Synthesis and Crystal Structure of New U(VI) and Np(VI) Benzoates, $K_{11}(AnO_2)_{23}(OOCC_6H_5)_{57}(H_2O)_{18+x}$

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Abstract—The structure of new double benzoates of hexavalent actinides, $K_{11}(AnO_2)_{23}(O_2C_2H_4)_{57}(H_2O)_{18+x}$ ($An = U$, Np), was studied. There are five crystallographically independent actinide atoms in the crystals. The coordination polyhedra of $An(1)$, $An(3)$, $An(4)$, and $An(5)$ are distorted hexagonal bipyramids, and that of $An(2)$ is a distorted pentagonal bipyramid. Ten crystallographically independent benzoate ions have been found in the crystals. All but one anions are bidentate chelating and form with $AnO_2^{2-}$ ions either electrically neutral [$AnO_2(O_2C_2H_4)(H_2O)]_2 [An(1)O_2^{2-}$ cations] or negatively charged [$AnO_2(O_2C_2H_4)(H_2O)]_2 [An(3)O_2^{2-}$, $An(4)O_2^{2-}$, $An(5)O_2^{2-}$ cations] complexes. The bidentate bridging benzoate ion links two adjacent $An(2)O_2^{2-}$ cations with the formation of peculiar electrically neutral cyclic fragments $AnO_2(O_2C_2H_4)(H_2O)]_6$, arranged perpendicular to the $c$-axis. There are three independent $K^+$ cations in the structure. The coordination surrounding of $K(1)^+$ (coordination number CN 6) is formed by oxygen atoms of two electrically neutral [$AnO_2(O_2C_2H_4)(H_2O)]_2$ fragments and of the complex anion $[AnO_2(O_2C_2H_4)(H_2O)]_5$. The coordination surrounding of $K(2)^+$ (CN 6) consists of oxygen atoms of three complex anions $[AnO_2(O_2C_2H_4)(H_2O)]_5$. The disordered $K(3)^+$ cation is arranged near the sixfold axis between the cyclic fragments $[AnO_2(O_2C_2H_4)(H_2O)]_6$. An important structure-forming factor in the crystals is hydrogen bonding involving coordinated water molecules. In the coordination polyhedra of actinides, the An–O bond lengths regularly decrease in going from U to Np owing to actinide contraction.

Key words: actinides(VI), benzoates, crystal structure, single crystal X-ray diffraction

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Published data on benzoate compounds of transuranium elements are very limited. They include only data on the synthesis, structure, and some properties of simple Np(V) benzoates [1, 2] and on complexes of An(V) benzoates with nitrogen-containing molecular ligands of the general composition [$AnO_2(Bipy)(OOCC_6H_5)]_2 (An = Np and Pu) [3, 4], [$NpO_2(Bipy)(OOCC_6H_4F)]_2 [5], and [$NpO_2(Phen)(OOCC_6H_5)]_2 [6], where Bipy is 2,2’-bipyridine and Phen is phenanthroline. These compounds have interesting systems of mutual coordination of $AnO_2^-$ ions (cation–cation interaction), including formation of dimeric ions [$AnO_2^-]_2$, observed for the first time in the structure of neptunyl(V) mellite $Na_4[NpO_2]_2C_12O_7$·5$H_2O$ [7]. We found no data on the structure of benzoates of hexavalent transuranium elements. However, there are a number of papers concerning the synthesis, structure, and properties of simple [8], double (with sodium and ammonium ions) [9–11], and mixed-ligand [12–15] benzoate compounds of uranyl. At the same time, it should be noted that the analogy in the preparation conditions, composition, and structure of compounds of U(VI) and hexavalent transuranium elements is not always observed [16, 17]. In this context, the goal of this study was to synthesize simple neptunyl(VI) benzoates and its double benzoates with alkali metal ions and to examine their structure. The result of the first step of this study was preparation of a complex double potassium neptunium(VI) benzoate in the form of single crystals and determination of its structure. The similar complex was prepared with uranyl. A single crystal X-ray diffraction study showed that the compounds are isostructural and have the composition $K_{11}(AnO_2)_{23}(O_2C_2H_4)(H_2O)_{18+x}$, where $An = U$ (I) and Np (II).

EXPERIMENTAL

We used weakly acidic 0.505 M $UO_2(NO_3)_2$ and 0.175 M $NpO_2(NO_3)_2$ aqueous solutions. The uranyl nitrate solution was prepared from the corresponding
analytically pure grade chemical. Its concentration was determined gravimetrically (precipitation from a sample with ammonia and calcination of the precipitate to U₃O₈). The initial NpO₂(NO₃)₂ solution was prepared by heating of a weighed portion of NpO₂ with concentrated HNO₃, followed by the solution evaporation to wet salts and dissolution of the residue in water. Neptunium was preliminarily purified by anion exchange and precipitation of Np(C₂O₄)₂·6H₂O, which was calcined to the dioxide. The other working solutions used in this study were prepared by common procedures from chemically pure or ultrapure grade chemicals using double-distilled water.

The procedure for preparing single crystals of I was as follows. To 0.5 ml of a 0.5 M UO₂(NO₃)₂ solution we added 5 ml of water and 1 ml of a 1 M KOOC₆H₅OH solution. After stirring, the reaction mixture transformed into a gelatinous mass which slowly underwent syneresis with the formation of a yellow supernatant. Prolonged storage (10–16 days) led to recrystallization of the precipitate and formation of a set of brownish-yellow prismatic crystals. The mother liquor over the precipitate decreased to ~0.2 ml. On further storage, the black prisms disappeared and the precipitated after 5-day storage in an open test tube. On small amount of fine light brown cubic crystals precipitated after 5-day storage in an open test tube. On further storage, the black prisms disappeared and the cubic crystals increased in size. The final volume of the mother liquor in the test tube decreased to ~0.2 ml owing to evaporation. Prolonged storage (10–16 days) led to syneresis with the formation of a yellow supernatant. A small amount of fine light brown cubic crystals precipitated after 5-day storage in an open test tube. On further storage, the black prisms disappeared and the cubic crystals increased in size. The final volume of the mother liquor in the test tube decreased to ~0.2 ml owing to evaporation.

The oxygen atoms of water molecules of crystallization O(1w), O(2w), and O(3w) in the structure of I, and O(5w), O(6w) in the structure of II were refined in the isotropic approximation. The H atoms at the C atoms were introduced into the calculated positions and refined with the site occupancy factor of 1/6 led to zero value of Ueq(H). Attempts to replace the K atom by the Na or Cs atom or by an oxygen atom (assuming the presence of oxonium ion, OH⁻) also failed. Furthermore, the alternative formula suggests that the carboxy group COOH of the randomly distributed benzoic acid molecule should be coordinated to An(VI) in the bidentate fashion. However, analysis of structural data [20] revealed no such examples.

The atomic coordinates for both structures were filed at the Cambridge Crystallographic Data Center (CCDC 734915 and 734916). The main crystallographic data and the characteristics of the X-ray structural experiment are given in Table 1, and the selected bond lengths in the coordination surrounding of U, Np, and K, in Table 2.

RESULTS AND DISCUSSION

In the crystals of I and II, there are five crystallographically independent actinide atoms: three of them [An(1), An(2), An(3)] occupy general positions; An(4), special position 3(c) on axis 2; and An(5), special position 2(b) on axis 3. The surrounding of actinide atoms and the numbering of nonhydrogen atoms...