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Cr(VI) Trioxide as a Starting Material for the Synthesis of Novel Zero-, One-, and Two-Dimensional Uranyl Dichromates and Chromate-Dichromates

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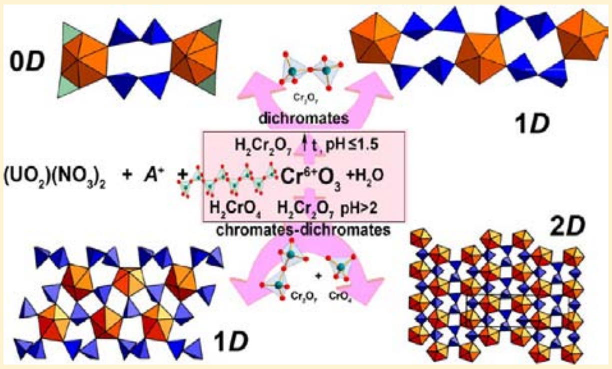
Supporting Information

ABSTRACT: Six different dichromate-based uranyl compounds were obtained. Their structures belong to four principally different but related structure types with different dimensionality of basic structural units. The units in $Cs_2(UO_2)(Cr_2O_7)(NO_3)_2$ (**1**) and $(C_6H_{11}N_2)_2(UO_2)(Cr_2O_7)_2(H_2O)$ (**2**) are unique, and these are the first "pure" uranyl-dichromates known to date. The compounds $Rb_2(UO_2)(CrO_4)(Cr_2O_7)$ (**3**), $(C_2NH_8)_2(UO_2)(CrO_4)(Cr_2O_7)$ (**4**), $(C_2NH_8)_2(UO_2)(CrO_4)_2(Cr_2O_7)(H_2O)_2$ (**5**), and $(C_3NH_{10})_2(UO_2)(CrO_4)_2(Cr_2O_7)(H_2O)_2$ (**6**) are novel representatives of a rather small group of inorganic compounds containing both isolated CrO_4 tetrahedra and dichromate Cr_2O_7 groups. The structures of **5** and **6** contain compositionally identical but topologically different ${}^{2}_{\infty}[(UO_2)(CrO_4)_2(Cr_2O_7)]^{2-}$ sheets (thus corresponding to different geometrical isomers), which have not been reported previously in inorganic compounds. All novel phases have been prepared with an excess of CrO_3. "Pure" dichromates are formed at pH < 1.5 and with prior hydrothermal treatment of uranyl-chromate solution, whereas mixed chromate-dichromates are formed at higher pH > 2 values.



■ INTRODUCTION

Investigations of oxocompounds of hexavalent uranium and chromium are of great importance due to the environmental issues and fundamental crystal chemical aspects. Highly mobile CrO_4^{2-} is a significant groundwater pollutant at the U.S. Department of Energy (DOE) Hanford Site,[1] which may have a considerable impact upon the transport of actinides in contaminated soils. Hexavalent chromium is also one of the significant constituents of spent nuclear fuel (SNF).[2] $K_2Cr^{6+}{}_2O_7$ was used as an oxidant in the REDOX process to manipulate the valence states of Pu and U.[3] $K_2Cr^{6+}O_4$ is used as an effective corrosion inhibitor for magnesium alloys used in some SNF rod arrays.[4] The extremely high oxidation potential of Cr^{6+} makes its coordination chemistry limited. Uranyl oxocompounds containing tetrahedral oxoanions formed by hexavalent cations of the group VI elements of the Periodic Table, T^{6+} (T = S, Cr, Se, Mo), constitute one of the most diverse and structurally rich groups of uranium compounds. For each of these elements, specific structural trends can be distinguished due to different electronic structure and ionic size. Despite the large number of uranyl compounds described almost on a weekly basis, there are several underexplored classes with unforeseen structural topologies and applications. Most of the structures containing uranyl coordination polyhedra and TO_4^{2-} tetrahedra are based upon linkage of these polyhedra via common anions that results in structural units of different topology and dimensionality. Edge-sharing of actinyl polyhedra and $T^{6+}O_4$ tetrahedra is very common for sulphates[5] and had also been observed for several chromates.[6] On the other hand, many structures of uranyl chromates are isotypic with uranyl selenates.[7] These observations can be explained by the fact that Cr^{6+} cation is larger than S^{6+} and smaller than Se^{6+}. It is well-known that the CrO_4^{2-} ions display the ability to polymerize,[8] which results in the formation of multiple groups such as $Cr_2O_7^{2-}$ dimers,[9] $Cr_3O_{10}^{2-}$ trimers,[10] or even $Cr_4O_{13}^{2-}$ tetramers.[11] However, in the majority of uranyl-chromates known to date,[12] chromate ions are not polymerized, which may well be the consequence of the use of A_nCrO_4 and $A_nCr_2O_7$, $n = 1-2$ (A = Na, K, Rb, Cs, Tl, Ca, Mg), as starting reagents in their synthesis. Recently, we have demonstrated that alternative synthetic procedures that employ CrO_3 as a starting material may result in novel structures with unusual architectures and topologies.[6,13] The structure of CrO_3 is formed by one-dimensional infinite chains of corner-sharing tetrahedra[14] and therefore can be considered as the primary source of chromate building units of different dimensionality. Chromium trioxide is a Lewis acid and easily reacts with different Lewis bases. Well-known is the formation of H_2CrO_4 chromic acid (red) after addition of H_2O to solid CrO_3, or $H_2Cr_2O_7$ dichromic acid (orange) if CrO_3 is used in excess. $Cr_3O_{10}^{2-}$ trichromates and $Cr_4O_{13}^{2-}$ tetrachromates are formed with decreasing pH value. There is only one uranyl chromate-dichromate known to date,[15] whereas "pure" uranyl dichromates are unknown.

Herein, we report on a chromate/dichromate/uranium system with various inorganic or organic monovalent cations. This system

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Table 1. Crystal Structure Data for Compounds $Cs_2(UO_2)(Cr_2O_7)(NO_3)_2$ (1), $(C_6H_{11}N_2)_2(UO_2)(Cr_2O_7)_2(H_2O)$ (2), $Rb_2(UO_2)(CrO_4)(Cr_2O_7)$ (3), $(C_2NH_8)_2(UO_2)(CrO_4)(Cr_2O_7)$ (4), $(C_2NH_8)_2(UO_2)(CrO_4)_2(Cr_2O_7)(H_2O)_2$ (5), and $(C_3NH_{10})_2(UO_2)(CrO_4)_2(Cr_2O_7)(H_2O)_2$ (6)

	1	2	3	4	5	6
T [K]	120	120	120	120	120	120
M_r [g mol^{-1}]	875.84	734.36	772.95	664.12	1114.23	1144.30
crystal system	triclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$C2/c$	Cc
a [Å]	8.148(3)	7.5410(18)	13.236(4)	6.9964(15)	22.0207(7)	23.5965(19)
b [Å]	8.299(3)	8.7776(9)	13.764(4)	7.8744(17)	7.2088(2)	7.0484(6)
c [Å]	11.805(4)	17.9493(18)	14.857(4)	15.811(4)	31.9884(11)	32.482(3)
α [deg]	70.881(8)	90	73.880(6)	82.387(4)	90	90
β [deg]	88.966(9)	102.973(2)	88.865(7)	83.862(4)	106.7060(10)	105.758(2)
γ [deg]	79.339(9)	90	89.841(7)	84.762(4)	90	90
V [Å^3]	740.5(4)	2693.1(5)	2599.7(13)	855.8(3)	4863.6(3)	5199.2(7)
ρ_{calcd} [g cm^{-3}]	3.93	2.265	3.95	2.631	2.994	2.862
μ [mm^{-1}]	17.271	7.633	22.360	11.346	15.081	14.111
refln collected	10 291	20 745	26 663	9795	65 392	21 589
ind reflns (R_{int})	3561 (0.0483)	6468 (0.0237)	12 255 (0.1322)	4142 (0.1179)	5878 (0.0531)	10 234 (0.0437)
GOF	1.048	1.022	0.963	0.958	1.372	1.014
R_1 [$I > 2\sigma(I)$]	0.0282	0.0291	0.0715	0.0510	0.0525	0.0404
wR_2	0.0707	0.0799	0.1773	0.1251	0.1245	0.0769
R_1 (all data)	0.0303	0.0348	0.1215	0.0931	0.0567	0.0551
wR_2	0.0719	0.0849	0.1919	0.1407	0.1263	0.0816
largest diff. peak and hole [e Å^3]	1.649, −3.004	1.830, −1.037	4.628, −2.182	2.543, −1.412	3.025, −4.351	2.235, −1.362

differs from our previous works by the higher concentration of chromate ions involved in syntheses. The six new compounds described here illustrate the complexity of the system and new pathways for synthesis of uranyl-chromate-dichromates.

■ EXPERIMENTAL SECTION

Syntheses. ***$Cs_2(UO_2)(Cr_2O_7)(NO_3)_2$ (1).*** Single crystals of **1** were obtained by the combination of hydrothermal method and evaporation from aqueous solution from the mixture of 0.12 g of CrO_3 (Vekton 99.5%), 0.05 g of $(UO_2)(NO_3)_2{\cdot}6H_2O$ (Vekton 99.7%), 0.015 g of $CsNO_3$ (Vekton 99.5%), and 8 mL of distilled H_2O. The reactants were placed in a 23 mL Teflon-lined steel autoclave and heated to 90 °C for 2 days. The autoclave was allowed to cool slowly to room temperature over a 24 h period. The resulted bright-red transparent solution was recovered and allowed to slowly evaporate in air in a fume hood for 3 days. Clusters and spherolites of prismatic orange crystals of **1** up to 0.1 mm were recovered after this period. The products were filtered and washed with hexane. The yield of the synthesis of **1** is 19% based on U.

$(C_6H_{11}N_2)_2(UO_2)(Cr_2O_7)_2(H_2O)$ (2). Crystals of **2** were obtained by a procedure similar to that for **1** from the mixture of 0.12 g of CrO_3 (Vekton 99.5%), 0.05 g of $(UO_2)(NO_3)_2{\cdot}6H_2O$ (Vekton 99.7%), 0.022 g of 1-ethyl-3-methylimidazolium bromide ($C_6H_{11}BrN_2$) (Sigma-Aldrich 97%), and 8 mL of distilled H_2O. Elongated orange platy crystals of **1** up to 0.4 mm were recovered after a 72 h period. The products were filtered and washed with hexane. The yield of the synthesis of **1** is 15% based on U.

$Rb_2(UO_2)(CrO_4)(Cr_2O_7)$ (3). Single crystals of **3** were obtained from aqueous solutions of 0.075 g of CrO_3 (Vekton 99.5%), 0.025 g of $(UO_2)(NO_3)_2{\cdot}6H_2O$ (Vekton 99.7%), 0.019 g of $RbNO_3$ (Vekton 99.5%), and 10 mL of distilled H_2O. The solution was left to evaporate in a fume hood. Sable-like ruby-red crystals of **3** up to 0.4 mm, dark-red CrO_3, and colorless $RbNO_3$ were formed after approximately 24 h. It is of interest that crystals of **3** were obtained also by the mixing of 0.050 g of RbCl (Vekton, 99.5%), 0.100 g of CrO_3 (Vekton, 98%), and 0.025 g of $(UO_2)(NO_3)_2{\cdot}6H_2O$ (Vekton, 99.7%). The produced mixture was loaded into a platinum crucible and kept at 240 °C for 10 h in air, followed by cooling to 100 °C with a cooling rate of 3 °C/h and then cooling to room temperature with a rate of 7 °C/h. The product consisted of ruby-red prismatic crystals of **3** in the mass of

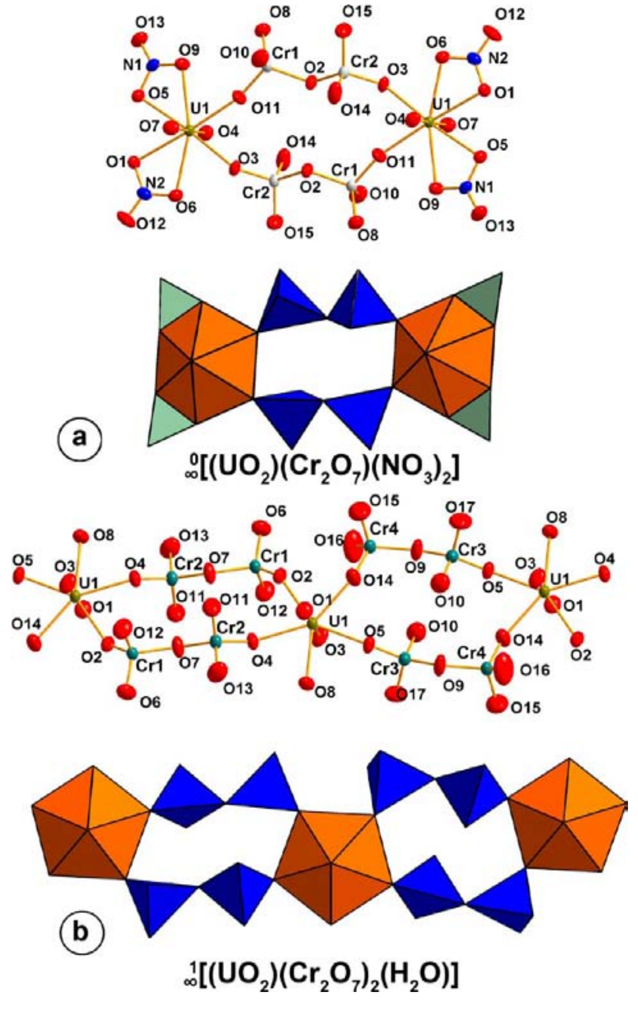

Figure 1. General projection of uranyl-dichromate units observed in the structures of **1** (a) and **2** (b) (designations: NO_3 = green; UO_7, UO_8 = orange; CrO_4 = blue). Ellipsoids are drawn at 50% probability level.

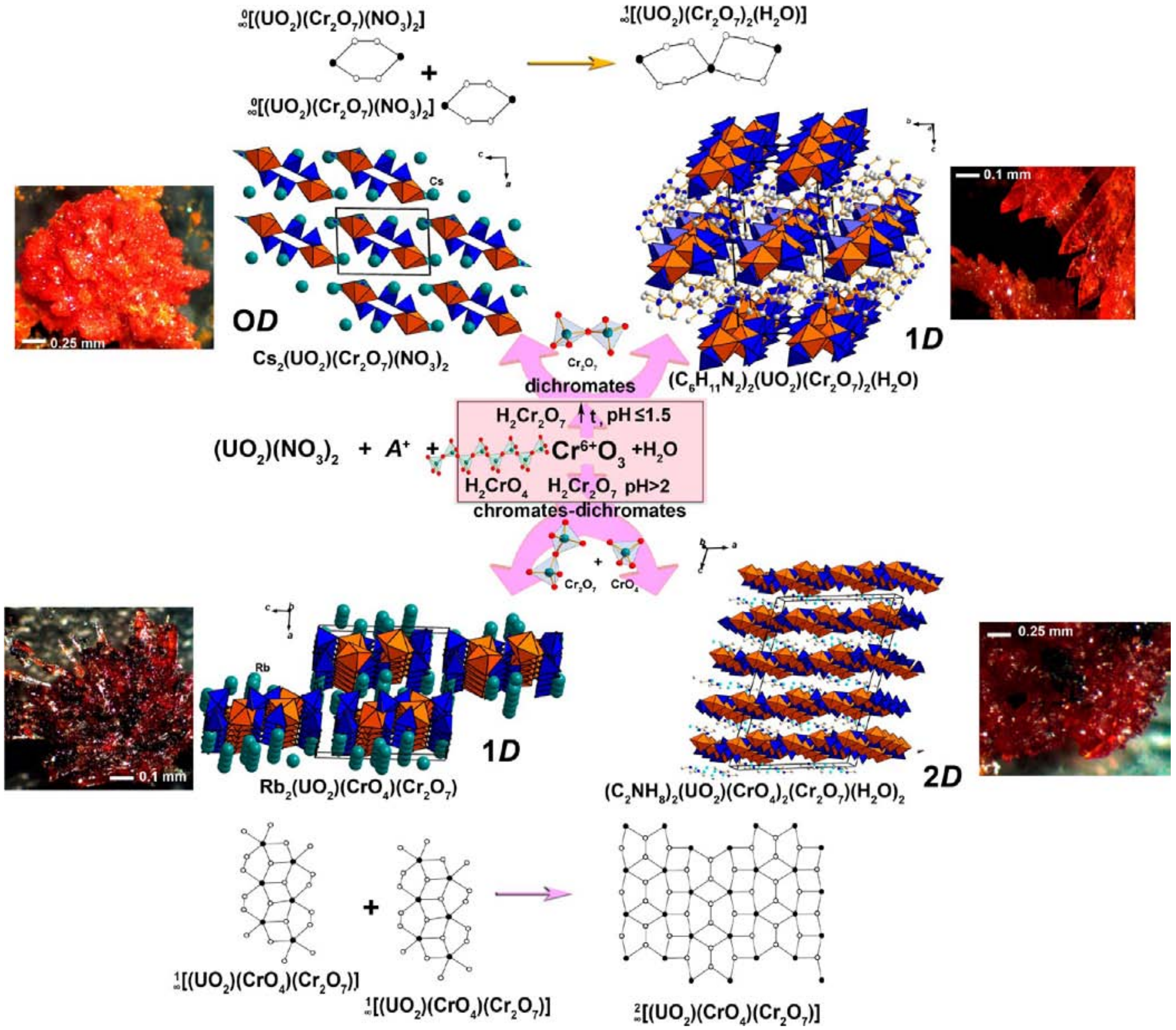

Figure 2. Structural diversity (from 0D to 2D) for the chromate/dichromate/uranium system with different monovalent organic and inorganic cations when using CrO_3 as primary source providing chromate building units at different pH's of initial solution (legend: NO_3 = green; UO_7, UO_8 = orange; CrO_4 = blue). Evolution of topology of $^{0}_{\infty}[(UO_2)(Cr_2O_7)(NO_3)_2]^{2-}$ into $^{1}_{\infty}[(UO_2)(Cr_2O_7)_2(H_2O)]^{2-}$ (up) and $^{1}_{\infty}[(UO_2)(CrO_4)_2(Cr_2O_7)]^{2-}$ into $^{2}_{\infty}[(UO_2)(CrO_4)_2(Cr_2O_7)]^{2-}$ (down) shown as black and white graphs in the structures of **1**, **2** and **3**, **4**, **5**, **6** dichromates and chromate-dichromates, respectively. See text for details.

amorphous Cr_2O_3. Yet the obtained crystals by this method were found to be of poor quality for single-crystal X-ray measurements.

$(C_2NH_8)_2(UO_2)(CrO_4)(Cr_2O_7)$ (4). Single crystals of **4** were obtained from aqueous solutions of 0.075 g of CrO_3 (Vekton 99.5%), 0.025 g of $(UO_2)(NO_3)_2{\cdot}6H_2O$ (Vekton 99.7%), 0.05 mL of dimethylamine (40 wt % in H_2O Sigma-Aldrich), and 10 mL of distilled H_2O. The solution was left to evaporate in a fume hood. Prismatic ruby-red crystals of 4 up to 0.1 mm and dark-red CrO_3 were formed after approximately 60 h.

$(C_2NH_8)_2(UO_2)(CrO_4)_2(Cr_2O_7)(H_2O)_2$ (5). Single crystals of **5** were obtained from aqueous solutions of 0.03 g of CrO_3 (Vekton 99.5%), 0.025 g of $(UO_2)(NO_3)_2{\cdot}6H_2O$ (Vekton 99.7%), 0.015 mL of dimethylamine (40 wt % in H_2O Sigma-Aldrich), and 8 mL of distilled H_2O. The solution was left to evaporate in a fume hood. Prismatic ruby-red crystals of **5** up to 0.1 mm and dark-red CrO_3 were formed after approximately 7 days.

$(C_3NH_{10})_2(UO_2)(CrO_4)_2(Cr_2O_7)(H_2O)_2$ (6). Single crystals of **6** were obtained from aqueous solutions of 0.03 g of CrO_3 (Vekton 99.5%), 0.025 g of $(UO_2)(NO_3)_2{\cdot}6H_2O$ (Vekton 99.7%), 0.015 mL of isopropylamine ($(CH_3)_2CHNH_2$) (Sigma-Aldrich 99.5%), and 8 mL of distilled H_2O. The solution was left to evaporate in a fume hood. Isometric ruby-red crystals of **6** up to 0.05 mm and dark-red CrO_3 were formed after approximately 7 days.

The electron-microprobe analyses (LINK AN-10000 EDS system) were performed for **1**−**6**. Qualitative electron microprobe analysis in **2**, **4**, **5**, **6** revealed no other elements, except U(VI) and Cr(VI), with the atomic number greater than 11 (Na). The averaged of 10 points (for **3**) gave the empirical formula calculated on the basis of 13 total oxygen atoms: $Rb_{1.97}U_{0.96}Cr_{3.045}O_{13}$. The averaged of 10 points (for **1**) gave the empirical formula calculated on the basis of N = 2: $Cs_{1.97}U_{0.98}Cr_{1.98}N_2O_{14.87}$.

Crystallographic Studies. Single crystals of all compounds were mounted on thin glass fibers for X-ray diffraction analysis using a Bruker APEX II DUO X-ray diffractometer with a microfocus X-ray tube operated with Mo Kα radiation at 50 kV and 40 mA. The data were integrated and corrected for absorption using an multiscan type

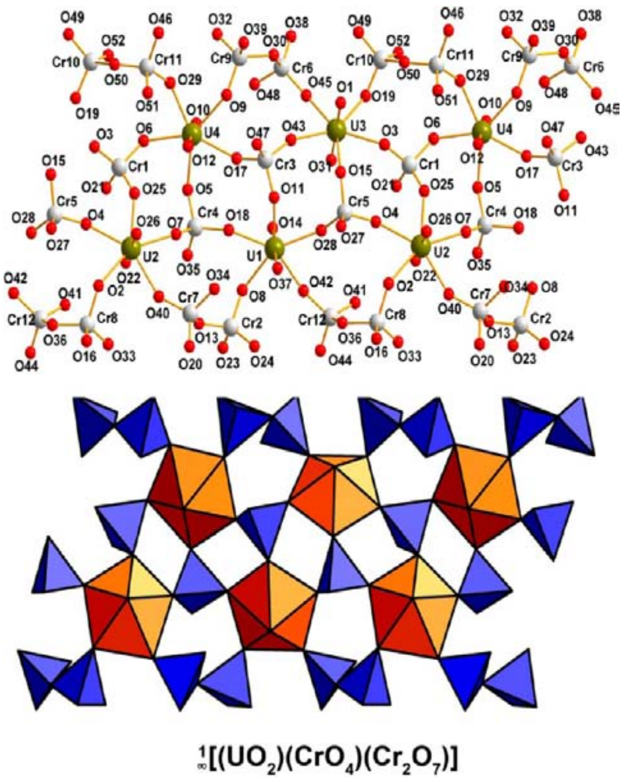

Figure 3. General projection of the $^{1}_{\infty}[(UO_2)(CrO_4)_2(Cr_2O_7)]^{2-}$ uranyl-chromate-dichromate chain observed in the structure of **3** (legend: NO_3 = green; UO_7, UO_8 = orange; CrO_4 = blue).

model using the Bruker programs APEX and SADABS. More than a hemisphere of X-ray diffraction data was collected for each crystal. Crystallographic information for all obtained phases is summarized in Table 1. Atomic coordinates and additional structural information are provided in the Supporting Information (CIF).

■ RESULTS AND DISCUSSION

Crystals of **1** formed at the high concentration of chromate ions and low pH of 1,4. In the structure of **1**, symmetrically independent U atom forms a uranyl cation $[UO_2]^{2+}$ coordinated in the equatorial plane by six O atoms. The two symmetrically independent NO_3 triangles share an edge with the UO_8 hexagonal bipyramid each, thus forming the $[UO_2(NO_3)_2O_2]^{4-}$ unit with distorted equatorial coordination of the uranyl ion, which have been reported in uranyl nitrates previously.[16] There are two Cr^{6+} positions tetrahedrally coordinated by four O atoms each. The Cr–O bonds in the CrO_4 tetrahedra are in the range 1.56–1.68 Å. The Cr(1)O4 and Cr(2)O4 tetrahedra share a common O atom to form a dichromate group, $[Cr_2O_7]^{2-}$. Two $[UO_2(NO_3)_2O_2]^{4-}$ units are linked via two $[Cr_2O_7]^{2-}$ dimers (Figure 1a) to form $^{0}_{\infty}[(UO_2)_2(Cr_2O_7)_2(NO_3)_4]^{4-}$ novel zero-dimensional (0D) units that have not been observed previously in inorganic compounds. The $^{0}_{\infty}[(UO_2)_2(Cr_2O_7)_2(NO_3)_4]^{4-}$ units are centrosymmetric. Their negative charge is compensated by the Cs^+ cations (Figure 2).

Crystals of **2** form under nearly the same pH 1,5 in the presence of 1-ethyl-3-methylimidazolium. As compared to **1**, formation of crystals of **2** requires more time, but they are more stable at ambient conditions. In contrast to the structure of **1**, uranyl ions in **2** are coordinated by five O atoms so that pentagonal bipyramids are formed. Equatorial U–O bond lengths in **2** range from 2.335(3) to 2.475(4) Å, with an average bond length of 2.38 Å. The UO_7 pemtagonal bipyramids share corners with $[Cr_2O_7]^{2-}$ groups, which results in the formation of $^{1}_{\infty}[(UO_2)(Cr_2O_7)_2(H_2O)]^{2-}$ chains running parallel to the *a* axis (Figure 1b). The cohesion between the chains in the *ab* plane is provided by hydrogen bonds emanating from the H_2O groups bonded to uranyl cations. The space between the chains is filled by protonated $C_6H_{11}N_2$ molecules (Figure 2). To improve the understanding of relation and evolution of structural topologies from the structure of **1** to **2**, we use their black and white nodal representations.[17] Within this approach, each black node represents a uranyl polyhedron, whereas each white node represents a CrO_4 tetrahedron. Nodes are connected if the corresponding polyhedra share at least one common vertex. The resulting black and white graphs represent the topologies of the interpolyhedral linkage within respective structural units. The topologies observed in the structures of **1** and **2** (Figure 2, up) are closely related, as they contain the same six-membered rings of two black (U) and four white (Cr) nodes as fundamental building blocks. These rings are isolated from each other in the structure of **1**, whereas they form chains in the structure of **2**. The transition from the graph of **1** to the graph of **2** can be simply achieved by sharing common black vertices. Both uranyl chromate structural units and their graphs found in the structures of **1** and **2** are novel and were not observed previously in inorganic compounds.[17] It may be speculated that the 0D six-membered rings (**1**) exist in crystallization chromate solutions as prenucleation building blocks and their condensation results in one-dimensional topology observed in the structure of **2**.

Crystals of **3** and **4** were obtained under pH 2.2 from the aqueous solution. It seems feasible that these experimental conditions are the key to obtain mixed chromate-dichromate uranyl compounds. In the crystal structures of **3** and **4**, each symmetrically independent U atom forms a uranyl cation $(UO_2)^{2+}$ coordinated in the equatorial plane by five O atoms. Each equatorial vertex of the UO_7 bipyramids is shared with either isolated CrO_4 tetrahedron or a Cr_2O_7 group. In the structure of **4**, there is an orientational disorder with the Cr(3) site split into the Cr(3A) and Cr(3B) sites. Except for this disorder, the uranyl-chromate-dichromate units are topologically identical in both compounds, and we restrict ourselves to the description of the structure of **3** only. There are 12 Cr sites in the structure of **3**. The Cr(1), Cr(3), Cr(4), and Cr(5) sites form isolated CrO_4 tetrahedra, whereas the Cr(2), Cr(6), Cr(7), Cr(8), Cr(9), Cr(10), Cr(11), and Cr(12) sites belong to dichromate groups, $[Cr_2O_7]^{2-}$. Each of isolated CrO_4 tetrahedra is 3-connected, sharing three of its four vertices with UO_7 bipyramids, thus forming $[UO_2(CrO_4)O_2]^{4-}$ chains previously observed in uranyl-chromates,[12d,i] -sulphates,[18] and -selenates.[19] The Cr_2O_7 dimers decorate the $[UO_2(CrO_4)O_2]^{4-}$ chain (Figure 3). The resulting $^{1}_{\infty}[(UO_2)(CrO_4)_2(Cr_2O_7)]^{2-}$ one-dimensional units are surrounded and linked into three-dimensional structure by Rb atoms (Figure 2).

The formation of crystals of **5** and **6** was observed under conditions (pH 2.4) similar to those used for the preparation of crystals of **3** and **4**. It is noteworthy that compound **5** crystallizes in the centrosymmetric space group *C*2/*c*, whereas **6** is noncentrosymmetric (space group *Cc*). The formation of noncentrosymmetric **6** is surprising because the majority of all known uranyl structures except for borates[20] are centrosymmetric. Analysis of the black and white graphs for structural units observed in the structures of **3**–**6** (Figure 2) reveals that compounds **3**,**4** and **5**,**6** are structurally related. The $^{1}_{\infty}[(UO_2)(CrO_4)_2(Cr_2O_7)]^{2-}$ chains observed in **3** and **4** fused together by sharing dichromate groups produced the $^{2}_{\infty}[(UO_2)(CrO_4)_2(Cr_2O_7)]^{2-}$ layers observed in **5** and **6**. Layers of

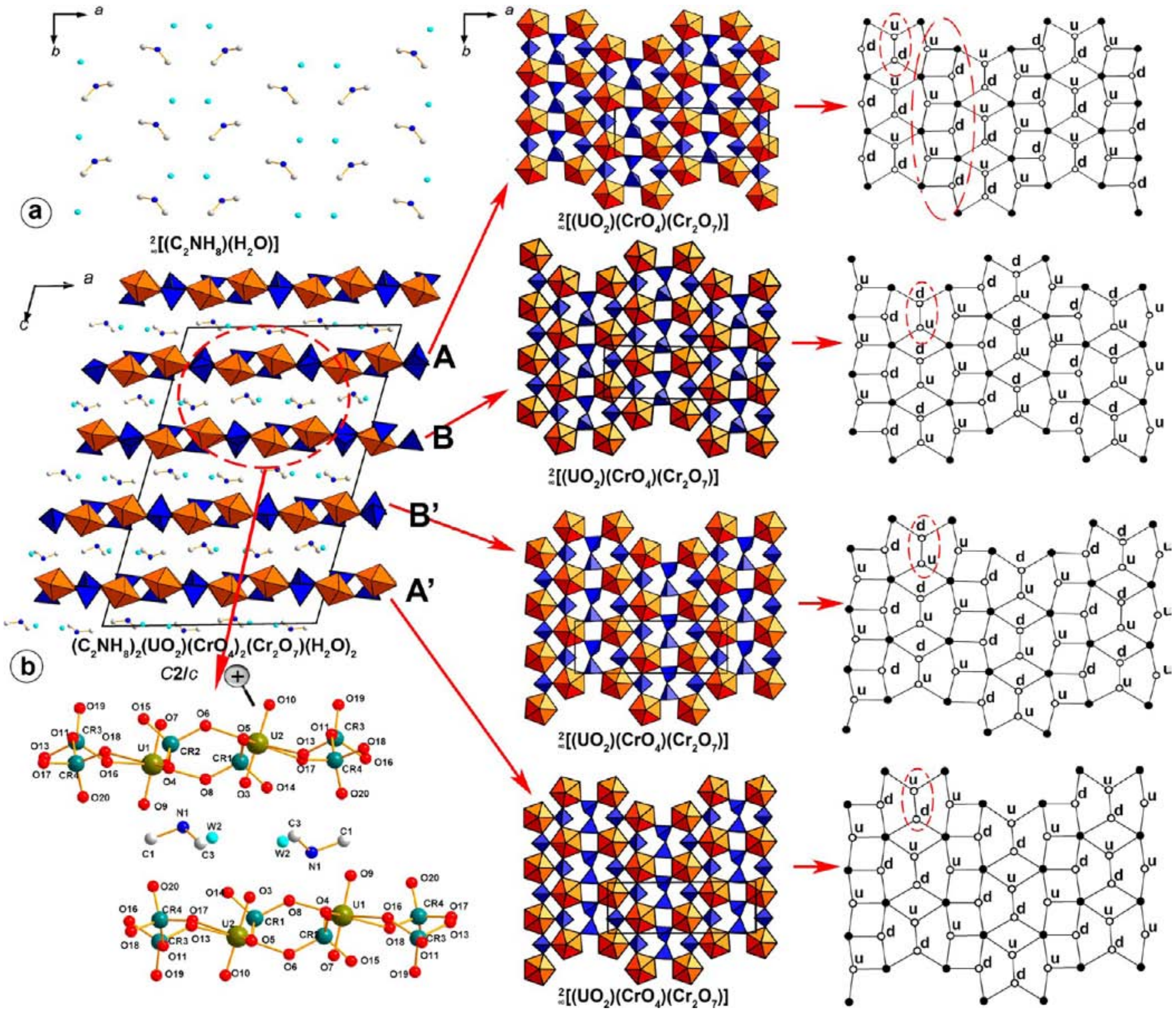

Figure 4. General projection of centrosymmetric (*C*2/*c*) crystal structure of **5** (b) and structure of ${}^{2}_{\infty}[(C_2NH_8)(H_2O)]^+$ organic interlayer (a) (legend as in Figure 1). Polyhedral representation of the ${}^{2}_{\infty}[(UO_2)(CrO_4)_2(Cr_2O_7)]^{2-}$ layers and their nodal representations with the u and d symbols written near the white and black vertices. The u and d symbols identify "up" and "down" orientations of the Cr−O$_t$ bonds in the CrO$_4$ tetrahedra.

this type are similar to those observed in uranyl polyarsenates,[21] but have never been described for uranyl oxysalts with T^{6+} (T = S, Cr, Se, Mo). Protonated dimethylamine (**5**), isopropylamine (**6**), and H_2O molecules are located in the interlayer, providing linkage of the adjacent layers through the system of hydrogen bonds with the shortest layer−interlayer N(1)···O(1), N(2)···O(5) contacts equal to 2.95(1), 3.02(1) Å, respectively, in the structure of **5** and N(1)···O(6), N(2)···O(19), N(3)···O(37), N(4)···O(9) contacts equal to 2.97(1), 2.95(1), 2.92(1), 3.11(1) Å, respectively, in the structure of **6**. Topological analysis of uranyl-chromate-dichromate units in the structures of **5** and **6** allows one to investigate the origin of chirality in **6** and to recognize topological similarities and differences between the ${}^{2}_{\infty}[(UO_2)(CrO_4)_2(Cr_2O_7)]^{2-}$ layers in the two structures. The orientations of the isolated CrO$_4$ tetrahedra alternate with the apex of the chromate tetrahedra pointing up and down within the ${}^{2}_{\infty}[(UO_2)(CrO_4)_2(Cr_2O_7)]^{2-}$ layers observed in the structure of **5**. Generally, the layers in **5** are positioned in such a way that hydrogen bonds are formed between the inorganic ${}^{2}_{\infty}[(UO_2)(CrO_4)_2(Cr_2O_7)]^{2-}$ and the ${}^{2}_{\infty}[(C_2NH_8)(H_2O)]^+$ organic sheets and fit in a somewhat expanded close-packed array. The pairs of layers designated as A, A′ and B, B′ have similar graphs with the same up−down orientations of the chromate tetrahedra (Figure 4). A and B as well as B′ and A′ are inverted relative to each other. Thus, the structure of **5** has the ...ABB′A′... stacking sequence of compositionally identical ${}^{2}_{\infty}[(UO_2)(CrO_4)_2(Cr_2O_7)]^{2-}$ layers. The orientation of isolated CrO$_4$ tetrahedra and the resulting sequence of the ${}^{2}_{\infty}[(UO_2)(CrO_4)_2(Cr_2O_7)]^{2-}$ layers in **6** is more complicated (Figure 5). The crystal structure of **6** is built up by stacking layers of identical composition, but with different mutual disposition of the layers as compared to the structure of **5**. Isolated tridentate CrO$_4$ tetrahedra are all in down orientation in layer A (Figure 5) and in up orientation in layer B, which means that the layers are chiral. A similar origin of chirality in uranyl oxysalts has already been described in the structures of layered uranyl selenates.[24] Note that the orientation of Cr$_2$O$_7$ is identical in both A and B layers. Figure 5 provides also the scheme of packing of the

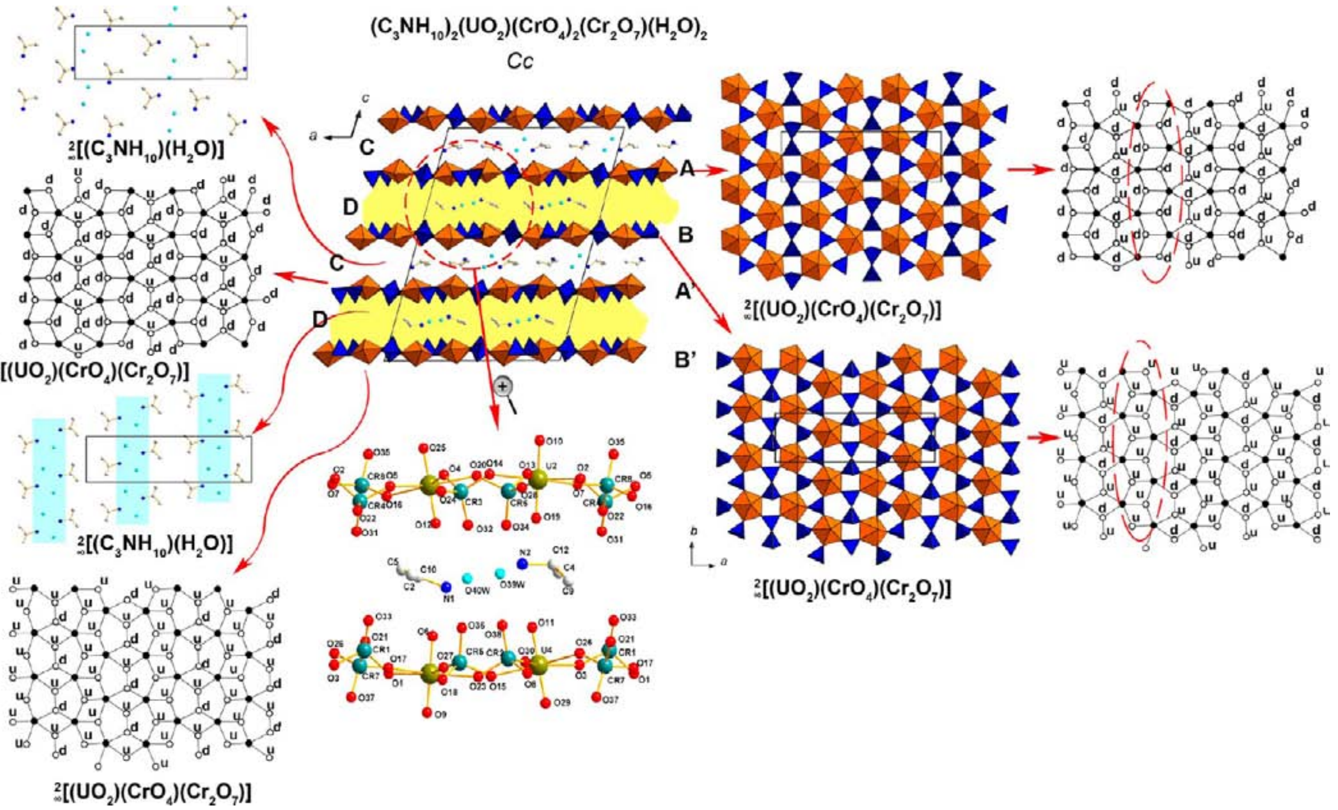

Figure 5. General projection of noncentrosymmetric (*Cc*) sandwich-like crystal structure of **6** and the C and D $^2_\infty[(C_3NH_{10})(H_2O)]^+$ organic interlayers (legend as in Figure 1). The D interlayer can be subdivided into hydrophobic and hydrophilic (highlighted by blue) zones. Polyhedral representation of the $^2_\infty[(UO_2)(CrO_4)_2(Cr_2O_7)]^{2-}$ layers and their nodal representation with the u and d symbols written near the white and black vertices in the structure of **6**. The ...dddd... and ...uuuu... sequences of isolated CrO_4 in A and B layers are highlighted by red dashed ovals. The sandwich consisting of two uranyl-chromate layers and one $[(C_3NH_{10})(H_2O)]$ organic-water interlayer is marked by yellow.

protonated isopropylamine molecules between uranyl chromate-dichromate layers. Because the aliphatic components of the isopropylamine molecules are hydrophobic, the packing can be subdivided into hydrophobic and hydrophilic (highlighted) zones in the D interlayers. The formation of hydrophilic zones in the C interlayer in **6** is not so pronounced and is not observed at all in the structure of **5**. The formation of a complex hydrogen-bonding system in hydrophilic regions in the D interlayer plays an essential role in the structural organization and consequent chirality of uranyl chromate layers and the whole structure of **6**. The nonshared vertices of isolated CrO_4 tetrahedra are oriented toward the arrangements of protonated isopropylamine and H_2O molecules. Generally, the structure of **6** can be described as sandwich-like similar to those observed in layered silicate minerals.[23] The sandwich in **6** consists (Figure 5) of two uranyl-chromate layers and one $[(C_3NH_{10})(H_2O)]$ organic-water interlayer. Hydrophilic–hydrophobic interactions are known already for their importance in structural chemistry of uranyl-selenates.[22,24]

■ CONCLUSION

Six different dichromate-based uranyl compounds were obtained. Their structures belong to four principally different but related structure types with different dimensionality of basic structural units. The units in the structures of **1** and **2** are unique, and these are the first "pure" uranyl-dichromates known to date. Compounds **3**–**6** are novel representatives of a rather small group of inorganic compounds containing both isolated CrO_4 tetrahedra and dichromate Cr_2O_7 groups.[25] The structures of **5** and **6** contain compositionally identical but topologically different $^2_\infty[(UO_2)(CrO_4)_2(Cr_2O_7)]^{2-}$ sheets (thus corresponding to different geometrical isomers[12e,f]), which have not been reported previously in inorganic compounds. The conformation geometries of the $[Cr_2O_7]^{2-}$ anions in **1**–**6** are different with the Cr–O–Cr angle varying in the range from 121.9° (in **1**) to 145.5° (in **3**).

All phases reported herein have been prepared with an excess of CrO_3. "Pure" dichromates are formed at pH < 1.5 and with prior hydrothermal treatment of uranyl-chromate solution, whereas mixed chromate-dichromates are formed at higher pH > 2 values. Further attempts of syntheses of uranyl chromates using CrO_3 may result in the fabrication of novel compounds with polymerized chromate ions. Decreasing pH of initial uranyl-chromate solution may lead to the formation of uranyl compounds with $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ anions, which has not been reported before.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

File of X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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