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Short communication

Host-guest structural architectures in hydrous alkaline (Li, K) uranyl chromates and dichromates

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Two new $(Cr_2O_7)^{2-}$ and/or $(CrO_4)^{2-}$ containing uranyl compounds with K and Li: $[K_{10}(Cr_2O_7)_2(H_2O)_2]|(UO_2)(CrO_4)_4|$ (**1**) and $|Li_2(H_2O)_5|[(UO_2)(CrO_4)_2]$ (**2**) were obtained via two various synthesis routes in the $K_2Cr_2O_7$–CrO_3–$(UO_2)(NO_3)_2{\cdot}6H_2O$–$H_2O$ (**1**) and LiCl–CrO_3–$(UO_2)(NO_3)_2{\cdot}6H_2O$ (**2**) systems. The key feature of the crystal structure of **1** is the formation of hydrous potassium dichromate $[K_{10}(Cr_2O_7)_2(H_2O)_2]^{6+}$ 2*D* units acting as hosts for guest $|(UO_2)(CrO_4)_4|^{6-}$ clusters. $(Cr_2O_7)^{2-}$ groups are not bonded via common oxygen atoms to $(UO_2)^{2+}$ in **1** which is the first example of such structural architecture in uranyl oxysalts with tetrahedral TO_4 ($T = Si^{4+}, As^{5+}, P^{5+}, Cr^{6+}$, etc.) anions. In the structure of **2**, UrO_5 and CrO_4 coordination polyhedra share corners to produce $[(UO_2)(CrO_4)_2]^{2-}$ layers with $|Li_2(H_2O)_5|^{2+}$ tetramers guest species in the interlayer.

Designing a uranium immobilization strategy in various types of media and solid-state phases that can accommodate diverse waste types is important from both environmental and technological point of views. Alkali metals represent significant constituent of spent nuclear fuel (SNF) [1,2]. These metals are present in SNF in concentrations high enough to form independent phases. Knowledge of the structures of these compounds is essential for understanding their behavior in a wide range of environmental and technological processes. Strong oxidant $K_2Cr_2O_7$ was used in the REDOX process to manipulate the valence states of actinides [3] and as an effective corrosion inhibitor for magnesium alloys used in some SNF rod arrays [4]. LiCl taken as one of starting reagents in described below synthesis is used in electrorefining processes of SNF [5,6]. The crystal chemistry of uranyl compounds with tetrahedral TO_4 ($T = Si^{4+}, P^{5+}, S^{6+}, Cr^{6+}, As^{5+}, Se^{6+}, Mo^{6+}, V^{5+}$, etc.) oxoanions is mainly dominated by two-dimensional (2*D*) or one-dimensional (1*D*) structural motifs resulting from the strong directional anisotropy of bond distribution observed in $(UO_2)^{2+}$ coordination geometries [7,8]. The diversity of 0*D* and 3*D* structural architectures are much scarcer. Note, TO_4 tetrahedral groups nearly always share common corners or edges with UO_n ($n = 6,7,8$) bipyramids to form different $[(UO_2)_n(TO_4)_m]^x$ units in uranyl oxysalts. $T^{6+}O_4$ units outside of structural entities with uranyl are unknown for chromates and molybdates but few were described for selenates and sulfates and are limited to electroneutral acidic groups of H_2SeO_4 [9,10] or H_2SO_4 [11].

Here we report on the syntheses, structures and properties of two Cr_2O_7 and/or CrO_4 containing uranyl compounds with K and Li: $[K_{10}(Cr_2O_7)_2(H_2O)_2]|(UO_2)(CrO_4)_4|$ (**1**) and $|Li_2(H_2O)_5|[(UO_2)(CrO_4)_2]$ (**2**) obtained via two various synthesis routes in the $K_2Cr_2O_7$–CrO_3–$(UO_2)(NO_3)_2{\cdot}6H_2O$–$H_2O$ (**1**) and LiCl–CrO_3–$(UO_2)(NO_3)_2{\cdot}6H_2O$ (**2**) systems [12,13]. The structural architecture of **1** is unknown, whereas general organization of uranyl–chromate and alkaline units in **2** is frequently observed in uranyl oxysalts.

The structure of **1** is triclinic ($P\bar{1}$) and contains one independent U^{6+} cation (Fig. 1a), which is bonded to two O atoms, forming $(UO_2)^{2+}$ uranyl ions (*Ur*) with two symmetrically equivalent U–O_{Ur} bond lengths of 1.82 Å. The uranyl ion is coordinated by four O atoms arranged at the equatorial vertices of UrO_4 tetragonal bipyramids. The $<$U–$O_{eq}>$ (*eq*: equatorial) bond lengths range from 2.23 to 2.25 Å. There are four symmetrically independent Cr^{6+} cations in **1**, which are tetrahedrally coordinated by four O atoms each. Each equatorial vertex of the UrO_4 bipyramids is shared with isolated $Cr(1)O_4$ or $Cr(2)O_4$ tetrahedron thus forming $|(UO_2)(CrO_4)_4|^{6-}$ 0*D* units or isles. The Cr–O bonds sharing common oxygen atoms with UrO_4 are elongated. The $Cr(3)O_4$ and $Cr(4)O_4$ tetrahedra share a common O atom to form a dichromate $(Cr_2O_7)^{2-}$ group. The structure of **1** contains five independent K sites forming the following irregular polyhedra: $K(1)O_8(H_2O)$, $K(2)O_8$, $K(3)O_8$, $K(4)O_7$, $K(5)O_6$. All of K–O bond $<$3.55 Å were taken into consideration. K-centered polyhedra share common oxygen atoms with $(Cr_2O_7)^{2-}$ groups to form $[K_{10}(Cr_2O_7)_2(H_2O)_2]^{6+}$ layers (Fig. 2a) with voids in the interlayer. $|(UO_2)(CrO_4)_4|^{6-}$ isolated 0*D* units are embedded into these cavities in between of hydrous potassium dichromate layers.

U(1) atom is coordinated by five oxygen atoms in equatorial plane thus forming UrO_5 pentagonal bipyramids in monoclinic ($P2_1/n$) structure of **2**. The two uranyl oxygen atoms occupy the axial positions

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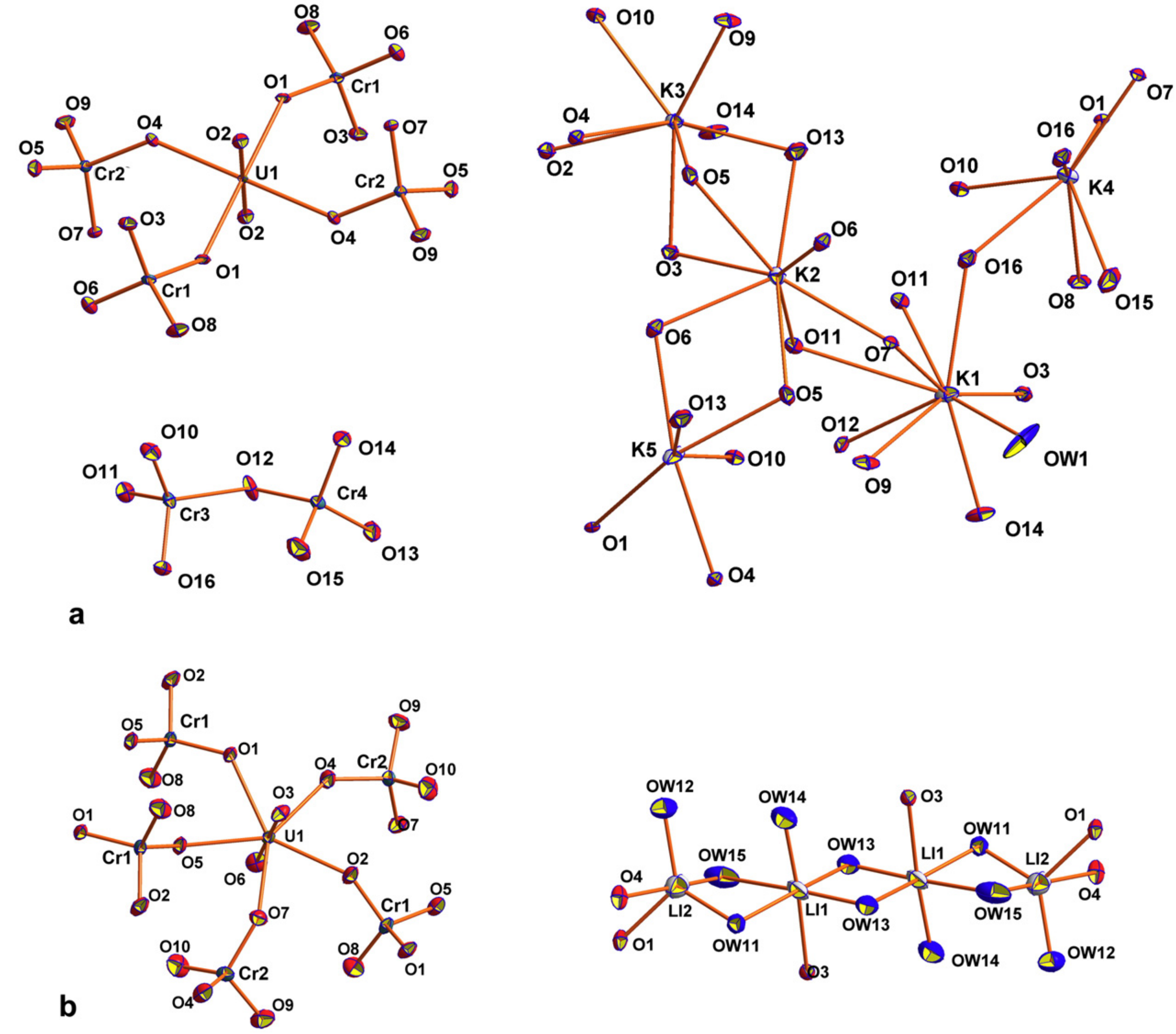

Fig. 1. General projection of cations coordination environments in the structures of **1** (a) and **2** (b). For K atoms all of K–O bonds ≤3.5 Å are shown.

(Fig. 1b). In the structure of **2**, UrO_5 and CrO_4 coordination polyhedra share corners to produce 2-dimensional layers with the chemical composition of $[(UO_2)(CrO_4)_2]^{2-}$. $Cr(1)O_4$ tetrahedra share three corners with adjacent uranyl polyhedra, whereas $Cr(2)O_4$ — only two (Fig. 2b).

The Cr–O_{br} (O_{br} = O atom bridging between U and Cr polyhedra) bonds are longer (1.64–1.70 Å) than the Cr–O_t bonds (1.59–1.61 Å; O_t = terminal O atom in a chromate group). Topologically similar layers were previously described in a number of uranyl–molybdates [16], — selenates [17] and.

$Tl_2(UO_2)(CrO_4)_2$ [16]. Li(1) atom is coordinated by five water molecules and one oxygen atom, whereas Li(2) is coordinated by three H_2O and two O atoms. Structural architecture of **2** is typical for uranyl oxysalts. $|Li_2(H_2O)_5|^{2+}$ tetramers guest species are packed in the interlayer of $[(UO_2)(CrO_4)_2]^{2-}$ 2*D* units and compensate for its negative charge (Fig. 2a). The linkages between the interlayer $|Li_2(H_2O)_5|^{2+}$ species and uranyl chromate sheets are provided through H bonds associated with H_2O and additional Li–O bonds. There is only one Li uranyl chromate reported to date [18]. It is based on topologically different $[(UO_2)_2(CrO_4)_3]^{2-}$ layers containing dimers of two UrO_5 bipyramids sharing common edge.

Despite the difference in number of symmetrically independent K atoms, hydrous potassium dichromate $[K_{10}(Cr_2O_7)_2(H_2O)_2]^{6+}$ layers in **1** are similar to those described previously in triclinic α-$K_2Cr_2O_7$ [19] and β-$K_2Cr_2O_7$ [20]. However packings of $(Cr_2O_7)^{2-}$ groups in these crystal structures demonstrate some considerable differences. $(Cr_2O_7)^{2-}$ groups are parallel shifted and face toward one to each other in all dichromate structures shown in Fig. 3. The shortest distances between CrO_4 tetrahedra in $(Cr_2O_7)^{2-}$ are about 3.4 Å in α-$K_2Cr_2O_7$ and β-$K_2Cr_2O_7$. However pairs of $(Cr_2O_7)^{2-}$ are moved apart with the significant distance increase to 5.0 Å in the structure of **1**. This enlargement of distance is the result of incorporation of $|(UO_2)(CrO_4)_4|^{6-}$ clusters into the $K_2Cr_2O_7$ matrix that induces modification of the latter.

In conclusion, we reported on two chromate and chromate–dichromate compounds with U^{6+} and alkali metals (Li, K). The key feature of the crystal structure of **1** is the formation of hydrous potassium dichromate $[K_{10}(Cr_2O_7)_2(H_2O)_2]^{6+}$ 2*D* units acting as hosts for guest uranyl-chromate clusters. Recently reported uranyl–dichromates [21,22], — diarsenates [23], — diphosphates [24] and –disilicates [25] demonstrate T_2O_7 ($T = Cr^{6+}, As^{5+}, P^{5+}, Si^{4+}$) bitetrahedral units strongly bonded to uranyl. In this sense structural organization of **1** is unique. **1** provides also additional knowledge about phase formation in chromate containing solutions with hexavalent uranium at low pH. In contrast, the structure of **2** has a common type of structural architecture observed in majority of known uranyl oxysalts with alkali metals and water in between negatively charged $[(UO_2)_n(TO_4)_m]^x$. Preparation of **2** from lithium chloride may be of interest in the frame of nuclear fuel treatment by pyrochemical processes.