Synthesis and characterization of uranyl chromate sheet compounds containing edge-sharing dimers of uranyl pentagonal bipyramids

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ABSTRACT

Eight uranyl chromates have been crystallized from aqueous solution and characterized: $Mg(H_2O)_6[(UO_2)_2(CrO_4)_2(OH)_2](H_2O)_3$ (**1**), $(NH_4)_2[(UO_2)_2(CrO_4)_2(OH)_2](H_2O)_3$, $Rb_2[(UO_2)_2(CrO_4)_2(OH)_2](H_2O)_3$ (**3**), $Cs[(UO_2)(CrO_4)(OH)]H_2O$ (**4**), $Rb[(UO_2)(CrO_4)(OH)]H_2O$ (**5**) $Co(H_2O)_4(Co(H_2O)_6)_2[(UO_2)_4(CrO_4)_6(OH)_2](H_2O)_4$ (**6**), $Li_2[(UO_2)_2(CrO_4)_3](H_2O)_7$ (**7**), and $Zn(H_2O)_6[(UO_2)_2(CrO_4)_3](H_2O)_3$ (**8**). The structural units of **1** through **8** each consist of a sheet of uranyl pentagonal bipyramids and $(Cr(VI)O_4)^{2-}$ tetrahedra. In each case two uranyl pentagonal bipyramids share an equatorial edge, giving a dimer that is linked into the sheet through vertex sharing with $(Cr(VI)O_4)^{2-}$ tetrahedra. The sheets are based upon three distinct sheet anion topologies, and the sheets based on a given anion topology can differ in the orientations of the non-bridging O atoms of $(CrO_4)^{2-}$ tetrahedra. The interlayers of these compounds contain either monovalent or divalent cations, as well as H_2O groups that are either bonded to the interlayer cation or are held in place by H bonding only. We explore the relationships between sheet topologies and interlayer configuration in these compounds.

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1. Introduction

Uranyl chromate compounds are interesting because of their potential importance in nuclear fuel cycles, and also because of the considerable structural diversity exhibited by uranyl compounds containing tetrahedrally coordinated hexavalent cations [1–11]. Of the dozens of unique uranyl compounds containing TO_4 anions (T=S, Se, Mo, or Cr) that have been examined in recent years, the most unusual are composed of nanoscale tubules built from uranyl polyhedra and selenate tetrahedra [12]. Most uranyl compounds containing TO_4 tetrahedra are built from UO_7 uranyl pentagonal bipyramids that are linked by sharing their equatorial vertices with the TO_4 tetrahedra forming structures with sheet topologies. As such, the U–O–T bond angles influence the details of the structure topologies. Krivovichev and Burns examined the distributions of these bond angles, and found significant differences between the T cations, with the widest distribution for the case of T=Mo [13]. The corresponding bond angles in the relatively few known uranyl Cr(VI) compounds range from ~125 to 175°, with a maximum at ~140–145°. Given the apparent pliability of the U–O–Cr(VI) linkages, considerable structural diversity should occur in this understudied class of compounds.

Here we report the synthesis and characterization of eight compounds that contain dimers of edge-sharing uranyl pentagonal bipyramids that are linked through tetrahedral $(CrO_4)^{2-}$ anions into extended sheets, and explore the influence of interlayer cations and H bonding on the sheet topologies. Seven uranyl compounds containing dimers of uranyl pentagonal bipyramids linked through XO_4 (X=P, S, Cr, Mo) into sheet topologies have been previously reported [14–20] (Table 1). In these, the uranyl pentagonal bipyramids share either two OH^- or two F^- equatorial anions. The resulting dimers are linked into extended sheets through tetrahedra by vertex sharing. These sheets are based on two sheet anion topologies, $6^15^24^23^2$ and $5^44^13^2$-I [13]. Sheets with the same anion topology can differ in the orientation of the non-bridging O atom(s) of the tetrahedra, which are related to the locations and types of interlayer constituents. Four different tetrahedral orientations are known for the anion topology $6^15^24^23^2$, and two have been reported for the $5^44^13^2$-I anion topology [13]. The eight new uranyl chromate compounds reported here introduce both new tetrahedral orientations of the $6^15^24^23^2$ and $5^44^13^2$-I anion topologies, and a new anion topology.

2. Materials and methods

Caution: chromium(VI) compounds are carcinogenic. All uranium used in these experiments was isotopically depleted. However, standard safety precautions for working with radioactive materials should be followed.

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Table 1
Compounds containing dimers of edge-sharing uranyl pentagonal bipyramids linked through tetrahedral oxyanions.

Formula	Anion topology	TO_4 orientation[a]	$U-O_{br}-Cr$ (deg.)	Dihedral (deg.)	Ref.
$Sr[UO_2(OH)(CrO_4)](H_2O)_8$	$6^15^24^23^2$	ududud	133.2–159.2	180.0	[6]
$Cu[(UO_2)_2(OH)_2(SO_4)_2](H_2O)_8$	$6^15^24^23^2$	ududud	145.3–151.9	180.0	[5]
$[C(NH_2)_3][(UO_2)(OH)(MoO_4)]$	$6^15^24^23^2$	ududud	129.4–157.9	173.3	[9]
$(UO_2)_3(MoO_4)_2(OH)_2(H_2O)_{10}$	$6^15^24^23^2$	uuuudd, dddduu	128.6–150.3	180.0	[8]
$[N_2C_6H_{16}][UO_2F(SO_4)]_2$	$6^15^24^23^2$	dduddu, uuduud	139.4–155.3	166.7	[10]
$Mg(H_2O)_6[(UO_2)_2(CrO_4)_2(OH)_2](H_2O)_3$	$6^15^24^23^2$	dduddu, uuduud	135.3–135.4	170.1	This study
$Rb(UO_2)F(HPO_4)$	$6^15^24^23^2$	uuuuuu	135.8–166.8	159.2	[11]
$Co(H_2O)_4(Co(H_2O)_6)_2[(UO_2)_4(CrO_4)_6(OH)_2](H_2O)_8$	$6^15^24^23^2$	dudduuu, uduuddd	124.2–173.4	152.8	This study
$K_2[(UO_2)_2(CrO_4)_2(OH)_2](H_2O)_3$	$5^44^13^2$-I	uuuuuu	131.4–163.3	168.6	[7]
$(NH_4)_2[(UO_2)_2(CrO_4)_2(OH)_2](H_2O)_3$	$5^44^13^2$-I	uuuuuu	136.3–166.2	167.3	This study
$Rb_2[(UO_2)_2(CrO_4)_2(OH)_2](H_2O)_3$	$5^44^13^2$-I	uuuuuu	129.2–159.4	168.3	This study
$Cs[(UO_2)(CrO_4)(OH)]H_2O$	$5^44^13^2$-I	uuuddd	130.7–165.2	180.0	This study
$Rb[(UO_2)(CrO_4)(OH)]H_2O$	$5^44^13^2$-I	uuuddd	136.5–165.2	180.0	This study
$Cs(UO_2)F(HPO_4)\cdot 0.5H_2O$	$5^44^13^2$-I	uuuuud, dddddu	139.6–165.5	158.9	[10]
$Li_2[(UO_2)_2(CrO_4)_3](H_2O)_7$	$5^24^43^2$	uuudduud, ddduudduu	123.9–151.9	145.8	This study
$Zn(H_2O)_6[(UO_2)_2(CrO_4)_3](H_2O)_3$	$5^24^43^2$	uuuduudd, ddduuudu	123.8–150.4	146.5	This study

[a] Orientation of a TO_4 tetrahedron is in reference to the orientation of the non-bridging O atom(s) of the tetrahedron (u=up, d=down), relative to the plane defined by the sheet of polyhedra.

2.1. Synthesis

Our objective in this study was to synthesize compounds containing uranyl chromate sheets with a range of topologies, and to gain insight into the role of interlayer cations in influencing the topologies of the resulting sheets. Each synthesis experiment was done in aqueous solution, mostly at a pH of 4.0 or 5.0. In some cases a heat treatment was used, but in all cases the crystals of compounds **1** through **8** formed under ambient conditions. Our experiments were designed to explore the effect of solution pH and counter ion, as well as uranyl to chromate ratio, on the final product. Some experiments gave no crystals suitable for diffraction study and those are excluded. Others gave uranyl chromate compounds that contained structural units other than sheets, and those will be reported elsewhere.

Cs_2CrO_4 (99.9%, Alfa Aesar), $(NH_4)_2CrO_4$ (98%, Aldrich), $MgCrO_4\cdot H_2O$ (98%, Aldrich), Rb_2CrO_4 (98%, Aldrich), $Co(NO_3)_2$ (98%, Aldrich), CsOH (99%, Aldrich), $Zn(NO_3)_2\cdot 6(H_2O)$ (99.0%, Fluka Analytical), CrO_3 (98%, Aldrich), LiOH (98%, Alfa Aesar), HNO_3 (70%, Fisher), and $UO_2(NO_3)_2\cdot 6H_2O$ (International Bio-Analytical Int.) were used as received from their respective suppliers. Millipore-filtered ultrapure water (18 MΩ resistance) was used in all reactions. In all cases, crystals were produced by slow evaporation of a solution containing uranium and chromium. Yields were ~10% by wt. based on U concentration; uranium remained in the solutions over the crystals.

Crystals of $Mg(H_2O)_6[(UO_2)_2(CrO_4)_2(OH)_2](H_2O)_3$ (**1**) were synthesized by the addition of 3 mL of 0.1 M aqueous uranyl nitrate solution to a 10 mL glass test tube with 3 mL of 0.1 M aqueous $MgCrO_4$ solution. The pH of the resulting solution was adjusted to 5.0 using 2 M aqueous LiOH. An aliquot of 300 μL of the resulting liquid was transferred to a 4 mL glass vial where it was allowed to evaporate under ambient conditions. After two weeks yellow blades were harvested from the remaining solution.

Crystals of $(NH_4)_2[(UO_2)_2(CrO_4)_2(OH)_2](H_2O)_3$ (**2**) were synthesized by adding 1 mL of 0.2 M aqueous uranyl nitrate solution to a 4 mL polypropylene vial containing 0.0310 g of $(NH_4)_2CrO_4$. The pH of the resulting solution was adjusted to 4.95 by adding 160 μL of 1 M aqueous LiOH. The vial was then capped, placed inside a 125 mL Teflon-lined reaction vessel, and heated for 96 h at 150 °C. After cooling to room temperature, an aliquot of 250 μL of the resulting clear, yellow solution was transferred to a 4 mL glass vial, where it was covered with 300 μL of toluene to foster crystallization and capped. Yellow blade crystals formed within 2 weeks.

$Rb_2[(UO_2)_2(CrO_4)_2(OH)_2](H_2O)_3$ (**3**) crystals were grown from a solution created by combining 3 mL of 0.1 M aqueous uranyl nitrate solution in a 10 mL glass test tube and 3 mL of 0.1 M aqueous Rb_2CrO_4 solution. The resulting solution was adjusted to a pH of 4.0 with 1.0 M aqueous LiOH. An aliquot of 500 μL was then transferred to a 4 mL glass vial and was allowed to evaporate under ambient conditions. After two weeks yellow blades were harvested from the remaining solution.

Crystals of $Cs[(UO_2)(CrO_4)(OH)]H_2O$ (**4**) were grown at room temperature from a heat-treated solution. 2.5 mL of 0.2 M aqueous uranyl nitrate solution, 0.5 mL of 0.2 M aqueous CrO_3 solution, and 0.5 mL of 0.2 M aqueous CsOH solution were combined and the pH was adjusted to 4.0 by adding 380 μL of 2 M aqueous LiOH. The resulting solution and precipitate were heated at 220 °C for 7 day in a 23 mL Teflon liner contained in a stainless steel vessel. The vessel was then allowed to cool to room temperature and the remaining solution was left to evaporate under ambient conditions. Yellow crystals of the compound were collected after 3 day.

Crystals of $Rb[(UO_2)(CrO_4)(OH)]H_2O$ (**5**) were formed when 0.5 mL of 0.1 M aqueous uranyl nitrate solution was combined with 0.5 mL of a 0.1 M aqueous Rb_2CrO_4 solution and 4 mL of ultrapure water in a 20 mL glass vial. The pH of the solution was 5.0, and it was allowed to evaporate under ambient conditions. After five days yellow crystals measuring 200 μm in maximum dimension were recovered from the remaining solution.

Crystals of $Co(H_2O)_4(Co(H_2O)_6)_2[(UO_2)_4(CrO_4)_6(OH)_2](H_2O)_4$ (**6**) were synthesized starting with a 10 mL glass vial with the addition of 3 mL of 0.2 M aqueous uranyl nitrate solution, 50 μL of 0.6 M CrO_3 solution, and 150 μL of 0.2 M aqueous $Co(NO_3)_2$. The pH of the resulting solution was adjusted to 6.4 using 2 M aqueous LiOH. An aliquot of 300 μL of the clear yellow solution was then transferred to a 4 mL glass vial and allowed to evaporate under ambient conditions. After two months, yellow blocky crystals were recovered from the remaining solution.

$Li_2[(UO_2)_2(CrO_4)_3](H_2O)_7$ (**7**) crystals were synthesized starting with 3 mL of 0.2 M aqueous uranyl nitrate solution that was added to 1.5 mL of a 1.0 M aqueous CrO_3 solution and 1.5 mL of a 0.2 M aqueous $Tl(NO_3)$ solution in a 10 mL glass vial. The pH of the resulting solution was adjusted to 4 by adding 2 M aqueous LiOH. An aliquot of 300 μL of the solution was then transferred to a 4 mL glass vial and allowed to evaporate under ambient conditions. After two weeks, yellow blade crystals measuring 300 μm in the maximum dimension were recovered from the remaining solution.

$Zn(H_2O)_6[(UO_2)_2(CrO_4)_3](H_2O)_3$ (**8**) crystals were synthesized by the combination of 0.4 mL of 0.2 M aqueous uranyl nitrate solution, 1.2 mL of 0.2 M aqueous CrO_3 solution, and 1.2 mL of 0.2 M aqueous zinc nitrate hexahydrate solution in a 10 mL glass vial. The pH of the resulting solution was adjusted to 4.0 with 2 M aqueous lithium hydroxide solution. An aliquot of 1 mL of the final solution was transferred to a polypropylene vial and heated in a Teflon-lined Parr reaction vessel at 140 °C for 24 h. Once the reaction vessel returned to ambient temperature, the solution was transferred to a 4 mL glass vial and allowed to slowly evaporate under ambient conditions until crystal formation. Yellow, blade-shaped crystals measuring 200 μm in maximum dimension were recovered after three weeks.

2.2. Infrared spectroscopy

Infrared spectra were obtained for each compound using a SensIR technology IlluminatIR FT-IR Microspectrometer. A single crystal of each was placed on a glass slide and the spectrum was collected using a diamond ATR objective over 600–4000 cm^{-1} with a beam aperture of 100 μm. Spectra are in the Supplemental Material. The spectra contain modes indicative of H_2O bending (1630 cm^{-1}) and H bonding (3000–3500 cm^{-1}). Numerous

modes in the range of 650–1000 cm^{-1} are attributed to asymmetric stretches of uranyl ions and various Cr–O stretches, but peak overlap precludes definitive assignment. The mode at 1350 cm^{-1} that is present in some of the spectra is due to nitrate from the aqueous solution.

2.3. X-ray crystallography

A suitable crystal of each compound was attached to a tapered glass fiber and mounted on a Bruker PLATFORM three-circle X-ray diffractometer equipped with an APEX I or II CCD detector. The data were collected at room temperature using Mo Kα X-radiation from a conventional tube with frame widths of 0.5° in ω. Selected crystallographic data and collection parameters are provided in Table 1. Unit cell parameters were refined by least-squares techniques using the Bruker SMART software [21] and data integration was handled using SAINT software [22]. Intensity data were corrected for Lorentz, polarization, and background effects using the Bruker program APEX II. An empirical correction for adsorption was applied using the program XPREP. The SHELXTL version 5 series of programs[23] were used for the solution and refinement of the crystal structures. For compounds **1**, **2**, **4**, **5**, **6**, **7**, and **8** anisotropic parameters were refined for all atoms. For

Table 2
Crystallographic and refinement parameters for compounds **1** through **8**.

	1	2	3	4
Formulae	$Mg(H_2O)_6[(UO_2)_2(CrO_4)_2(OH)_2](H_2O)_3$	$(NH_4)_2[(UO_2)_2(CrO_4)_2(OH)_2](H_2O)_3$	$Rb_2[(UO_2)_2(CrO_4)_2(OH)_2](H_2O)_3$	$Cs[(UO_2)(CrO_4)(OH)]H_2O$
Color and habit	Yellow blade	Yellow blade	Yellow blade	Yellow blade
T/K	296(2)	296(2)	296(2)	296(2)
λ/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$Cmcm$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	7.1695(16)	13.4430(18)	13.5998(21)	8.080(5)
b/Å	19.018(4)	9.5141(13)	9.4926(14)	12.072(8)
c/Å	16.588(4)	13.2561(18)	13.2429(20)	9.380(6)
β/deg.	90	103.535(2)	103.486(2)	112.745(7)
Max. 2θ for data/deg.	58.28	50.18	51.14	56.16
Reflectinos coll.	15,541	17,087	17,992	9817
R_{INT}	0.0799 (1683)	0.0722 (2918)	0.0812 (3097)	0.0502 (2023)
Parameters	81	208	123	109
S	1.034	1.003	1.072	1.027
$R1^a$ for $|F_o| \geq 4\sigma F$	0.0315	0.0322	0.0357	0.0255
$wR2^b$ all data	0.0970	0.0705	0.0718	0.0473

	5	6	7	8
Formulae	$Rb[(UO_2)(CrO_4)(OH)]H_2O$	$Co(H_2O)_4(Co(H_2O)_6)_2[(UO_2)_4(CrO_4)_6(OH)_2](H_2O)_4$	$Li_2[(UO_2)_2(CrO_4)_3](H_2O)_7$	$Zn(H_2O)_6[(UO_2)_2(CrO_4)_3](H_2O)_3$
Color and habit	Yellow blade	Yellow blocks	Yellow blade	Yellow blade
T/K	296(2)	296(2)	296(2)	296(2)
λ/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_12_12_1$
a/Å	7.9697(13)	9.8822(6)	9.2281(9)	9.1273(6)
b/Å	11.8350(18)	17.3444(11)	10.8264(11)	10.9329(7)
c/Å	9.2366(14)	13.8215(9)	19.793(2)	21.1262(13)
β/deg.	113.071(2)	108.926(1)	99.2470(10)	90
Max. 2θ for data/deg.	54.28	52.78	55.82	66.00
Reflections coll.	9822	27,614	22,908	40,540
R_{INT}	0.0641 (1770)	0.0924 (4568)	0.0796 (4589)	0.0666 (7898)
Parameters	109	295	259	280
S	1.032	1.013	1.044	1.006
$R1^a$ for $|F_o| \geq 4\sigma F$	0.0283	0.0423	0.0404	0.0372
$wR2^b$ all data	0.0534	0.0937	0.0822	0.0938

[a] $R1 = [\Sigma||F_o| - |F_c||]/\Sigma|F_o| \times 100$.
[b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma(F_o^4)]^{0.5}$.

compound **3**, the data supported refinement of anisotropic displacement parameters for U, Rb, and Cr only. As is typical for most actinide compounds, the X-ray data did not reveal the positions of the H atoms in most of the compounds. However, for compounds **4** and **5**, H atoms were included in the structural model. These were refined with the constraint that O–H bond distances be ~0.96 Å. Full details of the crystal structures are provided in the Supporting Information. Table 2 provides a summary.

3. Results

Each of compounds **1–8** contain U^{6+} cations that are present as typical $(UO_2)^{2+}$ uranyl (*Ur*) dioxo cations. The U–O_{Ur} bonds in these compounds range from 1.744(7) to 1.785(9) Å, and the average O–U–O bond angle is 178.7(6)°, within the range for well-refined uranyl compounds [1,24]. The average U–O_{eq} (*eq*: equatorial) bond length is 2.36(3) Å across the compounds. In each structure, two pentagonal bipyramids share an edge, forming a dimer of pentagonal bipyramids. These are linked into sheet structures through the $(CrO_4)^{2-}$ tetrahedra, with low-valence cations and H_2O groups located in the interlayer regions.

The U–O_{Ur} triple bonds satisfy much of the bond-valence requirements of the corresponding O atoms, and these usually do not form additional strong bonds within the structural unit. Uranyl polyhedra are usually linked through equatorial vertices, either directly with other uranyl polyhedra or with a wide variety of oxyanions in inorganic compounds. As a result, sheets of polyhedra are the dominant structural unit in inorganic uranyl compounds [1]. In 1996 the concept of a sheet anion topology was introduced for hierarchical studies of uranyl compounds [25]. In this approach the topological arrangement of anions that are at least two-connected within the sheet is considered. The sheet anion topology is a two dimensional representation of the polygons defined by the anions in the sheet. Those separated by less than ~3.2 Å are connected by lines. This construct has proven useful because a variety of sheets can correspond to a single sheet anion topology.

The compounds reported herein contain sheets of uranyl pentagonal bipyramids and $(CrO_4)^{2-}$ tetrahedra that are each based upon one of three sheet anion topologies. Consider first the topology shown in Fig. 1a, which is designated the phosphuranylite topology because it corresponds to the uranyl phosphate sheets contained in this mineral group [1]. The topology contains hexagons, pentagons, squares, and triangles and has the shorthand notation $6^1 5^2 4^2 3^2$ in which the number of vertices of each polygon is indicated, as well as their ratios. About 20 previously reported compounds have sheets based upon this anion topology [1].

The sheets in compounds **1** and **6** are based upon the phosphuranylite anion topology (Fig. 1a, b, and d). In each case the hexagons of the topology are vacant, the pentagons are populated by $(UO_2)^{2+}$ cations, and the triangles correspond to faces of $(CrO_4)^{2-}$ tetrahedra. In **1**, the uranyl pentagonal bipyramids share an edge that consists of two OH^- groups, and each bipyramid is coordinated by three monodentate $(CrO_4)^{2-}$ tetrahedral (Fig. 1b). The non-bridging O atoms of these tetrahedra are on the upper (**u**) or lower (**d**) side of the sheet, and around any dimer of pentagonal bipyramids they are in either of the sequences **dduddu** or **uuduud**. This sheet is isotypic to that in the compound $[N_2C_6H_{16}][UO_2F(SO_4)]_2$ [14]. Relative to the sheet in **1**, that in **6** contains an additional $(CrO_4)^{2-}$ tetrahedron. The uranyl pentagonal bipyramids in **6** share an edge defined by one OH^- group and an O atom of the added $(CrO_4)^{2-}$ tetrahedron (Fig. 1d). The anion topology of **6** is the same as **1** because the added $(CrO_4)^{2-}$ tetrahedron is located within the hexagon of the topology, where it shares only one of its vertices with the sheet. The non-bridging O atoms about the dimers of pentagonal bipyramids point either **uduuddd** or **dudduuu**.

The sheets of uranyl pentagonal bipyramids and $(CrO_4)^{2-}$ tetrahedra in compounds **2** through **5** are based upon the sheet anion topology shown in Fig. 2a. It consists of pentagons, squares, and triangles with the representation $5^4 4^1 3^2$-I. Two-thirds of the pentagons are occupied by uranyl ions and all of the triangles of the anion topology correspond to faces of $(CrO_4)^{2-}$ tetrahedra. The remaining polygons, one-third of the pentagons and all of the squares, are unpopulated in the case of the sheets in compounds
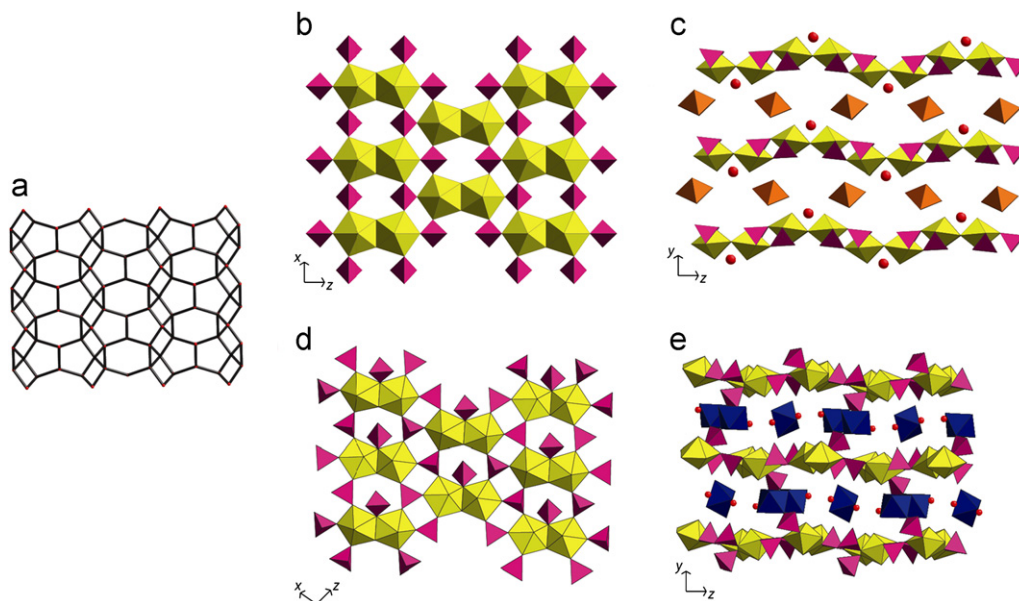

Fig. 1. Representations of the crystal structures of compounds **1** and **6**. (a) The phosphuranylite sheet anion topology. (b) The sheet of uranyl pentagonal bipyramids and $(CrO_4)^{2-}$ tetrahedra in **1**. (c) The extended structure of **1**. (d) The sheet of uranyl pentagonal bipyramids and $(CrO_4)^{2-}$ tetrahedra in **6**. (e) The extended structure of **6**. Uranyl and chromate polyhedra are shown in yellow and magenta, respectively. Mg and Co octahedra are shown in orange and blue, respectively, and those H_2O groups that are held in the interlayer by H bonding only are shown as red spheres. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
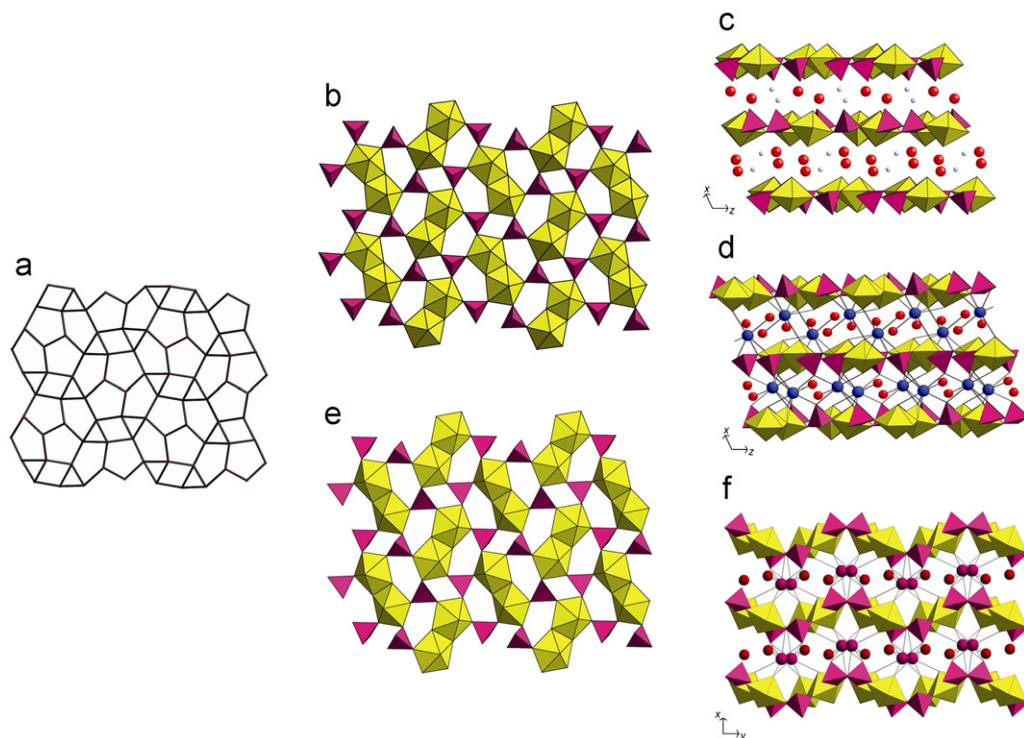
Fig. 2. Representations of the crystal structures of compounds **2** through **5**. (a) The $5^4 4^1 3^2$-I sheet anion topology. (b) The sheet of uranyl pentagonal bipyramids and $(CrO_4)^{2-}$ tetrahedra in **2** and **3**. (c) The extended structure of **2**. (d) The extended structure of **3**. (e) The sheet of uranyl pentagonal bipyramids and $(CrO_4)^{2-}$ tetrahedra in **4** and **5**. (f) The extended structures of **4** and **5**. Legend as in Fig. 1, except that N atoms are shown in light blue, Rb atoms in blue, and Cs atoms in purple. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2–5. In all, the edges that are shared within the dimers of pentagonal bipyramids correspond to two OH$^-$ groups. Each dimer of bipyramids is coordinated by six monodentate $(CrO_4)^{2-}$ tetrahedra. In compounds **2** and **3**, the orientations of all the non-bridging O atoms of the tetrahedra point in the same direction within a given sheet, with adjacent sheets being in opposite orientations (Fig. 2b). Compound **3** is isostructural to K[(UO$_2$)(CrO$_4$)(OH)]·1.5(H$_2$O) [19]. In the cases of compounds **4** and **5**, the non-bridging O atoms of tetrahedra connected to a single dimer of bipyramids is **uuuddd** (Fig. 2e).

Compounds **7** and **8** present a sheet of uranyl pentagonal bipyramids and $(CrO_4)^{2-}$ tetrahedra (Fig. 3b and d) with a novel anion topology (Fig. 3a). It contains pentagons, squares and triangles with the representation $5^1 4^2 3^1$. The uranyl pentagonal bipyramids share an edge that is defined by two O atoms of different modentate $(CrO_4)^{2-}$ tetrahedra. One of these tetrahedra shares a vertex with one other dimer of bipyramids, whereas the other is linked to two other dimers of bipyramids. Each uranyl ion is coordinated by three additional monodentate $(CrO_4)^{2-}$ tetrahedra. For a given dimer of uranyl pentagonal bipyramids, the orientations of the non-bridging O atoms for **7** are **uuudduud** or **dddudduu**, and for **8** the orientations are **uuuduudd** or **dddduuddu**.

The uranyl chromate sheets in compounds **1** through **8** each carry a net negative charge that is balanced by cations located between the sheets. In compounds **1**, **2**, **7**, and **8** the linkages between the interlayer cations and uranyl chromate sheets are either entirely (**1**, **2**, and **8**) or mostly (**7**) through H bonds associated with either H$_2$O groups that coordinate the cations in the interlayer or that are held in the interlayer by H bonding alone. In compounds **3** through **6**, there are direct linkages between the interlayer cations and adjacent uranyl chromate sheets.

In compound **1**, there is a single symmetrically distinct Mg cation as well as four H$_2$O groups. The Mg cation is octahedrally coordinated by two of these H$_2$O groups, with bond lenghts of 2.05(1) and 2.06(1) Å. The other two H$_2$O groups are held in place by H bonding only, and linkages between the interlayer consti-tuents and the uranyl chromate sheets are also only through H bonds (Fig. 1c). In compound **2**, the interlayer contains two symmetrically distinct (NH$_4$)$^+$ groups as well as three H$_2$O groups that are held in the structure by H bonds only (Fig. 2c). Again, linkages between the interlayer constituents and the uranyl chromate sheets are through H bonds only. For compound **8**, the interlayer contains a single unique Zn cation and nine symmetrically distinct H$_2$O groups (Fig. 3e). Six of the intersitial H$_2$O groups are bonded to the Zn cation in a octahedral coordina-tion with bond lengths ranging from 2.07(1) to 2.11(7) Å, and three are held in the structure by H bonding only. Similar to **1** and **2**, the interlayer constituents and uranyl chromate sheets of **8** are only linked through H bonds. In compound **7**, the interlayer contains two symmetrically distinct Li cations as well as seven H$_2$O groups (Fig. 3c). Five of the H$_2$O groups are bonded to Li cations, and two are held in the structure by H bonding only. Each Li cation is coordinated by five ligands in approximate square pyramidal [Li(1)] and trigonal bipyramidal [Li(2)] arrangements. The Li(1) coordination polyhedron includes a single O$_{Ur}$ atom, but otherwise both coordination polyhedra include only H$_2$O groups.

In compound **3**, the interlayer contains two symmetrically distinct Rb cations as well as three H$_2$O groups, each of which are bonded to a single Rb cation (Fig. 2d). In contrast to compounds **1** and **2**, there are many direct connections between the cations in the interlayer and the uranyl chromate sheets. The Rb coordina-tion environments include O$_{Ur}$ atoms of adjacent sheets, atoms that are at equatorial positions of uranyl polyhedra, and O atoms of $(CrO_4)^{2-}$ tetrahedra that do not bridge within the sheet.
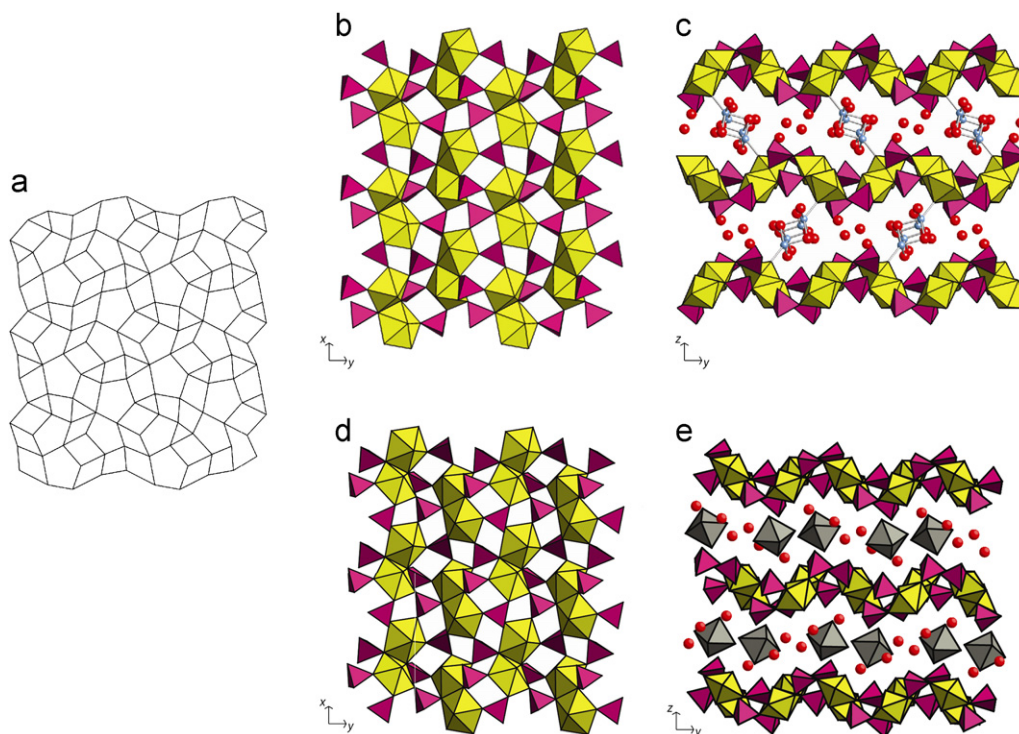
Fig. 3. Representations of the crystal structures of compounds **7** and **8**. (a) The $5^14^23^1$ sheet anion topology. (b) The sheet of uranyl pentagonal bipyramids and $(CrO_4)^{2-}$ tetrahedra in **7**. (c) The extended structure of **7**. (d) The sheet of uranyl pentagonal bipyramids and $(CrO_4)^{2-}$ tetrahedra in **8**. (e) The extended structure of **8**. Legend as in Fig. 1, except that Li atoms are shown in light blue and Zn octahedra are shown in gray. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Compounds **4** and **5** are isostructural. The interlayer of compound **4** contains a single symmetrically unique Cs cation as well as one H_2O group that is bonded to two Cs cations at distances of 3.098(6) and 3.240(6) Å (Fig. 2f). The Cs coordination environments include O_{Ur} atoms, O atoms located at the equatorial positions of uranyl polyhedra, and O atoms of $(CrO_4)^{2-}$ tetrahedra that do not bridge within the sheet. The interlayer in compound **5** contains a single symmetrically distinct Rb cation, as well as a single H_2O group that is bonded to two Rb cations at distances of 2.916(7) and 3.117(8) Å (Fig. 2f). The Rb coordination polyhedra are the same as for the Cs in **4**. Compound **6** has a complex interlayer that contains two symmetrically distinct Co cations and nine H_2O groups, seven of which are each bonded to a single Co cation and two of which are held in the structure by H bonds only. Each Co cation is octahedrally coordinated, but they assume substantially different structural roles (Fig. 1e). Co(1) is coordinated by six H_2O groups with bond lengths in the range of 2.045(9)–2.130(9) Å, and the only possible linkages between these octahedra and the uranyl chromate sheets is through H bonding. In contrast, the Co(2) octahedron contains four H_2O groups and two $(CrO_4)^{2-}$–O atoms that do not bridge within the uranyl chromate sheet. These two O atoms are from different sheets, thus the Co(2) site provides a direct linkage between the sheets, in addition to any linkages from the H_2O groups to the sheets through H bonds.

4. Discussion

The structures reported herein demonstrate some of the relationships between the structural units and interlayer constituents in uranyl compounds built from sheets. Consider first the two sheets that are based upon the phosphuranylite anion topology, corresponding to compounds **1** and **6**. In compound **1**,

the $(CrO_4)^{2-}$ tetrahedra are all in the same orientation, relative to the interlayer. Linkages between the uranyl chromate sheets and the interlayer constituents are only through H bonds, which presumably allows flexibility in the geometric details of the sheet. In the case of compound **6**, the $(CrO_4)^{2-}$ tetrahedra of the sheet are oriented such that the non-bridging O atoms point both up and down, and an additional $(CrO_4)^{2-}$ tetrahedron is present, relative to the sheet in compound **1**. Relative to the structural sheet, addition of the $(CrO_4)^{2-}$ tetrahedron increased the charge of the sheet, as it replaced one OH^- group. The interlayer of **6** therefore contains more octahedrally coordinated divalent cations than in **1**, and this extra $(CrO_4)^{2-}$ tetrahedron is linked directly to interlayer cations.

Compounds **2** and **3** contain the same uranyl chromate sheet in which all of the non-bridging O atoms of the $(CrO_4)^{2-}$ tetrahedra point in the same direction. In both compounds, adjacent sheets have the $(CrO_4)^{2-}$ tetrahedra in opposite orientations. This results in two distinct interlayers, one sandwiched between two sheets with all of the non-bridging O atoms of $(CrO_4)^{2-}$ tetrahedra directed into the interlayer, and one where no such O atoms are available for linkages to the sheets. The two interlayer configurations are most apparent in the case of compound **3** because the linkages between the Rb cations and the uranyl chromate sheets are well-defined. The details of these two interlayers are shown in Fig. 4, in which the Cr–O, U–O, and Rb–O bonds are shown in magenta, yellow, and black, respectively. The lower interlayer region in the figure contains the Rb(2) cations, each of which are bonded to three O atoms of $(CrO_4)^{2-}$ tetrahedra that do not bridge within the sheet. The coordination environment also includes two O_{Ur} atoms, one OH^- group that is shared between two uranyl pentagonal bipyramids, and one H_2O group. The upper interlayer contains the Rb(1) cation that is bonded to two O_{Ur} atoms and two H_2O groups. The remainder of the coordination sphere is completed by O atoms that are at
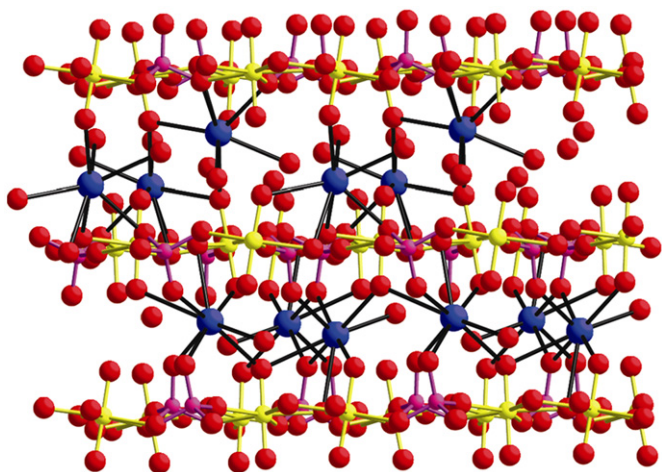
Fig. 4. Details of the interlayers and uranyl chromate sheets in compound **3**. U, O, Rb, and Cr are shown as yellow, red, blue, and magenta spheres, respectively. U–O, Cr–O, and Rb–O bonds are shown as yellow, magenta, and black lines, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

equatorial vertices of the uranyl pentagonal bipyramids, one of which is an OH$^-$ group and two of which belong to $(CrO_4)^{2-}$ tetrahedra.

The isostructural compounds **4** and **5** present an interesting contrast to the structures of compounds **2** and **3**. The compounds **3** and **5** differ compositionally only in the quantity of H_2O in the interlayer. In compound **5**, the $(CrO_4)^{2-}$ tetrahedra point both up and down relative to the sheet, adjacent sheets are in the same orientation, and only one interlayer configuration exists. The single symmetrically distinct Rb cation is bonded to four O_{Ur} atoms and one O atom of a $(CrO_4)^{2-}$ tetrahedron that does not bridge within the sheet. The sheet is corrugated, in contrast to the essentially planar sheets in compounds **2** and **3**.

Schindler and Hawthorne [26–28] examined the relationships between sheets containing uranyl polyhedra and the interstitial (interlayer) complexes, focusing mostly on minerals. They developed a binary representation that considered the average Lewis basicity of the structural unit (sheet), and related this to the Lewis acidity of the interstitial complex. This approach is effective in understanding the limiting factors for structure formation, specifically whether a given type of interlayer cation is compatible with a specific sheet containing uranyl polyhedra, and how many H_2O groups are required to stabilize the structure. The study showed that structures can be stable over a relatively limited range of the combinations of Lewis basicity of the structural unit, Lewis acidity of the interstitial components, and number of transformer H_2O groups. The structures of compounds **3** and **5** are examples of two compounds in which the number of transformer H_2O groups differs, while the Lewis basicity of the structural unit and Lewis acidity of the interstitial complex remain the same.

Supporting information

Supporting information includes crystallographic information files (CIFs) and crystallographic tables for compounds **1**–**8** as well as infrared spectra.

Acknowledgment

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2011.11.033.

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