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Uranyl Nitrates: By-Products of the Synthetic Experiments or Key Indicators of the Reaction Progress?

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Abstract: Six novel uranyl nitrate compounds $K_3[(UO_2)(NO_3)Cl_3](NO_3)$ (**1**, **2**), $\alpha\text{-Cs}_2[(UO_2)(NO_3)Cl_3]$ (**3**), $[(UO_2)(NO_3)_2(H_2O)_2][(CH_3NH_3)_2(NO_3)_2]$ (**4**), $Cs_2[(UO_2)(NO_3)_4]$ (**5**), and $[(UO_2)_2(OH)_2(NO_3)_2(H_2O)_3](H_2O)$ (**6**) have been prepared from aqueous solutions. Their structures were analyzed using single-crystal X-ray diffraction technique. Structural studies have shown that the crystals of **1** and **2** are isotypic but differ in the distortion at the counter ion's sites. The crystal of **3** is a low-temperature polymorph modification of the recently studied compound. The crystal structure of **4** is composed of uranyl-dinitrate-dihydrate and methylamine-nitrate electroneutral complexes linked through the system of H-bonds. The crystal structure of **5** is based on the finite $[(UO_2)(NO_3)_4]^{2-}$ clusters that are arranged in pseudo-chained complexes extended along [100] and are arranged according to a hexagonal packing or rods. The crystal of **6** is also a novel polymorph modification of previously studied compound, the structure of which is based on the very rare topological type of the finite clusters. Nowadays, uranyl nitrate finite clusters of nine various topological types are known. We give herein a short review of their topological features and relationships. Crystallization of uranyl nitrates usually occurs when all other competitive anions in the system have already formed crystalline phases, or the reaction of reagents have slowed down or even stopped. Thus it is suggested that crystallization of uranyl nitrates can be used as a key indicator of the reaction progress, which points to the necessity of the initial concentrations of reagents correction, or to the replacement of reagents and adjustment of the thermodynamic (P,T) parameters of the synthesis.

Keywords: uranyl; nitrate; chloride; crystal structure; X-ray diffraction; topology

1. Introduction

Uranyl nitrate is a very important compound in nuclear wastes management and modern synthetic chemistry of U. Uranyl nitrate is obtained after dissolution of spent nuclear fuel in nitric acid, prior to the preparation of UF_6 , which is used in uranium enrichment [1,2]. Besides, the first amounts of plutonium were obtained after irradiation of uranyl nitrate [3]. Uranyl nitrate hexahydrate was used in photographic processes since the 19th century and in the porcelain industry [4], and currently, it is one of the most popular reagents in laboratories to carry out various U-bearing phase formation experiments.

Nowadays, there are 108 inorganic and organically templated uranyl nitrate compounds that are listed in the Cambridge Crystallographic Data Centre (CCDC; version 2020.2.0, May 2020 update) and Inorganic Crystal Structure Database (ICSD; version 4.5.0) [5,6]. The majority of them (89) have their structure built on the finite clusters, 16 structures are based on the chained complexes and

the structures of three compounds are built by nanoclusters. Among those 89 structures 9 various topologies of clusters were described, some of which are very common, while another was found only in the structures of a single compound.

Herein we report on the synthesis and structural investigation of six novel uranyl nitrates. Two of them represent new polymorph modification of previously studied compounds. Two more compounds crystallize in isotypic structures but differ in the distortion at the counter ion's sites. In addition to the structural studies, we present a short topological review of uranyl nitrate finite clusters and discuss some crystal growth features of the named compounds.

2. Materials and Methods

2.1. Synthesis

Uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99%, Vekton), potassium chloride (KCl, 99%, Vekton), cesium chloride (CsCl, 99%, Vekton), lithium carbonate (Li_2CO_3 , 99%, Vekton), potassium carbonate (K_2CO_3 , 99%, Vekton), cesium carbonate (Cs_2CO_3 , 99%, Vekton), selenium dioxide (SeO_2 , 99%, Vekton), methylamine (CH_3NH_2 , 99%, Sigma-Aldrich), hydrochloric acid (HCl, 14%, Vekton), nitric acid (HNO_3 , 65%, Sigma-Aldrich), and sulphuric acid (H_2SO_4 , 98%, Sigma-Aldrich) were used as received. $\text{K}_3[(\text{UO}_2)(\text{NO}_3)\text{Cl}_3](\text{NO}_3)$ (**1**, **2**), $\alpha\text{-Cs}_2[(\text{UO}_2)(\text{NO}_3)\text{Cl}_3]$ (**3**), $[(\text{UO}_2)(\text{NO}_3)_2(\text{H}_2\text{O})_2][(\text{CH}_3\text{NH}_3)_2(\text{NO}_3)_2]$ (**4**), $\text{Cs}_2[(\text{UO}_2)(\text{NO}_3)_4]$ (**5**), and $[(\text{UO}_2)_2(\text{OH})_2(\text{NO}_3)_2(\text{H}_2\text{O})_3](\text{H}_2\text{O})$ (**6**) have been prepared from aqueous solutions (Figure 1).

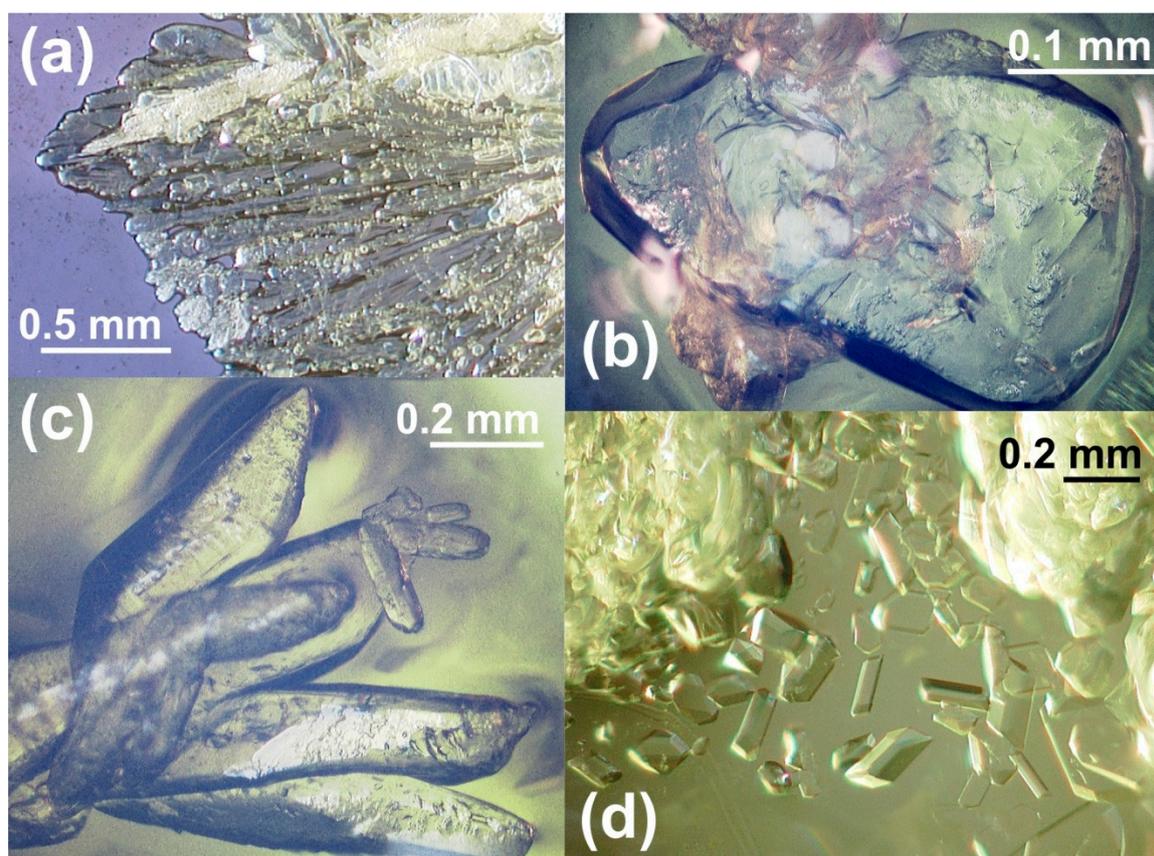


Figure 1. Crystals of **1–3** (a–c) and **6** (d) formed in the described synthetic experiments.

The crystals of **1** have been synthesized during evaporation at room temperature of 3 mL of preliminary heated for 2 days at 55 °C in an aqueous solution of uranyl nitrate (0.218 g), 0.097 g of KCl, 0.041 g of SeO_2 , and 0.2 mL of HCl. Se has not been detected in crystalline phases formed during the

synthesis of **1**. The crystals of **2** were obtained by evaporation at room temperature of 2 mL aqueous solution of uranyl nitrate (0.0904 g), potassium carbonate (0.0478 g), and 0.26 mL of HCl. The crystals of **3** were obtained by evaporation at room temperature of 2 mL aqueous solution of uranyl nitrate (0.1107 g), 0.0312 g of cesium carbonate, and 0.2 mL of HCl. The crystals of **4** were obtained by evaporation at room temperature of 2 mL aqueous solution of uranyl nitrate (0.2 g), 0.023 mL of methylamine, and 0.003 mL of sulfuric acid. At the first stage, crystals of $[\text{CH}_3\text{NH}_3]_2[(\text{UO}_2)_2(\text{SO}_4)_3]$ [7] formed approximately in 2 days, presumably capturing all the sulfate ions from the solution. Afterwards, the crystals of **4** appeared in the system. The crystals of **5** were obtained during 2 days of hydrothermal synthesis (in a steel autoclave with a Teflon liner at 55 °C) of uranyl nitrate (0.217 g), 0.07 g of CsCl, 0.042 g of SeO_2 , and 0.2 mL of HCl. Se has not been detected in crystalline phases formed during the synthesis of **5**. The crystals of **6** were obtained by evaporation at room temperature of 2 mL aqueous solution of uranyl nitrate (0.227 g), 0.0205 g of lithium carbonate, and 0.03 mL of nitric acid. Li has not been detected in crystalline phases formed during the synthesis of **6**.

The chemical analyses of small fragments of crystals **1–6** were performed using a TM 3000 scanning electron microscope equipped with an Oxford EDX spectrometer, with an acquisition time of 15 s per point in energy dispersive mode (acceleration voltage 15 kV). Single crystals have been first checked using single-crystal X-ray diffraction (SC XRD) technique, then crushed, pelletized, and carbon-coated.

Analytical calculations: Compound **1**, atomic ratio from structural data: U 1.0, Cl 3.0, K 3.0; found by EDX: U 0.92 Cl 3.05 K 3.03. Compound **2**, atomic ratio from structural data: U 1.0, Cl 3.0, K 3.0; found by EDX: U 0.89 Cl 3.06 K 3.05. Compound **3**, atomic ratio from structural data: U 1.0, Cl 3.0, Cs 2.0; found by EDX: U 1.16 Cl 2.93 Cs 1.91. Compound **5**, atomic ratio from structural data: U 1.0, Cs 2.0; found by EDX: U 1.08 Cs 1.92. The results of EDX analyses of **4** and **6** didn't reveal the presence of any element between O and U.

2.2. Single-Crystal X-ray Diffraction Study

Single crystals of **1–6** were selected under a binocular microscope, coated in oil-based cryoprotectant, and mounted on cryoloops. Diffraction data were collected using a Bruker Smart diffractometer (Bruker AXS, Madison, WI, USA) operated with monochromated $\text{MoK}\alpha$ radiation ($\lambda[\text{MoK}\alpha] = 0.71073 \text{ \AA}$) at 45 kV and 30 mA or a Bruker Kappa Duo diffractometer (Bruker AXS, Madison, WI, USA) operated with monochromated microfocused $\text{MoK}\alpha$ radiation at 45 kV and 0.6 mA, equipped with a CCD (charge-coupled device) Apex II detectors. Diffraction data were collected with frame widths of 0.5° in ω and φ , and exposures of 10 to 90 s per frame. Diffraction data were integrated and corrected for polarization, background, and Lorentz effects using Bruker software APEX2 [8] and XPREP [9] or *CrysAlisPro* program [10]. An empirical absorption correction based on spherical harmonics implemented in the SCALE3 ABSPACK algorithm was applied in the *CrysAlisPro* program [10] or using the *SADABS* program [11]. The unit-cell parameters (Table 1) were refined using the least-squares techniques. The structures were solved by a dual-space algorithm and refined using the *SHELX* programs [12,13] incorporated in the *OLEX2* program package [14]. The final models include coordinates and anisotropic displacement parameters for all non-H atoms. The carbon- and nitrogen-bound H atoms were placed in calculated positions and were included in the refinement in the 'riding' model approximation, with $U_{\text{iso}}(\text{H})$ set to $1.5U_{\text{eq}}(\text{C})$ and C–H 0.96 Å for CH_3 groups, and with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}(\text{N})$ and N–H 0.86 Å for NH_3 groups. The H atoms of OH groups and H_2O molecules were localized from different Fourier maps and were included in the refinement with $U_{\text{iso}}(\text{H})$ set to $1.5U_{\text{eq}}(\text{O})$ and O–H bond-length restraints to 0.95 Å. Selected bond lengths are listed in Table 2. The crystal structures of **1** and **2** were refined as inversion twins introducing the (-100/0-10/00-1) matrix, and with Flack parameters equal to c.a. 0.5 in both cases. Supplementary crystallographic data for **1–6** (See Supplementary Materials) have been deposited in the Structural Databases (ICSD or CCDC) and can be obtained via <https://www.ccdc.cam.ac.uk/structures/>.

Table 1. Crystallographic data for 1–6.

Compound	1	2	3	4	5	6
Space group	$P2_1$	$P2_1$	$P-2_1/c$	$P-1$	$P-2_1/n$	$P-1$
a (Å)	7.8106 (1)	7.8596 (2)	12.145 (5)	5.7104 (5)	6.6866 (5)	10.9048 (2)
b (Å)	15.6882 (2)	15.8675 (3)	7.926 (3)	7.6993 (7)	7.9932 (4)	10.9944 (2)
c (Å)	10.5935 (1)	10.6823 (2)	11.648 (5)	10.2304 (9)	12.6165 (10)	17.0902 (3)
α (°)	90	90	90	78.072 (2)	90	73.445 (2)
β (°)	90.147 (1)	90.141 (2)	97.050 (8)	75.750 (2)	99.603 (7)	89.421 (1)
γ (°)	90	90	90	75.623 (2)	90	86.382 (1)
V (Å ³)	1298.06 (3)	1332.21 (5)	1112.8 (8)	417.19 (6)	664.87 (8)	1960.06 (6)
μ (mm ⁻¹)	14.11	13.75	21.74	9.821	17.69	24.85
Temperature (K)	100 (2)	293 (2)	100 (2)	100 (2)	293 (2)	100 (2)
Z	4	4	4	1	2	6
D_{calc} (g/cm ³)	3.161	3.08	4.203	2.461	3.916	3.915
Crystal size (mm ³)	0.16 × 0.10 × 0.07	0.24 × 0.18 × 0.13	0.24 × 0.17 × 0.10	0.12 × 0.10 × 0.01	0.34 × 0.27 × 0.20	0.25 × 0.13 × 0.10
Diffractometer, Bruker	Kappa Apex II Duo		Smart Apex II		Kappa Apex II Duo	
Total reflections	13,057	22,471	12,780	4763	5896	23,202
Unique reflections	5961	11,537	2546	2336	1529	9006
Angle range 2θ (°), MoK α	3.84–55.00	3.84–72.84	6.15–55.00	4.16–60.00	3.06–55.00	3.87–55.00
Reflections with $ F_o \geq 4\sigma_F$	5802	8552	2328	2294	1238	6988
$R_{\text{int}}, R_{\sigma}$	0.0186, 0.0213	0.0216, 0.0325	0.0354, 0.0266	0.0503, 0.0364	0.0322, 0.0271	0.0331, 0.0362
R_1, wR_2 ($ F_o \geq 4\sigma_F$)	0.0151, 0.0333	0.0254, 0.0449	0.0164, 0.0324	0.0172, 0.0446	0.0288, 0.0723	0.0287, 0.0560
R_1, wR_2 (all data)	0.016, 0.0336	0.0475, 0.0501	0.0206, 0.0337	0.0198, 0.0463	0.0410, 0.0774	0.0439, 0.0608
S	1.03	1.02	1.05	1.04	1.05	1.02
$\rho_{\text{min}}, \rho_{\text{max}}, \varepsilon/\text{Å}^3$	−0.416, 0.542	−0.695, 1.018	−0.890, 0.870	−1.412, 1.411	−1.153, 1.789	−1.364, 1.279
CSD/CCDC	2,045,071	2,045,072	2,045,073	2,045,074	2,045,075	2,045,076

Table 2. Selected bond lengths (Å) in the structure of **1–6** ($X = O, Cl$).

1		U2–O6	1.737 (15)	5		U3–HO36	2.374 (5)
U1–O1	1.770 (5)	U2–O7	1.769 (12)	U1–O1 x2	1.754 (4)	U3–HO37	2.375 (4)
U1–O2	1.762 (5)	<U2–O _{Ur} >	1.753	<U1–O _{Ur} >	1.754	U3–H ₂ O38	2.400 (5)
<U1–O _{Ur} >	1.767	U2–O8	2.488 (14)	U1–O2 x2	2.413 (4)	U3–H ₂ O39	2.445 (5)
U1–O3	2.499 (5)	U2–O9	2.514 (13)	U1–O5 x2	2.521 (4)	U3–H ₂ O40	2.404 (5)
U1–O4	2.480 (5)	U2–Cl4	2.681 (6)	U1–O6 x2	2.506 (4)	<U3–O _{eq} >	2.400
U1–Cl1	2.6826 (15)	U2–Cl5	2.692 (6)	<U1–O _{eq} >	2.480	U4–O7	1.761 (5)
U1–Cl2	2.6998 (17)	U2–Cl6	2.708 (6)	<Cs1–O>	3.362	U4–O8	1.774 (4)
U1–Cl3	2.7143 (16)	<U2–X _{eq} >	2.617			<U4–O _{Ur} >	1.768
<U1–X _{eq} >	2.615	<K1–X>	3.090	6		U4–O19	2.576 (4)
U2–O6	1.772 (5)	<K2–X>	3.007	U1...U2	3.9331 (3)	U4–O21	2.554 (4)
U2–O7	1.755 (5)	<K3–X>	3.007	U3...U4	3.9419 (3)	U4–O22	2.514 (4)
<U2–O _{Ur} >	1.764	<K4–X>	2.969	U5...U6	3.9358 (3)	U4–O24	2.524 (5)
U2–O8	2.503 (4)	<K5–X>	3.020	U1–O1	1.771 (4)	U4–HO36	2.360 (5)
U2–O9	2.506 (5)	<K4–X>	3.091	U1–O2	1.775 (4)	U4–HO37	2.360 (5)
U2–Cl4	2.7022 (16)			<U1–O _{Ur} >	1.773	<U4–O _{eq} >	2.481
U2–Cl5	2.7197 (17)	3		U1–HO31	2.376 (4)	U5–O9	1.759 (4)
U2–Cl6	2.6956 (15)	U1–O1	1.766 (3)	U1–HO32	2.361 (4)	U5–O10	1.768 (5)
<U2–X _{eq} >	2.625	U1–O2	1.768 (3)	U1–H ₂ O33	2.404 (5)	<U5–O _{Ur} >	1.764
<K1–X>	3.079	<U1–O _{Ur} >	1.767	U1–H ₂ O34	2.441 (5)	U5–HO41	2.391 (5)
<K2–X>	2.995	U1–O3	2.508 (3)	U1–H ₂ O35	2.414 (5)	U5–HO42	2.342 (4)
<K3–X>	2.992	U1–O4	2.497 (3)	<U1–O _{eq} >	2.399	U5–H ₂ O43	2.3935 (2)
<K4–X>	2.968	U1–Cl1	2.7133 (12)	U2–O3	1.772 (4)	U5–H ₂ O44	2.478 (4)
<K5–X>	3.017	U1–Cl2	2.6772 (12)	U2–O4	1.756 (4)	U5–H ₂ O45	2.393 (5)
<K6–X>	3.204	U1–Cl3	2.6960 (13)	<U2–O _{Ur} >	1.764	<U5–O _{eq} >	2.400
		<U1–X _{eq} >	2.618	U2–O13	2.540 (4)	U6–O11	1.777 (4)
2		<Cs1–X>	3.358	U2–O15	2.502 (4)	U6–O12	1.754 (5)
U1–O1	1.752 (14)	<Cs2–X>	3.492	U2–O16	2.567 (5)	<U6–O _{Ur} >	1.766
U1–O2	1.780 (15)			U2–O18	2.552 (5)	U6–O25	2.503 (5)
<U1–O _{Ur} >	1.766	4		U2–HO31	2.372 (4)	U6–O27	2.487 (5)
U1–O3	2.492 (16)	U1–O1 x2	1.771 (2)	U2–HO32	2.368 (4)	U6–O28	2.528 (5)
U1–O4	2.488 (16)	<U1–O _{Ur} >	1.771	<U2–O _{eq} >	2.484	U6–O30	2.561 (5)
U1–Cl1	2.695 (6)	U1–O2 x2	2.502 (2)	U3–O5	1.762 (4)	U6–HO41	2.370 (4)
U1–Cl2	2.722 (5)	U1–O3 x2	2.525 (2)	U3–O6	1.762 (5)	U6–HO42	2.360 (4)
U1–Cl3	2.700 (6)	U1–H ₂ O5 x2	2.397 (2)	<U3–O _{Ur} >	1.762	<U6–O _{eq} >	2.468
<U1–X _{eq} >	2.619	<U1–O _{eq} >	2.475				

3. Results

3.1. Description of the Structures

The crystal structures of **1** and **2** contain two symmetrically nonequivalent U^{6+} atoms with two short $U^{6+} \equiv O^{2-}$ bonds (in the range of 1.737(15)–1.780(15) Å) forming linear (within 2 and 5° for **1** and **2**, respectively) UO_2^{2+} uranyl ions (*Ur*). *Ur* are coordinated in the equatorial plane by three Cl atoms (with average bond lengths equal to 2.702 and 2.700 Å for **1** and **2**, respectively) and two O atoms, which belong to the edge-shared NO_3 group ($\langle U-O_{eq} \rangle = 2.497$ and 2.497 Å for **1** and **2**, respectively), resulted in the formation of pentagonal bipyramids as coordination polyhedra for the U^{6+} atoms (Figure 2a). The crystal structures of **1** and **2** are based on the isolated $[(UO_2)(NO_3)Cl_3]^{2-}$ complexes arranged according to the principle of the hexagonal closest packing in a projection along the [100] around the isolated nitrate groups, non-shared with *Ur* (Figure 3a).

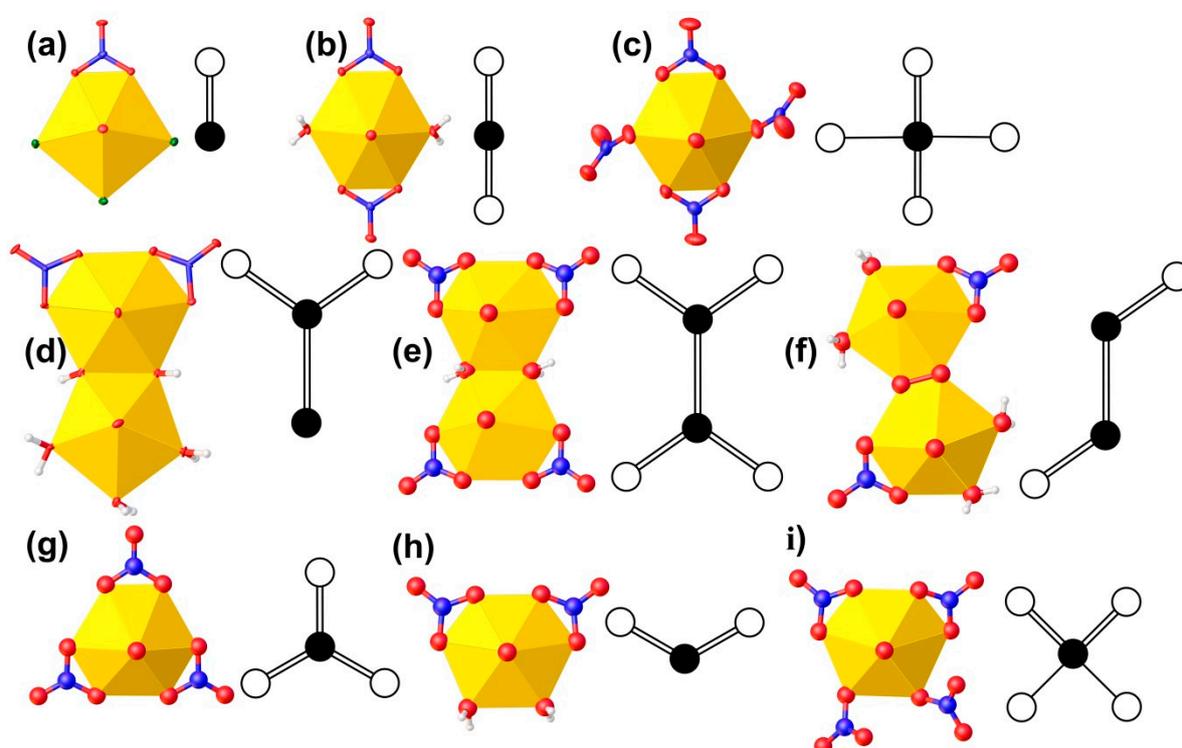


Figure 2. Finite clusters and their respective topologies that were described in the crystal structures of uranyl nitrate compounds, including those found in the structures of **1–3** (a), **4** (b), **5** (c), and **6** (d). Finite clusters shown in (e–i) are drawn according to the literature data (see text for details). Legend: U-bearing coordination polyhedra = yellow; O atoms = red; N atoms = blue; Cl atoms = green; H atoms = light grey; black nodes = U atoms, white nodes = N atoms.

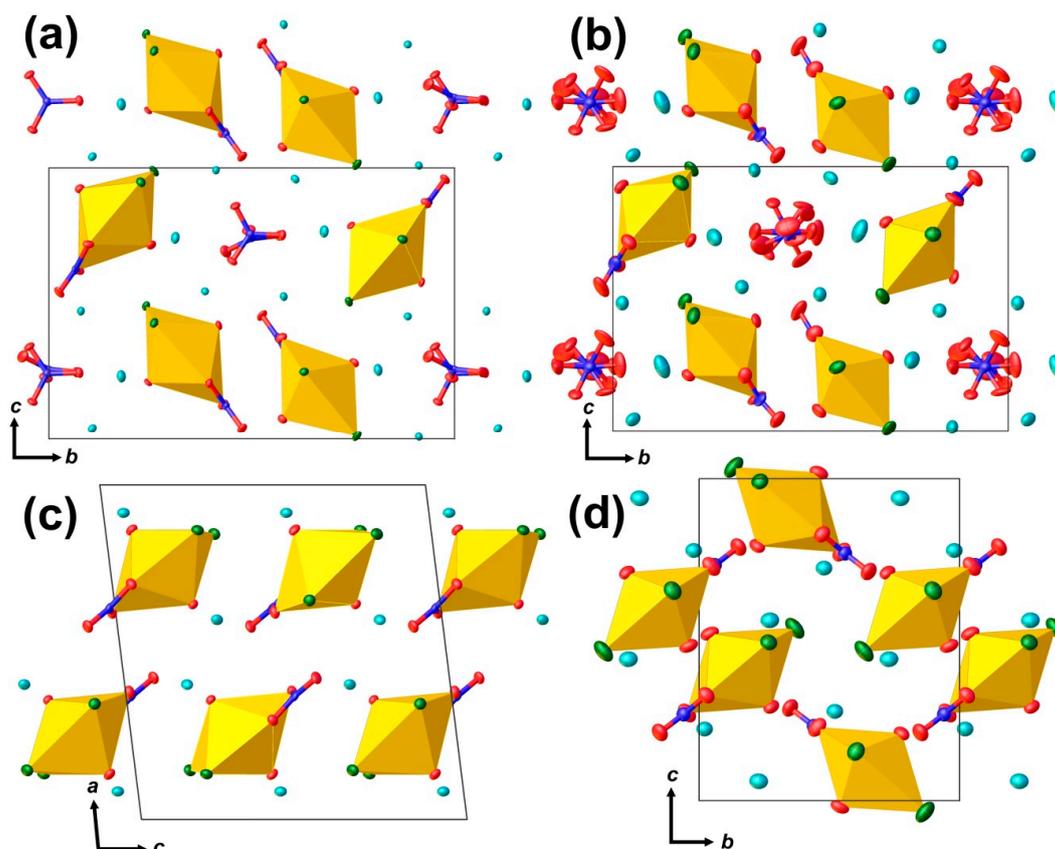


Figure 3. Crystal structures of **1** (a), **2** (b), **3** (c), and β -Cs₂[(UO₂)(NO₃)Cl₃] [15] (d). Legend: see Figure 2; K and Cs atoms = cyan.

Isolated U-bearing bipyramidal complexes are arranged in such a way that equatorial planes of *Ur* are oriented approximately parallel to (021) or (0-21). Six crystallographically nonequivalent K⁺ ions are arranged in octahedral-like interstitial sites of the closest packing. Coordination of K atoms includes various combinations of O and Cl atoms (3O + 5Cl, 3O + 4Cl, 5O + 3Cl and 6O + 3Cl), but keeping nearly similar average K–X distance (X = Cl, O) in the ranges of 2.968–3.204 and 2.969–3.091 Å for **1** and **2**, respectively. Compounds **1** and **2** have a similar arrangement of the U-centered polyhedra and K⁺ ions, and differ only in the disorder of the non-shared NO₃ groups (rotation around central N atom in the plane of the group with the total site occupancy factors equal to 1.0) in the latter crystal structure (Figure 3b). Rotation of the nitrate groups results in turn in a slight alteration of K⁺ ions coordination geometry. The origin of this disorder is not quite clear. The crystals of **1** were synthesized from the solution heated to 55 °C, while the crystals of **2** were obtained at room temperature conditions. SC XRD data were collected at 100 K for **1** and at room temperature for **2**. One could expect that the disorder had come as a result of temperature differences. However, the crystals with the disordered structure were also detected in the synthesis of **1** and kept the disorder during the XRD data collection at 100 K. Thus, it is more likely that the disorder is not a T effect, but the result of some instability during the growth process of particular crystals.

The crystal structure of **3** contains one symmetrically nonequivalent U⁶⁺ atom forming *Ur* ($\langle \text{U}-\text{O}_{Ur} \rangle = 1.767 \text{ \AA}$), equatorial plane of which is built by three Cl atoms ($\langle \text{U}-\text{Cl}_{eq} \rangle = 2.696 \text{ \AA}$) and two O atoms ($\langle \text{U}-\text{O}_{eq} \rangle = 2.503 \text{ \AA}$) from the edge-shared NO₃ group. The resulting coordination polyhedron of U atoms is the same pentagonal bipyramid as was described in the structures of **1** and **2** (Figure 2a). The crystal structure of **3** is based on the isolated [(UO₂)(NO₃)Cl₃]²⁻ moieties that are arranged in pseudo-chained complexes extended along [001] (Figure 3c). In this direction, the distance between U atoms is equal to c.a. 5.8 Å, while in other directions such spacing is significantly larger (7.8–8.2 Å).

Equatorial planes of Ur are arranged approximately parallel to (20-1). Two crystallographically nonequivalent Cs^+ ions are arranged in between the $[(UO_2)(NO_3)Cl_3]^{2-}$ complexes, forming $5O + 4Cl$ and $3O + 6Cl$ coordination geometries with average bond lengths of 3.358 and 3.492 Å, respectively. The crystal structure of **3** is a polymorph modification of the $Cs_2[(UO_2)(NO_3)Cl_3]$ phase recently reported in [15], and which was obtained following 4 days of hydrothermal synthesis at 205 °C. Thus, compound **3** should be regarded as α -modification since it was obtained at room temperature conditions. The crystal structure of β - $Cs_2[(UO_2)(NO_3)Cl_3]$ modification [15] differs from the structure of **3** by the Ur polyhedra arrangement: in the first structure, equatorial planes are arranged approximately parallel to (011) or (01-1) (Figure 3d), while in the structure of **1** equatorial planes of Ur are coplanar.

The crystal structure of **4** contains one symmetrically nonequivalent U^{6+} atom forming Ur ($U-O_{Ur} = 1.771(2)$ Å), equatorial plane of which is built by four O atoms from two *trans*-arranged edge-shared NO_3 groups ($\langle U-NO_{eq} \rangle = 2.514$ Å), and another two O atoms that belong to H_2O molecules ($U-H_2O_{eq} = 2.397(2)$ Å) and separate nitrate groups, thus resulting in the formation of hexagonal bipyramids as coordination polyhedra for the U^{6+} atoms (Figure 2b). The crystal structure of **4** is based on the isolated electroneutral $[(UO_2)(NO_3)_2(H_2O)_2]^0$ moieties that are arranged in pseudo-chained complexes extended along the [010] (Figure 4a), which in turn are arranged in layers parallel to (001). There is one crystallographically nonequivalent nitrate group and one protonated methylamine molecule arranged in between the U-bearing layers. These molecules are interlinked via a system of H-bonds, thus forming electroneutral slabs of $[(CH_3NH_3)_2(NO_3)_2]^0$ composition, which combines Ur layers through another system of H-bonds.

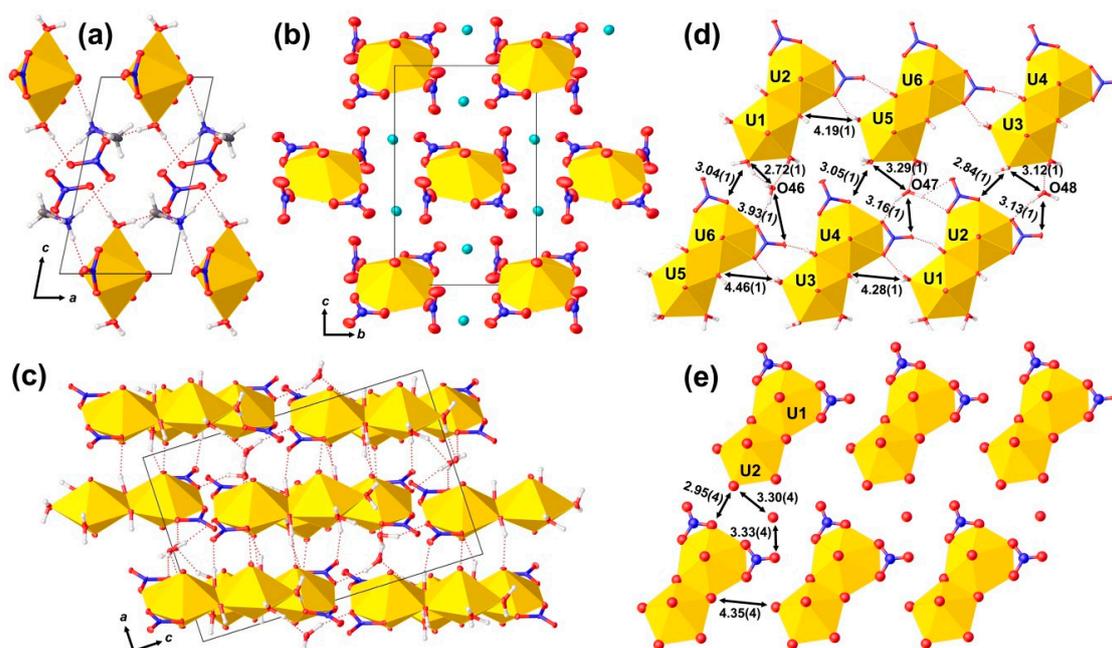


Figure 4. Crystal structures of **4** (a), **5** (b) and **6** (c); differences in the uranyl nitrate cluster arrangement in the structures of **6** (d) and α - $[(UO_2)_2(OH)_2(NO_3)_2(H_2O)_3](H_2O)$ [16] (e). Legend: see Figures 2 and 3; dashed red lines = H-bonds.

The crystal structure of **5** contains one symmetrically nonequivalent U^{6+} atom forming Ur ($U-O_{Ur} = 1.754(4)$ Å), equatorial plane of which is built by four O atoms from two *trans*-arranged edge-shared NO_3 groups ($\langle U-NO_{eq_edge} \rangle = 2.514$ Å), and another two O atoms that belong to one-connected NO_3 groups ($U-NO_{eq_vert} = 2.413(4)$ Å), which are arranged between the edge-shared ones, thus resulting in the formation of hexagonal bipyramids as coordination polyhedra for the U^{6+} atoms (Figure 2c). Equatorial planes of Ur are arranged approximately parallel to (10-2). The crystal structure of **5** is based on the finite $[(UO_2)(NO_3)_4]^{2-}$ clusters that are arranged in pseudo-chained

complexes extended along [100] (Figure 4b) and are arranged according to a hexagonal packing or rods. The negative charge of the clusters is compensated by the Cs⁺ cations, which are arranged in the hollow channels between the chains, and having complex 11-fold coordination geometry with an average $\langle \text{Cs-O} \rangle = 3.362 \text{ \AA}$.

The crystal structure of **6** contains six crystallographically nonequivalent U⁶⁺ atoms forming *Ur* ($\langle \text{U-O}_{Ur} \rangle$ ranges from 1.762 to 1.773 Å), which are arranged in pairs through the common equatorial HO–OH edge to form three isotypic dimers ($\text{U-O}_{eq}\text{H} = 2.342(4) - 2.391(5) \text{ \AA}$; $\langle \text{U}\cdots\text{U} \rangle = 3.937 \text{ \AA}$). One *Ur* in the dimer is linked to two edge-shared *cis*-arranged NO₃ groups ($\langle \text{U-NO}_{eq} \rangle = 2.520 - 2.542 \text{ \AA}$) to form hexagonal bipyramids [(UO₂)(OH)₂(NO₃)₂]. While the second *Ur* from the dimer is surrounded in the equatorial plane by three H₂O molecules ($\text{U-O}_{eq}\text{H}_2\text{O} = 2.393(5) - 2.478(4) \text{ \AA}$) to form pentagonal bipyramids [(UO₂)(OH)₂(H₂O)₃]. As a result of the U⁶⁺ coordination polyhedra linkage, electroneutral [(UO₂)₂(OH)₂(NO₃)₂(H₂O)₃] finite clusters are formed (Figure 2d), with equatorial planes arranged approximately parallel to (2-10). U-bearing clusters are crosslinked via branchy H-bonding system, which includes OH[−] groups and H₂O molecules from the neighbor clusters. The tightest linkage of the clusters is observed within the layered complexes (Figure 4c) arranged approximately parallel to (201). In between these layers, interstitial H₂O molecules are arranged, linking neighbor layers through the additional H-bonding system. This cluster is also quite remarkable due to the presence of edge-shared hexa- and pentagonal uranyl bipyramids. There are no other finite clusters to our knowledge, which have such a type of polyhedral combination. It should be also noted that the crystal structure of **6** is a polymorph modification of the [(UO₂)₂(OH)₂(NO₃)₂(H₂O)₃](H₂O) phase, reported by Perrin [16]. Both compounds crystallize in the triclinic *P*-1 space group, but instead of the structure of **6**, where there are three nonequivalent dimers and H₂O molecules, the structure reported by Perrin [16] contains only one dimer and H₂O molecule. The difference between the structures is in the arrangement of interstitial H₂O molecules (Figure 4d,e). A slight shift of the H₂O₄₆ molecule from an average position reported in [16], which also matches the geometry of the other two H₂O₄₇ and H₂O₄₈ sites in **6**, results in the displacement of U₅–U₆ dimer, which in turn triples the unit cell volume of **6**. Both compounds were synthesized at room temperature, but compound **6** was obtained from a pure inorganic system, whereas crystals of the previously reported phase were grown by a rather complex method of slow diffusion of water vapor to dihydroxyl diuranyl nitrate through the solution of hexachlorobutadiene and acetonitrile. Thus, compound **6** should be regarded as a novel β-modification.

3.2. Structural Topology

The topology of the uranyl nitrate clusters in the structures of **1–6** can be described using graphical representation, in which black nodes correspond to *Ur* and white nodes to NO₃ groups; the presence of a single or double line between the nodes corresponds to a vertex- or edge-sharing mechanism between the coordination polyhedra, respectively. This methodology was first proposed by Hawthorne [17] and subsequently modified by Krivovichev [18,19].

The topology of the uranyl-nitrate-chloride cluster in the structures of **1–3** (Figure 2a) is one of the simplest, being formed only by two coordination polyhedra that share a common edge and belong to the *cc*0-1:1-5 type [19]. But never the less, this type of topology is rather rare, it has been previously observed in six crystal structures only, five of which are organically templated uranyl compounds [20–22] and the one pure inorganic β-Cs₂[(UO₂)(NO₃)Cl₃] [15]. It is of special interest that this topological type has been found exclusively in the structures with three halogen ions arranged in the equatorial plane of *Ur* pentagonal bipyramid.

The topology of the uranyl dinitrate dihydrate cluster in the structure of **4** (Figure 2b), in contrast to those found in **1–3**, is the most common among both inorganic and organically templated uranyl compounds. It belongs to the *cc*0-1:2-7 type and was described as the fundamental structural unit in the structures of 25 organically templated and another 6 inorganic U-bearing uranyl compounds, for example, see [23–26]. The graph of the cluster represents a dumbbell with the central black node

and apical white nodes, linked via double bonds. This topological type is of special importance, because it is the basic cluster in the structure of, probably, the most common chemical source for U^{6+} -uranyl nitrate hexahydrate [27].

The topology of the cluster in the structure of **5** (Figure 2c) can be obtained from the previous one, if two additional white nodes will be linked through single bonds to the central black node at a right angle to the present dumbbell, thus forming a cross. From the crystal-chemical point of view, it means that two H_2O molecules, which were arranged between the edge-shared nitrate groups in the equatorial plane of *Ur* in the structure of **5** are replaced during the dehydration process by two NO_3 groups, each of which has a common vertex with U^{6+} atom. The topology belongs to the *cc0-1:4-2* type, and is rather common, being found in the structures of nine organically templated compounds and four inorganic uranyl nitrates (e.g., [28–31]).

The topology of the diuranyl dihydroxyl dinitrate trihydrate cluster (Figure 2d) in the structure of **6** belongs to the very rare *cc0-1:1-6* type. It has been previously found in the only structure of the α -modification [16] of the compound under investigation. The graph of the cluster can be described as a triangle in which one black node is arranged in its center and another black node occupies the vertex of the triangle, while the other two vertices are occupied by the white nodes. All three nodes that are arranged in the vertices of a triangle are linked to the central black node via double bonds, representing a tight edge-sharing mechanism of uranyl and nitrate polyhedra arrangement.

The variety of uranyl nitrate finite clusters is not limited to only the four aforementioned topologies. Figure 2e–i shows the rest of 0D structural units that were described in the structures of U- and NO_3 -bearing compounds. The cluster shown in Figure 2e belongs to the *cc0-1:2-8* type and is the second most common uranyl nitrate isolated structural unit, being found in the structures of 22 compounds; however, all of them are organically templated. There is no information available on the presence of such complexes in the pure inorganic systems. Another distinctive feature of this topology is that the common edge between *Ur* hexagonal bipyramids is commonly performed by the OH groups (e.g., [32,33]), while lower amount of structures hydroxyl groups are replaced by H_2O molecules (e.g., [34,35]).

The only known compound, which structure is based on the *cc0-1:1-7* type (Figure 2f), is an organic-inorganic composite, where the electroneutral uranyl nitrate clusters are templated by crown ether molecules [36]. The topology looks quite similar to the previous type with deleted diagonal pair of white nodes. However, the differences are much more significant from the crystal-chemical point of view. Edge-shared nitrate groups (white nodes) are not simply deleted, but replaced with two H_2O molecules, each, which results in elongation of the H_2O-OH_2 edge, and thus in alteration of symmetrical hexagonal geometry of the bipyramid. The second possibility, which also violates the hexagonal geometry, is the replacement of the common HO–OH (or H_2O-OH_2) edge between the two U-centered coordination polyhedra, by the peroxide group.

Uranyl trinitrate cluster shown in Figure 2g belongs to the *cc0-1:3-2* type, which is much more common for uranyl carbonates [6], but it also occupies not the last place among nitrates. This rather simple structural type appeared to be more common among inorganic compounds (9). Those are mostly uranyl trinitrates of mono valent cations (e.g., [37–40]). And only four organically templated structures are known (e.g., [24,41]).

Replacement of one NO_3 group from the previous cluster by two H_2O molecules results in the formation of the *cc0-1:2-9* topological type (Figure 2h), which was found in the structure of one inorganic uranyl nitrate $[UO_2(NO_3)_2(H_2O)_2] \cdot H_2O$ [42] and one organic-inorganic composite structure with uranyl nitrate clusters templated by cucurbit[6]uril molecules [43].

And the last topological type was found in the structures of the only two uranyl nitrate compounds, templated by $[Co(bipy)_3]^{3+}$ groups [44] and recently reported $K_2[(UO_2)(NO_3)_4]$ [45]. This topology can be attributed to the *cc0-1:4-3* type (Figure 2i) and actually should be regarded as the topological isomer of the much more common *cc0-1:4-2* type (Figure 2c). The difference is in arrangement with edge- and vertex-shared NO_3 groups. In *cc0-1:4-2* type, similar groups are arranged in *trans* position, whereas they

are cis-arranged in $cc0-1:4-3$ type. The $[\text{Co}(\text{bipy})_3]_2[\text{UO}_2(\text{NO}_3)_4]_2[(\text{UO}_2)_2(\text{NO}_3)_4(\text{OH})_2]$ [44] is also remarkable since it is the only, to our knowledge, compound which structure contains two various types of uranyl nitrate finite clusters, $cc0-1:4-3$ type, and $cc0-1:2-8$.

4. Discussion

Uranyl nitrates quite often form at various stages of synthetic experiments when trying to obtain other uranyl compounds, such as chromates [46], phosphates [47], sulfates [48], selenites [49], selenates [50], etc. In the structures of these compounds NO_3 groups can solely coordinate Ur , as it was shown for finite clusters, or can enter the coordination sphere along with other low- or high-valence anions [20–22,46–50]. In the majority of cases such compounds are regarded as “by-products”, but in fact, the presence of these phases can be of significant assistance in the crystal growth process within the system under investigation and in the correction of the reaction conditions.

The phase formation of uranyl compounds in various Cr(VI)-bearing systems can be considered as an example. Thus, the crystals of $\text{K}[\text{UO}_2(\text{NO}_3)_3]$ [39] were obtained during the evaporation synthesis at room temperature of potassium chromaturanylates [51], in which K_2CrO_4 was used as the reagent. Crystallization of $\text{K}[\text{UO}_2(\text{NO}_3)_3]$ occurred in the system with the highest U:Cr molar ratio (6:1). The details of another system targeted to obtain novel uranyl chromates were reported in [52]. Crystallization of $\text{K}[(\text{UO}_2)_2(\text{UO}_4)(\text{OH})(\text{NO}_3)_2]\text{H}_2\text{O}$ and $\text{Ba}[(\text{UO}_2)_4(\text{UO}_4)_2(\text{OH})_2(\text{NO}_3)_4]\text{H}_2\text{O}$ [52] occurred as the result of hydrothermal experiments in the presence of nitrate salts of K and Ba, respectively, and CrO_3 with the U:Cr molar ratio equal to 5:1. When the concentration of Cr in the systems increases up to 1:1, crystallization of uranyl-chromate-nitrates occurs [53], and when the ratio increases to c.a. 1:10, pure uranyl chromates crystallize [46].

Similar behavior of phase formation has been observed within the uranyl sulfate systems. Crystallization of **4** illustrates this tendency. Very low amounts of sulfate oxyanions (U:S~10:1) in the initial solution have completely reacted at first to form $[\text{CH}_3\text{NH}_3]_2[(\text{UO}_2)_2(\text{SO}_4)_3]$ [7] crystals. Concentration of Ur , nitrate, and methylamine ions afterwards was still high, so as soon as the system reached supersaturation after evaporation of the solvent, formation of $[(\text{UO}_2)(\text{NO}_3)_2(\text{H}_2\text{O})_2][(\text{CH}_3\text{NH}_3)_2(\text{NO}_3)_2]$ (**4**) crystals started.

An issue that is also related to low concentrations of the sulfate or fluorine anions was found during dissolution of U-bearing framework structures in the presence of large amounts of NO_3 anions, which resulted in the recrystallization of $[\text{N}(\text{CH}_3)_4][(\text{UO}_2)(\text{NO}_3)_3]$ [41] and $(\text{C}_4\text{H}_{12}\text{N})[\text{UO}_2(\text{NO}_3)(\text{SO}_4)]$ [48] compounds.

Another case of actinyl nitrate compounds formation can be attributed to the change of the direction or blocking of the initially supposed reaction. Thus, $\gamma\text{-K}[\text{UO}_2(\text{NO}_3)_3]$ [54] was obtained from the hydrothermal synthesis in the presence of V_2O_5 and Np(V)-bearing nitrates were grown from the solution containing selenic acid [45], and the crystals of **5** were grown in the presence of SeO_2 . In all of these cases vanadate, selenate, and selenite oxyanions didn't react with the respective actinyl ions to form the novel phases.

5. Conclusions

Thus, we have reported on the synthesis and characterization of six novel uranyl nitrate phases, in which crystal structures are based on the finite clusters of various topological types. The crystals of **1** and **2** are isotypic but differ in the distortion at the nitrate groups. The crystal structures of **3** and **6** are appeared to be novel polymorph modifications of the respective compounds. The crystal structure of **4** is composed of uranyl-dinitrate-dihydrate and methylamine-nitrate electroneutral complexes linked through the system of H-bonds. The crystal structure of **5** is based on the finite $[(\text{UO}_2)(\text{NO}_3)_4]^{2-}$ clusters that are arranged in pseudo-chained complexes extended along [100], and are arranged according to a hexagonal packing or rods.

Uranyl nitrates are well known for their high solubility, a property which has been in use for many years in a spent nuclear fuel reprocessing. After the dissociation of salts occurs in the initial

solution, crystallization starts with the evaporation of solvent and/or pressure and temperature variations. Solubility of uranyl nitrate is c.a. 120 g per 100 g of H₂O at room temperature, whereas that, e.g., uranyl sulfate is equal to c.a. 27 g. It means that at ambient conditions uranyl sulfate phases are expected to be grown first. High solubility of nitrates can also explain the fact that uranyl nitrates are not known as mineral species, and most likely it even prevents the incorporation of NO₃ ions in the structures of secondary U-bearing minerals. Considering the rare occurrence of chlorine ions in *Ur* coordination sphere in such systems, one can assume that the formation of crystals similar to 1–3 can be expected at high concentrations of Cl[−] anions, low amount of nitrate groups, and substantial residues of *Ur* and additional cations in the system. At high NO₃ concentration, crystallization of nitrates will be favored, which was shown by the formation of 5, where Cl[−] was also present in the initial solution. Thus, crystallization of uranyl nitrates can be used as a key indicator of the reaction progress in the system, which means that all other competitive anions in the system have already formed crystalline phases and the initial concentrations of reagents should be corrected, or the reaction of reagents have slowed down or even stopped. In the latter case, it may be necessary to replace the reagents or to adjust the thermodynamic (P,T) parameters of the synthesis.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4352/10/12/1122/s1>, Cif files for 1–6.

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