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Structure Determination of Neptunium(VI) μ_3-Hydroxobenzoate, $[(NpO_2)_2(\mu_3\text{-}OH)_2(H_5C_6COO)_2]\cdot 2H_2O$

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Neptunium(VI) benzoate with μ_3-OH$^-$ has been isolated and studied by the X-ray method. The main structural motive in the crystal is corrugated ribbons $[(NpO_2)_2(\mu_3\text{-}OH)_2(C_7H_5O_2)_2]_n$ extended along the *c* axes in which three neptunium pentagonal bipyramids are linked through the μ_3-OH$^-$ ligand. The benzoate ions are arranged at both sides of the ribbons, and each anion binds two adjacent NpO_2. The water molecules are arranged in the channels along the *c* axis.

Carboxylates of the transuranium elements (TRU) in higher oxidation states (V and VI) have very interesting and various structures. However, literature data on the benzoate compounds of TRU are rather restricted. They are represented only by the data on the synthesis, structure, and selected properties of simple neptunium(V) benzoates[1] and complex actinide(V) benzoates with N-containing molecular ligands with the general composition $[AnO_2(Bipy)(C_7H_5O_2)]_2$ (An = Np^V and Pu^V),[2] $[NpO_2(Bipy)(C_7H_4FO_2)]_2$, and $[NpO_2(Phen)(C_7H_5O_2)]_2$,[3] where Bipy is bipyridine and Phen is phenanthroline. Interesting systems with the mutual coordination of AnO_2^+ ions (cation−cation interaction), including that with the formation of the dimeric ions $[AnO_2^+]_2$, which have been found for the first time in the structure of neptunium(V) mellitate,[4] were observed in the compounds with Bipy and Phen.

We failed to find any data on the structure of benzoates of hexavalent TRU. The only exception is the neptunium(VI) compound $K_{11}(NpO_2)_{23}(C_7H_5O_2)_{57}(H_2O)_{18+x}$,[5] which has only recently been studied by X-ray diffractometry and shown to be isostructural to the uranium(VI) compound.

It should be mentioned that uranium(VI) benzoates were widely studied. Several works have been published on the synthesis, structures, and properties of simple,[6] binary (with Na^+ and NH_4^+ ions),[7] and mixed-ligand[8] uranium(VI) benzoates. At the same time, the preparation conditions, composition, and structures of the compounds of uranium(VI) and hexavalent TRU are often different.[9] Therefore, we decided to study the synthesis and crystal structures of simple neptunium(VI) benzoates and complex neptunium(VI) benzoates with alkali cations in the outer sphere. Neptunium(VI) hydroxobenzoate $[(NpO_2)_2(\mu_3\text{-}OH)_2(C_7H_5O_2)_2]\cdot 2H_2O$ (**1**) was prepared and structurally studied. In this compound, unique for TRU, each hydroxyl ion is simultaneously coordinated to three NpO_2^{2+} cations.

In the present time, there are several works on the crystal structures of the uranium(VI) compounds with OH$^-$ common for three UO_2^{2+} cations.[10−14] In this report, we considered in detail the crystal structure of **1** and compared its characteristics with those of the uranium(VI) compounds with a μ_3-OH$^-$ ligand.

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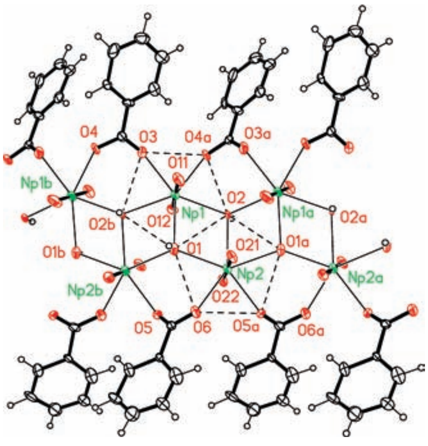

Figure 1. Ribbon $[(NpO_2)_2(\mu_3\text{-}OH)_2(C_7H_5O_2)_2]_n$ (30% ellipsoids). Selected interatomic distances (Å): Np1=O11 1.765(11), Np1=O12 1.734(13), Np1−O1 2.461(15), Np1−O2 2.363(12), Np1−O2b 2.388(12), Np1−O3 2.350(12), Np1−O4a 2.418(11), Np2=O21 1.722(14), Np2=O22 1.716(14), Np2−O1 2.355(13), Np2−O1a 2.437(14), Np2−O2 2.408(12), Np2−O5a 2.323(12), Np2−O6 2.396(12), Np1···Np2 3.901(1), Np1···Np2b 3.836(1), Np2···Np2a 4.366(1). Symmetry operations: a, $1 - y$, $1 - x$, $z - {}^1/_2$; b, $1 - y$, $1 - x$, $z + {}^1/_2$.

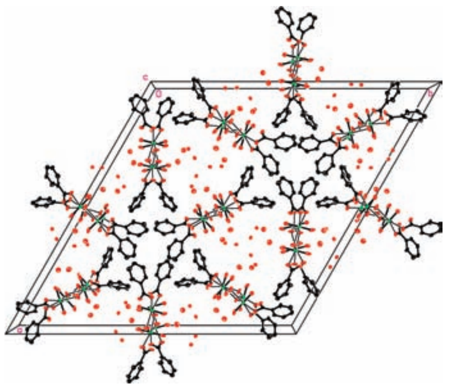

Figure 2. View of the crystal packing in **1**.

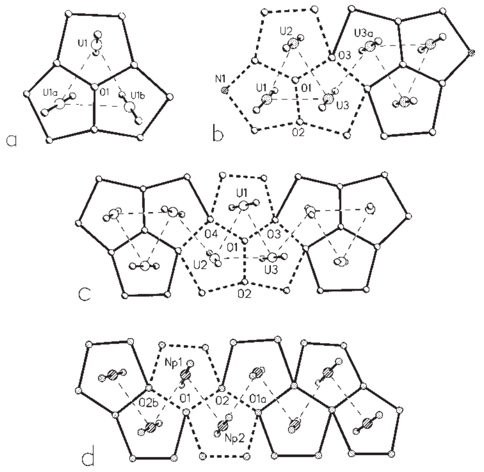

Figure 3. Types of the uranium(VI) and neptunium(VI) complexes with the μ_3-OH$^-$ ligand: (a) **2**; (b) **3**; (c) **4**; (d) **1**. The repeated fragment is shown by the dashed lines.

Single crystals of **1** were isolated,[15] and one of them was chosen for X-ray diffraction studies.[16] Compound **1** is unstable and transformed into light-brown prismatic crystals upon storage for 2 days under the mother liquor layer. The crystals turned out to be identical with the above-mentioned salt $K_{11}(NpO_2)_{23}(C_7H_5O_2)_{57}(H_2O)_{18+x}$.

Structure **1** contains two crystallographically independent Np1 and Np2 atoms with the coordination environment in the shape of distorted pentagonal bipyramids (Figure 1). The equatorial plane of each bipyramid contains two O atoms of two benzoate ions and three OH$^-$ ions, and each OH$^-$ is common for three neptunium bipyramids. A considerable scattering in the Np−O bond lengths in the equatorial plane of the bipyramids should be mentioned. The Np−μ_3-O bonds with a μ_3-hydroxyl differ in the Np1 and Np2 bipyramids by ~0.1 and ~0.08 Å, respectively. The Np−O$_{\text{benzoate}}$ bonds differ by 0.07 Å. The O atoms of the μ_3-OH$^-$ ligand deviate strongly from the plane of three Np atoms: O1 deviates from the Np1−Np2−Np2b plane by −0.58(2) Å, and O2 deviates from the Np1−Np1a−Np2 plane by +0.44(2) Å. The benzoate ions are located as shown in Figure 1, and each anion links two adjacent NpO_2^{2+} cations. As a result, infinite electroneutral ribbons $[(NpO_2)_2(\mu_3\text{-}OH)_2(C_7H_5O_2)_2]_n$ extending along the *c* axes are formed in the crystal. The water molecules are located in the channel-type cavities along the *c* axis (Figure 2).

Unlike rather numerous and various uranium(VI) complexes with the μ_3-O^{2-} ligand (see the Supporting Information), only several structures with the OH$^-$ common for three UO_2^{2+} are known. The environment of the uranyl groups in such complexes is shown in Figure 3.

In the complex compound $[(UO_2)_3(\mu_3\text{-}OH)(C_2H_6OS)_3(C_{198}H_{247}O_{18})]\cdot(C_2H_3N)_{11}(H_2O)_6$ (**2**),[10] three pentagonal bipyramids of uranium form a trimer (Figure 3a). The O1 atom of the μ_3-OH$^-$ ligand deviates from the plane formed by three U atoms by 0.65 Å, and the average U−μ_3-O bond length is 2.41 Å. The U···U interatomic distance is 4.020 Å.

The compounds $[(UO_2)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}OH)(C_7H_3NO_4)(H_2O)_2]_n\cdot nH_2O$ (**3**),[11] $[(UO_2)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)_2(C_7H_4NO_4)(C_7H_3NO_4)_{0.5}]_n$ (**4**),[11] $[C_6H_{13}N_2][(UO_2)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)(CHO_2)_2]\cdot 4H_2O$ (**5**),[12] $[H_3O][(UO_2)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)_3(C_6H_4NO_2)_2]$ (**6**)[13] and $K[(UO_2)_3(\mu_3\text{-}OH)_3(\mu_2\text{-}O)(C_7H_4NO_4)_2]\cdot H_2O$ (**7**)[14] contain both ligands: μ_3-O^{2-} and μ_3-OH$^-$. Compound **3** is based on two trimers joined through one equatorial edge into the electroneutral hexameric complex (Figure 3b).

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[15] ***Caution!*** *Np-237 is a high-specific-activity, α-emitting radionuclide. The use of radioactive materials is subject to statutory controls.* Np was prepurified by the anion-exchange method and precipitation of $Np(C_2O_4)_2\cdot 6H_2O$, which was calcined to NpO_2. The initial 0.145 M $NpO_2(NO_3)_2$ (pH ~5) solution was prepared by the heating of NpO_2 with concentrated HNO_3, followed by the careful evaporation of the solution to dryness and dissolution of the residue in water. The $NpO_2(NO_3)_2$ solution was placed in a tube, and a 10-fold volume of water and 0.2 M $KC_7H_5O_2$ were added to neptunium(VI) in a molar ratio of 2:1. The amorphous precipitate that formed dissolved upon heating of the suspension at 50°C. After cooling to ambient temperature, druses of dark-brown needle-like crystals were formed in ~2 h.

[16] Diffraction data were collected using a Bruker Kappa APEX-II diffractometer. Crystal data for **1**: $C_{14}H_{16}O_{12}Np_2$, M = 850.27, a = 38.4784(5) Å, c = 8.7086(2) Å, V = 11166.4(3) Å^3, trigonal, space group $R\bar{3}c$, Z = 18, T = 100(2) K, μ = 8.376 mm^{-1}, reflections collected/unique = 35 033/4962, R1 [$I > 2\sigma(I)$] = 0.0553, and wR2 [$I > 2\sigma(I)$] = 0.1380. The structure was solved by direct methods. The H atoms of the OH and ring C atoms were introduced into the calculated positions and refined with $U_H = 1.2U_{eq}$(O,C). Four positions for the O atoms of the water molecules were revealed in the structure. The overestimated temperature factors of Ow atoms indicate that the positions of the water molecules in the crystal are partially disordered. The positional and thermal parameters of the Ow atoms were refined with the halved occupancy factor. The H atoms at the water molecules were not localized.

Compounds **4**−**7** have the ribbons arrangement with periodically repeated trimers. The structure of such ribbons is shown for compound **4** chosen as an example (Figure 3c). In a crystal of **4**, the trimers form infinite electroneutral ribbons, whereas in crystals **5**−**7**, the trimers are joined into infinite anionic ribbons. It will be remarked that, according to the geometric parameters of the trimers, the formula of **7** should be written as $K[(UO_2)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)_2(\mu_2\text{-}OH)(C_7H_4NO_4)_2]\cdot H_2O$.

The general characteristic for the trimers in **3**−**7** is that the central atom of the trimer is the μ_3-O^{2-} atom (O1 in Figure 3b,c). In **3**−**7**, the μ_3-O atom lies in the plane of three U atoms (exept for **4**, where the deviation is 0.19 Å). Interatomic distances U···U are 3.762−3.978 Å (the average value is 3.864 Å), and the lengths of the U−O bonds with the O atom range from 2.19 to 2.26 Å (average 2.22 Å).

The O atoms of the μ_3-OH groups (atom O3 in Figure 3b and atoms O3 and O4 in Figure 3c) are the common vertices for four equatorial edges of three pentagonal bipyramids (two edges are not conjugated). The anionic ribbons in crystals **5**−**7** are similar in their oxygen environments to the electroneutral ribbon of **4**, with the only difference that the O2 atom in **5**−**7** belongs to the μ_2-OH group, whereas in **4**, the O atom belongs to $C_7H_4NO_4$.

In the bipyramids, the lengths of the U−μ_3-O bonds with μ_3-OH^- range from 2.39 to 2.57 Å and have an average value of 2.48 Å. Note that for comparison the bonds with the O atom of the μ_2-OH groups in **3** and **5**−**7** (atom O2 in Figure 3b) are noticeably shorter, being 2.347−2.406 Å (average 2.37 Å). In **3**−**7**, the μ_3-O atoms of the hydroxyl ions deviate strongly from the plane of three surrounding U atoms (0.55−0.71 Å; the average value is 0.66 Å). The distances between the central atoms of the bipyramids, which are not conjugated by the common edge (for instance, U2···U3a in Figure 3b), range from 4.403 to 4.507 Å (average 4.469 Å). All of the ribbons are nonplanar, the dihedral angles between the equatorial planes of the repeated trimers are ~30°, and the inflection passes through the μ_3-O−μ_3-O edge formed by the O atoms of the μ_3-OH groups.

The principal difference between **1** and earlier studied **4**−**7** is that the periodically repeated fragment of the ribbon is the dimer composed of two pentagonal bipyramids of Np1 and Np2 (Figure 3d). The equatorial zones of the dimeric fragments planar within 0.19(2) Å form a dihedral angle of 41.7° (inflection along the O1···O2b or O1a···O2 edges), and the ribbon becomes corrugated.

Although the compared neptunium(VI) and uranium(VI) compounds differ in composition and structure, we can observe a trend of decreasing bond length with increasing atomic number, as expected from the actinide contraction. The An═O bonds decrease upon going from U to Np (average values are 1.774 and 1.734 Å, respectively). The average Np−μ_3-O bond is shorter than the average U−μ_3-O bond (2.402 and 2.48 Å, respectively). The An···An distance between the central atoms of the bipyramids, which are not conjugated along the common edge, also shortens upon going from U to Np (4.469 and 4.366 Å, respectively). However, this characteristic depends on the geometric parameters of the An−O ribbons. For compounds **3**−**7**, a dependence of the U···U interatomic distance on the angle of bending in the line of the μ_3-O−μ_3-O edge is observed: the larger the dihedral angle between the equatorial plane of repeated trimers, the shorter the distance U···U.

An alternative formula with the μ_3-O^{2-} ligand was considered for **1**. In the crystal packing of such a compound, the negative charge of the anionic fragments $[(NpO_2)_2(\mu_3\text{-}O)_2(C_7H_5O_2)_2]_n^{2-}$ can be compensated for by oxonium ions. A notable feature of such a structure is the presence of $[H_3O]^+$ units strongly hydrogen-bonded to O atoms. In the structure **1**, the O···O distances are more than 2.74(4) Å. In addition, the Np−μ_3-O bond lengths and a large value of deviation of μ_3-O from the plane of three Np atoms indicate unambiguously the structure with the μ_3-OH^- ligand.

Attempts to isolate crystalline a uranium(VI) benzoate analogous to **1** by the procedure presented above were unsuccessful, so a slightly modified method was applied.[17] Calcination of weighed samples at 800 °C showed that the uranium content in the compound was close to the theoretical value for $[(UO_2)_2(\mu_3\text{-}OH)_2(C_7H_5O_2)_2]\cdot 3H_2O$.[18] The larger amount of water molecules for the uranium compound can be explained by the presence in the structure of channel-like cavities in which the larger number of water molecules of crystallization can be accommodated easily. Unfortunately, the fine crystals obtained are not usable for X-ray diffraction studies. Nevertheless, a crystal was found that allowed us to determine the *R* unit cell with parameters a = 38.32 Å and c = 8.729 Å. This confirms that the uranium(VI) and neptunium(VI) compounds are isostructural.

The structure reported here represents the first complex TRU with the μ_3-OH^- ligand. We are continuing to develop synthetic routes for the preparation of crystalline samples of the plutonium(VI) analogue of complex **1**.

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Supporting Information Available: Detailed crystallographic information in CIF format and structures of uranium(VI) complexes with the μ_3-O^{2-} ligand. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] A solution of $UO_2(NO_3)_2$ was prepared according to a known procedure.[5] Samples of 0.5 M $UO_2(NO_3)_2$ were placed in tubes and diluted 5-fold with water, 0.5 M $LiC_7H_5O_2$ was added to $UO_2(NO_3)_2$ in the molar ratio of 1.1:1.5, and then the pH of the solution was brought to 5−6 with a 0.2 M solution of LiOH. After the solutions were stored for 5 days and longer, druses of thin needle-like crystals were formed. It was also established that the dry uranium(VI) compound decomposed gradually. This was confirmed by the X-ray studies; additional reflections appeared with time in the powder X-ray diffraction pattern.

[18] The uranium content was determined by calcination of two samples at 800 °C to U_3O_8. Elem anal. Calcd for $[(UO_2)_2(OH)_2(C_7H_5O_2)_2]\cdot 3H_2O$: U, 54.71. Found: U, 54.33 and 54.66.