

ELECTRONIC SUPPLEMENTARY INFORMATION

Halogen bonding in uranyl and neptunyl trichloroacetates with alkali metals and improved crystal chemical formulae for coordination compounds

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DESCRIPTION OF CRYSTAL STRUCTURES

Crystal structure of $\text{K}_2\text{UO}_2(\text{tca})_4(\text{tcaH})_2$ (I). All atoms in I (space group $P2_1/c$, $Z' = 1$) occupy general positions. The single independent uranium atom realizes the most common coordination number of 7. The uranyl ion coordinates five oxygen atoms of four trichloroacetate ions in the equatorial plane (Fig. S1 top). In relation to the U atom (disregarding the coordination of K atoms), three crystallographically independent trichloroacetate ions in I show monodentate coordination mode M^1 , and the fourth is bidentate of mode B^{01} . The designations of coordination modes hereinafter follow the notation provided in ref. ¹. The counterions for the $[\text{UO}_2(\text{tca})_4]^{2-}$ complexes (Fig. S1 top) are potassium ions. Both independent potassium atoms form centrosymmetric dimers with short K...K distances ($d = 3.72$ and 4.00 Å for K1...K1 and K2...K2, respectively, Fig. S1 middle, bottom). For comparison, in the structure of metallic potassium, $d(\text{K}...\text{K}) = 4.54$ Å.² K1 atoms are bound into dimers due to four trichloroacetic acid molecules, while pairs of K2 atoms form dimers due to four trichloroacetate ions (Fig. S1 middle, bottom).

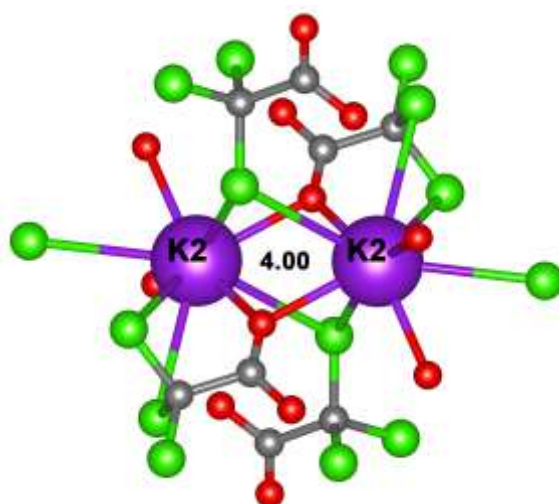
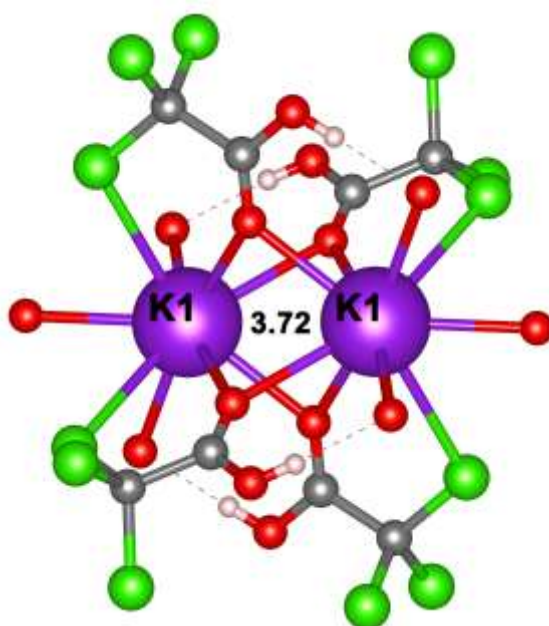
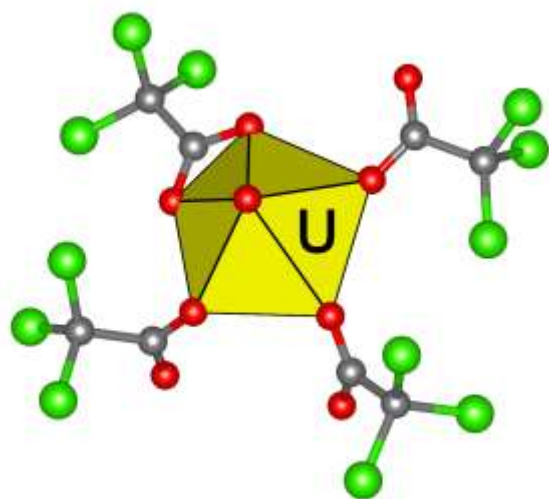


Fig. S1. Fragments of crystal structure of $K_2UO_2(tca)_4(tcaH)_2$ (I). Hereinafter U, Np, K, Rb, Cs, O, Cl, Br, I, C and H atoms/coordination polyhedra are depicted with yellow, charcoal, purple, cerise, spring green, red, green, brown, dark purple, grey and pink colors respectively.

Both independent molecules of trichloroacetic acid are coordinated only to K1 atoms showing the B^{11-5} coordination mode. This mode implies coordination through one oxygen atom of the carboxylate group and one Cl atom (Fig. S1 middle). Due to the bridging function of carboxylate ligands, the $[\text{UO}_2(\text{tca})_4]^{2-}$ complexes and potassium-containing dimers are packed into 2D layers parallel to the (001) plane with the composition of $\text{K}_2\text{UO}_2(\text{tca})_4(\text{tcaH})_2$. The distance between adjacent layers corresponds to $c/2$ and is equal to ca. 12.06 Å. Neighboring layers are interconnected by XB's (see article text) and other van der Waals interactions. Such a layered structure of crystals is easily detected experimentally – the crystals of I show perfect cleavage along the (001) plane: stacks of very thin layers easily separate by cutting the crystals.

Crystal structures of $\text{K}_4\text{NpO}_2(\text{tca})_6(\text{tcaH})(\text{H}_2\text{O})_3$ (II) and $\text{Rb}_4\text{UO}_2(\text{tca})_6(\text{tcaH})(\text{H}_2\text{O})_3$ (III). Compounds II and III are isostructural (space group $P2_1/n$, $Z' = 1$) with all atoms occupying general positions. Actinide atoms An (An = U or Np) form almost linear dioxocations AnO_2^{2+} . Uranyl and neptunyl ions in the equatorial plane coordinate the oxygen atoms of five monodentate trichloroacetate ions, forming the $[\text{AnO}_2(\text{tca})_5]^{3-}$ mononuclear complexes (Fig. S2 top). The counter ions for such complexes are four independent potassium (in II) or rubidium (in III) ions. Potassium and rubidium atoms in pairs form non-centrosymmetric dimers with short distances between metal atoms ($d = 3.94$ and 3.87 Å for K1...K3 and K2...K4 and $d = 4.07$ and 3.99 Å for Rb1...Rb3 and Rb2...Rb4, respectively, Fig. S2 middle, bottom). For comparison, the K...K and Rb...Rb distances in the structures of the corresponding metals are ca. 4.54 and 4.85 Å.² The K1 and K3 atoms (as well as Rb1 and Rb3) are linked into dimers by one trichloroacetate ion, one trichloroacetic acid molecule and one water molecule, while K2 and K4 atoms (as well as Rb2 and Rb4) form dimers due to three trichloroacetate ions (Fig. S2 middle, bottom). In addition, the atoms K3, K4, Rb3 and Rb4 coordinate one terminal water molecule each.

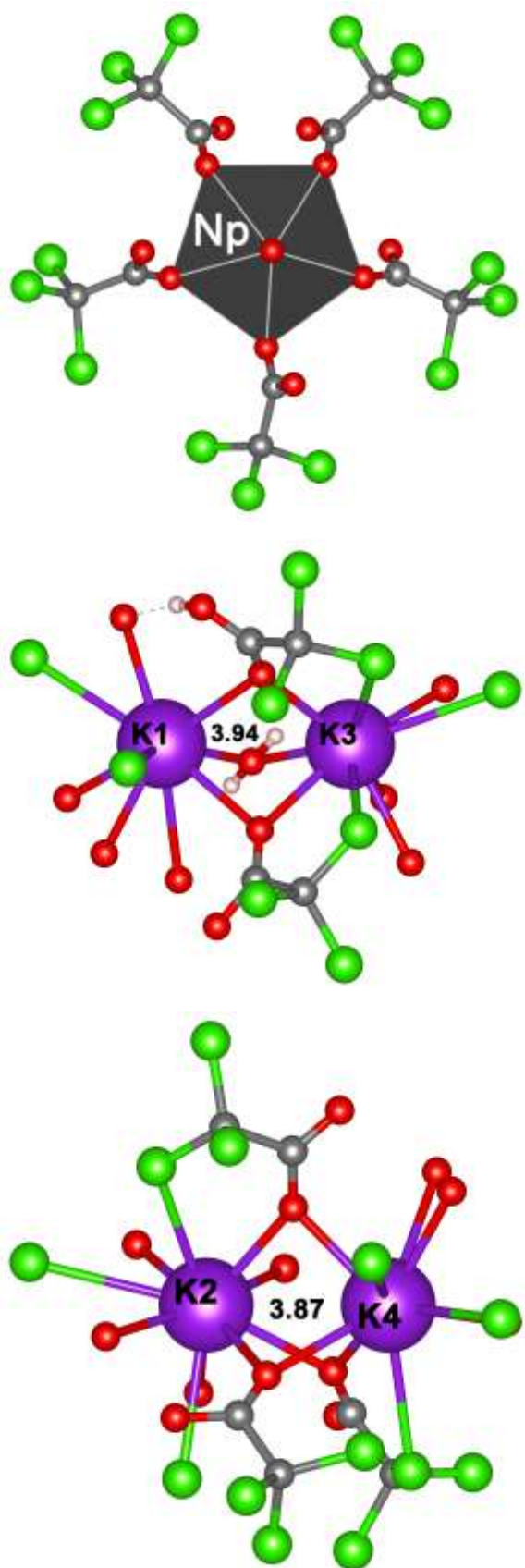


Fig. S2. Fragments of crystal structure of $\text{K}_4\text{NpO}_2(\text{tca})_6(\text{tcaH})(\text{H}_2\text{O})_3$ (II). Similar pictures correspond to the isostructural compound $\text{Rb}_4\text{UO}_2(\text{tca})_6(\text{tcaH})(\text{H}_2\text{O})_3$ (III).

In structures of II and III, five crystallographically independent trichloroacetate ions, which are bound to An atoms, realize the M^1 coordination mode in respect to An atoms (given in disregard of coordination to K and Rb atoms), while the sixth trichloroacetate ion is coordinated only by alkali metal atoms with coordination mode $T^{21}-5$, i.e. with the participation of O and Cl atoms. The single trichloroacetic acid molecule in II and III is also linked to K or Rb by the O and Cl atoms according to the coordination mode $Q^{12}-55$. Due to the bridging function of the carboxylate ligands in structures of II and III, the AnO_2^{2+} and R^+ ions ($R = K$ or Rb) are bound into 1D chains propagating along the $[001]$ direction (Fig. S3). Such chains are interconnected by trichloroacetate groups, XB's (see article text) and other van der Waals interactions and form quasi-hexagonal 3D frameworks (Fig. S3).

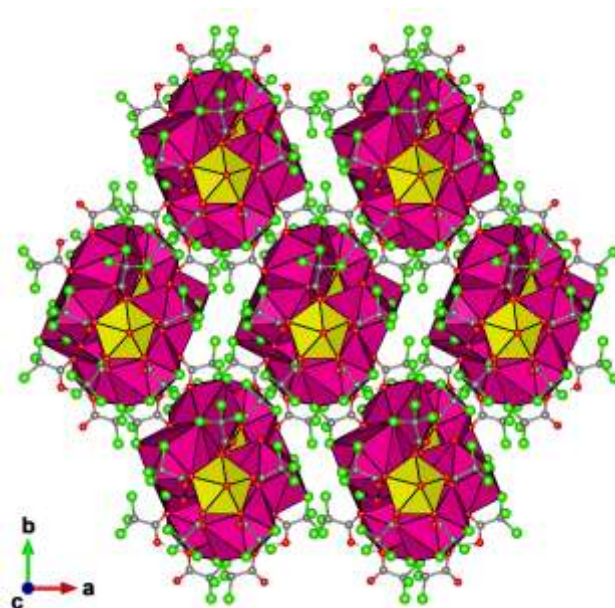


Fig. S3. Fragment of crystal structure of $Rb_4UO_2(tca)_6(tcaH)(H_2O)_3$ (III) in the projection along the c axis.

Crystal structure of $Cs_3UO_2(tca)_5(tcaH)_2 \cdot H_2O$ (IV). In the structure of IV (space group $P2_12_12_1$, $Z' = 1$) all atoms occupy general positions. The single independent uranyl ion in the equatorial plane coordinates oxygen atoms of five monodenate trichloroacetate ions and forms $[UO_2(tca)_5]^{3-}$ mononuclear complexes (Fig. S4 top). Three crystallographically independent cesium atoms act as

counterions. In contrast to I–III, in IV the cesium atoms form trimers with short distances between cesium atoms ($d = 4.59, 4.68$ and 5.69 Å, Fig. S4 bottom). Note that in the structure of metallic cesium $d(\text{Cs}\dots\text{Cs})$ is equal to ca. 5.25 Å.² Cs atoms are linked into trimers due to bridging trichloroacetate ions and oxygen atoms of the uranyl ion (Fig. S4 bottom). The Cs1 and Cs2 atoms also coordinate two independent trichloroacetic acid molecules (Fig. S4 bottom). In addition, the structure of IV contains one molecule of crystallization water.

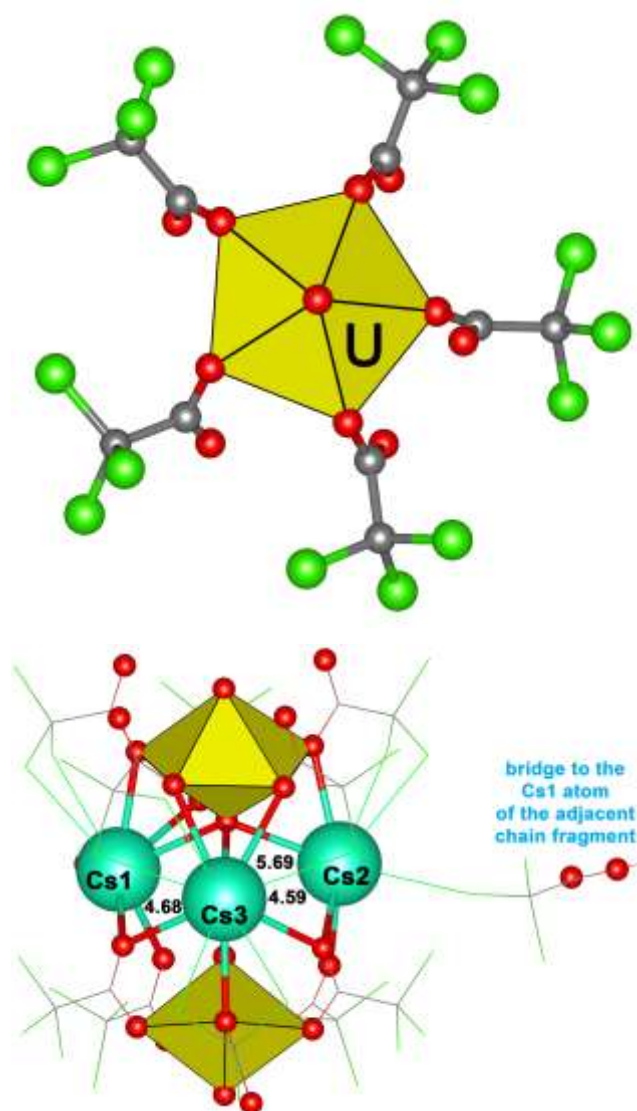


Fig. S4. Fragments of crystal structure of $\text{Cs}_3\text{UO}_2(\text{tca})_5(\text{tcaH})_2 \cdot \text{H}_2\text{O}$ (IV).

In relation to the uranyl ion, all five independent trichloroacetate ions in the structure of IV realize coordination mode M^1 (provided in disregard of coordination to Cs atoms). Both molecules of trichloroacetic acid in IV are coordinated only by

Cs atoms, while one of the molecules implements the M^1 coordination mode and is terminal, and the second molecule implements the B^2 coordination mode (coordination via one O atom and one Cl atom) and is bridging between the Cs1 and Cs2 atoms. Due to the bridging function of the ligands, the uranyl ions and cesium cations are linked into a three-dimensional framework. As in the case of compounds II and III, in the structure of IV, 1D chain fragments propagating along the [010] direction can be distinguished (Fig. S5). Neighboring chain fragments form a quasi-hexagonal packing in the structure of IV (Fig. S5) and are interconnected by the single trichloroacetic acid molecule (the one that bridges the Cs1 and Cs2 atoms, Fig. S4 bottom), as well as XB's (see article text) and other types of van der Waals interactions.

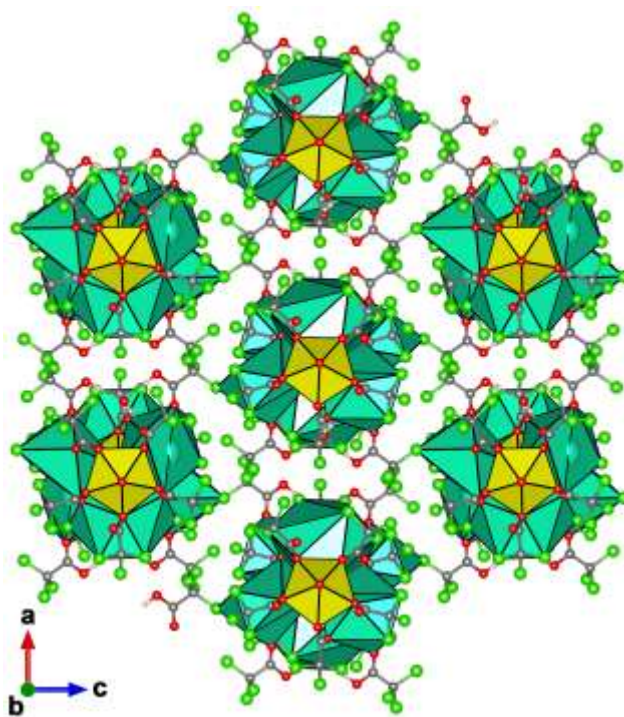


Fig. S5. Fragment of crystal structure of $\text{Cs}_3\text{UO}_2(\text{tca})_5(\text{tcaH})_2 \cdot \text{H}_2\text{O}$ (IV) in the projection along the b axis.

Crystal structure discussion. All four compounds I–IV feature actinyl-cation interactions between the oxygen atoms of actinyl ions and K, Rb, or Cs atoms (Fig. S6).^{3,4} It should be noted that actinyl-cation interactions are most often observed in cesium-containing compounds of uranyl ions with anions of aliphatic

monocarboxylic acids, whereas potassium and rubidium cations most often do not form such interactions.⁵⁻⁹ In the structures of compounds II and III, bifurcate actinyl-cation interactions are observed, and in the structure of compound IV, there are trifurcate actinyl-cation interactions (Fig. S6).

In crystals of compound IV, the uranyl ion is tilted in respect to its equatorial plane (the angle between the line passing through the O atoms of the uranyl ion and the average equatorial plane of the uranyl ion is equal to 85.4°). This case is similar to that described in ref. ¹⁰ for two uranyl maleate complexes, where the corresponding angles were 84.8 and 84.6° . However, if in those maleate complexes the cause of such a distortion was the repulsion of the O atoms of the uranyl ion from the O atoms of the carboxylate groups, then in the case of compound IV, apparently, on the contrary, two O atoms of the uranyl ion attract to Cs3 cations in opposite directions (Fig. S6 bottom).

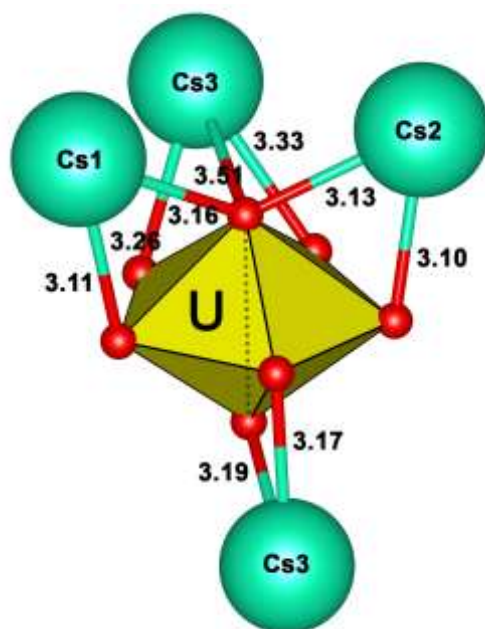
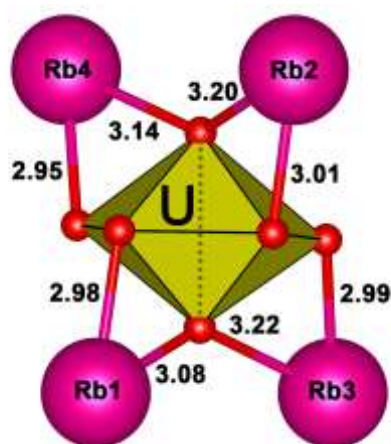
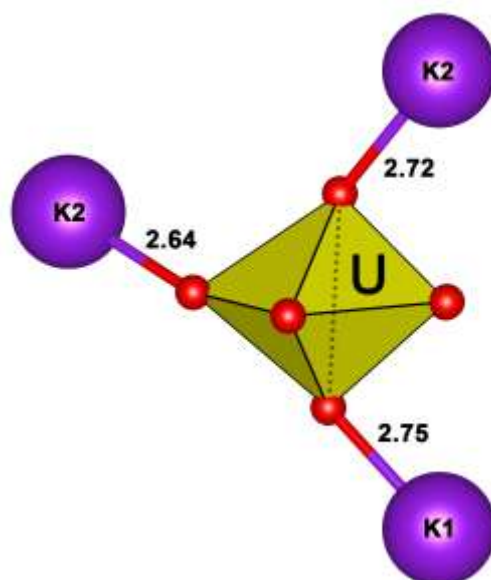


Fig. S6. Mono-, bi- and trifurcate actinyl-cation interactions and coordination polyhedra of actinides in crystal structures of I (top), III (middle), and IV (bottom). Orientation of uranyl ions is indicated with dotted lines. Similar middle picture corresponds to the isostructural compound II.

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