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Complex Uranyl Dichromates Templated by Aza-Crowns

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Received: 3 November 2018; Accepted: 7 December 2018; Published: 10 December 2018



Abstract: Three new uranyl dichromate compounds templated by aza-crown templates were obtained at room temperature by evaporation from aqueous solutions: (H₂diaza-18-crown-6)₂[(UO₂)₂(Cr₂O₇)₄(H₂O)₂](H₂O)₃ (**1**), (H₄[15]aneN₄)[(UO₂)₂(CrO₄)₂(Cr₂O₇)₂(H₂O)](H₂O)_{3.5} (**2**) and (H₄Cyclam)(H₄[15]aneN₄)₂[(UO₂)₆(CrO₄)₈(Cr₂O₇)₄](H₂O)₄ (**3**). The use of aza-crown templates made it possible to isolate unprecedented and complex one-dimensional units in **2** and **3**, whereas the structure of **1** is based on simple uranyl-dichromate chains. It is very likely that the presence of relatively large organic molecules of aza-crown ethers does not allow uranyl chromate chain complexes to condense into the units of higher dimensionality (layers or frameworks). In general, the formation of **1**, **2**, and **3** is in agreement with the general principles elaborated for organically templated uranyl compounds. The negative charge of the [(UO₂)(Cr₂O₇)₂(H₂O)]^{2−}, [(UO₂)₂(CrO₄)₂(Cr₂O₇)₂(H₂O)]^{4−} and [(UO₂)₃(CrO₄)₄(Cr₂O₇)₂]^{6−} one-dimensional inorganic motifs is compensated by the protonation of all nitrogen atoms in the molecules of aza-crowns.

Keywords: uranium; chromium; dichromates; aza-crowns; organically templated uranyl compounds

1. Introduction

The crystal chemistry of hexavalent uranium oxysalts is remarkable for its extremely rich diversity of structural types [1]. Among these, uranyl compounds containing tetrahedrally coordinated hexavalent cations (S, Cr, Se, Mo) form one of the most numerous groups [2]. Structural chemistry of uranyl oxysalts is mostly represented by layered structural architectures which results from strong directional anisotropy of the bond distribution in UO₂²⁺ coordination geometries. However, each of the chemical classes of compounds bearing T⁶⁺O₄ tetrahedral anions (i.e., uranyl sulfates, chromates, selenates and molybdates) exhibits its own characteristic structural trends and features. Uranyl sulfates demonstrate remarkable structural diversity [1]. The sulfate anions may coordinate to the uranyl group in both monodentate and bidentate manner via corner and edge sharing, respectively, between the UO₇ pentagonal bipyramid and the SO₄ tetrahedron. However, just a few of uranyl polysulfates (disulfates in fact) are known to date [3]. Polymerization is unknown for selenates in uranyl compounds. The chemistry of organically templated uranyl selenates is also diverse and many contributions were reported in the last decade [4]. Bidentate bridging of SeO₄^{2−} anion with the UO₇ bipyramid cannot be realized due to the relatively large size of Se⁶⁺ cation and high repulsive forces between the U⁶⁺ and Se⁶⁺. Uranyl molybdates tend to form framework structures [5] due to the

flexibility and broad variation of U-O-Mo bond angles. Uranyl chromates constitute a particularly versatile class among the compounds considered as they exhibit all the features listed above: both mono- [6–16] and bidentate [17–19] linkage modes of CrO_4 tetrahedra to UO_7 uranyl bipyramids, formation of corner-sharing tetrahedral chromate polyanions [19–21], flexibility and variation of U-O-Cr angles similar to those in uranyl molybdates and formation of framework structures [22], and variability of coordination environments [23–25]. The tendency of the CrO_4^{2-} to form isopolyanions in acidic media leads to formation of structures involving simultaneously several polychromate moieties such as $\text{Cr}_2\text{O}_7^{2-}$ dimers, $\text{Cr}_3\text{O}_{10}^{2-}$ trimers and $\text{Cr}_4\text{O}_{13}^{2-}$ tetramers [26].

Organically templated uranyl-based materials [27] are characterized by the structures consisting of weakly bonded inorganic and organic substructures. The majority of organic molecules used as templates in uranyl compounds are structurally non-rigid nitrogen-based hydrogen bond donors. It is of interest to explore a template effect when employing organic species with restricted adaptability and fixed mutual positioning of the donor atoms. Macrocycles including crown ethers and particularly their aza derivatives seem to be the most proper candidates due to their applications in actinide partitioning [28,29], given their high selectivity for uranium [30] and neptunium [31,32]. Recently, crown ether complexes with alkali metals [33] and aza-crown ether complexes with Ni [34] were used as assemblers and linkers in uranyl-organic coordination polymers. In addition to metal-organic compounds, a number of works were devoted to the preparation of uranyl oxysalts templated by crown ethers [35–38]. In some cases, the use of crown ethers as templates has resulted in highly porous framework structures [39]. We note that, in most of the reported structures of crown ether-templated uranyl compounds, both inorganic units and the crown ether molecules remain electroneutral leading to formation of the so-called organic-inorganic composite structures [4,19,38]. This clear demonstration of the template effect in organically templated uranyl-based materials sheds light at further perspectives of the macrocycles in the structural design of uranyl compounds. Therefore, one can expect that incorporation of nitrogen donor atoms, capable of accepting protons, into the structures of macrocyclic templates would further expand the structural chemistry of the templated uranium compounds. Uranyl compounds templated by aza-crowns have not been reported to date. Chromates were chosen due to their higher structural diversity in terms of composition, including formation of polyanions as discussed above.

Herein, we report syntheses and structural data for the first three uranyl dichromate compounds based on aza-crown templates: $(\text{H}_2\text{diaz-18-crown-6})_2[(\text{UO}_2)_2(\text{Cr}_2\text{O}_7)_4(\text{H}_2\text{O})_2](\text{H}_2\text{O})_3$ (**1**), $(\text{H}_4[15]\text{aneN}_4)[(\text{UO}_2)_2(\text{CrO}_4)_2(\text{Cr}_2\text{O}_7)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_{3.5}$ (**2**) and $(\text{H}_4\text{Cyclam})(\text{H}_4[15]\text{aneN}_4)_2[(\text{UO}_2)_6(\text{CrO}_4)_8(\text{Cr}_2\text{O}_7)_4](\text{H}_2\text{O})_4$ (**3**) obtained at room temperature in the aza-crown— CrO_3 — $(\text{UO}_2)(\text{NO}_3)_2$ systems by evaporation from aqueous solutions. A small set of relatively simple aza-crown molecules has resulted in two new unprecedented and complex one-dimensional units in the structures of **2** and **3**, respectively. The structure of **1** is based on more simple uranyl-dichromate chains previously reported in an imidazole-templated compound [20].

2. Materials and Methods

2.1. Synthesis

Caution: Depleted uranium is radioactive and chemically toxic so its compounds should be handled with care. Chromium (VI) compounds are carcinogenic. Suitable safety measures for precautions and protection should be taken.

Single crystals of **1**, **2** and **3** were obtained from aqueous solutions of 0.08 g of CrO_3 (Vekton 99.5%), 0.03 g of $(\text{UO}_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Vekton 99.7%), 0.01 g of 1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane (diaz-18-crown-6) ($\geq 96\%$, Sigma-Aldrich, Saint Louis, MO, USA) (for **1**), 0.01 g of 1,4,8,12-Tetraazacyclopentadecane ([15]aneN₄) (97%, Sigma-Aldrich) (for **2**), mixture of 0.005 g of [15]aneN₄ and 0.005 g of 1,4,8,11-Tetraazacyclotetradecane (Cyclam) (97%, Sigma-Aldrich) (for **3**) and 10 mL of

distilled H₂O. The pH of the resulted solutions was about 2. The solutions were left to evaporate in a fume hood. Prismatic ruby-red crystals of **1–3** were formed after approximately 7 days. The estimated yields are ca. 10%. Qualitative electron microprobe analysis of **1–3** (Hitachi TM3000 system, Hitachi, Tokyo, Japan) revealed no other elements, except U and Cr with atomic number greater than 11 (Na).

2.2. X-ray Experiments

The crystals of **1–3** selected for data collection were examined under an optical microscope and mounted on glass fibers. The single crystal X-ray data were collected at 120 K on a Bruker SMART diffractometer equipped with an APEX II CCD detector operating with MoK α radiation at 50 kV and 40 mA. A single dark red translucent prismatic crystal of **1** with dimensions of 0.10 \times 0.12 \times 0.04 mm³, a dark red plate of **2** with dimensions of 0.12 \times 0.12 \times 0.02 mm³ and one of **3** with similar habit measuring 0.20 \times 0.20 \times 0.10 mm³ were chosen. For each crystal, more than a hemisphere of data was collected with a frame width of 0.5° in ω , and 10 s counting time spent for each frame. The data were integrated and corrected for absorption using a multi-scan type model using the Bruker programs APEX and SADABS [40]. The crystals of **1–3** decay after approximately 3 h of X-ray exposure. Their structures were solved by direct methods. **1** is monoclinic, space group $P2_1/c$, $a = 17.587(3)$ Å, $b = 11.0803(16)$ Å, $c = 33.410(4)$ Å, $\beta = 112.265(6)^\circ$, $V = 6025.2(15)$ Å³. **2** is also monoclinic, space group $P2_1/c$, $a = 20.916(4)$ Å, $b = 11.1898(16)$ Å, $c = 16.948(3)$ Å, $\beta = 106.367(8)^\circ$, $V = 3806.0(10)$ Å³, whereas **3** is triclinic, $P\bar{1}$, $a = 8.6749(10)$ Å, $b = 17.076(2)$ Å, $c = 17.921(2)$ Å, $\alpha = 67.767(2)^\circ$, $\beta = 81.969(2)^\circ$, $\gamma = 83.691(2)^\circ$, $V = 2428.5(5)$ Å³ (Table 1). All structures were successfully refined with the use of SHELX software package [41]. For **1**, all atoms except split sites Cr8 and O27 were refined anisotropically. The final model for **2** included anisotropic displacement parameters for all atoms. For **3**, only all of the U and Cr and most of O atoms in uranyl chromate units could be refined anisotropically. The hydrogen atoms in protonated aza-crowns molecules were added to their ideal positions using HFIX command. Hydrogen atoms belonging to H₂O molecules could not be localized in all structures. Further details of the data collection and refinement are given in Table 1 and selected bond lengths in Tables 2–4.

Table 1. Crystallographic data and refinement parameters for **1–3**.

	1	2	3
a (Å)	17.587(3)	20.916(4)	8.6749(10)
b (Å)	11.0803(16)	11.1898(16)	17.076(2)
c (Å)	33.410(4)	16.948(3)	17.921(2)
α (°)			67.767(2)
β (°)	112.265(6)	106.367(8)	81.969(2)
γ (°)			83.691(2)
V (Å ³)	6025.2(15)	3806.0(10)	2428.5(5)
Radiation	MoK α	MoK α	MoK α
Total reflections	18,459	19,233	22,459
Unique reflections	8379	7355	13,436
Unique $ F_o \geq 4\sigma_F$	4699	4825	9874
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Θ range	1.25–23.72	2.04–26.20	1.42–29.68
Crystal size (mm)	0.10 \times 0.12 \times 0.04	0.12 \times 0.12 \times 0.02	0.20 \times 0.20 \times 0.10
μ (mm ^{−1})	7.004	10.223	11.778
ρ_{calc} (g cm ^{−3})	2.29	2.56	2.72
GoF	0.937	0.988	1.059
R_1	0.057	0.052	0.052

Note: hydrogen atoms belonging to H₂O molecules could not be localized.

Crystallographic data in cif format have been deposited with the Cambridge Crystallographic Data Center (1883671 (for **1**), 1883670 (for **2**), 1883669 (for **3**)). Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44-1223-366033, email: deposit@ccdc.cam.ac.uk or on the web at <http://www.ccdc.cam.ac.uk>.

3. Results

3.1. Cation Coordination

3.1.1. $(\text{H}_2\text{diaz-18-crown-6})_2[(\text{UO}_2)_2(\text{Cr}_2\text{O}_7)_4(\text{H}_2\text{O})_2](\text{H}_2\text{O})_3$

The structure of **1** (Figure 1) contains two symmetrically independent U^{6+} cations and eight Cr^{6+} cations. Each of two U atoms is strongly bonded to two O atoms thus forming linear UO_2^{2+} uranyl cations and further coordinated by five atoms of O arranged at the equatorial vertices of $\text{UO}_6(\text{H}_2\text{O})$ pentagonal bipyramids. OW1 and OW2 atoms belong to the H_2O molecules. Individual U– O_{eq} (O_{eq} = equatorial O atom) bond lengths are in the range 2.361(13)–2.505(12) Å for U1 and 2.362(11)–2.453(11) Å for U2. U1–OW1 and U2–OW2 bonds (Table 2) are significantly elongated in comparison to the other.

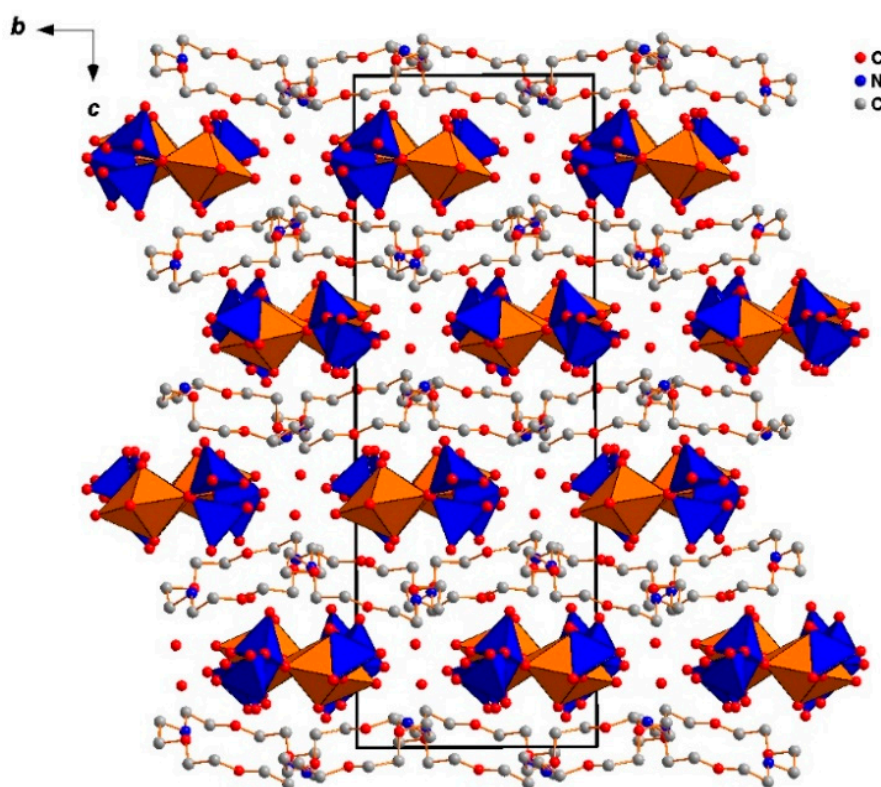


Figure 1. General projection of the crystal structure of **1** along the a -axis (designations: UO_7 = orange; CrO_4 = blue). Pseudolayers formed by $[(\text{UO}_2)_2(\text{Cr}_2\text{O}_7)_4(\text{H}_2\text{O})_2]^{4-}$ units and water molecules alternate with organic layers of $[\text{H}_2\text{diaz-18-crown-6}]^{2+}$ cations. Hydrogen atoms are omitted for clarity.

Each of the eight Cr atoms is tetrahedrally coordinated by four O atoms. CrO_4 tetrahedra are distorted with the Cr–O bond lengths varying from 1.562(12) to 1.793(12) Å. This feature is typical for all previously reported uranyl polychromates [19,20]. There is an orientational disorder observed for Cr8-centered tetrahedron with the Cr8 site split into the Cr8A, Cr8B sites and O27 site split into O27A and O27B sites. The Cr1O_4 and Cr2O_4 , Cr3O_4 and Cr7O_4 , Cr4O_4 and Cr5O_4 , Cr6O_4 and Cr8O_4 tetrahedra share a common O atom to form dichromate groups, $\text{Cr}_2\text{O}_7^{2-}$ (Figure 2a).

In all three structures, the C–C, C–N and C–O bond lengths as well as the bond angles in aza-crown molecules are within the limits typically observed for these molecules. Some strong distortions in several bond-lengths values are due to the instability of grown crystal under X-ray beam.

Table 2. Selected interatomic distances (Å) in **1**.

U1-O4	1.744(12)	Cr2-O18	1.599(12)	Cr6-O23	1.604(13)
U1-O3	1.767(11)	Cr2-O2	1.602(13)	Cr6-O24	1.618(13)
U1-O15	2.361(13)	Cr2-O19	1.651(11)	Cr6-O10	1.650(12)
U1-O10	2.371(12)	Cr2-O21	1.793(12)	Cr6-O32	1.741(14)
U1-O20	2.381(12)				
U1-O1	2.388(11)	Cr3-O22	1.585(12)	Cr7-O26	1.562(12)
U1-OW1	2.505(12)	Cr3-O13	1.601(12)	Cr7-O16	1.579(12)
		Cr3-O7	1.628(12)	Cr7-O15	1.635(12)
U2-O5	1.765(11)	Cr3-O14	1.779(12)	Cr7-O14	1.747(12)
U2-O6	1.765(12)				
U2-O9	2.362(11)	Cr4-O30	1.584(13)	Cr8A *-Cr8B *	1.031(7)
U2-O19	2.368(10)	Cr4-O28	1.600(12)	Cr8A-O31	1.569(13)
U2-O7	2.374(12)	Cr4-O9	1.662(12)	Cr8A-O17	1.574(14)
U2-O31	2.374(12)	Cr4-O25	1.782(12)	Cr8A-O27A *	1.58(2)
U2-OW2	2.453(11)			Cr8A-O32	1.804(15)
				Cr8B-O31	1.512(13)
Cr1-O8	1.603(12)	Cr5-O11	1.587(14)	Cr8B-O27B *	1.613(7)
Cr1-O12	1.604(13)	Cr5-O29	1.585(12)	Cr8B-O17	1.682(15)
Cr1-O1	1.621(11)	Cr5-O20	1.642(12)	Cr8B-O32	1.729(14)
Cr1-O21	1.718(12)	Cr5-O25	1.729(14)		

* S.O.F. = 0.5.

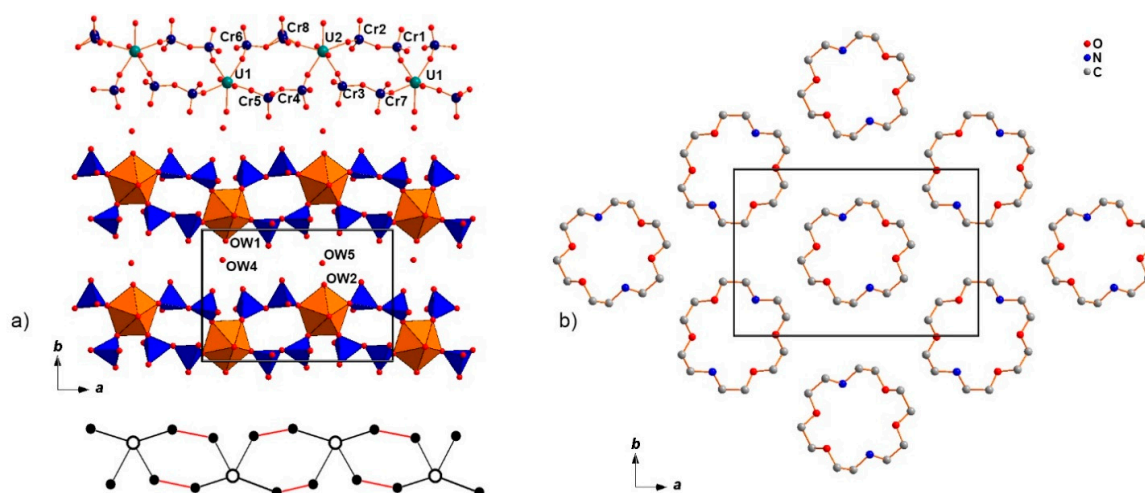


Figure 2. Ball-and-stick and polyhedral representation of $[(\text{UO}_2)(\text{Cr}_2\text{O}_7)_2(\text{H}_2\text{O})]^{2-}$ uranyl-dichromate units in the structure of **1** (a) (designations: UO_7 = orange; CrO_4 = blue). Black-and-white graph (U = white circles, Cr = black circles) of the $[(\text{UO}_2)_2(\text{Cr}_2\text{O}_7)_4(\text{H}_2\text{O})_2]^{4-}$ unit is given below. Red single lines highlight the Cr_2O_7 groups. Arrangement of $[\text{H}_2\text{diza-18-crown-6}]^{2+}$ cations in the interlayer (b). Hydrogen atoms are omitted for clarity.

3.1.2. $(\text{H}_4[15]\text{aneN}_4)[(\text{UO}_2)_2(\text{CrO}_4)_2(\text{Cr}_2\text{O}_7)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_{3.5}$

The monoclinic structure of **2** contains two symmetrically independent U^{6+} cations also forming linear UO_2^{2+} ion each coordinated by five oxygen atoms at the equatorial vertices of pentagonal bipyramids similar to those observed in **1**. Water molecules are absent in the coordination sphere of U1 atom in **2**, whereas U2 coordination environments are similar to those in **1** with the formation of $\text{UO}_6(\text{H}_2\text{O})$ pentagonal bipyramids (Table 3, Figure 3a,b).

There are four distinct Cr^{6+} sites tetrahedrally coordinated by four O atoms each. There are six Cr sites in the structure of **2**. The Cr1 and Cr2 form isolated CrO_4 tetrahedra, whereas the Cr3, Cr4, Cr5 and Cr6 sites belong to dichromate groups, $\text{Cr}_2\text{O}_7^{2-}$. Cr-O_{br} (O_{br} = bridging O atom in $\text{Cr}_2\text{O}_7^{2-}$ group) bonds are significantly elongated in comparison to the Cr-O_t (O_t = terminal O atom) (Table 3).

Table 3. Selected interatomic distances (Å) in **2**.

U1-O2	1.752(9)	Cr1-O18	1.578(9)	Cr4-O17	1.592(10)
U1-O1	1.775(8)	Cr1-O11	1.614(8)	Cr4-O15	1.622(9)
U1-O8	2.318(9)	Cr1-O8	1.648(9)	Cr4-O5	1.628(9)
U1-O9	2.322(8)	Cr1-O14	1.653(9)	Cr4-O12	1.760(9)
U1-O6	2.326(8)				
U1-O5	2.443(9)	Cr2-O20	1.558(10)	Cr5-O19	1.575(11)
U1-O15	2.462(9)	Cr2-O7	1.636(9)	Cr5-O23	1.584(11)
		Cr2-O6	1.666(9)	Cr5-O16	1.647(10)
		Cr2-O9	1.671(8)	Cr5-O13	1.764(10)
U2-O3	1.774(8)				
U2-O4	1.803(8)				
U2-O14	2.299(9)	Cr3-O22	1.591(12)	Cr6-O26	1.53(2)
U2-O7	2.358(9)	Cr3-O21	1.605(11)	Cr6-O24	1.550(14)
U2-O10	2.358(9)	Cr3-O10	1.640(9)	Cr6-O25	1.784(17)
U2-O16	2.363(10)	Cr3-O12	1.792(9)	Cr6-O13	1.803(11)
U2-OW1	2.485(9)				

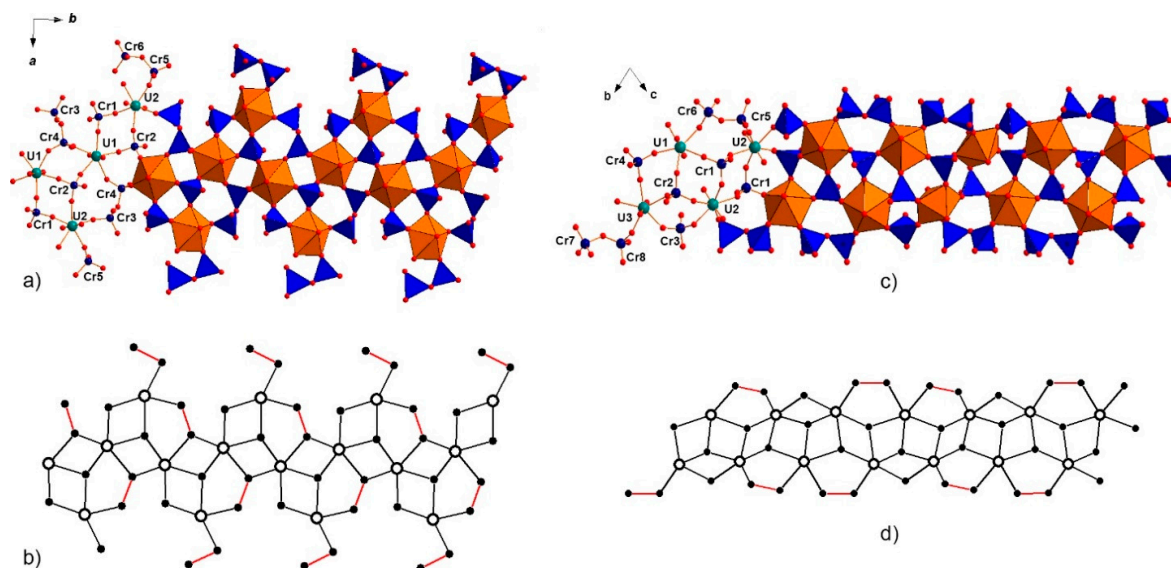


Figure 3. Ball-and-stick and polyhedral representation of $[(\text{UO}_2)_2(\text{CrO}_4)_2(\text{Cr}_2\text{O}_7)_2(\text{H}_2\text{O})]^{4-}$ and $[(\text{UO}_2)_6(\text{CrO}_4)_8(\text{Cr}_2\text{O}_7)_4]^{12-}$ uranyl-dichromate units in the structures of **2** (a) and **3** (c), respectively (designations: UO_7 = orange; CrO_4 = blue). Black-and-white graphs (U = white circles, Cr = black circles) of $[(\text{UO}_2)_2(\text{CrO}_4)_2(\text{Cr}_2\text{O}_7)_2(\text{H}_2\text{O})]^{4-}$ (b) and $[(\text{UO}_2)_6(\text{CrO}_4)_8(\text{Cr}_2\text{O}_7)_4]^{12-}$ (d) one-dimensional units. Red single lines highlight Cr_2O_7 groups.

3.1.3. $(\text{H}_4\text{Cyclam})(\text{H}_4[15]\text{aneN}_4)_2[(\text{UO}_2)_6(\text{CrO}_4)_8(\text{Cr}_2\text{O}_7)_4](\text{H}_2\text{O})_4$

There are three symmetrically independent U atoms in the triclinic structure of **3** (Table 4), all forming linear uranyl cations equatorially coordinated by five O atoms to form pentagonal bipyramids. Water molecules are absent in the coordination sphere of uranium atoms in **3**.

Eight independent Cr positions are tetrahedrally coordinated by four O atoms each. Cr1-, Cr2-, Cr3- and Cr4-centered tetrahedra are isolated. Pairs of Cr5-, Cr6-centered and Cr7, Cr8-centered tetrahedra form the $\text{Cr}_2\text{O}_7^{2-}$ dichromate groups (Figure 3c,d).

Table 4. Selected interatomic distances (Å) in **3**.

U1-O2	1.790(7)	Cr1-O16	1.613(8)	Cr5-O28	1.585(9)
U1-O1	1.797(7)	Cr1-O14	1.643(7)	Cr5-O22	1.619(8)
U1-O13	2.303(7)	Cr1-O10	1.658(8)	Cr5-O25	1.629(11)
U1-O23	2.318(8)	Cr1-O17	1.667(8)	Cr5-O21	1.758(9)
U1-O14	2.333(7)				
U1-O18	2.357(8)	Cr2-O9	1.588(8)	Cr6-O26	1.580(11)
U1-O19	2.362(8)	Cr2-O11	1.662(8)	Cr6-O29	1.586(12)
		Cr2-O13	1.663(7)	Cr6-O19	1.659(9)
U2-O3	1.770(7)	Cr2-O12	1.678(7)	Cr6-O21	1.818(10)
U2-O4	1.793(7)				
U2-O17	2.335(8)	Cr3-O20	1.591(9)	Cr7-O35	1.51(2)
U2-O12	2.340(7)	Cr3-O24	1.599(8)	Cr7-O31	1.560(10)
U2-O7	2.343(7)	Cr3-O8	1.687(7)	Cr7-O18	1.638(9)
U2-O10	2.356(7)	Cr3-O7	1.698(8)	Cr7-O34	1.914(3)
U2-O22	2.395(8)				
		Cr4-O32	1.529(15)	Cr8-O33	1.541(16)
U3-O6	1.763(9)	Cr4-O27	1.616(10)	Cr8-O30	1.609(11)
U3-O5	1.775(8)	Cr4-O23	1.623(9)	Cr8-O34	1.696(3)
U3-O8	2.326(7)	Cr4-O15	1.662(8)	Cr8-O36	1.73(3)
U3-O15	2.355(8)				
U3-O30	2.357(9)				
U3-O27	2.389(9)				
U3-O11	2.398(7)				

3.2. Structure Description

3.2.1. $(\text{H}_2\text{dianza-18-crown-6})_2[(\text{UO}_2)_2(\text{Cr}_2\text{O}_7)_4(\text{H}_2\text{O})_2](\text{H}_2\text{O})_3$

The UO_7 pentagonal bipyramids share some of their common vertices with $\text{Cr}_2\text{O}_7^{2-}$ groups, which results in the formation of $[(\text{UO}_2)(\text{Cr}_2\text{O}_7)_2(\text{H}_2\text{O})]^{2-}$ chains running parallel to the *a*-axis (Figure 2a). The $[(\text{UO}_2)(\text{Cr}_2\text{O}_7)_2(\text{H}_2\text{O})]^{2-}$ chains are parallel one to each other and packed in a layered arrangement. Additional crystallization water molecules are located between the chains. Protonated $[\text{H}_2\text{dianza-18-crown-6}]^{2+}$ molecules compensate for the negative charge of $[(\text{UO}_2)(\text{Cr}_2\text{O}_7)_2(\text{H}_2\text{O})]^{2-}$ chains and also form layers (Figure 2b).

3.2.2. $(\text{H}_4[15]\text{aneN}_4)[(\text{UO}_2)_2(\text{CrO}_4)_2(\text{Cr}_2\text{O}_7)_2(\text{H}_2\text{O})](\text{H}_2\text{O})_{3.5}$

The Cr1O_4 isolated tetrahedra are bidentate, whereas Cr2O_4 are tridentate in the structure of **2** (Figure 3a,b). U1-centered UO_7 pentagonal bipyramids share all of its vertices with the chromate tetrahedra. U2-centered UO_7 pyramids are four coordinated. $\text{Cr}_2\text{O}_7^{2-}$ dichromate group centered by Cr3 and Cr4 shares three common vertices with UO_7 polyhedra, whereas that one formed by Cr5 and Cr6 atoms is attached to UO_7 polyhedron by the one common oxygen vertex only. The resulting $[(\text{UO}_2)_2(\text{CrO}_4)_2(\text{Cr}_2\text{O}_7)_2(\text{H}_2\text{O})]^{4-}$ units are unique in topology for uranyl oxysalts and have not been reported to date. $[(\text{UO}_2)_2(\text{CrO}_4)_2(\text{Cr}_2\text{O}_7)_2(\text{H}_2\text{O})]^{4-}$ chains are oriented parallel to the *b*-axis (Figure 4a,b). Similar to **1**, structural architecture of **2** can be described as pseudo-layered. $[\text{H}_4[15]\text{aneN}_4]^{4+}$ aza-crown moieties and additional water molecules form layers parallel to *ab* plane (Figure 4c). Aza-crown molecules are interconnected with uranyl chromate units by the relatively weak hydrogen bonds only.

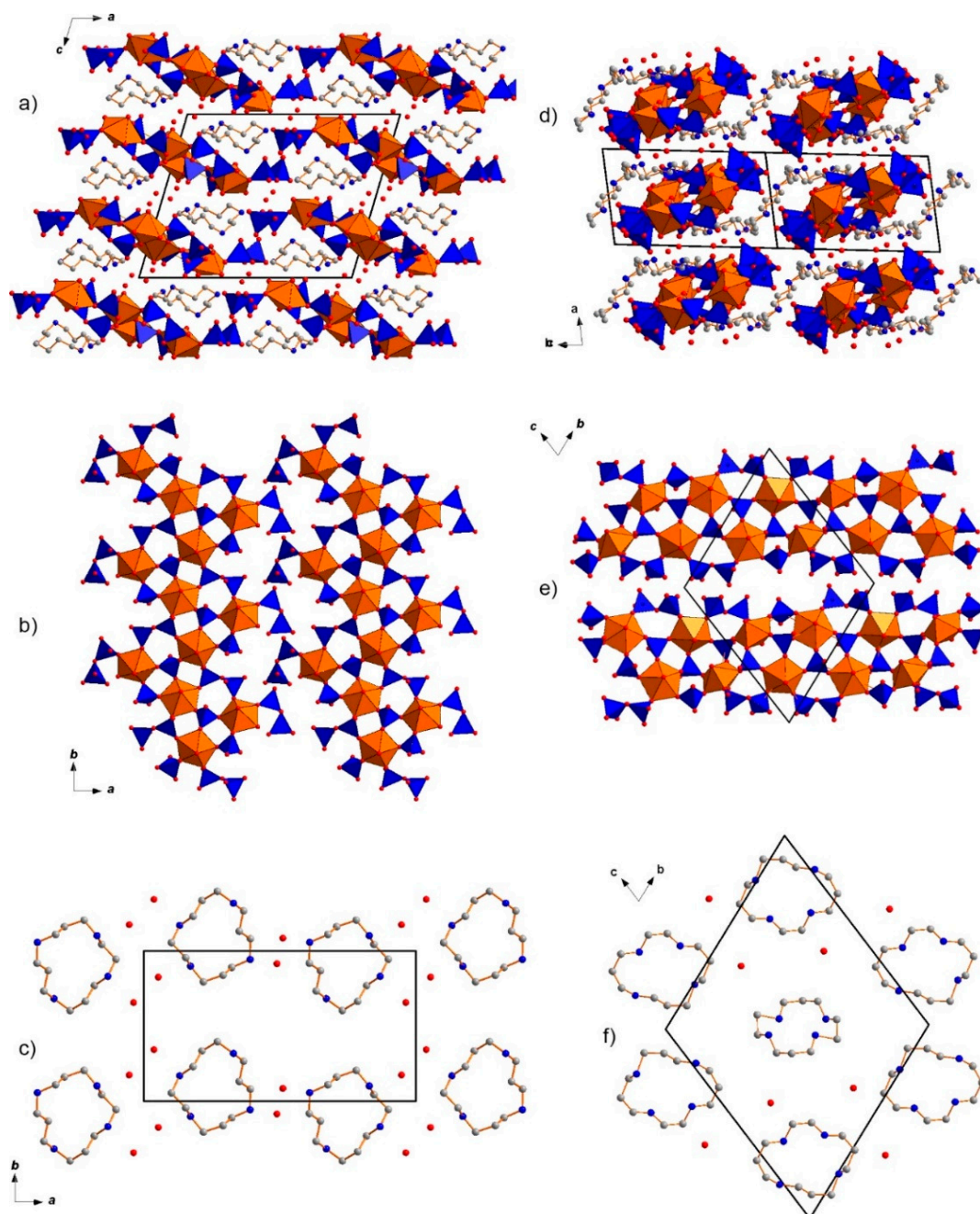


Figure 4. General projection of the structure of **2** (designations: UO_7 = orange; CrO_4 = blue) along the b -axis (a). Mutual arrangement of $[(\text{UO}_2)_2(\text{CrO}_4)_2(\text{Cr}_2\text{O}_7)_2(\text{H}_2\text{O})]^{4-}$ complex chromate-dichromate units projected along the c -axis (b); interlayer formed by $[\text{H}_4[15]\text{aneN}_4]^{4+}$ cations and water molecules in **2** (c); general projection of the structure of **3** (d); pseudolayered arrangement of $[(\text{UO}_2)_6(\text{CrO}_4)_8(\text{Cr}_2\text{O}_7)_4]^{12-}$ units projected along the a -axis (e); arrangement of water molecules, $[\text{H}_4\text{Cyclam}]^{4+}$ and $[\text{H}_4[15]\text{aneN}_4]^{4+}$ ions in the interlayer in **3** (f); hydrogen atoms are omitted for clarity.

3.2.3. $(\text{H}_4\text{Cyclam})(\text{H}_4[15]\text{aneN}_4)_2[(\text{UO}_2)_6(\text{CrO}_4)_8(\text{Cr}_2\text{O}_7)_4](\text{H}_2\text{O})_4$

Novel $[(\text{UO}_2)_3(\text{CrO}_4)_4(\text{Cr}_2\text{O}_7)_2]^{6-}$ uranyl chromate-dichromate chain in the structure of **3** is built on the similar principles described above in **2**. The black-and-white graph depicted in Figure 3d reveals that the $[(\text{UO}_2)_3(\text{CrO}_4)_4(\text{Cr}_2\text{O}_7)_2]^{6-}$ chain is based on the simple $[(\text{UO}_2)(\text{CrO}_4)\text{O}_2]$ block with topology described previously in a number of uranyl oxysalts with different tetrahedrally coordinated cations [13]. However, in **3**, the way of decoration of $[(\text{UO}_2)(\text{CrO}_4)\text{O}_2]$ block by the

isolated CrO_4^{2-} tetrahedra and $\text{Cr}_2\text{O}_7^{2-}$ groups is new and has not been described before. Every two $\text{Cr}_2\text{O}_7^{2-}$ groups alternate with one single CrO_4^{2-} tetrahedron on the both sides of the chain. We note also strong corrugation of $[(\text{UO}_2)_3(\text{CrO}_4)_4(\text{Cr}_2\text{O}_7)_2]^{6-}$ chains in the structure of **3**. The $[\text{H}_4\text{Cyclam}]^{4+}$ and $[\text{H}_4[15]\text{aneN}_4]^{4+}$ cations are located in the form of undulating layers (Figure 4d,f) between the uranyl chromate units (Figure 4e).

4. Discussion

Three novel uranyl chromate-dichromate compounds were obtained and their crystal structures solved. Both uranyl chromate structural units and their graphs found in the structures of **2** and **3** are novel and were not described previously in inorganic compounds. Moreover, **2** and **3** belong to the relatively small group of inorganic compounds with crystal structures containing both isolated and dichromate tetrahedral groups. In general, formation of **1–3** is in agreement with the general principles elaborated for organically templated uranyl compounds [4]. The formation of negatively charged $[(\text{UO}_2)(\text{Cr}_2\text{O}_7)_2(\text{H}_2\text{O})]^{2-}$, $[(\text{UO}_2)_2(\text{CrO}_4)_2(\text{Cr}_2\text{O}_7)_2(\text{H}_2\text{O})]^{4-}$ and $[(\text{UO}_2)_3(\text{CrO}_4)_4(\text{Cr}_2\text{O}_7)_2]^{6-}$ one-dimensional inorganic motifs requires positively charged units to keep electroneutrality. The latter is achieved by the protonation of all nitrogen atoms in the molecules of aza-crowns. Such a structural mechanism is typical of uranyl compounds with various tetrahedral oxoanions, and uranyl chromates in particular, templated by different amine molecules [20]. Planes of the rings of protonated aza-crown molecules in **1–3** are nearly parallel (Figures 1 and 4a,d) to the planes of the uranyl chromate-dichromate chains. It is very likely that the presence of relatively large organic molecules of aza-crowns does not allow uranyl chromate chain complexes to condense into the units of higher dimensionality (layers or frameworks). It may be speculated that the $[(\text{UO}_2)_2(\text{CrO}_4)_2(\text{Cr}_2\text{O}_7)_2(\text{H}_2\text{O})]^{4-}$ and $[(\text{UO}_2)_3(\text{CrO}_4)_4(\text{Cr}_2\text{O}_7)_2]^{6-}$ chains represent the transitional structures between one- and two-dimensional structural topologies very typical for uranyl oxysalts [16]. We also note that **1–3** were formed in the case of relatively nitrogen-rich templates (tetra-aza compounds) where the mutual positioning of the hydrogen donor centers (protonated nitrogen atoms) is more or less fixed. In **1**, the relatively large separation between the nitrogen atoms permits to position the semi-rigid template in such a way to be able to fit to the known $[(\text{UO}_2)_2(\text{Cr}_2\text{O}_7)_4(\text{H}_2\text{O})_2]^{4-}$ motif. Therefore, both the number and mutual positioning of the nitrogen atoms (hydrogen bond donor centers) within the macrocycle are structure-determining parameters while the effect of the macrocycle size is yet unclear. Evidently, a broader set of examples would shed more light on the relative role of these factors.

The presence of polychromate groups in the structures of three novel reported compounds can be explained, on the one hand, by the relatively high pH and Cr^{6+} concentration in the mother liquids [16]. On the other hand, formation of novel moieties is likely to exemplify the particular flexibility and adaptability of the uranyl chromate systems towards the size and shape of the template, as noted in the Introduction. Compared to amines commonly used in previous studies, the aza-crowns employed in this study are relatively large molecules bearing just several cationic centers (protonated nitrogen atoms). Therefore, the positive charge density in these structures is relatively low compared at least to some other templates to provide electroneutrality, and the inorganic backbone should also keep a relatively low charge density. The latter can be easily achieved by the incorporation of low-charged large spacers, for instance, polychromates. Hence, formation of two unique uranyl-chromate units in **2** and **3** is an illustration of the template effect of the organic moieties. The chromate-based systems are likely to be most responsive to the size and shape of the complex templates and promise existence of other, even more complex structural architectures. In the structures of sulfates and selenates where formation of polyanionic chains is not feasible, the inorganic units are characterized by the relatively high negative charge densities; this excess charge is easily compensated by protonated solvent molecules (water in the most common case [35]). This compensation mechanism with formation of hydronium cations is less common while known for uranyl chromates [19]. Formation of low charge-density nets upon use of spacer ligands is also common for another numerous class of uranyl

compounds, the phosphonates [42]. Related patterns may be also expected for phosphates where polymeric chains are also common. Some of these investigations are now in progress.

Author Contributions: O.I.S. designed the study; O.I.S. and E.V.N. performed and interpreted single crystal X-ray diffraction experiments; E.V.N., A.I.Z. and D.O.C. performed synthesis; O.I.S. and D.O.C. wrote the paper; S.N.K. provided work in the radiochemical laboratory.

Funding: This work was financially supported by the Russian Science Foundation through Grant No. 16-17-10085.

Acknowledgments: Technical support by the SPbSU (Saint-Petersburg State University) X-Ray Diffraction and Microscopy and Microanalysis Resource Centers is gratefully acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

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