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Technetium - The Unknown Center of the Periodic Table

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It took 78 years from Mendeleev's proposal of an existence of "eka-manganese" (1869) until it was finally named as technetium (Tc) in 1947. Another 78 years have passed since then. This provides a good occasion to pinpoint what we know and what we still do not know of this radioelement. Technetium is placed near the center of the Periodic Table, in the center of the groups 6, 7, and 8. Some chemical properties of the elements surrounding technetium show trends within the columns or along the rows of the Periodic Table, but a consistent interpretation of these trends is lacking as long as the knowledge on technetium remains incomplete. This is especially remarkable as, on the other hand, the isotope ^{99m}Tc is applied on a daily basis in nuclear medicine. The aim of this paper is to review the fundamental understanding of technetium chemistry, mostly focusing on the research of the last decade, its implications, and its future perspectives. These developments show a picture of growing connections between physicochemical data, fundamental inorganic chemistry, organometallic and coordination chemistry, computational chemistry, and geochemistry.

Introduction

A Brief History of Technetium

The existence of an element below manganese (eka-manganese) was proposed as early as 1869 by Mendeleev.[1] The story of its final discovery has been told often, e.g.by Zingales.[2] It was finally discovered[3] and named as technetium,[4] 78 years after Mendeleev's proposal.

Tc turned out to be a radioelement, with isotopes ranging from ^{85}Tc to ^{120}Tc, and varied half–lives from ns to My. There is an extremely low natural abundance of Tc on Earth as a consequence of spontaneous fission of primordial ^{238}U, however, the isotope ^{99}Tc (half-life 211,000 years) is mostly anthropogenic since it is one of the major fission products of nuclear fission of ^{235}U and ^{239}Pu, with a fission yield of around 6%.[5] A typical nuclear power reactor today produces around 20 kg of ^{99}Tc annually. So it is to no surprise that especially in the earlier days, when radiation safety measures were less strict, a lot of studies have been performed to characterize technetium physically and chemically. A good overview of these works is given in Schwochau - Technetium: Chemistry and Radiopharmaceutical Applications.[6]

Since the naming of technetium, nearly another 78 years have passed, and today, its short–lived isomer ^{99m}Tc (half-life 6 hours) is the most applied radioisotope in medicine with roughly 25 million applications per year (that is, almost one every second), mostly for SPECT (single photon emission computer tomography), for which the 140 keV gamma is very convenient.[7] For this purpose, roughly 1 g of ^{99}Mo are produced annually by reprocessing neutron-irradiated highly enriched ^{235}U.[8] ^{99}Mo is fixated on commercial alumina columns (generators) from which Tc is eluted as pertechnetate $[TcO_4]^-$ in physiological NaCl solution. For this reason, Tc has a great significance for humanity despite its artificial origin.

Even though ^{99m}Tc is such an important nuclide for radiopharmacy, radiation protection rules have become more restrictive, and research, particularly on ^{99}Tc, has been stagnating in the last decades (see Figure 1). However, apart from general regulatory and safety measures, ^{99}Tc is chemically easy to handle even in gram amounts. It emits mostly low energy beta radiation (297 keV), which can be easily shielded.

General Differences in the Chemistry Between ^{99}Tc and ^{99m}Tc

Contrary to ^{99}Tc, the chemistry of ^{99m}Tc is mostly performed with nanomolar amounts due to its higher specific radioactivity. This strongly influences reaction kinetics and therefore might open different reaction pathways. ^{99m}Tc chemistry has been focused around medical applications, establishing certified "kits" that allow the easy preparation of different ^{99m}Tc

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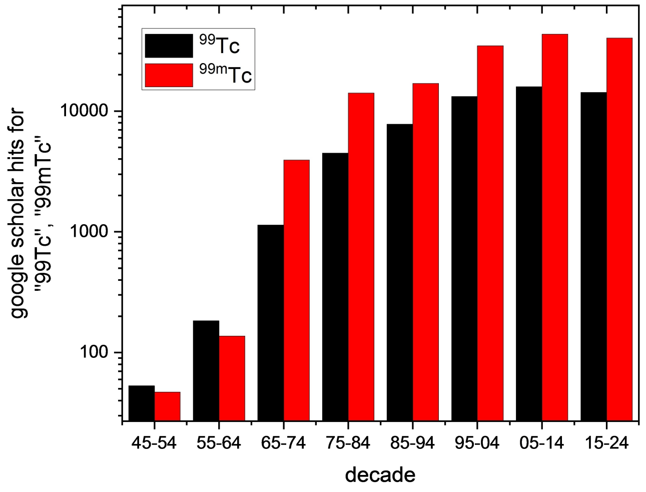


Figure 1. Number of publications referring to searches on google scholar for "99Tc" and "99mTc" per decade.[9]

compounds. Because the final preparations will always have to be performed with nanomolar amounts, also characterization of the final products is very challenging, while trying to use the more stable ^{99}Tc may yield different results due to kinetic differences, as the synthesis of ^{99}Tc complexes is carried out at much higher concentrations than that of ^{99m}Tc complexes.[10] Consequently, such differences turn out to be interesting from the viewpoint of fundamental chemistry. For example, macroscopic amounts of $[^{99}TcO_4]^-$ do not form arene sandwich complexes while ^{99m}Tc (in imperatively low concentration) leads to a yield of 90% under otherwise similar conditions.[10] This is a common concern in radiopharmacy: because the comparison of nanomolar and micromolar amounts of products might fail and X-ray diffraction (XRD) is not available for nanomolar amounts, the structure of some ^{99m}Tc pharmaceuticals must be considered unknown, presenting a challenge for licensing processes. But even if the structures of ^{99m}Tc compounds might not be replicated with ^{99}Tc due to kinetics - the existing database of ^{99}Tc still lists far fewer compounds than that of the surrounding elements of the Periodic Table (Figure 2). The geochemistry of Tc in the context of a final disposal of nuclear waste might face similar problems, e.g., when leaching of nanomolar amounts might still lead to considerable dissolution of material over a time span of several days, years or even millennia.

Other Isotopes of Technetium

Recently, further Tc isotopes have attracted interest: The short-lived ^{101}Tc (half-life 14 min) has been suggested for possible theragnostic applications,[12,13] and can be produced using neutron generators[13] or secondary neutrons of the $^{18}O(p, n)^{18}F$ reaction in a cyclotron.[12] This simultaneous production provides a possible alternative route to isotopes of Tc suitable for use in radiopharmacy. The isotopes ^{96}Tc (half-life 4,28 d) and ^{97}Tc (half-life 4.2 My) have been considered as a tracer/spike pair in ultra-trace analysis of ^{99}Tc with AMS (Accelerator Mass Spectrometry).[14] In addition, ^{94m}Tc (half-life 52 min) has been used in the past and might be a possible nuclide for positron emission tomography.[15,16] All these possible applications are subject to the same restrictions comparing nanomolar and micromolar amounts described above. Thus, in all these cases, a deep understanding of fundamental Tc inorganic chemistry is a prerequisite for a successful utilization of these isotopes.

Scope of this Work

Recent findings and scientific surprises, which are detailed below, have inspired a small but very diverse and lively community to continue ^{99}Tc research. The aim of this concept paper is to set a focus on these important developments of the last decade and their implications and future perspectives. Consequently, the sections of this are devoted to different aspects of technetium chemistry, dealing with

I) physicochemical data
II) fundamental inorganic chemistry
III) organometallic and coordination chemistry

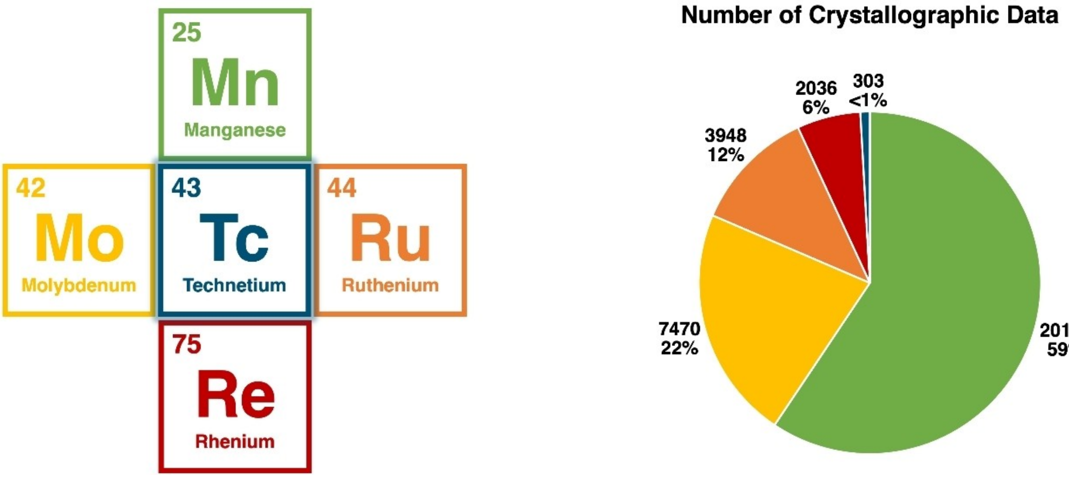


Figure 2. Number of structures in the Inorganic Crystal Structure Database (ICSD) database for Tc and its neighbors in the Periodic Table.[11]

IV) computational chemistry
V) geochemistry

We will not focus on radiopharmaceutical applications in detail, and only touch on these where they provide relevant material as a starting point for ^{99}Tc chemistry. Extensive coverage has been provided by others elsewhere, e.g., the recent review of Duatti and references therein.[17]

I Physicochemical Data

Many measurements of classical physicochemical data of Tc compounds or alloys (like melting points, thermodynamic data, critical temperatures, etc.) require macroscopic amounts of Tc, i.e., more than just a few mg that are sufficient for XRD (X-ray Diffraction) or X-ray absorption spectroscopy (XAS) methods. Therefore, most of these data originate from earlier times in which fewer lab restrictions have been in place, see Schwochau - Technetium: Chemistry and Radiopharmaceutical Applications.[6] Nevertheless, there are some recent results, namely heat capacity measurements,[18] and a book on electrochemistry.[19]

From our point of view, there are two important developments in the field of physicochemical data in a wider sense, which are important for the characterization of Tc compounds using instrumental analytics: The first development concerns DFT (Density Functional Theory) calculations of chemical shifts in ^{99}Tc nuclear magnetic resonance (NMR). This work, e.g. Chatterjee et al., Bühl, or Hall et al. is generally ambitious because the number of experimental chemical shift data for Tc comprises about only 500 data points (not corrected for doubles).[20–23] However, recent developments show that if solvatisation is taken into account and multi-step calculations are being used, Tc shifts in radiopharmaceuticals can be satisfactorily determined[24] and Kuznetsov *et al.* have recently pointed out the "pivotal role of ^{99}Tc in solid-state and molecular chemistry".[25] Secondly, the measurement of XAS at the L_3 edge using synchrotron radiation has proven suitable for the characterization of Tc oxidation states.[26,27] XANES (X-ray Absorption Near Edge Spectroscopy) can determine oxidation states and can give clues to electronic structure and geometry while EXAFS (Extended X-Ray Absorption Fine Structure) can be used to probe the Tc neighboring atoms and give accurate inter-atomic distances."; both techniques work very well with mg or even μg amounts. Besides these recent developments it is worth to mention that already Schwochau[6] reported on IR (infrared), Raman or UV-visible as well as EPR (electromagnetic paramagnetic resonance) spectroscopy, LPAS (laser induced photoacoustic spectroscopy) or mass spectrometry. All these methods are utilized to characterize Tc compounds whenever the necessary amounts are available, but we are not aware of significant recent method developments. The only exception here might be the detection of Tc with liquid electrode plasma optical emission spectrometry.[28]

II Fundamental Inorganic Chemistry

Despite the fact that Tc has been known for over 80 years now, less is known about its systematics within the Periodic Table, compared to most other transition elements. Recent developments concerning fundamental inorganic technetium chemistry consider the binary, ternary and quarternary technetium complexes with simple ligands, like halides or oxyhalides as well as pertechnetate chemistry in water, in super acidic and in super basics conditions. Especially, Tc polyoxometallate structures have been identified; several of these developments are strongly influenced by redox processes which often mitigate the easy transfer of rhenium chemistry to Tc.

Binary, Ternary and Quarternary Technetium Complexes with Simple Ligands

When examining crystallographically characterized technetium compounds in the inorganic database,[11] it seems reasonable to begin by comparing binary technetium salts. Although relatively few technetium compounds are known compared to those of other d-block elements, a selected range of important technetium salts can be discussed. Besides the few characterized technetium hydrides and borides, such as TcH, Tc_3B, Tc_7B_3, and TcB_2, salts of the group 14 elements remain scarcely studied by XRD.[29,30]

Hydrides are potential starting materials for Tc chemistry with acidic ligands that serve as a source for various anions. The recent reinvestigation of $[TcH_3(PPh_3)_4]$ and its reaction product with CO, *mer-trans*-$[TcH(CO)_3(PPh_3)_2]$, made a hydride complex of Tc available in sufficient quantity. *Mer-trans*-$[TcH(CO)_3(PPh_3)_2]$ reacts with HX to give corresponding di- or tricarbonyl complexes. The parallel oxidation of the two *trans*-PPh_3 ligands leads to an isomerization under formation of the *fac*-$Tc\{CO\}_3^+$ core. The reactions are easily monitored by ^{99}Tc NMR.[31]

However, the crystal structures of technetium's pentel and chalcogen compounds are better explored. The structure chemistry of certain binary halides has also been known since 1966.[32] Four halogen compounds have been elucidated through X–ray crystallography, with $TcBr_3$, $TcBr_4$ $TcCl_3$, and $TcCl_4$ featuring technetium in the +3 and +4 oxidation states.[32–35]

The discovery of new binary halides of technetium is important to understand the potential speciation of technetium in halide-containing media, but also offers an intriguing possibility for the study of coordination chemistry. Like for other elements of the Periodic Table, binary halides in some cases represent self-adducted dimers of coordinatively unsaturated species that may govern the reactivity of such compounds, making them ideal starting materials. Additionally, such compounds shed light on the intrinsic differences of manganese, technetium and rhenium within group 7 as well as differences to group 6 and 8,[36–38] e.g., for Tc and Fe, only 2 fluorides (TcF_5 and TcF_6) are known. Fe is the only other element within these nine elements for which only 2 fluorides are known. Several similarities between elements are observed across their group boundaries, as exemplarily illustrated in Figure 3. In this light,

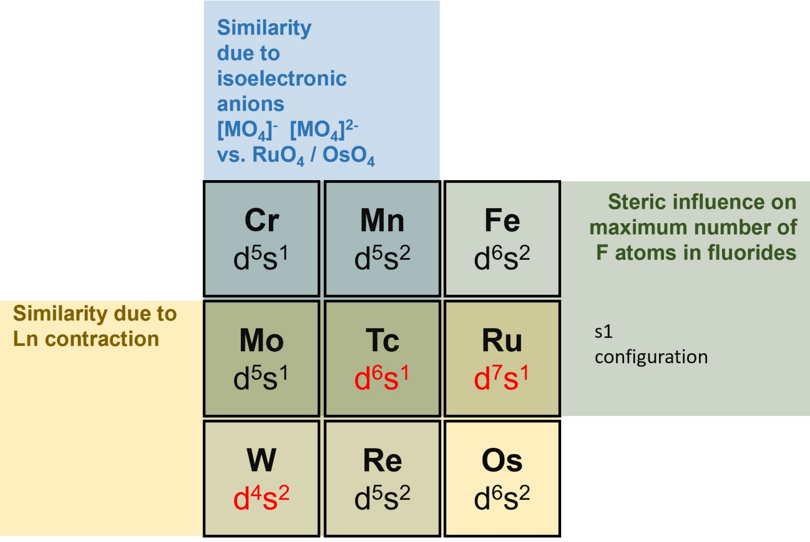


Figure 3. Groups 6 and 7 show a similarity to their isoelectronic oxoanions. While there is a general similarity of the ionic radii of period 5 and 6 due to the lanthanoid contraction, e.g. the formation of ReF_7 is observed, but not of TcF_7. The "odd" ground state electron configurations of d^6s^1 (Tc), d^7s^1 (Ru) and d^4s^2 (W) occur only once and are distributed apparently randomly across groups and periods.

understanding the chemistry of Tc which is in the center of this "block-of-nine" will lead to a deeper understanding of trends of chemistry of these elements.

Among the most important class of inorganic compounds are technetium oxyfluorides and fluorides, due to their role in the nuclear fuel cycle. Relatively few of these have been prepared. Some relevant contributions in recent years include $[TcO_3F]$, $[TcOF_5]$, $[Tc_2O_2F_9]^+$ and $[TcOF_4]^+$.[39–41] Adsorption enthalpies of oxychlorides and oxyfluorides of group 7 elements (inter alia) have been correlated with their respective boiling points.[42] Earlier results of this work were used for the characterization of bohrium (element 107) as the 4th member of the group 7 elements.[43] After the development of a new synthesis for $[TcF_6]^{2-}$ a number of nitrosyl-containing technetium fluoride complexes in low oxidation states have been prepared. There is a remarkable range of oxidation states in these compounds (I, II, III, IV and VI).[39,44–50]

Of the pnictogens, in addition to the nitrogen compound Tc_4N_3,[51] three phosphorus-containing compounds with technetium in oxidation states $+1$, $+2$, and $+3$ (TcP_3, TcP_4, Tc_2P_3, Tc_3P) have long been synthesized,[52–54] occurring as phosphides or polyphosphides. In contrast, only two technetium oxides have been thoroughly characterized via X-ray techniques. Tc_2O_7 and TcO_2, which can be obtained by heating Tc_2O_7.[55,56]

When expanding the focus from binary to ternary and quaternary technetium compounds, the number of crystallographically characterized structures increases significantly. Beginning with halogen oxides, four single-crystal structures have been identified. In addition to the oxyfluorides mentioned above there are $TcOF_4$, TcO_2F_3, and $TcO_2F_3{\cdot}TcO_3F$, which crystallize with technetium in high oxidation states of $+6$ and $+7$.[39–41] *Via* fluoride ion donation of TcO_2F_3 even a xenon compound with the formula $TcO_2F_3{\cdot}XeO_2F_2$ as well as the antimony species $TcO_2F_3{\cdot}SbF_5$ has been crystallized.[44] In 2008, $Bi_2Tc_2O_6$ was synthesized from Bi_2O_3 and TcO_2 at 700 °C, with Bi_3TcO_8 subsequently obtained through further reaction with Bi_2O_3.[57] Additionally, a spinel-type compound with the composition $TcCo_2O_4$ has been structurally characterized in detail.[58,59]

Moreover, compounds such as TcA_2O_4 ($A=$ Mg, Mn, Sr), with technetium in the $+4$ oxidation state, have also been synthesized. The perovskite structure $SrTcO_3$ is a compound that has been extensively investigated, including temperature-dependent measurements and investigations of its magnetic behavior. Apart from the aforementioned perovskite, related compounds with the formula $A'TcO_3$ ($A'=$ Ba, Ca, Cd, Pb) have also been structurally elucidated.[58,60] Compounds containing higher oxygen content are $A''_2Tc_2O_7$ ($A''=$ Cd, Dy, Er, Nd, Sm).[58–63]

Recent Developments in Pertechnetate Chemistry

Many technetium compounds were synthesized starting from pertechnetates, because the pertechnetate anion $[TcO_4]^-$ is the typical chemical form of Tc when separated from the fission product cocktail. Therefore, it is essential to consider both earlier findings and the most recent developments regarding pertechnetates.

Pertechnetates in Water

Up until recently, only six pertechnetate salts have been known, while for its neighbors (chromate, molybdate, tungstate) several species are known already as mineralogical samples, and even more from chemical research.[11] Extending the library of known pertechnetate salts across the Periodic Table showed, for instance, the unexpected formation of a yellow manganese pertechnetate complex.[64] In the presence of mercury, both the formation of a mercury(I) pertechnetate and a mercury(II) pertechnetate could be observed, which may open the path to mixed oxidation state complexes, allowing to study the redox properties of such compounds in more detail. In lanthanoid complexes it could be shown that these may form with varying degrees of hydration, indicating that water plays indeed a pivotal role in Tc coordination chemistry, and that the removal of water may not just alter the solid-state structure, but also its redox chemistry. It is remarkable that, with exceptions, many compounds of Re and Tc of the s, p and d block were observed to be isostructural, while significant differences occur between the lanthanoid pertechnetates and the lanthanoid perrhenates, see Strub et al.[64] The library of pertechnetate salts was also furthered extended with the synthesis of tetravalent zirconium, hafnium, and thorium pertechnetates.[65,66] Investigations by small-angle X-ray scattering (SAXS) suggested that the M^{IV}–TcO_4^- (M=Zr, Hf and Th) bonding persists in solution, and pertechnetate shows more extensive binding to $Zr/Hf/Th^{IV}$ than perrhenate in solution.[65,66] Simulating nuclear fuel reprocessing, Zr–XO_4 solvent extraction studies showed that pertechnetate can enhance extraction of Zr^{IV}.[65]

Pertechnetate in Super Acidic Conditions

Likewise, as the solubility of Tc in water has been the most useful aspect of its chemistry in terms of biological applications, little is known about the edges of the pH scale and how pertechnetate reacts in super acidic or super basic solutions. Remarkable progress in the detection of Tc species in solution of sulfuric acid (H_2SO_4), perchloric acid ($HClO_4$), nitric acid (HNO_3), and triflic acid (CF_3SO_3H) has been made over the last years. Investigations by XAS and UV-VIS spectroscopy revealed, that the dominating species contain the metal in the oxidation states VII, V, and even VI.[67–69] In order to understand the redox chemistry of Tc in these acids it is necessary to investigate the formed compounds in the solid state.

Pertechnetate is auto-reduced in triflic acid solutions, that is without the addition of a reducing agent. This is one indicator that reduction to lower valent species may occur given the right conditions, potentially even in the environment. Given different cations, more complex systems and solid-state networks could be synthesized,[70,71] see Figure 4. Structurally, $TcO_3[CF_3SO_3]$ is very similar to the fluorosulfate $TcO_3[FSO_3]$, one of the few known oxoanionic technetium compounds.[72]

The formation of polyoxometallates (POMs) of Tc from pertechnetate is another mystery that slowly gets solved,[73] see Zegke et al.[70] In solutions of pertechnetic acid these may form upon concentrating the stock solution, forming dark red materials that are highly oxygen- and moisture-sensitive. These Tc POMs contain Tc in different oxidation states (+V and +VII), and emerge from auto-reduction processes that depend on the Tc redox potentials and have not been observed by homolog Re compounds.

Synthetically, it will be challenging to transfer the chemistry of pertechnetic acid into non–aqueous systems. However, excluding water as a competing ligand, it may allow the isolation of systems that are too hygroscopic at ambient conditions, such as chromium pertechnetate. Further including redox-active cations in this system may help to analyze how strong the oxidation capacity of Tc is in the solid state, and whether reduced Tc(VI) species could be formed.

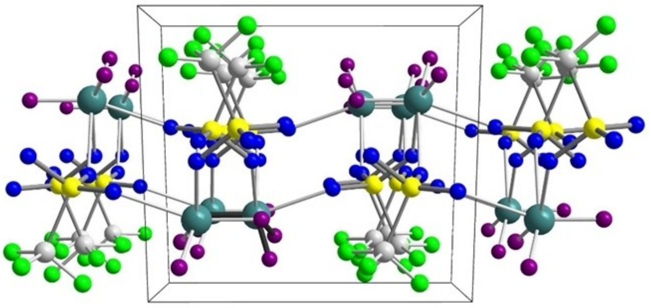


Figure 4. Crystal structure of $TcO_3[CF_3SO_3]$.[69] The distances to the oxide ligands (violet) are by about 0.5 Å shorter than the respective distances to the triflate oxygens (blue), justifying the description of the compound as pertechnetyl triflate.

It has also not yet been achieved to synthesize pertechnetates with cations with a charge of +4 or higher, or for oxocations. More importantly though, the redox chemistry of technetium itself needs to be ultimately advanced to the chemistry of lower valent technetium. In particular, the chemistry of Tc(II), Tc(III) and Tc(VI) is very poorly understood, and these species may very likely play a key role in the reduction of Tc(VII) to Tc(I).[21,74]

Pertechnetate in Super Basic Conditions

Contrary to this, in super basic conditions, pertechnetate shows the activation of the NH_4^+ ion, resulting in the formation of a nitridospecies.[75,76]

The number of published studies on reactions of pertechnetates with strongly basic media is even smaller than that of reactions in super acidic media, especially when focusing on results validated with single crystal X-ray results. One major focus is on the radiolysis of pertechnetates in radioactive wastewater.[77,78] A result of these studies is, for example, the reductive formation of $TcO_2 \cdot n\ H_2O$. If ammonium pertechnetate is used in hydroflux reactions the incorporation of nitrogen in form of $[TcO_3N]^{2-}$ anions can be observed, see also recent work.[75,76] Accordingly, the oxidation state of +VII remains unchanged and seems to be the most dominant one besides + IV even under extremely alkaline conditions. However, in an electrochemical cell relatively stable compounds with the +V oxidation state can also be obtained. However, the latter disproportionate also to +IV und +VII species.[79]

III Organometallic and Coordination Chemistry

The overall picture in organometallic chemistry of Tc is that there are several "islands" of knowledge developing around stable core structures that are partly originating from an interest in radiopharmaceuticals. Despite the general motivation to develop stable, polydentate ligands which allow a tailoring of their coordinating properties and robust anchoring for the conjugation of technetium to biovectors, also the development of new, reasonably stable small fundamental structural motifs containing ligands that do not usually undergo further reactions (such motifs are referred to as „cores“; e.g. *fac*-$\{Tc(CO)_3\}^+$, $\{TcO\}^{3+}$, $\{TcN\}^{2+}$, $\{TcO_3\}^+$) are on-going. These allow for the systematic study of the coordination chemistry of Tc as has been exemplified in a number of different ways in recent years as will be outlined in this section. One major challenge for Tc chemistry is still to understand the fundamental binding properties and differences of and between ligands or ligand classes as well as their influence on the reactivity of Tc. Some compound classes, such as side-on bonded alkyne complexes, are completely missing, while others such as carboxylates or thioureas are rare while having implications for the geo-ecological context as they can stabilize intermediate oxidation states and modify the redox and solubility properties of Tc.[80]

Advances Towards Radiopharmacy

Given their well-known tendency to provide systematic insights into the chemistry of transition metals, carbonyl complexes were among the first well-defined technetium coordination compounds.[81–83] Despite a few long-known compounds, however, technetium carbonyls have received more attention in recent years not only due to their potential application in radiopharmaceuticals,[84,85] but also as they may be relevant to the nuclear waste problem. Compounds containing the *fac*-$\{Tc(CO)_3\}^+$ core are stable *in vivo* and readily available for the medicinally relevant nuclear isomer ^{99m}Tc by one-pot reduction of $^{99m}TcO_4^-$.[86] The water ligands of the intermediate *fac*-$[^{99(m)}Tc(CO)_3(H_2O)_3]^+$ readily exchange for a variety of ligands. In the radiopharmaceutical context the most relevant are potentially chelating three-dentate ligands that can be linked to biological markers examples include chelators based on iminodiacetate,[87,88] pyridine, imidazole,[89–92] or cyclopentadienyl (Cp),[85,93,94] while also exotic ligands such as coated gold nanoparticles have been used.[95] The lipophilicity can be adjusted by both the technetium core structure as well as the ligand motifs. Exemplarily, $^{99m}Tc(CO)_3$–mebrofenin is more lipophilic compared to compounds with a different ^{99m}Tc core structure.[96] Similarly and remarkably, the small size of the $[^{99m}Tc(CO)_3(\eta^5\text{-}C_5H_4R)]$ (R = bioactive moiety) unit makes it biologically equivalent to the attachment of a phenyl group, indicating that it shows little influence on the biological activity of a conjugated biomarker compared to the unconjugated biomarker.[97] An orthogonal approach to three-dentate chelators is the use of bidentate chelators e.g. bipyridines or picolinic amides together with an additional capping ligand e.g. isocyanides or imidazoles in a “1 + 2” approach that offers the possibility for two orthogonal ways of bioconjugation and tailoring of the complex properties.[98–102] Some examples for these radiopharmaceutical principles with illustrative examples for the *fac*–$\{Tc(CO)_3\}^+$ core are given in Figure 5.

Advances in Fundamental Carbonyl Chemistry

Beyond potential radiopharmaceutical applications, Tc carbonyl species were identified in liquid nuclear waste supernatants at the Hanford Site by X-ray absorption spectroscopy and ^{99}Tc NMR spectroscopy.[20,74,103] The formation of *fac*-$\{Tc(CO)_3\}^+$ such as $[^{99}Tc(CO)_3(gluconate)]^{2-}$ or *fac*-$\{Tc(CO)_2(NO)\}^{2+}$ is possibly the result of Tc(VII) reduction by the radiolysis products of nitrate, water and organic components.[104] The classic starting materials for group 7 carbonyl chemistry are $[M_2(CO)_{10}]$ and $[MX(CO)_5]$ (M = Mn, Tc, Re; X = Cl, Br, I). The high-pressure syntheses for the volatile $[Tc_2(CO)_{10}]$ and its equally volatile halogenation products $[TcX(CO)_5]$ (X = Cl, Br, I) are unfortunately mostly incompatible with radiation protection requirements, making them essentially inaccessible. Therefore, considerable efforts for legislation-compliant low-pressure alternatives have been made in recent years and even the ^{99m}Tc analogs have been studied.[102,105–111] In a related line of research, work on the iconic, but elusive higher carbonyl compounds $[Tc(CO)_6]^+$, $[TcH(CO)_5]$ and $[TcF(CO)_5]$ provided a plethora of Tc carbonyl chemistry and a variety of decomposition pathways. Decarbonylation

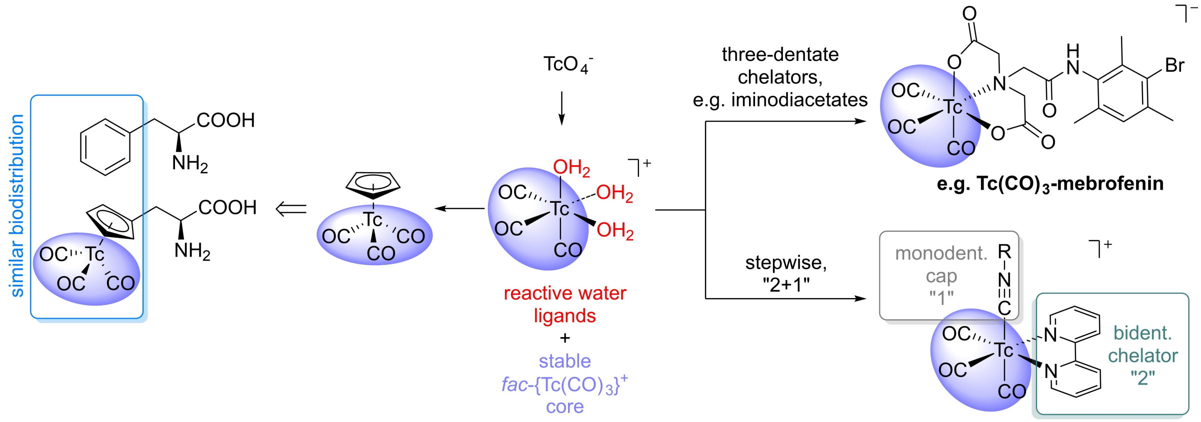


Figure 5. Examples for the functionalization of the fac-$\{Tc(CO)_3\}^+$ core.

followed by aggregation to multi-nuclear clusters is the "normal" decomposition pathway. Particularly ligands with either a large *trans*-influence or those exerting a strong *cis*-effect (i.e., strong π-donors) facilitate decarbonylation of the CO ligands in *trans*- or *cis*-position respectively. Both effects play a role in stabilizing the *fac*–$\{Tc(CO)_3\}^+$ core over the isomeric *mer*-$\{Tc(CO)_3\}^+$. Similarly, they make molecules such as $[Tc(CO)_6]^+$ and $[TcF(CO)_5]$ relatively unstable with respect to decarbonylation. Very recently, the extremely volatile and sensitive $[TcH(CO)_5]$ was finally authenticated by NMR and vibrational spectroscopy. It is surprisingly more inert towards CO-displacement reactions than previously thought, especially in comparison to its group neighbors. That being said, the quest for $[TcF(CO)_5]$ and related mixed carbonyl fluoride complexes has not yet been settled as only one clustered decomposition product has been identified in this line of research so far.[84,105–112]

A sterically shielded series of isocyanide analogs of the archetypical $[TcH(CO)_5]$, $[Tc(CO)_5]$ and $[Tc(CO)_5]^-$ was developed to study the fundamental properties of technetium complexes with more exotic co-ligands. $[TcH(CO)(CNp\text{–}F\text{-}Ar^{DarF2})_4]$, $[Tc(CO)(CNp\text{–}F\text{-}Ar^{DarF2})_4]$ and $[Tc(CO)(CNp\text{–}F\text{-}Ar^{DarF2})_4]^-$ represent rare examples of an unambiguously confirmed technetium hydride, a molecular, monomeric technetium(0) species and the first authenticated and structurally characterized technetium complex with the central metal in a formally negative oxidation state of -I.[113–115] Consistent with the formally negative oxidation state and providing a proof of concept for the envisioned reactivity, the technetium atom in $[Tc(CO)(CNp\text{–}F\text{-}Ar^{DarF2})_4]^-$ is nucleophilic undergoing nucleophilic substitution at $ClSnMe_3$ to give the first compound with a technetium-tin bond: $[Tc(SnMe_3)(CO)(CNp\text{–}F\text{–}Ar^{DarF2})_4]$. A reaction with HCl first leads to $[TcH(CO)(CNp\text{–}F\text{-}Ar^{DarF2})_4]$, which is protonated under H_2 loss to give the original starting material $[TcCl(CO)(CNp\text{–}F\text{-}Ar^{DarF2})_4]$. Such protonation reactions under coordination of the corresponding acid anion have in the meantime also been reported for $[TcH(CO)_5]$.

The underlying reactivity seems to be general as the phosphine analog *mer–trans*–$[TcH(CO)_3(PPh_3)_2]$ reacts similarly. The retention of the stereochemistry in the phosphine complexes indicates that the loss of H_2 and coordination of the anion are very quick. Reactions of *mer–trans*–$[TcH(CO)_3(PPh_3)_2]$ with protic acids of weakly coordinating anions instead enable the stabilization and preparation of highly reactive solvent complexes *mer–trans*–$[Tc(L)(CO)_3(PPh_3)_2]^+$ (L = solvent). These complexes can be prepared at the gram scale and act as synthons for the coordinatively unsaturated $16e^-$ species $[Tc(CO)_3(PPh_3)_2]^+$. Therefore, they represent a convenient platform for the study of technetium complexes with a large variety of ligands largely retaining the parent compound's structure. The reaction products retain the *mer*-$\{Tc(CO)_3\}^+$ core or decarbonylate once to yield *cis*-$\{Tc(CO)_2\}^+$ for bidentate or sufficiently π-donating ligands (see below). In this way technetium(I) complexes of MO_4^- (M = Tc, Re), ER_2 (E = S, Se, Te), BH_4^-, NO_2^-, NO_3^-, *cyclo*-oxycarbenes, organyl and other previously elusive ligands could be synthesized (some examples are shown in Figure 6).

Alkynyl complexes in particular were prepared from lithium alkynyls and envisioned as promising intermediates having in mind the on-going challenge of preparing technetium complexes with a side-on bonded alkyne ligand. A different strategy that has often been successful for the isolation of transition metal complexes with elusive ligands such as N_2, H_2, alkenes or alkynes is the use of pincer-type ligands with a *P,N,P* donor set. Such complexes have only recently been reevaluated and studied somewhat systematically. The complexes show *fac-mer*-isomerism, decarbonylation reactions and HX activation. The latter is thought to be enabled by internal deprotonation with an amido-type aromatization/dearomatization metal-ligand cooperativity pathway providing another route to Tc alkynyl complexes. Such reactions are postulated to proceed via transiently coordinated alkyne ligands, but no experimental evidence for such complexes was observed.[116–118] Contrastingly, the protonation of the alkynyl ligands in *mer–trans*-$[Tc(CCR)(CO)_3(PPh_3)_2]$ indeed led to new ^{99}Tc NMR resonances potentially consistent with a side-on bonded alkyne ligand or its isomeric vinylidene carbene analog, one carbonyl ligand is lost in the process resulting in an inseparable 1 : 1 mixture of *cis,trans*-$[Tc(L)(CO)_2(PPh_3)_2]^+$ and *trans*-$[Tc(CO)_4(PPh_3)_2]^+$. The synthesis of the first technetium alkynyl complexes and their methyl and phenyl analogs emphasizes the marked importance of the choice of organometallic reagents in organotechnetium chemistry. Grignard reagents that work well for the preparation of high-valent organotechnetium chemistry, lead to halide transfer instead of aryl or alkyl transfer, while organolithium reagents lead to the desired organotechnetium species. The strategy has also been extended to the replacement of chlorido complexes with the $\{Tc^VN\}^{2+}$ core.[119–122]

Advances in transmetallation reactions

In similar reactions, the treatment of both the Tc^{IV} starting material $[TcCl_4(PR_3)_2]$ (PR_3 = PPh_3 and PEt_2Ph), and the Tc^{III} starting materials $[TcCl_3(PR_3)_3]$ (PR_3 = PMe_2Ph, $PMePh_2$, and PEt_2Ph) and $[TcCl_3(PPh_3)_2(CH_3CN)]$ with arylmagnesium bromides in benzene yields deep blue η^1-aryl Tc^{III} complexes of the composition $[Tc(\eta^1\text{-aryl})_3(PR_3)_2]$. These are only moderately stable depending on the phosphine used ($PMe_2Ph < PEt_2Ph < PMePh_2 < PPh_3$), and they decompose by forming oily brown products. Interestingly, while the triphenylphosphine complex $[Tc(Ph)_3(PPh_3)_2]$ is stable on air. As its rhenium analog, the latter product is not soluble in any common solvents preventing an unambiguous structural elucidation and ongoing reactions. This problem was overcome by preparation of an analogous complex containing trifluoromethylated aryl ligands: the well-soluble complex $[Tc\{Ph(CF_3)_2\}_3(PPh_3)_2]$. While Grignard reagents readily led to displacement of the chlorido and acetonitrile ligands from $[TcCl_3(PPh_3)_2(CH_3CN)]$, the corresponding aryl lithium reagent attacks the coordinated acetonitrile forming the first azavinylidene complex of technetium: $[Tc\{NC(CH_3)Ph(CF_3)_2\}\{Ph(CF_3)_2\}_2(PPh_3)_2]$.[123]. Contrastingly, $[TcCl_3(PPh_3)_2(CH_3CN)]$ reacts with lithium aryl tellurolates and selenolates under selective halide replacement to give the corresponding $[Tc^{III}(ArE)_3$

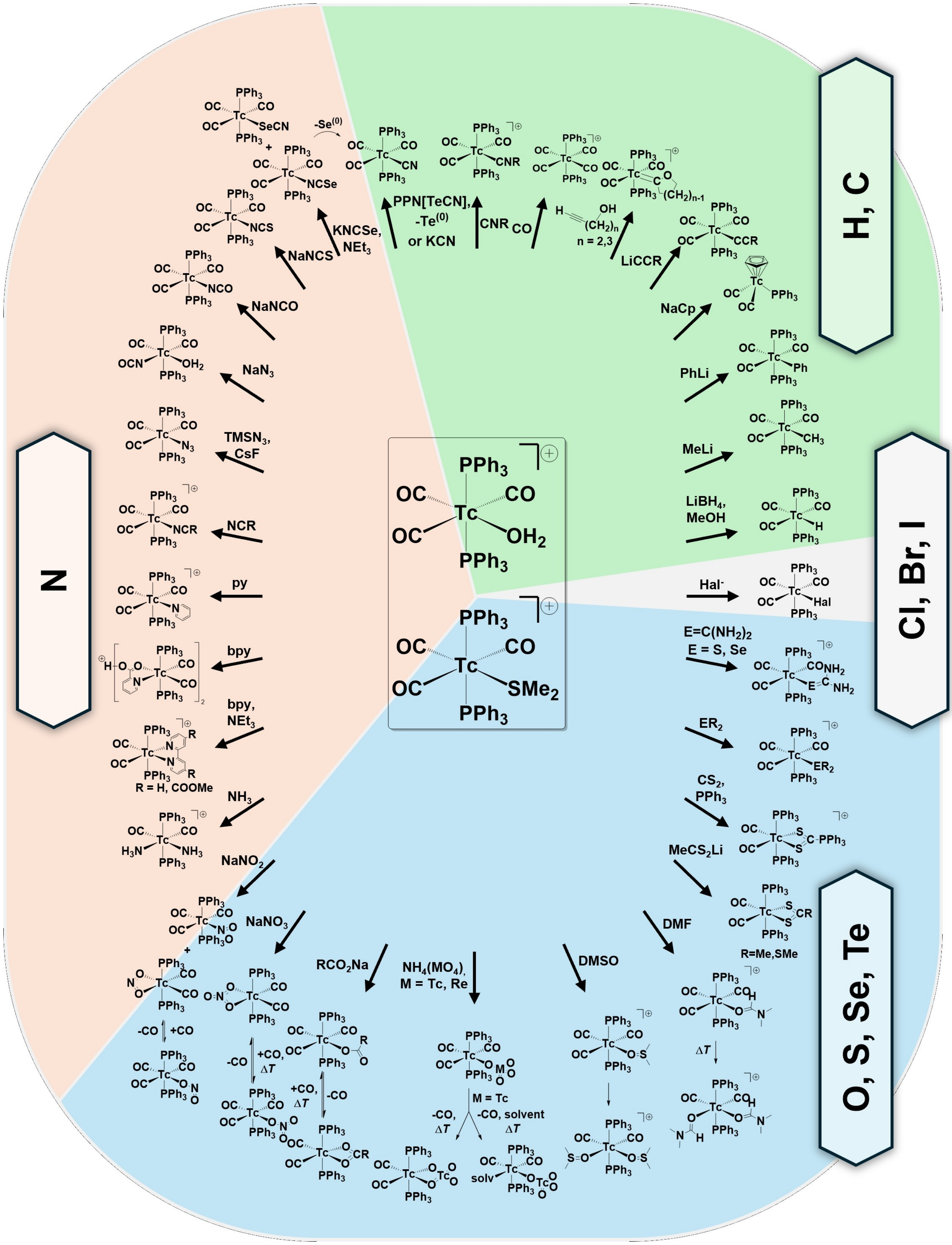


Figure 6. Systematic reactions enabled by mer–trans-$[Tc(L)(CO)_3(PPh_3)_2]^+$ (L = solvent).

$(PPh_3)(CH_3CN)]$ (E = Se, Te; Ar = phenyl, 2,6-Me_2phenyl, mesityl) retaining one acetonitrile and one PPh_3 ligand, while reactions of the technetium(V) starting material $[TcOCl_4]^-$ give $[Tc^VO(ArE)_4]^-$ (E = Se, Te; Ar = phenyl).[124] Although similar complexes with other simple ligands such as technetium(III) carboxylates have rarely been reported despite their obvious importance in geoecological systems, the recent development of potential Tc carboxylate starting materials is encouraging.[125–127]

Another interesting class of compounds are the water- and air-stable organometallic phenyl complexes with a nitridotechnetium(V) core. A transmetallation from PhLi to Starting from $[TcNCl_2(PPh_3)_2]$ yields $[TcNPh_2(PPh_3)_2]$. Moreover, when starting with $(NBu_4)[TcNCl_4]$ and the N-heterocyclic carbene (NHC) 1,3,4-triphenyl-1,2,4-triazol-5-ylidene (HL^{Ph} or its methoxo-protected form), the chlorido compound $[TcNCl_2(HL^{Ph})_2]$ is formed, while no reaction was observed between the NHC and $[TcNPh_2(PPh_3)_2]$. The desired mixed NHC/aryl complex $[TcNPh_2(HL^{Ph})_2]$ had to be accessed by transmetallation from PhLi to $[TcNCl_2(HL^{Ph})_2]$ instead. Interestingly, the chemistry of the NHC is entirely different from its Re analog, in which CH activation and orthometalation are dominating reactions.[128] In addition to this, Braband and co-workers have been successful in synthesizing water-stable organometallic ^{99}Tc-NHC complexes. Starting from the ethylene glycolato complex $[Tc^VO(glyc)_2]^-$ the authors have characterized three different $^{99}Tc^VO_2$-NHC complexes (with NHC = 1,3-dimethylimidazoline-2-ylidene (L1), 1,1′-methylene-3,3′-dimethyl-4,4′-diimidazoline-2,2′-diylidene (L2), and 1,1′-methylene-3,3′-diethyl-4,4′-diimidazoline-2,2′-diylidene (L3)). It was shown that monodentate NHC complexes are hydrolytically unstable, while bidentate complexes are water-stable over a broad pH range, allowing the interconversion of the $[^{99}Tc^VO_2(NHC)_2]^+$ into $[^{99}Tc^VOCl(NHC)_2]^{2+}$ in the presence of aqueous HCl. While these $^{99}Tc^VO_2$–NHC complexes can also be made *via in situ* deprotonation of imidazolium salts (avoiding the use of free NHCs), the remarkable stability and pH-dependent reactivity may serve as a steppingstone towards ^{99m}Tc–NHC complexes.[129] Of similar medicinal interest are the surprisingly robust bis(arene) cations $[Tc(arene)_2]^+$ that were recently reinvestigated and developed towards bioconjugates. Interestingly, they were found to be much more easily and reliably formed at the low concentrations governing the chemistry of ^{99m}Tc compared to their ^{99}Tc analogs.[130]

Advances in Isocyanide Chemistry

While NHC and arene complexes may be promising radiopharmaceuticals, the Tc isocyanide complex under the tradename cardiolite© is one of the most frequently applied radiopharmaceuticals to date. The fundamental study of transition metal isocyanide chemistry was governed by the long standing believe that isocyanides are a homogeneous compound class with little electronic variability behaving equivalently to the commercialized small alkyl isocyanides CN^tBu or CNCy and were usually considered as tailorable electronic equivalents of CO. The disparity between seemingly random but sometimes strongly reducing behavior with an often nearly non-existent π-acceptor behavior in these alkyl isocyanides was largely ignored. This believe was recently challenged for technetium using the sterically demanding terphenyl isocyanides $CNAr^{Dipp2}$ ($CN(C_6H_3$(*o*,*o*-bis(2,6-diisopropylphenyl)) and $CNAr^{Mes2}$ ($CN(C_6H_3$(*o*,*o*-bis(2,4,6-trimethylphenyl)). In contrast to the previous believe-set, not only low-valent, i.e. Tc(I) and Tc(III) complexes with additional carbonyl, nitrosyl and chlorido co-ligands, could be isolated, but surprisingly stable Tc^V complexes with complementary nitrido- and aryl imido ligands have been prepared. Particularly the *cis*-trans configuration of the isocyanide ligands to the PPh_3 co-ligands in the Tc^V complexes was surprising and can be fine-tuned by careful choice of the ligand, with the $CNAr^{Dipp2}$ supporting the *trans* arrangement, while the $CNAr^{Mes2}$ allows for the *cis* geometry.[131] A common rationale that enabled the prediction of the coordination behavior of isocyanide ligands as well as the stability of the high-valent complexes was developed: the Surface-Averaged-Donor-Acceptor-Potential (SADAP) combining steric and electronic effects in the uncoordinated ligands. The SADAP concept was originally designed, however, to understand the marked differences in isocyanide reactivity towards Tc^I carbonyl starting materials and the potential of different isocyanides to replace carbonyl ligands. Treatment of *fac*-$[Tc(CO)_3(CNR)_2Cl]$ (CNR = CN^nBu or CN^tBu) with the sterically demanding isocyanide CN*p*-FAr^{DarF2} [DArF = 3,5-$(CF_3)_2C_6H_3$] results in the loss of the CO groups forming *mer*,*trans*-$[Tc(CN$*p*-$FAr^{DarF2})_3(CNR)_2Cl]$, which in turn can be substituted in a halide exchange reaction, culminating in a Tc complex with three different isocyanide groups when the initial material contains CN^nBu and the last step is performed with CN^tBu. Using *p*-fluorophenyl isocyanide, $CNPh^{pF}$ leads to the hexakis(isocyanide)technetium(I) cation through an exchange of all ligands in both $[Tc_2(CO)_6(\mu\text{-}Cl)_3]^-$ or *fac*-$[Tc(CO)_3(CNR)_2Cl]$.[132] The hexakis(isocyanide)technetium(I) cation can also be made with *p*-isocyanoethynylbenzene $CNPh^{pC\equiv CH}$ as the ligand.[133]

Advances in the Chemistry with Face-Capping Ligands

Another remarkable example of a single ligand forming stabile complexes with the seven most common oxidation states of technetium is the „Kläui ligand“, η^5-(cyclopentadienyl)tris-(dimethyl phosphito-*P*)cobaltate(III) (L^{OMe}, Figure 7).[134] Tc is coordinated via the oxo group on the P atoms of the ligand, while the coordination sphere is complemented by strongly bound nitrosyl, oxido or nitrido ligands, or less tightly binding halido and phosphine coligands. Interestingly, all members of this series ($[Tc^I(NO)Cl(PPh_3)(L^{OMe})]$, $[Tc^{II}(NO)Cl_2(L^{OMe})]$, $[Tc^{III}Cl_2(PPh_3)(L^{OMe})]$, $[Tc^{IV}Cl_3(L^{OMe})]$, $[Tc^VOCl_2(L^{OMe})]$, $[Tc^VNCl(PPh_3)(L^{OMe})]$, $[Tc^{VI}NCl_2(L^{OMe})]$, and $[Tc^{VII}O_3(L^{OMe})]$ are stable in water and on air. They thus provide unique starting materials, particularly for the study of technetium chemistry with the metal in rarer oxidation states +2 and +6, where few examples of suitable starting material platforms have been reported and the corresponding chemistry seen little advancement in recent times. Unfortunately the replacement of the chlorido ligand in

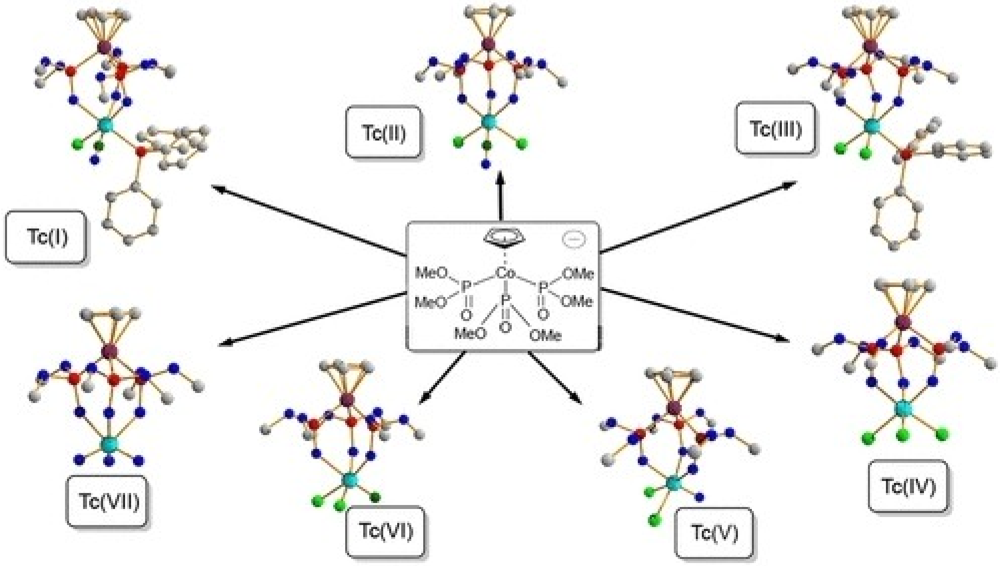


Figure 7. The "Kläui ligand" and its complexes with Tc from oxidation states +1 to +7. Figure taken from Grunwald.[134]

$[Tc^I(NO)Cl(PPh_3)(L^{OMe})]$ by Ag^+ as halide scavenger in hopes to isolate reactive solvent complexes for on-going ligand exchange reactions led to the formation of a complex mixture of redox-pairs between $[Tc^I(NO)Cl(PPh_3)(L^{OMe})] + Ag^+$ and the crystallographically and spectroscopically characterized adduct $[\{Tc^I(NO)(PPh_3)(L^{OMe})\mu\text{-}Cl\}Ag\{\mu\text{-}ClTc^I(NO)(PPh_3)(L^{OMe})\}]^+$ and the oxidation/reduction products.[135]

The "Kläui ligand" is often considered a structural and electronic equivalent to cyclopentadienyl (Cp). In contrast to several hundred structurally characterized rhenium cyclopentadienyl complexes, little is known about the chemistry of Cp complexes with Tc beyond complexes of the type $[Tc(CO)_3(Cp^R)]$. A platform for the systematic study of technetium Cp chemistry was identified by Abram and co-workers. The relatively robust $\{Tc(NO)(Cp)(PPh_3)\}^+$ core was prepared by a much simpler route than its rhenium analog: KCp and $[Tc^I(NO)X_2(PPh_3)_2(CH_3CN)]$ (X = Cl, Br) react to the air-stable starting materials $[Tc^I(NO)(Cp)(PPh_3)X]$.[136] Stable complexes under exchange of the coordinated halide anions can be prepared by direct ligand exchange using the protic acids or halide scavenging salts of ligands such as I^-, I_3^-, $F_3CSO_3^-$, CF_3COO^-, or SCN^- as well as suitable neutral donor ligands such as phosphine chalcogenides. In contrast to the difficulties outlined for the "Kläui"-analog above, the halido ligands can also easily be scavenged in the presence of suitable solvent ligands such as acetonitrile or pyridine and at least the acetonitrile compound shows promise as a starting material for ligand exchange reactions.[137] One prerequisite is, however, that the incoming ligands binds stronger to the $\{Tc(NO)(Cp)(PPh_3)\}^+$ fragment than the chlorido moiety in the starting material, since a self-quenching process otherwise leads to the brick-stable, unreactive chloride-bridged dimer $[\{Tc^I(NO)(Cp)(PPh_3)\}\mu\text{-}Cl\{Tc^I(NO)(Cp)(PPh_3)\}]^+$. This is for example the case in reactions aimed at the coordination of alkynes. Nevertheless, multifacetted decomposition reactions take place when such reactions are performed in the presence of both alcohols and alkynes leading to rare examples of phosphonium stabilized Fischer-type carbene complexes.[138]

The Connection of Organometallic Chemistry to Applied Fields

Overall, the fundamental coordination chemistry of technetium and the influence of different ligands on the spectroscopic signatures remain underdeveloped. The focus of fundamental studies needs to aim at providing comprehensive insights about the coordination properties of the element with various ligands. Organometallic chemistry interconnects applied fields such as radiopharmacy, geoecology and nuclear waste. Recently, radiopharmaceutical compounds have been proposed for the use in environmental remediation.[139] In the latter fields this may include the identification of potential coordination modes and the development of model systems that could lead to less ambiguous interpretation of speciation data obtained by powerful and specialized techniques such as XAS and ^{99}Tc NMR but also to understand the electrochemical behavior of the element. In terms of radiopharmacy and although the synthetic chemistry of ^{99}Tc usually not directly translatable to the chemistry of ^{99m}Tc, where entirely different protocols have to be developed due to the different kinetic regimes, knowledge about the interaction of technetium with simple and complex ligands can help to understand issues regarding surprising biodistribution or stability and finally guide the optimization of ligand systems and linkers for bioconjugation. Some distinct differences between technetium and rhenium may add an additional layer of fog to the understanding of ^{99m}Tc chemistry, when comparing its chemistry to a rhenium surrogate instead of actual technetium given redox, reactional and structural differences between the elements.

IV Computational Chemistry

The role of "applied" DFT calculations for the understanding of Tc chemical shifts in NMR has already been emphasized above (section I). This part deals with the more fundamental approach understanding the Tc bonding behavior in certain pertechnetate and related compounds.

Utilization of Pertechnetate and Related Compounds in Crystal Engineering: A Focus on Matere Bonds

The role of technetium compounds, particularly pertechnetate in crystal engineering has gained significant attention due to their ability to participate in non-covalent interactions.[140] These interactions often involve technetium acting as an electron acceptor, facilitating the formation of so called matere bonds - a recently recognized type of interaction specific to the group 7 elements **ma**nganese, **te**chnetium and **r**h**e**nium, equivalent to the well known halogen bonds in group 17.[141] Matere bonds (MaBs) are characterized by the attractive interaction between an electron-rich atom, such as oxygen, and the metal center, in most cases belonging to a permetalate anion, such as $[TcO_4]^-$, $[ReO_4]^-$, or $[MnO_4]^-$.[140–145] This section highlights the significance of these bonds in crystal engineering focusing on technetium, underpinned by specific examples drawn from the Cambridge Structural Database (CSD) and recent theoretical studies.

Matere Bonds in Pertechnetate and Perrhenate Compounds

Recent research has highlighted the distinctive behavior of pertechnetate and perrhenate anions in forming anion-anion interactions. These anions serve, despite their negative charge, as relatively strong electron acceptors, with technetium and rhenium participating in highly directional and often linear non-covalent interactions. These interactions are driven by σ-holes —regions of reduced electron density—located on the metal centers of the anions. For instance, a study by Daolio *et al.* provided both experimental and theoretical evidence for the presence of anion···anion interactions in crystalline perrhenate and pertechnetate salts.[141] This concept was first described for halogens ("halogen bonds") and has been established in most groups of the Periodic Table since. In these structures, the oxygen atom of one anion interacts with the metal center (Tc or Re) of another anion, leading to the formation of well-defined supramolecular structures such as anionic dimers or extended polymeric chains. These supramolecular motifs significantly influence the overall architecture and stability of the crystal structures, making matere bonds a critical element in the design of functional materials.

Two specific examples illustrate the significance of these interactions. The first example, corresponding to CSD refcode AMOGIS,[146] shows pertechnetate anions forming infinite zigzag 1D chains through directional matere bonds (O···Tc–O, 172.9°) flanked by 3,4,6,7,8,9-Hexahydro-2H-pyrimidino(1,2-a)pyridinium cations (Figure 8). The second example, represented by refcode NAPVUZ,[141] involves melaminium perrhenate (2,4,6-triamino-1,3,5-triazin-1-ium perrhenate). In the solid state (Figure 8b), this compound exhibits anion···anion interactions where the oxygen of one anion approaches the rhenium atom of another along the extension of a Re–O covalent bond, forming linear infinite chains. The strong directionality of these interactions (177.7°) aligns with the small size of the σ-hole and helps to minimize repulsion with the O-atoms of the adjacent anion.

Selected examples from the Cambridge Structural Database (CSD)

A comprehensive analysis of the Cambridge Structural Database (CSD) reveals numerous instances where pertechnetate and perrhenate anions engage in matere bonds. Previous studies have shown that approximately 19% of structures containing $[ReO_4]^-$ anions exhibit these interactions, with a significant proportion (around 75%) involving anion···anion contacts.[141] These interactions are characterized by highly directional geometries, with distances shorter than the sum of van der Waals radii, indicating strong, close-range interactions between the involved atoms. Such directional interactions frequently lead to

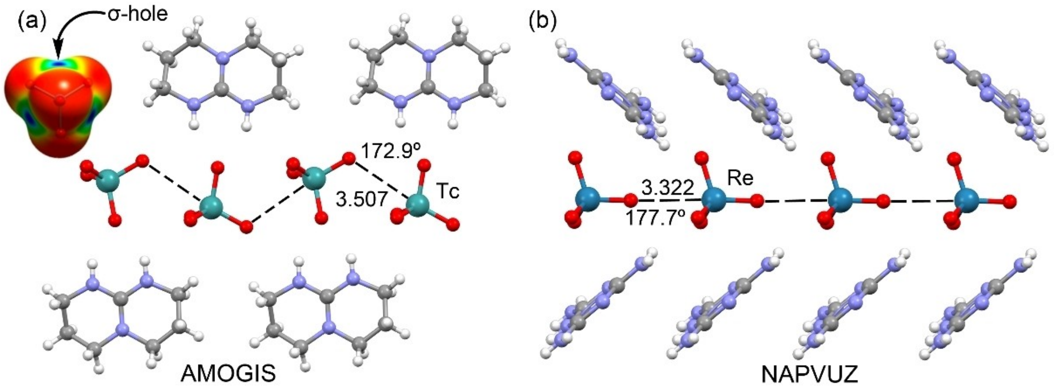


Figure 8. Ball and stick representation of the X-ray structures AMOGIS (a) and AZEMUO (b). Distances in Å. Color code: Carbon grey, Oxygen red, Nitrogen blue, Technetium teal, Hydrogen light grey.

the formation of linear chains, as depicted in Figure 8, infinite anionic networks, or other extended supramolecular assemblies, highlighting the potential of $[TcO_4]^-$ and $[ReO_4]^-$ as versatile building blocks in crystal engineering.[140–142]

However, matere bonds are not confined to oxoanionic species alone. An intriguing example is illustrated in Figure 9, where anion···anion MaBs drive the formation of an infinite 1D assembly.[147] In this structure, the lone pair on the nitrogen atom of one chlorido–nitrido–technetate(VI) anion is directed towards the Tc atom of the adjacent $[TcNCl_4]^-$ anion, opposite to the Tc–N bond (at the σ-hole location, see Figure 9, right). This 1D assembly is flanked by catena-((μ2–18-crown-6)-cesium) counterions, creating an "infinite sandwich" structure with Cs^+ cations intercalated between crown ether molecules.

In addition to anion···anion interactions shown in Figures 8 and 9a, the CSD also documents cases where $[TcO_4]^-$ and $[ReO_4]^-$ anions participate in interactions with atoms that can donate electrons from non-bonding orbitals, such as nitrogen or chlorine.[140] These interactions further expand the utility of these anions in constructing diverse supramolecular architectures. Although the number of structures containing $[TcO_4]^-$ and $[MnO_4]^-$ anions is relatively limited compared to $[ReO_4]^-$,[141] the observed matere bonds in these systems are consistent with the general trend that heavier elements in a group (such as Re compared to Tc or Mn) are more prone to act as electrophilic centers, forming stronger and more directional non-covalent interactions.

Beyond $[TcO_4]^-$ and $[ReO_4]^-$ anions acting as electron acceptors, neutral Tc derivatives have also been described as matere bond donors, significantly influencing the solid-state structure of these compounds.[142,144] An illustrative example is shown in Figure 9b, featuring bis(μ^2–acetato)-tetrachlorido-di-technetium(III), refcode OSICUP.[33–35] This structure consists of two bridging trans-acetate ligands and four terminal chlorido ligands. Notably, the compound propagates in the solid state through four symmetrically equivalent Tc···Cl MaBs, forming a supramolecular 1D assembly. The Tc···Cl distance is remarkably short, only 0.4 Å longer than the sum of the covalent radii, highlighting the strength of these interactions. This represents a unique example of a MaB involving Tc in a low oxidation state, where the σ-hole is located opposite the Tc–Tc bond (see Figure 11, right).

Finally, matere bonds have also been observed in metal-coordinated $[TcO_4]^-$ anions. One notable structure is illustrated in Figure 10. It corresponds to a hydrated magnesium pertechnetate with the formula $Mg(H_2O)_4[TcO_4]_2$. In this structure, the Mg metal center is coordinated in an elongated octahedral geometry by four water molecules in the equatorial plane and two oxygen atoms from $[TcO_4]^-$ units that are trans to each other. In the extended structure, this compound forms two-

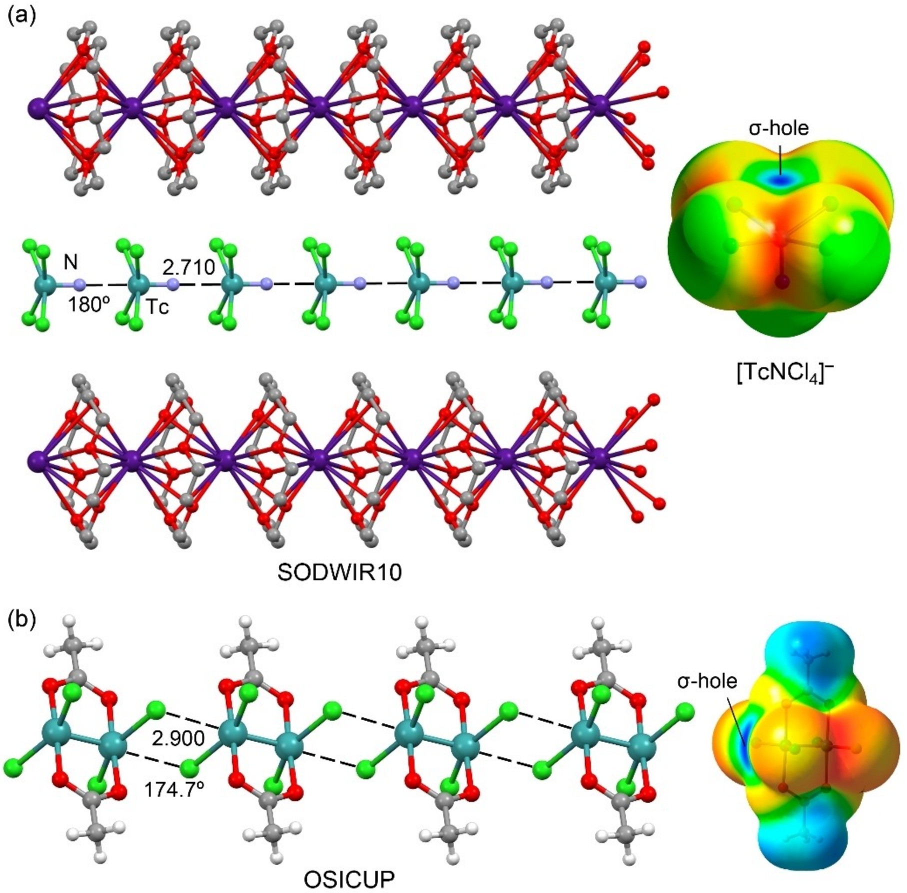


Figure 9. (a) Left: Ball and stick representation of the X-ray structure SODWIR10. Distance in Å. Right: MEP surface of $[TcNCl_4]^-$ anion. (b) Left: Ball and stick representation of the X-ray structure OSICUP. Distance in Å. Right: MEP surface of bis(μ2-acetato)-tetrachlorido-di-technetium(III).

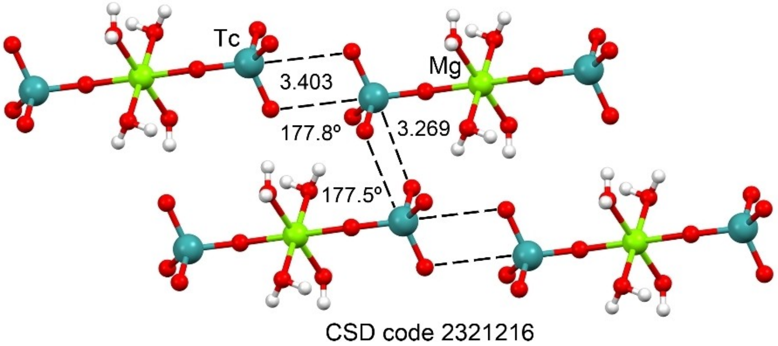


Figure 10. Partial view of the X-ray structure of $Mg(H_2O)_4[TcO_4]_2$. Distances in Å.

dimensional assemblies characterized by two types of MaBs, as shown in Figure 11b and similar to those observed in HETRUT. One MaB is formed opposite to the Tc–O bond that coordinates to the Mg^{2+} ion (3.403 Å), with a nearly linear O–Tc···O angle (177.8°), which is typical of σ-hole interactions. The second MaB is formed opposite to a Tc═O bond, with a shorter distance (3.269 Å) and comparable linearity (177.5°).

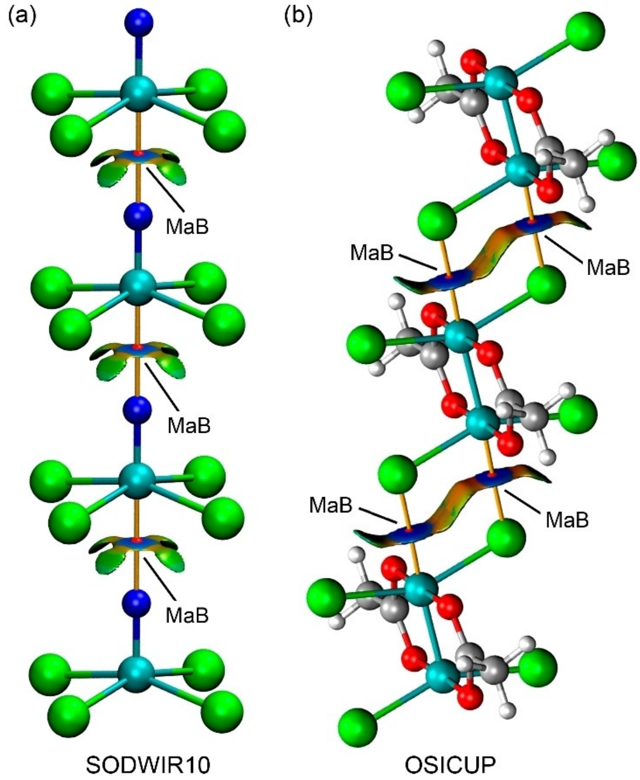


Figure 11. QTAIM/NCIPlot analyses of the homotetramer of SIDWIR10 (a) and the homotrimer of OSICUP (b). The NCIplot settings used are: RDG = 0.45, density cut-off 0.04 a.u., and color range ±0.03 for (sign λ_2) ρ. Blue and green are used for attractive interactions and red and yellow for repulsive interactions.

Theoretical Insights into Matere Bond Formation

To gain a deeper understanding of the nature of matere bonds, several theoretical approaches have been employed, including molecular electrostatic potential (MEP) surface calculations, quantum theory of atoms-in-molecules (QTAIM), and non-covalent interaction (NCI) plot analyses. These methods offer detailed insights into the electronic environments that facilitate the formation of these interactions. For instance, MEP calculations, such as those depicted in Figures 8-10, reveal that the σ-holes on the metal centers of $[TcO_4]^-$, $[ReO_4]^-$ and $[TcNCl_4]^-$ are critical sites for electron donation from neighboring molecules or anions. This electron donation results in the formation of strong and directional matere bonds.

Other computational tools, such as QTAIM and NCIplot analyses, are equally valuable for confirming the existence and character of these bonds. QTAIM identifies bond critical points (BCPs) and bond paths that connect the interacting atoms, while NCIplot analysis uses reduced density gradient (RDG) isosurfaces to visualize noncovalent interactions in real space. These isosurfaces are color-coded to indicate the nature of the interactions: yellow and red represent weak and strong repulsive interactions, while green and blue denote weak and strong attractive interactions. Thus, these analyses not only allow for the visualization of matere bonds within crystal structures but also quantify the strength and directionality of these interactions, offering a deeper understanding of how these non-covalent forces contribute to the overall stability and organization of the crystal lattice.

Figure 11 provides such analyses for two of the examples discussed above: SODWIR10 and OSICUP.[33–35] In the former, a tetrameric assembly is illustrated, where the combined QTAIM/NCIplot analysis reveals a BCP (red sphere) and bond path (orange line) connecting the Tc atom of one monomer to the N-atom of the adjacent monomer. This confirms the existence of the MaB and its role in directing the structure, as there are no additional BCPs or bond paths interconnecting the monomers. The MaB is further characterized by a dark blue RDG isosurface, coinciding with the location of the BCP, indicating a strong and attractive interaction as denoted by the blue color in the NCI plot analysis.

For the OSICUP structure, a trimeric assembly is shown in Figure 11b, where the combined QTAIM/NCIplot analysis demonstrates that the central monomer is connected to the adjacent monomers by four BCPs and bond paths linking the Tc atoms to the Cl atoms. Each pair of MaBs that connects two monomers is characterized by two dark blue RDG isosurfaces, coinciding with the BCPs, which indicate the attractive nature of both symmetrically equivalent Tc⋯Cl contacts. The blue RDG isosurfaces are connected by an elongated yellow-reddish region, indicating the presence of Cl⋯Cl repulsion.

V Geochemistry

Research on Tc is relevant from the geo- and radiological point of view. In this case, the work so far available in the literature deals with the remediation technologies of Tc, with special focus on the long-term safety assessment of nuclear waste repositories and decontamination of Tc-polluted sites. Thus, multiple works report the scavenging of aqueous Tc by using naturally occurring minerals or materials to be present in the nuclear waste repository. Among them, clays and clay derivatives,[148] cementicious matrices as ettringite[149] and species that can be present in the repository, like microorganisms,[150] or minerals such as pyrite,[151] magnetite[152] or chukanovite.[153] In addition, in the last decade an increased interest has been oriented towards using other innovative materials, i.e., metal organic frameworks, as Tc scavengers, although the studies carried out so far only used rhenium as a Tc analogue.[154–157]

Despite the large variety of oxidation states of Tc, it is considered that only Tc(VII) and Tc(IV) are environmentally relevant under oxidizing and reducing conditions, respectively. While Tc(VII) is inert against interaction with minerals and is, hence, very mobile in aqueous fluxes,[158] Tc(IV) can be immobilized by different mechanisms. Tc(IV) retention mechanisms include the surface complexation on mineral (e.g., sorption on layered double hydroxides[159,160] or on chukanovite[153]), the incorporation into mineral structures (e.g., in magnetite and hematite[161]), or the precipitation as poorly soluble solids such as TcO_2,[162,163] or TcS_X.[164]

Technetium Removal by Using Reducing Sorbents

Based on this, most of the reported studies deal with the Tc removal by using sorbents that can induce Tc(VII) reduction, such as Fe(II)-, Sn(II)-, S(−II)-containing materials,[165] or microorganisms.[166] These sorbents have been the most explored against Tc immobilization – being Fe(II)-minerals the main focus – since they will be relevant phases in the nuclear waste repository, and they are ubiquitous. Likewise these studies usually cover a range of pH from 4 to 9, and Eh from 400 to -400 mV, due to being very common environmental conditions.[167] However, Tc immobilization is sometimes studied considering very limited parameter variability, which might not convey a proper understanding of the actual Tc environmental chemistry.

Even though it is important, not all of the works have considered all the variables (time, pH, ionic strength and Tc concentration). Likewise, only a minority of the possible minerals have yet been explored, and only some of the molecular interactions of Tc with the minerals have been studied and reported. However, the knowledge generated over the last decades shows that redox-active sorbents induce the highest removal of Tc.

The majority of the available literature is based on Tc immobilization in binary systems, i.e., the interaction of Tc with a selected sorbent (mineral or microorganism) as a function of multiple parameters. However, this is an unrealistic scenario under environmental conditions. Hence, there is a need of studying the influence of the coexisting species in solution, as much as studying the sorbent materials to evaluate whether the presence of different species i) induces competition for Tc immobilization, ii) triggers the formation of soluble Tc species that do not interact with sorbents, iii) and/or affects Tc scavenging by their presence. Few studies report how the presence of other species can alter Tc immobilization. For example the competition for the immobilization by ettringite of technetium with other anions chromate and iodate,[149] or the effect of organic ligands on the complexation of Tc in solution such as EDTA (Ethylenediaminetetraacetic acid),[168] or on the solubility of TcO_2.[80]

Identification of the Immobilization Mechanism of Tc

Due to the few spectroscopic techniques by which Tc molecular environment can be identified, the immobilization mechanisms of Tc are primarily evaluated by XAS, which is a highly sophisticated method only available in synchrotron facilities. Therefore, user accessibility to this technique is limited and, in turn, a thorough mechanistic understanding of Tc immobilization by given sorbents is a time-demanding process. However, due to the high similitudes of the Fe(II)-, Fe(III)-, and Fe(II/III) mineral structures, it is tremendously tedious to unambiguously identify the exact interaction of Tc in the solid phase by XAS.[159,169,170] In addition, usually, after the reduction of Tc(VII) by the selected Fe(II) mineral, Tc(IV) does not interact with the initial sorbent, but with its oxidation products. There are multiple examples in the literature, as an example, when Fe(II)-Al(III)-layered double hydroxide was used as sorbent, Tc(IV) formed surface complexes on hematite and incorporated into hematite structure.[159]

Tc(VII) Reduction Mechanism and Lower-Valence Tc Species

It is remarkable that all the studies mentioned above have one thing in common: it has been historically assumed that the only relevant Tc species in the environment are inorganic Tc(VII) and Tc(IV) species. Nevertheless, this is not always the case. In 2004, it was found that in the Hanford nuclear waste site in the USA, a Tc(I)-carbonyl species was stable in solution.[74] In the same direction, other Tc species with oxidation states different than Tc(IV) or Tc(VII) are used for radiopharmaceutical purposes,[171] and in fact, they are daily released via the patients' urine into the sewage systems and from there to the environment. Despite the environmental relevance of such Tc species, little is known to date about their interaction with sorbents such as minerals or microorganisms, although there are a few earlier publications dealing with microbial reduction of Tc.[172–175]

Moreover, although the reduction of Tc(VII) to Tc(IV) is clearly the step limiting Tc migration in the environment, little is known about this reduction mechanism, and whether there are intermediary species. So far, electrochemical analyses have been done under extreme pH conditions.[79] The only systematic work performed at different pH values shows that pH has a clear influence on Tc(VII) reduction,[176] indicating that Tc(VII) reduction to Tc(IV) in $NaClO_4$ is a direct process from pH 4 to. In addition, the techniques available to explore *in situ* the molecular changes of Tc as a function of the redox potential are very limited. So far, the only method used for this purpose is the coupling of electrochemistry and UV-vis, which has often been used to evaluate the changes of absorption of aqueous Tc species. [176–178] However, the characterization of Tc complexes takes part generally only *ex situ*, which can be hinder keeping a given redox potential.

In order to address this further, more thermodynamic data, in particular reduction potentials, are needed to understand the redox chemistry of Tc - not only for Tc(VII)–Tc(IV) redox pair. For example, the most critically evaluated thermodynamic database of Tc solely reports the reduction of $[TcO_4]^-$ to TcO_2 and the reduction of $[TcO_4]^-$ to $[TcO_4]^{2-}$.[179]

Consequently, there are multiple knowledge gaps that need to be addressed in future studies from a chemical point of view (Figure 12).

Conclusions

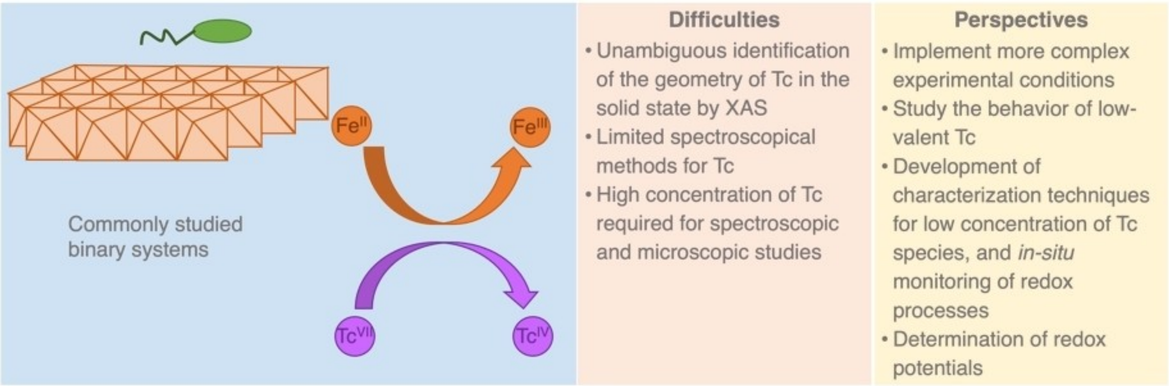
Even though technetium is radiopharmaceutically important, radioecologically relevant, and from a health and safety point of view relatively easy to handle, the numbers of papers on Tc chemistry has remained relatively constant over the last three decades. Compared to the general growing trends in scientific literature this shows that Tc chemistry is still under-researched, even though are significant knowledge gaps, in particular considering the differences in ^{99m}Tc chemistry and ^{99}Tc chemistry. This shows in many fields, such as spectroscopic data, particularly NMR and XAS. The lack of structural data is also underlined the relatively small number of inorganic and organic structures in the databases.

However, while physicochemical data, requiring often amounts >1 mg of material are somewhat stagnating, both inorganic chemistry and organometallic chemistry of Tc made significant progress in that time and some gaps in understanding fundamental bond interactions and geochemistry are slowly being filled.

Inorganic chemistry and organometallic chemistry both are strongly influenced by the redox behavior of Tc, which is often the key in understanding the fundamental differences between Tc and its homolog Re, just as much as the difference of ^{99}Tc and ^{99m}Tc is often affected by effects of low concentrations and temperature. Both these aspects are interconnected, and we believe that an expansion of Tc research both towards comparison with its neighbors as well as between its nuclear isomers will tell us a lot more about which drugs to synthesize, which form of waste disposal to choose or how to analyze our data.

A famous quote (probably misattributed to E. Rutherford) states that science is "either physics or stamp collecting". While this is probably a sarcastic classification, we would emphasize that any conceptual interpretation must be preceded by some kind of data collection, at best in a systematic way. Looking at Tc chemistry, e.g., the knowledge on organometallic chemistry seems to consist of several islands developing around structures that are known from radiopharmaceutical applications. We are convinced that once these islands are connected, the resulting map of Tc organometallic chemistry will also contribute to deeper understanding and "physical" science.

In this respect, we may conclude with a few key points that may be of interest to the wider community, as they apply as



Difficulties
- Unambiguous identification of the geometry of Tc in the solid state by XAS
- Limited spectroscopical methods for Tc
- High concentration of Tc required for spectroscopic and microscopic studies

Perspectives
- Implement more complex experimental conditions
- Study the behavior of low-valent Tc
- Development of characterization techniques for low concentration of Tc species, and *in-situ* monitoring of redox processes
- Determination of redox potentials

Figure 12. Usually studied Tc removal conditions in binary systems (blue box). Fe^{II} as an example of a reducing agent in solution or coming from microbial or mineral sources. Highlighted difficulties on Tc immobilization studies (orange box) and future perspectives (yellow box) of Tc geochemistry.

much to inorganic and geochemistry as to radiopharmacy and organic chemistry.

We do need to further our understanding of

I) the chemistry of Tc at low concentrations in comparison with high concentrations
II) Tc in the environment, and particularly focus on the difference between Tc and Re
III) the oxidation states of Tc other than +4 and +7
IV) spectroscopic data, and advance our usage of XAS as a versatile tool at hand to do this

Pertechnetate and related anions such as perrhenate can serve as versatile building blocks in crystal engineering due to their ability to form strong and directional matere bonds. These interactions not only stabilize the resulting crystal structures but also allow for the design of new materials with tailored properties. The examples from the CSD, combined with theoretical insights, underscore the significance of technetium and its congeners in advancing our understanding of non-covalent interactions in solid-state chemistry, paving the way for future innovations in the design of supramolecular materials, and understanding its interactions with other such oxoanions, both in the lab and in the environment.

Carbonyl complexes have been shown to be extremely relevant for radiopharmacy as well as for Tc speciation in environmental samples, and *vice versa*, radiopharmaceutical compounds have been proposed for the use in environmental remediation. The picture that Tc is mainly Tc(VII) or Tc(IV) under environmental conditions is probably oversimplified due to the fact that fundamental Tc chemistry is still under-researched. The inorganic chemiistry of Tc is also highly relevant for medical applications – any metabolism resulting in pertechnetate anions will result in an uptake of $[TcO4]^-$ into the thyroid where it is interchangeable with iodide.

Also, the future perspectives of Tc geochemistry are connected to the research results of redox and/or organometallic chemistry. In order to draw a realistic picture of the behavior of Tc in the environment, two fields of work have to be addressed. On the one hand, the Tc immobilization experiments need to be carried out under more realistic conditions. This implies the following points.

I) Widening the experimental conditions in binary systems (time, pH, Tc concentration, salinity) and explore those that have not yet been deeply analyzed (temperature, imposed redox potentials). This will not only help to understand the basis of Tc removal under the most expected environmental conditions, but also it will help to assess the chemical behavior of Tc when the chemical surrounding induces speciation changes e.g., the mineral transformation.
II) Expanding Tc immobilization studies to complex environments (ternary and quaternary systems) when multiple components coexist in suspension.
III) Developing techniques that allow for identifying the Tc geometry under low Tc concentrations. They will offer a more realistic understanding of the actual behavior of Tc in the environment.
IV) Always analyzing the changes in the mineralogy of the sorbent after Tc interaction with redox-active sorbents. This will help to overcome the difficulties on the identification of the Tc mechanistic scavenging process by XAS.
V) Exploring the Tc scavenging behavior of new, synthetic, sorbents.
VI) Limiting the use of Re as Tc analogue or carrying out more comparative studies between Re and Tc. In most of the cases, Re geochemistry is not analogue to Tc, and comparative works will help to assess their chemical differences.
VII) The immobilization of other Tc species different than Tc(VII) and Tc(IV) needs to be analyzed. These includes Tc(I) species (identified in Hanford site) and other Tc complexes in low oxidation states that are used in radiodiagnostics.

On the other hand, the redox chemistry of Tc requires a deep expansion. The following steps need to be fulfilled.

VII) Studying Tc reduction potentials in presence of (in)organic ligands in a wide range of pH values. This will help to evaluate the effect of such ligands on the redox processes of Tc and to describe new thermodynamic parameters: Tc reduction potentials, and the complexation of aqueous Tc-ligand species that might be formed. Expanding the so far limited thermodynamic data of Tc will enormously benefit the use of modelling tools to predict the geochemical behavior of Tc, which in turn will support the long-term safety assessment of Tc in the nuclear waste repository.
IX) Developing and optimizing the use of coupled electrochemical and spectroscopic methods. They will allow for studying in situ the changes in Tc chemistry and Tc molecular environment in solution or at the solid-water interphase at given potentials. These methodologies will provide the most accurate picture of Tc geochemistry under any possible environmental conditions.

These are a few aspects that we think are potential valuable starting points for anyone interested in enhancing this field. It's a large field, but the goals are open. Tc is still an unknown, right at the center of the Periodic Table.

Author Contributions

E.S.: concept, writing, editing, graphics, D.B.: writing, J.B.: writing, A.F.: writing, graphics, N.M.H.: writing, graphics, A. S.: writing, M.R.J.: writing, graphics, M.W.: writing, C.Y.: writing, editing, graphics, M.Z.: writing, editing

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Conflict of Interests

The authors declare no conflict of interest.

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