}$
	$\gamma = 62.861(2)^{\circ}$
Volume	473.23(5) Å ³
Ζ	1
Density (calculated)	3.812 g/cm ³
Absorption coefficient	11.492 mm ⁻¹
F(000)	506
Crystal size	0.226 x 0.068 x 0.063 mm ³
2θ Range for data collection	$4.332 - 54.986^{\circ}$
Index range	$-9 \le h \le 9, -9 \le k \le 9, -12 \le l \le 12$
Reflections collected	67407
Independent reflections	2180 [$R_{\text{int}} = 0.0404, R_{\sigma} = 0.0097$]
Completeness	100%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7480/0.5435
Refinement method	Least Squares

Data/Restraints/Parameters	2180/0/153
Goodness-of-fit on F^2	1.139
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0098, wR_2 = 0.0252$
R Indices (all data)	$R_1 = 0.0099, wR_2 = 0.0252$
Largest diff. peak and hole	$0.39/-0.39 \mathrm{e}\cdot\mathrm{\AA}^{-3}$
CCDC Deposition Number	2310269

Table 132: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters ($\mathring{A}^2 \times 10^3$) for Rb₃Ag₃[CH(SO₃)₃]₂.

Atom	X	у	Z.	U(eq)
Ag1	7197.2(2)	-259.5(2)	245.9(2)	11.60(4)
Ag2	10000	5000	0	10.62(5)
Rb1	1379.9(2)	6874.5(2)	6237.2(2)	8.56(4)
Rb2	5000	10000	5000	11.64(5)
C1	2928(2)	6019(2)	1850(2)	7.4(3)
S 1	3181.5(6)	3625.5(5)	2445.9(4)	7.05(7)
S2	281.2(6)	8047.7(6)	2405.5(4)	7.84(8)
S 3	4841.9(6)	6656.6(6)	2229.0(4)	6.87(7)
011	2075(2)	4002(2)	3932(1)	10.9(2)
O12	5397(2)	2289(2)	2206(1)	11.2(2)
013	2249(2)	2989(2)	1518(1)	10.2(2)
O21	-144(2)	8789(2)	3869(1)	11.1(2)
O22	229(2)	9522(2)	1415(1)	15.3(2)
O23	-1023(2)	7153(2)	2206(1)	16.4(3)
O31	4328(2)	8636(2)	1772(1)	13.0(2)
O32	4662(2)	6614(2)	3746(1)	9.8(2)
O33	6797(2)	5085(2)	1358(1)	9.9(2)

Table 133: Anisotropic Displacement Parameters $(Å^2 \times 10^3)$ for $Rb_3Ag_3[CH(SO_3)_3]_2$.

Atom	U_{11}	U_{22}	<i>U</i> 33	U_{23}	U_{13}	U_{12}
Rb1	8.45(7)	8.86(7)	7.72(7)	1.19(5)	-2.07(5)	-3.50(6)
Rb2	13.3(1)	10.3(1)	12.3(1)	1.54(8)	-3.78(8)	-6.07(8)
Ag1	12.73(7)	11.13(6)	9.69(6)	0.14(4)	-3.16(4)	-4.39(5)
Ag2	7.76(8)	15.47(9)	9.04(8)	0.45(6)	-2.04(6)	-5.81(7)
C1	6.5(7)	7.8(7)	7.6(7)	0.0(5)	-2.0(5)	-3.1(6)
S 1	7.3(2)	6.6(2)	7.4(2)	0.5(1)	-1.7(1)	-3.5(1)

S2	6.0(2)	8.3(2)	7.7(2)	-0.5(1)	-2.4(1)	-1.8(1)
S 3	7.0(2)	7.3(2)	7.5(2)	1.1(1)	-2.8(1)	-4.0(1)
O11	13.1(6)	11.9(5)	8.3(5)	1.3(4)	-1.4(4)	-7.0(5)
O12	7.8(5)	8.0(5)	15.9(6)	0.8(4)	-2.6(4)	-2.3(4)
O13	12.7(6)	9.7(5)	10.6(5)	0.6(4)	-4.3(4)	-6.6(5)
O21	11.2(5)	9.7(5)	8.6(5)	-1.1(4)	-2.4(4)	-2.0(4)
O22	12.2(6)	14.4(6)	11.2(6)	5.8(5)	-2.1(4)	-0.1(5)
O23	7.9(5)	16.9(6)	22.9(7)	-8.1(5)	-3.2(5)	-4.7(5)
O31	15.8(6)	9.4(5)	18.0(6)	5.5(4)	-8.1(5)	-7.6(5)
O32	10.1(5)	12.7(5)	7.3(5)	0.0(4)	-2.7(4)	-5.8(4)
O33	7.1(5)	12.5(5)	9.5(5)	-0.4(4)	-1.2(4)	-4.6(4)

 Table 134: Selected Bond Lengths for Rb₃Ag₃[CH(SO₃)₃]₂.

Bond	Length [pm]	Bond	Length [pm]
S1-O11	144.6(1)	Ag2-O23	242.8(1)
S1-O12	145.9(1)	Ag2-O13	247.4(1)
S1-O13	146.5(1)	Ag2-O33	242.8(1)
S2-O21	144.3(1)	Rb1-O21	289.3(1)
S2-O22	145.8(1)	Rb1-O32 ⁴	293.8(1)
S2-O23	146.4(1)	Rb1-O21 ¹⁰	297.3(1)
S3-O31	145.5(1)	Rb1-O11	291.7(1)
S3-O32	145.2(1)	Rb1-O11 ¹¹	299.1(1)
S3-O33	145.8(1)	Rb1-O13 ¹¹	302.6(1)
S1-C1	183.0(2)	Rb1-O23 ¹¹	347.2(1)
S2-C1	182.1(2)	Rb1-O33 ⁴	302.1(1)
S3-C1	181.9(2)	Rb1-O32	295.7(1)
C1-H1	95(2)	Rb1-O12 ⁴	341.6(1)
Ag1-O23	282.4(1)	Rb1-O22 ¹⁰	314.6(1)
Ag1-O12	237.7(1)	Rb2-O12	323.4(1)
Ag1-O22 ⁵	248.0(1)	Rb2-O31	353.0(1)
Ag1-O22	271.4(2)	Rb2-O23	337.1(1)
Ag1-O13	251.2(1)	Rb2-O21	322.8(1)
Ag1-O31 ⁵	252.9(1)	Rb2-O32	297.8(1)
Ag1-O31	276.5(2)	Rb2-O11	315.8(1)

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
O11-S1-O12	112.65(7)	S2-C1-S3	113.68(8)
O12-S1-O13	112.41(7)	S3-C1-S1	113.24(8)
O13-S1-O11	113.39(7)	O13-S1-C1	103.40(7)
O21-S2-O22	113.58(7)	O21-S2-C1	108.87(7
022-82-023	111.48(8)	O22-S2-C1	104.38(7)
O23-S2-O21	112.70(7	O23-S2-C1	105.09(7)
031-S3-O32	113.33(7)	S31-S3-C1	105.64(7)
032-\$3-033	113.45(7)	\$32-\$3-C1	107.10(7)
033-S3-O31	113.15(7)	\$33-\$3-C1	103.10(7)
O11-S1-C1	107.70(7)	S1-C1-H1	105(1)
O12-S1-C1	106.50(7)	S2-C1-H1	105(1)
S1-C1-S2	113.05(8)	S3-C1-H1	106(1)

Table 135: Selected Bond Angles for Rb₃Ag₃[CH(SO₃)₃]₂.

$Ag_9[C(SO_3)_4]_2Cl\cdot 4 H_2O$

Table 136: Crystal Data and Structure Refinement for $Ag_9[C(SO_3)_4]_2Cl \cdot 4H_2O$ measured at 100 K.

Empirical formula	$Ag_9C_2ClO_{28}S_8$
Formula Weight	6939.12 g/mol
Temperature	100 K
Wavelength	71.073 pm (Mo _{Kα})
Crystal system	triclinic
Space group	PĪ
Unit cell parameters	<i>a</i> = 1361.27(8) pm
	<i>b</i> = 1381.66(9) pm
	c = 160.47(1) pm
	$\alpha = 100.752(2)^{\circ}$
	$\beta = 90.052(2)^{\circ}$
	$\gamma = 111.267(2)^{\circ}$
Volume	2755.5(3) Å ³
Ζ	4
Density (calculated)	4.182 g/cm ³

Absorption coefficient	7.071 mm ⁻¹
F(000)	3216
Crystal size	0.212 x 0.116 x 0.117 mm ³
2θ Range for data collection	$3.978 - 60.0^{\circ}$
Index range	−19≤h≤18, −19≤k≤19, −22≤l≤22
Reflections collected	318051
Independent reflections	16073 [$R_{\text{int}} = 0.0274, R_{\sigma} = 0.0132$]
Completeness	99.9%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7465/0.6043
Refinement method	Least Squares
Data/Restraints/Parameters	16073/0/878
Goodness-of-fit on F^2	1.107
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0365, wR_2 = 0.1067$
R Indices (all data)	$R_1 = 0.0369, wR_2 = 0.1070$
Largest diff. peak and hole	$10.71/-4.26 \text{ e} \cdot \text{\AA}^{-3}$
CCDC Deposition Number	2314360

Table 137: Fractional Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Ag_9[C(SO_3)_4]_2Cl \cdot 4$ H₂O measured at 100 K.

Atom	X	У	Z,	U(eq)
Ag1	6534.4(3)	1290.6(3)	3873.5(2)	9.52(7)
Ag2	1063.9(3)	1242.5(3)	3899.1(2)	10.93(7)
Ag3	3881.3(3)	1088.2(3)	7930.6(2)	10.73(7)
Ag4	5017.3(3)	4574.7(3)	3839.2(2)	11.33(7)
Ag5	2203.0(3)	4467.4(3)	4271.3(2)	13.54(7)
Ag6	51.4(3)	4501.0(3)	6364.0(2)	11.90(7)
Ag7A	4292.7(4)	4236.6(4)	8373.9(3)	16.39(12)
Ag7B	5116(5)	4593(4)	8907(4)	45.9(18)
Ag8	6618.6(3)	4966.2(3)	9152.8(3)	19.19(8)
Ag9	-122.1(3)	5319.3(3)	8611.3(2)	15.39(8)
Ag10	6067.3(3)	8567.5(3)	7023.3(2)	10.62(7)
Ag11	3953.4(3)	8684.7(3)	8629.4(2)	10.50(7)
Ag12	6353.0(3)	11093.6(3)	8726.6(2)	10.05(7)
Ag13	4028.6(3)	8891.8(3)	3580.7(2)	9.87(7)
Ag14	1142.4(3)	8752.5(3)	-468.0(2)	10.17(7)

Ag15	1118.5(3)	8764.9(3)	4545.6(2)	10.07(7)
Ag16	1446.7(3)	11150.8(3)	6294.7(2)	9.53(7)
Ag17	-1476.9(3)	8722.3(3)	8766.3(2)	9.90(7)
Ag18	974.4(3)	11133.5(3)	8832.2(2)	9.95(7)
C1	918(3)	7831(3)	2131(3)	6.6(7)
C2	4180(3)	2285(3)	5448(3)	6.0(7)
C3	782(3)	7656(3)	7115(3)	5.8(7)
C4	5830(3)	7699(3)	9686(3)	6.6(7)
S11	1839.5(8)	7314.0(8)	2579.3(7)	6.8(2)
S12	764.2(9)	7391.7(9)	960.6(7)	8.1(2)
S13	-398.4(8)	7277.5(9)	2558.3(7)	7.5(2)
S14	1438.3(8)	9298.8(8)	2410.9(7)	6.6(2)
S21	4300.1(8)	2670.2(8)	6627.7(6)	6.7(2)
S22	3657.1(8)	816.8(8)	5131.3(6)	5.4(2)
S23	3256.9(8)	2798.8(8)	4992.6(7)	6.0(2)
S24	5503.6(8)	2862.2(8)	5038.2(7)	6.7(2)
S 31	1324.0(8)	9125.1(8)	7376.5(6)	5.7(2)
S32	559.7(8)	7213.1(8)	5944.2(6)	6.1(2)
S 33	-494.5(8)	7117.1(8)	7604.5(7)	6.8(2)
S34	1735.6(8)	7136.4(8)	7515.5(7)	6.7(2)
S 41	6348.9(8)	9169.1(8)	9872.3(6)	5.7(2)
S42	4538.4(8)	7213.8(9)	10163.5(7)	8.1(2)
S43	6774.0(8)	7264.0(8)	10201.8(7)	8.4(2)
S44	5642.7(8)	7125.8(9)	8523.6(7)	8.1(2)
0111	2719(3)	7495(3)	2040(2)	12.3(6)
O112	1249(3)	6197(3)	2554(2)	10.5(6)
0113	2143(3)	7927(3)	3449(2)	10.1(6)
0121	1708(3)	8104(3)	648(2)	12.0(6)
O122	708(3)	6307(3)	798(2)	13.7(6)
0123	-198(3)	7503(3)	677(2)	12.3(6)
0131	-960(3)	7961(3)	2419(2)	11.7(6)
0132	-862(3)	6202(3)	2073(2)	12.1(6)
0133	-181(3)	7330(3)	3458(2)	10.5(6)
O141	906(3)	9623(3)	1799(2)	11.0(6)
O142	1153(3)	9546(3)	3274(2)	10.7(6)

O143	2575(3)	9638(3)	2346(2)	11.5(6)
O211	4346(3)	3755(3)	6847(2)	12.2(6)
O212	5271(3)	2563(3)	6902(2)	10.0(6)
O213	3358(3)	1919(3)	6904(2)	10.6(6)
O221	4175(3)	454(3)	5730(2)	9.8(6)
O222	2526(3)	481(3)	5198(2)	9.9(6)
O223	3951(3)	601(3)	4269(2)	10.1(6)
O231	2376(3)	2615(3)	5532(2)	9.8(6)
O232	3858(3)	3912(3)	5016(2)	9.6(6)
O233	2946(3)	2174(3)	4127(2)	9.2(6)
O241	6078(3)	2190(3)	5186(2)	10.5(6)
O242	5952(3)	3932(3)	5530(2)	10.7(6)
O243	5288(3)	2795(3)	4136(2)	10.8(6)
O311	1106(3)	9410(3)	8256(2)	10.4(6)
O312	2442(3)	9428(3)	7257(2)	11.0(6)
O313	763(3)	9456(3)	6788(2)	9.2(6)
O321	1476(3)	7931(3)	5608(2)	9.4(6)
O322	-434(3)	7308(3)	5717(2)	9.8(6)
O323	507(3)	6127(3)	5765(2)	10.6(6)
O331	-209(3)	7207(3)	8499(2)	11.1(6)
O332	-988(3)	6028(3)	7152(2)	10.4(6)
O333	-1070(3)	7793(3)	7475(2)	10.9(6)
O341	2568(3)	7292(3)	6932(2)	11.5(6)
O342	2104(3)	7766(3)	8375(2)	10.4(6)
O343	1131(3)	6028(3)	7520(2)	9.9(6)
O411	6081(3)	9520(3)	10720(2)	10.5(6)
O412	7477(3)	9480(3)	9796(2)	10.5(6)
O413	5807(3)	9415(3)	9209(2)	10.6(6)
O421	3976(3)	7872(3)	9973(2)	12.0(6)
O422	4795(3)	7353(3)	11070(2)	12.6(6)
O423	4031(3)	6103(3)	9758(2)	11.9(6)
O431	7119(3)	7983(3)	11027(2)	11.4(6)
O432	6163(3)	6171(3)	10280(2)	14.1(7)
O433	7614(3)	7336(3)	9635(2)	12.6(6)
O441	5607(3)	6045(3)	8459(2)	13.1(6)

O442	6562(3)	7790(3)	8152(2)	11.2(6)
O443	4658(3)	7191(3)	8241(2)	12.7(6)
Cl1	8.1(6)	14.9(7)	8.8(6)	2.6(5)
C12	7.8(6)	12.7(6)	7.9(6)	1.6(5)
C13	8.5(4)	16.4(5)	8.0(4)	3.2(3)
01	14(2)	9(1)	12(2)	-1(1)
O2	15(2)	12(2)	13(2)	1(1)
03	14(2)	11(2)	13(2)	2(1)
O4	13(2)	12(2)	15(2)	2(1)
05	19(2)	14(2)	33(2)	2(2)
06	15(2)	15(2)	16(2)	1(1)
07	17(2)	21(2)	16(2)	0(1)
08	20(2)	17(2)	13(2)	2(1)

Table 138: Anisotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Ag_9[C(SO_3)_4]_2Cl \cdot 4 H_2O$ measured at 100 K.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag1	10.5(1)	8.7(1)	9.1(1)	2.5(1)	2.9(1)	2.8(1)
Ag2	7.6(1)	8.4(1)	16.6(2)	0.8(1)	-0.8(1)	3.6(1)
Ag3	13.2(2)	11.3(2)	7.5(1)	2.1(1)	-1.4(1)	4.2(1)
Ag4	9.9(2)	10.3(2)	13.5(2)	4.1(1)	2.0(1)	2.6(1)
Ag5	12.7(2)	15.0(2)	13.1(2)	2.2(1)	2.2(1)	5.6(1)
Ag6	11.6(2)	10.1(2)	14.5(2)	5.6(1)	2.4(1)	3.0(1)
Ag7A	19.9(2)	17.6(2)	10.8(2)	4.7(2)	4.4(1)	5.1(2)
Ag7B	75(4)	15(2)	55(3)	21(2)	38(3)	18(2)
Ag8	23.9(2)	19.9(2)	15.4(2)	4.6(1)	3.9(1)	9.5(2)
Ag9	16.2(2)	12.7(2)	17.0(2)	6.9(1)	1.7(1)	3.1(1)
Ag10	12.1(2)	12.0(2)	8.3(1)	1.9(1)	-0.2(1)	5.2(1)
Ag11	7.2(1)	10.6(2)	13.2(2)	2.4(1)	-0.4(1)	2.6(1)
Ag12	11.5(2)	9.2(1)	9.7(1)	2.9(1)	3.6(1)	3.5(1)
Ag13	7.5(1)	8.8(1)	13.3(2)	1.5(1)	-0.6(1)	3.4(1)
Ag14	14.1(2)	9.2(2)	7.4(1)	2.4(1)	-1.6(1)	4.1(1)
Ag15	13.0(2)	9.0(2)	8.3(1)	2.8(1)	-1.2(1)	3.7(1)
Ag16	9.6(1)	9.4(1)	9.1(1)	2.5(1)	2.8(1)	2.7(1)
Ag17	10.2(1)	9.3(1)	8.7(1)	0.2(1)	2.2(1)	2.6(1)
Ag18	8.4(1)	9.5(1)	13.3(2)	2.9(1)	0.7(1)	4.5(1)

C1	8(2)	8(2)	5(2)	2(1)	0(1)	4(1)
C2	8(2)	8(2)	4(2)	2(1)	2(1)	4(1)
C3	7(2)	8(2)	3(2)	1(1)	0(1)	4(1)
C4	6(2)	8(2)	7(2)	3(1)	1.(1)	3(1)
S11	6.5(4)	7.9(4)	8.1(4)	3.8(3)	0.9(3)	3.9(3)
S12	11.6(4)	9.2(4)	5.9(4)	2.6(3)	1.5(3)	6.1(4)
S13	5.7(4)	8.6(4)	8.3(4)	2.2(3)	1.2(3)	2.7(3)
S14	6.7(4)	6.4(4)	7.6(4)	2.3(3)	0.7(3)	3.0(3)
S21	8.1(4)	6.8(4)	5.3(4)	0.7(3)	0.0(3)	3.4(3)
S22	5.9(4)	4.1(4)	6.2(4)	1.0(3)	0.1(3)	2.0(3)
S23	6.4(4)	6.2(4)	6.7(4)	2.4(3)	0.5(3)	3.3(3)
S24	5.2(4)	6.6(4)	8.2(4)	2.3(3)	1.7(3)	1.7(3)
S 31	6.2(4)	4.7(4)	6.0(4)	0.8(3)	0.2(3)	2.1(3)
S32	8.5(4)	5.8(4)	4.6(4)	0.7(3)	0.3(3)	3.5(3)
S33	5.8(4)	7.1(4)	7.0(4)	0.8(3)	0.8(3)	2.1(3)
S34	6.3(4)	7.5(4)	7.6(4)	3.2(3)	0.7(3)	3.3(3)
S41	6.0(4)	4.7(4)	6.4(4)	1.1(3)	0.0(3)	2.0(3)
S42	6.3(4)	8.5(4)	8.6(4)	2.3(3)	1.4(3)	1.5(3)
S43	7.5(4)	7.0(4)	11.8(5)	3.2(4)	-0.4(3)	3.2(3)
S44	7.9(4)	8.2(4)	6.9(4)	-1.3(3)	0.5(3)	2.7(3)
0111	10(1)	16(2)	16(2)	8(1)	6(1)	8(1)
0112	14(2)	9(1)	12(2)	5(1)	2(1)	6(1)
0113	10(1)	13(2)	8(1)	2(1)	-2(1)	5(1)
0121	14(2)	15(2)	9(1)	6(1)	3(1)	6(1)
0122	22(2)	10(2)	11(2)	2(1)	1(1)	8(1)
0123	16(2)	14(2)	10(1)	0(1)	-3(1)	9(1)
0131	9(1)	16(2)	14(2)	4(1)	2(1)	8(1)
0132	9(1)	10(2)	15(2)	-1(1)	1(1)	3(1)
0133	9(1)	13(2)	10(1)	4(1)	2(1)	4(1)
0141	14(2)	9(1)	12(2)	4(1)	-1(1)	6(1)
0142	15(2)	10(2)	8.(1)	2(1)	3(1)	6(1)
0143	8(1)	11(2)	15(2)	4(1)	2(1)	1(1)
O211	17(2)	9(1)	10(1)	0(1)	-2(1)	6(1)
O212	11(1)	12(2)	9(1)	1(1)	-4(1)	8(1)
O213	11(1)	13(2)	9(1)	5(1)	2(1)	4(1)

O221	12(1)	8(1)	12(1)	4(1)	-1(1)	5(1)
O222	7(1)	8(1)	12(2)	1(1)	0(1)	1(1)
O223	14(2)	10(1)	7(1)	1(1)	2(1)	5(1)
O231	8(1)	11(2)	12(2)	5(1)	2(1)	5(1)
O232	13(2)	7(1)	11(1)	4(1)	2(1)	4(1)
O233	8(1)	12(2)	8(1)	1(1)	-2(1)	4(1)
O241	8(1)	12(2)	14(2)	4(1)	3(1)	6(1)
O242	7(1)	8(1)	15(2)	1(1)	1(1)	1(1)
O243	10(1)	15(2)	9(1)	6(1)	2(1)	4(1)
O311	16(2)	9(1)	6(1)	-1(1)	1(1)	6(1)
O312	8(1)	10(2)	14(2)	2(1)	2(1)	2(1)
O313	11(1)	8(1)	11(1)	4(1)	-1(1)	4(1)
O321	12(1)	9(1)	7(1)	5(1)	3(1)	3(1)
O322	10(1)	11(2)	10(1)	0(1)	-4(1)	6(1)
O323	16(2)	7(1)	9(1)	1(1)	2(1)	6(1)
O331	11(1)	14(2)	8(1)	4(1)	2.(1)	3(1)
O332	10(1)	7(1)	13(2)	1(1)	0.(1)	2(1)
O333	8(1)	13(2)	15(2)	3(1)	3(1)	6(1)
O341	11(1)	14(2)	14(2)	6(1)	4(1)	8(1)
O342	8(1)	15(2)	9(1)	2(1)	-3(1)	4(1)
O343	12(1)	9(1)	11(1)	5(1)	2(1)	5(1)
O411	15(2)	10(1)	7(1)	0(1)	2(1)	6(1)
O412	6.(1)	11(2)	13(2)	1(1)	0(1)	1(1)
O413	12(1)	10(1)	12(2)	5(1)	-2(1)	5(1)
O421	9(1)	13(2)	16(2)	3(1)	3(1)	6(1)
O422	11(2)	16(2)	8(1)	3(1)	2(1)	2(1)
O423	11(1)	8(1)	15(2)	3(1)	1(1)	1(1)
O431	10(1)	14(2)	11(2)	4(1)	-2(1)	4(1)
O432	16(2)	8(2)	21(2)	7(1)	1(1)	5(1)
O433	10(1)	12(2)	18(2)	3(1)	0(1)	7(1)
O441	14(2)	10(2)	13(2)	-1(1)	1(1)	4(1)
O442	10(1)	15(2)	7(1)	1(1)	2(1)	3(1)
O443	9(1)	15(2)	12(2)	0(1)	-3(1)	4(1)
Cl1	8.1(6)	14.9(7)	8.8(6)	2.6(5)	0.6(5)	5.5(5)
Cl2	7.8(6)	12.7(6)	7.9(6)	1.6(5)	0.4(5)	4.4(5)

C13	8.5(4)	16.4(5)	8.0(4)	3.2(3)	0.9(3)	6.2(4)
O1	14(2)	9.1(1)	12(2)	-1(1)	0(1)	4(1)
O2	15(2)	12(2)	13(2)	1(1)	3(1)	5(1)
O3	14(2)	11(2)	13(2)	2(1)	2(1)	5(1)
O4	13(2)	12(2)	15(2)	2(1)	2(1)	5(1)
O5	19(2)	14(2)	33(2)	2(2)	2(2)	6(1)
O6	15(2)	15(2)	16(2)	1(1)	0(1)	7(1)
O7	17(2)	21(2)	16(2)	0(1)	-1(1)	3(1)
08	20(2)	17(2)	13(2)	2(1)	3(1)	8(1)

Table 139: Selected Bond Lengths for $Ag_9[C(SO_3)_4]_2Cl \cdot 4H_2O$ measured at 100 K.

Bond	Length [pm]	Bond	Length [pm]
C1-S11	185.6(4)	C3-S31	185.4(4)
C1-S12	185.0(4)	C3-S32	185.3(5)
C1-S13	186.3(4)	C3-S33	186.4(4)
C1-S14	185.3(4)	C3-S34	186.0(5)
S11-O111	145.3(3)	S31-O311	145.4(3)
S11-O112	145.1(4)	S31-O312	144.8(4)
S11-O113	146.3(3)	S31-O313	144.8(5)
S12-O121	146.3(4)	S32-O321	146.1(4)
S12-O122	144.6(5)	S32-O322	145.8(5)
S12-O123	145.5(5)	S32-O323	144.9(4)
S13-O131	145.9(5)	S33-O331	145.8(4)
S13-O132	144.9(4)	S33-O332	145.0(4)
S13-O133	145.7(4)	S33-O333	146.0(5)
S14-O141	144.5(5)	S34-O341	145.2(4)
S14-O142	145.1(4)	S34-O342	146.5(3)
S14-O143	145.5(4)	S34-O343	145.3(4)
C2-S21	185.9(4)	C4-S41	185.6(4)
C2-S22	185.7(4)	C4-S42	186.2(4)
C2-S23	185.9(4)	C4-S43	185.5(5)
C2-S24	186.2(4)	C4-S44	186.4(5)
S21-O211	145.2(4)	S41-O411	145.0(4)
S21-O212	145.9(3)	S41-O412	144.9(4)
S21-O213	145.8(3)	S41-O413	145.2(4)

S22-O221	145.1(3)	S42-O421	145.4(5)
S22-O222	144.9(3)	S42-O422	145.6(4)
S22-O223	144.8(3)	S42-O423	145.4(4)
S23-O231	145.5(3)	S43-O431	146.0(3)
S23-O232	145.0(3)	S43-O432	146.6(4)
S23-O233	146.3(3)	\$43-0433	144.8(4)
S24-O241	146.2(3)	S44-O441	146.0(5)
S24-O242	144.6(3)	S44-O442	146.2(4)
S24-O243	145.6(3)	S44-O443	145.3(4)
Cl1-Ag2	273.83(4)	Cl3-Ag1	270.2(1)
Cl1-Ag15	268.04(5)	Cl3-Ag3	268.0(1)
Cl1-Ag16	268.54(3)	Cl3-Ag10	268.4(1)
Cl2-Ag18	270.49(4)	Cl3-Ag11	267.4(1)
Cl2-Ag17	268.18(3)	Cl3-Ag12	271.18(9)
Cl2-Ag14	272.34(5)	Cl3-Ag13	273.3(1)

Table 140: Selected Bond Angles for $Ag_9[C(SO_3)_4]_2Cl \cdot 4 H_2O$ measured at 100 K.

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
S11-C1-S12	109.1(2)	S31-C3-S32	108.8(2)
S12-C1-S13	108.5(2)	S32-C3-S33	109.2(2)
S13-C1-S14	110.2(2)	S33-C3-S34	109.0(2)
S14-C1-S11	110.2(2)	S34-C3-S31	110.1(2)
S14-C1-S12	109.6(2)	S34-C3-S32	109.1(2)
S11-C1-S13	109.1(2)	S31-C3-S33	110.7(2)
O111-S11-C1	106.1(2)	O311-S31-C3	105.5(2)
O112-S11-C1	106.4(2)	O312-S31-C3	105.1(2)
O113-S11-C1	105.2(2)	O313-S31-C3	105.8(2)
O121-S12-C1	105.5(2)	O321-S32-C3	105.1(2)
O122-S12-C1	105.8(2)	O322-S32-C3	105.7(2)
O123-S12-C1	106.4(2)	O323-S32-C3	106.0(2)
O131-S13-C1	105.9(2)	O331-S33-C3	105.5(2)
O132-S13-C1	104.4(2)	O332-S33-C3	105.2(2)
O133-S13-C1	105.7(2)	O333-S33-C3	105.3(2)
O141-S14-C1	105.3(2)	O341-S34-C3	106.3(2)
O142-S14-C1	104.7(2)	O342-S34-C3	105.2(2)

O143-S14-C1	105.9(2)	O343-S34-C3	105.6(2)
O111-S11-O112	112.8(2)	O311-S31-O312	113.1(2)
O112-S11-O113	112.4(2)	O312-S31-O313	113.5(2)
O113-S11-O111	113.1(2)	O313-S31-O311	112.9(2)
O121-S12-O122	112.5(2)	O321-S32-O322	113.6(2)
O122-S12-O123	113.5(2)	O322-S32-O323	112.9(2)
O123-S12-O121	112.4(2)	O323-S32-O321	112.7(2)
O131-S13-O132	114.2(2)	0331-\$33-0332	113.1(2)
O132-S13-O133	113.2(2)	O332-S33-O333	113.9(2)
O133-S13-O131	112.4(2)	O333-S33-O331	112.9(2)
O141-S14-O142	113.2(2)	O341-S34-O342	113.2(2)
O142-S14-O143	113.1(2)	O342-S34-O343	112.1(2)
O143-S14-O141	113.6(2)	O343-S34-O341	113.5(2)
S21-C2-S22	109.1(2)	S41-C4-S42	109.6(2)
S22-C2-S23	109.0(2)	S42-C4-S43	108.6(2)
S23-C2-S24	108.9(2)	S43-C4-S44	109.7(2)
S24-C2-S21	109.2(2)	S44-C4-S41	110.4(2)
S24-C2-S22	110.4(2)	S44-C4-C42	109.2(2)
S21-C2-S23	110.1(2)	S41-C4-S43	109.3(2)
O211-S21-C2	107.4(2)	O411-S41-C4	105.8(2)
O212-S21-C2	105.6(2)	O412-S41-C4	105.1(2)
O213-S21-C2	105.2(2)	O413-S41-C4	104.9(2)
O221-S22-C2	108.8(2)	O421-S42-C4	105.6(2)
O222-S22-C2	105.7(2)	O422-S42-C4	105.7(2)
O223-S22-C2	104.8(2)	O423-S42-C4	105.7(2)
O231-S23-C2	108.9(2)	O431-S43-C4	105.8(2)
O232-S23-C2	105.7(2)	O432-S43-C4	105.2(2)
O233-S23-C2	105.3(2)	O433-S43-C4	106.1(2)
O241-S24-C2	105.8(2)	O441-S44-C4	104.9(2)
O242-S24-C2	104.6(2)	O442-S44-C4	105.8(2)
O243-S24-C2	105.0(2)	O443-S44-C4	105.0(2)
O211-S21-O212	112.6(2)	O411-S41-O412	113.3(2)
O212-S21-O213	112.7(2)	O412-S41-O413	113.4(2)
O213-S21-O211	112.6(2)	O413-S41-O411	113.2(2)
O221-S22-O222	112.9(2)	O421-S42-O422	113.2(2)

0222-822-0223	113.6(2)	O422-S42-O423	112.2(2)	
0223-\$22-0221	113.1(2)	O423-S42-O421	113.5(1)	
O231-S23-O232	113.5(2)	O431-S43-O432	112.4(2)	
0232-S23-O233	113.0(2)	O432-S43-O433	112.7(2)	
O233-S23-O231	112.6(2)	O433-S43-O431	113.8(2)	
O241-S24-O242	113.7(2)	O441-S44-O442	112.7(2)	
O242-S24-O243	114.3(2)	O442-S44-O443	113.1(2)	
O243-S24-O241	112.2(2)	O443-S44-O441	114.2(2)	

Table 141: Atomic Occupancy for $Ag_9[C(SO_3)_4]_2Cl \cdot 4H_2O$ measured at 100 K.

Atom	Occupancy	Atom	Occupancy
Ag7A	0.884(2)	Ag7B	0.116(2)

Table 142: Crystal Data and Structure Refinement for $Ag_9[C(SO_3)_4]_2Cl \cdot 4H_2O$ measured at 301 K.

Empirical formula	$Ag_9C_2ClO_{28}S_8$
Formula Weight	1734.78 g/mol
Temperature	100 K
Wavelength	71.073 pm (Mo _{Kα})
Crystal system	triclinic
Space group	PĪ
Unit cell parameters	a = 792.3(2) pm
	<i>b</i> = 796.5(2) pm
	c = 1287.7(3) pm
	$\alpha = 86.099(9)^{\circ}$
	$\beta = 80.049(8)^{\circ}$
	$\gamma = 61.073(7)^{\circ}$
Volume	700.5(3) Å ³
Ζ	1
Density (calculated)	4.113 g/cm ³
Absorption coefficient	6.954 mm ⁻¹
F(000)	804
Crystal size	0.212 x 0.119 x 0.117 mm ³
2θ Range for data collection	$5.844 - 52.994^{\circ}$
Index range	−9≤h≤9, −9≤k≤9, −16≤l≤16
Reflections collected	64426

Independent reflections	2887 [$R_{int} = 0.0482, R_{\sigma} = 0.0177$]
Completeness	99.7%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7479/0.4423
Refinement method	Least Squares
Data/Restraints/Parameters	2887/0/224
Goodness-of-fit on F^2	1.196
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0811, wR_2 = 0.1954$
R Indices (all data)	$R_1 = 0.0816, wR_2 = 0.1957$
Largest diff. peak and hole	3.10/−2.79 e · Å ⁻³
CCDC Deposition Number	2314359

Table 143: Fractional Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Ag_9[C(SO_3)_4]_2Cl \cdot 4$ H₂O measured at 301 K.

Atom	x	У	Z.	U(eq)
Ag1	-3555(2)	12051(2)	3756.7(11)	32.7(4)
Ag2	-1192(7)	6238(7)	482(4)	66(1)
Ag3	2149(2)	1127.2(18)	3806.0(11)	29.9(4)
Ag4	6765(3)	2707(3)	401.5(14)	52.2(5)
Ag5	2603(2)	3242(2)	6183.4(11)	30.4(4)
C1	2314(19)	6630(20)	2728(11)	14(3)
S 1	252(5)	8766(5)	2273(3)	20.5(8)
S 2	1929(5)	6602(5)	4193(3)	16.2(7)
S 3	2473(6)	4421(5)	2195(3)	20.7(8)
S 4	4636(5)	6683(6)	2230(3)	20.4(8)
O11	-192(17)	10331(16)	2982(10)	30(3)
O12	-1333(17)	8323(18)	2374(9)	29(3)
O13	930(20)	9060(20)	1202(10)	39(3)
O21	2558(18)	7899(18)	4514(9)	29(3)
O22	-142(16)	7246(18)	4518(9)	27(2)
O23	3147(17)	4616(16)	4471(9)	26(2)
O31	947(18)	4141(16)	2850(9)	28(2)
O32	4403(17)	2936(15)	2291(10)	29(3)
O33	2183(19)	4884(18)	1123(9)	30(3)
O41	6061(16)	5310(17)	2864(10)	27(2)
O42	5140(17)	6074(19)	1140(9)	30(3)

O43	4203(18)	8644(18)	2370(10)	30(3)
01	6300(30)	-110(30)	830(20)	96(9)
O2	9380(20)	3030(20)	1180(30)	105(10)
Cl1	5000	0	5000	28(1)

Table 144: Anisotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $Ag_9[C(SO_3)_4]_2Cl \cdot 4 H_2O$ measured at 301 K.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag1	20.6(6)	33.7(8)	33.5(7)	-1.0(5)	-3.4(5)	-5.3(5)
Ag2	71(3)	65(3)	76(3)	20(2)	-27(2)	-40(2)
Ag3	35.2(7)	19.6(6)	31.1(7)	-1.5(5)	-5.1(5)	-10.1(5)
Ag4	56.6(11)	56.7(11)	37.2(9)	-14.5(7)	2.7(7)	-23.8(9)
Ag5	33.8(7)	37.5(8)	29.5(7)	0.6(5)	-4.5(5)	-24.8(6)
C1	9(6)	13(6)	21(7)	-1(5)	0(5)	-6(5)
S 1	18(2)	18(2)	22(2)	2(1)	-3(1)	-6(1)
S2	16(2)	15(2)	17(2)	0(1)	-2(1)	-8(1)
S 3	23(2)	17(2)	25(2)	-2(1)	-4(1)	-12(2)
S4	18(2)	24(2)	22(2)	-3(1)	1(1)	-13(2)
O11	24(6)	15(5)	41(7)	-7(5)	-5(5)	-1(5)
O12	20(6)	37(7)	27(6)	13(5)	-8(5)	-13(5)
O13	39(7)	40(8)	28(7)	8(5)	-3(5)	-13(6)
O21	36(7)	30(6)	27(6)	0(5)	-12(5)	-18(5)
O22	21(6)	42(7)	18(5)	-5(5)	5(4)	-17(5)
O23	31(6)	17(5)	22(6)	6(4)	-3(5)	-7(5)
O31	37(7)	20(6)	31(6)	3(5)	-3(5)	-19(5)
O32	29(6)	10(5)	42(7)	-6(5)	-12(5)	-2(5)
O33	38(7)	34(7)	26(6)	-7(5)	-1(5)	-24(6)
O41	14(5)	27(6)	37(7)	-3(5)	-6(5)	-8(5)
O42	25(6)	40(7)	23(6)	-4(5)	5(5)	-17(5)
O43	30(6)	30(6)	30(6)	-4(5)	11(5)	-18(5)
01	55(11)	58(11)	220(30)	72(15)	-79(15)	-50(10)
O2	31(8)	12(7)	280(30)	22(12)	-43(13)	-13(6)
Cl1	23(3)	19(3)	48(3)	1(2)	-10(2)	-12(2)

Table 145: Selected Bond Lengths for $Ag_9[C(SO_3)_4]_2Cl \cdot 4 H_2O$ measured at 301 K.

Bond	Length [pm]	Bond	Length [pm]

C1-S1	185(1)	Ag2-O2	250(2)
C1-S2	186(2)	Ag2-O33	262(2)
C1-S3	187(1)	Ag2-O2	256(3)
C1-S4	186(1)	Ag2-O33	268(2)
S1-O11	146(1)	Ag2-O1	262(2)
S1-O12	144(1)	Ag2-O42	295(2)
S1-O13	144(1)	Ag3-Cl1	270.6(2)
S2-O21	146(1)	Ag3-O43	251(1)
S2-O22	145(1)	Ag3-O32	316(1)
S2-O23	146(1)	Ag3-O31	244(1)
S3-O31	145(1)	Ag3-O11	262(2)
S3-O32	143(1)	Ag3-O22	246(1)
S3-O33	143(1)	Ag3-O21	255(1)
S4-O41	146(1)	Ag4-O33	316(1)
S4-O42	144(1)	Ag4-O1	246(3)
S4-O43	145(1)	Ag4-O42	255(1)
Cl1-Ag1	271.4(2)	Ag4-O13	249(1)
Cl1-Ag5	271.8(1)	Ag4-O33	295(1)
Cl1-Ag3	270.6(2)	Ag4-O2	258(3)
Ag1-Cl1	271.4(2)	Ag4-O42	252(1)
Ag1-O21	250(1)	Ag4-O32	276(1)
Ag1-O12	311(1)	Ag5-Cl1	271.8(1)
Ag1-O11	139(1)	Ag5-O23	246(1)
Ag1-O32	254(1)	Ag5-O43	312(1)
Ag1-O41	267(1)	Ag5-O41	240(2)
Ag1-O23	247(1)	Ag5-O31	270(1)
Ag2-O12	300(1)	Ag5-O12	250(1)

Table 146: Selected Bond Angles for $Ag_9[C(SO_3)_4]_2Cl \cdot 4 H_2O$ measured at 301 K.

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]	
S1-C1-S2	109.8(7)	O11-S1-O12	112.1(8)	
S2-C1-S3	109.8(7)	O12-S1-O13	113.2(8)	
S3-C1-S4	108.8(7)	O13-S1-O11	112.8(8)	
S4-C1-S1	109.8(7)	O21-S2-O22	113.7(7)	
S4-C1-S2	109.6(7)	O22-S2-O23	112.6(7)	

S1-C1-S3	109.1(7)	O23-S2-O21	112.9(7)	
O11-S1-C1	105.4(7)	O31-S3-O32	113.5(7)	
O12-S1-C1	106.2(7)	O32-S3-O33	113.2(8)	
O13-S1-C1	106.4(7)	O33-S3-O31	114.5(7)	
O21-S2-C1	105.4(7)	O41-S4-O42	111.7(7)	
O22-S2-C1	105.7(6)	O42-S4-O43	113.4(7)	
O23-S2-C1	105.7(6)	O43-S4-O41	113.8(7)	
O31-S3-C1	106.0(6)	Ag1 ⁸ -Cl1-Ag5 ⁷	91.92(4)	
O32-S3-C1	104.6(6)	Ag1 ¹ -Cl1-Ag5 ⁷	88.08(4)	
O33-S3-C1	103.6(7)	Ag3-Cl1-Ag5 ⁷	92.74(4)	
O41-S4-C1	105.8(7)	Ag3 ⁷ -Cl1-Ag5 ⁷	87.26(4)	
O42-S4-C1	105.6(7)	Ag3-Cl-Ag1 ⁸	89.18(4)	
O43-S4-C1	105.7(7)	Ag3 ⁷ -Cl-Ag1 ⁸	90.82(4)	

K[Cl₃CSO₃] · H₂O

Table 147: Crystal Data and Structure Refinement for K[Cl₃CSO₃] H₂O.

Empirical formula	CH ₂ Cl ₃ KO ₄ S
Formula Weight	255.54 g/mol
Temperature	100 K
Wavelength	71.073 pm (Mo _{Kα})
Crystal system	triclinic
Space group	PĪ
Unit cell parameters	a = 656.67(7) pm
	b = 1094.0(1) pm
	c = 1241.1(1) pm
	$\alpha = 73.416(4)^{\circ}$
	$\beta = 85.008(5)^{\circ}$
	$\gamma = 89.921(5)^{\circ}$
Volume	851.0(2) Å ³
Ζ	4
Density (calculated)	1.995g/cm ³
Absorption coefficient	1.767 mm ⁻¹
F(000)	504

Crystal size	$0.251 \text{ x } 0.132 \text{ x } 0.076 \text{ mm}^3$
2θ Range for data collection	$3.886 - 60.0^{\circ}$
Index range	−19≤h≤9, −15≤k≤15, −17≤l≤17
Reflections collected	46039
Independent reflections	4947 [$R_{int} = 0.0399, R_{\sigma} = 0.0250$]
Completeness	99.7%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7468/0.6566
Refinement method	Least Squares
Data/Restraints/Parameters	4947/0/197
Goodness-of-fit on F^2	1.085
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0435, wR_2 = 0.1089$
R Indices (all data)	$R_1 = 0.0503, wR_2 = 0.1144$
Largest diff. peak and hole	$1.43/-0.57 \mathrm{e}\cdot\mathrm{\AA}^{-3}$
CCDC Deposition Number	2120005

Table 148: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters ($\mathring{A}^2 \times 10^3$) for K[Cl₃CSO₃] H₂O.

Atom	X	у	Z.	U(eq)
K1	6307.9(8)	6066.0(5)	860.3(5)	18.5(1)
K2	11283.0(8)	8432.2(5)	847.1(5)	18.3(1)
C1	16417(5)	8852(3)	3257(2)	24.1(5)
C2	11371(4)	3971(2)	3219(2)	19.8(5)
S 1	15799.4(9)	9180.6(6)	1785.2(5)	15.9(1)
S 2	10862.5(9)	4689.6(6)	1733.3(5)	15.2(2)
011	17716(3)	9611(2)	1123(2)	21.0(4)
O12	14260(3)	10153.1(2)	1662(2)	24.9(4)
013	15020(3)	7970(2)	1723(2)	23.3(4)
O21	12804(3)	4657(2)	1100(2)	20.1(4)
O22	10159(3)	5953(2)	1696(2)	21.3(4)
O23	9286(3)	3864(2)	1547(2)	22.6(4)
Cl11	17441(2)	10256(1)	3447.4(8)	47.0(2)
Cl12	18246(1)	7642.7(9)	3505.3(7)	37.4(2)
Cl13	14192(1)	8341(1)	4166.6(7)	40.6(2)
O1	3675(3)	7382(2)	-626(2)	20.4(4)

O2	8676(3)	8061(2)	-628(2)	21.1(4)
	0010(0)	0001(=)	0=0(=)	====(.)

Atom	U_{11}	U ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
K1	13.1(2)	19.4(2)	24.2(3)	-8.1(2)	-3.0(2)	0.8(2)
K2	12.9(2)	17.6(2)	24.5(3)	-6.0(2)	-2.8(2)	1.2(2)
C1	25(1)	27(1)	23(1)	-11(1)	-2(1)	3(1)
C2	19(1)	20(1)	21(1)	-5.6(9)	-3.2(9)	1.2(9)
S 1	13.4(3)	14.6(3)	20.4(3)	-5.8(2)	-2.7(2)	1.9(2)
S2	12.6(3)	14.3(2)	19.4(3)	-5.8(2)	-2.6(2)	0.4(2)
O11	16.9(9)	20.1(8)	25.0(9)	-5.2(7)	-0.2(7)	2.6(7)
O12	18(1)	19.0(9)	36(1)	-5.3(8)	-2.0(8)	7.6(7)
O13	18(1)	19.0(9)	36(1)	-5.3(8)	-2.0(8)	7.6(7)
O21	15.0(9)	23.3(9)	22.9(9)	-8.5(7)	0.4(7)	0.3(7)
O22	23(1)	15.3(8)	26.2(9)	-6.5(7)	-3.8(7)	4.1(7)
O23	17.2(9)	23.2(9)	30(1)	-11.1(8)	-5.2(7)	-3.1(7)
Cl11	59.3(6)	47.8(5)	46.2(5)	-31.0(4)	-11.7(4)	-9.0(4)
Cl12	35.5(4)	45.7(5)	27.1(3)	-2.4(3)	-9.1(3)	17.9(4)
Cl13	37.1(5)	52.7(5)	27.3(4)	-7.6(3)	10.9(3)	2.8(4)
O1	15.7(9)	17.4(8)	29(1)	-7.5(8)	-6.1(8)	-0.1(7)
O2	16(1)	21.1(9)	29(1)	-11.4(8)	-5.4(8)	4.3(7)

Table 149: Anisotropic Displacement Parameters $(Å^2 \times 10^3)$ for $K[Cl_3CSO_3]$ H₂O.

Table 150: Selected Bond Lengths for K[Cl₃CSO₃] H₂O.

Bond	Length [pm]	Bond	Length [pm]
S1-O11	144.3(2)	K1-O21 ¹	271.8(2)
S1-O12	145.2(2)	K1-O21	278.2(2)
S1-O13	144.5(2)	K1-O23	307.6(2)
S1-C1	184.0(3)	K1-O22	278.2(2)
C1-Cl11	176.2(4)	K1-O2	279.3(2)
C1-Cl12	176.5(3)	K1-O13	270.4(2)
C1-Cl13	175.4(3)	K1-O1	273.8(2)
S2-O21	144.4(2)	K2-Cl12	358.3(1)
S2-O22	144.6(2)	K2-O22	269.3(2)
S2-O23	145.0(2)	K2-O2	272.4(2)
S2-C2	184.6(2)	K2-O1	279.7(2)
C2-Cl21	176.9(3)	K2-O13	275.8(2)
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C2-C122	175.8(3)	K2-O11	278.0(2)
C2-Cl23	176.2(2)	K2-O12	313.5(2)
K1-Cl21	361.66(9)	K2-O11 ¹	271.5(2)

¹-1+X,+Y,+Z.

Table 151: Selected Bond Angles for K[Cl₃CSO₃] H₂O.

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
O11-S1-O12	114.2(1)	O21-S2-O22	115.0(1)
O12-S1-O13	113.3(1)	O22-S2-O23	113.2(1)
O13-S1-O11	114.9(1)	O23-S2-O21	114.2(1)
O11-S1-C1	104.4(1)	O21-S2-C1	104.3(1)
O12-S1-C1	104.5(1)	O22-S2-C1	104.4(1)
O13-S1-C1	103.9(1)	O23-S2-C1	104.2(1)
Cl11-C1-S1	108.8(2)	Cl21-C2-S2	108.3(1)
Cl12-C1-S1	108.0(1)	Cl22-C2-S2	108.7(1)
Cl13-C1-S1	109.4(2)	Cl23-C2-S2	108.9(1)
Cl11-C1-Cl12	110.0(2)	Cl21-C2-Cl22	110.0(1)
Cl12-C1-Cl13	110.1(2)	Cl22-C2-Cl23	110.7(2)
Cl13-C1-Cl11	110.6(2)	Cl23-C2-Cl21	110.2(2)

Table 152: Torsion Angles for K[Cl₃CSO₃] H₂O.

Atom-Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom-Atom	Angle [°]
O21-S2-C2-Cl23	-60.0(2)	Cl12-C1-S1-O13	59.6(2)
Cl23-C2-S2-O23	60.1(2)	O13-S1-C1-Cl13	-60.3(2)
O23-S2-C2-Cl22	-60.6(2)	Cl13-C1-S1-O12	58.8(1)
Cl22-C2-S2-O22	58.4(2)	O12-S1-C1-Cl11	-62.1(1)
O22-S1-C1-Cl21	-61.1(2)	Cl11-C1-S1-O11	58.2(2)
Cl21-C2-S2-O21	59.9(2)	O11-S1-C1-Cl12	-61.2(2)

Table 153: Hydrogen Atom Coordinates ($\mathring{A} \times 10^4$) and Isotropic Displacement Parameters ($\mathring{A}^2 \times 10^3$) for K[Cl₃CSO₃] H₂O.

Atom	X	у	Z.	U(eq)
H1A	2850(70)	7070(40)	-930(30)	31(10)
H1B	4080(80)	7970(50)	-1070(40)	49(14)
H2A	7960(70)	8540(40)	-940(30)	29(10)

H2B	9160(90)	7750(60)	-1050(50)	65(17)
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O_D -H···O _A	d _{D-A} [pm]	$\angle O_D$ -H-O _A [°]
O1-H1A-O23	286.9(3)	174(4)
O1-H1B-O12	291.4(3)	153(5)
O2-H2A-O12	285.8(3)	174(4)
O2-H2B-O23	293.7(3)	153(6)

Table 154: Hydrogen Bonding within $K[Cl_3CSO_3] H_2O$.

Rb[Cl₃CSO₃]

Table 155: Crystal Data and Structure Refinement for Rb[Cl₃CSO₃].

Empirical formula	$C_3Cl_9O_9Rb_3S_3$
Formula Weight	851.67 g/mol
Temperature	100 K
Wavelength	71.073 pm (Mo-K _α)
Crystal system	triclinic
Space group	PĪ
Unit cell parameters	a = 601.32(6) pm
	b = 1228.5(1) pm
	c = 1578.6(2) pm
	$\alpha = 106.241(3)^{\circ}$
	$\beta = 90.832(3)^{\circ}$
	$\gamma = 100.862(4)^{\circ}$
Volume	1096.7(2) Å ³
Ζ	2
Density (calculated)	1.579g/cm ³
Absorption coefficient	8.083 mm ⁻¹
F(000)	804
Crystal size	0.244 x 0.1 x 0.083 mm ³
2θ Range for data collection	$3.77 - 52.996^{\circ}$
Index range	$-7 \le h \le 7, -15 \le k \le 15, -19 \le l \le 19$
Reflections collected	87029
Independent reflections	4559 [$R_{\text{int}} = 0.0378, R_{\sigma} = 0.0154$]

Completeness	99.9%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7479/0.4246
Refinement method	Least Squares
Data/Restraints/Parameters	4559/0/244
Goodness-of-fit on F^2	1.049
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0334, wR_2 = 0.0910$
R Indices (all data)	$R_1 = 0.0338, wR_2 = 0.0914$
Largest diff. peak and hole	$1.82/-0.57 \text{ e} \cdot \text{\AA}^{-3}$
CCDC Deposition Number	2041090

Table 156: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters ($\mathring{A}^2 \times 10^3$) for Rb[Cl₃CSO₃].

Atom	X	у	Z.	U(eq)
Rb1	-1647.3(5)	6735.7(3)	6842.2(2)	18.2(1)
Rb2	-2518.7(5)	4831.2(3)	9092.0(2)	145.0(1)
Rb3	2044.1(5)	4148.6(3)	6446.2(2)	18.4(1)
S 1	3260(1)	6278.1(6)	8504.2(5)	11.8(2)
011	1002(4)	6155(2)	8111(2)	17.5(5)
O12	3322(4)	5926(2)	9300(2)	17.9(5)
013	4832(4)	5830(2)	7871(2)	16.4(5)
C1	4408(5)	7852(3)	8851(2)	16.5(6)
Cl11	2870(2)	8544.9(7)	9695.6(6)	23.4(2)
Cl12	4202(2)	8362.0(7)	7913.1(6)	23.2(2)
Cl13	7284(1)	8076.0(8)	9206.6(6)	27.0(2)
S2	1274(1)	2960.5(7)	8356.2(6)	17.7(2)
O21	31(5)	3464(2)	7820(2)	24.6(5)
O22	814(5)	3289(2)	9278(2)	22.7(5)
O23	3622(5)	3018(3)	8170(2)	38.3(8)
C2	-37(6)	1406(3)	7947(2)	15.8(6)
Cl21	-2987(1)	1253.7(8)	8011.0(6)	23.4(2)
Cl22	578(2)	877.2(8)	6831.0(6)	28.3(2)
Cl23	1063(2)	632.4(8)	8574.8(7)	32.0(2)
S 3	6484(1)	3558.1(7)	4869.6(5)	12.5(2)
O31	4103(4)	3603(2)	4828(2)	18.5(5)
O32	7735(4)	4279(2)	5685(2)	21.2(5)

O33	7572(4)	3630(2)	4074(2)	20.9(5)
C3	6443(5)	2062(3)	4914(2)	15.8(6)
Cl31	5473(2)	1947.2(8)	5939.5(6)	27.6(2)
C132	9228(1)	1786.2(7)	4819.2(6)	21.1(2)
C133	4638(2)	1071.9(7)	4042.9(6)	25.6(2)

Table 157: Anisotropic Displacement Parameters $(Å^2 \times 10^3)$ for $Rb[Cl_3CSO_3]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rb1	16.3(2)	25.4(2)	14.5(2)	7.6(1)	3.0(1)	5.0(1)
Rb2	14.7(2)	17.1(2)	14.0(2)	5.5(1)	0.8(1)	4.1(1)
Rb3	20.5(2)	18.7(2)	12.9(2)	2.1(1)	1.2(1)	0.4(1)
S 1	12.6(3)	10.9(3)	11.9(3)	3.9(3)	1.1(3)	1.6(3)
O11	14(1)	17(1)	22(1)	6.5(9)	-1.8(9)	1.3(9)
O12	23(1)	20(1)	14(1)	8.4(9)	2.4(9)	5.6(9)
O13	17(1)	18(1)	14(1)	4.4(9)	4.0(9)	3.7(9)
C1	16(2)	13(2)	19(2)	4(1)	1.(1)	0(1)
Cl11	24.5(4)	19.3(4)	22.0(4)	-1.3(3)	7.1(3)	4.6(3)
Cl12	31.4(4)	17.8(4)	24.1(4)	12.1(3)	5.1(3)	4.4(3)
Cl13	16.3(4)	26.9(4)	31.3(5)	2.1(4)	-4.9(3)	-1.2(3)
S 2	15.7(4)	10.9(4)	22.7(4)	0.7(3)	4.0(3)	-0.3(3)
O21	37(2)	19(1)	21(1)	9(1)	8(1)	6(1)
O22	31(1)	15(1)	18(1)	-1.0(9)	-5(1)	5(1)
O23	18(1)	22(1)	61(2)	-7(1)	9(1)	-3(1)
C2	19(2)	11(1)	15(2)	1(1)	2(1)	1(1)
Cl21	15.7(4)	24.0(4)	25.9(4)	3.9(3)	3.6(3)	-2.4(3)
C122	30.2(5)	25.5(5)	20.4(4)	-4.7(3)	7.7(3)	1.2(4)
C123	44.3(6)	20.5(4)	35.1(5)	9.4(4)	-3.5(4)	14.1(4)
S 3	13.1(3)	12.4(3)	11.7(4)	3.8(3)	1.1(3)	0.9(3)
O31	14(1)	20(1)	23(1)	9(1)	1.8(9)	3.1(9)
O32	28(1)	15(1)	19(1)	2(1)	-7(1)	4(1)
O33	24(1)	19(1)	20(1)	7(1)	10(1)	3(1)
C3	14(1)	18(2)	16(2)	7(1)	0(1)	1(1)
Cl31	35.3(5)	30.3(5)	26.8(4)	19.5(4)	11.7(4)	12.1(4)
C132	17.1(4)	18.3(4)	26.0(4)	1.8(3)	0.1(3)	5.9(3)
C133	25.3(4)	16.1(4)	29.7(5)	3.7(3)	-9.4(3)	-4.6(3)

Bond	Length [pm]	Bond	Length [pm]
S1-O11	144.8(3)	Rb1-O33 ⁴	290.8(3)
S1-O12	144.1(3)	Rb1-O32	300.9(2)
S1-O13	145.3(3)	Rb1-O31 ³	288.9(3)
S1-C1	184.6(3)	Rb1-O33	372.4(3)
C1-Cl11	174.8(3)	Rb1-O13 ¹	293.0(3)
C1-Cl12	177.3(4)	Rb2-Cl13	396.4(1)
C1-Cl13	175.7(3)	Rb2-O13 ¹	311.9(3)
S2-O21	145.1(3)	Rb2-O12 ¹	303.6(3)
S2-O22	144.3(3)	Rb2-O23 ¹	293.4(3)
S2-O23	144.9(3)	Rb2-O12 ²	295.4(3)
S2-C2	184.8(3)	Rb2-O22	306.9(3)
C2-Cl21	175.5(4)	Rb2-O21	289.4(3)
C2-C122	177.0(3)	Rb2-O12	349.2(2)
C2-C123	175.2(4)	Rb2-O11	311.9(3)
S3-O31	144.5(3)	Rb2-O22 ²	295.1(2)
S3-O32	144.6(2)	Rb3-Cl31	362.6(1)
S3-O33	144.1(3)	Rb3-Cl32	342.61(8)
S3-C3	185.4(4)	Rb3-O31	282.0(3)
C3-Cl31	176.2(4)	Rb3-O32 ¹	289.1(3)
C3-C132	177.1(3)	Rb3-O33 ⁴	303.3(3)
C3-Cl33	175.3(3)	Rb3-O11	322.2(2)
Rb1-Cl12 ¹	363.2(1)	Rb3-O13	285.0(2)
Rb1-Cl13	375.3(1)	Rb3-O21	275.5(3)
Rb1-Cl12	380.90(9)	Rb3-O23	357.4(4)
Rb1-Cl32 ⁴	375.1(1)	Rb3-O32	363.3(3)
Rb1-O11	286.3(3)		

 Table 158: Selected Bond Lengths for Rb[Cl₃CSO₃].

¹-1+X,+Y,+Z; ²-X,1-Y,2-Z; ³-X,1-Y,1-Z; ⁴1-X,1-Y,1-Z.

Table 159: Selected Bond Angles for Rb[Cl₃CSO₃].

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]	
O11-S1-O12	114.7(2)	Cl21-C2-S2	108.5(2)	
O12-S1-O13	113.8(1)	C122-C2-S2	108.7(2)	
013-S1-O11	113.6(1)	Cl23-C2-S2	110.4(2)	

O11-S1-C1	104.7(1)	Cl21-C2-Cl22	109.5(2)
O12-S1-C1	105.4(2)	Cl22-C2-Cl23	109.1(2)
O13-S1-C1	103.0(2)	Cl23-C2-Cl21	110.7(2)
Cl11-C1-S1	110.0(2)	031-S3-O32	114.2(2)
Cl12-C1-S1	107.8(2)	032-\$3-033	115.2(2)
Cl13-C1-S1	108.0(2)	O33-S3-O31	113.7(2)
Cl11-C1-Cl12	110.7(2)	O31-S3-C3	102.9(1)
Cl12-C1-Cl13	109.1(2)	O32-S3-C3	104.0(2)
Cl13-C1-Cl11	111.1(2)	O33-S3-C3	104.9(2)
O21-S2-O22	113.3(2)	Cl31-C3-S3	108.2(2)
O22-S2-O23	116.3(2)	Cl32-C3-S3	109.1(2)
O23-S2-O21	113.6(2)	C133-C3-S3	109.8(2)
O21-S2-C2	102.5(2)	Cl31-C3-Cl32	109.8(2)
O22-S2-C2	104.5(2)	Cl32-C3-Cl33	109.5(2)
O23-S2-C2	104.7(2)	Cl33-C3-Cl31	110.4(2)

Table 160: Torsion Angles for Rb[Cl₃CSO₃].

Atom-Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom-Atom	Angle [°]
Cl11-C1-S1-O11	66.1(2)	Cl22-C2-S2-O23	-53.5(2)
O11-S1-C1-Cl12	-54.7(2)	O23-S2-C2-Cl23	66.1(2)
Cl12-C1-S1-O13	64.3(2)	Cl23-C2-S2-O22	-56.6(2)
O13-S1-C1-Cl13	-53.4(2)	Cl31-C3-S3-O31	-68.3(2)
Cl13-C1-S1-O12	66.2(2)	O31-S3-C3-Cl33	52.2(2)
O12-S1-C1-Cl11	-55.3(2)	Cl33-C3-S3-O33	-67.0(2)
O22-S2-C2-Cl21	64.8(2)	O33-S3-C3-Cl32	53.1(2)
Cl21-C2-S2-O21	-53.7(2)	Cl32-C3-S3-O32	-68.3(2)
O21-S2-C2-Cl22	65.3(2)	O32-S3-C3-Cl31	51.2(2)

Rb3[Cl3CSO3]3Cl

 Table 161: Crystal Data and Structure Refinement for Rb3[Cl3CSO3]3Cl.

Empirical formula	$C_2Cl_7O_6Rb_3S_2$
Formula Weight	688.70 g/mol
Temperature	100 K

Wavelength	71.073 pm (Mo _{Kα})
Crystal system	monoclinic
Space group	<i>I</i> 2/ <i>a</i>
Unit cell parameters	a = 2554.7(6) pm
	<i>b</i> = 613.15(9) pm
	c = 2324.0(4) pm
	$\beta = 103.343(3)^{\circ}$
Volume	3542(1) Å ³
Ζ	8
Density (calculated)	2.583g/cm ³
Absorption coefficient	9.560 mm ⁻¹
F(000)	2576
Crystal size	0.12 x 0.1 x 0.7 mm ³
2θ Range for data collection	$4.274 - 53.006^{\circ}$
Index range	-31≤h≤31, -7≤k≤7 -29≤l≤29
Reflections collected	53358
Independent reflections	3657 [$R_{\text{int}} = 0.0483, R_{\sigma} = 0.0186$]
Completeness	99.9%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.554/0.393
Refinement method	Least Squares
Data/Restraints/Parameters	3657/0/183
Goodness-of-fit on F^2	1.161
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0237, wR_2 = 0.0501$
R Indices (all data)	$R_1 = 0.0254, wR_2 = 0.0506$
Largest diff. peak and hole	$1.01/-0.72 \text{ e} \cdot \text{\AA}^{-3}$
CCDC Deposition Number	2041089

Table 162: Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters ($\mathring{A}^2 \times 10^3$) for $Rb_3[Cl_3CSO_3]_2Cl$.

Atom	X	у	Z.	U(eq)
Rb1	6034.7(2)	4956.0(4)	3669.4(2)	16.32(7)
Rb2	5000	5000	5000	14.52(9)
Rb3	8775.7(2)	465.3(4)	4778.2(2)	15.85(7)

Rb4	7500	-5280.0(6)	5000	14.55(9)
S 1	7133.5(3)	-99(1)	4059.9(3)	11.9(1)
011	7657.1(8)	436(4)	4416.6(9)	21.2(5)
O12	6712.1(8)	1355(3)	4146.8(9)	19.6(4)
013	6996.8(9)	-2382(3)	4045(1)	21.8(5)
C1	7202(1)	479(5)	3304(1)	17.4(6)
Cl11	7749.1(4)	-1041(1)	3176.5(4)	29.6(2)
Cl12	7317.5(4)	3296(1)	3242.6(4)	30.0(2)
Cl13	6606.6(4)	-267(2)	2793.7(4)	37.4(2)
S 2	5026.2(3)	9970(1)	3897.6(3)	13.3(1)
O21	5334.1(8)	11862(3)	4145.0(9)	18.2(4)
O22	5304.8(9)	8493(4)	3590(1)	23.2(5)
O23	4741.6(9)	8941(4)	4294.5(9)	20.9(5)
C2	4484(1)	11125(5)	3310(1)	14.7(6)
Cl21	4759.1(3)	12498(1)	2781.4(3)	23.4(2)
C122	4064.0(3)	8997(1)	2959.3(3)	22.5(2)
C123	4108.1(3)	12963(1)	3642.2(3)	19.5(2)
Cl1	8740.3(3)	-4526(1)	4910.2(3)	15.4(1)

Table 163: Anisotropic Displacement Parameters $(Å^2 \times 10^3)$ for $Rb_3[Cl_3CSO_3]_2Cl$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Rb1	14.2(1)	15.3(1)	19.6(1)	1.6(1)	4.0(1)	2.9(1)
Rb2	10.1(2)	14.1(2)	19.8(2)	1.3(1)	4.2(1)	1.1(1)
Rb3	13.1(1)	10.4(1)	24.7(2)	-1.2(1)	5.7(1)	0.1(1)
Rb4	9.9(2)	14.1(2)	19.0(2)	0	1.9(1)	0
S 1	11.0(3)	12.7(3)	12.4(3)	1.8(2)	3.5(3)	1.4(2)
O11	14(1)	31(1)	16(1)	-5.8(9)	-1.3(8)	1.0(9)
O12	17(1)	19(1)	24(1)	3.9(9)	8.0(9)	7.8(8)
O13	24(1)	13(1)	29(1)	5.1(9)	9(1)	-0.5(9)
C1	26(2)	13(1)	12(1)	0.2(1)	2(1)	1(1)
Cl11	39.6(5)	28.4(4)	27.1(4)	-0.8(3)	20.7(4)	7.5(4)
Cl12	50.6(5)	14.8(3)	30.0(4)	5.0(3)	20.3(4)	-2.2(3)
Cl13	44.6(5)	31.1(4)	24.1(4)	-3.0(3)	-17.9(4)	3.2(4)
S2	11.4(3)	13.7(3)	14.3(3)	1.3(3)	1.9(3)	2.4(3)
O21	14(1)	20(1)	20(1)	-1.2(9)	1.1(8)	-1.2(8)

O22	21(1)	23(1)	27(1)	-3.9(9)	5.7(9)	8.6(9)
O23	19(1)	24(1)	20(1)	8.8(9)	4.9(9)	0.5(9)
C2	17(1)	15(1)	12(1)	-0.3(1)	4(1)	0(1)
Cl21	26.3(4)	27.5(4)	17.1(4)	6.8(3)	6.8(3)	-1.1(3)
Cl22	19.5(4)	23.0(4)	22.2(4)	-6.0(3)	-0.8(3)	-4.4(3)
Cl23	17.0(3)	19.9(3)	20.8(4)	-1.4(3)	2.6(3)	6.7(3)
Cl1	12.9(3)	11.2(3)	23.4(4)	1.9(3)	6.9(3)	0.6(2)

Table 164: Selected Bond Lengths for Rb3[Cl3CSO3]2Cl.

Bond	Length [pm]	Bond	Length [pm]
S1-O11	144.0(2)	Rb1-O21	299.0(2)
S1-O12	144.7(2)	Rb1-O22	283.8(3)
S1-O13	144.1(2)	Rb1-O12	286.6(2)
S1-C1	184.0(3)	Rb1-O13	291.2(2)
C1-Cl11	176.0(3)	Rb2-O23	290.9(2)
C1-Cl12	176.3(3)	Rb2-O21	302.7(2)
C1-Cl13	176.0(3)	Rb2-Cl1	319.0(1)
S2-O21	144.5(2)	Rb2-Cl23	365.91(8)
S2-O22	144.0(2)	Rb3-Cl1	307.89(8)
S2-O23	144.5(2)	Rb3-Cl1	309.00(8)
S2-C2	184.8(3)	Rb3-Cl23	362.56(9)
C2-Cl21	176.5(3)	Rb3-O12	308.7(2)
C2-C122	176.4(3)	Rb3-O11	278.7(2)
C2-C123	176.9(3)	Rb3-O23	296.0(2)
Rb1-Cl1	323.3(1)	Rb3-O21	308.9(2)
Rb1-Cl21 ¹	374.8(1)	Rb4-Cl1	325.6(1)
Rb1-Cl21 ²	384.09(9)	Rb4-O12	322.5(2)
Rb1-Cl22	378.1(1)	Rb4-O13	290.1(2)
Rb1-Cl12	377.6(1)	Rb4-O11	302.5(2)

¹+X,-1+Y,+Z; ²1-X,-1/2+Y,1/2-Z.

 Table 165: Selected Bond Angles for Rb3[Cl3CSO3]2Cl.

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]	
O11-S1-O12	113.7(1)	O21-S2-O22	114.6(1)	
O12-S1-O13	114.7(1)	O22-S2-O23	115.0(1)	
O13-S1-O11	115.0(1)	O23-S2-O21	113.9(1)	

O11-S1-C1	103.0(1)	O21-S2-C2	103.5(1)
O12-S1-C1	104.7(1)	O22-S2-C2	104.3(1)
O13-S1-C1	103.9(1)	O23-S2-C2	103.7(1)
Cl11-C1-S1	108.3(2)	Cl21-C2-S2	110.2(2)
Cl12-C1-S1	108.7(2)	Cl22-C2-S2	109.3(2)
Cl13-C1-S1	109.6(2)	Cl23-C2-S2	108.2(2)
Cl11-C1-Cl12	110.6(2)	Cl21-C2-Cl22	109.2(2)
Cl12-C1-Cl13	109.5(2)	Cl22-C2-Cl23	109.9(2)
Cl13-C1-Cl11	110.2(2)	Cl23-C2-Cl21	110.1(2)

Table 166: Torsion Angles for Rb3[Cl3CSO3]2Cl.

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom-Atom	Angle [°]
O11-S1-C1-Cl12	-64.4(2)	O21-S2-C2-Cl23	-60.3(2)
Cl12-C1-S2-O12	54.7(2)	Cl23-C2-S2-O23	58.8(2)
O12-S1-C1-Cl13	-65.0(2)	O23-S2-C2-Cl22	-60.8(2)
Cl13-C1-S1-O13	55.6(2)	Cl22-C2-S2-O22	59.9(2)
O13-S1-C1-Cl11	-64.5(2)	O22-S2-C2-Cl21	-60.1(2)
Cl11-C1-S1-O11	55.7(2)	Cl21-C2-S2-O21	60.1(2)

$[Cu(H_2O)_4(Cl_3CSO_3)_2]$

Table 167: Crystal Data and Structure Refinement for $[Cu(H_2O)_4(Cl_3CSO_3)_2]$.

Empirical formula	$C_2H_8Cl_6CuO_{10}S_2$
Formula Weight	532.44 g/mol
Temperature	250 K
Wavelength	71.073 pm (Mo _{Kα})
Crystal system	monoclinic
Space group	C2/m
Unit cell parameters	a = 747.11(6) pm
	<i>b</i> = 988.01(8) pm
	c = 2352.7(2) pm
	$\beta = 90.415(3)^{\circ}$
Volume	1736.6(3) Å ³
Ζ	4

Density (calculated)	2.037 g/cm ³
Absorption coefficient	2.457 mm ⁻¹
F(000)	1052
Crystal size	0.512 x 0.347 x 0.211 mm ³
2θ Range for data collection	$5.194 - 53.0^{\circ}$
Index range	−9≤h≤9, −12≤k≤12, −29≤l≤29
Reflections collected	19369
Independent reflections	1909 [$R_{\text{int}} = 0.0428, R_{\sigma} = 0.0192$]
Completeness	99.4%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7467/0.5644
Refinement method	Least Squares
Data/Restraints/Parameters	1909/2/152
Goodness-of-fit on F^2	1.193
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0847, wR_2 = 0.1892$
R Indices (all data)	$R_1 = 0.0898, wR_2 = 0.1892$
Largest diff. peak and hole	$0.71/-1.01 \text{ e} \cdot \text{\AA}^{-3}$
CCDC Deposition Number	2324855

Table 168: Fractional Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $[Cu(H_2O)_4(Cl_3CSO_3)_2]$.

Atom	X	у	Z	U(eq)
Cu1	0	5000	5000	30.7(5)
Cu2	5000	5000	0	37.6(6)
S 1	4279(4)	5000	4157(1)	31.2(6)
011	2652(13)	5000	4452(5)	68(3)
O12	5340(8)	6233(6)	4225(3)	45.5(15)
C1	7534(14)	5000	602(6)	88(4)
Cl1A	6510(110)	5000	3153(19)	110(20)
Cl1B	5320(20)	5000	2958(5)	72(3)
Cl2A	2730(60)	6460(14)	3223(10)	161(8)
Cl2B	2197(12)	6459(14)	3303(5)	51(4)
S2	9299(4)	5000	843.0(12)	34.1(7)
O21	7534(14)	5000	602(6)	88(4)
O22	10300(8)	3794(7)	727(3)	47.2(16)
C2	9030(40)	5000	1620(7)	92(7)

Cl3A	10570(70)	5000	1994(10)	108(10)
C13B	11700(40)	5000	1835(8)	72(7)
Cl4A	7370(50)	6458(8)	1712(7)	87(7)
Cl4B	8430(40)	6452(12)	1903(11)	82(6)
01	1154(8)	6389(8)	5441(4)	73(3)
02	6195(9)	6380(8)	-430(4)	70(2)

Table 169: Anisotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $[Cu(H_2O)_4(Cl_3CSO_3)_2]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu1	27(1)	20.0(9)	45(1)	0	-0.9(8)	0
Cu2	27(1)	20.0(9)	45(1)	0	-0.9(8)	0
S 1	28(1)	33(2)	32(1)	0	-1(1)	0
011	35(5)	109(10)	60(6)	0	10(4)	0
O12	36(3)	29(3)	72(4)	-10(3)	-7(3)	0(3)
C1	118(14)	33(7)	26(6)	0	-6(7)	0
Cl1A	180(50)	61(11)	88(19)	0	70(30)	0
Cl1B	79(8)	91(5)	46(4)	0	37(4)	0
Cl2A	320(20)	46(5)	117(10)	13(6)	-129(12)	19(10)
Cl2B	52(7)	53(5)	49(4)	0(3)	-18(3)	25(3)
S2	32.2(15)	37(2)	33.0(14)	0	1(1)	0
O21	34(6)	108(11)	122(11)	0	-19(6)	0
O22	40(3)	36(4)	65(4)	-14(3)	12(3)	-5(3)
C2	190(20)	42(9)	47(9)	0	38(12)	0
Cl3A	150(30)	111(9)	61(8)	0	-42(13)	0
Cl3B	89(15)	90(8)	38(6)	0	-26(7)	0
Cl4A	148(17)	45(3)	69(5)	-3(3)	43(8)	20(5)
Cl4B	104(13)	63(5)	78(9)	-28(5)	41(9)	11(6)
01	32(3)	48(4)	139(8)	-47(5)	-22(4)	8(3)
O2	39(4)	47(4)	124(7)	42(5)	22(4)	10(3)

Table 170: Selected Bond Lengths for $[Cu(H_2O)_4(Cl_3CSO_3)_2]$.

Bond	Length [pm]	Bond	Length [pm]
S1-O11	140(1)	S2-O21	143(1)
S1-O12	146.1(6)	S2-O22	143.4(6)
S1-C1	182(1)	S2-C2	184(2)

C1-Cl1A	226(7)	C2-Cl3A	144(4)
C1-Cl1B	168(2)	C2-Cl3B	205(4)
C1-Cl2A	164(2)	C2-Cl4A	192(3)
C1-Cl2B	180(2)	C2-Cl4B	165(1)
Cu1-O1	192.1(8)	Cu2-O2	192.2(8)
Cu1-O11	237(1)	Cu2-O21	236(1)

Table 171: Selected Bond Angles for $[Cu(H_2O)_4(Cl_3CSO_3)_2]$.

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
O11-S1-O12	114.7(3)	O21-S2-O22	113.9(4)
O12-S1-O12	113.0(5)	O22-S2-O22	114.7(3)
O11-S1-C1	114.7(3)	O21-S2-C2	107(1)
O12-S1-C1	104.5(4)	O22-S2-C2	104.4(5)
Cl1A-C1-S1	90(2)	Cl3A-C2-S2	121(2)
Cl1B-C1-S1	121.4(9)	Cl3B-C2-S2	98(1)
Cl2A-C1-S1	111.7(8)	Cl4A-C2-S2	101(1)
Cl2B-C1-S1	107.3(6)	Cl4B-C2-S2	116(1)
Cl1A-C1-Cl2A	108(2)	Cl3A-C2-Cl4A	117(2)
Cl2A-C1-Cl2A	123(2)	Cl4A-C2-Cl4A	97(2)
Cl1B-C1-Cl2B	110.8(7)	Cl3B-C2-Cl4B	100(2)
Cl2B-C1-Cl12B	106(1)	Cl4B-C2-Cl4B	121(1)

Table 172: Hydrogen Atom Coordinates $(\mathring{A} \times 10^4)$ and Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $[Cu(H_2O)_4(Cl_3CSO_3)_2]$.

Atom	x	У	Z	U(eq)
H1A	641.63	6924.32	5677.39	109
H1B	2268.14	6413.92	5534.69	109
H2A	5663.81	7052.77	-590.8	105
H2B	7139.01	6252.67	-630.3	105

Table 173: Atomic Occupancy for $[Cu(H_2O)_4(Cl_3CSO_3)_2]$.

Atom	Occupancy	Atom	Occupancy
Cl1A	0.30(5)	Cl1B	0.70(5)
Cl2A	0.54(4)	Cl2B	0.46(4)
Cl3A	0.54(6)	C13B	0.46(6)
Cl4A	0.56(5)	Cl4B	0.44(5)

[C0(H₂O)₆][Cl₃CSO₃]₂

Empirical formula	$C_2H_{12}Cl_6CoO_{12}S_2$
Formula Weight	563.87 g/mol
Temperature	250 K
Wavelength	71.073 pm (Mo _{Kα})
Crystal system	monoclinic
Space group	$P2_{1}/n$
Unit cell parameters	a = 661.32(2) pm
	<i>b</i> = 648.54(3) pm
	c = 2319.9(1) pm
	$\beta = 91.257(3)^{\circ}$
Volume	994.75(7) Å ³
Ζ	2
Density (calculated)	1.883 g/cm ³
Absorption coefficient	1.923 mm ⁻¹
F(000)	562
Crystal size	0.170 x 0.315 x 0.602 mm ³
2θ Range for data collection	$6.37 - 56.646^{\circ}$
Index range	-8≤h≤8, -8≤k≤8, -30≤l≤30
Reflections collected	15224
Independent reflections	2475 [$R_{\text{int}} = 0.0431, R_{\sigma} = 0.0275$]
Completeness	99.6%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7457/0.5686
Refinement method	Least Squares
Data/Restraints/Parameters	2475/2/113
Goodness-of-fit on F^2	1.068
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0409, wR_2 = 0.1048$
<i>R</i> Indices (all data)	$R_1 = 0.0464, wR_2 = 0.1093$
Largest diff. peak and hole	$0.99/-0.85 \text{ e} \cdot \text{\AA}^{-3}$
CCDC Deposition Number	2324853

Table 174: Crystal Data and Structure Refinement for [Co(H₂O)₆][Cl₃CSO₃]₂.

Atom	X	У	Z	U(eq)
Co1	10000	0	5000	26.5(2)
S 1	4689.8(9)	4111.5(9)	4007.4(3)	27.7(2)
011	4732(3)	1888(3)	40101)	45.8(6)
O12	6207(3)	5044(3)	4380.7(8)	33.6(4)
013	2686(3)	4973(3)	4063(1)	41.8(5)
C1	5450(6)	4865(5)	3280(1)	45.6(8)
Cl11	7938(2)	4024(3)	3183.9(5)	88.8(4)
Cl12	3794(3)	3746(2)	2772.4(5)	94.5(5)
Cl13	5320(2)	7585(2)	3234.6(4)	63.1(3)
01	7189(3)	-864(3)	4662(1)	43.2(5)
O2	9723(3)	2951(3)	4685(1)	39.0(5)
O3	8541(4)	881(3)	5751(1)	45.0(5)

Table 175: Fractional Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $[Co(H_2O)_6][Cl_3CSO_3]_2$.

Table 176: Anisotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $[Co(H_2O)_6][Cl_3CSO_3]_2$.

Atom	U_{11}	U_{22}	<i>U</i> 33	U_{23}	U_{13}	U_{12}
Co1	24.2(2)	16.5(2)	38.6(3)	-2.7(2)	-2.0(2)	0.6(2)
S 1	26.9(3)	19.5(3)	36.8(3)	1.1(2)	2.2(2)	1.9(2)
O11	44(1)	19.7(9)	74(2)	1(1)	-5(1)	2.3(8)
O12	39(1)	29(1)	33(1)	0.3(7)	-2.3(8)	1.1(8)
O13	30(1)	31(1)	65(2)	8(1)	7.3(9)	5.8(8)
C1	44(1)	19.7(9)	74(2)	1(1)	-5(1)	2.3(8)
Cl11	73.9(7)	130(1)	63.6(7)	-1.1(7)	35.3(6)	34.3(8)
Cl12	130(1)	93.7(9)	57.5(6)	-26.7(6)	-42.3(7)	7.4(8)
Cl13	90.3(7)	51.1(5)	48.1(5)	20.6(4)	9.2(5)	-4.0(5)
01	37(1)	26(1)	66(2)	-4(1)	-18(1)	-1.2(8)
O2	31(1)	23.5(9)	63(1)	9.6(9)	1.2(9)	1.9(8)
O3	50(1)	29(1)	57(1)	-9(1)	16(1)	-2.1(9)

Table 177: Table of Selected Bond Lengths for $[Co(H_2O)_6][Cl_3CSO_3]_2$.

Bond	Length [pm]	Bond	Length [pm]
S1-O11	144.2(2)	C1-Cl12	174.8(4)
S1-O12	144.4(2)	C1-Cl13	176.9(3)

S1-O13	144.6(2)	Co1-O1	207.8(2)
S1-C1	183.8(3)	Co1-O2	205.5(2)
C1-Cl11	175.2(4)	Co1-O3	209.0(2)

Table 178: Selected Bond Angles for $[Co(H_2O)_6][Cl_3CSO_3]_2$.

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
O11-S1-O12	113.8(1)	Cl11-C1-S1	108.1(2)
O12-S1-O13	114.3(1)	Cl12-C1-S1	109.2(2)
O13-S1-O11	113.8(1)	Cl13-C1-S1	107.8(2)
O11-S1-C1	105.3(2)	Cl11-C1-Cl12	111.2(2)
O12-S1-C1	103.8(2)	Cl12-C1-Cl13	110.2(2)
O13-S1-C1	104.4(2)	Cl13-C1-Cl11	110.3(2)

Table 179: Torsion Angles for $[Co(H_2O)_6][Cl_3CSO_3]_2$.

Atom-Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom-Atom	Angle [°]
Cl13-C1-S1-O13	57.2(2)	O11-S1-C1-Cl11	-63.4(2)
O13-S1-C1-Cl12	-62.5(2)	Cl11-C1-S1-O12	54.5(2)
Cl12-C1-S1-O11	57.7(2)	O12-S1-C1-Cl13	-62.8(2)

Table 180: Hydrogen Atom Coordinates $(\mathring{A} \times 10^4)$ and Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $[Co(H_2O)_6][Cl_3CSO_3]_2$.

Atom	x	у	Z.	U(eq)
H1A	7035.81	-2057.48	4505.37	65
H1B	6525.75	-38.89	4438.08	65
H2A	8596.41	3564.04	4608.12	59
H2B	10582.74	3549.3	4468.35	59
H3A	8182.39	2153.21	5724.43	67
H3B	7421.09	215.01	5776.33	67

Table 181: Hydrogen Bonding within $[Co(H_2O)_6][Cl_3CSO_3]_2$.

O_D -H···O _A	d _{D-A} [pm]	$\angle O_D$ -H-O _A [°]
O1-H1A-O12	280.6(3)	161.2(1)
O1-H1B-O11	283.0(3)	172.1(2)
O2-H2A-O12	277.1(3)	174.9(1)
O2-H2B-O13	278.8(3)	152.8(1)
O3-H3A-O13	284.4(3)	161.6(1)

O3-H3B-O11

[Fe(DMSO)6][Cl₃CSO₃]

Table 182	: Crystal	Data and	Structure	Refinement	for	Fe(DMSC	$D)_{6}[Cl_{3}CSO_{3}]$
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Empirical formula	$C_{15}H_{36}Cl_9FeO_{15}S_9$
Formula Weight	1119.88 g/mol
Temperature	100 K
Wavelength	71.073 pm (Mo _{Kα})
Crystal system	monoclinic
Space group	$P2_{1}/c$
Unit cell parameters	a = 1100.25(3) pm
	b = 1100.45(3) pm
	c = 3565.8(1) pm
	$\beta = 90.996(1)^{\circ}$
Volume	4316.7(2) Å ³
Ζ	4
Density (calculated)	1.723 g/cm ³
Absorption coefficient	1.396 mm ⁻¹
F(000)	2276
Crystal size	0.584 x 0.368 x 0.29 mm ³
2θ Range for data collection	$3.702 - 52.998^{\circ}$
Index range	−13≤h≤13, −13≤k≤13, −44≤l≤44
Reflections collected	60969
Independent reflections	8934 [$R_{\text{int}} = 0.0293, R_{\sigma} = 0.0167$]
Completeness	99.9%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7466/0.6212
Refinement method	Least Squares
Data/Restraints/Parameters	8934/0/596
Goodness-of-fit on F^2	1.243
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0357, wR_2 = 0.0728$
R Indices (all data)	$R_1 = 0.0367, wR_2 = 0.0733$
Largest diff. peak and hole	$0.94/-0.63 \text{ e} \cdot \text{\AA}^{-3}$

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Atom	X	у	Z.	U(eq)
Fe1	7437.6(3)	7394.9(3)	6410.3(2)	9.87(8)
S 1	6966.0(6)	2482.7(6)	7496.2(2)	13.94(13)
011	6884(2)	1745(2)	7162.6(5)	22.1(4)
O12	6289(2)	3606(2)	7477.7(6)	24.7(4)
013	6845(2)	1821(2)	7843.9(5)	19.6(4)
C1	8577(2)	2973(3)	7510.2(7)	18.0(5)
Cl11	8862.2(7)	3866.4(7)	7912.9(2)	28.4(2)
Cl12	8892.5(6)	3840.6(7)	7106.5(2)	23.1(2)
Cl13	9512.3(7)	1665.4(7)	7524.1(2)	32.8(2)
S2	2257.5(6)	2250.4(6)	6371.5(2)	13.2(1)
O21	3350(2)	2485(2)	6591.9(5)	18.5(4)
O22	1863(2)	1000(2)	6368.3(5)	18.9(4)
O23	1298(2)	3126(2)	6417.5(6)	20.2(4)
C2	2771(2)	2509(2)	5885.2(7)	15.1(5)
Cl21	3295.9(6)	4023.6(6)	5838.6(2)	19.33(1)
C122	3972.6(6)	1502.3(6)	5788.3(2)	19.6(1)
C123	1535.7(6)	2276.0(7)	5570.4(2)	22.8(1)
S 3	7014.3(6)	12411.6(6)	5341.7(2)	16.1(1)
O31	7751(2)	13328(2)	5524.9(6)	27.1(5)
O32	7005(2)	11255(2)	5529.3(6)	27.6(5)
O33	5845(2)	12834(2)	5210.4(6)	29.2(5)
C3	7813(3)	12114(3)	4899.5(8)	19.7(6)
Cl31	9311.6(7)	11612(1)	4996.4(2)	43.7(2)
C132	7824.4(9)	13450.8(7)	4628.0(2)	35.4(2)
C133	7051.8(8)	10952.5(7)	4647.0(2)	30.1(2)
01	7777(2)	9134(2)	6311.2(5)	15.3(4)
O2	7039(2)	5655(2)	6518.3(5)	15.9(4)
O3	9181(2)	6995(2)	6351.3(5)	13.1(4)
O4	7236(2)	7067(2)	5854.4(5)	18.3(4)
O5	7749(2)	7640(2)	6956.6(5)	17.5(4)
O6	5680(2)	7787(2)	6456.0(5)	13.3(4)

Table 183: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\mathring{A}^2 \times 10^3$) for [Fe(DMSO)₆][Cl₃CSO₃].

S 11	9050.6(5)	9727.7(6)	6345.6(2)	12.4(1)
S21	5884.3(5)	5006.8(6)	6364.2(2)	12.6(1)
S 31	9742.0(5)	5719.5(6)	6403.8(2)	12.3(1)
S41	6118.9(6)	7170.6(6)	5589.9(2)	15.6(1)
S 51	6810.4(6)	7796.4(7)	7265.3(2)	19.1(1)
S61	4986.8(5)	8940.8(6)	6326.2(2)	12.5(1)
C11	8695(3)	11297(2)	6363.2(9)	18.0(5)
C12	9619(3)	9623(3)	5883.3(8)	20.4(6)
C21	6309(3)	3451(2)	6363.2(8)	16.7(5)
C22	4878(3)	4996(3)	6746.4(8)	18.9(6)
C31	11322(2)	6044(3)	6428.7(8)	16.8(5)
C32	9637(3)	5059(3)	5949.8(9)	20.9(6)
C41	6430(3)	8439(3)	5299.7(9)	24.9(6)
C42	6351(4)	5971(3)	5262.9(10)	31.6(8)
C51	7509(4)	8876(3)	7570.6(10)	34.3(8)
C52	7009(5)	6476(3)	7549.9(10)	40.4(9)
C61	3455(2)	8440(3)	6338.1(8)	18.6(5)
C62	5008(3)	9926(3)	6721.6(8)	20.2(6)

Table 184 : Anisotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for	r
Tuble 104. Anisotropic Displacement 1 drameters (A ×10) jo	'
$[Fe(DMSO)_6][Cl_3CSO_3].$	

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	9.5(2)	9.3(2)	10.9(2)	0(1)	1.4(1)	0.3(1)
S 1	15.5(3)	13.4(3)	12.9(3)	1.1(2)	0.0(2)	-4.1(2)
O11	29(1)	22(1)	15.6(9)	-2.8(8)	-0.3(8)	-9.0(9)
O12	23(1)	19(1)	32(1)	4.6(9)	2.2(9)	1.4(8)
013	23(1)	21(1)	15.1(9)	3.7(8)	2.1(7)	-6.0(8)
C1	20.(1)	18(1)	16(1)	3(1)	-1(1)	-4(1)
Cl11	40.1(4)	29.7(4)	15.2(3)	1.1(3)	-6.0(3)	-19.5(3)
Cl12	28.4(4)	25.7(3)	15.3(3)	4.5(3)	3.3(3)	-11.6(3)
Cl13	19.8(3)	28.7(4)	49.9(5)	9.9(3)	3.4(3)	3.9(3)
S2	13.6(3)	12.0(3)	14.2(3)	0.8(2)	1.5(2)	0.3(2)
O21	18.8(9)	23(1)	13.2(9)	1.0(8)	-0.8(7)	-2.0(8)
O22	21(1)	13.8(9)	22(1)	3.0(8)	3.2(8)	-2.5(8)
O23	17.5(9)	19(1)	25(10)	1.4(8)	5.1(8)	4.8(8)
C2	15(1)	15(1)	16(1)	0(1)	-1(1)	-3(1)

Cl21	24.0(3)	14.6(3)	19.5(3)	3.3(2)	1.2(2)	-3.9(2)
Cl22	19.0(3)	19.5(3)	20.3(3)	-4.2(3)	4.3(2)	2.6(2)
Cl23	21.2(3)	28.2(4)	18.8(3)	-0.5(3)	-5.8(2)	-3.6(3)
S 3	20.9(3)	14.0(3)	13.6(3)	-0.2(2)	1.2(2)	-0.8(2)
O31	36(1)	26(1)	20(1)	-8.1(9)	1.5(9)	-10.8(9)
O32	44(1)	19(1)	20(1)	4.7(8)	0.0(9)	-2.2(9)
O33	23(1)	35(1)	30(1)	3(1)	4.1(9)	5.7(9)
C3	20(1)	23(1)	16(1)	-1(1)	-2(1)	1(1)
Cl31	23.8(4)	77.8(7)	29.3(4)	-11.3(4)	-2.1(3)	16.3(4)
C132	57.4(5)	27.2(4)	21.8(4)	5.7(3)	8.9(3)	-11.5(4)
C133	47.5(5)	23.2(4)	19.2(3)	-6.2(3)	-6.0(3)	-3.2(3)
01	10.9(8)	10.9(9)	24(1)	1.9(7)	1.5(7)	-0.6(7)
O2	10.8(8)	11.7(9)	25(1)	2.6(7)	-1.7(7)	-2.6(7)
03	10.4(8)	10.7(8)	18.3(9)	0.3(7)	1.8(7)	0.9(7)
O4	15.9(9)	26(1)	12.6(9)	-2.1(8)	-2.5(7)	2.8(8)
05	14.7(9)	27(1)	11.1(8)	-1.1(8)	2.2(7)	1.2(8)
O6	11.8(8)	9.7(8)	18.3(9)	1.6(7)	0.5(7)	2.2(7)
S11	11.8(3)	11.2(3)	14.1(3)	0.6(2)	0.2(2)	-0.5(2)
S21	11.2(3)	10.3(3)	16.2(3)	1.0(2)	0.2(2)	-0.1(2)
S 31	9.9(3)	11.7(3)	15.1(3)	1.7(2)	0.6(2)	0.7(2)
S41	16.8(3)	15.5(3)	14.6(3)	0.3(2)	-2.2(2)	0.1(2)
S51	17.0(3)	27.2(4)	13.1(3)	0.7(3)	4.0(2)	2.8(3)
S 61	10.9(3)	11.9(3)	14.9(3)	1.1(2)	1.1(2)	0.8(2)
C11	18(1)	12(1)	24(2)	-2(1)	4(1)	-1(1)
C12	17(1)	19(1)	27(2)	-10(1)	-5(1)	5(1)
C21	16(1)	12(1)	22(1)	-2(1)	1(1)	1(1)
C22	14(1)	19(1)	24(2)	-3(1)	6(1)	-2(1)
C31	9(1)	18(1)	24(1)	-5(1)	-1(1)	1(1)
C32	17(1)	19(1)	27(2)	-10(1)	-5(1)	5(1)
C41	34(2)	20(2)	21(2)	6(1)	-3(1)	-4(1)
C42	49(2)	19(2)	26(2)	-9(1)	-20(2)	7.8(2)
C51	68(3)	13(2)	22(2)	-5(1)	11(2)	-4(2)
C52	76(3)	26(2)	20(2)	1(1)	6(2)	-19(2)
C61	11(1)	21(1)	24(2)	5(1)	0(1)	-1(1)
C62	23(2)	14(1)	23(2)	-7(1)	-5(1)	5(1)

Bond	Length [pm]	Bond	Length [pm]
S1-O11	144.2(2)	S3-O31	144.3(2)
S1-O12	144.4(2)	S3-O32	143.8(2)
S1-O13	144.6(2)	S3-O33	143.8(2)
S1-C1	185.3(2)	S3-C3	184.7(3)
C1-Cl11	176.4(3)	C3-Cl31	176.7(3)
C1-Cl12	176.7(3)	C3-Cl32	176.1(3)
C1-Cl13	176.9(3)	C3-C133	176.6(3)
S2-O21	144.8(2)	Fe1-O1	198.3(2)
S2-O22	144.3(2)	Fe1-O2	200.4(2)
S2-O23	144.1(2)	Fe1-O3	198.3(2)
S2-C2	185.5(3)	Fe1-O4	202.3(2)
C2-Cl21	177.3(2)	Fe1-O5	199.0(2)
C2-Cl22	176.4(2)	Fe1-O6	199.0(2)
C2-C123	176.6(2)		

 Table 185: Selcted Bond Lengths for [Fe(DMSO)₆][Cl₃CSO₃].

Table 186: Selected Bond Angles within [Fe(DMSO)₆][Cl₃CSO₃].

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]
O11-S1-O12	114.8(1)	Cl21-C2-S2	109.7(1)
O12-S1-O13	114.6(1)	C122-C2-S2	109.2(1)
O13-S1-O11	114.7(1)	Cl23-C2-S2	109.2(1)
O11-S1-C1	103.4(1)	Cl21-C2-Cl22	109.0(1)
O12-S1-C1	104.2(1)	Cl22-C2-Cl23	110.8(1)
O13-S1-C1	103.0(1)	Cl23-C2-Cl21	109.0(1)
Cl11-C1-S1	109.9(2)	O31-S3-O32	114.6(1)
Cl12-C1-S1	109.7(1)	032-S3-O33	115.1(1)
Cl13-C1-S1	108.6(1)	033-S3-O31	114.5(1)
Cl11-C1-Cl12	109.1(2)	O31-S3-C3	103.8(1)
Cl12-C1-Cl13	109.9(2)	O32-S3-C3	104.3(1)
Cl13-C1-Cl11	109.6(2)	O33-S3-C3	102.5(1)
O21-S2-O22	114.9(1)	Cl31-C3-S3	110.2(1)
O22-S2-O23	114.7(1)	Cl32-C3-S3	109.2(2)
O23-S2-O21	114.9(1)	Cl33-C3-S3	109.6(2)
O21-S2-C2	102.5(1)	Cl31-C3-Cl32	109.4(2)

O22-S2-C2	103.6(1)	Cl32-C3-Cl33	109.4(2)
O23-S2-C2	103.9(1)	Cl33-C3-Cl31	107.8(2)

Table 187: Torsion Angles within [Fe(DMSO)₆][Cl₃CSO₃].

Atom-Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom-Atom	Angle [°]
Cl11-C1-S1-O12	61.8(2)	Cl21-C2-S2-O21	-60.1(1)
O12-S1-C1-Cl12	-58.8(2)	O21-S2-C2-Cl22	59.3(2)
Cl12-C1-S1-O11	61.6(2)	Cl22-C2-S2-O22	-60.5(1)
O11-S1-C1-Cl13	-58.5(2)	Cl31-C3-S3-O31	59.2(2)
Cl13-C1-S1-O13	61.3(2)	O31-S3-C3-Cl32	-52.6(2)
O13-S1-C1-Cl11	-58.7(2)	Cl32-C3-S3-O33	56.8(2)
O22-S2-C2-C123	60.8(2)	O33-S3-C3-C133	-63.0(2)
Cl23-C2-S2-O23	-59.4(2)	Cl33-C3-S3-O32	57.3(2)
O23-S2-C2-Cl21	59.9(2)	O32-S3-C3-Cl31	-61.2(2)

Table 188: Hydrogen Atom Coordinates ($\mathring{A} \times 10^4$) and Isotropic Displacement Parameters ($\mathring{A}^2 \times 10^3$) for [Fe(DMSO)₆][Cl₃CSO₃].

Atom	x	у	Z.	U(eq)
H11A	9390(30)	11730(30)	6369(9)	18(8)
H11B	8320(30)	11400(30)	6586(11)	34(10)
H11C	8210(30)	11490(30)	6157(10)	32(10)
H12A	10380(30)	10020(30)	5871(9)	27(9)
H12B	9740(30)	8790(40)	5833(11)	39(10)
H12C	9050(30)	9970(30)	5715(10)	26(9)
H21A	6610(30)	3250(30)	6601(10)	29(9)
H21B	6860(30)	3380(30)	6175(9)	20(8)
H21C	5610(30)	2980(30)	6287(9)	27(9)
H22A	4640(30)	5790(30)	6793(9)	19(8)
H22B	4180(30)	4550(30)	6670(8)	16(8)
H22C	5270(30)	4660(30)	6945(10)	22(8)
H31A	11720(30)	5260(30)	6428(10)	29(9)
H31B	11500(30)	6580(30)	6231(9)	21(8)
H31C	11480(30)	6460(30)	6665(10)	30(9)
H32A	9970(30)	5590(30)	5767(10)	27(9)
H32B	10060(30)	4360(30)	5956(10)	31(9)
H32C	8790(30)	4930(30)	5888(9)	26(9)

H41A	6380(30)	9090(30)	5448(9)	21(8)
H41B	7240(30)	8320(30)	5207(9)	23(8)
H41C	5810(30)	8470(30)	5107(11)	36(10)
H42A	6210(40)	5240(40)	5404(11)	41(11)
H42B	5760(30)	6080(30)	5071(11)	34(10)
H42C	7210(40)	6080(40)	5152(12)	58(13)
H51A	7050(30)	8910(30)	7801(11)	34(10)
H51B	7410(40)	9560(40)	7457(13)	56(13)
H51C	8300(40)	8620(40)	7631(13)	57(14)
H52A	7930(50)	6440(40)	7634(13)	68(15)
H52B	6750(40)	5860(40)	7392(13)	59(13)
H52C	6430(40)	6600(40)	7732(13)	59(14)
H61A	3350(30)	8080(30)	6567(9)	20(8)
H61B	2960(30)	9150(30)	6316(9)	27(9)
H61C	3350(30)	7880(40)	6132(11)	37(10)
H62A	4680(30)	9480(30)	6933(9)	21(8)
H62B	5830(30)	10130(30)	6762(9)	27(9)
H62C	4520(30)	10570(30)	6654(10)	29(9)

$[La_{2}(H_{2}O)_{10}(NO_{3})_{2}(\mu-Cl_{3}CSO_{3})_{2}](Cl_{3}CSO_{3})_{2} \cdot 2 H_{2}O$

Table 189: Crystal Data and Structure	Refinement for $[La_2(H_2O)_{10}(NO_3)_2(\mu -$
$Cl_3CSO_3)_2](Cl_3CSO_3)_2 \cdot 2 H_2O.$	

Empirical formula	$C_4H_{24}Cl_{12}La_2N_2O_{30}S_4$
Formula Weight	705.86 g/mol
Temperature	100 K
Wavelength	71.073 pm (Mo _{Kα})
Crystal system	triclinic
Space group	PĪ
Unit cell parameters	<i>a</i> = 639.17(4) pm
	<i>b</i> = 1289.39(6) pm
	c = 1445.80(8) pm
	$\alpha = 63.542(2)^{\circ}$
	$\beta = 88.816(2)^{\circ}$

	$\gamma = 75.698(2)^{\circ}$
Volume	1028.2(1) Å ³
Ζ	1
Density (calculated)	2.280 g/cm ³
Absorption coefficient	3.126 mm ⁻¹
F(000)	684
Crystal size	0.154 x 0.046 x 0.038 mm ³
2θ Range for data collection	$3.588 - 54.996^{\circ}$
Index range	-8≤h≤8, -16≤k≤16, -18≤l≤18
Reflections collected	25914
Independent reflections	4705 [$R_{int} = 0.0265, R_{\sigma} = 0.0197$]
Completeness	99.8%
Absorption correction	Multi-Scan
Max./Min. Transmission	0.7482/0.6526
Refinement method	Least Squares
Data/Restraints/Parameters	4705/2/282
Goodness-of-fit on F^2	1.085
Final <i>R</i> Indices $[I \ge 2\sigma(I)]$	$R_1 = 0.0165, wR_2 = 0.0372$
R Indices (all data)	$R_1 = 0.0174, wR_2 = 0.0377$
Largest diff. peak and hole	$0.68/-0.61 \text{ e} \cdot \text{\AA}^{-3}$
CCDC Deposition Number	2324854

Table 190: Fractional Atomic Coordinates $(\times 10^4)$ and Equivalent Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $[La_2(H_2O)_{10}(NO_3)_2(\mu - Cl_3CSO_3)_2](Cl_3CSO_3)_2 \cdot 2 H_2O$.

Atom	X	у	Z,	U(eq)
La1	5573.3(2)	3913.8(2)	3359.1(2)	7.37(3)
S 1	447.8(7)	6631.8(4)	-139.5(3)	11.75(9)
011	2778(2)	6218(1)	-129(1)	14.5(3)
O12	-786(2)	6543(1)	-918(1)	18.2(3)
013	-329(2)	6169(1)	882(1)	15.4(3)
C1	-70(4)	8255(2)	-563(2)	18.5(4)
Cl11	1351(1)	8436.4(5)	363.7(4)	25.9(1)
Cl12	841(1)	8934.7(5)	-1788.3(4)	31.4(1)
Cl13	-2881(1)	8877.1(6)	-636.5(4)	32.8(1)
S2	7176.7(7)	6225.0(4)	4085.6(3)	8.14(8)

O21	9395(2)	6296(1)	4117(1)	12.1(3)
O22	6151(2)	6064(1)	5024(1)	12.1(3)
O23	6904(2)	5402(1)	3693(1)	11.8(3)
C2	5657(3)	7719.6(16)	3078(1)	12.2(4)
Cl21	6946.6(8)	8026.9(4)	1932.2(4)	18.5(1)
C122	5691.1(8)	8789.1(4)	3506.4(4)	17.5(1)
C123	2973.2(8)	7698.3(4)	2865.1(4)	17.3(1)
N1	4332(3)	1593(1)	3939(1)	11.9(3)
01	1803(2)	5274(1)	2840(1)	13.9(3)
O2	5692(3)	5651(1)	1601(1)	15.7(3)
O3	4609(3)	3519(1)	1836(1)	14.8(3)
O4	9029(2)	3346(1)	2700.(1)	17.2(3)
05	8561(2)	2772(1)	4795.(1)	12.9(3)
O6	6310(2)	1573(1)	4013(1)	15.0(3)
07	2960(2)	2562(1)	3818(1)	12.0(3)
08	3749(2)	745(1)	3974(1)	21.5(3)
09	9965(3)	-373(1)	4130(1)	19.2(3)

Table 191: Anisotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $[La_2(H_2O)_{10}(NO_3)_2(\mu - Cl_3CSO_3)_2](Cl_3CSO_3)_2 \cdot 2 H_2O$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
La1	7.20(5)	8.34(5)	7.89(5)	-4.72(4)	0.86(4)	-2.26(4)
S 1	10.6(2)	16.6(2)	8.9(2)	-6.4(2)	1.1(2)	-3.9(2)
011	11.0(6)	19.2(7)	14.0(7)	-8.7(6)	1.4(5)	-2.9(5)
O12	14.9(7)	30.7(8)	13.6(7)	-12.9(6)	1.0(5)	-8.1(6)
013	15.5(7)	21.2(7)	9.9(6)	-6.3(6)	3.3(5)	-7.1(6)
C1	22.(1)	16.5(9)	13.0(9)	-5.7(8)	2.2(8)	-1.0(8)
Cl11	37.6(3)	21.7(2)	24.0(3)	-14.6(2)	1.8(2)	-9.0(2)
Cl12	50.6(4)	21.7(3)	16.1(3)	-3.5(2)	11.9(2)	-10.4(2)
Cl13	27.4(3)	34.3(3)	21.7(3)	-10.8(2)	-3.5(2)	13.8(2)
S2	9.1(2)	8.2(2)	8.4(2)	-4.8(2)	1.4(2)	-2.9(2)
O21	10.0(6)	13.7(6)	14.5(7)	-7.6(5)	2.1(5)	-4.0(5)
O22	14.3(7)	13.1(6)	9.2(6)	-5.6(5)	3.0(5)	-3.4(5)
O23	15.8(7)	10.6(6)	12.8(6)	-7.6(5)	1.9(5)	-5.5(5)
C2	14.2(9)	13.2(8)	10.4(9)	-6.3(7)	1.9(7)	-3.6(7)
Cl21	24.3(3)	16.4(2)	11.1(2)	-3.6(2)	6.8(2)	-4.6(2)

Cl22	25.2(3)	10.6(2)	18.3(2)	-8.6(2)	-0.3(2)	-3.1(2)
Cl23	12.6(2)	21.1(2)	16.6(2)	-7.8(2)	-1.9(2)	-2.7(2)
N1	12.7(8)	10.6(7)	12.7(8)	-5.5(6)	0.5(6)	-2.8(6)
O1	11.3(6)	17.0(7)	11.6(7)	-7.8(6)	-0.3(5)	1.7(5)
O2	15.2(7)	19.3(7)	10.6(7)	-3.2(6)	-0.7(6)	-8.3(6)
O3	12.1(7)	24.7(8)	12.7(7)	-11.5(6)	3.4(6)	-7.8(6)
O4	9.3(6)	30.8(8)	12.5(7)	-12.5(6)	1.3(5)	-1.8(6)
05	14.2(7)	11.4(7)	13.3(7)	-6.4(6)	-3.0(5)	-1.7(6)
O6	9.4(6)	13.0(6)	22.5(7)	-7.9(6)	-0.6(5)	-2.6(5)
O7	10.1(6)	10.7(6)	16.7(7)	-8.2(5)	1.4(5)	-1.3(5)
08	20.7(8)	14.8(7)	35.5(9)	-14.9(7)	1.9(7)	-8.7(6)
09	18.1(8)	15.2(7)	22.6(8)	-8.0(6)	0.7(6)	-2.3(6)

Table 192: Selected Bond Lengths for $[La_2(H_2O)_{10}(NO_3)_2(\mu-Cl_3CSO_3)_2](Cl_3CSO_3)_2 \cdot 2 H_2O.$

Bond	Length [pm]	Bond	Length [pm]
S1-O11	145.1(1)	C2-Cl22	175.0(3)
S1-O12	144.8(2)	C2-C123	175.8(2)
S1-O13	145.4(1)	La1-O1	250.2(1)
S1-C1	184.1(2)	La1-O2	254.7(1)
C1-Cl11	176.3(3)	La1-O3	258.9(2)
C1-Cl12	175.3(2)	La1-O4	246.1(1)
C1-Cl13	176.1(3)	La1-O5	248.5(1)
S2-O21	144.6(2)	La1-O6	264.6(2)
S2-O22	144.7(2)	La1-O7	257.5(2)
S2-O23	145.4(2)	La1-O22	257.3(2)
S2-C2	184.7(2)	La1-O23	250.7(2)
C2-Cl21	176.0(2)	La1-La1	644.84(5)

Table 193: Selected Bond Angles for $[La_2(H_2O)_{10}(NO_3)_2(\mu-Cl_3CSO_3)_2](Cl_3CSO_3)_2 \cdot 2 H_2O.$

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom	Angle [°]	
O11-S1-O12	113.49(8)	O21-S2-O22	114.98(8)	
012-\$1-013	114.09(8)	O22-S2-O23	113.58(8)	
O13-S1-O11	114.13(8)	O23-S2-O21	112.61(8)	
O11-S1-C1	104.41(9)	O21-S2-C2	104.71(8)	

O12-S1-C1	104.99(9)	O22-S2-C2	105.42(8)
O13-S1-C1	104.29(9)	O23-S2-C2	104.20(8)
Cl11-C1-S1	107.6(1)	Cl21-C2-S2	108.0(1)
Cl12-C1-S1	109.3(1)	Cl22-C2-S2	108.7(1)
Cl13-C1-S1	108.9(1)	Cl23-C2-S2	109.1(1)
Cl11-C1-Cl12	110.6(1)	Cl21-C2-Cl22	110.5(1)
Cl12-C1-Cl13	109.7(1)	Cl22-C2-Cl23	110.3(1)
Cl13-C1-Cl11	110.7(1)	Cl23-C2-Cl21	110.2(1)

Table 194: Torsion Angles for $[La_2(H_2O)_{10}(NO_3)_2(\mu - Cl_3CSO_3)_2](Cl_3CSO_3)_2 \cdot 2 H_2O$.

Atom-Atom-Atom	Angle [°]	Atom-Atom-Atom-Atom	Angle [°]
Cl12-C1-S1-O11	58.9(1)	Cl21-C2-S2-O21	54.0(1)
O11-S1-C1-Cl11	-61.3(1)	O21-S2-C2-Cl22	-65.9(1)
Cl11-C1-S1-O13	58.7(1)	Cl22-C2-S2-O22	55.8(1)
O13-S1-C1-Cl13	-61.3(1)	O22-S2-C2-Cl23	-64.6(1)
Cl13-C1-S1-O12	59.0(1)	Cl23-C2-S2-O23	55.3(1)
O12-S1-C1-Cl12	-60.8(1)	O23-S2-C2-Cl21	-64.5(1)

Table 195: Hydrogen Atom Coordinates $(\mathring{A} \times 10^4)$ and Isotropic Displacement Parameters $(\mathring{A}^2 \times 10^3)$ for $[La_2(H_2O)_{10}(NO_3)_2(\mu - Cl_3CSO_3)_2](Cl_3CSO_3)_2 \cdot 2 H_2O.$

Atom	x	у	Z.	U(eq)
H1A	1040.9	5611.27	2238.39	21
H1B	1015.4	5571.85	3205.91	21
H2A	4970(50)	5850(20)	1110(20)	25(7)
H2B	6720(50)	5810(30)	1420(20)	33(9)
H3A	3540(60)	3520(30)	1600(30)	41(9)
H3B	5360(60)	3590(30)	1420(30)	41(9)
H4A	10272.74	2976.8	3078.45	26
H4B	9334.31	3478.05	2074.77	26
H5A	9120(50)	3030(20)	5070(20)	25(7)
H5B	9040(50)	2100(30)	5080(20)	37(9)
H9A	10840(60)	30(30)	4040(30)	47(10)
H9B	8740(50)	110(30)	4200(20)	37(8)

5.2. Powder X-Ray Diffraction

Ag[H₃CSO₃]



Figure 100: Powder diffraction pattern and Rietveld refinement of $Ag[H_3CSO_3]$. The sample was measured with $MO_{K\alpha 1}$ radiation in a 0.3 mm capillary.

Table 196:	Rietveld	Refinement	of Ag[H ₃ CSO ₃]
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Parameters	Rietveld Refinement	Single Crystal
<i>a</i> [pm]	872.8(3)	869.1(1)
<i>b</i> [pm]	579.6(3)	574.18(6)
<i>c</i> [pm]	829.7(4)	823.4(1)
V [Å ³]	413.05(3)	404.23(9)
T [K]	293	100
Rwp	12.220	
Rexp	7.101	
Rp	8.509	
gof	1.721	

$Rb_2[H_3CSO_3]_2 \cdot H_2O$



Figure 101: X-ray powder diffraction pattern of the remaining sample after the DSC measurement of Rb₂[H₃CSO₃]₂ · H₂O, heated with 5 K/min to a maximum temperature of 1260 K. Simulated pattern for Rb₂SO₄ is given in blue.^[147] The sample was measured as flat preparation in Bragg-Brentano geometry with Cu_{Kal} radiation.

Methanedisulphonic Acid (MSA)



Figure 102: X-ray powder diffraction pattern of MSA in black with simulated pattern from $(H_3O)_2[CH_2(SO_3)_2]$ from Sartori in blue.^[109] The sample was measured as a flat preparation with MO_{Kal} radiation.

$Rb_2[CH_2(SO_3)_2]$



Figure 103: Powder diffraction pattern and Rietveld refinement of Rb2[CH2(SO3)2]. The sample was measured with $Mo_{K\alpha l}$ radiation in a 0.3 mm capillary.

able 197: Rietveld Refinement of Rb ₂ [CH ₂ (SO ₃) ₂]				
Parameters	Rietveld Refinement	Single Crysta		
<i>a</i> [pm]	1295.2(3)	1282.05(6)		
<i>b</i> [pm]	778.8(1)	771.93(4)		
<i>c</i> [pm]	758.7(1)	756.62(3)		
β[°]	90.85(9)	91.310(2)		
V [Å ³]	765.3(3)	748.60(6)		
T [K]	293	100		
Rwp	2.531			
Rexp	2.210			

1.649

1.145

Rp

gof



Figure 104: *X*-ray powder diffraction pattern of the remaining sample after the DSC measurement of Rb₂[CH₂(SO₃)₂], heated with 5 K/min to a maximum temperature of 973 K. The sample was measured as flat preparation in Bragg-Brentano geometry with Cu_{Kal} radiation. Simulated pattern for Rb₂SO₄ is added in blue.^[147]

$BaK_2[CH_2(SO_3)_2]_2$



Figure 105: X-ray powder diffraction pattern of the residual sample after the reaction of $K_2[CH_2(SO_3)_2]$ with $BaCl_2$ (black) and simulated pattern for $BaSO_4$ for comparison (red).^[115] The sample was measured in a 0.3 mm capillary with Mo_{Kal} radiation.

$K_3[CH(SO_3)_3] \cdot H_2O$



Figure 106: X-ray powder diffraction pattern of the remaining sample after the DSC measurement of $K_3[CH(SO_3)_3] \cdot H_2O$ heated with 7 K/min to a maximum temperature of 823 K. The sample was measured in a 0.3 mm capillary with $Mo_{K\alpha l}$ radiation. Simulated pattern for K_2SO_4 is added in red.^[148]

$(H_3O)_3[CH(SO_3)_3]$



Figure 107: X-ray powder diffraction pattern of $(H_3O)_3[CH(SO_3)_3]$, measured in a 0.3 mm capillary with Mo_{Kal} radiation (black, cross) with Rietveld refinement for the modification, crystallising in P6₃.^[101] The difference curve is added in blue.

Parameters	Rietveld Refinement	Single Crystal
<i>a</i> [pm]	1391.5(2)	1365.48(2)
<i>b</i> [pm]	1391.5(2)	1365.48(2)
<i>c</i> [pm]	942.9(1)	931.93(1)
V [Å ³]	1538(2)	1504.82(5)
T [K]	293	150
Rwp	18.802	
Rexp	14.157	
Rp	15.040	
gof	1.328	

Table 198: Rietveld Refinement of (H₃O)₃[CH(SO₃)₃] for the Hexagonal Modification



Figure 108: X-ray powder diffraction pattern of $(H_3O)_3[CH(SO_3)_3]$, measured in a 0.3 mm capillary with Mo_{Kal} radiation (black, cross) with Rietveld refinement for the modification, crystallising in R3c. The difference curve is added in blue.

Rietveld Refinement	Single Crystal
1327.9(1)	1322.13(4)
1327.9(1)	1322.13(4)
980.57(8)	977.40(5)
1492(2)	1479.6(1)
293	99
25.528	
20.907	
19.515	
1.221	
	Rietveld Refinement 1327.9(1) 1327.9(1) 980.57(8) 1492(2) 293 25.528 20.907 19.515 1.221

Table 199: Rietveld Refinement of (H₃O)₃[CH(SO₃)₃] for the Trigonal Modification

 $Ag_9[C(SO_3)_4]_2Cl \cdot 4 H_2O$



Figure 109: X-ray Powder diffraction pattern of the collected sample from the ampoule, delivering the $Ag_9[C(SO_3)_4]_2Cl \cdot 4 H_2O$ single crystal. The sample was measured with Mo_{Kal} radiation in a 0.3 mm capillary. Simulated pattern for Ag_2SO_4 is added in red.^[108]

K[Cl₃CSO₃] · H₂O



Figure 110: Measured powder diffraction pattern (black) and simulated pattern from the single crystal (green) for $K[Cl_3CSO_3] \cdot H_2O$. The sample was measured with MO_{Kal} radiation in a 0.3 mm capillary.

5.3. Thermal Analysis

K[H₃CSO₃]



Figure 111: DTA/TG curve for K[H₃CSO₃], heated with 5 K/min under steady nitrogen gas flow to a maximum temperature of 1268 K.
5.4. Vibrational Spectroscopy

$(H_{3}O)_{2}[CH_{2}(SO_{3})_{2}]$



Figure 112: Measured IR-spectrum for $(H_3O)_2[CH_2(SO_3)_2]$ in black with calculated bands for the $[CH_2(SO_3)_2]^{2-}$ anion in olive green. For the calculated data a scaling factor of 0.97 was applied.

Alkali Salts of MDA



Figure 113: Measured IR-spectra of Li-Cs methanedisulphonate with calculated bands for the $[CH_2(SO_3)_2]^{2-}$ anion in black. The measured IR-spectra are normalised and an offset is applied.



Figure 114: Excerpt of the measured IR-spectra of all alkali methanedisulphonates with calculated vibrational bands in black.



*Figure 115: IR-Spectrum of a sample of Rb*₃[*CH*(*SO*₃)₃] *prepared under inert conditions in a glovebox without addition of solvent.*



Figure 116: Excerpt of the measured and calculated IR data for silver-, potassium-, lithium- and rubidium methanetrisulphonate from 1500 to 500 cm⁻¹.

5.5. NMR-Spectroscopy

$CH_2(SO_2Cl)_2$



Figure 117: DEPTQ ¹³C-NMR (75 MHz) of a sample of CH₂(SO₂Cl)₂ measured in CDCl₃.



Figure 118: ¹H-NMR spectrum (300 mHz) of a sample of $CH_2(SO_2Cl)_2$ measured in CDCl₃. Small traces of the acid are visible ($\delta/ppm = 11.68$).

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Erklärung zur Dissertation

Hiermit versichere ich an Eides statt, dass ich die vorliegende Dissertation selbstständig und ohne die Benutzung anderer als der angegebenen Hilfsmittel und Literatur angefertigt habe. Alle Stellen, die wörtlich oder sinngemäß aus veröffentlichten und nicht veröffentlichten Werken dem Wortlaut oder dem Sinn nach entnommen wurden, sind als solche kenntlich gemacht. Ich versichere an Eides statt, dass diese Dissertation noch keiner anderen Fakultät oder Universität zur Prüfung vorgelegen hat; dass sie – abgesehen von unten angegebenen Teilpublikationen und eingebundenen Artikeln und Manuskripten - noch nicht veröffentlicht worden ist, sowie, dass ich eine Veröffentlichung der Dissertation vor Abschluss der Promotion nicht ohne Genehmigung des Promotionsausschusses vornehmen werde. Die Bestimmungen dieser Ordnung sind mir bekannt. Darüber hinaus erkläre ich hiermit, dass ich die Ordnung zur Sicherung guter wissenschaftlicher Praxis und zum Umgang mit wissenschaftlichen Fehlverhalten der Universität zu Köln gelesen und sie bei der Durchführung der Dissertation zugrundeliegenden Arbeiten und der schriftlich verfassten Dissertation beachtet habe und verpflichte mich hiermit, die dort genannten Vorgaben bei allen wissenschaftlichen Tätigkeiten zu beachten und umzusetzen. Ich versichere, dass die eingereichte elektronische Fassung der eingereichten Druckfassung vollständig entspricht.

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Teilpublikationen

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Alisha Mertens, David van Gerven, Hyunsong Lee and Mathias S. Wickleder Synthesis and Characterization of the Trichlates [N(CH₃)4][Cl₃CSO₃], [NH4][Cl₃CSO₃], and the Dichlate [NH4][Cl₂CHSO₃]

Eur. J. Inorg. Chem. 2023, e202300535, 1-7.

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Alisha Mertens, Katrin Eppers, David van Gerven and Mathias S. Wickleder The Molecular Structures of Lithium Trichlate, Li[Cl₃CSO₃] · 2 H₂O, and Lithium Tribrate, Li[Br₃CSO₃] · 2 H₂O

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