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A contribution to the perrhenate crystal chemistry: the crystal structures of new CdTh[MoO$_4$]$_3$-type compounds

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Abstract: Singe crystals of four new $A^{I}M^{II}[ReO_4]_3$ perrhenates (A^{I} = Na, M^{II} = Pb; A^{I} = Na, M^{II} = Sr, Ag, K) have been prepared from the respective $A^{I}[ReO_4]$ and $M^{II}[ReO_4]_2$ perrhenates using melt and solution evaporation techniques. All new compounds belong to the hexagonal CdTh[MoO$_4$]$_3$ structure type, similar to previously known NaCa[ReO$_4$]$_3$. We discuss the crystal chemical relationships within this structure type and suggest existence of some more representatives involving other tetrahedral anions.

Keywords: CdTh[MoO$_4$]$_3$-type; crystal structure; perrhenates; synthesis.

1 Introduction

Found in nature mostly as an isomorphous substituent for molybdenum in sulfide minerals [1, 2], rhenium also exhibits some structural analogies to molybdenum in their highest oxidation states, *e.g.* in oxoanions (ReO_4^- vs. MoO_4^{2-}). For instance, alkali-metal and thallium(I) perrhenates, $A^{I}[ReO_4]$, adopt the same scheelite structure type [3, 4] as alkaline earth-metal and lead molybdates, $M^{II}[MoO_4]$ [5]. Analogies exist also among several more complex structure types, including CdTh[MoO$_4$]$_3$. This arrangement, first observed for molybdates [6, 7], and among perrhenates of alkali metal cations and rare earths [8]. The coordination polyhedra of the lower- and higher-charged cations can be regarded as almost regular octahedra and tricapped trigonal prisms sharing oxygen vertices with the tetrahedral anions. This structure is sometimes considered as a filled version of an “expanded” UCl$_3$ type with the tetrahedral groups replacing the halide anions. The latter structure, with octahedral positions vacant, is observed for anhydrous perchlorates and perrhenates of rare earths; it is partially filled in the structure of $NaNd[ReO_4]_4 \equiv 4/3 \times (Na_{0.5})(Nd_{0.75}Na_{0.25})[ReO_4]_3$ ([8] and references therein).

Recently, a full structural Group 1–Group 2 perrhenate analog of CdTh[MoO$_4$]$_3$, namely NaCa[ReO$_4$]$_3$, was reported by Conrad and Schleid [9]. This structure type was also proposed for some more exotic compositions like LiCa[AlH$_4$]$_3$ [10, 11]. In an attempt to find more representatives of this architecture, we observed formation of four more double perrhenates among compounds of monovalent (Na^+, Ag^+, and K^+) and divalent (Sr^{2+} and Pb^{2+}) cations. In addition, single crystals of some anhydrous and hydrated divalent metal perrhenates were observed and their structures determined.

2 Experimental

2.1 Synthesis

The starting compounds were perrhenates of the moonooo- and divalent cations whereof most were obtained by dissolution of metal carbonates ($M^{II}CO_3$, M^{II} = Cd, Ca, Sr, Ba, Pb, and Li_2CO_3) or hydrogen carbonates $A^{I}HCO_3$ (A = Na or K) in perrhenic acid (prepared from metallic rhenium and hydrogen peroxide). Ammonium perrhenate was prepared directly from solutions of ammonia and perrhenic acid. The solutions formed were evaporated to dryness upon heating at 80–100 °C and the solid residues dried at 140 °C, except thermally unstable NH_4ReO_4 which was obtained by evaporation at room temperature. Heating the perrhenates at higher temperatures resulted in formation of colored (yellow or black) admixtures. The hygroscopic anhydrous perrhenates of alkaline earth metals and cadmium were stored in a desiccator. The perrhenates of silver and rubidium were obtained by mixing solutions of the corresponding nitrates and perrhenic acid in a 1:1 M ratio and cooling the solutions to 0 °C, to increase the yield. The silver perrhenate obtained in this way is light sensitive and was stored in darkness. Attempts to prepare Sn[ReO$_4$]$_2$ starting from SnSO$_4$ and Ba[ReO$_4$]$_2$ solutions were not successful. The transparent colorless solution formed after filtering off barium sulfate turned turbid within several minutes with precipitation of some dark substance, probably, a mixture of $SnO_2{\cdot}aq$ and $ReO_2{\cdot}aq$. Based on this

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result, no attempt was made for $Eu[ReO_4]_2$ as Eu^{2+} ($E°$ (Eu^{3+}/Eu^{2+}) = −0.36 V) is a much stronger reducer compared to Sn^{2+} ($E°$ (Sn^{IV}/Sn^{2+}) = +0.15 V). For the reduction of ReO_4^- to ReO_2, $E°$ = +0.51 V [12].

Two synthetic approaches were employed. In the first case, 1:1 mixtures of A^IReO_4 and $M^{II}[ReO_4]_2$ were thoroughly ground, dried at 140 °C for 1 h, places in silica-jacketed alumina crucibles, and annealed at 500 (M^{II} = Pb and Cd) – 850 (M^{II} = Ca, Sr, Ba) °C (heating rate 50 °C/h, soak time 48 h; cooling rate 20 °C/h). The solidified melts were blackish due to partial reduction of rhenium and possibly of silver; however, in some cases, colorless, rather hygroscopic crystals could be selected. Crystals of four new representatives of the $CdTh[MoO_4]_3$ structure type, namely $NaPb[ReO_4]_3$, $NaSr[ReO_4]_3$, $AgSr[ReO_4]_3$, and $KSr[ReO_4]_3$, could be prepared this way. In most other case, no reaction between the components was observed. As a side result, low-quality, very hygroscopic crystals of anhydrous calcium perrhenate $Ca[ReO_4]_2$ were also observed.

The other approach was based on evaporation of aqueous solutions containing A^IReO_4 (including the thermally unstable ammonium compound) and $M^{II}[ReO_4]_2$. Room-temperature evaporation is not appropriate in case of sparingly or poorly soluble perrhenates of lead, barium (as tetrahydrate), ammonium, potassium and rubidium. Single crystals of $NaSr[ReO_4]_3$ could however be prepared similar to $NaCa[ReO_4]_3$ [9]. This procedure also resulted in crystals of what appeared to be an elusive lead perrhenate dihydrate [13]. Evaporation upon mild heating yielded inhomogeneous, slightly blackened (most likely due to partial reduction of Re^{VII} into Re^{IV}) polycrystalline residues. Crystals of more new compounds, according to the cell metrics, were observed in most systems; these will be addressed in a following report. Formation of both target and some new compounds was verified also by powder X-ray studies. The highest yield exceeding 50% was observed for $NaCa[ReO_4]_3$ (test experiment, in agreement with [9]), $NaPb[ReO_4]_3$, and $NaSr[ReO_4]_3$.

2.2 Single-crystal X-ray studies

Single-crystal X-ray data of new compounds were collected using a Rigaku XtaLAB Synergy-S diffractometer equipped with a PhotonJet-S detector operating with MoKα radiation at 50 kV and 1 mA. A single crystal of each compound was chosen and more than a hemisphere of data collected with a frame width of 0.5° in ω, and 1.26–5.5 s spent counting for each frame. The data were integrated and corrected for absorption applying a multi-scan type model using the Rigaku Oxford Diffraction programs CrysAlis Pro. The structures of compounds were successfully refined with the use of Shelx software package. Atom coordinates and thermal displacement parameters for each temperature are collected in the corresponding cif files (Supplement 1); experimental parameters are provided in Table 1.

3 Results and discussion

The crystal structure of the lead sodium perrhenate representative is shown in Figures 1–3. This is yet an only lead-containing compound; no reaction was observed between $Pb[ReO_4]_2$ and $Li[ReO_4]$, $Ag[ReO_4]$, or $K[ReO_4]$ both in “dry” (high-temperature) and “wet” (room-temperature and mild heating) experiments.

Lead and ammonium perrhenates also crystallize separately from aqueous solutions. On the contrary, Sr^{2+} contributes to this structure with a richer set of monovalent cations (Na^+, Ag^+, and K^+). Neither Cd^{2+}, nor Ba^{2+} were found to contribute to this structure among perrhenates

Table 1: Crystallographic data and refinement parameters for $A^IM^{II}[ReO_4]_3$ perrhenates (A^I = Na, M^{II} = Pb; A^I = Na, M^{II} = Sr, Ag, K).

Compound	**$NaPb[ReO_4]_3$**	**$NaSr[ReO_4]_3$**	**$AgSr[ReO_4]_3$**	**$KSr[ReO_4]_3$**
Crystal system	Hexagonal	Hexagonal	Hexagonal	Hexagonal
Space group	$P6_3/m$ (# 176)	$P6_3/m$ (# 176)	$P6_3/m$ (# 176)	$P6_3/m$ (# 176)
a, Å	9.9558(15)	9.9376(5)	10.0234(4)	10.3155(2)
c, Å	6.6053(10)	6.5619(4)	6.5739(3)	6.47810(10)
V, Å^3	567.0(2)	561.21(7)	571.98(5)	596.98(2)
Z	2	2	2	2
$F(000)$	828	740	812	840
Radiation, wavelength, Å	MoKα, 0.71073	MoKα, 0.71073	MoKα, 0.71073	MoKα, 0.71073
Ranges of h, k, l	$-10 \le h \le 10$, $-10 \le k \le 10$, $-7 \le l \le 7$	$-13 \le h \le 10$, $-7 \le k \le 13$, $-8 \le l \le 7$	$-12 \le h \le 12$, $-13 \le k \le 13$, $-8 \le l \le 6$	$-15 \le h \le 15$, $-15 \le k \le 13$, $-9 \le l \le 9$
Number of reflections	3835	1875	4258	11902
Number of unique reflections	275	491	502	799
R_{int}	2.02	2.62	2.92	0.85
R_{equ}	5.98	2.59	6.05	2.30
R_{all}	2.24	2.12	2.79	1.87
R_1 [$F > 4\sigma(F)$]	1.59	1.91	2.63	1.77
wR_1 [$F > 4\sigma(F)$]	3.10	3.40	6.19	3.54
GOF	1.154	1.128	1.088	1.294
CCDC	2190510	2190512	2190509	2190511

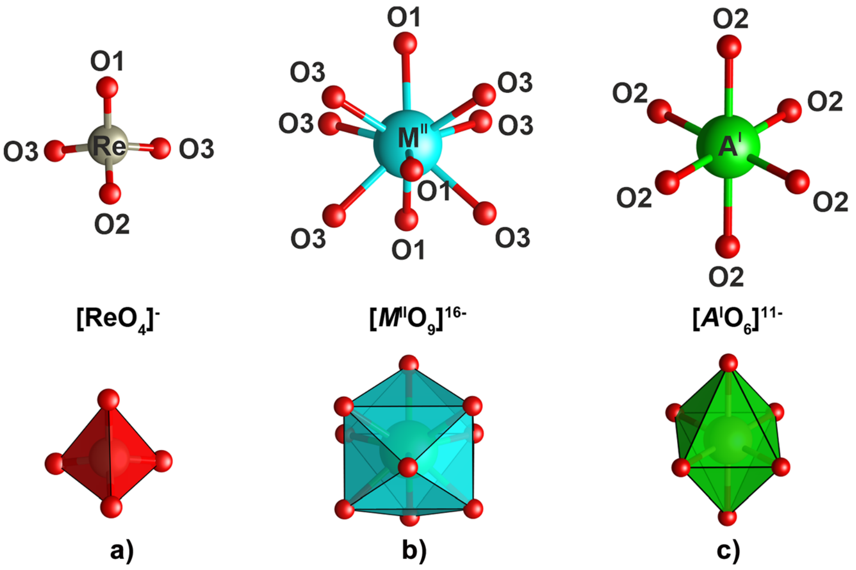

Figure 1: Coordination environments of metal cations in $A^IM^{II}[ReO_4]_3$ perrhenates (A^I = Na, M^{II} = Pb; A^I = Na, M^{II} = Sr, Ag, K).

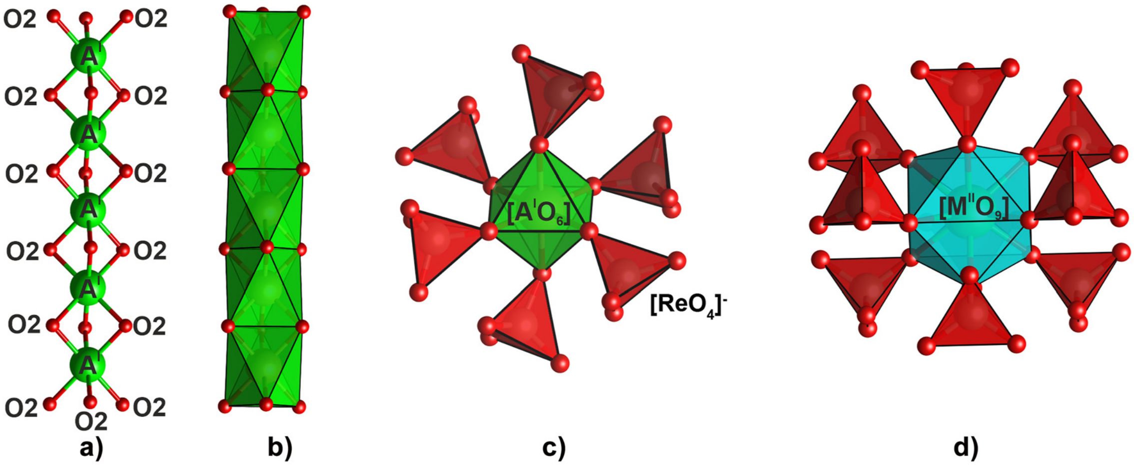

Figure 2: Structural units in $A^IM^{II}[ReO_4]_3$ perrhenates (A^I = Na, M^{II} = Pb; A^I = Na, M^{II} = Sr, Ag, K).

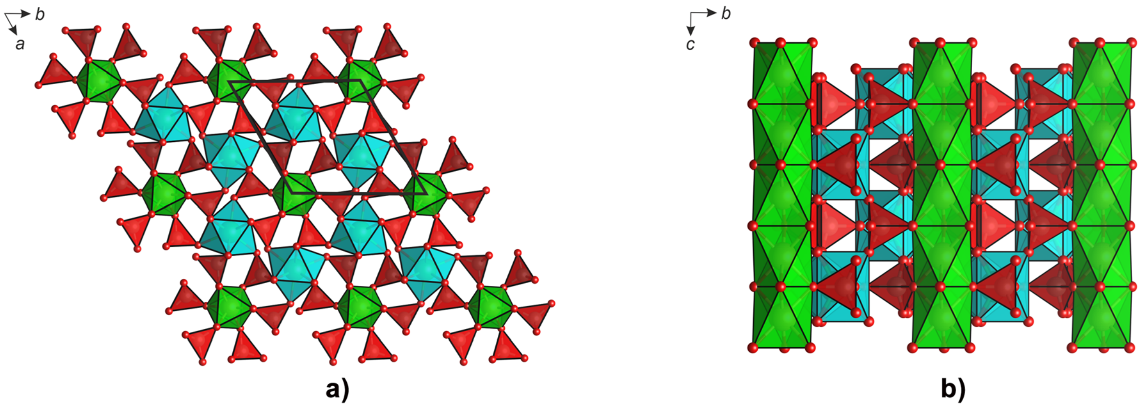

Figure 3: General projection of the crystal structure of $A^IM^{II}[ReO_4]_3$ perrhenates (A^I = Na, M^{II} = Pb; A^I = Na, M^{II} = Sr, Ag, K).

Table 2: Selected interatomic distances (Å) in $A^{I}M^{II}[ReO_4]_3$ perrhenates (A^{I} = Na, M^{II} = Pb; A^{I} = Na, M^{II} = Sr, Ag, K) and known $NaCa[ReO_4]_3$.

	$NaCa[ReO_4]_3$ [9]	$NaPb[ReO_4]_3$	$NaSr[ReO_4]_3$	$AgSr[ReO_4]_3$	$KSr[ReO_4]_3$
Re – O1	1.712(6)	1.737(9)	1.724(5)	1.719(6)	1.707(5)
Re – O2	1.727(6)	1.704(10)	1.737(4)	1.728(6)	1.724(5)
Re – O3 (2×)	1.712(5)	1.712(7)	1.725(3)	1.716(5)	1.697(4)
A^{I} – O2 (6×)	2.414(4)	2.455(7)	2.429(3)	2.472(5)	2.573(4)
M^{II} – O1 (3×)	2.538(6)	2.603(8)	2.600(4)	2.607(6)	2.660(4)
M^{II} – O3 (6×)	2.485(5)	2.636(7)	2.592(3)	2.604(5)	2.585(4)

under the conditions employed. Selected bond distances for the new $CdTh[MoO_4]_3$-type compounds are provided in Table 2. The monovalent cations center slightly distorted octahedra (Figure 1) which share opposite faces to form columns aligned along (001). These octahedra also share vertices (Figure 2) with the slightly distorted $[ReO_4]^-$ tetrahedra. In the series $NaM^{II}[ReO_4]_3$ (M^{II} = Ca, Pb, Sr), the Na–O distances remain nearly constant. Along the $A^{I}Sr[ReO_4]_3$ series (A^{I} = Na, Ag, K), the A^{I}–O distances increase but not so rapidly as could be expected from the ionic radii (Na^+: 1.02 Å, Ag^+: 1.15 Å, K^+: 1.38 Å [14]). It is curious to note that the $KSr[ReO_4]_3$ compound is characterized by a much smaller c/a ratio of 0.628 which for the three other compound is nearly the same (0.656–0.663). It is even smaller than those for $LiCa[AlH_4]_3$ (0.660) and $CdTh[MoO_4]_3$ (0.648) but close to that of (Cu, Mn)$U[MoO_4]_3$ (0.633).

The M^{2+} cations center tricapped trigonal prisms which share only vertices with the ReO_4 tetrahedra, to form vertex-sharing $[M^{II}(ReO_4)_9]^{7-}$ species (Figure 2). As follows from Table 2, all Sr–O distances in $NaSr[ReO_4]_3$ and $AgSr[ReO_4]_3$ are nearly equal; the difference between "face" (6-fold) and "cap" (3-fold) distances are relatively small in $NaPb[ReO_4]_3$ but quite noticeable in $NaCa[ReO_4]_3$ and $KSr[ReO_4]_3$. This difference reflects the distortions of the capped antiprisms which may be the "weak point" of the overall structure. It should also be noted that the regular environment of Pb^{2+} shows no evidence of the stereochemically active lone pair which is clearly manifested in the structure of anhydrous $Pb[ReO_4]_2$ [15]. In accordance with the closeness of ionic radii, the Sr–O and Pb–O distances are rather similar.

The perrhenate tetrahedron shares three of its vertices to three $[M^{II}O_9]^{16-}$ tricapped prisms (two to the bases and one to the cap) while the fourth is shared with an $[A^{I}O_6]^{11-}$ octahedron. The radial and angular distortions of these tetrahedra are relatively small indicating that they are the most rigid part of the structure (Figure 3).

The relative size of partaking cations and anions seem to strongly affect the stability of the respective structures. Among the structures of perrhenates, $CdTh[MoO_4]_3$ has the greatest number of representatives (seven) and some more can be experted upon more systematic studies of rare-earth compounds. Considering the systems wherein the targeted compounds were not produced, we may assume that the size of both the monovalent and divalent cations is important. The best "fit" is observed for Sr^{2+} for which the tricapped trigonal coordination is rather commonly observed among various perrhenate structures; it is reflected in the largest (yet three) number of representatives; the same is true for Na^+ for which octahedral coordination is quite common. For Ca^{2+}, the coordination number of nine is already somewhat high; this is reflected by the low number of representatives (only one) and its high hygroscopicity. The answer to this question can possible be obtained from systematic studies of various $(A^{I}_{0.5})(Ln_{0.75}A^{I}_{0.25})[ReO_4]_3$ compounds wherein the (mean) radius of the nine-coordinated cation varies more smoothly. There is evidence that a number of such compound actually exist among complex perrhenates of rare-earths and monovalent elements [16, 17]. Yet, the structural data on these compounds have not been published, to the best of our knowledge; more to the point, the mixed and incomplete site occupancies are expected to affect the stability of the structure, which additionally complicates the overall pattern.

The cation:anion size ratio is also likely to be important as Ca^{2+} contributes to this structure type in the company of a smaller cation, Li^+, and a smaller anion, $[AlH_4]^-$ [10, 11]. It would be of interest to see if this structure type could be also reproduced among tetrahydridoborates or tetrafluoroborates of calcium. Note that Cd^{2+}, despite of almost the same size as Ca^{2+}, does not contribute to this structure type: coordination number of 8 and 9 are probably too high for Cd^{2+} which more commonly adopts an octahedral coordination with oxygen. Indeed, it does so in the structure of $CdTh[MoO_4]_3$ itself. On the contrary, the coordination number of nine may be too small for Ba^{2+}; in addition, the relative size of $[BaO_9]^{16-}$ and $[A^{I}O_6]^{11-}$ polyhedra may fall beyond the stability limit of the structure in discussion. More data are evidently necessary to draw the conclusions, including systematic studies in the respective anhydrous and hydrated systems, which are currently underway.

The structural analogies between perrhenates and the respective anions centered by non-transition elements like perchlorates are restricted to the alkali salts and some compounds of rare-earths [8]. Yet, existence of $A^{I}M^{II}[ClO_4]_3$ or $A^{I}M^{II}[BrO_4]_3$ seems quite possible from a crystal chemical viewpoint. In addition, there exist at least some transition metal-based monoanions which may occasionally contribute to the structure types discussed here: $[MnO_4]^-$, $[TcO_4]^-$, $[CrO_3F]^-$, or $[OsO_3N]^-$. Though some of these are unstable towards thermal decomposition, hydrolysis or reduction, cases are accumulating when solution approaches bring fruitful results [18–20]; studies aimed to check some of these predictions are now in progress.

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