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Aqueous Reactions of U(VI) at High Chloride Concentrations: Syntheses and Structures of New Uranyl Chloride Polymers

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The reactions of UO_3 with acidic aqueous chloride solutions resulted in the formation of two new polymeric U(VI) compounds. Single crystals of $Cs_2[(UO_2)_3Cl_2(IO_3)(OH)O_2]\cdot 2H_2O$ (**1**) were formed under hydrothermal conditions with HIO_3 and CsCl, and $Li(H_2O)_2[(UO_2)_2Cl_3(O)(H_2O)]$ (**2**) was obtained from acidic LiCl solutions under ambient temperature and pressure. Both compounds contain pentagonal bipyramidal coordination of the uranyl dication, UO_2^{2+}. The structure of **1** consists of infinite $[(UO_2)_3Cl_2(IO_3)(\mu_3\text{-}OH)(\mu_3\text{-}O)_2]^{2-}$ ribbons that run down the *b* axis that are formed from edge-sharing pentagonal bipyramidal $[UO_6Cl]$ and $[UO_5Cl_2]$ units. The Cs^+ cations separate the chains from one another and form long ionic contacts with terminal oxygen atoms from iodate ligands, uranyl oxygen atoms, water molecules, and chloride anions. In **2**, edge-sharing $[UO_3Cl_4]$ and $[UO_5Cl_2]$ units build up tetranuclear $[(UO_2)_4(\mu\text{-}Cl)_6(\mu_3\text{-}O)_2(H_2O)_2]^{2-}$ anions that are bridged by chloride to form one-dimensional chains. These chains are connected in a complex network of hydrogen bonds and interactions of uranyl oxygen atoms with Li^+ cations. Crystal data: **1**, orthorhombic, space group *Pnma*, $a = 8.2762(4)$ Å, $b = 12.4809(6)$ Å, $c = 17.1297(8)$ Å, $Z = 4$; **2,** triclinic, space group $P\bar{1}$, $a = 8.110(1)$ Å, $b = 8.621(1)$ Å, $c = 8.740(1)$ Å, $Z = 2$.

Introduction

The hydrolysis of uranium(VI) exhibits a complex chemistry with mono- and polynuclear solution species and has been studied repeatedly during the last 50 years. Renewed interest in the structure, formation, and stability of uranyl oxide minerals is triggered by the alteration of UO_2 and spent nuclear fuel by oxidative dissolution and the formation of secondary minerals.[1,2] The structural chemistry of uranyl(VI) oxides is based on uranyl units that are linked by oxo or hydroxo groups to form extensive polyhedral $(UO_2)_kO_l(OH)_m$ chains or layers.[3] The generally linear uranyl dication, UO_2^{2+}, is coordinated with four, five, or six ligands in the equatorial plane forming square, pentagonal, or hexagonal bipyramids, respectively. The systematic classification of U(VI) minerals and inorganic phases based on the polymerization of uranyl polyhedra was recently reviewed by Burns et al.[3]

Chloride ligation alters the stability and structural properties of uranyl oxohydroxo compounds in solution and in the solid state. Chloride anions have been shown to undergo exchange reactions with terminal water molecules bound to uranyl cations in both solution and solid state. For example, the $[UO_2Cl_4]^{2-}$ anion is well-known to crystallize from a large number of highly acidic aqueous systems concentrated in chloride.[4,5] The mixed dimeric U(VI) hydrolysis product, $[(UO_2)_2Cl_2(OH)_2(H_2O)_4]$, crystallizes from less acidic chloride solution and maintains two bridging hydroxo groups.[6] Partial ligand exchange between chloride and water was also observed in the uranyl compounds $M_2[(UO_2)_4O_2Cl_8(H_2O)_4]$[7] (M = Rb, Cs) and $[(UO_2)_4Cl_2O_2(OH)_2(H_2O)_6]\cdot 4H_2O$.[8] Four

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edge-sharing $[UO_6Cl]$ polyhedra make up the structure of $[(UO_2)_4Cl_2O_2(OH)_2(H_2O)_6]\cdot 4H_2O$, which also contains six terminal water molecules. In the anionic cluster $[(UO_2)_4O_2Cl_8(H_2O)_4]^{2-}$, which is built from two $[UO_6Cl]$ and two $[UO_5Cl_2]$ polyhedra, two of these terminal water molecules are replaced by chloride. Both compounds are derivatives of the tetranuclear uranyl cluster, $[(UO_2)_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_4(H_2O)_6]$, where two of the four bridging μ-OH groups are replaced by chloride ligands. The triangular μ_3-O groups that link three uranyl moieties are not available for ligand exchange and therefore remain intact throughout these reactions. Interestingly, both compounds maintain a substantial number of uranyl-coordinated water molecules that were not replaced by chloride, while bridging hydroxo groups undergo partial replacement. The ligand exchange of chloride into the inner-coordination sphere of U(VI) reduces the dimensionality of the compounds, and the reported solid chlorohydroxo uranium(VI) compounds contain discrete molecular complexes. We report here the syntheses and structures of two new uranium(VI) chlorohydroxo compounds that are based upon one-dimensional infinite anionic chains.

Experimental Section

Syntheses. UO_3 (99.8%, Alfa-Aesar), HIO_3 (99.5%, Alfa-Aesar), CsCl (99.999%, Alfa-Aesar), HCl (12 M, Aldrich), and LiOH (1 M, Aldrich) were used as received. Distilled and Millipore filtered water with a resistance of 18.2 MΩ was used in all reactions. *CAUTION: Although UO_3 contains depleted U, standard precautions for the handling and disposing of radioactive materials should be followed.* Heavy element ratios were determined using X-ray fluorescence spectra that were obtained using a SEM JEOL 840/Link Isis instrument with an EDX attachment. IR spectra for **1** were collected with a Nicolet 5PC FT-IR spectrometer from KBr pellets. The IR and Raman spectra for **2** were collected on a Nicolet Magna 560 FT-IR/Raman spectrometer. KBr pellets were used for IR, and 20-mg crystalline samples in NMR tubes were used for Raman.

$Cs_2[(UO_2)_3Cl_2(IO_3)(OH)O_2]\cdot 2H_2O$ (1). UO_3 (286 mg, 1 mmol), HIO_3 (176 mg, 1 mmol), CsCl (168 mg, 1 mmol), and 1 mL water were loaded in a 23-mL PTFE-lined autoclave. The autoclave was sealed, placed in a box furnace, and heated to 180 °C. After 72 h the furnace was cooled at 9 °C/h to 23 °C. The product consisted of a yellow solution over a mixture of golden columns of **1** and bright yellow truncated tetragonal bipyramids of $UO_2(IO_3)_2(H_2O)$, which have been previously characterized.[13] The mother liquor was decanted from the crystals, which were then washed with methanol and allowed to dry. Yield: 69 mg (10% yield based on U) for $Cs_2[(UO_2)_3Cl_2(IO_3)(OH)O_2]\cdot 2H_2O$ and 346 mg (54% yield based on U) for $UO_2(IO_3)_2H_2O$. EDX analysis for **1** provided a Cs/U/I/Cl ratio of 2:3:1:2. IR (KBr, cm^{-1}): ν_{as}(U═O) 907 (s); ν(U═O$_s$, U−O, and I═O) 892 (s, sh), 871 (m), 858 (m), 821 (m), 800 (s), 776 (s), 751 (s), 715 (w, sh), 698 (w), 668 (m), 517 (s), 420 (s).

$Li(H_2O)_2[(UO_2)_2Cl_3(O)(H_2O)]$ (2). UO_3 (50 mg, 0.175 mmol) was dissolved in concentrated HCl, and 1 M LiOH was added to adjust the pH to 4. The precipitate that formed was separated by filtration (450 nm pore size), and the filtrate was left to stand undisturbed for several months. The reaction gradually produced yellow powder with a small amount of golden plates. Yield: 4.3 mg (9% yield based on U). The largest crystals were isolated manually and characterized by single-crystal X-ray diffraction. IR (KBr, cm^{-1}): ν_{as}(U═O) 913 (s); ν_s(U═O and U−O) 815 (s, sh), 490 (s). Raman (cm^{-1}): ν_s(U═O) 843 (s), 827 (s); $\nu(\mu_3\text{-}O)$ 575 (w); ν(U−OH) 405 (m), 335 (w); ν(U−Cl) 218 (m, sh), 199 (m), 179 (w, sh), 156 (w), 135 (w).

Crystallographic Studies. $Cs_2[(UO_2)_3Cl_2(IO_3)(OH)O_2]\cdot 2H_2O$ (1). A yellow single crystal of suitable size and uniform shape was selected, mounted on a glass fiber with epoxy, and aligned on a Bruker SMART APEX CCD X-ray diffractometer. Intensity measurements were performed using graphite monochromated Mo Kα radiation from a sealed tube and a monocapillary collimator. SMART was used for preliminary determination of the cell constants and data collection control.[9] The intensities of reflections of a sphere were collected by a combination of three sets of exposures (frames). Each set had a different ϕ angle for the crystal, and each exposure covered a range of 0.3° in ω. A total of 1800 frames were collected with an exposure time per frame of 40 s. The determination of integral intensities and global cell refinement were performed with the Bruker SAINT (version 6.02) software package using a narrow-frame integration algorithm.[9] A face-indexed, analytical absorption correction was applied in XPREP prior to SADABS corrections.[9] To accomplish this, individual shells of unmerged data were corrected analytically and exported in the same format. These files were subsequently treated by SADABS with a $\mu \times t$ parameter of 0. The program suite SHELXTL was used for space group determination (XPREP), structure solution (XS), and refinement (XL).[10] The final refinement included anisotropic displacement parameters for all atoms and a secondary extinction parameter. Some crystallographic details are listed in Table 1; additional details can be found in the Supporting Information.

$Li(H_2O)_2[(UO_2)_2Cl_3(O)(H_2O)]$ (2). A gold portion of a multifaceted block crystal of **2** was attached to a glass fiber using a spot of silicone grease. The crystal was placed on a Bruker P4/CCD/PC X-ray diffractometer and cooled to 203 K using a Bruker LT-2 temperature device. The data were collected using a sealed, graphite monochromated Mo Kα X-ray source. A hemisphere of data was collected using a combination of φ and ω scans, with 10-s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell refinement were handled using SMART software.[9] Frame integration and final cell parameter calculations were carried out using SAINT software.[9] The data were corrected for absorption using SADABS.[9] Decay of reflection intensity was not observed. The final cell parameters were determined using a least-squares fit to 4402 reflections. The structure was solved in space group $P\bar{1}$ using Patterson methods and difference Fourier techniques. The initial solution revealed the uranium, chlorine, lithium, and majority of all non-hydrogen atom positions. The remaining atomic positions were determined from subsequent Fourier synthesis. The final refinement included anisotropic temperature factors on all non-hydrogen atoms except O(5), which was refined isotropically, and a secondary extinction parameter. Structure solution, refinement, graphics, and creation of publication tables were performed using SHELXTL-97.[20] Some crystallographic details are listed in Table 1; additional details can be found in the Supporting Information.

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Table 1. Crystallographic Data for $Cs_2[(UO_2)_3Cl_2(IO_3)(OH)O_2]\cdot 2H_2O$ (**1**) and $Li(H_2O)_2[(UO_2)_2Cl_3(O)H_2O)]$ (**2**)

formula	$Cs_2[(UO_2)_3Cl_2(IO_3)(OH)O_2]\cdot 2H_2O$	$Li(H_2O)_2[(UO_2)_2Cl_3(O)(H_2O)]$
formula mass (amu)	1405.74	723.40
space group	*Pnma* (No. 62)	$P\bar{1}$ (No. 2)
a (Å)	8.2762(4)	8.110(1)
b (Å)	12.4809(6)	8.621(1)
c (Å)	17.1297(8)	8.740(1)
α (deg)	90	112.228(2)
β (deg)	90	96.378(2)
γ (deg)	90	93.665(2)
V (Å^3)	1769.4(2)	558.4(1)
Z	4	2
T (°C)	−80	−70
λ (Å)	0.71073	0.71073
ρ_{calcd} (g cm^{-3})	5.262	4.302
μ(Mo Kα) (cm^{-1})	335.48	296.92
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)^a$	0.0471	0.0402
$R_w(F_o^2)^b$	0.0870	0.1034

^{a} $R(F) = \{\sum||F_o| - |F_c||\}/\{\sum|F_o|\}$. ^{b} $R_w(F_o^2) = [\{\sum[w(F_o^2 - F_c^2)^2]\}/\{\sum wF_o^4\}]^{1/2}$.

Results and Discussion

Synthesis. It is well-established that hydrolysis of UO_2^{2+} produces a series of mono- and polynuclear species in solution of general formula $(UO_2)_k(OH)_l^{2k-l}$.[17] In the presence of other anionic ligands (i.e., chloride), hydrolysis of uranyl in aqueous solutions may form ternary chlorohydroxo compounds, $(UO_2)_k(OH)_l(X)_m^{2k-l-m}$, where X is a monovalent anionic ligand (i.e., Cl^-).[17] The major product of the reaction of UO_3 with HIO_3 and CsCl under mild hydrothermal conditions is $UO_2(IO_3)_2(H_2O)$, which is an unavoidable byproduct of hydrothermal reactions of UO_3 with iodate.[11−14] The remaining uranium is maintained in these highly acidic solutions in the form of uranyl chloride complexes that can be crystallized as salts of $[UO_2Cl_4]^{2-}$ and $[UO_2Cl_4(H_2O)]^{2-}$ through slow evaporation of the mother liquors. When we used solid $UO_2(OH)_2$ as starting material to prepare compound **2** by evaporation at slightly acidic pH, unreacted uranyl hydroxide is the main product. The dimeric and trimeric uranium(VI) hydroxo species, $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3(OH)_5^+$, respectively, remain in solution.[17] However, the use of UO_3 as starting material results in approximately 10% yield of crystalline $Li(H_2O)_2[(UO_2)_2Cl_3(O)(H_2O)]$ (**2**).

Both compounds **1** and **2** are quite difficult to prepare, and significant changes in water content or uranium/chloride ratios or alterations of the reaction temperatures preclude their formation. We believe that the sensitivity of **1** to changes in reaction conditions indicates that it is not thermodynamically stable. This is in contrast to the syntheses of $M_2[(UO_2)_3(IO_3)_4O_2]$ (M = K,[14] Rb,[11] Tl[11]) and $M'[(UO_2)_2(IO_3)_2O_2](H_2O)$ (M′ = Sr,[11] Ba,[14] Pb[11]), all of which can be prepared in moderate to high yields under these conditions. Compounds **1** and **2** are air-stable and golden in color.

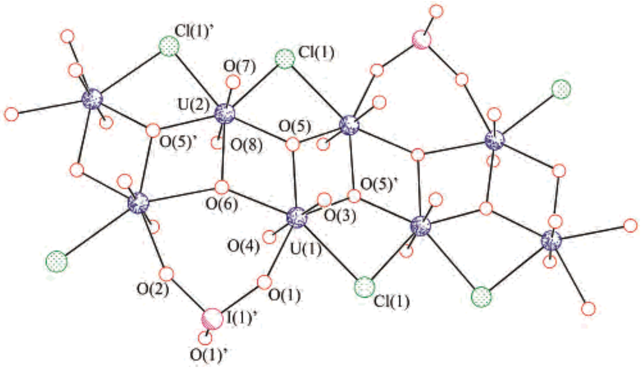

Figure 1. Part of the structure of $Cs_2[(UO_2)_3Cl_2(IO_3)(OH)O_2]\cdot 2H_2O$ (**1**) showing the infinite one-dimensional ${}^{1}_{\infty}[(UO_2)_3Cl_2(IO_3)(OH)O_2]^{2-}$ ribbons that run down the *b* axis. These ribbons are formed from edge-sharing pentagonal bipyramidal units of $[UO_6Cl]$ and $[UO_5Cl_2]$.

Structures. Both compounds contain uranium bound to two apical oxygen atoms (O_{Ur}) with average bond distances and angles of 1.80(1) Å and 178.0(6)° in **1** and 1.78(1) Å and 178.1(5)° in **2**, which are within expected ranges for U═O bonds in U(VI) compounds. The uranyl oxygen atoms form the apexes of pentagonal bipyramids with oxygens from water, hydroxide, or iodate ligands, and chlorides in the equatorial positions. Common to both compounds are the triangular arrangements of the uranyl groups with single oxygen atoms, μ_3-O(5) for **1** and **2**, in the center. However, significant structural variations exist in the linkage of these trinuclear clusters to form dense ribbon **(1)** or sequential band **(2)** topologies.

$Cs_2[(UO_2)_3Cl_2(IO_3)(OH)O_2]\cdot 2H_2O$ (1). The structure of **1** consists of infinite one-dimensional ${}^{1}_{\infty}[(UO_2)_3Cl_2(IO_3)(OH)O_2]^{2-}$ ribbons that run down the *b* axis. These ribbons are formed from edge-sharing pentagonal bipyramidal $[UO_6Cl]$ and $[UO_5Cl_2]$ units as shown in Figure 1. This type of topology for uranium oxide chains has not been observed before in either naturally occurring or synthetic systems.[18] The edges of the uranium oxide chains are terminated by iodate and chloride anions that also serve to bridge between the pentagonal bipyramids. The $[UO_6Cl]$ units containing U(1) are joined by one iodate and one chloride anion,

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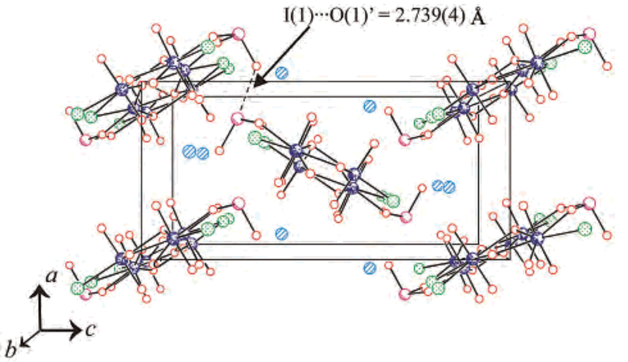

Figure 2. Depiction of the unit cell of $Cs_2[(UO_2)_3Cl_2(IO_3)(OH)O_2]\cdot 2H_2O$ (**1**) viewed down the *b* axis showing the Cs^+ cations that separate the $[{}^{1}_{\infty}(UO_2)_3Cl_2(IO_3)(OH)O_2]^{2-}$ ribbons. The water molecules have been omitted for clarity.

Table 2. Selected Bond Distances (Å) for $Cs_2[(UO_2)_3Cl_2(IO_3)(OH)O_2]\cdot 2H_2O$ (**1**)

U(1)−O(3)	1.797(9)	U(2)−O(7)	1.79(1)
U(1)−O(4)	1.808(9)	U(2)−O(8)	1.79(1)
U(1)−O(5)	2.240(9)	U(2)−O(5)	2.220(8) (×2)
U(1)−O(5)′	2.243(9)	U(2)−O(6)	2.52(1)
U(1)−O(1)	2.421(9)	U(2)−Cl(1)	2.848(3) (×2)
U(1)−O(6)	2.453(4)	I(1)−O(2)	1.79(1)
U(1)−Cl(1)	2.858(3)	I(1)−O(1)	1.805(9) (×2)

whereas the pentagonal bipyramids containing U(2) are connected along the edges of the ribbons only through two bridging chloride anions. The coordination polyhedra of the uranium atoms are completed by μ_3-O and μ_3-OH ligands that are shared by both pentagonal bipyramidal environments. The Cs^+ cations separate the chains from one another and form long ionic contacts with terminal oxygen atoms from the iodate ligands, uranyl oxygen atoms, water molecules, and chloride anions. The Cs−O distances range from 3.023(2) to 3.469(2) Å, and the Cs−Cl distance is 3.362(5) Å. A view of the complete unit cell showing the Cs^+ cations separating the $[{}^{1}_{\infty}(UO_2)_3Cl_2(IO_3)(OH)O_2]^{2-}$ chains is depicted in Figure 2.

The complex variety of ligands (OH^-, O^{2-}, IO_3^-, and Cl^-) around the two crystallographically unique uranyl units creates substantial variation in the equatorial U−X bond lengths. For instance, in the $[UO_6Cl]$ units the U−O bond lengths vary from 2.240(1) to 2.450(5) Å. The U−Cl bond is considerably longer with a bond distance of 2.856(4) Å. The bond lengths for the $[UO_5Cl_2]$ units range from 2.219(1) to 2.52(2) Å for U−O bonds and are 2.847(4) Å for the two U−Cl bonds in the equatorial plane. Selected bond lengths for **1** are given in Table 2. Bond valence sum calculations[15,16] result in values of 5.998 for U(1) and 6.084 for U(2). Parameters for seven-coordinate U(VI) from Burns et al. were used in this calculation.[18]

The iodate ligands serve to bridge U(1) centers along the edge of the chains and show only small variations in the I═O bond distances, which range from 1.79(2) to 1.812(1) Å. Close I···O contacts of 2.769(4) Å exist between the terminal oxygen from a bridging iodate ligand on one chain and an adjacent iodine atom belonging to the next closest chain, as shown in Figure 2. These types of interactions are common in iodate compounds in the solid state.[11−14]

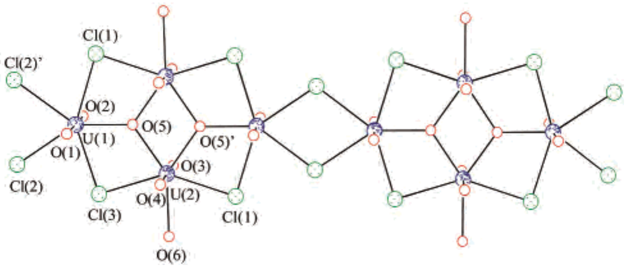

Figure 3. Infinite one-dimensional tetranuclear $[{}^{1}_{\infty}(UO_2)_4(\mu\text{-}Cl)_6(\mu_3\text{-}O)_2(H_2O)_2]^{2-}$ chains of $Li(H_2O)_2[(UO_2)_2Cl_3(O)(H_2O)]$ (**2**) constructed from four edge-sharing pentagonal bipyramids with two crystallographically independent uranyl polyhedra, $[UO_5Cl_2]$ and $[UO_3Cl_4]$.

The oxo and hydroxo oxygen atoms can be distinguished from one another on the basis of both the U−O bond lengths and the pyramidalization of the oxygen atom. The longest U−O distances of 2.453(4) and 2.52(2) Å are with the O(6) atom, which is an μ_3-OH ligand. This μ_3-OH ligand links one $[UO_5Cl_2]$ and two $[UO_6Cl]$ units. The shortest U−O distances of 2.219(1) and 2.240(1) Å are found with the μ_3-O(5) atom, which also joins one $[UO_5Cl_2]$ and two $[UO_6Cl]$ units. The deviations from planarity for O(4) and O(5) are 0.20 and 0.11 Å, respectively. The greater degree of pyramidalization should occur on the hydroxo ligand as the present formulation indicates.

$Li(H_2O)_2[(UO_2)_2Cl_3(O)(H_2O)]$ (2). Compound **2** consists of one-dimensional chains that are made up of tetranuclear $[{}^{1}_{\infty}(UO_2)_4(\mu\text{-}Cl)_6(\mu_3\text{-}O)_2(H_2O)_2]^{2-}$ anions linked by bridging chloride ligands. Each tetranuclear uranyl cluster is formed from four edge-sharing pentagonal bipyramids with two crystallographically independent uranyl polyhedra, $[UO_5Cl_2]$ and $[UO_3Cl_4]$ (Figure 3). The $[UO_3Cl_4]$ units of U(1) contain only one μ_3-O(5) atom and provide two chloride atoms that serve to bridge the tetranuclear subunits. The $[UO_5Cl_2]$ polyhedra of U(2) contain two μ_3-O(5) atoms, two internally bridging chlorides, and one oxygen from a terminal water molecule in the equatorial plane. This arrangement of edge-sharing pentagonal bipyramids is similar to those found in many uranyl(VI) oxides and is essentially identical to those in the molecular structures of $M''_2[(UO_2)_4Cl_4O_2(OH)_2(H_2O)_6]$ ($M'' = K, Rb, NH_4$)[7] and $[(UO_2)_4Cl_2O_2(OH)_2(H_2O)_6]\cdot 4H_2O$.[8] The chains are positioned approximately parallel to each other with four nearest neighboring $[Li(H_2O)]_2^{2+}$ moieties. Each row of $[Li(H_2O)]_2^{2+}$ cations is surrounded by four $[{}^{1}_{\infty}(UO_2)_4(\mu\text{-}Cl)_6(\mu_3\text{-}O)_2(H_2O)_2]^{2-}$ chains. A view down the chain axis of **2** is shown in Figure 4.

The U−Cl bond distances in the $[UO_5Cl_2]$ and $[UO_3Cl_4]$ polyhedra span a relatively narrow range of 2.807(4) to 2.840(4) Å. These distances are significantly longer than the average U−Cl bond distance of 2.67(1) Å reported for the $[UO_2Cl_4]^{2-}$ unit[5] because of the increased coordination of uranium in the equatorial plane. As expected, the U−O bond distances within the triangle are short with 2.21(1) Å for U(1)−O(5) and 2.24(1) Å for U(2)−O(5). The additional U−O(6) bond distance of 2.49(1) Å in the $[UO_5Cl_2]$ polyhedra agrees well with those reported in the literature for uranyl(VI) bound water and is far too short to be assigned as a terminal chloride. Coordination between the uranyl

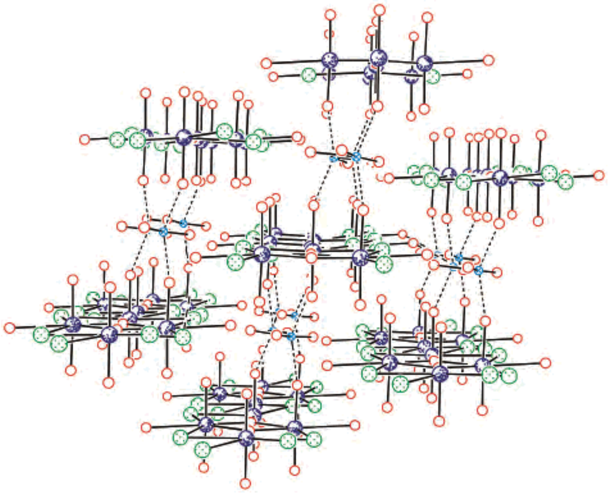

Figure 4. View down the chains of $Li(H_2O)_2[(UO_2)_2Cl_3(O)(H_2O)]$ (**2**) and the four nearest neighboring $[Li(H_2O)]_2^{2+}$ cations, illustrating the bonding between the lithium atoms with the uranyl oxygen atoms.

Table 3. Selected Bond Distances (Å) for $[Li(H_2O)_2][(UO_2)_2(Cl)_3(O)(H_2O)]$ (**2**)

U(1)−O(2)	1.75(1)	U(2)−O(4)	1.77(1)
U(1)−O(1)	1.78(1)	U(2)−O(3)	1.75(1)
U(1)−O(5)	2.21(1)	U(2)−O(5)	2.24(1)
U(1)−Cl(1)	2.802(4)	U(2)−O(5)′	2.26(1)
U(1)−Cl(3)	2.807(4)	U(2)−O(6)	2.48(1)
U(1)−Cl(2)	2.821(4)	U(2)−Cl(1)	2.811(4)
U(1)−Cl(2)′	2.840(4)	U(2)−Cl(3)	2.822(4)

chains and the $[Li(H_2O)]_2^{2+}$ cations is accomplished through interaction between lithium and uranyl oxygen atoms. The Li−O_{Ur} distance of 2.04(3) Å is longer than the 1.89(2) Å reported for Li−O_{Ur} in $[Li(12\text{-crown-}4)]_2[UO_2Cl_4]$,[5] as it represents a weaker interaction, but it is within the range of Li−O distances (1.9−2.3 Å) observed in Li_2UO_4.[19] Selected bond lengths for **2** are given in Table 3. Bond valence sum calculations[15,16] present values of 6.050 and 6.123 for U(1) and U(2), respectively. Parameters for seven-coordinate U(VI) from Burns et al. were used in this calculation.[18]

Conclusion

While the previously reported uranyl iodate compounds, $M_2[(UO_2)_3(IO_3)_4O_2]$ (M = K,[14] Rb,[11] Tl[11]) and $M'[(UO_2)_2(IO_3)_2O_2](H_2O)$ (M′ = Sr,[11] Ba,[14] Pb[11]), display previously unknown uranium oxide architectures, in all of these compounds the uranyl moiety is solely complexed by oxygen atoms. $Cs_2[(UO_2)_3Cl_2(IO_3)(OH)O_2]\cdot 2H_2O$ (**1**) is unique in this respect since this is the first example of a mixed-anion chloroiodate compound where bridging chloride anions are incorporated into the uranyl iodate structures. The ribbon-forming $[UO_2X_5]$ pentagonal bipyramids have been found in the one-dimensional $M'[(UO_2)_2(IO_3)_2O_2](H_2O)$ (M′ = Sr,[11] Ba,[14] Pb[11]) structures that contain both terminal and bridging iodate ligands. However, in **1** the terminal iodates are replaced by bridging chloride ligands. This changes the connectivity of the polyhedra from the sharing of two and four edges in $M'[(UO_2)_2(IO_3)_2O_2](H_2O)$ to three and four shared edges in **1**.

The formation of mixed hydroxochloro complexes of U(VI) in chloride media has been debated for years, and it remains uncertain if such species exist in high chloride solutions.[17] Partial exchange of terminal water and bridging hydroxo groups was reported in the solid-state structures containing discrete tetranuclear uranyl(VI) clusters.[7,8] In compound **2**, all four μ-OH groups within the tetramer are replaced by chloride, and for the first time, chloride atoms are connecting the tetranuclear clusters to form infinite chains. Interestingly, the terminal water groups in the $[UO_6Cl]$ polyhedra of the molecular structures and in the $[UO_5Cl_2]$ polyhedra of **2** are resistant toward ligand exchange. However, in **1**, the iodate ligand replaces the water and serves as a bridge between the $[UO_6Cl]$ units. The more extensive ligand exchange observed in **2** results in the condensation of tetranuclear moieties and the formation of one-dimensional chains. This is important for chloride-rich environments, such as nuclear disposal sites in underground salt formations, where most likely mixed hydroxochloro or pure chloro compounds may precipitate as secondary phases. These increasingly complex phases may alter the solubility and release kinetics and thus could have a great impact on the long-term risk assessment of those disposal sites.

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Supporting Information Available: An anisotropic picture showing 50% ellipsoids of $Cs_2[(UO_2)_3Cl_2(IO_3)(OH)O_2]\cdot 2H_2O$ (**1**) and X-ray crystallographic files for $Cs_2[(UO_2)_3Cl_2(IO_3)(OH)O_2]\cdot 2H_2O$ (**1**) and $Li(H_2O)_2[(UO_2)_2Cl_3(O)(H_2O)]$ (**2**) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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