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Synthesis and Characterization of $A_3[ReO_4][ReO_3N]$ and $A'_2[ReO_3N]$ (A = Rb, Cs; A' = K, Cs)

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Crystallographically phase-pure samples of $A_3[ReO_4][ReO_3N]$ with A = Rb, Cs are obtained from the reaction of $NH_4[ReO_4]$ in an alkali metal hydroxide flux. Both compounds are isotypic to the known compound $K_3[ReO_4][ReO_3N]$ and crystallize in the space group $R\bar{3}m$.[1] $A'_2[ReO_3N]$ with A' = K, Cs are also synthesized from the respective alkali metal hydroxides, but with an increased amount of the nitrogen source via adding ammonium chloride to the starting mixture. $K_2[ReO_3N]$ crystallizes in the space group $C2/m$, whereas $Cs_2[ReO_3N]$ crystallizes in the space group $Pnma$. Along with the characterization of the four novel crystal structures, the experimental results are further supported by Raman spectroscopy and quantum chemical calculations.

1. Introduction

Oxometallates and nitridooxometallates represent two interesting classes of inorganic compounds that have garnered significant attention over decades.[2–8] Considering the nitridotrioxidometallates of transition metals, it is noticeable that only a few publications on technetium and rhenium in form of the nitridotrioxidotechnetate(VII) and nitridotrioxidorhenate(VII) salts $[MO_3N]^{2-}$ (M = Tc, Re) are reported. Some of them have been published only recently.[1,3,9,10] The nitridotrioxidometallates of other transition metals, such as $K[OsO_3N]$, $Ba_3[WO_3N]_2$, and $Ba_2[VO_3N]$ have been studied in more detail.[2,11,12] In the literature, the reactions are performed either by using gaseous/liquid NH_3 or by salt metathesis of an already existing nitridotrioxidometallate.[3,4,9,11] Pure nitrides, usually synthesized by high-temperature reactions involving nitrogen or ammonia as the nitrogen source,[13,14] are already known for their challenging synthesis. Similarly, the preparation of nitridotrioxidometallates can also be demanding. However, recently we were able to show that nitrogen from ammonium permetallates can be converted to a nitridotrioxidometallate in metal hydroxide hydrofluxes even at moderate temperatures.[1,10]

The recent work focuses on nitridotrioxidorhenates. $K_2[ReO_3N]$, the first compound featuring the respective $[ReO_3N]^{2-}$ anion has been published in 1960.[9] The latter has been obtained from the reaction of Re_2O_7 with KNH_2 in liquid NH_3. However, the obtained sample was not characterized via single crystal X-ray diffraction but by means of vibrational spectroscopy.[3,15] One crystallographic hint for the existence of the free anion $[ReO_3N]^{2-}$ was achieved via the characterization of a compound with the sum formula $K_3[ReO_4][ReO_3N]$, which has been synthesized via a hydroflux approach from ammonium perrhenate in a mixture of potassium hydroxide and water.[1,10] Similarly, $Ba[TcO_3N]$ has been obtained from ammonium pertechnetate in a mixture of barium hydroxide and water.[10] Similar to the two previously described syntheses, the title compounds $A_3[ReO_4][ReO_3N]$ (A = Rb, Cs) can be synthesized from $NH_4[ReO_4]$ in a flux of the respective alkali metal hydroxides, making these reactions less complex than working with liquid or gaseous ammonia. Furthermore, the amount of nitrogen in the synthesized compounds can be increased by adding more of a suitable ammonium compound as nitrogen source. Accordingly, it is possible to synthesize the nitridotrioxidorhenates $A'_2[ReO_3N]$ (A' = K, Cs).

2. Results and Discussion

Crystallographically phase-pure $A_3[ReO_4][ReO_3N]$ (A = Rb, Cs) could be obtained from $NH_4[ReO_4]$ in an alkaline flux of RbOH or CsOH, respectively. Both compounds were characterized by means of single-crystal structure analysis and via powder X-ray diffraction. The crystal structure of $Rb_3[ReO_4][ReO_3N]$ is shown in **Figure 1** and will be depicted in the following as an example for the two isotypic species $A_3[ReO_4][ReO_3N]$ (A = Rb, Cs). Both crystallize in the trigonal space group $R\bar{3}m$ and are isotypic to $K_3[ReO_4][ReO_3N]$, see **Table 1**.[1] The structures contain two crystallographically distinguishable alkali metal cations, whereas only one unique rhenium atom is present. Since the bond lengths give no hint for a predominant location of nitrogen all three distinguishable oxygen positions are refined as partially occupied by nitrogen with a fixed N:O ratio of 1:7, resulting in the total

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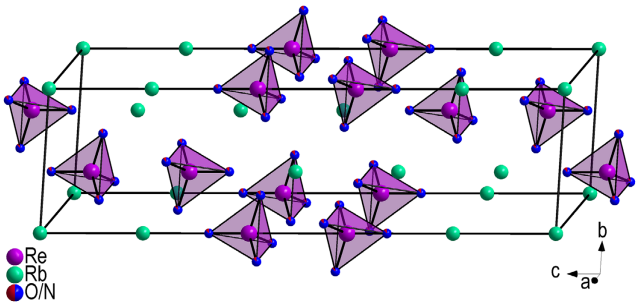

Figure 1. Crystal structure of $Rb_3[ReO_4][ReO_3N]$ with $[ReO_4]^-$ and $[ReO_3N]^{2-}$ polyhedra, whereas the mixed colored atoms are occupied with a ratio of 12.5% by N (red) and 87.5% by O (blue).

Table 1. Selected crystallographic data of $A_3[ReO_4][ReO_3N]$ with $A = Rb$, Cs.

Empirical formula	$Rb_3[ReO_4][ReO_3N]$	$Cs_3[ReO_4][ReO_3N]$
Formula weight	754.82 g mol^{-1}	897.14 g mol^{-1}
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Trigonal	Trigonal
Space group	$R\bar{3}m$ (no. 166)	$R\bar{3}m$ (no. 166)
Unit cell dimensions	$a = 6.1747(3)$ Å	$a = 6.3947(2)$ Å
	$c = 22.062(1)$ Å	$c = 23.160(1)$ Å
Volume	728.46(8) Å^3	820.18(6) Å^3
Z	3	3
Density (calculated)	5.16 g cm^{-3}	5.45 g cm^{-3}
$F(000)$	972	1134
Crystal size	0.10 × 0.06 × 0.01 mm^3	0.10 × 0.05 × 0.07 mm^3
2θ range for data collection	5.54° to 59.91°	5.28° to 57.95°
Index ranges	$-8 \le h \le 8$, $-8 \le k \le 8$, $-30 \le l \le 30$	$-8 \le h \le 8$, $-8 \le k \le 8$, $-31 \le l \le 31$
Reflections collected	6254	18322
Independent reflections	306 [$R_{int} = 0.0371$, $R_{sigma} = 0.0122$]	308 [$R_{int} = 0.0436$, $R_{sigma} = 0.0090$]
Completeness to θ	100%	100%
Absorption correction	Multi-scan	Multi-scan
Data/parameters	306/18	308/19
Goodness-of-fit on F^2	1.265	1.159
Final R indices [$I \ge 2\sigma(I_o)$]	$R_1 = 0.0197$, $wR_2 = 0.0474$	$R_1 = 0.0125$, $wR_2 = 0.0327$
R indices (all data)	$R_1 = 0.0207$, $wR_2 = 0.0477$	$R_1 = 0.0125$, $wR_2 = 0.0327$
Largest diff. peak and hole	1.69/–1.64 e Å^{-3}	1.91/–1.34 e Å^{-3}
CCDC number	2414620	2414618

composition $A_3[ReO_{3.5}N_{0.5}]_2$ (A = Rb, Cs), in the following written as $A_3[ReO_4][ReO_3N]$.

The same holds true for the previously published structure of $K_3[ReO_4][ReO_3N]$.[1] A detailed crystallographic analysis is provided in the literature from 2023, where the possibility of an O/N ordering has already been studied.[1] A comparison of the bond lengths within the $[ReO_3N]^{2-}$ tetrahedra across the three known mixed anionic species reveals consistent values. The Re–O/N bond lengths fall in the narrow range of 1.710(8)–1.747(4) Å.[1] **Figure 2** shows the coordination polyhedra of both crystallographically distinguishable rubidium cations.

Rb1 is coordinated by 12 O/N atoms with distances of 2.912(4) Å up to 3.5673(4) Å, building an icosahedron as confirmed by the program Polynator.[16] By using CHARDI2015, the coordinating ligands were verified.[17,18] In contrast, Rb2 is coordinated by 10 O/N atoms and forms the rather unusual polyhedron "mono-capped trigonal cupola" as determined by Polynator.[16,18] The bond lengths for Rb2 range from 2.825(8) Å to 3.185(1) Å. Similar metal-oxygen polyhedra are found for the potassium and cesium salts, with the respective distances depending on the central cation.[1]

Figure 3 shows the powder X-ray data and Rietveld refinement patterns, whereas Raman spectroscopy data can be found in **Figure 4**. The spectra were recorded for single crystals of the respective compounds. All spectra show the characteristic Re-N vibration in the range of 1010–1023 cm^{-1} and Re–O vibrations in the range of 966–971 cm^{-1}. The vibrations at lower wavenumbers are assigned to the symmetric and antisymmetric bending modes of the compounds and agree with the literature.[1] The bands shift to lower wavenumbers with increasing size of the alkali metal cations.

In addition to $A_3[ReO_4][ReO_3N]$ (A = Rb, Cs), single crystals of $K_2[ReO_3N]$ and $Cs_2[ReO_3N]$ could be obtained from a CsOH flux and a KOH hydroflux, respectively. Therefore, ammonium chloride as an additional nitrogen source was added. However, so far it was not possible to crystallize $Rb_2[ReO_3N]$. Furthermore, it was not possible to increase the amount of nitrogen in the oxo-anions even further.

$K_2[ReO_3N]$ crystallizes in the monoclinic space group $C2/m$ with four formula units per unit cell. The latter is not isotypic to $Cs_2[ReO_3N]$, which crystallizes in the orthorhombic space group $Pnma$ with four formula units per unit cell, see **Figure 5** and **6**, and **Table 2**.

As described for the mixed anionic compounds before, the nitrogen atoms are refined with a fixed N:O ratio of 1:3 as distributed over all four ligand positions in the tetrahedra of $A'_2[ReO_3N]$ with A' = K, Cs. Even though, freely refined oxygen atoms give

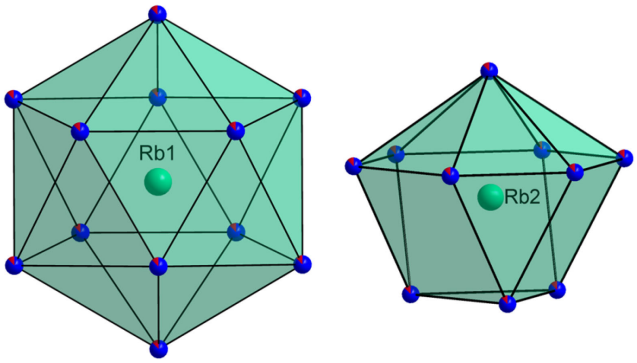

Figure 2. Rb-O/N polyhedra of $Rb_3[ReO_4][ReO_3N]$.

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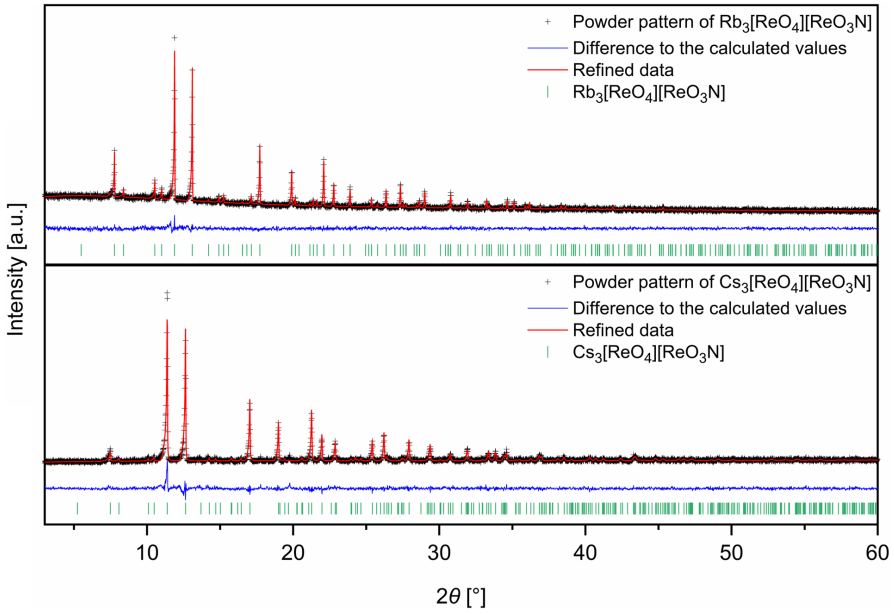

Figure 3. Powder X-ray data and Rietveld refinement patterns of $Rb_3[ReO_4][ReO_3N]$ and $Cs_3[ReO_4][ReO_3N]$.

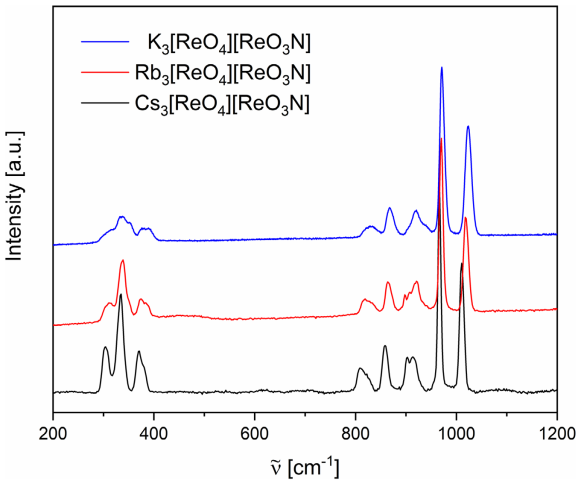

Figure 4. Raman spectra of $A_3[ReO_4][ReO_3N]$ (A = K, Rb, Cs).[1]

hint for a preferred occupancy of the O3 position in $K_2[ReO_3N]$ and the O2 and O3 position in $Cs_2[ReO_3N]$ with nitrogen, a localization of the nitrogen atom is not doubtless since the metal–ligand bond lengths do not differ significantly. Furthermore, a stable refinement failed due to strong correlation effects. Both, $K_2[ReO_3N]$ and $Cs_2[ReO_3N]$ contain one distinguishable rhenium atom which is coordinated by four O/N ligands and exhibit three crystallographically distinguishable O/N atoms. **Table 3** shows the bond lengths of the $[ReO_3N]^{2-}$ tetrahedra. It is noticeable that no significant differences in the bond lengths of both compounds can be observed. $K_2[ReO_3N]$ exhibits Re-ligand bond lengths of 1.764(3) Å, 1.779(4) Å and 1.756(3) Å, whereas $Cs_2[ReO_3N]$ has Re-ligand bond lengths of 1.770(2) Å, 1.737(4) Å and 1.762(3) Å. Compared to the mixed anionic species $A_3[ReO_4][ReO_3N]$ (A = K, Rb, Cs), the homoleptic compounds reveal slightly longer Re-O/N bonds.[1]

Examining the coordination polyhedra of the potassium and cesium cations, only irregular polyhedra can be determined

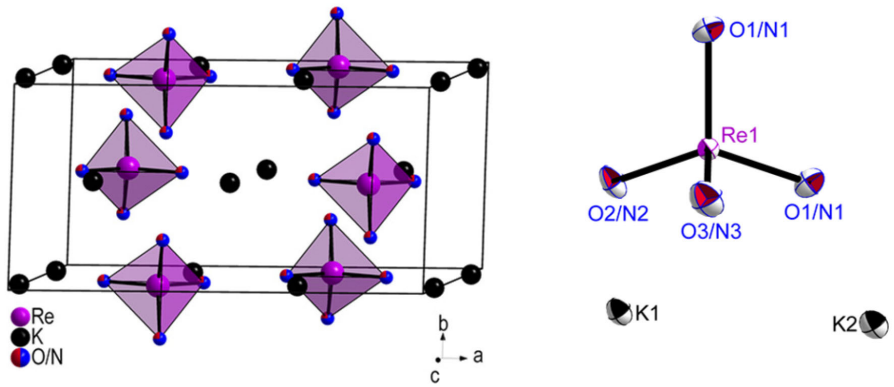

Figure 5. Crystal structure of $K_2[ReO_3N]$ (left) and the extended asymmetric unit with ellipsoid representation (70% probability, right). The mixed colored atoms are occupied with a ratio of 25% by N (red) and 75% by O (blue).

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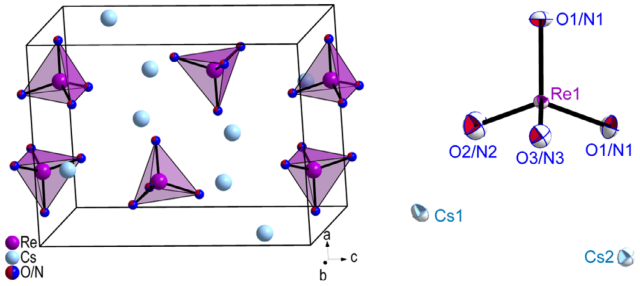

Figure 6. Extended unit cell of the crystal structure of $Cs_2[ReO_3N]$ (left) and the extended asymmetric unit with ellipsoid representation (70% probability, right). The mixed colored atoms are occupied 25% by N (red) and 75% by O (blue).

Table 2. Selected crystallographic data of $A'_2[ReO_3N]$ with $A' = K$, Cs.

Empirical formula	$K_2[ReO_3N]$	$Cs_2[ReO_3N]$
Formula weight	326.41 g mol^{-1}	514.03 g mol^{-1}
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Orthorhombic
Space group	*C*2/*m* (no. 12)	*Pnma* (no. 62)
Unit cell dimensions	$a = 12.3380(8)$ Å	a = 8.5375(2) Å
	$b = 6.0361(4)$ Å	$b = 6.4813(2)$ Å
	$c = 7.4694(5)$ Å	$c = 11.5049(3)$ Å
	$\beta = 114.687(3)°$	
Volume	505.43(6) Å^3	636.61(3) Å^3
Z	4	4
Density (calculated)	4.29 g cm^{-3}	5.36 g cm^{-3}
F(000)	576	864
Crystal size	0.04 × 0.03 × 0.03 mm^3	0.40 × 0.30 × 0.10 mm^3
2θ range for data collection	6.00° to 51.98°	5.94° to 61.19°
Index ranges	$-15 \le h \le 15$, $-7 \le k \le 7$, $-9 \le l \le 9$	$-12 \le h \le 12$ $-9 \le k \le 9$, $-16 \le l \le 16$
Reflections collected	5525	29483
Independent reflections	551 [$R_{int} = 0.0432$, $R_{sigma} = 0.0205$]	1062 [$R_{int} = 0.0814$, $R_{sigma} = 0.0202$]
Completeness to θ	99.8%	100%
Absorption correction	Multi-scan	Multi-scan
Data/parameters	551/40	1062/41
Goodness-of-fit on F^2	1.119	1.157
Final *R* indices [$I \ge 2\sigma(I_o)$]	$R_1 = 0.0113$, $wR_2 = 0.0258$	$R_1 = 0.0149$, $wR_2 = 0.0339$
R indices (all data)	$R_1 = 0.0116$, $wR_2 = 0.0259$	$R_1 = 0.0162$, $wR_2 = 0.0343$
Largest diff. peak and hole	0.59/–0.58 e Å^{-3}	2.41/–1.28 e Å^{-3}
CCDC number	2414619	2414617

with Polynator.[16] The coordinating ligands were verified with CHARDI2015.[17,18] **Figure 7** and **8** show the irregular polyhedra of the counter cations in $K_2[ReO_3N]$ and $Cs_2[ReO_3N]$, respectively.

Table 3. Selected bond lengths of $A'_2[ReO_3N]$ with $A' = K$, Cs.

$K_2[ReO_3N]$		$Cs_2[ReO_3N]$	
Atoms	Bond length [Å]	Atoms	Bond length [Å]
Re-O1/N1	1.764(3)	Re-O1/N1	1.770(2)
Re-O2/N2	1.779(4)	Re-O2/N2	1.737(4)
Re-O3/N3	1.756(3)	Re-O3/N3	1.762(3)

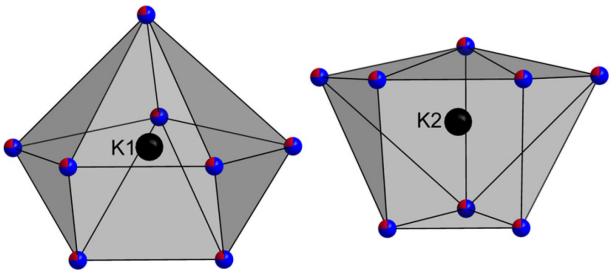

Figure 7. K-O/N polyhedra of $K_2[ReO_3N]$.

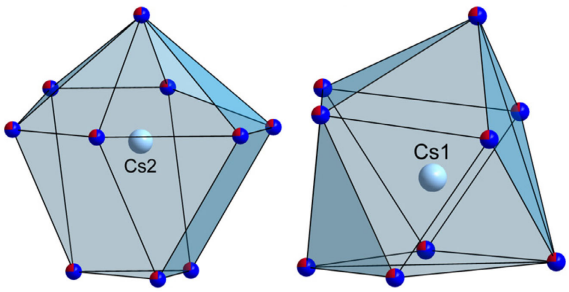

Figure 8. Cs-O/N polyhedra of $Cs_2[ReO_3N]$.

Raman spectra measured on single crystals of $K_2[ReO_3N]$ and $Cs_2[ReO_3N]$ are shown in Figure 6. A suitable reference compound is $Ba[TcO_3N]$.[10] Similar to the technetium salt, $A'_2[ReO_3N]$ ($A' = K$, Cs) exhibit bands in the range between 306 and 381 cm^{-1}, which can be identified as the Re–O/N bending vibrations. In the range of 814–869 cm^{-1} the stretching modes can be assigned.

The bands at wavenumbers >1000 cm^{-1} can be attributed to the Re–N stretching vibrations. Compared to $Ba[TcO_3N]$,[10] where only one band for the Re-N vibrations has been found at large wavenumbers, $K_2[ReO_3N]$ and $Cs_2[ReO_3N]$ clearly reveal two bands above 1000 cm^{-1}. Since the spectra were recorded on single crystals, no impurities are assumed to be present. Moreover, the additional band observed for $K_2[ReO_3N]$ and $Cs_2[ReO_3N]$ appears at wavenumbers comparable to those associated with the Re-N stretching vibration. This distinction can likely be attributed to differences in their crystal structures compared to $Ba[TcO_3N]$[10] and should be investigated by means of quantum chemical calculations (**Figure 9**).

As a representative compound, quantum chemical calculations on the solid-state structure of $K_2[ReO_3N]$ were performed using the CRYSTAL program suite, see Section 3 for detail on utilized basis sets and functionals. Calculated Raman spectra were obtained

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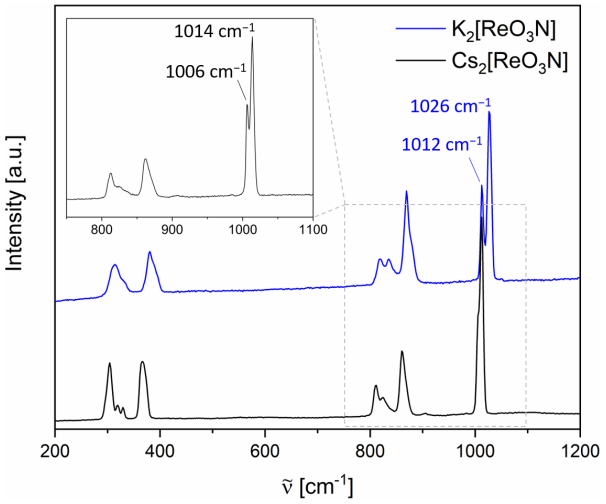

Figure 9. Raman spectra of $A'_2[ReO_3N]$ (A' = K, Cs). The top-left cutout of the $Cs_2[ReO_3N]$ spectrum was measured using the same single crystal but at a higher resolution compared to the overall measurement range of 200–1200 cm^{-1}.

for geometry optimized structures with either nitrogen on the O2 or O3 site, naming according to **Figure 10** and Figure S4, Supporting Information. These in silico obtained Raman spectra agree very well with experimental result, besides the fact that all bands are slightly shifted to higher wavenumbers which has been observed frequently in quantum chemical calculations.[19,20] The obtained bands at wavenumbers above 1000 cm^{-1} are almost identical for both nitrogen positions and reveal values of 1025 and 1019 cm^{-1}, see **Table 4**. Since the structure in *C*2/*m* shows two crystallographically identical ligand sites (O1), calculations with nitrogen on these different positions are impossible. Thus, the symmetry was reduced to space group *C*2 and the calculations were repeated with nitrogen on the two new different sites O1 and $O1^2$, respectively. See Figure S4, Supporting Information for the different positions in both symmetries. With reduced symmetry the maxima for nitrogen on both sites (O1 and $O1^2$) differ a little more, revealing values of 1039 and 1042 cm^{-1}, but are still consistent with the experimental data, see Table 4. All calculated spectra can be found in the Supporting Information.

Accordingly, the different crystallographic positions of the oxygen and nitrogen atoms seem to have a significant influence

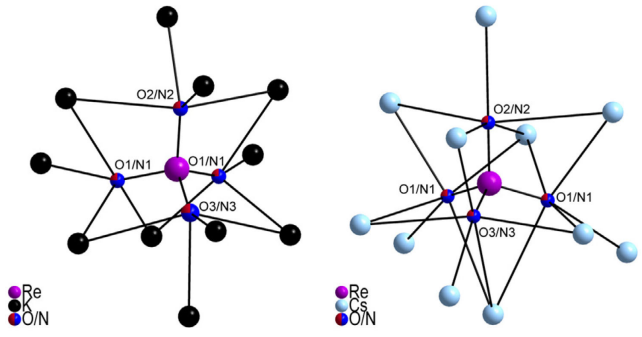

Figure 10. Structure of the coordination of O/N atoms by K/Cs in $K_2[ReO_3N]$ (left) and $Cs_2[ReO_3N]$ (right).

Table 4. Calculated Raman shifts when using the four different N positions in the $[ReO_3N]^{2-}$ tetrahedra, see also Figure S4, Supporting Information.

$K_2[ReO_3N]$ in *C*2/*m*		$K_2[ReO_3N]$ in *C*2	
N position	Raman shift [cm^{-1}]	N position	Raman shift [cm^{-1}]
2	1025.38	1	1039.11
3	1019.42	1^2	1041.86

on the vibrational modes. Figure 10 shows the different coordination spheres of $K_2[ReO_3N]$ (*C*2/*m*) and $Cs_2[ReO_3N]$ (*Pnma*). Overall, the finding of more than one band at highest wavenumbers is in good agreement with results of the similar $[VO_3N]^{4-}$ anion in Ba_2VO_3N exhibiting nonzero occupancies for nitrogen and oxygen as well as C_s symmetry.[2] In contrast, one band has been observed for an anion in C_{3v} symmetry like for $[ReO_3N]^{2-}$ in the herein presented mixed-anionic species and $[OsO_3N]^-$ in the respective sodium salt.[21]

Since it was now possible for the first time to determine the crystal structure of $K_2[ReO_3N]$, the results can be compared to known data of a bulk sample.[3,9] However, the latter has so far only been characterized by means of IR spectroscopy. The powder pattern of $K_2[ReO_3N]$ simulated from single crystal X-ray data from this publication does not agree with the pattern obtained for the species synthesized via the already published synthesis route with liquid ammonia, see Figure S1, Supporting Information.[3,9] However, the Raman spectra of the compounds from the two different routes agree very well, except a less pronounced splitting of the band at highest wavenumbers for the compound obtained from liquid ammonia, see Figure S2, Supporting Information.[9]

In summary, the syntheses of the nitridotrioxidometallates were obtained from flux reactions with water being present in small to moderate amounts. $Rb_3[ReO_4][ReO_3N]$ and $Cs_3[ReO_4][ReO_3N]$ are isotypic to $K_3[ReO_4][ReO_3N]$ and crystallize in the space group $R\bar{3}am$.[1] Both compounds have been investigated by powder X-ray diffraction, Rietveld refinement, and Raman spectroscopy. By increasing the nitrogen content in the starting mixture by simply adding ammonium chloride it was also possible to obtain $A'_2[ReO_3N]$ (A' = K, Cs). While the mixed anionic compounds crystallize in the same space group, $A'_2[ReO_3N]$ (A' = K, Cs) are not isotypic. $K_2[ReO_3N]$ crystallizes in the space group *C*2/*m*, whereas $Cs_2[ReO_3N]$ crystallizes in the orthorhombic space group *Pnma*. Raman spectroscopic measurements support the crystallographic results and prove the presence of Re-N bands. Quantum chemical calculations support the experimentally obtained Raman spectra.

3. Experimental Section

Syntheses

Colorless crystals of $A_3[ReO_4][ReO_3N]$ (A = Rb, Cs) were obtained from a flux reaction with alkali metal hydroxides by using a Teflon-lined stainless-steel autoclave. A batch contained 1 equivalent $NH_4[ReO_4]$ and 10–20 equivalents alkali metal hydroxide. The detailed batch information can be found in **Table 5**. The closed

Table 5. Detailed batch information for the syntheses of $A_3[ReO_4][ReO_3N]$ (A = Rb, Cs).

Reagent	*n* [mmol]	*m* [mg]	Equation	Product
$NH_4[ReO_4]$ (*Sigma–Aldrich*, ≥99%)	0.1	26.8	1	$Rb_3[ReO_4][ReO_3N]$
RbOH·xH_2O (*Thermo Scientific*, 99%)	2.0[a)]	205.0	20[a)]	
$NH_4[ReO_4]$ (*Sigma–Aldrich*, ≥99%)	0.3	80.5	1	$Cs_3[ReO_4][ReO_3N]$
CsOH·H_2O (*Acros Organics*, 99.95%)	3.0	503.8	10	

[a)]RbOH was purchased as a x-hydrate. The molar mass and equivalents were calculated based on RbOH anhydrate (102.48 g mol^{-1}).

autoclaves were heated at 200 °C for 10 h and cooled to room temperature with a cooling rate of 0.1 K min^{-1}. Single crystals of $A_3[ReO_4][ReO_3N]$ (*A* = Rb, Cs) were isolated after washing the reaction mixture with methanol. For the synthesis of phase-pure bulk samples, longer cooling times are required, specifically 0.02 K min^{-1} for $Rb_3[ReO_4][ReO_3N]$ and 0.03 K min^{-1} for $Cs_3[ReO_4][ReO_3N]$.

Colorless single crystals of $A'_2[ReO_3N]$ (*A*′ = K, Cs) were obtained from an alkali metal hydroxide flux by using a Teflon-lined stainless-steel autoclave. A batch contained 1 equivalent $NH_4[ReO_4]$ and 49–110 equivalents alkali metal hydroxide. Additionally, ammonium chloride as a nitrogen source was added. For $K_2[ReO_3N]$, 50 equivalents H_2O were added, so this reaction might be called hydroflux reaction. The detailed batch information can be found in **Table 6**. The closed autoclaves were heated at 200 °C for 10 h and cooled to room temperature with a cooling rate of 0.1 K min^{-1}. Single crystals of $A'_2[ReO_3N]$ (*A*′ = K, Cs) were mechanically removed from the flux. Phase-pure syntheses of bulk material were not successful.

Powder X-Ray Diffraction (P-XRD) and Rietveld Refinement

P-XRD data were collected on a Stoe Stadi-P powder diffractometer with a Mythen detector and a Debye−Scherrer geometry by using Mo–Kα_1 radiation of $\lambda = 0.70930$ Å. The samples were ground and sealed in glass capillaries with 0.3 mm diameter. The data was recorded in a range of $2\theta = 0°$–60° within 30 min. The Rietveld refinement was performed with Topas, refining the lattice parameters freely using the Thompson–Cox–Hastings profile function, see Table S1 and S2, Supporting Information.[22,23] For $Rb_3[ReO_4][ReO_3N]$ the atomic displacement parameters were also refined freely. The background was described with six Chebychev polynomials. The diffractogram was plotted using Origin software.[24]

Table 6. Detailed batch information for the syntheses of $A'_2[ReO_3N]$ (A′ = K, Cs).

Reagent	n [mmol]	m [mg]	Equation	Product
$NH_4[ReO_4]$ (*Sigma–Aldrich*, ≥99%)	0.2	53.7	1	$K_2[ReO_3N]$
NH_4Cl (stock, not specified)	0.6	32.1	3	
KOH (*Thermo Scientific*, ≈85%)	22.0	1234.3	110	
H_2O	10.0	180.2	50	
$NH_4[ReO_4]$ (*Sigma–Aldrich*, ≥99%)	0.1	26.8	1	$Cs_2[ReO_3N]$
NH_4Cl (stock, not specified)	0.3	16.1	3	
CsOH·H_2O (*Acros Organics*, 99.95%)	4.9	824.6	49	

Single-Crystal X-Ray Diffraction (SC-XRD)

The single-crystal XRD data were collected with a Bruker D8 Venture by using Mo-Kα radiation of $\lambda = 0.71073$ Å. The crystals were prepared under a polarization microscope and measured at a temperature of 100(2) K. The lattice parameters, the refinement details, the atomic parameters and selected bond lengths are given in Table 1 and 3. Further data can be found in Table S3–S22, Supporting Information. The solution and refinement of the structures were carried out using ShelXL/ShelXT in Olex2.[25,26] The pictures of the structures were generated using the Diamond software.[27]

Deposition Numbers 2414620 (for $Rb_3[ReO_4][ReO_3N]$), 2414618 (for $Cs_3[ReO_4][ReO_3N]$), 2414619 (for $K_2[ReO_4]$) and 2414617 (for $Cs_2[ReO_4]$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Raman Spectroscopy

Raman spectra of single crystals were obtained with a Renishaw InVia Qontor spectrometer by a frequency-doubled Ne:YAG laser with 532 nm wavelength and 100 mW output energy in 180 °C backscatter geometry, a slit opening of 65 μm, a Rayleigh edge filter with a cut-off below approx. 50 cm^{-1} and a back-illuminated CCD Centrus detector. The estimated spectral resolutions are about 0.7 cm^{-1} (1800 lines mm^{-1} grating) and 0.4 cm^{-1} (3000 lines mm^{-1} grating), respectively. The spectrometer was calibrated to a Si single crystal before measurements. Spectra were recorded at room temperature with a transmission filter of 5% over 20–60 times for 5 s using a 50x LWD objective. The data was plotted using the Origin Software.[24]

Quantum Chemical Calculations

DFT calculations were carried out with the Crystal 17 program suite[28–32] using the PBEsol[33] functional at pob-TZVP[34,35] basis set quality with an 8,8 k space grid. Raman spectra were calculated using geometry optimizations with subsequent frequency calculations ensuring optimized structures to be a minimum. See Figure S3 and Table 23–26, Supporting Information.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: flux · oxoanion · Raman spectroscopy quantum chemistry · rhenium

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