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Carbonate Complexes $[C(NH_2)_3]_6[An(CO_3)_5] \cdot nH_2O$ (An = Th, U, Np, and Pu; $n = 3$ and 4): Synthesis and Structures

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Abstract—Two series of isostructural double An(IV) and guanidinium carbonates were obtained as single crystals of the formula $[C(NH_2)_3]_6[An(CO_3)_5] \cdot nH_2O$ (An = Th, U, Np, and Pu; $n = 3$ (**I**) and 4 (**II**)) and examined by X-ray diffraction. For the Pu(IV) complexes, $a = 10.490(2)$ Å, $b = 33.798(5)$ Å, $c = 10.519(2)$ Å, $\beta = 119.414(7)°$, space group $P2_1/c$, $Z = 4$, $R = 0.0369$ (**I**) and $a = 16.0895(18)$ Å, $b = 13.1458(14)$ Å, $c = 16.6951(18)$ Å, $\beta = 108.116(6)°$, space group $C2/c$, $Z = 4$, $R = 0.0171$ (**II**). Both series of complexes contain the anions $[An(CO_3)_5]^{6-}$, in which the An atom is coordinated to five chelating bidenate carbonate ions. The coordination polyhedra of the An atoms are distorted bicapped square antiprisms. Within both the series, the An–O bond lengths decrease monotonically only for the sequence Th–U–Np. The average Np–O and Pu–O bond lengths in both tri- and tetrahydrates are virtually equal. The IR and electronic absorption spectra of the complexes obtained were studied. The absorption bands due to the *f–f* transitions experience bathochromic shifts in the spectra of the U^{4+} and Pu^{4+} carbonate complexes and hypsochromic shifts in the spectra of the Np^{4+} complexes.

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Much research dealing with the behavior of various forms of actinides (An) in carbonate solutions is due to the natural desire to gain better insight into processes that can occur in natural aqueous systems often containing noticeable amounts of carbonate ions [1]. In addition to the study of the forms in which actinide ions exist in aqueous solutions, possible ways of coordination of the carbonate ion to An atoms upon crystallization are also of interest. However, available data seem to give a one-sided view of the matter because the overwhelming majority of relevant studies are focused on the behavior of the uranyl ion under different experimental conditions.

The behavior of other actinyl ions in the presence of CO_3^{2-} is less understood. The greatest attention is currently given to interactions with Np(V) carbonate ions as the most stable and labile ionic form of neptunium under natural conditions. A study of the complexation and stability of tetravalent actinides in carbonate solutions is complicated mainly by accompanying hydrolysis leading to mixed An(IV) hydroxo carbonates. Obviously, possible transformations of ionic forms of actinides in natural carbonate systems can substantially influence the mobility of radioactive nuclides. According to [2], the uranyl ion in bicarbonate solutions can be reduced to U(IV) by Fe(II) ions (the content of the latter in underground water can be considerable); similar redox processes are possible for oxygenated Np and Pu cations. Since the chemistry of aqueous solutions of An(IV) is sophisticated, data on the solid-state structures of tetravalent actinides can be quite useful for the prediction of their behavior in the presence of carbonate ions. Nevertheless, solid-state An(IV) complexes with carbonate ions are poorly studied. We have retrieved the structural data only for three Th and two Pu complexes: $[C(NH_2)_3]_6[Th(CO_3)_5] \cdot 4H_2O$ [3, 4], $Na_6[Th(CO_3)_5] \cdot 12H_2O$ [5], $Na_6BaTh(CO_3)_6 \cdot 6H_2O$ [6], $[Na_6Pu(CO_3)_5]_2Na_2CO_3 \cdot 33H_2O$ [7], and $Na_8Pu_2(O_2)_2(CO_3)_6 \cdot 12H_2O$ [8].

Here we present data for two isostructural series of the complexes $[C(NH_2)_3]_6[An(CO_3)_5] \cdot 3H_2O$ (**I**) and $[C(NH_2)_3]_6[An(CO_3)_5] \cdot 4H_2O$ (**II**) (An = Th, U, Np, and Pu). The tetrahydrates belong to the known structural type $[C(NH_2)_3]_6[Th(CO_3)_5] \cdot 4H_2O$. However, the structure of $[C(NH_2)_3]_6[Th(CO_3)_5] \cdot 4H_2O$ has been identified in the noncentrosymmetric space group *Cc* [3]; later, this structure has been found to be centrosymmetric (space group *C*2/*c* [4]) without further refinement in this space group. That is why we performed new identification of this structure and did not use the data from [3].

EXPERIMENTAL

Synthesis. The starting materials for the synthesis of carbonate complexes of thorium, neptunium, and plutonium were their oxalate tetrahydrates. These salts (~20 mg) were dissolved in ~50-μL portions in a magnetically stirred ~1 M solution of guanidinium carbonate at room temperature. Heating of the reaction mixture above 40°C always gave finely crystalline and jelly-like products. Their dissolution resulted in the formation of a two-phase system (solution–oil) in which complexes **I** rapidly crystallized as large oblong plates. Subsequent recrystallization gave prismatic crystals of complexes **II**. The plutonium complexes were recrystallized most rapidly: in some cases, the process was completed in 15 min. For uranium(IV), UF_4, $U(SO_4)_2 \cdot 4H_2O$, $U(C_2O_4)_2 \cdot 6H_2O$, and $U(DMSO)_8(ClO_4)_4 \cdot CH_3CN$ [9] were tried as starting reagents; the last compound proved to be most suitable. The synthesis of U(IV) complexes was carried out in sealed glass tubes for uranium(IV) is appreciably oxidized in air during its dissolution in carbonate solution. Crystallization of the resulting uranium complexes in a two-phase system occurred most slowly. The yields of the carbonate complexes did not exceed ~40% because of their relatively high solubilities.

The uranium carbonate complexes are bright green. The neptunium complexes exhibit noticeable dichroism (greenish gray under normal light); the plutonium complexes are light green. Both the tri- and tetrahydrates of the Th, U, Np, and Pu complexes obtained are stable in air.

X-ray diffraction experiments were carried out on a Bruker KAPPA APEX II automated four-circle diffractometer [10] equipped with an area detector (MoK_α radiation, $\lambda = 0.71073$ Å). A preliminary X-ray data collection from a single crystal of $[C(NH_2)_3]_6[Np(CO_3)_5] \cdot 3H_2O$ showed that the diffraction pattern is sharply deteriorated at 100 K, probably because of a phase transition. For this reason, all X-ray diffraction experiments were conducted at room temperature. The unit cell parameters were refined for all the reflection intensities collected [11]. Absorption corrections were applied with the SADABS program [12]. The structures were solved by the direct methods with the SHELXS-97 program [13] and refined by the full-matrix least-squares method on F^2 in the anisotropic approximation for all non-hydrogen atoms (SHELXL-97 [13]). The H atoms of the guanidinium cations were located geometrically with isotropic thermal parameters of $1.2U_{\text{equiv}}(N)$. The H atoms of the molecules of crystallization water in the trihydrates were not located and were ignored in the refinement procedure. In the tetrahydrates, the water H atoms were located objectively and refined under the constraints that the O–H bond lengths and the H···H distances tend toward 0.85(2) and 1.35(2) Å, respectively, and that the isotropic thermal parameters are $1.5U_{\text{equiv}}(O)$.

The crystallographic parameters and the data collection and refinement statistics for structures **I** and **II** are summarized in Tables 1 and 2; the bond lengths at the An atoms are given in Tables 3 and 4. Comprehensive structural data for the complexes $[C(NH_2)_3]_6[An(CO_3)_5] \cdot 3H_2O$ (An = Th, U, Np, and Pu; $n = 3$ and 4) have been deposited with the Cambridge Crystallographic Data Collection (nos. 854432–854439; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

The IR and electronic absorption spectra of crystalline samples (pellets with molten NaCl) were recorded at room temperature on Specord M80 (Germany) and Shimadzu UV-3100 (Japan) spectrophotometers, respectively. The content of any carbonate complex in the matrix was 2 wt % for IR spectroscopic measurements. In recording the electronic absorption spectra, the content was calculated with allowance for the molar absorption coefficients of the An^{4+} ions.

RESULTS AND DISCUSSION

The double An(IV) and guanidinium carbonates of two isostructural series $[C(NH_2)_3]_6[An(CO_3)_5] \cdot 3H_2O$ and $[C(NH_2)_3]_6[An(CO_3)_5] \cdot 4H_2O$ (An = Th, U, Np, and Pu) contain the complex anions $[An(CO_3)_5]^{6-}$, in which the An atom is coordinated to five chelating bidenate carbonate ions (Fig. 1). The An atoms in the trihydrates occupy a general position; those in the tetrahydrates are on a twofold axis and so are the C and O_{term} atoms of one carbonate ion. In both cases, the coordination polyhedra of the An atoms are distorted bicapped square antiprisms. The carbonate ions occupy similar positions in both types of the coordination polyhedra (Fig. 2). The shortened edges between the atoms of one carbonate ion link one base of the bicapped square antiprism to the other or one base to its "cap" but do not link two vertices of the same base. Such an arrangement of the chelating bidenate ligands with shortened distances between the donor atoms agrees with that predicted in terms of the rigid sphere model [14].

Voliotis et al. [5] maintain that the coordination polyhedron of the Th atom in $Na_6[Th(CO_3)_5] \cdot 12H_2O$ is an irregular dioctahedron. For $[Na_6Pu(CO_3)_5]_2Na_2CO_3 \cdot 33H_2O$ [7], the coordination polyhedron of the Pu atom is described as a pseudohexagonal bipyramid with three equatorial and two axial CO_3^{2-} anions. However, we believe that the coordination polyhedra of the An atoms in these complexes can be described as clinocrowns.

The guanidinium cations and the molecules of crystallization water act as proton donors in numerous hydrogen bonds. On the whole, the H bonds formed by the guanidinium cations are weaker than those with water molecules as proton donors. The parameters of the water-formed hydrogen bonds in $[C(NH_2)_3]_6[Pu(CO_3)_5] \cdot 4H_2O$ are given in Table 5.

Table 1. Crystallographic parameters and the data collection and refinement statistics for $[C(NH_2)_3]_6[An(CO_3)_5] \cdot 3H_2O$ (An = Th, U, Np, and Pu)

Parameter	Value			
	Th	U	Np	Pu
M	946.67	952.66	951.63	953.63
T, K	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Crystal dimensions, mm	0.22 × 0.18 × 0.06	0.20 × 0.10 × 0.06	0.20 × 0.10 × 0.04	0.36 × 0.10 × 0.04
a, Å	10.5642(6)	10.5029(4)	10.4873(6)	10.490(3)
b, Å	33.9518(13)	33.8134(13)	33.7933(18)	33.798(5)
c, Å	10.5767(5)	10.5333(4)	10.5120(6)	10.5190(18)
β, deg	119.313(2)	119.3535(17)	119.360(2)	119.414(7)
V, Å^3	3307.8(3)	3260.5(2)	3246.9(3)	3248.8(11)
Z	4	4	4	4
ρ_{calcd}, g/cm^{-3}	1.901	1.941	1.947	1.950
μ, mm^{-1}	4.606	5.078	2.143	2.218
θ_{max}, deg	30.00	30.00	30.00	27.50
Number of measured reflections	31511	47382	50693	76902
Number of independent reflections	9568	9371	9409	7389
Number of reflections with ($I > 2\sigma(I)$)	6177	7982	6400	5885
R_{int}	0.0875	0.0376	0.0778	0.0865
T_{min}, T_{max}	0.572, 0.770	0.610, 0.750	0.739, 0.922	0.649, 0.919
Number of parameters refined	433	433	433	433
GOOF	1.018	1.146	1.020	1.098
R_1, wR_2 ($I > 2\sigma(I)$)	0.0549, 0.0941	0.0363, 0.0757	0.0412, 0.0707	0.0369, 0.0734
R_1, wR_2 (for all reflections)	0.1039, 0.1068	0.0459, 0.0788	0.0794, 0.0800	0.0541, 0.0784
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.751, –2.948	1.420, –3.641	1.010, –1.416	1.290, –2.842

Table 2. Crystallographic parameters and the data collection and refinement statistics for $[C(NH_2)_3]_6[An(CO_3)_5] \cdot 4H_2O$ (An = Th, U, Np, and Pu)

Parameter	Value			
	Th	U	Np	Pu
M	964.68	970.67	969.64	971.64
T, K	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$C2/c$	$C2/c$
Crystal dimensions, mm	0.22 × 0.16 × 0.12	0.32 × 0.10 × 0.08	0.24 × 0.08 × 0.06	0.36 × 0.10 × 0.04
a, Å	16.2075(8)	16.1359(6)	16.1014(3)	16.0895(18)
b, Å	13.2493(5)	13.2103(4)	13.1554(2)	13.1458(14)
c, Å	16.7510(8)	16.7107(6)	16.6752(3)	16.6951(18)
β, deg	108.419(2)	108.257(2)	108.137(1)	108.116(6)
V, Å^3	3412.8(3)	3382.7(2)	3356.65(10)	3356.1(6)
Z	4	4	4	4
ρ_{calcd}, g/cm^{-3}	1.878	1.906	1.919	1.923
μ, mm^{-1}	4.468	4.898	2.075	2.150
θ_{max}, deg	27.50	27.50	30.00	35.00
Number of measured reflections	12660	24894	24302	56786
Number of independent reflections	3905	3855	4892	7334
Number of reflections with ($I > 2\sigma(I)$)	3387	3376	4322	6862
R_{int}	0.0537	0.0498	0.0527	0.0294
T_{min}, T_{max}	0.490, 0.616	0.531, 0.695	0.758, 0.913	0.811, 0.968
Number of parameters refined	235	235	235	235
GOOF	0.992	1.037	1.008	1.040
R_1, wR_2 ($I > 2\sigma(I)$)	0.0316, 0.0555	0.0254, 0.0528	0.0279, 0.0538	0.0171, 0.0381
R_1, wR_2 (for all reflections)	0.0418, 0.0584	0.0350, 0.0560	0.0365, 0.0563	0.0201, 0.0390
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	0.984, –0.711	1.549, –0.855	1.330, –0.635	1.294, –0.590

Table 3. Bond lengths at the An atoms in $[C(NH_2)_3]_6[An(CO_3)_5] \cdot 3H_2O$ (An = Th, U, Np, and Pu)

Bond	d, Å			
	Th	U	Np	Pu
An–O(1)	2.510(5)	2.456(3)	2.439(3)	2.439(4)
An–O(2)	2.526(4)	2.480(3)	2.471(3)	2.462(3)
An–O(4)	2.507(5)	2.460(3)	2.447(3)	2.447(4)
An–O(5)	2.523(5)	2.479(3)	2.460(3)	2.461(4)
An–O(7)	2.525(4)	2.479(3)	2.465(3)	2.461(4)
An–O(8)	2.501(4)	2.448(3)	2.432(3)	2.424(4)
An–O(10)	2.516(4)	2.469(3)	2.454(3)	2.453(4)
An–O(11)	2.548(4)	2.507(3)	2.485(3)	2.492(4)
An–O(13)	2.476(5)	2.417(3)	2.399(3)	2.397(4)
An–O(14)	2.475(5)	2.430(3)	2.412(3)	2.417(4)
Average	2.511	2.462	2.446	2.446

The variation of the An–O bond lengths with the atomic number of the actinide atom is of particular interest (Fig. 3). Within both the series of complexes, the An–O bond lengths monotonically decrease (as a result of the actinide compression [15]) only for the sequence Th–U–Np. The average Np–O and Pu–O bond lengths in both the tri- and tetrahydrates are virtually equal. This can hardly be attributed to the coordination sphere "saturation" alone (i.e., the greatest possible decrease in the number of O···O contacts for adjacent carbonate ions). In the complex $Na_6BaTh(CO_3)_6 \cdot 6H_2O$ [6], the Th atom is coordinated to six bidentate carbonate ions. The average O···O distance for the atoms of different carbonate ions is 2.88 Å, while that in $[C(NH_2)_3]_6[Pu(CO_3)_5] \cdot 4H_2O$ is 3.00 Å.

Because of their structural similarity, the carbonate complexes $[C(NH_2)_3]_6[An(CO_3)_5] \cdot nH_2O$ studied have similar IR spectra both within either series and in trihydrate–tetrahydrate pairs of the same actinide.

Table 4. Bond lengths at the An atoms in $[C(NH_2)_3]_6[An(CO_3)_5] \cdot 4H_2O$ (An = Th, U, Np, and Pu)

Bond	d, Å			
	Th	U	Np	Pu
An–O(1)	2.515(2)	2.475(2)	2.4573(19)	2.4498(9)
An–O(3)	2.500(3)	2.445(2)	2.433(2)	2.4270(12)
An–O(4)	2.516(3)	2.473(2)	2.4532(19)	2.4518(10)
An–O(6)	2.498(3)	2.452(2)	2.433(2)	2.4410(11)
An–O(7)	2.499(3)	2.465(2)	2.442(2)	2.4433(11)
Average	2.506	2.462	2.444	2.443

The IR spectra of Pu(IV) carbonates are shown as examples in Fig. 4.

In the spectra of all the complexes obtained, the main absorption peaks of carbonate ions, guanidinium cations, and water molecules appear in close frequency ranges. Some differences are observed in the 4000–3000 cm^{-1} range showing wide intense bands due to the molecules of crystallization water (ν(OH) stretches) and the guanidinium cation (ν(NH) stretches). In the spectrum of the tetrahydrate, this integral band consists of more observed components and has a greater half-width compared to the trihydrate ($\Delta\nu_{1/2}$ = 750 and 480 cm^{-1}, respectively) because of more hydrogen bonding. In the 1700–500 cm^{-1} range, the most intense peaks at ~1680 cm^{-1} are due to the guanidinium cation (ν_{as}(CN) stretches). The high intensity of these stretches has been attributed to a partial π-character of the C–N bonds [16].

Table 5. Geometrical parameters of the hydrogen bonds in $[C(NH_2)_3]_6[Pu(CO_3)_5] \cdot 4H_2O$ (An = Th, U, Np, Pu)

D–H···A	Distance, Å			Angle D–H···A, deg	Symmetry operation code for A
	D–H	H···A	D···A		
O(1*w*)–H(1*C*)···O(7)	0.859(17)	2.020(17)	2.849(2)	162(3)	*x*, *y*, *z*
O(1*w*)–H(1*D*)···O(2*w*)	0.860(16)	2.050(19)	2.874(2)	160(3)	*x*, *y*, *z*
O(2*w*)–H(2*C*)···O(2)	0.805(16)	1.963(17)	2.7670(17)	178(3)	$x - 1/2, y + 1/2, z$
O(2*w*)–H(2*D*)···O(5)	0.812(16)	2.16(2)	2.883(2)	149(3)	*x*, *y*, *z*

Table 6. IR spectra of the crystalline complexes $[C(NH_2)_3]_6[An(CO_3)_5] \cdot nH_2O$*

Type of the vibration	Position of the absorption peak, cm^{-1}*			
	1	2	3	4
ν(NH), ν(OH)	3452, 3364, 3248, 3160	3448, 3408, 3344, 3252, 3164	3464, 3372, 3304, 3224, 3084	3472, 3440, 3412, 3378, 3352, 3316, 3276, 3160, 3098, 3052
ν_{as}(CN), δ(HOH)	1668, 1648sh	1684, 1660, 1644	1680, 1660	1698, 1668,1648, 1640
$\nu_3(CO_3)$, δ(NH)	1502, 1364	1496, 1368	1520, 1508, 1468, 1352,	1586, 1540sh, 1498, 1460, 1376
ν_s(CN), $\nu_1(CO_3)$	1148, 1052	1156, 1048	1136, 1084, 1046	1160, 1052, 1004
$\nu_2(CO_3)$	896, 865sh	860	896, 872	860
$\nu_4(CO_3)$	732, 664	736, 648	724, 668	728
δ(NCN)	548		516	588, 552

* The numbers 1, 2, 3, and 4 refer to $[C(NH_2)_3]_6[U(CO_3)_5] \cdot 3H_2O$, $[C(NH_2)_3]_6[Np(CO_3)_5] \cdot 3H_2O$, $[C(NH_2)_3]_6[Pu(CO_3)_5] \cdot 3H_2O$, and $[C(NH_2)_3]_6[Pu(CO_3)_5] \cdot 4H_2O$, respectively.

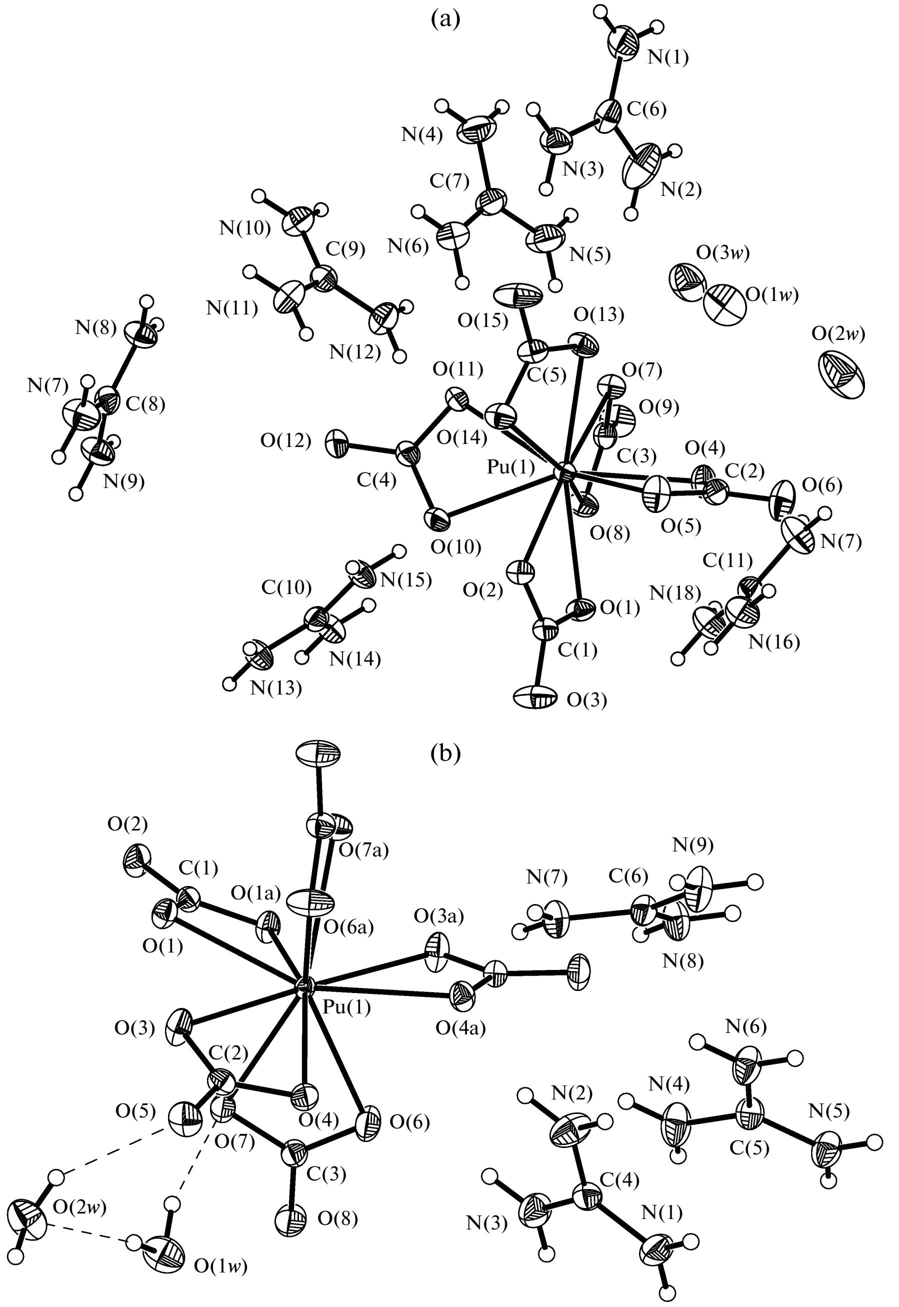

Fig. 1. Fragments of (a) $[C(NH_2)_3]_6[Pu(CO_3)_5] \cdot 3H_2O$ and (b) $[C(NH_2)_3]_6[Pu(CO_3)_5] \cdot 4H_2O$ with atomic thermal displacement ellipsoids (30% probability). The hydrogen atoms are indicated with arbitrary radius spheres.

The bending vibrations of water molecules appear as ill-resolved shoulders on the low-frequency side of the ν_{as}(CN) bands. The asymmetric carbonate ions seem to absorb at six fundamental frequencies (1500, 1360, 1050, 890, 740, and 650 cm^{-1}). The same range contains the ν_s(CN) bands of the guanidinium cation. The bending vibrations δ(NCN) of this fragment are manifested in the 540–520 cm^{-1} range. All the IR spectra are simple in shape allowing easy visual comparison. One can see that the vibrational frequencies of the coordinated carbonate ions do not change substantially when moving from uranium to plutonium within one series of isostructural complexes (Table 6). The exceptions are the frequencies of their in-plane and out-of-plane vibrations ν_2 and ν_4, which are most sensitive to structural and compositional variations in carbonate complexes [17–19].

Because of the coordination of the carbonate ions to the central U^{4+}, Np^{4+}, or Pu^{4+} ion, the electronic absorption spectra of solid-state carbonate complexes

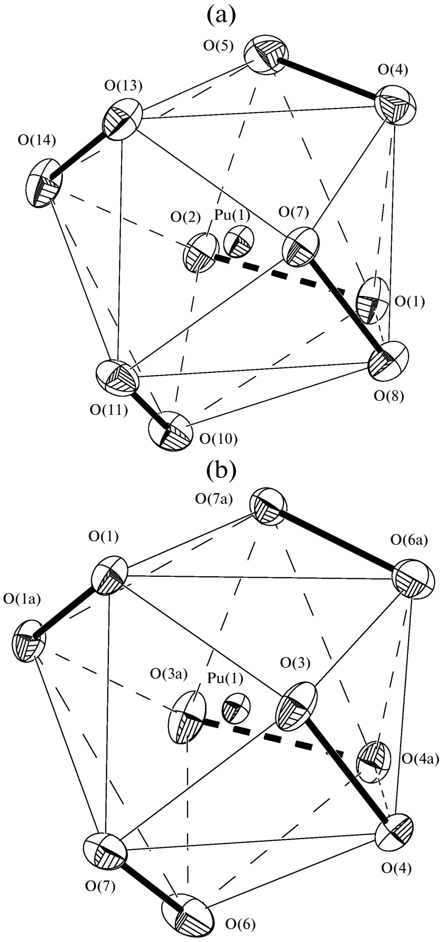

Fig. 2. Coordination polyhedra of the Pu atom in (a) $[C(NH_2)_3]_6[Pu(CO_3)_5] \cdot 3H_2O$ and (b) $[C(NH_2)_3]_6[Pu(CO_3)_5] \cdot 4H_2O$. The edges linking the O atoms of the same carbonate ion are indicated with heavy lines.

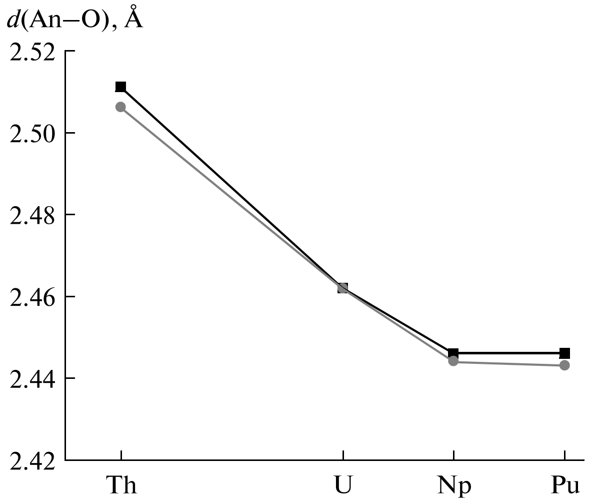

Fig. 3. Average An–O bond lengths in the complexes $[C(NH_2)_3]_6[An(CO_3)_5] \cdot nH_2O$ (squares and circles refer to the trihydrates and tetrahydrates, respectively).

differ from the spectra of the corresponding hydrated ions (Table 7). The influence of the ligand environment on the intensities and positions of the bands of the electronic *f–f* transitions in the spectra of the An^{4+} ions depends on both the structure of the complex and the electronic configuration of the actinide ion. For the series of the carbonate complexes studied, the spectra of the U^{4+} and Pu^{4+} complexes (these ions have even-electron configurations) show bathochromic shifts of the absorption peaks. Note that the solid-state complexes and solutions of the U^{4+} and Pu^{4+} ions in the presence of carbonate ions agree well in spectroscopic characteristics. According to spectrophotometric data on the equilibrium between tetra- and pentacarbonate U^{4+} complexes in CO_2/HCO_3^-, solution [20], the molar absorption coefficient of the main peak of the complex $[U(CO_3)_5]^{6-}$ at 660 nm is 35.5 L/(mol cm). The formation of pentacarbonate complexes is also assumed for carbonate solutions of other An(IV) ions [20]. The behavior of Pu^{4+} in the presence of Na_2CO_3 is described in [21]. The main absorption peak due to the *f–f* transition is shifted to 485 nm (ε_{calc} =

Table 7. Selected absorption bands in the electronic absorption spectra of the solid-state carbonate complexes

Complex		Position of the peak, nm
U(IV)	$[C(NH_2)_3]_6[U(CO_3)_5] \cdot 3H_2O$	406, 426, 447, 464, 493, 538, 614, 659, 675 (ε = 25 L/(mol cm)); 701, 740, 801
	U^{4+} aqua ion [22]	405, 426, 452, 469, 486, 495, 525, 590, 656, 670 (ε = 40 L/(mol cm)); 692, 762
Np(IV)	$[C(NH_2)_3]_6Np[(CO_3)_5] \cdot 3H_2O$	463, 502, 581, 658, 693, 704, 726, 740, 763, 799, 943 (ε = 30 L/(mol cm)); 1017
	Np^{4+} aqua ion [23]	504, 590, 723, 743, 825, 960 (ε = 150 L/(mol cm))
Pu(IV)	$[C(NH_2)_3]_6Pu[(CO_3)_5] \cdot 3H_2O$	423, 468, 486 (ε = 30 L/(mol cm)); 628, 684, 793, 824
	Pu^{4+} aqua ion [24]	470 (ε = 56); 655, 726, 730, 815

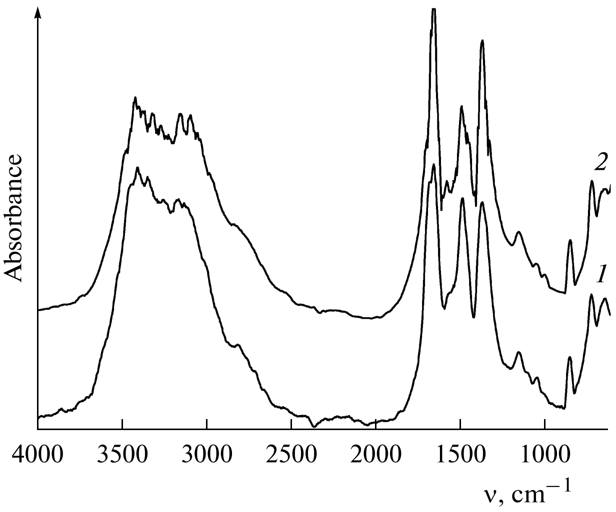

Fig. 4. IR spectra of the solid-state complexes (*1*) $[C(NH_2)_3]_6[Pu(CO_3)_5] \cdot 3H_2O$ and (*2*) $[C(NH_2)_3]_6[Pu(CO_3)_5] \cdot 4H_2O$.

95 L/(mol cm)) compared to the spectrum of the hydrated ion.

The electronic absorption spectrum of the complex $[C(NH_2)_3]_6[Np(CO_3)_5] \cdot 3H_2O$ differs substantially from the spectrum of the hydrated Np^{4+} ion in both the number and intensities of the observed transitions. The spectra of the solid-state complex and its solution in 1 M $HClO_4$ are shown in Fig. 5. Obviously, the influence of the coordinated carbonate ion in this complex on the spectral pattern is not the case of U^{4+} and Pu^{4+}, which can be attributed to the electronic configuration $5f^3$ of the Np^{4+} ion.

To sum up, we obtained two series of isostructural Th(IV), U(IV), Np(IV), and Pu(IV) carbonate complexes, determined their structures, and examined using IR and electronic absorption spectroscopy. An interesting feature of their synthesis is that crystallization initially gives trihydrate and then tetrahydrate, which is very uncommon; this effect was observed for all the elements studied. Such a unified behavior from thorium to plutonium seems to be somewhat surprising because these elements have substantially different hydrolytic and complexing properties.

For the complexes studied, we revealed that the plot of the An–O bond length vs. the atomic number of the central complexing ion becomes distinctly nonlinear at the end of the sequence Th–Pu (the linear plot agrees with the actinide compression concept and holds well for actinide dioxides). A similar nonlinearity at the end of the sequence Th–Am has been noted for complexes with "unsaturated" lacunar heteropoly anions $P_2W_{17}O_{61}^{10-}$ [25]. It is interesting to study this phenomenon in more detail with a greater number of experimental systems, along with theoretical methods of attacking this problem.

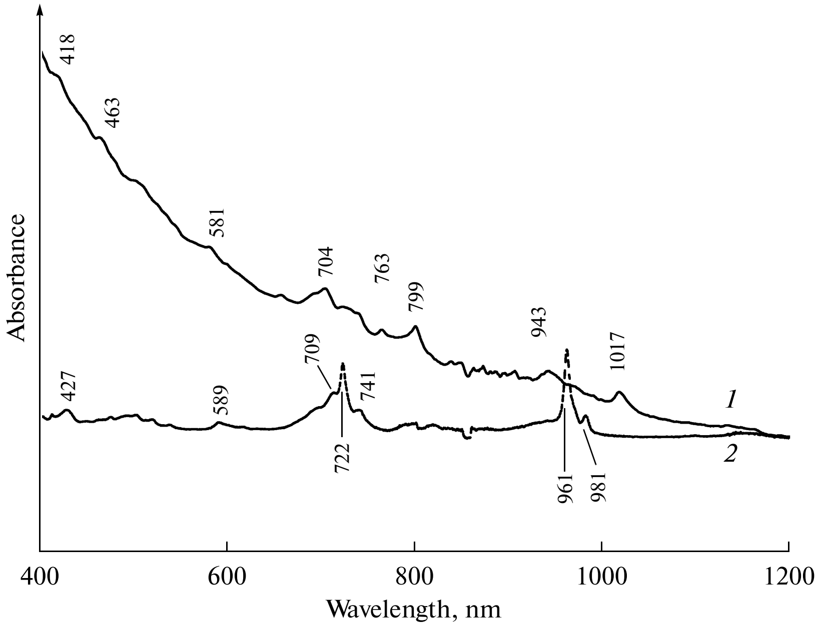

Fig. 5. Electronic absorption spectra of (*1*) the crystalline complex $[C(NH_2)_3]_6[Np(CO_3)_5] \cdot 3H_2O$ and (*2*) its solution in 1 M $HClO_4$.

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REFERENCES

1. Clark, D.L., Hobart, D.E., and Neu, M.P., *Chem. Rev.*, 1995, vol. 95, p. 25.
2. Gogolev, A.V., Zakharova, E.V., Rodygina, N.I., et al., *Radiokhimiya*, 2006, vol. 48, p. 224.
3. Voliotis, S. and Rimsky, A., *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1975, vol. 31, p. 2612.
4. Marsh, R.E. and Herbstein, F.H., *Acta Crystallogr., Sect. B: Struct. Sci.*, 1988, vol. 44, p. 77.
5. Voliotis, S. and Rimsky, A., *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1975, vol. 31, p. 2615.
6. Yamnova, N.A., Pushkarevskii, D.I., and Voloshin, A.V., *Dokl. Akad. Nauk SSSR*, 1990, vol. 35, p. 12.
7. Clark, D.L., Conradson, S.D., Keogh, D.W., et al., *Inorg. Chem.*, 1998, vol. 37, p. 2893.
8. Runde, W., Brodnax, L.F., Goff, G.S., et al., *Chem. Commun.*, 2007, p. 1728.
9. Budantseva, N.A., Grigor'ev, M.S., Mishkevich, V.I, et al., *Russ. J. Coord. Chem.*, 2011, vol. 37, no. 9, p. 701.
10. *APEX2*, Madison (WI, USA): Bruker AXS Inc., 2006.
11. *SAINT-Plus. Version 6.01*, Madison (WI, USA): Bruker AXS Inc., 1998.
12. Sheldrick, G.M., *SADABS*, Madison (WI, USA): Bruker AXS Inc., 2004.
13. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, p. 112.
14. Favas, M.C. and Kepert, D.L., *Prog. Inorg. Chem.*, 1981, vol. 28, p. 309.
15. *The Chemistry of the Actinide and Transactinide Elements*, Morss, L.R., Edelstein, N.M., Fuger, J., and Katz, J.J., Eds., Dordrecht: Springer, vol. 3, 2006.
16. Sension, R.J., Hudson, B., and Callis, P.R., *J. Phys. Chem.*, 1990, vol. 94, p. 4015.
17. Todorova, T., Krocher, O., and Delley, B., *J. Mol. Struct.*, 2009, vol. 907, p. 16.
18. Vagenas, N.V., Gatsonli, A., and Kontoyannis, C.G., *Talanta*, 2002, vol. 59, p. 831.
19. Frost, R.L. and Cejka, J., *J. Raman Spectrosc.*, 2007, vol. 38, p. 1488.
20. Bruno, J., Grenthe, I., and Robouch, P., *Inorg. Chim. Acta*, 1989, vol. 152, p. 221.
21. Charyulu, M.M., Pius, I.C., Kadem, A., et al., *J. Radioanal. Nucl. Chem.*, 1991, vol. 152, p. 479.
22. Stein, L., Williams, C.W., Fox, I.M., and Gebert, E., *Inorg. Chem.*, 1966, vol. 5, p. 662.
23. Lahalle, M.P., Krupa, J.C., Guillaumont, R., and Rizzli, C., *Less-Comm. Met.*, 1986, vol. 122, p. 65.
24. Cohen, D.J., *J. Inorg. Nucl. Chem.*, 1961, vol. 18, p. 211.
25. Sokolova, M., Fedosseev, A., Andreev, G., et al., *Inorg. Chem.*, 2009, vol. 48, p. 9185.