

## Synthesis and Structure of U(VI), Np(VI), and Pu(VI) 2-Fluorobenzoates

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**Abstract**—The compounds  $\text{NH}_4[\text{AnO}_2(\text{C}_6\text{H}_4\text{FCOO})_3]$ , where An = U (**I**), Np (**II**), or Pu (**III**),  $\text{C}_6\text{H}_4\text{FCOO}^-$  is the 2-fluorobenzoate anion, were synthesized and studied by single crystal X-ray diffraction. Compounds **I–III** are isostructural and crystallize in the cubic system, space group  $P2_13$ ,  $Z = 4$ . The main structural units of **I–III** are mononuclear complexes  $[\text{AnO}_2(\text{C}_6\text{H}_4\text{FCOO})_3]^-$  belonging to crystal-chemical group  $\text{AB}_3^{\text{O}1}$  (A =  $\text{AnO}_2^{2+}$ ,  $\text{B}^{\text{O}1} = \text{C}_6\text{H}_4\text{FCOO}^-$ ). The actinide contraction in the structures of **I–III** is manifested in a regular decrease in the lengths of the An=O bonds in the  $\text{AnO}_2^{2+}$  cations and in the volumes of the Voronoi–Dirichlet polyhedra (VDPs) of the An atoms in the series U–Np–Pu. The intermolecular interactions in crystal structures of **I–III** were analyzed by the method of molecular VDPs.

**Keywords:** uranyl(VI), neptunyl(VI), plutonyl(VI), fluorobenzoates, molecular Voronoi–Dirichlet polyhedra

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Mononuclear complexes  $[\text{UO}_2\text{L}_3]^-$  ( $\text{L}^-$  is a monobasic carboxylic acid anion) in which the U(VI) atoms have the hexagonal-bipyramidal coordination are among the most abundant types of uranyl complexes with anionic ligands [1]. Complexes containing anions of saturated or unsaturated aliphatic carboxylic acids have been characterized in the most detail (see, e.g., [1–5]). On the other hand, complexes with anions of monobasic aromatic carboxylic acids have been studied relatively poorly. Today data are available on the complexes  $[\text{UO}_2\text{L}_3]^-$  containing as ligands L anions of benzoic acid [6–8] or of some of its hydroxy, amino, and alkyl derivatives [9–13].

In this study, we examined the crystal structure of the previously unknown complexes  $\text{NH}_4[\text{AnO}_2\text{L}_3]$ , where An(VI) = U (**I**), Np (**II**), or Pu (**III**), and L is the anion of 2-fluorobenzoic acid  $\text{C}_6\text{H}_4\text{FCOOH}$ . These complexes are of interest for several reasons. First, crystal structure data on compounds containing halogen-substituted benzoate anions in the complexes  $[\text{AnO}_2\text{L}_3]^-$  are still lacking even for U(VI), not to speak of the less studied Np(VI) and Pu(VI). Second, because compounds **I–III** could be expected to be isostructural, it was interesting to evaluate for them the effect of the actinide contraction in the series U(VI)–

Np(VI)–Pu(VI). In addition, taking into account increased attention to halogen bonds [14], which are a new type of noncovalent interactions, only recently (in 2013) recognized by IUPAC [15], these compounds are of interest for analyzing the crystal-chemical role of fluorine atoms in organization of intermolecular interactions in the crystal structures of actinide compounds.

### EXPERIMENTAL

The compounds were prepared using 2-fluorobenzoic acid (Acros Organics), uranyl nitrate (analytically pure grade), and stock solutions of  $^{237}\text{Np}$  and  $^{239}\text{Pu}$  in 3 M  $\text{HNO}_3$ . An aqueous 1 M solution of 2-fluorobenzoic acid, neutralized with aqueous ammonia, was added to an aqueous solution of an actinide(VI) nitrate. Yellow (U), pink (Np), or brown (Pu) prismatic crystals were formed within 1–3 h at room temperature. All the compounds are stable in the solid phase for at least several days.

**X-ray diffraction analysis.** The structures of **I–III** were determined by single crystal X-ray diffraction. Measurements were performed with a Bruker Kappa Apex II automatic four-circle diffractometer. The unit cell parameters were refined over the whole dataset

**Table 1.** Crystallographic data and parameters of the experiment and refinement of the structures of **I–III**

Parameter	<b>I</b>	<b>II</b>	<b>III</b>
Chemical formula	NH <sub>4</sub> UO <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> FCOO) <sub>3</sub>	NH <sub>4</sub> NpO <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> FCOO) <sub>3</sub>	NH <sub>4</sub> PuO <sub>2</sub> (C <sub>6</sub> H <sub>4</sub> FCOO) <sub>3</sub>
Crystal system, space group, <i>Z</i>		Cubic, <i>P</i> 2 <sub>1</sub> 3, 4	
<i>a</i> , Å	13.1050(4)	13.0933(2)	13.0817(6)
<i>V</i> , Å <sup>3</sup>	2250.7(2)	2244.64(10)	2238.7(3)
<i>D</i> <sub>x</sub> , g cm <sup>-3</sup>	2.082	2.084	2.096
Radiation, λ, Å		MoK <sub>α</sub> (0.71073)	
μ, mm <sup>-1</sup>	7.362	3.207	3.334
<i>T</i> , K		100(2)	
Crystal size, mm	0.18 × 0.16 × 0.14	0.10 × 0.08 × 0.06	0.10 × 0.08 × 0.08
Account of absorption	Semiempirical, by equivalents		
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.325, 0.429	0.728, 0.809	0.706, 0.794
θ <sub>max</sub> , deg	29.95	29.98	29.96
Ranges of <i>h</i> , <i>k</i> , <i>l</i>	-18 ≤ <i>h</i> ≤ 18, -17 ≤ <i>k</i> ≤ 18, -18 ≤ <i>l</i> ≤ 18	-18 ≤ <i>h</i> ≤ 18, -17 ≤ <i>k</i> ≤ 18, -18 ≤ <i>l</i> ≤ 17	-18 ≤ <i>h</i> ≤ 18, -18 ≤ <i>k</i> ≤ 18, -18 ≤ <i>l</i> ≤ 18
Number of reflections: measured/unique ( <i>N</i> <sub>1</sub> ), <i>R</i> <sub>int</sub> / with <i>I</i> > 1.96σ( <i>I</i> ) ( <i>N</i> <sub>2</sub> )	26 461/2178, 0.0486/2114	38 981/2182, 0.1051/2080	40 828/2168, 0.0732/2112
Refinement method	Full-matrix least-squares method on <i>F</i> <sup>2</sup>		
Number of refined parameters		107	
<i>wR</i> <sub>2</sub> on <i>N</i> <sub>1</sub>	0.0297	0.0407	0.0322
<i>R</i> <sub>1</sub> on <i>N</i> <sub>2</sub>	0.0148	0.0202	0.0152
<i>S</i>	1.055	1.029	1.053
Absolute structure parameter, <i>x</i>	0.007(4)	-0.008(15)	-0.011(11)
Δρ <sub>max</sub> /Δρ <sub>min</sub> , e Å <sup>-3</sup>	0.283/-0.870	0.353/-0.441	0.334/-0.563

[16]. The experimental reflection intensities were corrected for absorption using SADABS program [17]. The structures were solved by the direct method (SHELXS97 [18]) and refined by the full-matrix least-squares method (SHELXL-2014 [19]) on *F*<sup>2</sup> for all the atoms in the anisotropic approximation for all nonhydrogen atoms. The H atoms of the fluorobenzoate ions were placed in the geometrically calculated positions with the isotropic temperature factors equal to 1.2*U*<sub>eq</sub>(C). The H atoms of the ammonium cations were localized on the difference Fourier electron density syntheses and were refined with the isotropic temperature factors equal to 1.2*U*<sub>eq</sub>(N), imposing the condition of equal N–H distances. The Flack parameters *x* [20] confirm the correctness of the determination of the absolute structures.

The crystallographic data and the parameters of the experiment and refinement of the structures of **I–III** are given in Table 1. The main bond lengths and bond angles and the parameters of the hydrogen bonds in **I–III** are given in Table 2. The coordination numbers (CN) of all the atoms were determined by the method of intersecting spheres [21]. The atomic coordinates and temperature parameters are filed at the Cambridge Cry-

tallographic Data Center, CCDC 1 833 119–1 833 121.

The absorption spectra of crystalline complexes were measured with IR Prestige21 and Shimadzu 3100 spectrometers in the ranges 4000–400 cm<sup>-1</sup> (resolution 2 cm<sup>-1</sup>, 60 scans) and 400–1300 nm (resolution 1 nm, slit width 1 nm), respectively, at room temperature in melted NaCl pellets.

## RESULTS AND DISCUSSION

Compounds **I–III** are isostructural and crystallize in space group *P*2<sub>1</sub>3. Actinide atoms (An) occupy sites with *C*<sub>3</sub> point symmetry and have CN 8. The An coordination polyhedra are hexagonal bipyramids. The O atoms of the actinyl groups AnO<sub>2</sub><sup>2+</sup> are located in the apical positions, and six O atoms of three 2-fluorobenzoate ions, in the equatorial plane of the AnO<sub>8</sub> bipyramids. Each anion exhibits bidentate coordination type B<sup>01</sup>, forming a four-membered metal chelate ring (Fig. 1). The main structural units of the crystals of **I–III** are mononuclear complexes [AnO<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>FCOO)<sub>3</sub>]<sup>-</sup> having the crystal-chemical formula AB<sub>3</sub><sup>01</sup> (A = AnO<sub>2</sub><sup>2+</sup>, B<sup>01</sup> = C<sub>6</sub>H<sub>4</sub>FCOO<sup>-</sup>).

The An=O distances in the structures of **I–III** are

**Table 2.** Selected bond lengths and bond angles in **I–III**

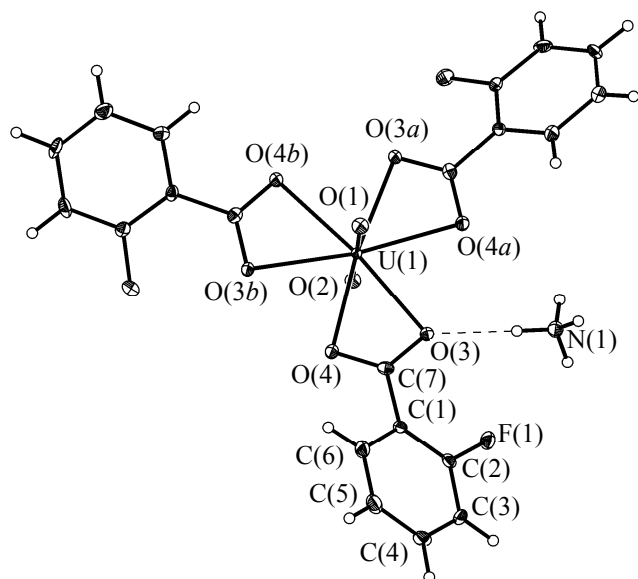
Distance, angle	I	II	III	Distance, angle	I	II	III
AnO <sub>2</sub> O <sub>6</sub> hexagonal bipyramid				N(1)–H(2)···O(3) H bond [for H(2)/O(3) face, rank = 0] <sup>a</sup>			
bond	<i>d</i> , Å			<i>d</i> [N(1)···O(3)], Å	2.953(3)	2.962(4)	2.957(3)
An(1)–O(1)	1.762(4)	1.750(5)	1.744(4)	<i>d</i> [N(1)–H(2)], Å	0.89(3)	0.86(4)	0.84(3)
An(1)–O(2)	1.766(4)	1.753(6)	1.751(4)	<i>d</i> [H(2)···O(3)], Å	2.07(3)	2.10(4)	2.12(3)
An(1)–O(3) (×3)	2.465(2)	2.464(3)	2.462(2)	Ω[H(2)···O(3)], % <sup>b</sup>	18.4	17.9	17.6
An(1)–O(4) (×3)	2.465(2)	2.465(3)	2.459(3)	N(1)–H(2)···O(3) angle, deg	175(4)	174(5)	173(4)
angle	ω, deg			C(4)–H(4)···O(1) H bond [for H(4)/O(1) face, rank = 0]			
O(1)An(1)O(2)	180.0	180.0	180.0	<i>d</i> [C(4)···O(1)], Å	3.200(5)	3.193(6)	3.186(5)
O(3)An(1)O(4) (×3)	52.70(7)	52.71(9)	52.92(8)	<i>d</i> [C(4)–H(4)], Å	0.95	0.95	0.95
O(3')An(1)O(4') (×3)	67.41(7)	67.40(9)	67.21(8)	<i>d</i> [H(4)···O(1)], Å	2.62	2.62	2.63
Fluorobenzoate anions				Ω[H(4)···O(1)], %	15.3	15.0	14.8
bond	<i>d</i> , Å			C(4)–H(4)···O(1) angle, deg	120	119	118
C(1)–C(2)	1.388(4)	1.384(6)	1.390(5)	C(4)–H(4)···F(1) H bond [for H(4)/F(1) face, rank = 0]			
C(2)–C(3)	1.380(4)	1.372(6)	1.381(5)	<i>d</i> [C(4)···F(1)], Å	3.014(4)	3.011(5)	3.002(4)
C(3)–C(4)	1.385(5)	1.396(7)	1.386(6)	<i>d</i> [C(4)–H(4)], Å	0.95	0.95	0.95
C(4)–C(5)	1.390(5)	1.393(7)	1.390(6)	<i>d</i> [H(4)···F(1)], Å	2.62	2.62	2.61
C(5)–C(6)	1.380(5)	1.384(6)	1.388(5)	Ω[H(4)···F(1)], %	12.7	12.7	12.8
C(6)–C(1)	1.399(5)	1.396(6)	1.402(5)	C(4)–H(4)···F(1) angle, deg	105	105	105
C(7)–C(1)	1.491(4)	1.488(6)	1.487(4)	C(6)–H(6)···O(2) H bond [for H(6)/O(2) face, rank = 0]			
C(7)–O(3)	1.272(4)	1.264(5)	1.274(4)	<i>d</i> [C(6)···O(2)], Å	3.489(4)	3.489(5)	3.481(4)
C(7)–O(4)	1.260(4)	1.271(5)	1.264(4)	<i>d</i> [C(6)–H(6)], Å	0.95	0.95	0.95
angle	ω, deg			<i>d</i> [H(6)···O(2)], Å	2.86	2.86	2.85
C(2)C(1)C(6)	117.5(3)	117.7(4)	117.5(3)	Ω[H(6)···O(2)], %	10.2	10.1	10.3
C(2)C(1)C(7)	123.3(3)	123.0(4)	123.4(3)	C(6)–H(6)···O(2) angle, deg	124	124	125
C(6)C(1)C(7)	119.2(3)	119.3(4)	119.1(3)				
C(1)C(2)C(3)	122.8(3)	123.2(4)	122.6(3)				
C(2)C(3)C(4)	118.3(3)	118.2(4)	118.7(4)				
C(3)C(4)C(5)	120.6(3)	120.3(4)	120.4(3)				
C(4)C(5)C(6)	119.9(4)	119.8(5)	120.0(4)				
C(5)C(6)C(1)	120.8(3)	120.8(4)	120.7(4)				
C(1)C(7)O(3)	121.3(3)	122.0(4)	121.3(3)				
C(1)C(7)O(4)	119.0(3)	118.7(4)	119.1(3)				
O(3)C(7)O(4)	119.6(3)	119.3(4)	119.5(3)				

<sup>a</sup> The rank of face (RF) indicates the minimal number of chemical bonds connecting the atoms whose VDPs share a common face. RF = 0 corresponds to intermolecular interactions, and RF > 1, to intramolecular interactions.

<sup>b</sup> (Ω) Solid angle (in percents of 4π sr) at which the common face of the VDPs of the indicated atoms is “seen” from the nucleus of any of them.

in the range 1.74–1.77 Å, and the An–O bond lengths in the equatorial plane, in the range 2.46–2.47 Å (Table 2). The mean length of each kind of bonds (An=O and An–O) regularly decreases in the order U–Np–Pu. The actinide contraction is also manifested in a regular decrease in the volume of the Voronoi–Dirichlet polyhedra (VDPs) of An atoms: 9.34, 9.26, and 9.22 Å<sup>3</sup> in **I–III**, respectively. On the other hand, the dimensionless second moment of inertia (*G*<sub>3</sub>) of the

VDP of the An atoms, which usually regularly increases in the series U(VI)–Np(VI)–Pu(VI) [4], showing that the degree of sphericity of the VDPs of the An atoms decreases with an increase in the number of their 5*f* electrons (for a sphere, *G*<sub>3</sub> = 0.077), in the series **I–III** varies nonmonotonically. Namely, *G*<sub>3</sub> increases only in going from U to Np (0.083474 and 0.083595, respectively), but does not further increase in going from Np to Pu.



**Fig. 1.** Molecular structure of  $\text{NH}_4[\text{UO}_2(\text{C}_6\text{H}_4\text{FCOO})_3]$  (**I**). Thermal displacement ellipsoids are shown on the 50% probability level.

The common feature of the complexes  $[\text{AnO}_2(\text{C}_6\text{H}_4\text{FCOO})_3]^-$ , which is also seen in Fig. 1, is a significant turn of the fluorobenzene ring around the  $\text{Fbz}-\text{COO}^-$  single bond. We can note in this connection that, in crystals of benzoic acid  $\text{Bz}-\text{COOH}$ , the dihedral angle  $\lambda$  between the planes passing through the C atoms of the benzene ring (Bz) and C and O atoms of the carboxy group is close to zero. In particular, according to the crystal data for {BENZAC02} [22], {BENZAC11} [23], and {BENZAC18} [24],  $\lambda$  in benzoic acid is about  $1.0^\circ$ ,  $0.7^\circ$ , and  $3.9^\circ$ , respectively. Here and hereinafter, the structure code in the Cambridge database is indicated in braces [25]. On the other hand, in five crystallographically different benzoate-containing complexes  $[\text{UO}_2(\text{L})_3]^-$ , present in the crystal structures of  $\text{Na}[\text{UO}_2(\text{C}_6\text{H}_5\text{COO})_3]\cdot 2\text{H}_2\text{O}$  {QQQFMA01} [6],  $\text{Na}[\text{UO}_2(\text{C}_6\text{H}_5\text{COO})_3]\cdot \text{C}_6\text{H}_5\text{COOH}\cdot 2\text{H}_2\text{O}$  {RACRES} [7], and  $\text{K}_{11}[(\text{UO}_2)_{23}(\text{H}_2\text{O})_{18}(\text{C}_6\text{H}_5\text{COO})_{57}]\cdot 7\text{H}_2\text{O}$  {AXUXAT} [8],  $\lambda$  for 11 different benzoate ions is larger by approximately  $10^\circ$  on the average. That is, the coordination of benzoate ions by uranyl ions is accompanied by an appreciable increase in  $\lambda$ . Similar effect is observed for 2-fluorobenzoate ions. In crystals of 2-fluorobenzoic acid (data for {FBENZA01} [26] and {FBENZA02} [27]), owing to the presence of fluorine atoms,  $\lambda$  increases to  $10.6^\circ$  and  $10.2^\circ$ , whereas in the crystals of **I–III**, on the average,  $\lambda = 30.1(3)^\circ$ ; i.e., the coordination of the 2-fluoro-

benzoate ions to the  $\text{AnO}_2^{2+}$  ions increases the angle of the turn of the Fbz ring about the  $\text{Fbz}-\text{COO}^-$  single bond by a factor of approximately 3.

The shortest distance between the H atoms of the adjacent carboxylate ions incorporated in the complex  $[\text{UO}_2(\text{L})_3]^-$  is relatively long ( $\approx 6$  Å). Therefore, the turn of the Bz or Fbz rings about the C–C single bonds in ligands L can be attributed to intermolecular interactions arising in packing of complexes  $[\text{UO}_2(\text{L})_3]^-$  and counterions and/or outer-sphere molecules in the crystal structures. The fact that the values of  $\lambda$  for crystallographically different benzoate ions in the same structure can differ significantly (e.g., in {AXUXAT} [8], from  $\approx 6^\circ$  to  $23^\circ$ ) counts in favor of this assumption.

The intermolecular interactions in the structures of **I–III** were analyzed by the method of molecular VDPs [28, 29], making it possible to reveal and characterize from the common standpoint, without using crystal-chemical radii, all the nonvalent contacts and not only the contacts commonly considered to be significant. The data obtained show (Table 3) that only 9 of 15 theoretically possible types of intermolecular contacts are observed in the structures of **I–III**. The major contribution to binding of complex groups (about 49% of the total area  $^0S$  of the faces of the molecular VDPs) is made by hydrogen bonds (H/O and H/F contacts, Table 3). The second largest contribution (total partial contribution about 46%) is made by the dispersion interactions (H/H, H/C, C/C, and F/F contacts, Table 3). The contribution of the other three types of contacts (O/F, C/F, and C/O) to  $^0S$  is as low as  $\sim 5\%$  in total). It should be noted that the mole fraction of the O atoms in **I–III** (16%) is almost 3 times larger than that of the F atoms (6%). Nevertheless, F/F intermolecular interactions are observed in the structures of **I–III**, whereas the O/O contacts are absent, although there are O/F contacts with  $\Delta$  about 1.5% of  $^0S$  (Table 3). The expected halogen bonds of type  $\text{C}-\text{F}\cdots\text{Z}$ , for which the  $\text{C}-\text{F}\cdots\text{Z}$  angle ( $\alpha$ ) should be close to  $180^\circ$  [15], in the structures of **I–III** are absent. The intermolecular contacts  $\text{C}(2)-\text{F}\cdots\text{O}(3)$ , for which  $\alpha \approx 159^\circ$ , are the closest to the linear ideal, but  $d[\text{F}\cdots\text{O}(3)] = 3.07$  Å, exceeding the sum of the van der Waals radii of the F and O atoms (2.99 Å [30]).

The structural features of **I–III** influence the electronic (UV, visible, and near-IR) absorption spectra differently. For U(VI) with electronic configuration  $5f^0$ ,  $f-f$  electronic transitions are impossible, and in the spectrum of the complex  $\text{NH}_4[\text{UO}_2(\text{C}_6\text{H}_4\text{FCOO})_3]$

**Table 3.** Main parameters of interatomic interactions in the structures of **I–III**<sup>a</sup>

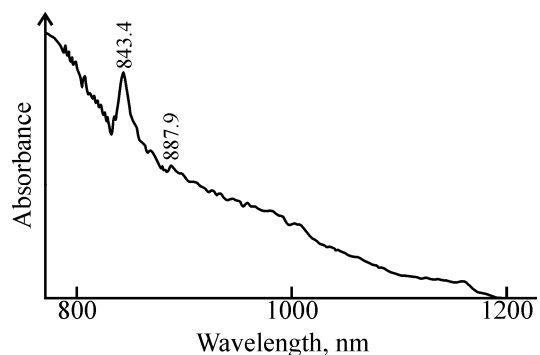
A/Z contact	<b>I</b>				<b>II</b>				<b>III</b>			
	$k_{AZ}$	$d, \text{Å}$	$S_{AZ}, \text{Å}^2$	$\Delta_{AZ}, \%$	$k_{AZ}$	$d, \text{Å}$	$S_{AZ}, \text{Å}^2$	$\Delta_{AZ}, \%$	$k_{AZ}$	$d, \text{Å}$	$S_{AZ}, \text{Å}^2$	$\Delta_{AZ}, \%$
F/F	6	3.11–3.11	10.60	1.7	6	3.09–3.09	10.84	1.8	6	3.07–3.07	10.97	1.8
O/F	6	3.07–3.07	9.05	1.5	6	3.07–3.07	8.78	1.4	6	3.07–3.07	9.09	1.5
C/F	30	3.02–3.52	20.64	3.4	30	3.02–3.51	20.11	3.3	30	3.00–3.51	20.02	3.3
H/F	24	2.51–2.94	69.66	11.3	24	2.53–2.95	68.94	11.3	24	2.51–2.93	68.36	11.2
C/O	18	3.20–3.70	1.78	0.3	18	3.19–3.69	1.93	0.3	18	3.19–3.66	2.23	0.4
H/O	102	2.06–5.14	232.52	37.9	102	2.10–5.17	231.64	37.8	102	2.12–5.18	230.43	37.8
C/C	96	3.36–5.01	40.36	6.6	96	3.36–5.01	40.51	6.6	102	3.36–5.02	40.52	6.6
H/C	108	2.93–4.61	104.90	17.1	108	2.94–4.61	105.50	17.2	108	2.94–4.59	105.61	17.3
H/H	102	2.93–4.59	124.32	20.3	102	2.91–4.61	123.91	20.2	102	2.90–4.62	123.00	20.2
Total	492	2.06–5.14	613.83	100.0	492	2.10–5.17	612.15	100.0	498	2.12–5.18	610.22	100.0

<sup>a</sup> ( $k_{AZ}$ ) Total number of the A/Z VDP faces with the rank equal to 0; ( $d$ ) range of the corresponding A–Z interatomic distances; ( $S_{AZ}$ ) total area of all the faces of this type in VDPs of atoms contained in one formula unit of the substance; ( $\Delta_{AZ}$ ) partial contribution (in percents) of the corresponding A/Z nonvalent contracts to the integral parameter  $^0S = \sum S_{AZ}$  (indicated in the bottom row) of the molecular VDP.

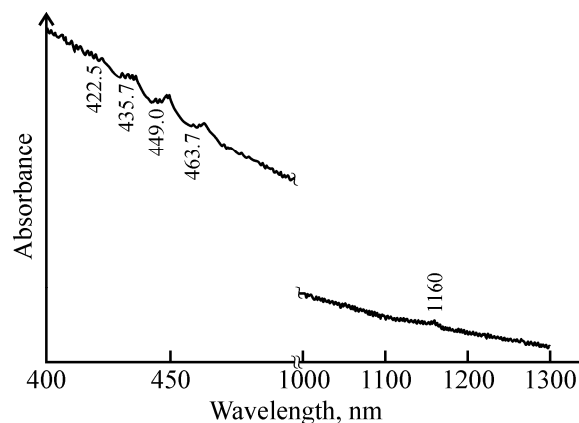
there is only a series of bands in the range 350–500 nm, typical of uranyl compounds. The strongest band is red-shifted relative to the hydrated  $\text{UO}_2^{2+}$  ion (409 nm) [31] and has a maximum at 424 nm. The electronic spectra of complexes **II** and **III** are more interesting, because the compounds in which the Np(VI) and Pu(VI) ions occurring in the hexagonal-bipyramidal surrounding are less numerous than in the case of uranyl. The spectra of compounds in which the actinyl(VI) ion has the symmetry close to  $D_{6h}$  usually contain in the visible range relatively strong bands of partially forbidden  $5f-5f$  electronic transition. Theoretically such absorption bands should not be manifested in the spectra of compounds containing  $\text{AnO}_2^{2+}$  in a symmetrical coordination surrounding. However, even small distortion of the equatorial surrounding of the actinyl(VI) ion in the structure due to differences in the  $\text{An}-\text{O}_{yl}$  interatomic distances can make such forbidden (in accordance with the Laporte rule) transitions experimentally observable. Indeed, the electronic absorption spectra of complexes **II** and **III** in the visible and near-IR range are not “empty” (Fig. 2). In the spectrum of  $\text{NH}_4[\text{PuO}_2(\text{C}_6\text{H}_4\text{FCOO})_3]$ , there is a weak but well-defined band of the  $^3H_4-^3H_6$   $f-f$  electronic transition with the maximum at 843.4 nm. The extinction coefficient in the maximum was determined to be  $\varepsilon \approx 20 \text{ L mol}^{-1} \text{ cm}^{-1}$ , which is considerably lower than in the spectrum of the hydrated Pu(VI) ion [32]. In the long-wave part of the absorption spectrum of  $\text{NH}_4[\text{NpO}_2(\text{C}_6\text{H}_4\text{FCOO})_3]$ , there is also a very weak band with a maximum at 1160 nm; its intensity is difficult to evaluate reliably. A distinctive feature of the spectrum

is the presence of a regular series (with the difference of approximately  $700 \text{ cm}^{-1}$ ) of well-defined bands in the range 400–500 nm (Fig. 3).

The IR spectra of isostructural compounds **I–III** are



**Fig. 2.** Fragment of the electronic absorption spectrum of  $\text{NH}_4[\text{PuO}_2(\text{C}_6\text{H}_4\text{FCOO})_3]$ .

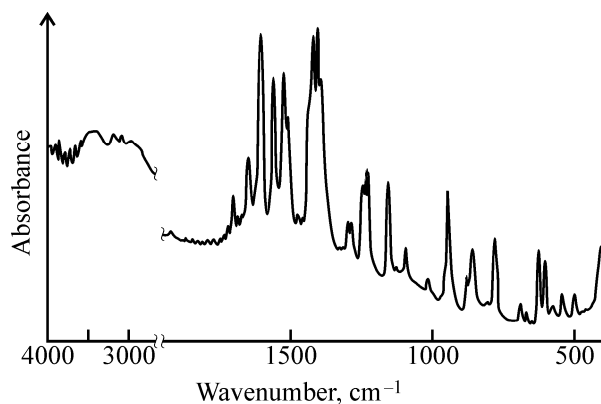


**Fig. 3.** Fragment of the electronic absorption spectrum of  $\text{NH}_4[\text{NpO}_2(\text{C}_6\text{H}_4\text{FCOO})_3]$ .

**Table 4.** Positions of the maxima of the major absorption bands in the IR spectrum of  $\text{NH}_4[\text{UO}_2(\text{C}_6\text{H}_4\text{FCOO})_3]$  and their possible assignment

Wavenumber, $\text{cm}^{-1}$	Assignment	Wavenumber, $\text{cm}^{-1}$	Assignment
3206 m	$\nu(\text{NH})$	1160 m, 1095 w, 1018 w	$\delta(\text{CH}), \nu(\text{CC})$
3092 m, 2966 w, 2944 w	$\nu(\text{CH})_{\text{arom}}$	956 m, 945 vs	$\nu(\text{C}-\text{COO})$
1612 vs, 1560 m	$\nu(\text{CC})_{\text{ring}}$	936 m	$\nu_{\text{as}}(\text{UO}_2)$
1524 s, 1512 s	$\delta(\text{COS}) + \nu(\text{CC})_{\text{arom}}$	860 m	$\delta(\text{CH})_{\text{ip}}$
1436 s, 1420 s	$\nu(\text{COO}) + \delta(\text{NH})$	784 vs	$\delta(\text{CH})_{\text{oop}}$
1396 vs	$\nu(\text{CO})$	694 m	$\delta(\text{CS})_{\text{oop}}$
1336 vs	$\nu(\text{CC})$	564 m	$\delta(\text{CC})_{\text{ring}}$
1298 s	$\delta(\text{CH})_{\text{ip}}$	496 w	$\rho(\text{COO})$
1236 w	$\nu(\text{CF})$		

similar in the number and shape of the absorption bands. Figure 4 shows as an example the spectrum of the uranyl complex. The possible band assignment (Table 4) is suggested taking into account the published data [33–37]. In the high-frequency range, there is a broad medium-intensity absorption band. Its diffuse constituent is due to the presence of occluded water in the sample. Also, the components at 3206, 3086, 2966, and 2864  $\text{cm}^{-1}$  have been identified; the first of them corresponds to the stretching vibrations  $\nu(\text{NH})$  of the outer-sphere ammonium ion. The other three bands were assigned to vibrations of the methine groups of the ring; their frequency is somewhat higher than for benzoic acid, which is due to the presence of the fluorine atom in the aromatic system [37]. The coordination of the fluorobenzoate ion by the uranyl ion is accompanied by the disappearance of the band of the nonionized carboxy group (1686  $\text{cm}^{-1}$  for the free ligand) and appearance of the stretching vibration band of the carboxylate ion. The  $\nu(\text{CF})$  stretching vibrations give a well-defined medium-intensity band at

**Fig. 4.** IR spectrum of  $\text{NH}_4[\text{UO}_2(\text{C}_6\text{H}_4\text{FCOO})_3]$ .

1236  $\text{cm}^{-1}$ . In the interval 970–900  $\text{cm}^{-1}$ , there is a narrow and very strong band at 945  $\text{cm}^{-1}$  with two shoulders at 956 and 936  $\text{cm}^{-1}$ . The lower frequency should probably be assigned to the uranyl vibrations, because this value is more typical of  $\nu_{\text{as}}(\text{UO}_2)$ .

It should be noted in conclusion that crystals of cubic symmetry are formed in  $\text{An}(\text{VI})$  compounds relatively seldom. In this context, it is interesting that compounds **I–III** crystallize in the same cubic space group  $P2_13$  as the majority of the previously known related complexes  $\text{R}[\text{AnO}_2\text{L}_3]$  do. Notably, the carboxylate ligands  $\text{L}$  in the previously characterized compounds are anions of aliphatic acids (acetate, propionate, *n*-butyrate, acrylate, or methacrylate ions [38]). Thus, compounds **I–III** are the first studied complexes  $\text{R}[\text{AnO}_2\text{L}_3]$  containing anions of an aromatic carboxylic acid. In view of the data of [38], nonlinear optical properties of crystals of **I–III** can be expected.

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## CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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