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# Polymeric Structure of Oxalato-Bridged Complexes of Tetravalent Actinides Th, U, Np and Pu

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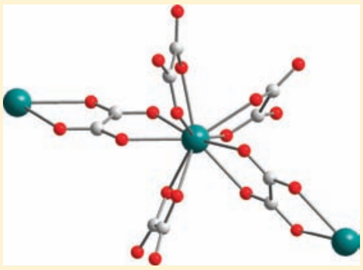
S Supporting Information

**ABSTRACT:** A series of isostructural oxalates of Th, U, Np, and Pu have been synthesized. The crystal structure of $\{C(NH_2)_3\}_4[An(C_2O_4)_4]\cdot 2H_2O$ comprises infinite $[An(C_2O_4)_4]^{4n-}$ chains, guanidinium cations and water molecules. Each An atom is connected to five oxalate anions, two of which act as bridging tetradentate ligands, while the other three function as terminating bidentate ligands. Electron and IR spectra of the compounds as well as the results of thermal analysis correlate with their structure. An actinide contraction effect is demonstrated by a decrease in the An−O interatomic distances and the volumes of An atom coordination polyhedra and Voronoi−Dirichlet polyhedra. Ten-coordinate An oxalates are discussed in terms of continuous shape measures approach.



## ■ INTRODUCTION

Oxalate anion complexes are one of the traditional research objects within actinide chemistry. Significant attention has been paid to the interaction of actinides with oxalate ion in aqueous solution because of the role of oxalic acid in chemical processing of actinides. For example, oxalate precipitation is one of the important steps in the separation and purification of uranium and transuranium elements. The use of oxalate ion as a precipitating agent is warranted by the sufficiently low solubility of An oxalates even in acidic solutions. There is a large body of information regarding oxalate solubility for actinides in various oxidation states from 3 to 6.[1] The formation of complexes in solutions has been also studied for Th, U, and transuranium elements.

At the same time, the structural chemistry of actinide oxalates is characterized by certain unilaterality. The vast majority of structurally studied actinide oxalates are complexes of uranium(VI). Linearity of uranyl-ion dictates the bipyramidal geometry of U coordination polyhedron, but relative flexibility of the oxalate-ion permits a formation of various crystal structures. Depending on uranyl/oxalate ratio, mononuclear,[2] dimeric,[3,4] infinite chained,[5,6] or layered[7,8] structures can be formed with oxalate anions usually playing the role of tetradentate bridging or bidentate chelate ligands. Several complexes of neptunyl(V) have been also structurally characterized[9,10] including 3D structure $NH_4NpO_2C_2O_4\cdot nH_2O$.[11] As for plutonium oxocation, among the known Pu(VI) oxalates the only structurally characterized are $[Co(NH_3)_6]_2[(PuO_2)_2(C_2O_4)_4]\cdot 6H_2O$[12] and $[PuO_2(C_2O_4)]\cdot 3H_2O$.[13]

Characteristic of actinides in lower oxidation states are their higher coordination numbers. Numerous EXAFS studies of actinide(IV) hydration number show that An(IV)−O bond lengths correlates with the coordination number 9[14−16] with the exception of U for which CN 10 has been proposed.[17] However, Torapava et al.[16] suggested CN 9 even for U from the analysis of their own and literature data and basing on the fact that the higher symmetrical tricapped trigonal prismatic configuration of $An^{4+}$ cation surrounding is more probable.

Crystallographic studies of solid $An^{4+}$ oxalates indicate the high diversity of coordination polyhedra of the central atoms. Several simple An(IV) oxalate hydrates are known including $[U(C_2O_4)_2(H_2O)_2]$,[18] $[Th(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$,[19] $[U(C_2O_4)_2]\cdot 6H_2O$, and $[Np(C_2O_4)_2]\cdot 6H_2O$.[20] In the structures of hexahydrates, the oxygen atoms of oxalate-ions form a distorted cubic environment of the actinide atoms resulting in untypical CN equal to 8. Metal atoms are connected into four-membered rings through bis-chelating oxalate-ions with the formation of neutral layers $[An(C_2O_4)_2]_\infty$; the water molecules are localized in the interlayer space. The crystal structure of $[U(C_2O_4)_2(H_2O)_2]$ also contains layers, but in this case two water molecules enter in the coordination sphere of U atom and the interlayer space remains empty. Ten-fold coordination surrounding of An atom has been also found in the structure of Th oxalate with potassium, $K_4[Th(C_2O_4)_4]\cdot 4H_2O$.[21] Tetradentate bridging oxalate-ions join Th atoms into infinite chains parallel to [110] while other three oxalate-ions coordinating metal atom play the role of bidentate ligands. The coordination polyhedron of Th atom is a bicapped square antiprism with very small deviations from the ideal $D_{4d}$ symmetry. In the double U oxalate with Ba, $Ba_2[U(C_2O_4)_4(H_2O)]\cdot 7H_2O$, the coordination sphere of the central atom is formed by oxygen atoms of four bidentate oxalate-ions and one water molecule. The coordination polyhedron of U atom is an intermediate

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between tricapped trigonal prism and capped square antiprism.[22]

By this means, actinides in lower oxidation states can form with oxalate ion structures of various topologies with tendency to polymerization. Oxalate ions function as bidentate terminating or tetradentate bridging ligands forming a five-membered ring with the An atom. Depending on the composition and structure of the compound, a central An atom is coordinated by up to five oxalate ions. The main structural units found in such An(IV) compounds are $\{An(\mu_2\text{-}C_2O_4)_5\}$, $\{An(\mu_2\text{-}C_2O_4)_2(C_2O_4)_3\}$, $\{An(C_2O_4)_4(H_2O)\}$, $\{An(\mu_2\text{-}C_2O_4)_4(H_2O)\}$, $\{An(\mu_2\text{-}C_2O_4)_4(H_2O)_2\}$. Other structural units can be found when additional anions (other than oxalate) are present in the structure.

In spite of the fact that the first identification of solid An oxalate was reported in 1901,[23] and numerous solid An compounds have been prepared and characterized since that time, most of these materials are binary oxalates of U(VI) and U(IV). Other actinides, especially TRU, have been significantly less studied, particularly with regard to structural determination. The rare examples of structural studies for transuranium elements in lower oxidation states are $K[Pu(C_2O_4)_2(OH)]\cdot 2.5H_2O$,[24] $[Pu_2(C_2O_4)_3(H_2O)_6]\cdot 3H_2O$,[24] $[Np(C_2O_4)_2]\cdot 6H_2O$,[20] $[Np_2(HC_2O_4)_2(C_2O_4)_3(H_2O)_4]\cdot 5H_2O$,[25] and $(Him)[Np(C_2O_4)(CH_3SO_3)_3(H_2O)_2]$.[26] We present here new oxalates of tetravalent Th, U, Np and Pu with guanidinium, $\{C(NH_2)_3\}_4[An(C_2O_4)_4]\cdot 2H_2O$ (**1**–**4**), which form a series of isostructural compounds.

## EXPERIMENTAL SECTION

***Caution!*** *$^{237}$Np and $^{239}$Pu are highly radioactive isotopes and must be handled in dedicated facilities with equipment suitable for radioactive materials.*

**Synthesis.** Complexes were synthesized by treatment of solid $An(C_2O_4)_2\cdot 6H_2O$ with an aqueous solution of $\{C(NH_2)_3\}_2C_2O_4$ (~0.1–0.5 mol/L), prepared by neutralizing 1.0 mol/L of guanidinium carbonate aqueous solution with 1.0 mol/L of oxalic acid solution up to an An:$\{C(NH_2)_3\}_2C_2O_4$ molar ratio of about 1:3–1:4 at temperatures of 30–60 °C. Particularly 50 mg (~0.095 mmol) of $An(C_2O_4)_2\cdot 6H_2O$ was completely dissolved by heating slightly and stirring in 0.8 mL of 0.5 mol/L (0.4 mmol) of $\{C(NH_2)_3\}_2C_2O_4$. Large well shaped prismatic crystals were obtained in a few hours when the resulting clear solutions were stored at room temperature. The yield was about 80%.

**X-ray Diffractometry.** The data were collected on Bruker KAPPA APEX II and Bruker Smart diffractometers with CCD area detectors using graphite monochromated MoK$\alpha$ ($\lambda$ = 0.71073 Å) radiation at $T$ = 100 K. The SAINT program was used to integrate the diffraction profiles,[27] and the data were corrected for Lorentz and polarization effects and for absorption using SADABS.[28] The crystal structures were solved by direct method and refined by full-matrix least-squares refinement against $F^2$. All the non-hydrogen atoms were readily located, and their positions were refined anisotropically. Hydrogen atoms were also located and refined isotropically. The main crystal data and details of the final refinement calculations are indicated in Table 1.

**Spectroscopy.** NIR and IR spectra were measured using Shimadzu UV3100 and Specord M80 spectrometers, respectively. Samples of ~2 wt % of the solids were prepared in NaCl pellets.

**Thermal analysis.** Simultaneous thermogravimetric and differential thermal analyses were conducted at a constant heating rate of 5 °C/min up to 800 °C using Paulik–Paulik–Erday Q-1500 system with a platinum sample holder.

**Table 1. Crystal Data and Details of Final Refinement Calculations for Compounds 1–4**

| compound | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $a$, Å | 19.5854(5) | 19.6703(4) | 19.6222(2) | 19.6361(4) |
| $b$, Å | 12.0780(3) | 11.9387(2) | 11.9186(2) | 11.8811(2) |
| $c$, Å | 12.9363(3) | 12.8072(2) | 12.7670(2) | 12.7195(2) |
| $\beta$, deg | 118.161(1) | 117.811(1) | 117.725(1) | 117.437(1) |
| $V$, Å$^3$ | 2697.87(10) | 2660.21(8) | 2643.01(7) | 2633.66(8) |
| no. collected reflns | 18 385 | 24 719 | 49 291 | 50 342 |
| no. unique reflns | 3592 | 5874 | 8705 | 7770 |
| no. params | 237 | 237 | 237 | 237 |
| 2$\theta$max | 58 | 70 | 82 | 78 |
| R | 0.0235 | 0.0345 | 0.0356 | 0.0325 |
| wR($F^2$) | 0.0555 | 0.0811 | 0.0884 | 0.0792 |

## RESULTS AND DISCUSSION

The An atoms in the crystal structures of **1**–**4** are coordinated by five chelating oxalate anions (Figure 1). Three of these oxalate anions are bidentate terminating ligands, while other two function as tetradentate bridging ligands. The An-O distances differ significantly depending on the role of the oxalate ligand to which the corresponding O atoms belong. Shorter distances are observed for O atoms of terminating oxalates with the lowest and the highest values equal to 2.3742(20) and 2.4810(25) Å found in Pu and Th complexes, respectively (Table 2). The An-O distances for bridging $\mu_2$-oxalates are in the range from 2.4942(25) (**3**) to 2.5524(22) Å (**1**).

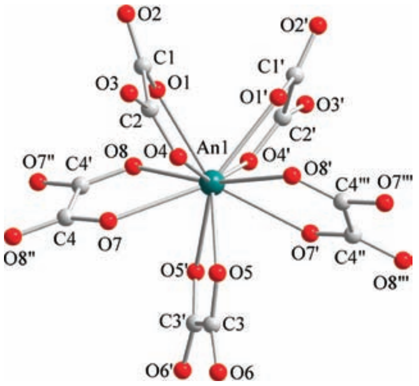

**Figure 1.** Coordination of An atom and atomic numbering in $\{C(NH_2)_3\}_4[An(C_2O_4)_4]\cdot 2H_2O$.

The coordination polyhedron of An atoms in 1–4 is a sphenocorona (Supporting Information Figure S1). Its volume depends on the atomic number of the central atom and decreases from 34.015 Å$^3$ for Th to 31.278 Å$^3$ for Pu, reflecting the "actinide contraction" effect (Table 2). This effect is also manifested by decreases in the values of other geometrical parameters such An–O bond lengths, volumes of packing polyhedra[29] (or Voronoi–Dirichlet polyhedra[30]) for An atoms. It should be noted that a monotonic dependence of unit cell parameters and volume is also observed with the exception of the $a$ parameter.

Bridging oxalate ions connect adjacent An atoms so that infinite $[An(C_2O_4)_4]^{4n-}$ chains are formed along the $c$ axis (Figure 2). Guanidinium cations and water molecules are located between these chains. The distances between adjacent

Table 2. Main Interatomic Distances in the Crystal Structures of 1−4

| distance, Å | Th | U | Np | Pu |
|---|---|---|---|---|
| An(1)−O(1) | 2.4682(22) | 2.4069(25) | 2.4029(19) | 2.3815(21) |
| An(1)−O(4) | 2.4810(25) | 2.4382(33) | 2.4209(29) | 2.4125(29) |
| An(1)−O(5) | 2.4407(22) | 2.4008(25) | 2.3809(19) | 2.3742(20) |
| An(1)−O(7) | 2.5498(24) | 2.5153(32) | 2.4942(25) | 2.4982(29) |
| An(1)−O(8) | 2.5524(22) | 2.5255(23) | 2.5200(17) | 2.4954(19) |
| average An−$O_{term}$ | 2.4633 | 2.4153 | 2.4016 | 2.3894 |
| average An−$O_{bridg}$ | 2.5511 | 2.5204 | 2.5071 | 2.4968 |
| volume of An coordination polyhedron, $Å^3$ | 34.015 | 32.278 | 31.774 | 31.278 |
| volume of An packing polyhedron, $Å^3$ | 11.665 | 11.092 | 10.898 | 10.756 |

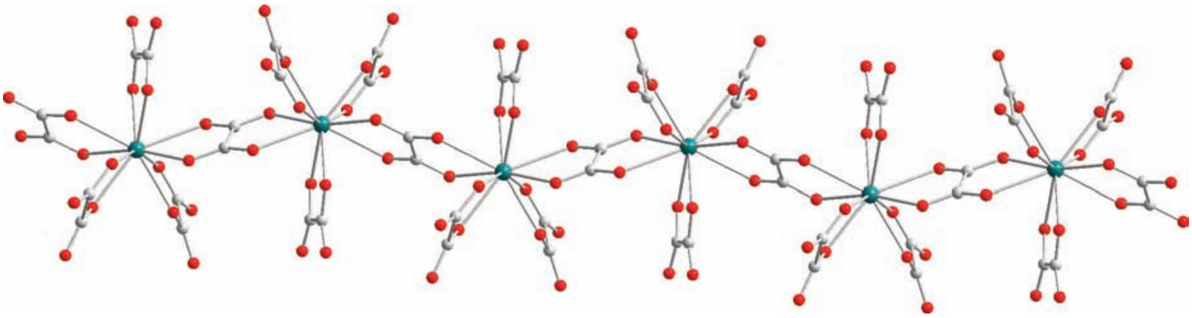

**Figure 2.** Infinite chains $[An(C_2O_4)_4]^{4n-}$ in structures of $\{C(NH_2)_3\}_4[An(C_2O_4)_4]\cdot 2H_2O$.

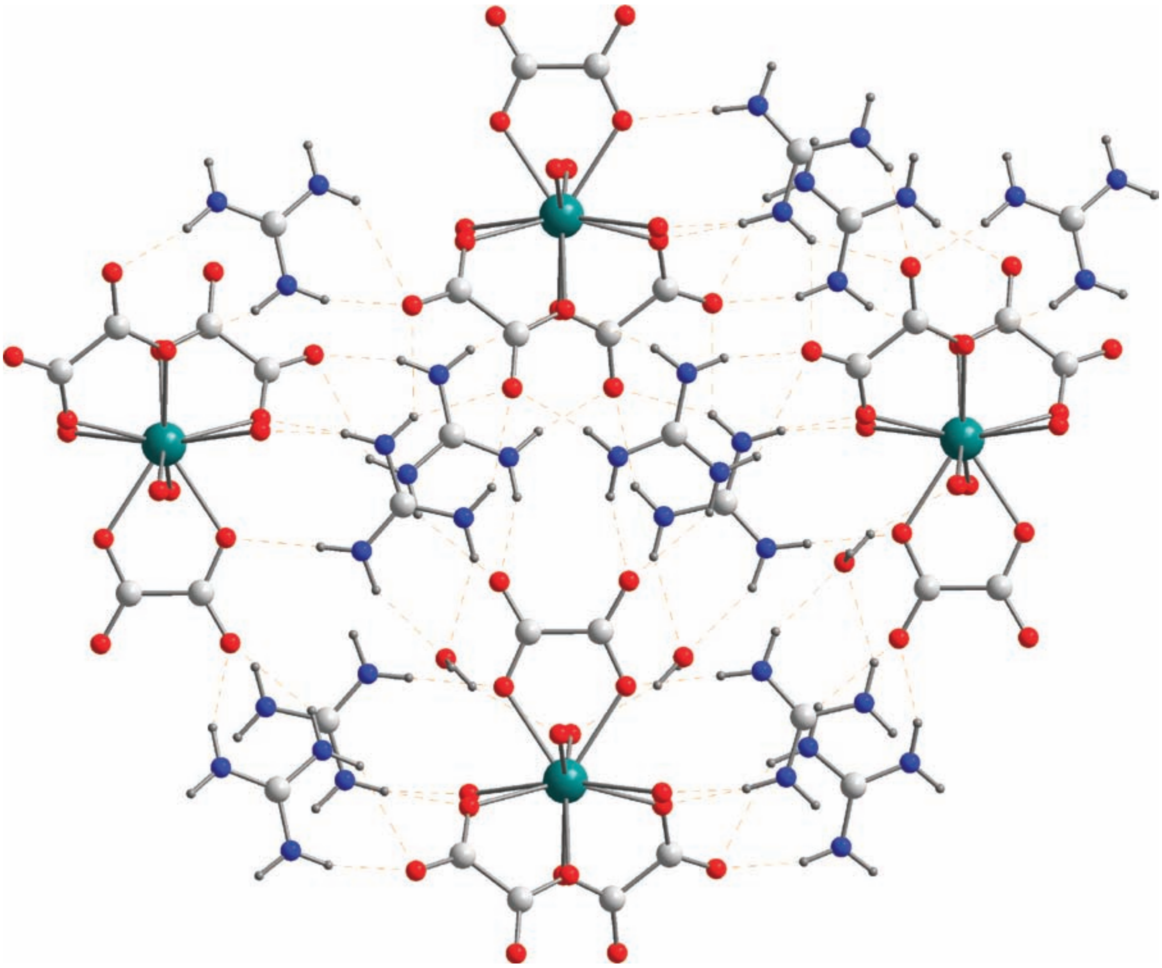

**Figure 3.** Structure of hydrogen bond network in **1−4**.

**Table 3. Maxima of Main Absorption Bands in the IR Spectra of 1−4 and Their Assignments**

| assignment | wavenumber, $cm^{-1}$ | | | |
|---|---|---|---|---|
| | 1 | 2 | 3 | 4 |
| $\nu(NH_2)$; $\nu(OH)$ | 3476; 3404; 3180 | 3484; 3412; 3188 | 3472; 3420; 3208 | 3480; 3384; 3168 |
| $\nu_{as}(COO)$; $\delta(H_2O)$; $\nu(CN)$; $\delta(NH_2)$; | 1680; 1644; 1612; 1580 | 1680; 1660; 1628; 1584 | 1672; 1640; 1624;1584 | 1696; 1664, 1648; 1572 |
| $\nu_s(COO)$; | 1440; 1420 | 1432; 1404 | 1432; 1404; 1356 | 1428; 1396 |
| $\delta(NH_2)$; $\delta(COO)$ | 1316; 1288; 1140−1008 | 1320; 1292; 1160−1012 | 1284; 1136−992 | 1292; 1136−1060 |
| $\nu(CC)$ | 900 | 904 | 904 | 892 |
| $\delta(COO)$; | 784 | 792 | 792 | 788 |
| $\rho(COO)$; $\delta(NCN)$ | 612; 544 | 604; 536 | 616; 528 | 592; 532 |
| $\delta(CN_3)$ | 484 | 496 | 472 | 488 |

An atoms within the same chains are equal to 6.589, 6.522, 6.495, and 6.475 Å for compounds 1−4, respectively. The shortest distances between An atoms belonging to different chains are very similar for all four structures (10.041−10.087 Å). The packing of the chains as viewed along the *c* axis is shown in Supporting Information Figure S2. Analogous 1D polymeric structures based on $[An(C_2O_4)_4]^{4n-}$ chains were found in orthorhombic and triclinic modifications of $K_4[U(C_2O_4)_4]\cdot4H_2O$,[31] as well as in $K_4[Th(C_2O_4)_4]\cdot4H_2O$,[21] which is isostructural with the triclinic modification of $K_4[U(C_2O_4)_4]\cdot4H_2O$.

Coordination to the An atom significantly influences the length of C−O bonds in oxalate ligands. The C−O distances for coordinating oxygen atoms are longer than for noncoordinating atoms and equal to 1.247(4)−1.259(4) Å and 1.263(4)−1.281(4) Å for bridging and terminating oxalates, respectively, while free oxygen atoms show distances ranging from 1.224(4) to 1.237(4) Å. The difference in C−O bond values within the same carboxylic group thus lie in the range from 0.027 to 0.054 Å. The C−C bonds have typical values from 1.530(6) to 1.554(4) Å.

Almost all hydrogen atoms of guanidinium cations participate in the formation of the H-bond network (Figure 3, Supporting Information Tables S1−S4). Two types of H-bonds formed by guanidinium cations can be distinguished: linear (2-center) and bifurcated (3-center). H1′, H5, and H5′ atoms take part in the formation of bifurcated bonds, while other H atoms (except H3 which does take part in any H-bond) form linear bonds. Oxygen atoms of oxalate ions act as acceptors. It is worth noting that each oxalate oxygen atom takes part in the formation of at least two bonds: either a coordination bond with An atom, or a hydrogen bond with a guanidinium cation or water molecule. O1, O4, and O7 atoms thus form by one coordination and one hydrogen bond, O5 and O8 atoms form by one coordination and two hydrogen bonds, O3 and O6 atoms form by two hydrogen bonds, and O2 atom forms three hydrogen bonds. The water molecule participates in the formation of three hydrogen bonds, one of which is linear (O9−H2W···N5), another is bifurcated (O9−H1W···O7, O9−H1W···O5). The H-bond network has layered topology and connects $[An(C_2O_4)_4]^{4n-}$ polymeric chains, guanidinium cations, and water molecules in a 3D structure.

The reported complexes represent ten-coordinate structures. Generally, ten-coordination is a rare phenomenon observed almost exclusively in f-element compounds,[32] of those the major proportion belongs to lanthanide compounds. Among the actinides, the most common examples of ten-coordination correspond to Th and U complexes. As for oxalates, the ten-coordination of An atom has been previously observed in simple hydrates, as well as in double and triple oxalates. Analysis of these compounds shows that their coordination polyhedra are mostly close to the sphenocorona or the bicapped square antiprism formed by oxygen atoms of five oxalate-ions bidentately linking to the An atom, with the exception of Th and U oxalate hydrates, $[Th(C_2O_4)_2(H_2O)_2]\cdot2H_2O$ and $[U(C_2O_4)_2(H_2O)_2]$. In the structure of $[U(C_2O_4)_2(H_2O)_2]$, oxygen atoms of four chelate oxalate-ions form a square antiprismatic surrounding of U atom which is completed by two water oxygen atoms capping two bases. Similarly, oxygen atoms of four oxalate-ions and two water molecules comprise sphenocoronal surrounding of Th atom in $[Th(C_2O_4)_2(H_2O)_2]\cdot2H_2O$.

To compare the coordination polyhedra of ten-coordinate An oxalates we applied the continuous shape measures (CShM) approach.[33] This approach provides a quantitative measure S(P,Q) of the difference between the shapes of two polyhedra, P and Q. It can be seen from the Supporting Information Table S5 that the "actinide contraction" effect does not influence the shape of CPs in compounds **1−4** while the volumes of these CPs change significantly. The S(P,Q) values close to 0 mean that the CPs contract isotropically with change of central atom from Th to Pu. At the same time, the more significant difference is observed in the shapes of CPs for **1−4** as compared to other two known An oxalates with sphenocoronal coordination of An atom, $K_4[U(C_2O_4)_4]\cdot4H_2O$ (orthorhombic) and $[Th(C_2O_4)_2(H_2O)_2]\cdot2H_2O$. As for the oxalates with bicapped square antiprismatic surrounding of An atom, the S(P,Q) values do not exceed 0.7 (Supporting Information Table S6) meaning that the shapes of these coordination polyhedra variate to a lesser degree than the shapes of sphenocoronal polyhedra. The more predefined shape of the bicapped square antiprismatic surrounding of the central atom reflects in more constant volumes of CPs. Supporting Information Table S7 shows that the volumes of the corresponding CPs in U oxalates lie in the range from 32.708 (for $(NH_4)_2[U_2(C_2O_4)_5]\cdot0.7H_2O$[34]) to 32.892 $Å^3$ (for $Mg_2K_2[U_2(C_2O_4)_7]\cdot11H_2O$[35]) with the exception of mixed site compound, $Na_{2.46}[U_{1.54}Nd_{0.46}(C_2O_4)_5]\cdot7.6H_2O$,[34] whose CP volume (33.815 $Å^3$) is more close to the corresponding value (33.890 $Å^3$) for Th oxalate, $K_4[Th(C_2O_4)_4]\cdot4H_2O$. The volumes of CPs for U oxalates with sphenocoronal surrounding have lower values, 32.278 and 31.857 $Å^3$ for compounds 2 and $K_4[U(C_2O_4)_4]\cdot4H_2O$ (orthorhombic), respectively. It is worth noting that the volumes of Voronoi-Dirichlet polyhedra show significantly less variance depending on the shape of the central atom surrounding and have very close values for a given metal atom, for example, from 11.061 to 11.152 $Å^3$ for U oxalates.

The structure of compounds 1−4 is in good agreement with their IR spectra (Supporting Information Figure S3). The maxima of the main absorption bands and their possible assignments based on the literature[36−40] are listed in Table 3. In the high-frequency spectral range (3500−3100 $cm^{-1}$), a large number of intensive bands are observed with the large number of shoulders corresponding to characteristic vibrational frequencies, typical of $C(NH_2)_3^+$ cation and water molecules. Very strong bands in the 1690−1620 $cm^{-1}$ range are present in spectra of all compounds and result from overlapping of stretching modes $\nu_{as}$(CO) of oxalate anions and deformation vibrations $\delta(H_2O)$ of water molecules. The further complication of this band can be attributed to the "scissors" vibration mode $\delta(NH_2)$ of guanidinium cations.[41] Besides the main maxima, it is possible to identify low-frequency components at ~1620 $cm^{-1}$ corresponding to $\nu_{as}$(CO) of tetradentate oxalate-ions.[42] As a rule in the spectra of compounds including tetradentate-bridged oxalate, only two stretching modes of $\nu_{as}$(CO) in the range of 1700−1630 and $\nu_s$(CO) in the range of 1350−1310 $cm^{-1}$ are observed. Very weak bands observed at ~1350 $cm^{-1}$ in the spectra of compounds 1−4 can be assigned to symmetrical modes of oxalate-ions. At the same time, in the IR spectrum of oxalate-ion in aqueous solution, the intensity of the analogous $\nu_s$(CO) band is practically equal to the intensity of $\nu_{as}$(CO).[43] Symmetrical modes of bidentate oxalate-ions are exhibited by strong bands at ~1420 $cm^{-1}$.

Optical spectra of $U^{4+}$, $Np^{4+}$, and $Pu^{4+}$ ions have been discussed in a number of works.[44−49] Theoretically the expected number of bands for electronic configurations $5f^2$ ($U^{4+}$), $5f^3$ ($Np^{4+}$), and $5f^4$ ($Pu^{4+}$) taking into account spin−orbital effects and ligand field influence is relatively high. In the actual spectra of solid compounds a considerably smaller number of absorption bands can be distinguished even if the actinide atom is present in a matrix as dilute impurity. The U(IV) spectrum in $\beta$-$ThGeO_4$ has 17 main peaks.[50] The experimental spectra of oxalate complexes **2−4** in the range 1200−400 nm contain a small number of absorption bands (Supporting Information Figures S4−S6). Evidently each band corresponds to several unresolved *ff*-transitions resulting in sufficiently large band half-widths. Parameters of the most intensive absorption bands of complexes are listed in Table 4.

**Table 4. Maxima of Main Absorption Bands in Electron Spectra of 2−4**

| compound | $\lambda$, nm |
|---|---|
| 2 | 505.9; 571.0; 626.4; 681.6; 1077.6; 1175.3 |
| 3 | 600.9; 715.2; 737.7; 831.7; 968.4; 988.1; 1157.4 |
| 4 | 487.8; 546.7; 660.6; 716.1; 853.2; 1058.5 |

Results of the thermal analysis are in good agreement with the structural data. For all compounds **1−4**, several weight losses corresponding to different degradation steps can be identified (Supporting Information Table S8). At the first stage, the crystallization water molecules are released with small endothermic effect. The destruction of organic components starts above 210 °C; at this stage, significant mass loss is observed that corresponds to the partial destruction of the compounds. According to the weight loss curves, compounds **1−4** decompose to $An(C_2O_4)_2$ in two overlapping steps through the formation of $\{C(NH_2)_2\}[An(C_2O_4)_3]$. TG curve shows corresponding decrease with an inflection point, while DTA curve contains one strong and two slight endothermic effects. At the fourth stage, endothermical decomposition of $An(C_2O_4)_2$ occurs leading to the formation of the $An(CO_3)_2$. Above 410 °C, the carbonate exothermically decomposes into $AnO_2$, which in the case of the uranium compound oxidizes to $U_3O_8$. This step is accompanied with the corresponding mass growth and a slight endothermic effect. The similarity in the thermal behavior counts in favor of the stability of 4+ oxidation state in the compounds **1−4**.

## CONCLUSION

A series of isostructural oxalates of Th, U, Np, and Pu have been synthesized. Their composition is described by the formula $\{C(NH_2)_3\}_4[An(C_2O_4)_4]\cdot 2H_2O$. The crystal structure comprises infinite $[An(C_2O_4)_4]^{4n-}$ chains, guanidinium cations and water molecules which are consolidated into an overall 3D structure by an extended network of hydrogen bonds. The difference in the ionic radii of An atoms results in a decrease of interatomic An−O distances and unit cell parameters as the atomic number of the central atom increases. Coordination polyhedra of An atom undergo isotropic contraction as shown using continuous shape measures analysis. Comparison with other ten-coordinate An oxalates has shown that the volumes of coordination polyhedra depends on the An atomic number and the shape of corresponding CPs, while do not depend on the presence of water molecules in the coordination sphere. At the same time, Voronoi−Dirichlet polyhedra have more constant volumes irrespective of the coordination surrounding geometry. The structure of the compounds 1−4 is confirmed by electron and IR spectroscopy. Thermal analysis shows that the decomposition of $\{C(NH_2)_3\}_4[An(C_2O_4)_4]\cdot 2H_2O$ in air starts with the dehydration and proceeds through the organic components decomposition leading to the successive formation of An anhydrous oxalates and carbonates. The carbonates decompose to $AnO_2$ which, in case of U compound, oxidizes to $U_3O_8$.

## ASSOCIATED CONTENT

### Supporting Information

Crystallographic data in CIF format, supplementary figures, and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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