

Structural Units in Three Uranyl Perrhenates

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Three uranyl perrhenates have been synthesized, and their structures have been determined. $(\text{UO}_2)_2(\text{ReO}_4)_4(\text{H}_2\text{O})_3$ (**1**) is triclinic, space group $P\bar{1}$, $a = 5.2771(7)$, $b = 13.100(2)$, $c = 15.476(2)$ Å, $\alpha = 107.180(2)$, $\beta = 99.131(3)$, $\gamma = 94.114(2)^\circ$, $V = 1001.12$ Å³, $Z = 2$. $[(\text{UO}_2)_4(\text{ReO}_4)_2\text{O}(\text{OH})_4(\text{H}_2\text{O})_7](\text{H}_2\text{O})_5$ (**2**) is also triclinic, space group $P\bar{1}$, $a = 7.884(1)$, $b = 11.443(2)$, $c = 16.976(2)$ Å, $\alpha = 83.195(4)$, $\beta = 89.387(4)$, $\gamma = 85.289(4)^\circ$, $V = 1515.70$ Å³, $Z = 2$. $\text{Na}(\text{UO}_2)(\text{ReO}_4)_3(\text{H}_2\text{O})_2$ (**3**) is monoclinic, space group $C2/m$, $a = 12.311(3)$, $b = 22.651(6)$, $c = 5.490(1)$ Å, $\beta = 109.366(6)^\circ$, $V = 1444.24$ Å³, $Z = 4$. These compounds are the first structurally characterized uranyl perrhenates that do not contain organic ligands. In each structure, perrhenate groups coordinate uranyl ions at the equatorial vertices of pentagonal bipyramids. **1** contains complex chains of uranyl pentagonal bipyramids that are bridged by vertex sharing with perrhenate groups. The structural units in **2** and **3** consist of three novel finite clusters that include the coordination of uranyl ions with perrhenate. In general, weakly coordinating ligands such as perchlorate, perrhenate, and pertechnetate are assumed not to form stable complexes with uranyl in solutions or solids. The current findings, together with other recently reported studies, indicate each of these ligands can coordinate uranyl, and novel structure types result.

1. Introduction

The crystal chemistry of inorganic uranyl compounds has been significantly advanced over the past decade, including a doubling of the number of well-determined structures.¹ Many of the newly reported structures possess complex topologies made possible by the linkage of uranyl polyhedra with oxyanions such as sulfate,^{2–4} molybdate,^{5–9} vanadate,^{10–13}

iodate,^{14–17} selenite,^{18–20} and silicate.^{21,22} Weakly coordinating ligands such as perchlorate, perrhenate, and pertechnetate are usually assumed not to form stable complexes with uranyl.²³ However, it is well-known that pertechnetate coextracts with uranyl in the PUREX (plutonium and uranium recovery by extraction) process,²⁴ an observation

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Table 1. Crystallographic Information for **1**, **2**, and **3**

	1	2	3
formula	(UO ₂) ₂ (ReO ₄) ₄ (H ₂ O) ₃	[(UO ₂) ₄ (ReO ₄) ₂ O(OH) ₄ (H ₂ O) ₇](H ₂ O) ₅	Na(UO ₂)(ReO ₄) ₃ (H ₂ O) ₂
fw	1594.91	1880.74	1047.65
space group	P1	P1	C2/m
a (Å)	5.2771(7)	7.884(1)	12.311(3)
b (Å)	13.100(2)	11.443(2)	22.651(6)
c (Å)	15.476(2)	16.976(2)	5.490(1)
α (deg)	107.180(2)	83.195(4)	
β (deg)	99.131(3)	89.387(4)	109.366(6)
γ (deg)	94.114(2)	85.289(4)	
V (Å ³)	1001.12	1515.70	1444.24
Z	2	2	4
D _{calcd} (g/cm ³)	5.291	4.121	4.818
μ (mm ⁻¹)	40.3	29.4	36.33
R1	0.0372	0.0559	0.0402
wR2	0.0638	0.0911	0.0767
largest diff. peak and hole (e/Å ³)	2.6 and -2.5	2.3 and -2.7	2.4 and -2.7

that has motivated several recent studies of the uranyl-pertechnetate and uranyl-perrhenate systems,^{25–30} as perrhenate is often utilized as a crystal-chemical analogue for pertechnetate. The structures of [UO₂(ReO₄)(TPPO)₃] (where TPPO is triphenylphosphine oxide)²⁶ and [UO₂(ReO₄)-(DPPMO₂)₂][ReO₄] (where DPPMO₂ is bis(diphenylphosphino)methane dioxide)³¹ contain uranyl pentagonal bipyramids with two monodentate perrhenate ligands. It has been shown that the structures of [UO₂(μ₂-ReO₄)(ReO₄)(TBPO)₂]₂ (where TBPO is tri-*n*-butylphosphine oxide) and [UO₂(μ₂-ReO₄)(ReO₄)(TiBP)₂]₂ (where TiBP is tri-*iso*-butyl phosphate) both contain dimeric uranyl complexes that are bridged by perrhenate.²⁵ On the basis of infrared data, the structure of [UO₂(ReO₄)₂·H₂O] is also thought to contain bridging perrhenate.²⁶ A structure determination has shown that pertechnetate bridges neptunyl pentagonal bipyramids to form infinite chains in [(NpO₂)(TcO₄)₄·3H₂O].³² In the case of perchlorate, the structure of [UO₂(ClO₄)₂(H₂O)₃] contains a uranyl pentagonal bipyramid with two perchlorate monodentate ligands.²³

Our ongoing interest in the structural topologies of uranyl compounds,¹ as well as applications of uranyl structural chemistry to nuclear waste management^{33–35} provided the impetus for the current study of the crystal chemistry of uranyl perrhenates. Here, we report the synthesis and

Table 2. Selected Interatomic Distances for **1**, **2**, and **3**

	1	2	3		
U1–O18	1.746(9)	U1–O6	1.738(9)	U1–O5	1.734(8)
U1–O15	1.759(8)	U1–O7	1.765(8)	U1–O3	1.747(8)
U1–O20	2.364(8)	U1–O19	2.356(8)	U1–O8	2.362(7) × 2
U1–O9	2.376(8)	U1–O19	2.367(7)	U1–O7	2.402(7)
U1–O21	2.382(8)	U1–O25	2.414(9)	U1–O1	2.416(6) × 2
U1–O7	2.387(8)	U1–O10	2.433(9)		
U1–O8	2.389(7)	U1–O23	2.457(9)	Re1–O9	1.703(7) × 2
				Re1–O1	1.720(6) × 2
U2–O5	1.753(7)	U2–O2	1.765(9)		
U2–O22	1.760(8)	U2–O8	1.777(8)	Re2–O6	1.682(6)
U2–O1	2.380(9)	U2–O17	2.199(9)	Re2–O10	1.689(6)
U2–O2	2.408(7)	U2–O26	2.417(9)	Re2–O4	1.723(7)
U2–O13	2.413(8)	U2–O18	2.428(8)	Re2–O8	1.750(7)
U2–O19	2.418(9)	U2–O22	2.452(9)		
U2–O10	2.453(9)	U2–O21	2.458(7)	Na1–O6	2.436(7) × 2
				Na1–O10	2.467(7) × 2
Re1–O11	1.702(9)	U3–O1	1.760(9)	Na1–O9	2.712(9) × 2
Re1–O16	1.707(8)	U3–O3	1.761(8)	Na1–O4	2.719(9) × 2
Re1–O2	1.736(7)	U3–O17	2.206(8)		
Re1–O9	1.752(8)	U3–O20	2.388(8)		
		U3–O9	2.428(9)		
Re2–O14	1.684(9)	U3–O21	2.441(8)		
Re2–O6	1.704(9)	U3–O24	2.483(8)		
Re2–O17	1.713(8)				
Re2–O20	1.732(9)	U4–O4	1.752(9)		
		U4–O5	1.789(8)		
Re3–O12	1.696(9)	U4–O17	2.209(8)		
Re3–O19	1.698(9)	U4–O20	2.420(8)		
Re3–O3	1.71(1)	U4–O18	2.444(8)		
Re3–O8	1.732(7)	U4–O27	2.457(9)		
		U4–O28	2.462(8)		
Re4–O23	1.69(1)				
Re4–O4	1.688(8)	Re1–O12	1.67(1)		
Re4–O7	1.757(8)	Re1–O16	1.69(1)		
Re4–O21	1.756(8)	Re1–O11	1.708(9)		
		Re1–O9	1.724(9)		
		Re2–O13	1.66(1)		
		Re2–O15	1.69(1)		
		Re2–O10	1.69(1)		
		Re2–O14	1.74(1)		

characterization of the first three compounds without organic molecules containing direct uranyl-perrhenate linkages.

2. Experimental Section

Sample Preparation. Crystals of (UO₂)₂(ReO₄)₄(H₂O)₃ (**1**) were obtained from a solution of equimolar amounts of UO₃ and Re₂O₇ in ultrapure water. The bright-yellow solution was evaporated to dryness in a desiccator over P₂O₅ and resulted in yellow crystals of **1** up to several hundreds of micrometers in maximum length.

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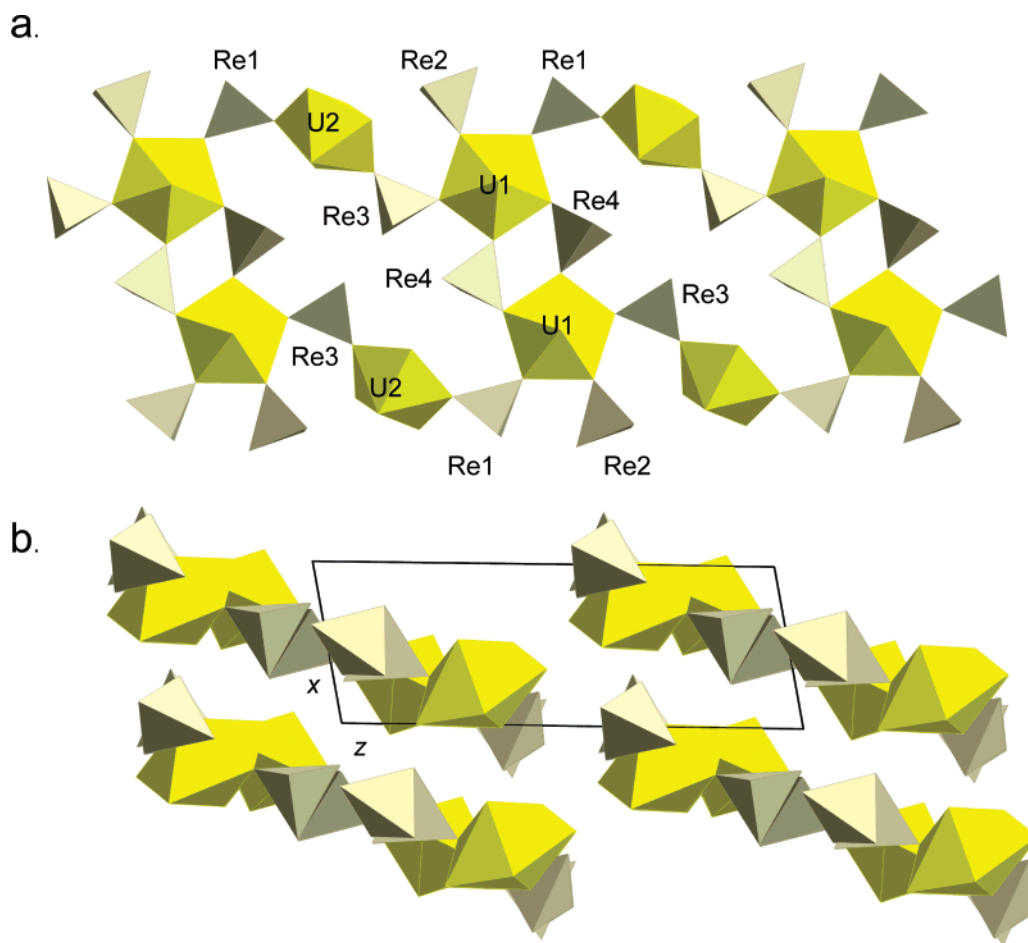


Figure 1. Polyhedral and ball-and-stick representations of the crystal structure of $(\text{UO}_2)_2(\text{ReO}_4)_4(\text{H}_2\text{O})_3$ (**1**). Uranyl polyhedra are yellow and perhenate tetrahedra are green.

The crystals are hygroscopic and soluble in water, acetone, and alcohol.

Crystals of $[(\text{UO}_2)_4(\text{ReO}_4)_2\text{O}(\text{OH})_4(\text{H}_2\text{O})_7](\text{H}_2\text{O})_5$ (**2**) were produced by combining 0.142 g UO_3 and 0.251 g HReO_4 and heating the resulting solution to a point of boiling ($\sim 170^\circ\text{C}$). The solution was then evaporated to dryness in air. Plate-shaped yellow transparent crystals with maximum dimensions of $\sim 100\ \mu\text{m}$ were obtained.

Crystals of $\text{Na}(\text{UO}_2)(\text{ReO}_4)_3(\text{H}_2\text{O})_2$ (**3**) were prepared by combining 0.142 g UO_3 with 0.502 g HReO_4 and heating the resulting solution to the point of boiling ($\sim 170^\circ\text{C}$). After heating, 0.20 mL of a 12.5% NaOH solution was added, and the resulting solution was allowed to evaporate to dryness over P_2O_5 . This procedure resulted in both crystals of **1** and yellow flattened prisms of **3** up to $200\ \mu\text{m}$ in maximum dimension.

Chemical Analyses. Crystals of each compound were mounted on glass slides, coated with carbon, and analyzed using a JEOL JXA 8600 electron superprobe. Qualitative energy dispersive analysis confirmed the elements present in each compound and their relative abundances.

Infrared Spectroscopy. Infrared spectra were obtained for single crystals of **1** using a SensIR technology IlluminatIR FTIR Microspectrometer. A single crystal was placed on a glass slide, and the spectrum was collected with a diamond ATR objective. The spectrum was taken from 400 to $3600\ \text{cm}^{-1}$ with an aperture of $100\ \mu\text{m}$.

Single-Crystal X-ray Diffraction. Single crystals of **1**, **2**, and **3** were mounted on tapered glass fibers for X-ray diffraction

analysis. A sphere of data was collected for each compound using a Bruker three-circle X-ray diffractometer equipped with an APEX CCD detector. Data were collected at 125 K for **1** and at room temperature for **2** and **3**. Data were collected using monochromatic $\text{Mo K}\alpha$ radiation with a frame width of 0.3 in omega. Unit-cell parameters were refined by least-square techniques using the Bruker *SMART* software, and the *SAINTE* software was used for data integration including Lorentz and polarization corrections. Semiempirical corrections for absorption were applied using the program *SADABS*. Selected data collection parameters and crystallographic information are provided in Table 1 and selected interatomic distances are in Table 2.

The structures of **1**, **2**, and **3** were solved using direct methods and were refined on the basis of F^2 for all unique data using the Bruker *SHELXTL* version 6 system of programs.³⁶ Atomic scattering factors for each atom were taken from the International Tables for X-ray Crystallography.³⁷ The structure refinements for **1** and **3** were straightforward and included anisotropic displacement parameters for the oxygen, rhenium, sodium, and uranium atoms, except for O2 in **3**, which corresponds to a H_2O group that was refined isotropically. The final model for **2** included anisotropic displacement parameters for uranium, oxygen, and rhenium atoms, except that isotropic parameters were used for terminal oxygen atoms of ReO_4 groups and oxygen atoms of H_2O groups held in the structure

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by hydrogen bonding only. The displacement parameters are large for the oxygen atoms of the interstitial H₂O groups, and it is possible that some of these sites are partially occupied.

3. Results

The structures of **1**, **2**, and **3** each contain sites that are occupied by U⁶⁺ cations, each of which is strongly bonded to two atoms of oxygen to give nearly linear (UO₂)²⁺ uranyl ions. The bond lengths within these uranyl ions range from 1.734(8) to 1.789(9) Å, with average bond lengths of 1.752 (**1**), 1.756 (**1**), 1.751 (**2**), 1.770 (**2**), 1.760 (**2**), 1.770 (**2**), and 1.740 (**3**). These uranyl ion bond lengths are generally shorter than the 1.79(3) Å average from 270 uranyl pentagonal bipyramids in 143 well-refined inorganic structures.¹ Each uranyl ion is coordinated by five equatorial ligands in these structures, giving pentagonal bipyramids. The Re⁺⁷ cations are tetrahedrally coordinated in each structure, with individual Re–O bond lengths ranging from 1.66(1) to 1.756(8) Å, consistent with other perrhenate structures.^{25,26}

1 is isostructural with its neptunyl pertechnetate analogue.³² There are two symmetrically distinct uranyl pentagonal bipyramids in the structure. The U(1) uranyl ion is monodentate coordinated by five perrhenate groups, with equatorial bond lengths ranging from 2.364(8) to 2.389(7) Å (Figure 1). The U(2) uranyl ion is coordinated by two perrhenate groups with equatorial U–O bond lengths of 2.408(7) and 2.418(9) Å, and by three H₂O groups, with equatorial bond lengths ranging from 2.380(9) to 2.453(9) Å. The Re(1), Re(3), and Re(4) perrhenate groups bridge between two uranyl polyhedra, whereas the Re(2) perrhenate is terminal. The uranyl–perrhenate linkages result in a chain of polyhedra that extends along [010], with adjacent chains connected solely through hydrogen bonds (Figure 1).

2 is a novel compound that contains two new finite clusters of uranyl pentagonal bipyramids and perrhenate tetrahedra (Figure 2). One of these clusters contains the U(1) uranyl ion that is coordinated by two hydroxyl groups, two H₂O groups, and one perrhenate tetrahedron. The resulting uranyl pentagonal bipyramid shares an OH–OH edge with a symmetrically equivalent U(1) bipyramid, resulting in a dimer with two terminal perrhenate groups in a trans arrangement (part a of Figure 2) and the composition [(UO₂)₂–(OH)₂(H₂O)₄(ReO₄)₂]. The second cluster (part b of Figure 2) contains all of the U(2), U(3), and U(4) uranyl bipyramids, which share a common O(17) vertex with U–O(17) bond lengths ranging from 2.199(9) to 2.209(8) Å. The cluster also contains three OH groups, each of which is shared between two bipyramids. The resulting trimer of edge-sharing bipyramids contains six equatorial vertices that are not shared between bipyramids. One of these, located in the U(3) bipyramid, corresponds to a perrhenate tetrahedron, whereas the other five are occupied by H₂O groups. This cluster is extraordinary in that it contains all of O, OH, and H₂O as equatorial ligands of uranyl polyhedra. The composition of this unusual cluster is [(UO₂)₃O(OH)₃(ReO₄)(H₂O)₅]. Both of the clusters in **2** are electroneutral. These clusters are unique in uranyl crystal chemistry, although the trimer of pentagonal bipyramids of the larger of these clusters has been

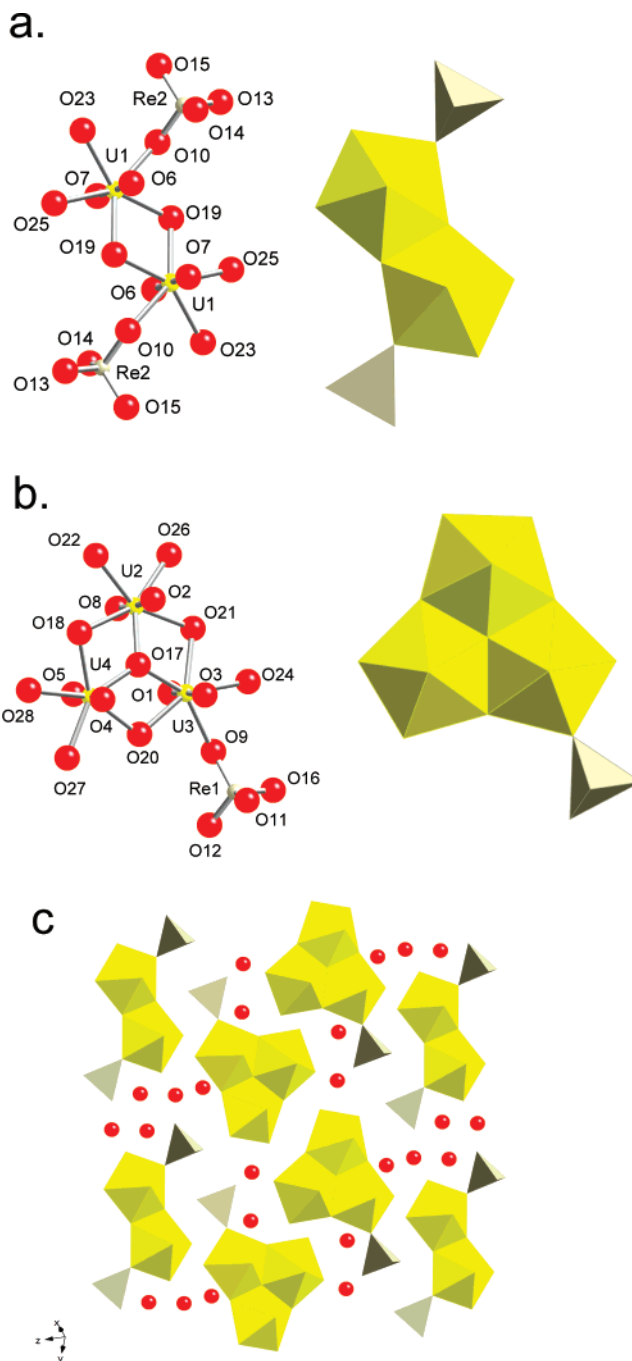


Figure 2. Polyhedral and ball-and-stick representations of the crystal structure of [(UO₂)₄(ReO₄)₂O(OH)₄(H₂O)₇](H₂O)₅. Isolated clusters of uranyl pentagonal bipyramids (yellow) and perrhenate tetrahedra (green) (a,b) and their arrangement within a layer parallel to (111) with oxygen atoms of interstitial H₂O groups shown in red (c).

observed in [(UO₂)₃O(OH)₃(H₂O)₆](NO₃)(H₂O)₄,³⁸ where the equatorial vertex occupied by perrhenate in **2** is replaced by an H₂O group. The interstitial regions contain an additional five H₂O groups, and the clusters are linked through a network of hydrogen bonds (part c of Figure 2).

3 contains a finite cluster of uranyl pentagonal bipyramids and perrhenate tetrahedra (Figure 3). The single symmetrically unique U(1) position is coordinated by four perrhenate tetrahedra and one H₂O group, and the Re(1)

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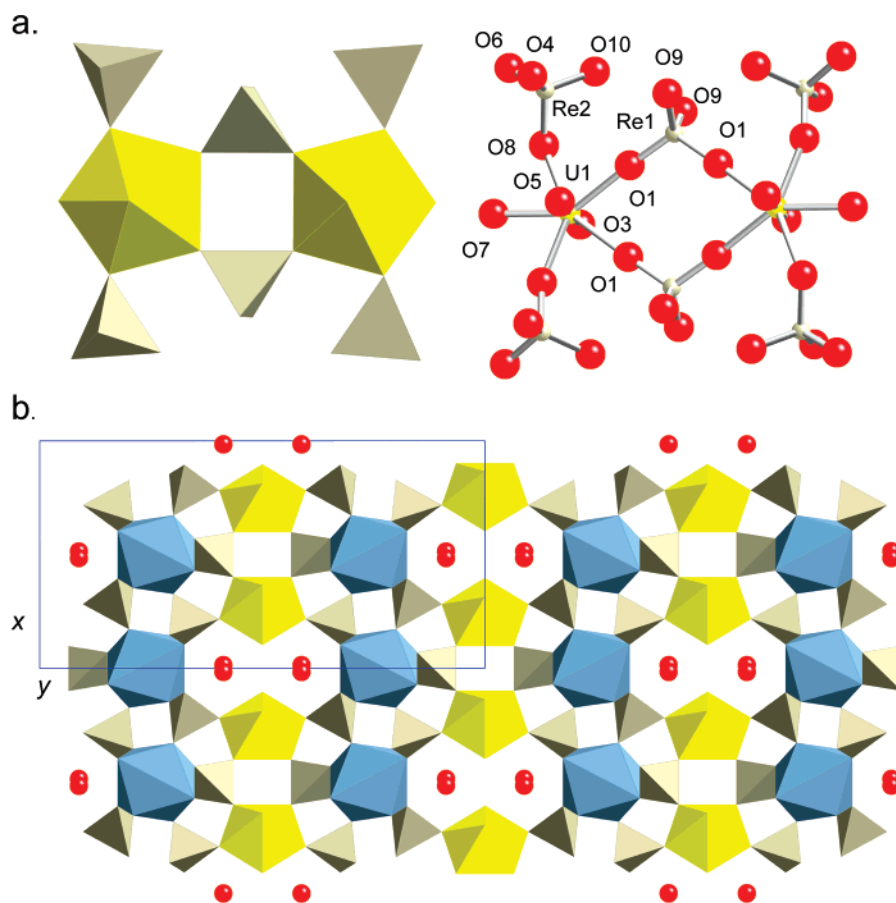


Figure 3. Polyhedral and ball-and-stick representations of the crystal structure of $\text{Na}(\text{UO}_2)(\text{ReO}_4)_3(\text{H}_2\text{O})_2$ showing an isolated cluster of uranyl pentagonal bipyramids (yellow) and perrhenate tetrahedra (green) (a), and the connection of these clusters through sodium polyhedra (blue) (b).

perrhenates bridge between symmetrically equivalent bipyramids, whereas the Re(2) perrhenate groups are terminal. The resulting cluster has the composition $[(\text{UO}_2)_2(\text{ReO}_4)_6(\text{H}_2\text{O})_2]^{2-}$. The charge of the cluster is balanced by sodium cations located in interstitial positions. The Na(1) site is bidentate coordinated by four perrhenate groups, and the eight bond lengths cluster into groups of four at ~ 2.45 and ~ 2.71 Å. There is also an H_2O group located at an interstitial position, and hydrogen bonds and Na–O bonds connect the uranyl perrhenate clusters into a 3D structure (part b of Figure 3).

The infrared spectrum for **1** exhibits a sharp peak at 590 and a broad envelope extending from about 600 to 950 cm^{-1} that are associated with the uranyl ion and perrhenate groups. A water bending mode is indicated by a peak at 1590 cm^{-1} , and multiple hydrogen bonds are revealed by peaks ranging from about 3130 to 3330 cm^{-1} .

4. Discussion

The average uranyl and equatorial U–O bond lengths in 270 pentagonal bipyramids from well-refined structures are 1.79(3) and 2.37(10) Å, respectively.¹ The coordination-specific bond-valence parameters³⁹ provide that these average bond lengths correspond to about 1.64 and 0.53 valence units, respectively. The expected bond valence for an Re–O bond in a symmetric perrhenate group is 1.75 valence units. This

suggests that the coordination of uranyl by perrhenate would lead to a bond-valence sum of about 2.28 valence units at the shared oxygen atom, indicating significant overbonding. Elongation of the corresponding U–O and Re–O bonds can elevate this to some extent, but interestingly this is not a pronounced feature of the structures of the uranyl perrhenates reported herein, although some elongation of the Re–O bonds is evident. Instead, the uranyl ion bond lengths are contracted in these structures. In **1**, where all of the equatorial vertices of the bipyramid are perrhenate groups, the uranyl ion bond lengths are contracted to 1.746(9) and 1.759(8) Å. This indicates that where uranyl ions are linked to weakly coordinating ligands such as perrhenate, the uranyl ion bonds are stronger, thereby lessening the amount of bonding associated with the equatorial ligands.

The structures of the three uranyl perrhenate compounds studied here contain structural units that are novel in uranyl crystal chemistry. About 60 inorganic uranyl compounds contain infinite chains,¹ and many of these contain tetrahedra such as chromate, molybdate, sulfate, and phosphate. The fragment of the chain in **1** consisting of two uranyl pentagonal bipyramids and eight perrhenate groups is topologically identical to the uranyl molybdate clusters found in $\text{Na}_6[(\text{UO}_2)(\text{MoO}_4)_2]$ ⁴⁰ and $\text{Na}_3\text{Ti}_3[(\text{UO}_2)(\text{MoO}_4)_4]$,⁴¹ but these clusters have not previously been found linked into a

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Structural Units in Three Uranyl Perrhenates

chain. More than 40 inorganic uranyl compounds contain finite clusters of polyhedra of higher bond valence,¹ but the three clusters found in **2** and **3** are unique. Note that the cluster in **3** is similar to that found in $\text{Na}_6[(\text{UO}_2)(\text{MoO}_4)_2]$ ⁴⁰ and $\text{Na}_3\text{Ti}_3[(\text{UO}_2)(\text{MoO}_4)_4]$,⁴¹ and that is contained in the chain of **1** but with two of the tetrahedral ligands replaced by H_2O groups. The inorganic components of the clusters in the structures of $[\text{UO}_2(\mu_2\text{-ReO}_4)(\text{ReO}_4)(\text{TBPO})_2]_2$ and $[\text{UO}_2(\mu_2\text{-ReO}_4)(\text{ReO}_4)(\text{TiBP})_2]_2$ ²⁵ are similar to that found in **3** in that they contain two uranyl pentagonal bipyramids that are bridged by two perrhenate tetrahedra. In $[\text{UO}_2(\mu_2\text{-ReO}_4)(\text{ReO}_4)(\text{TBPO})_2]_2$ and $[\text{UO}_2(\mu_2\text{-ReO}_4)(\text{ReO}_4)(\text{TiBP})_2]_2$,

there is only one terminal perrhenate tetrahedron linked to each of the uranyl pentagonal bipyramids, and the other two equatorial ligands are organic molecules.

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Supporting Information Available: Crystallographic data (CIF) for **1**, **2** and **3**. Infrared spectra for **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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