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# New calcium perrhenates: synthesis and crystal structures of $\text{Ca}(\text{ReO}_4)_2$ and $\text{K}_2\text{Ca}_3(\text{ReO}_4)_8 \cdot 4\text{H}_2\text{O}$

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**Abstract:** Single crystals of two new calcium perrhenates, anhydrous  $\text{Ca}(\text{ReO}_4)_2$  (**1**) and  $\text{K}_2\text{Ca}_3(\text{ReO}_4)_8 \cdot 4\text{H}_2\text{O}$  (**2**), were prepared during solid-state and solution attempts to prepare the potassium analog of  $\text{NaCa}(\text{ReO}_4)_3$ . Both structures can be regarded as frameworks comprised of vertex-sharing  $\text{CaO}_8$  and  $\text{ReO}_4$  polyhedra. **1** is a complete structural analog of  $\text{Sr}(\text{ReO}_4)_2$  while **2** corresponds to its own structure type. It is also the first hydrated binary perrhenate to date. We discuss the similarities and differences in the structures of alkaline earth perrhenates and pertechnetates; existence of more complex and elegant metal-perrhenate architectures is predicted.

**Keywords:** perrhenates; calcium; solid-state synthesis; crystal structure

## 1 Introduction

The interest to the compounds of rhenium has a complex background: they serve as model non-radioactive systems for further targeting compounds of technetium,<sup>1,2</sup> are involved in the separation of rhenium *per se*,<sup>3,4</sup> in addition, these are relatively sparsely studied and remain a “blank spot” when analyzing general trends in the chemistry of transition metals, particularly in higher oxidation states. For instance, inorganic perrhenates exhibit essential structural similarities evidently to pertechnates, but also to chromates,

molybdates, sometimes tungstates and perruthenates; less common are analogies to sulfates, selenates, perchlorates, etc. This mostly concerns the compounds of simple compositions, e.g. those corresponding to the scheelite or barite structures – which, amongst perrhenates, are adopted by compounds of univalent cations like alkali, thallium (I), and silver. Essentially less is known about double perrhenates or compounds of higher-valence cations. For instance, a small series of trigonal  $\text{M}^I\text{M}^{II}(\text{ReO}_4)_3$  compounds ( $\text{M}^I = \text{Na, K, Ag}$ ;  $\text{M}^{II} = \text{Ca, Sr, Pb}$ )<sup>5,6</sup> adopt the structure also observed for  $\text{CdTh}(\text{MoO}_4)_3$ <sup>7</sup> and  $(\text{Cu,Mn})\text{U}(\text{MoO}_4)_3$ ,<sup>8</sup> yet, not all combinations of  $\text{M}^I$  and  $\text{M}^{II}$  are possible. Just a single pertechnetate representative,  $\text{NaCa}(\text{TcO}_4)_3$ , is also known.<sup>9</sup> Several cation-deficient representatives,  $\text{M}^I\text{Ln}(\text{ReO}_4)_4$  ( $\text{M}^I = \text{Na, Ag}$ ),<sup>10,11</sup> as well as a single alumohydrate,  $\text{LiCa}(\text{AlH}_4)_3$ ,<sup>12</sup> have also been reported for the trigonal structure type. Among others, dihydrates of  $\text{Sr}(\text{ReO}_4)_2$ ,<sup>13</sup>  $\text{Pb}(\text{TcO}_4)_2$ , and  $\text{Pb}(\text{ReO}_4)_2$ <sup>9</sup> were reported to be isostructural yet the data for the latter are missing. Among perrhenates of alkaline earths, just a few compounds have been structurally characterized:  $\text{Ca}(\text{ReO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,<sup>14</sup>  $\text{Sr}(\text{ReO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,<sup>13</sup>  $\text{Ba}(\text{ReO}_4)_2 \cdot \text{H}_2\text{O}$ ,<sup>15</sup> and  $\text{Ba}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$ ,<sup>16</sup> as well as a single anhydrous compound  $\text{Sr}(\text{ReO}_4)_2$ .<sup>17,18</sup>

As we reported in<sup>5</sup>, attempts to prepare  $\text{KCa}(\text{ReO}_4)_3$  via solution and high-temperature approaches were not successful. However, these preparations resulted in formation of some new calcium perrhenates. Hereby we report the preparation and structural features of two new compounds,  $\text{Ca}(\text{ReO}_4)_2$  (**1**) and  $\text{K}_2\text{Ca}_3(\text{ReO}_4)_8 \cdot 4\text{H}_2\text{O}$  (**2**), obtained via these synthesis techniques.

## 2 Preparation of single crystals of $\text{Ca}(\text{ReO}_4)_2$ and $\text{K}_2\text{Ca}_3(\text{ReO}_4)_8 \cdot 4\text{H}_2\text{O}$

The  $\text{KReO}_4$ ,  $\text{Ca}(\text{ReO}_4)_2$  and  $\text{Ba}(\text{ReO}_4)_2$  precursors were obtained during reaction of  $\text{HReO}_4$  (prepared from 99.97 % Re powder and hydrogen peroxide) and analytically pure K, Ca, and Ca carbonates.  $\text{KReO}_4$  was dried in air while  $\text{Ca}(\text{ReO}_4)_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Ba}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$  were slowly heated to 140 °C and kept at this temperature for several hours. At higher temperatures, the color of the off-white powders thus obtained changes to yellow of gray which indicates loss or reduction of small amounts of rhenium and should be avoided.

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Strongly hygroscopic single crystals of  $\text{Ca}(\text{ReO}_4)_2$  were obtained during the search for new  $\text{CaTh}(\text{MoO}_4)_2$ -like perrhenates. In the solid-state experiments, 1 mmol  $\text{KReO}_4$  and 1 mmol dehydrated  $\text{Ca}(\text{ReO}_4)_2$  or  $\text{Ba}(\text{ReO}_4)_2$ , respectively, were placed into silica-jacketed alumina crucibles, rapidly ground, evacuated to 30 mTorr (*ca.* 4 Pa), sealed, and annealed in a programmable furnace to 560–750 °C with slow cooling (within 50 h) to room temperature. Single crystals could be picked out of the solidified melt which were identified as  $\text{KReO}_4$  and anhydrous  $\text{Ca}(\text{ReO}_4)_2$  (**1**). Formation of ternary perrhenates was observed indicating that no reaction took place and the system is probably eutectic. In the case of Ba-containing sample, good quality crystals were not formed. Attempts to crystallize pure dehydrated  $\text{Ca}(\text{ReO}_4)_2$  and  $\text{Ba}(\text{ReO}_4)_2$  in the same manner were not successful. The samples turned dark due to partial reduction of  $\text{Re}^{\text{VII}}$ , and the quality of crystals was too low for structural studies.

In the wet approach, an aqueous solution containing 2 mmol  $\text{KReO}_4$  and 2 mmol  $\text{Ca}(\text{ReO}_4)_2$  was evaporated on a hotplate until *ca.* 80 % of water was removed and a thick polycrystalline crust was formed. It was broken and the crystals separated from the slurry by vacuum filtration. Upon searching the polycrystalline sample, a crystal with relatively large cell dimensions was picked out (**2**). Subsequent structure determination (*vide infra*) revealed a rather complex calcium perrhenate framework containing large voids which were assumed to contain disordered potassium cations.

In both cases, the crystals were picked out of multiphase polycrystalline samples. Therefore, herein we restrict ourselves to the discussion and comparisons of the crystal structures of the new compounds.

### 3 Single-crystal X-ray experiments

Single crystals of studied compounds selected for X-ray diffraction analysis were glued onto glass filaments and arranged in a Rigaku XtaLAB Synergy-S diffractometer equipped with a PhotonJet-S detector operating with MoK $\alpha$  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  $\omega$ , and 10–50 s spent counting for each frame. The data were integrated and corrected for absorption applying a multiscan type model using the Rigaku Oxford Diffraction programs CrysAlis Pro. The unit cell parameters were calculated by the least-squares method. The cell metrics indicated close similarity to the low-temperature polymorph of  $\text{Sr}(\text{ReO}_4)_2$ ; hence, the initial atomic coordinates from<sup>17</sup> were used to refine the

structure of **1**. The structure of **2** was solved by direct methods. The parameters of the X-ray diffraction experiment and structure refinement are given in Table 1. The final model of compounds selected includes the coordinates and anisotropic thermal parameters of atoms. Selected interatomic distances are collected in Tables 2 and 3. Bond valence sums for  $\text{K}_2\text{Ca}_3(\text{ReO}_4)_8 \cdot 4\text{H}_2\text{O}$  (Table 4) were calculated using the parameters from Ref. 19.

## 4 Elemental analysis

Qualitative electron microprobe analysis of two compounds reported herein (LINK AN-10000 EDS system) revealed no other elements, except Ca and Re in  $\text{Ca}(\text{ReO}_4)_2$  and K, Ca and Re in  $\text{K}_2\text{Ca}_3(\text{ReO}_4)_8 \cdot 4\text{H}_2\text{O}$  with atomic number greater than 11 (Na).

## 5 Results

**Anhydrous  $\text{Ca}(\text{ReO}_4)_2$ .** The structure of anhydrous calcium perrhenate is shown in Figure 1. It contains one Ca, two Re,

**Table 1:** Crystallographic data and refinement parameters for  $\text{Ca}(\text{ReO}_4)_2$  and  $\text{K}_2\text{Ca}_3(\text{ReO}_4)_8 \cdot 4\text{H}_2\text{O}$ .

	$\text{Ca}(\text{ReO}_4)_2$	$\text{K}_2\text{Ca}_3(\text{ReO}_4)_8 \cdot 4\text{H}_2\text{O}$
<b>Crystal data:</b>		
Temperature (K)	293	100
Radiation	MoK $\alpha$	MoK $\alpha$
Crystal system	Monoclinic	Tetragonal
Space group	$P2_1/n$	$P4/ncc$
$a$ (Å)	6.0874(3)	12.7047(2)
$b$ (Å)	9.8178(5)	
$c$ (Å)	12.3120(6)	21.5501(7)
$\beta$ (°)	95.343(4)	
$V$ (Å <sup>3</sup> )	732.63(6)	3,478.39(16)
$Z$	4	4
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	4.900	4.325
$\mu$ (mm <sup>-1</sup> )	33.714	28.512
<b>Data collection:</b>		
$\theta$ Range (°)	3.324–27.998	3.709–27.995
$h, k, l$ ranges	–7 → 8, –12 → 10, –16 → 16	–14 → 11, –16 → 13, –25 → 28
Total reflections collected	7,809	15,719
Unique reflections ( $R_{\text{int}}$ )	1,619 (0.0494)	2,005 (0.0304)
<b>Structure refinement:</b>		
Weighting scheme $a, b$	0.0409, 62.7534	0.0, 73.2729
$R_1[F > 4\sigma F], wR_1[F > 4\sigma F]$	0.0450, 0.1175	0.0277, 0.0546
$R_{\text{all}}, wR_{\text{all}}$	0.0482, 0.1187	0.0300, 0.0552
Goodness-of-fit	1.143	1.268
CCDC	2415241	2415242

**Table 2:** Selected interatomic distances (Å) in  $\text{Ca}(\text{ReO}_4)_2$ .

Ca1–O7	2.351(12)	Re1–O2	1.704(13)
Ca1–O2	2.373(14)	Re1–O3	1.707(12)
Ca1–O1	2.401(14)	Re1–O4	1.720(12)
Ca1–O3	2.407(12)	Re1–O1	1.724(13)
Ca1–O4	2.423(12)	<Re1–O>	1.714
Ca1–O5	2.430(14)		
Ca1–O6	2.457(14)	Re2–O8	1.715(13)
Ca1–O8	2.758(14)	Re2–O5	1.722(14)
<Ca1–O>	2.450	Re2–O6	1.729(13)
		Re2–O7	1.739(12)
		<Re2–O>	1.726

**Table 3:** Selected interatomic distances (Å) in  $\text{K}_2\text{Ca}_3(\text{ReO}_4)_8 \cdot 4\text{H}_2\text{O}$ .

K1A–O6	2.86(2)	Ca1–Ow1	2.395(5)	× 4	Re1–O8	1.702(7)
K1A–Ow1	2.99(2)	Ca1–O4	2.488(5)	× 4	Re1–O6	1.717(6)
K1A–O8	3.07(2)	<Ca1–O>	2.442		Re1–O2	1.723(5)
K1A–O4	3.16(2)				Re1–O3	1.733(5)
K1A–Ow1	3.36(2)	Ca2–O2	2.430(6)	× 4	<Re1–O>	1.719
K1A–O6	3.47(2)	Ca2–O5	2.460(7)	× 4		
<K1A–O>	3.15	<Ca2–O>	2.445		Re2–O7A <sup>a</sup>	1.657(10)
					Re2–O7B <sup>b</sup>	1.843(10)
K1B–O8	2.69(1)	Ca3–O7A <sup>a</sup>	2.383(10)	× 4	Re2–O5	1.709(7)
K1B–O6	2.88(1)	Ca3–O3	2.434(6)	× 4	Re2–O4	1.710(6)
K1B–O8	3.13(1)	Ca3–O7B <sup>a</sup>	2.457(11)	× 4	Re2–O1	1.717(6)
K1B–O5	3.21(1)	<Ca3–O>	2.425		<Re2–O>	1.727
K1B–O2	3.23(1)					
K1B–O4	3.35(1)					
K1B–O6	3.39(1)					
<K1B–O>	3.13					

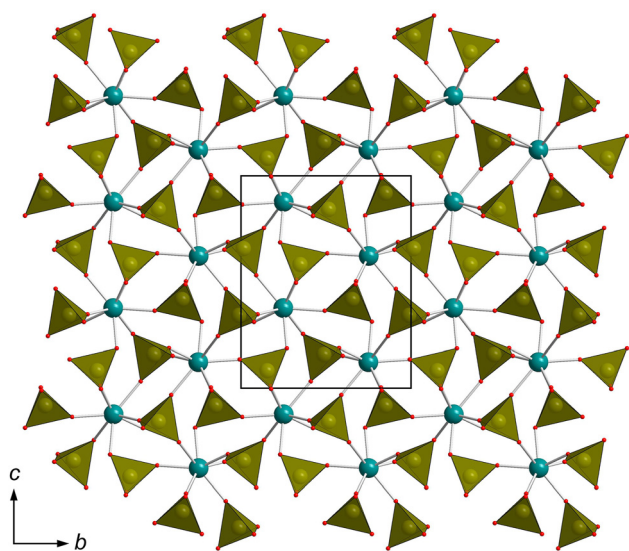
<sup>a</sup>O7A s.o.f. = 0.5; <sup>b</sup>O7B s.o.f. = 0.5.

and eight O sites (Figure 2). The compound is isostructural to the monoclinic polymorph or  $\text{Sr}(\text{ReO}_4)_2$ .<sup>17</sup>  $\text{Ca}^{2+}$  adopts a coordination number of eight with formation of a polyhedron which can be regarded as a bicapped trigonal prism. The Ca–O distances range from 2.353(2) Å to 2.758(5) Å all except the longest one lie between 2.353(2) Å and 2.457(1) Å. The environment of  $\text{Sr}^{2+}$  in  $\text{Sr}(\text{ReO}_4)_2$  is essentially more regular ( $d(\text{Sr} - \text{O}) = 2.59(2) - 2.68(2)$  Å). The Re–O bonds lie within 1.706(3)–1.723(3) Å for Re1 and 1.716(1)–1.735(1) Å for Re2. The distortions of the  $\text{ReO}_4$  tetrahedra are relatively small and comparable to those in  $\text{Sr}(\text{ReO}_4)_2$ :  $d(\text{Re1–O}) = 1.66(1) - 1.74(1)$  Å,  $d(\text{Re2–O}) = 1.68(1) - 1.73(1)$  Å. The angles are in the range 109.1(9)° – 110.2(7)° and 108.4(6)° – 110.9(6)° for  $\text{Re1O}_4$  and  $\text{Re2O}_4$  tetrahedra, respectively. The  $\text{CaO}_8$  and  $\text{ReO}_4$  polyhedra form a 3D framework (Figure 1).

**$\text{K}_2\text{Ca}_3(\text{ReO}_4)_8 \cdot 4\text{H}_2\text{O}$ .** This structure is symmetrical and complex and features three Ca, two Re, nine O sites one of which (O7) is split over O7A and O7B (50 %/50 % occupancy) and two weakly occupied K sites (20 and 30 %). The coordination polyhedra of all  $\text{Ca}^{2+}$  cations can be regarded as square antiprisms. Ca1 is coordinated by oxygen atoms from four perrhenate groups and from four water molecules ( $d(\text{Ca1–O4}) = 2.488(5)$  Å,  $d(\text{Ca–Ow}) = 2.395(5)$  Å, Figure 3) while Ca2 ( $d(\text{Ca2–O2}) = 2.430(6)$  Å,  $d(\text{Ca2–O5}) = 2.460(7)$  Å) and Ca3 ( $d(\text{Ca3–O3}) = 2.434(6)$  Å,  $d(\text{Ca3–O7A}) = 2.384(10)$  Å,  $d(\text{Ca–O7B}) = 2.457(11)$  Å), only by the perrhenate groups. The range of these bond distances is very similar to that for anhydrous  $\text{Ca}(\text{ReO}_4)_2$  (*vide supra*) and  $\text{CaCl}(\text{ReO}_4) \cdot 2\text{H}_2\text{O}$  (2.359(2) Å and 2.531(2) Å).<sup>20</sup> The rhenium atoms center

**Table 4:** Bond-valence values (in *vu*) in the crystal structure of  $\text{K}_2\text{Ca}_3(\text{ReO}_4)_8 \cdot 4\text{H}_2\text{O}$ .

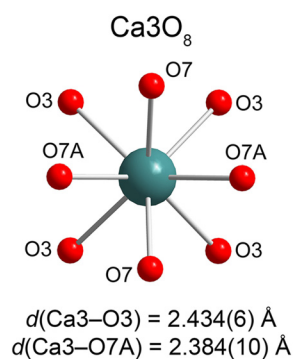
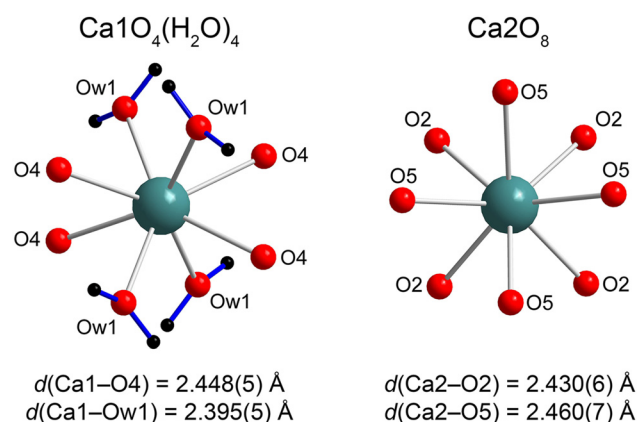
	O1	O2	O3	O4	O5	O6	O7A	O7B	O8	Ow1	Σ
							s.o.f. = 0.5	s.o.f. = 0.5			
Ca1				0.24 × 4→						0.30 × 4→	2.16
Ca2		0.28 × 4→			0.26 × 4→						2.16
Ca3			0.28 × 4→				0.16 × 4→	0.13 × 4→			2.28
							0.31 × 4↓	0.26 × 4↓			
Re1		1.73	1.69			1.73			1.82		6.97
Re2	1.73			1.78	1.78		1.01	0.65			6.95
K1A				0.06→		0.13→			0.08→	0.09→	0.43
s.o.f. = 0.2				0.01↓		0.03→			0.02↓	0.04→	
						0.03↓				0.02↓	
						0.01↓				0.01↓	
K1B		0.05→		0.04→	0.05→	0.12→			0.19→		0.55
s.o.f. = 0.3		0.02↓		0.01↓	0.02↓	0.03→			0.07→		
						0.04↓			0.06↓		
						0.01↓			0.02↓		
Σ	1.73	2.03	1.97	2.04	2.06	1.82	2.25	1.69	1.92	0.33	



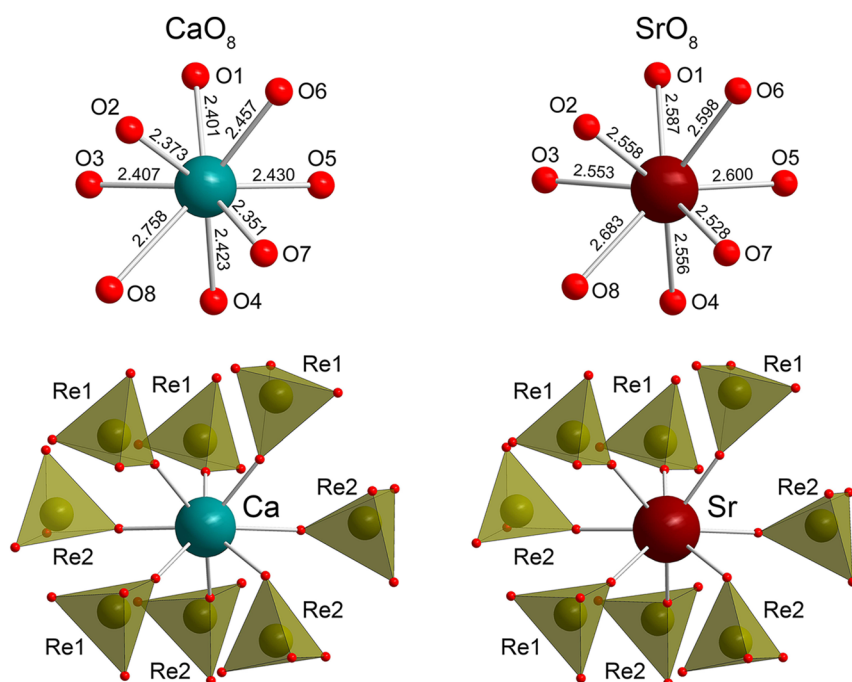
**Figure 1:** General projection of the crystal structure of  $\text{Ca}(\text{ReO}_4)_2$ .

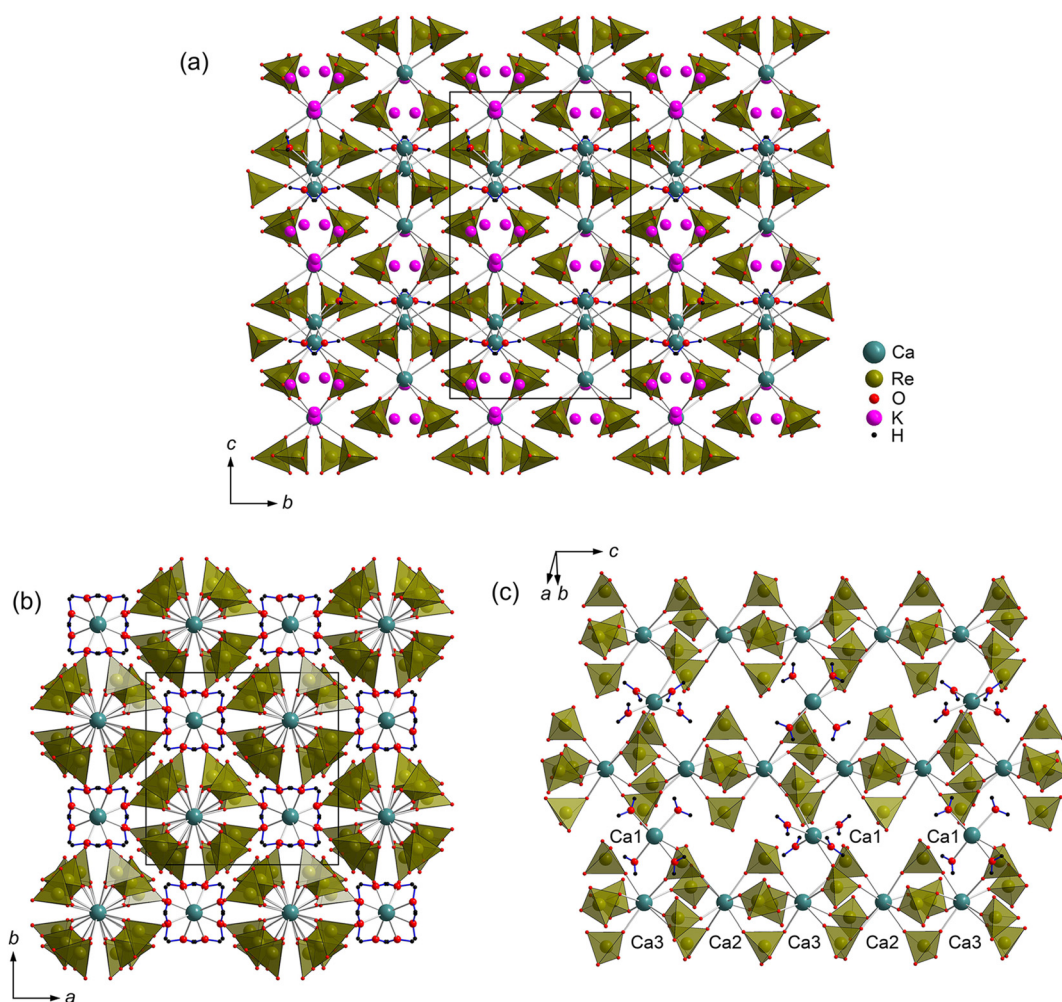
somewhat distorted tetrahedra ( $d(\text{Re1}-\text{O}) = 1.702(7) - 1.733(5) \text{ \AA}$ ;  $d(\text{Re2}-\text{O}) = 1.657(10) - 1.843(10) \text{ \AA}$ ). A large dissimilarity and lower precision in the bond distances for Re2 is due to orientational disorder of the  $\text{Re2O}_4^-$  tetrahedron, most likely caused by the partial occupancy of the neighboring K sites. The  $\text{CaO}_8$  antiprisms and  $\text{ReO}_4$  tetrahedra share vertices to form a holey heteropolyhedral framework with relatively large cavities gilled by disordered potassium cations (Figure 4). There is one symmetrically independent Ow1 water molecule in the structure of  $\text{K}_2\text{Ca}_3(\text{ReO}_4)_8 \cdot 4\text{H}_2\text{O}$ .  $\text{Ow1}-\text{H1} \cdots \text{O1}$  and  $\text{Ow1}-\text{H2} \cdots \text{O6}$

hydrogen bonds with  $D \cdots A$  distances 2.814(8) and 3.110(9)  $\text{ \AA}$  and  $\langle \text{DHA} \rangle$  angles 165.83° and 165.16°, respectively, are formed.



**Figure 3:** Coordination environments of Ca in the crystal structure of  $\text{K}_2\text{Ca}_3(\text{ReO}_4)_8 \cdot 4\text{H}_2\text{O}$ .





**Figure 4:** General projection of the crystal structure of  $\text{K}_2\text{Ca}_3(\text{ReO}_4)_8 \cdot 4\text{H}_2\text{O}$  along the  $a$  axis with voids filled by partially occupied K cations (a). K sites are omitted in two structure projections below for clarity (b,c).

## 6 Discussion and concluding remarks

As noted above, the sparsity of data on “simple” inorganic perrhenates permits yet little to conclude about the structural relationships between these and other compounds of  $d$ -metal-centered tetrahedral anions. The anhydrous calcium and strontium perrhenates are isostructural but not their dihydrates,<sup>13,21</sup> despite the essential difference in the ionic radii of  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$ .<sup>22</sup> This structure is totally different from that of anhydrous  $\text{Pb}(\text{ReO}_4)_2$ <sup>14</sup> while the radii of  $\text{Sr}^{2+}$  and  $\text{Pb}^{2+}$  are similar and  $\text{NaPb}(\text{ReO}_4)_3$  and  $\text{NaSr}(\text{ReO}_4)_3$  are again isostructural.<sup>5</sup>  $\text{Ca}(\text{TcO}_4)_2 \cdot 2\text{H}_2\text{O}$  is isostructural to its perrhenate analog,<sup>9</sup> the same applies to the iso-formula compounds of strontium and, probably, lead. Again,  $\text{Ba}(\text{ReO}_4)_2 \cdot 4\text{H}_2\text{O}$  is isostructural to the corresponding

pertechnetate while the anhydrous compounds adopt different structures.<sup>9</sup> Unfortunately, the structures of anhydrous  $\text{Ca}(\text{TcO}_4)_2$  and  $\text{Sr}(\text{TcO}_4)_2$  are as yet unknown.

The structures of  $\text{NaCa}(\text{ReO}_4)_3$  and  $\text{Ca}(\text{ReO}_4)_2$  contain relatively simple heteropolyhedral frameworks. An essentially more complex architecture is observed in that of  $\text{K}_2\text{Ca}_3(\text{ReO}_4)_8 \cdot 4\text{H}_2\text{O}$  (2) which also exhibits relatively high symmetry. Contrary to hygroscopic  $\text{Ca}(\text{ReO}_4)_2$  with the same coordination number of  $\text{Ca}^{2+}$ , this compound crystallizes from aqueous solutions. This is partially in line with the behavior of hydrated alkaline earth perrhenates which effloresce, rather than deliquesce, in air.<sup>23</sup> It is also very likely that formation of such complex and elegant frameworks, exemplified by the structure of  $\text{K}_2\text{Ca}_3(\text{ReO}_4)_8 \cdot 4\text{H}_2\text{O}$ , will, upon further studies, be observed in a variety of perrhenate-, and possible pertechnetate-based systems.

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**Data availability:** The raw data can be obtained on request from the corresponding author.

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