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New Complexes of Actinides with Monobromoacetate Ions: Synthesis and Structures

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ABSTRACT: Synthesis, FTIR spectral study, and X-ray diffraction analysis of single crystals of $(CH_3)_4N[UO_2(mba)_3]$ (**I**), $(CH_3)_4N[NpO_2(mba)_2(NO_3)]$ (**II**), $(CH_3)_4N[PuO_2(mba)_2(NO_3)]$ (**III**), and $(CH_3)_4N[NpO_2(mba)(NO_3)_2]$ (**IV**), where mba is a monobromoacetate ion $(CH_2BrCOO^−)$, were conducted. The main structural units of crystals **I−IV** are mononuclear anionic complexes of the $[AnO_2(mba)_3]^−$, $[AnO_2(mba)_2(NO_3)]^−$, or $[AnO_2(mba)(NO_3)_2]^−$ composition. All these complex units are characterized with the same crystal-chemical formula AB^{01}_3 ($A = AnO_2^{2+}$ and $B^{01} = CH_2BrCOO^−$ or $NO_3^−$). Using the method of molecular Voronoi− Dirichlet polyhedra, the contributions of various types of noncovalent interactions into the formation of supramolecular structures of the obtained complexes were characterized. The analysis of coordination modes of all monobromoacetate-containing compounds from the Cambridge Structural Database was accomplished. Actinide contraction in the studied compounds is discussed.
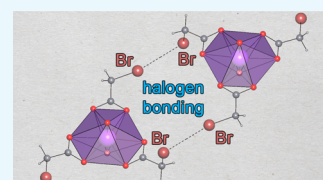
1. INTRODUCTION

A lot of attention currently is given to hybrid organo-inorganic compounds of hexavalent uranium, which frequently incorporate the $[UO_2(L)_3]^−$ anionic complex units (*L*, anions of saturated or unsaturated monocarboxylic acids) in their crystal structures. The prevalence of the tricarboxylatouranilate complex group has been shown by the example of the previously studied acetate-, propionate-, butyrate-, valerate-, acrylate-, methacrylate-, and crotonate-containing compounds.[1−12] The recently synthesized tribromopropionate-containing compounds of actinides are also constructed of the same $[AnO_2(L)_3]^−$ units (An, actinide).[13] However, the known compounds with a trichloroacetic acid anion as a ligand feature complex units of different compositions, $[AnO_2(L)_5]^{3−}$, in which trichloroacetate ions are coordinated to the AnO_2^{2+} cation in a monodentate mode.[14] For this reason, the investigation of the interaction between other halogen-substituted saturated and unsaturated monocarboxylate anions and hexavalent uranium and transuranic elements (neptunium and plutonium) seems to be valuable. This work is devoted to FTIR spectroscopic and X-ray diffraction analyses of the actinyl coordination compounds with monobromoacetate anions and tetramethylammonium: $(CH_3)_4N[UO_2(mba)_3]$ (**I**), $(CH_3)_4N[NpO_2(mba)_2(NO_3)]$ (**II**), $(CH_3)_4N[PuO_2(mba)_2(NO_3)]$ (**III**), and $(CH_3)_4N[NpO_2(mba)(NO_3)_2]$ (**IV**).

2. RESULTS AND DISCUSSION

2.1. Description of Crystal Structures. The structures of **I−IV** contain one crystallographic type of actinide atom. The coordination polyhedra of actinide atoms in the structures of all synthesized compounds are hexagonal bipyramids AnO_8 (An = U, Np, or Pu) with oxygen atoms of the AnO_2^{2+} cation in axial positions (Figure 1a). In the equatorial plane, the uranyl, neptunyl, and plutonyl ions coordinate three monobromoace-
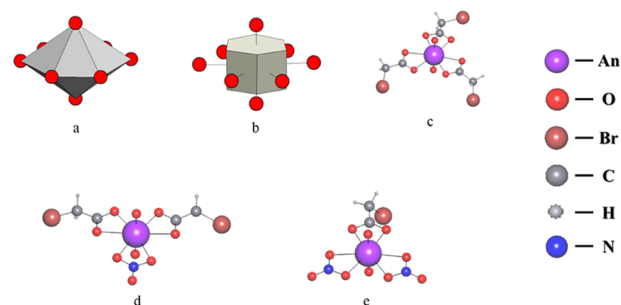

Figure 1. Coordination polyhedron (a), Voronoi−Dirichlet polyhedron (b), and the environment of actinide atoms (c−e) in crystal structures of **I−IV**.

tate ions in **I** (Figure 1c), two monobromoacetate ions and one nitrate ion in isostructural **II** and **III** (Figure 1d), or two nitrate ions and one monobromoacetate ion in **IV** (Figure 1e). All ligands implement the B^{01}-4-(O_2) coordination mode. The designations of coordination modes are given in accordance with ref 14. The geometric parameters of coordination polyhedra of actinide atoms in the structures of **I−IV** are
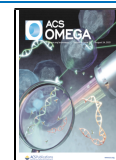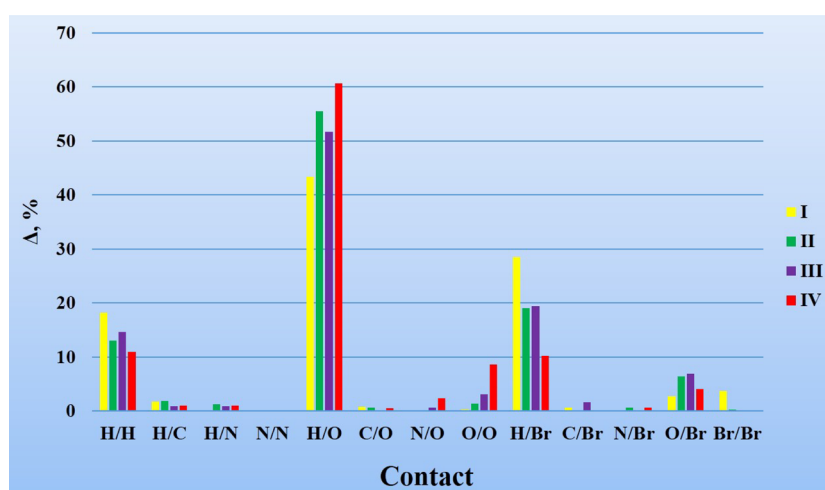
Figure 2. Partial contributions (Δ, %) of intermolecular noncovalent interactions in crystal structures of $(CH_3)_4N[UO_2(mba)_3]$ (**I**), $(CH_3)_4N[NpO_2(mba)_2(NO_3)]$ (**II**), $(CH_3)_4N[PuO_2(mba)_2(NO_3)]$ (**III**), and $(CH_3)_4N[NpO_2(mba)(NO_3)_2]$ (**IV**).

Table 1. Characteristics of Hydrogen Bonds in Crystal Structures of I−IV[a]

bond C−H···A	N^b	d(C···A) (Å)	d(C−H) (Å)	d(H···A) (Å)	angle (C−H···A) (deg)	Ω(H···A) (%)
			$C_{10}H_{18}Br_3NO_8U$, **I**			
C−H···Br	2	3.732–3.917	0.97	2.82–2.99	157.3–158.9	15.53–16.32
C−H···O	9	3.392–3.808	0.96–0.97	2.55–2.93	137.7–154.8	10.27–15.30
			$C_8H_{16}Br_2N_2NpO_9$, **II**			
C−H···O	8	3.251–3.826	0.96–0.97	2.41–2.92	131.6–159.5	11.21–15.75
			$C_8H_{16}Br_2N_2O_9Pu$, **III**			
C−H···O	7	3.267–3.753	0.96–0.97	2.37–2.87	148.0–164.3	10.41–17.42
			$C_6H_{14}BrN_3NpO_{10}$, **IV**			
C−H···O	8	3.173–3.683	0.96–0.97	2.40–2.77	137.4–164.0	10.01–17.04

[a]Allowance was made for contacts with C−H···A angle > 130°, d(H···A) < 3 Å, and Ω(H···A) > 10%. [b]N is the number of contacts of a specified type.

provided in the Supporting Information. The Voronoi−Dirichlet polyhedra (VDP) of U, Np, and Pu atoms are hexagonal prisms (Figure 1b). Their volumes (see the Supporting Information) are in good agreement with average values of 9.2(2), 9.2(2), and 9.20(9) Å^3 established for U(VI), Np(VI), and Pu(VI) atoms, respectively, surrounded by oxygen atoms.[15−17]

The AnO_2^{2+} ions in structures of **I−IV** are almost linear and equilateral (see the Supporting Information).[18] Actinide-containing structural units are the mononuclear complexes $[UO_2(CH_2BrCOO)_3]^-$ in **I**, $[AnO_2(CH_2BrCOO)_2(NO_3)]^-$ (An = Np or Pu) in **II** and **III**, and $[NpO_2(CH_2BrCOO)(NO_3)_2]^-$ in **IV**. The actinide-containing complex anions in the structures of all synthesized compounds are represented with a crystal chemical formula AB^{01}_3 (A = AnO_2^{2+} and B^{01} = CH_2BrCOO^- or NO_3^-). Due to the linkage of anionic complex units with outer-sphere cations with a developed network of noncovalent interactions (see below), the formation of supramolecular three-dimensional frameworks occurs in all the four structures.

2.2. Intermolecular Interactions. Anionic actinide-containing units in structures of **I−IV** are bound to tetramethylammonium cations into a three-dimensional supramolecular framework through electrostatic and intermolecular interactions. The existence of atoms of six chemical elements in the composition of each of the investigated compounds determines the theoretically possible presence of 21 types of pairwise noncovalent contacts. All intra- and intermolecular noncovalent

interactions in the structures of crystalline substances can be reliably evaluated with the method of molecular Voronoi−Dirichlet polyhedra.[19,20] The calculation of main parameters of noncovalent interactions was done with the program Intermol of the TOPOS program package.[21,22] The results of the calculation are given in the form of a diagram in Figure 2. The vertical axis of the diagram reflects the parameter Δ (%), the partial contribution of certain types of noncovalent interactions to the total surface area of all faces of Voronoi−Dirichlet polyhedra.

According to the derived data, the most considerable contribution into the formation of supramolecular frameworks of all synthesized compounds is provided by the H/O, H/Br, and H/H contacts, the total partial contribution of which is in the range of 82−90%. The characteristics of discovered hydrogen bonds in the examined structures are provided in Table 1. According to the classification proposed by Steiner,[23] all the mentioned hydrogen bonds can be attributed to medium or weak in strength.

A significant contribution of the Br/Br type of contacts was found for compound **I** with Δ_{BrBr} = 3.67%, while for the other compounds, Δ_{BrBr} does not exceed 1% (Figure 2). A more detailed study demonstrated the presence of a type II halogen bond[24] in the structure of **I** (Figure 3). The existence of such a halogen bond determines the deviation of one monobromoacetate ion from the equatorial plane of the uranyl group.

2.3. Coordination Modes. To summarize the available information on the structure and coordination modes of
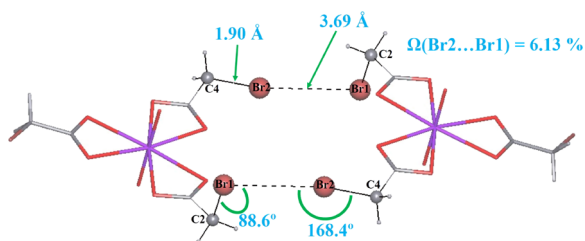
Figure 3. Halogen bond in the structure of **I**.

monobromoacetate ions, a crystal-chemical analysis of all monobromoacetate-containing compounds contained in the Cambridge Structural Database (CSD) was performed. The following requirements were imposed on the crystal structures for the preparation of the initial data set:

1) The crystal structure contains monobromoacetate ions bound to a metal atom.
2) The value of bond valence ($S = v/CN$, where v is the valence of the metal and CN is its coordination number in the structure) of the metal-oxygen bonds with mono-bromoacetate ions is ≥ 0.25.
3) The crystal structure does not possess disorder.
4) The crystal structure is determined with a nonzero R_1 factor that does not exceed 0.1.

The stated requirements resulted in the structures of 17 compounds containing 30 crystallographically independent monobromoacetate ions. Bi, Ce, Cu, Fe, Mn, Sb, Ti, and V served as metal atoms in the observed complexes. In the investigated compounds, monobromoacetate ions exhibit four different coordination modes (Figure 4). The most widespread
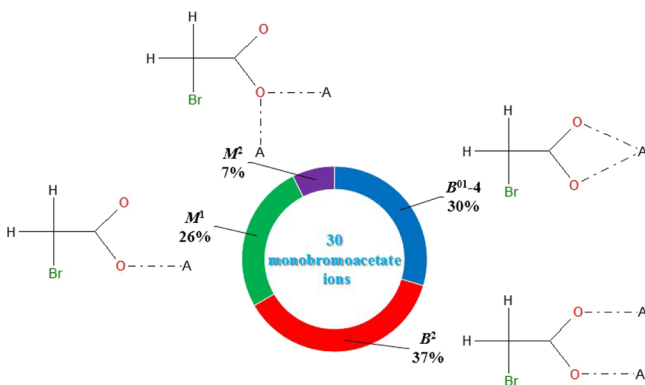

Figure 4. Four coordination modes of monobromoacetate ions in the crystal structures of all available coordination compounds in the CSD.

mode is B^2 (10 ions). The identified coordination modes show that monobromoacetate ions are able to act as terminal (M^1 and B^{01}-4) and bridging (B^2 and M^2) ligands and are able to coordinate without chelating effects (M^2, M^1, and B^2) or to form four-membered cycles with metal atoms (B^{01}-4). In all the studied cases, the donor atoms of ligands were exclusively oxygen atoms and no covalent bonding between Br and metal atoms was observed as opposed to the available information on other halogen-substituted carboxylate complexes.[14,25]

2.4. Actinide Contraction. The concept of actinide contraction represents the phenomenon of a regular decrease in the size of actinides with an increase in the atomic number. This effect is due to an increase in the effective charge of the atomic nucleus when filling the internal 5f electron shells. The

existence of 5f contraction is confirmed by crystal-chemical estimates and quantum-chemical calculations of various levels.[26−30] In An(VI) structures, actinide atoms are contained in the form of dioxocations AnO_2^{2+} with two short covalent An=O bonds, and actinide contraction is usually accompanied by a decrease in the lengths of the An=O bonds, while the average length of the equatorial An−O bonds changes insignificantly.[31−33]

The obtained results on the structures of **I−IV** confirm the opinion[29−31] that the average An=O distances in the actinyl group decrease with increasing actinide atomic number: 1.765(5) Å for U in **I**, 1.744(4) Å for Np in **II** and **IV**, and 1.709(26) Å for Pu in **III**. At the same time, the average An−O distances in the equatorial plane in the U−Np−Pu series almost do not change and coincide within the standard errors of the bond length estimation (2.459(4) Å approximately for all the four structures). These data also agree with the results of FTIR spectroscopy (see below): the asymmetric stretching vibrations of actinyl ions appear at 915, 922, and 948 cm^{-1} for An = U, Np, and Pu, respectively, implying a gradual decrease in the An=O distances in the sequence.

The implementation of Voronoi−Dirichlet polyhedra allows one to quantitatively characterize all atoms with the assistance of the V_{VDP} parameter (the volume of the Voronoi−Dirichlet polyhedron of an atom) or its one-dimensional analogue R_{SD} (the radius of a sphere with the volume equal to V_{VDP}). The volume of the Voronoi−Dirichlet polyhedron and, as a consequence, the radius of the spherical domain as integral characteristics depend on the length of all bonds of the central atom with its nearest neighbors in the crystal structure. In monobromoacetates **I−IV**, the radii of spherical domains of An(VI) atoms in the U−Np−Pu series are 1.31 Å (**I**), 1.30 Å (**II** and **IV**), and 1.29 Å (**III**) and are referred to as 1:0.996:0.987 to one another. A decrease in the distances in the actinyl group leads to an increase in the degree of nonsphericity of the Voronoi−Dirichlet polyhedron. According to the stereoatomic model of crystal structures,[34] the dimensionless second moment of inertia of the Voronoi−Dirichlet polyhedron (G_3) is a quantitative estimate of the uniformity of environment distribution. The minimum value of $G_3 = 0.077$ corresponds to a sphere, and the more non-uniform the environment is, the higher the value of this parameter. In the synthesized compounds **I−IV**, the G_3 parameter in the U−Np−Pu series increases sequentially: 0.0834 for **I**, 0.0837 for **II** and **IV**, and 0.0840 for **III**. These data are in good agreement with the previous results.[35] The possibility of reliable determination of the actinide contraction phenomenon in the synthesized compounds proves the undeniable value of the methods of analysis within the stereoatomic model of crystal structures.

3. EXPERIMENTAL SECTION

3.1. Synthesis. Solutions of tetramethylammonium hydroxide (1 mol/L) and monobromoacetic acid (0.58 mol/L) were added to the water solutions of hexavalent actinide nitrates ($UO_2(NO_3)_2$ (0.24 mol/L), $NpO_2(NO_3)_2$ (0.18 mol/L), and $PuO_2(NO_3)_2$ (0.21 mol/L)). The initial molar ratio of the reagents was $AnO_2(NO_3)_2:(CH_3)_4NOH:CH_2BrCOOH = 1:1:5$. The obtained transparent solutions were left for slow crystallization at a temperature of approximately 4−6 °C. The crystals, suitable for the X-ray diffraction experiment, were isolated after 4 (compounds **II** and **IV**), 5−7 (compound **III**), and 14 (compound **I**) days.

Table 2. Crystallographic Data, Experimental Parameters, and Results of Refinement of $(CH_3)_4N[UO_2(mba)_3]$ (I), $(CH_3)_4N[NpO_2(mba)_2(NO_3)]$ (II), $(CH_3)_4N[PuO_2(mba)_2(NO_3)]$ (III), and $(CH_3)_4N[NpO_2(mba)(NO_3)_2]$ (IV)

compound	I	II	III	IV
chemical formula	$C_{10}H_{18}Br_3NO_8U$	$C_8H_{16}Br_2N_2O_9Np$	$C_8H_{16}Br_2N_2O_9Pu$	$C_6H_{14}BrN_3O_{10}Np$
syngony, space group, Z	triclinic, $P\bar{1}$, 2	monoclinic, $P2_1/n$, 4	monoclinic, $P2_1/n$, 4	triclinic, $P\bar{1}$, 2
a (Å)	10.2846(5)	12.8188(3)	14.0745(4)	9.4165(2)
b (Å)	10.4846(5)	10.7726(2)	8.8946(2)	9.6346(2)
c (Å)	11.2692(6)	13.0405(2)	14.3877(4)	10.1237(2)
α (deg)	63.8330(10)	90	90	76.0690(10)
β (deg)	75.9080(10)	91.8340(10)	99.116(2)	64.8660(10)
γ (deg)	67.0570(10)	90	90	84.1920(10)
V (Å³)	1000.57(9)	1799.86(6)	1778.40(8)	807.04(3)
D_x (g/cm³)	2.516	2.513	2.562	2.490
radiation type		(λ; Å) MoK$_\alpha$; 0.71073		
μ (mm^{-1})	14.133	10.253	8.240	8.961
temperature		(K) 296(2)		
crystal dimensions (mm)	0.17 × 0.22 × 0.26	0.08 × 0.12 × 0.15	0.10 × 0.14 × 0.17	0.18 × 0.18 × 0.20
θ_{max} (deg)	29.993	30.000	24.594	29.994
hkl range	$-14 \leq h \leq 14$	$-18 \leq h \leq 17$	$-16 \leq h \leq 16$	$-13 \leq h \leq 13$
	$-14 \leq k \leq 14$	$-15 \leq k \leq 14$	$-10 \leq k \leq 10$	$-13 \leq k \leq 13$
	$-15 \leq l \leq 15$	$-18 \leq l \leq 18$	$-16 \leq l \leq 16$	$-14 \leq l \leq 14$
reflection number: collected/unique (N_1); R_{int}/with $I > 2\sigma(I)$ (N_2)	19,675/5824; 0.0265/5038	21,838/5240; 0.0390/3811	23,512/2984; 0.0554/2115	19,192/4697; 0.0232/4268
parameters refined	208	199	199	190
uncertainty values				
wR_2 on N_1	0.0879	0.0558	0.0683	0.0771
R_1 on N_2	0.0335	0.0284	0.0307	0.0273
S	1.023	1.006	1.022	1.057
$\Delta\rho_{min}/\Delta\rho_{max}$ (e/Å³)	−1.813/1.805	−0.899/1.151	−0.844/1.070	−1.447/1.987

Table 3. Assignment of Absorption Bands in FTIR Spectra of I−IV

	wavenumber (cm^{-1})[a]			
I	II	III	IV	assignment
1536 v.s.	1562 s.	1488 v.s.	1562 s.	$\nu_{as}(COO)$
1485 v.s.	1487 s.	1420 v.s.	1487 s.	$\nu_{as}(COO)$
	1448 m.		1448 m.	$\nu_{as}(COO)$
	1384 s.		1384 s.	$\nu(NO_3^-)$
1255 m.	1278 m.		1278 m.	$\nu_s(COO)$
1080 m.	1218 w.	1218 w.	1218 w.	$\nu(-C-N-)$
	1090 m.			$\nu(-C-N-)$
915 v.s.	922 s.	948 v.s.	922 s.	$\nu_{as}(AnO_2^{2+})$
	898 v.w.			$\delta(C-H)$
	836 m.		836 m.	$\delta(CH_2)$
	748 s.		748 s.	$\delta(CH_2)$
	692 m.	668 w.	692 m.	$\nu(C-Br)$
	570 m.			$\delta(CH_2)$

[a]Band intensities: v.s.: very strong; s.: strong; m.: medium; w.: weak; v.w.: very weak.

3.2. X-ray Diffraction Analysis. The data were collected on a Bruker KAPPA APEX II diffractometer with a CCD area detector using graphite monochromated MoKα (λ = 0.71073 Å) radiation at T = 298 K. The SAINT program was used to integrate the diffraction profiles, and the data were corrected for Lorentz and polarization effects as well as for absorption using SADABS.[36] The crystal structures were solved by direct methods and refined by full-matrix least-squares refinement against F^2 using SHELXTL software.[37] All nonhydrogen atoms were readily located, and their positions were refined anisotropically. The hydrogen atoms of the tetramethylammonium cations and monobromoacetate anions were placed in geometrically calculated positions and refined with $U_H = 1.2U_{eq}(N,C)$.

The coordinates of basis atoms and the values of thermal parameters of the crystal structures were deposited at the Cambridge Crystallographic Data Centre[38] under CCDC nos. 2078740, 2078743, 2078741, and 2078742 for I−IV, respectively. The parameters of the experiment and the final values of uncertainty factors for I−IV are given in Table 2. The main geometric parameters of synthesized compounds are provided in the Supporting Information.

3.3. FTIR Spectroscopy. FTIR spectra of compounds I−IV were measured in the range of 500−4000 cm^{-1} on an FTIR spectrometer (Shimadzu IR Prestige-21). The samples were prepared by careful grinding with melted NaCl. The assignment of absorption bands (Table 3) was preformed according to the literature data.[39−41]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02296.

Geometric parameters of coordination polyhedra of actinide atoms in crystal structures of I−IV (PDF)

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Notes

The authors declare no competing financial interest.

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