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Synthesis and Structure of Dimeric Complexes of U(VI) and Np(VI) with Isophthalic Acid Anions, $\{AnO_2[C_6H_4(COO)(COOH)]_2(H_2O)\}_2$

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Abstract—Two previously unknown isophthalate complexes $[AnO_2(C_8H_5O_4)_2(H_2O)]_2$ [An(VI) = U, Np] were synthesized, and their structure was studied by single crystal X-ray diffraction. The compounds are isostructural. Their structural unit is a centrosymmetrical dimeric complex. The coordination surrounding of the An(VI) atoms in the structure is formed by the O atoms of three acidic anions $[C_8H_5O_4]^-$ and of water molecules; the coordination polyhedra are pentagonal bipyramids with the oxygen atoms of the AnO_2 groups in the apical positions. One of the two independent $[C_8H_5O_4]^-$ anions is bidentate chelating, and the other is bidentate bridging. The different functions of the anions influence the bond lengths in the coordination polyhedra of the An(VI) atoms. The 3D network of hydrogen bonds additionally stabilizes the crystal structure, and the hydrogen bonding influences the geometric and conformational characteristics of the dimers.

Keywords: uranium(VI), neptunium(VI), acidic isophthalate, crystal structure

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Benzenecarboxylic acid anions are a subject of active research. They are sufficiently resistant to both oxidation and reduction, which allows their use as ligands coordinating actinide ions in different oxidation states. Among actinide complexes with benzenecarboxylic acid ions, benzoic and phthalic acid compounds are the most studied. The range of structurally studied actinide compounds with phthalic acid isomers, isophthalic (1,3-benzenedicarboxylic) and terephthalic (1,4-benzenedicarboxylic) acids, is considerably narrower, and studies dealing with these compounds, as a rule, mainly concerned synthesis and properties of uranyl complexes with these acids [1–5]. The structure and spectral properties of Np(VI) and Pu(VI) terephthalates isostructural with the complex $[UO_2(C_8H_4O_4)]$ were also studied [6]. For Np(V), papers [6, 7] concerning synthesis and structural characterization of Np(V) complexes with terephthalic and isophthalic acids can be noted. In Np(V) complexes with isophthalic acid [7], cation–cation interaction takes place even in anionic complexes with the metal : ligand ratio of 1 : 1.

In this work, we synthesized isostructural acidic isophthalates of Np(VI) and U(VI), $[UO_2(C_8H_5O_4)_2\cdot(H_2O)]_2$ (**I**) and $[NpO_2(C_8H_5O_4)_2(H_2O)]_2$ (**II**), and studied their structure.

EXPERIMENTAL

Uranyl complex **I** was synthesized as follows. Solid isophthalic acid was added to a ~1.0 M aqueous $UO_2\cdot(NO_3)_2$ solution to the molar ratio U : $C_6H_4(COOH)_2$ = 1 : 5 and higher. The mixture was heated in sealed glass ampules at ~180°C for ~100 h. As a result, light yellow crystals formed in a small yield.

Neptunium(VI) complex **II** was synthesized as follows. A ~0.4 M aqueous $NpO_2(ClO_4)_2$ solution was prepared by evaporation of a stock solution of NpO_2NO_3 with concentrated $HClO_4$ to wet salts, followed by dilution with water. Solid isophthalic acid was added to this solution to the molar ratio Np : $C_6H_4(COOH)_2$ = 1 : 3 and higher. The mixture was heated in sealed glass ampules at ~180°C for no more than ~10 h. As a result, light green crystals formed in the reaction mixture in a very low yield, and Np(V) accumulated in the mother liquor, as indicated by the

Table 1. Crystallographic data and characteristics of the X-ray diffraction experiment

Parameter	**I**	**II**
Empirical formula	$C_{32}H_{24}O_{22}U_2$	$C_{32}H_{24}O_{22}Np_2$
Molecular mass	1236.57	1234.51
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	6.6965(4)	6.6716(6)
b, Å	10.4463(6)	10.4440(8)
c, Å	13.0995(9)	13.0654(10)
α, deg	90.923(3)	91.020(4)
β, deg	95.340(3)	94.728(4)
γ, deg	108.497(3)	108.486(4)
Unit cell volume, $Å^3$; *Z*	864.24(9); 1	859.53(12); 1
ρ_{calc}, g cm^{-3}	2.376	2.385
$\mu(MoK_\alpha)$, mm^{-1}	9.065	3.958
Number of measured/ unique reflections	12646/4950	12878/12915
Number of unique reflections with $I > 2\sigma(I)$	4652	11579
Number of refined parameters	265	266
$R(F)$; $wR(F^2)$ $[I > 2\sigma(I)]$	0.0194; 0.0406	0.0250; 0.0545
$R(F)$; $wR(F^2)$ [whole dataset]	0.0218; 0.0413	0.0310; 0.0558
GOOF	1.039	1.059
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e $Å^{-3}$	1.544; –1.311	1.673; – 2.550

change in the color of the reaction mixture and by its absorption spectrum.

Attempted preparation of crystals of the related plutonium compound failed. Under similar conditions, with a ~0.3 M $PuO_2(ClO_4)_2$ solution, crystals of considerably smaller size, compared to those of the U(VI) and Np(VI) compounds, were obtained; in addition, a voluminous finely dispersed green precipitate formed, probably by reduction of Pu(VI) to the tetravalent state and subsequent hydrolysis of the reduction product.

The X-ray diffraction experiment was performed at the Center for Shared Use of Physical Methods of Investigation, Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, on a Bruker Kappa Apex II automatic four-circle diffractometer equipped with an area detector (MoK_α radiation, graphite monochromator) at 100 K. The unit cell parameters were refined over the whole dataset. The experimental intensities were corrected for absorption using SADABS program [8]. The structures were solved by the direct method (SHELXS97 [9]) and were refined by the full-matrix least-squares method (SHELXL97 [9]) on F^2 over the whole dataset in the anisotropic approximation for all nonhydrogen atoms. The refinement results and the main crystallographic data are given in Table 1. The crystal of **II** appeared to be an axial twin with the second domain turned by 180° about [100] direction. The experimental set of intensities for this crystal was processed using TWINABS program [10], and the final refinement was performed with introducing BASF instruction using HKLF 5 format.

The H atoms at the carbon atoms of the $[C_8H_5O_4]^-$ anions in both structures were placed in the geometrically calculated positions and refined with $U_H = 1.2U_{eq}(C)$. The H atoms at the oxygen atoms of the carboxy groups were localized in the difference Fourier syntheses and refined with $U_H = 1.2U_{eq}(O)$ and restricted O–H interatomic distances. The H atoms of the coordinated water molecule were localized in the difference Fourier syntheses and refined with $U_H = 1.5U_{eq}(O)$ and restricted O–H interatomic distances and H–O–H bond angles.

The bond lengths and angles in the structures of **I** and **II** are given in Table 2. The atomic coordinates were filed at the Cambridge Crystallographic Data Centre, CCDC 1042621 and 1042622.

RESULTS AND DISCUSSION

The structure of the centrosymmetrical dimers in **I** and **II** is shown in Fig. 1 for the neptunium compound as example. The coordination surrounding of the An atoms in the structures of **I** and **II** is constituted by the O atoms of three $[C_8H_5O_4]^-$ anions and of water molecule; the coordination polyhedra are pentagonal bipyramids with the O atoms of the AnO_2 groups in the apical positions. The bond lengths in the coordination polyhedron tend to decrease in going from U(VI) to Np(VI) (Table 1). The dimers in the crystal are arranged in the $(\bar{2}10)$ planes.

Two crystallographically independent $[C_8H_5O_4]^-$ anions have different functions in the structure. The first anion [carbon atoms C(11)–C(18)] is bidentate chelating, and the second anion [carbon atoms C(21)–C(28)] is bidentate bridging. Different functions of the anions influence the bond lengths in the coordination polyhedra of the An(VI) atoms: The An–O bonds with the O atoms of the bridging anion are shorter than those with the O atoms of the chelating anion (Table 2).

Table 2. Bond lengths (Å) and bond angles (deg) in the structures[a]

Bond	**I** (An = U)	**II** (An = Np)	Angle	**I** (An = U)	**II** (An = Np)
An(1)=O(1)	1.769(2)	1.7524(17)	O(1)=An(1)=O(2)	177.69(10)	178.38(8)
An(1)=O(2)	1.7694(19)	1.7461(17)	O(11)–An(1)–O(12)	52.48(6)	52.54(5)
An(1)–O(11)	2.4062(19)	2.3950(15)	O(11)–An(1)–O(21)	75.34(7)	75.69(5)
An(1)–O(12)	2.5326(18)	2.5317(15)	O(21)–An(1)–O(22*a*)	82.91(7)	83.33(5)
An(1)–O(21)	2.294(2)	2.2730(15)	O$_{\rm w}$(1)–An(1)–O(12)	72.37(6)	72.25(5)
An(1)–O(22*a*)	2.3031(18)	2.2962(15)	O$_{\rm w}$(1)–An(1)–O(22*a*)	77.19(7)	76.51(6)
An(1)–O$_{\rm w}$(1)	2.418(2)	2.4076(16)	O(11)–C(11)–O(12)	118.7(2)	118.58(18)
C(11)–O(11)	1.262(3)	1.266(2)	O(11)–C(11)–C(12)	118.8(2)	118.29(17)
C(11)–O(12)	1.279(3)	1.275(2)	O(12)–C(11)–C(12)	122.5(2)	123.13(18)
C(18)–O(13)	1.305(4)	1.311(3)	O(13)–C(18)–O(14)	122.9(3)	123.0(2)
C(18)–O(14)	1.237(3)	1.238(3)	O(13)–C(18)–C(14)	115.3(2)	115.41(18)
C(21)–O(21)	1.252(3)	1.257(2)	O(14)–C(18)–C(14)	121.8(3)	121.58(19)
C(21)–O(22)	1.262(3)	1.253(2)	O(21)–C(21)–O(22)	123.1(2)	123.04(18)
C(28)–O(23)	1.317(3)	1.315(3)	O(21)–C(21)–C(22)	119.0(2)	118.55(18)
C(28)–O(24)	1.229(3)	1.222(3)	O(22)–C(21)–C(22)	117.9(2)	118.41(17)
			O(23)–C(28)–O(24)	123.5(3)	124.2(2)
			O(23)–C(28)–C(24)	114.5(2)	113.97(19)
			O(24)–C(28)–C(24)	122.0(3)	121.88(19)

[a] Symmetry code: (*a*) (1 – *x*, –*y*, 1 – *z*).

The dimers are linked by hydrogen bonds in layers, as shown in Fig. 2 for compound **I** as example. Hydrogen bonds also arise between the layers, and the 3D system of hydrogen bonds thus formed additionally stabilizes the crystal packing of **I** and **II**. The H atoms of the carboxy groups of the anions participate in very strong hydrogen bonding. Being arranged in the ($\bar{2}$10) planes, the dimers are linked along [001] direction by hydrogen bonds involving H(4) atoms of the carboxy groups [C(21)–C(28)] and H(2) atoms of the coordinated water molecules O$_{\rm w}$(1). The H(3) atoms of the carboxy groups [C(11)–C(18)] also link the dimers in the layer with the formation of centrosymmetrical H bonds (Fig. 2). The coordinated water molecules O$_{\rm w}$(1) via H(1) atoms link the layers with each other, and these hydrogen bonds are appreciably weaker than the other hydrogen bonds (Fig. 3, Table 3).

Hydrogen bonding influences the geometric and conformational characteristics of the dimers. For example, the O(12) atom participates in hydrogen bonding as proton acceptor, the C(11)–O(12) bond is longer than the C(11)–O(11) bond (Table 2), and within the An coordination polyhedron the An(1)–O(12) bond is the longest. The carboxy group with the C(18) atom is turned relative to the benzene ring plane by 20.68(11)° in **I** and 20.01(9)° in **II**, whereas the carboxy group with the C(28) atom is turned by 12.91(12)° in **I** and 12.96(10)° in **II**. In the equatorial plane of the bipyramid, the O atom of the water molecule deviates from this plane by 0.210(3) Å in **I** and 0.218(3) Å in **II**.

It should be noted that the dimeric structures of

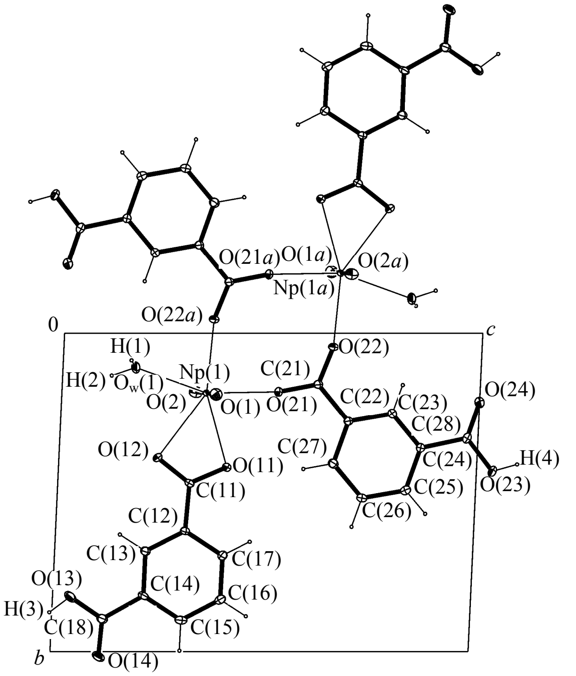

Fig. 1. Centrosymmetrical dimer in the structure of **II**. Ellipsoids of thermal vibrations of nonhydrogen atoms are given on the 50% probability level. The symmetry code is the same as in Table 2.

Table 3. Hydrogen bonds in the structures

D–H···A	D–H, Å	H···A, Å	D···A, Å	D–H···A, deg	Symmetry code
$[(UO_2)(C_8H_5O_4)_2(H_2O)]_2$ (**I**)					
$O_w(1)$–H(1)···O(14)	0.843(17)	1.948(19)	2.785(3)	172(4)	$x, y-1, z$
$O_w(1)$–H(2)···O(24)	0.849(18)	1.801(19)	2.647(3)	174(3)	$x, y, z-1$
O(13)–H(3)···O(14)	0.816(18)	1.837(19)	2.649(3)	173(4)	$2-x, 2-y, -z$
O(23)–H(4)···O(12)	0.818(19)	1.85(2)	2.651(3)	168(4)	$x, y, z+1$
$[(NpO_2)(C_8H_5O_4)_2(H_2O)]_2$ (**II**)					
$O_w(1)$–H(1)···O(14)	0.855(16)	1.944(18)	2.789(3)	169(3)	$x, y-1, z$
$O_w(1)$–H(2)···O(24)	0.837(16)	1.820(18)	2.645(2)	169(3)	$x, y, z-1$
O(13)–H(3)···O(14)	0.813(17)	1.837(18)	2.651(2)	178(4)	$2-x, 2-y, -z$
O(23)–H(4)···O(12)	0.805(17)	1.846(18)	2.643(2)	170(4)	$x, y, z+1$

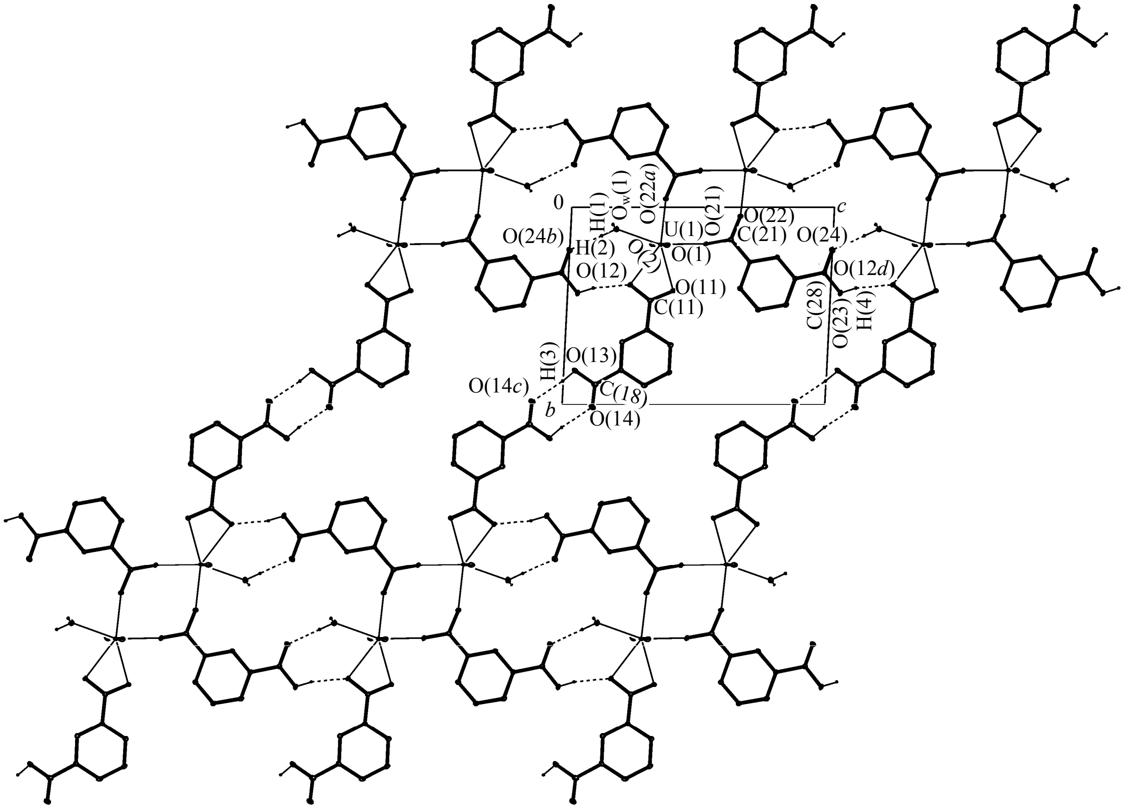

Fig. 2. Hydrogen bonds linking the dimers in the layer. Symmetry codes: (*a*) $(1-x, -y, 1-z)$, (*b*) $(x, y, z-1)$, (*c*) $(2-x, 2-y, -z)$, and (*d*) $(x, y, z+1)$.

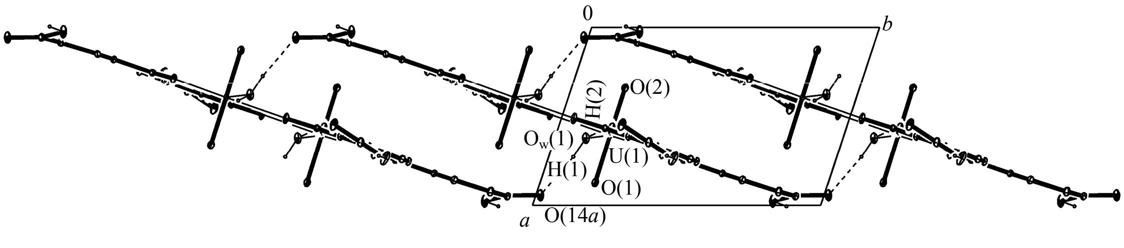

Fig. 3. Hydrogen bonds linking the dimers lying in the $(\bar{2}10)$ planes. Symmetry code: (*a*) $(x, y-1, z)$.

uranyl compounds in which the same ligand is coordinated in different fashions, as bridging and as chelating ligand, are quite frequent in uranyl carboxylates [11–16]. The examples are dimeric complexes of uranyl with benzoic acid and dimethylformamide (DMF) [11, 12] and salts with 4-halobenzoic acids, where the halogen is Cl, Br, or I [13, 14]. As a rule, in such dimers the bimetallic eight-membered heterocycle constituted by the U, O, and C atoms has the chair conformation in which the metal atoms deviate from the mean plane formed by the C and O atoms. The largest and the smallest deviations of the U atom from the mean plane are observed in the iodobenzoate $[(UO_2)(IC_7H_4O_2)_2\cdot(H_2O)]_2$ [13] (±1.281 Å) and in the complex $[(UO_2)\cdot(C_7H_5O_2)_2(DMF)]_2$ [12] (±0.346 Å), respectively. In **I** and **II**, these deviations are ±0.206 and ±0.186 Å, respectively.

The conformational characteristics of the dimers are primarily influenced by steric hindrance, which is particularly manifested in the compounds with halobenzoic acids. Hydrogen bonding also plays an important role, e.g., in uranyl acetates [15, 16] and in compounds **I** and **II**. However, the effect of so-called weak interactions is no less important. It is highly probable that the planar structure of dimeric complexes **I** and **II** is due to the interaction of the π systems of the benzene rings. Weak π–π interaction occurs between molecules located in different layers [17, 18], all the benzene rings overlap by 1/3, and the distances between the adjacent layers $d_{\bar{2}10}$ are 3.334 and 3.324 Å in the structures of **I** and **II**, respectively.

Thus, we have isolated two new dimeric complexes of An(VI) with isophthalic acid, in which the isophthalate acts as a single-charged anion $[C_8H_5O_4]^-$. The structure of the dimeric complexes is influenced by hydrogen bonding and by weak interaction between the π systems of the benzene rings.

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