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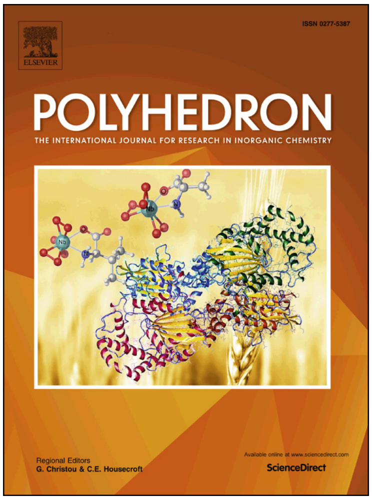

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Mg, Ca and Ba glutaratouranylates – synthesis and structure

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Abstract

Three novel uranyl coordination polymers were synthesized and structurally characterized by single crystal X-ray diffraction - $[Mg(H_2O)_6][UO_2(glt)(Hglt)]_2 \cdot 6H_2O$ (**1**), $[Ca(H_2O)_4][UO_2(glt)(Hglt)]_2 \cdot 4H_2O$ (**2**) and $[Ba(H_2O)_5][UO_2(glt)(Hglt)]_2 \cdot 2H_2O$ (**3**), where glt = $C_5H_6O_4^{2-}$ (glutarate) and Hglt = $C_5H_7O_4^-$ (hydroglutarate) anions. The structures of compounds **1-3** contain 1D $[UO_2(glt)(Hglt)]^-$ units that belong to the $AQ^{02}B^{01}$ ($A = UO_2^{2+}$, Q^{02} = glt, B^{01} = Hglt) crystallochemical group. The different roles of alkaline earth R^{2+} cations in the structures and the flexibility of the glutarate anions account for the structural distinctions of **1-3**. The diverse ways for the connection between the R^{2+} ions and the $[UO_2(glt)(Hglt)]^-$ chains, the water content and the geometry of the uranyl-glutarate units present the main structural features of the new complexes. A comparative analysis based on Pauling's second rule of **1-3** and alkali glutaratouranylates has allowed an explanation of their structural dissimilarity.

Keywords: Uranium, Coordination polymer, Glutarate

1. Introduction

Coordination polymers and metal-organic frameworks with the uranyl ion have been under scrutiny over the past decade [1-3]. Utilizing a variety of O- and N-donor linkers in the synthesis, many new structurally and topologically diverse compounds of this group have been obtained, some of which possess notable optical properties [4-7]. The development of rational approaches to the design of new coordination polymer materials with predetermined dimensionality, topology and functionality remains challenging nowadays. In this connection, the stepwise study of systems with the uranyl ion and certain linker molecules under controlled synthetic conditions is necessary.

Anions of dicarboxylic acids are very common linkers for the synthesis of new uranium coordination polymers. We should note that examples of dicarboxylate uranium complexes have been reported for the first thirteen homologues of the saturated dicarboxylic acid family. The largest structurally characterized group of dicarboxylates is the oxalate group. Crystal structures of uranium oxalates include complexes with all possible dimensionalities and a wide topological variety. The increase of the dicarboxylate linker length may induce the appearance of very peculiar structures. The most remarkable examples of this peculiarity are the Borromean-type association of 2D units in $[Mn(C_{12}H_8N_2)_3][(UO_2)_2(C_{11}H_{22}(COO)_2)_3]$ [10] and polycatenation of the 2D network in $[UO_2(C_6H_8O_4)(C_{10}H_8N_2)]$ [13]. The major contribution in the study of compounds with long chain linkers (six or more carbon atoms) belongs to Thuéry's [8-11] and Cahill's [12-15] groups.

Recently we have obtained a group of compounds with the $R[UO_2(glt)(Hglt)]\cdot H_2O$ (R^+ = Na^+, K^+, Rb^+ or Cs^+) formula which contain glutaric acid anions as linkers [16]. Herein we carry on our comprehensive study of uranyl-glutarate coordination polymers by replacing the monovalent cations with bivalent alkaline earth cations.

We report the synthesis and structures of three alkaline earth glutaratouranylates: $[Mg(H_2O)_6][UO_2(glt)(Hglt)]_2\cdot 6H_2O$ (**1**), $[Ca(H_2O)_4][UO_2(glt)(Hglt)]_2\cdot 4H_2O$ (**2**) and $[Ba(H_2O)_5][UO_2(glt)(Hglt)]_2\cdot 2H_2O$ (**3**). The title compounds illustrate the influence of the incorporation of auxiliary cations on the dimensionality of the structural units in the uranyl glutarate series.

2. Experimental

2.1 Synthesis

Uranium (VI) oxide (UO_3) and commercially available glutaric acid (H_2glt), calcium oxide, magnesium and barium chlorides were all used for synthesis of **1-3** as received. UO_3 was obtained by the thermal decomposition of uranyl nitrate, $UO_2(NO_3)_2·6H_2O$, in air at 330 °C for 24 h.

*$Mg(UO_2)_2(glt)_2(Hglt)_2·12H_2O$ (**1**)*

$MgCl_2·6H_2O$ (0.033 g, 0.16 mmol), UO_3 (0.100 g, 0.35 mmol) and H_2glt (0.185 g, 1.40 mmol) were used for the synthesis. First, glutaric acid was dissolved in 4 ml of distilled water and then uranium oxide powder was added. The reaction was moderately heated to dissolve the oxide, resulting in a yellow solution, which was treated with 2 ml of magnesium chloride solution. Slow evaporation of the solution (pH ≈ 2.0) at room temperature yielded yellow crystals of **1**. Yield: 39% based on uranium. Chem. analysis, found (calculated): U 36.8% (36.5%).

*$Ca(UO_2)_2(glt)_2(Hglt)_2·8H_2O$ (**2**)*

Crystals of **2** were obtained as follows: UO_3 (0.100 g, 0.35 mmol) was mixed with an H_2glt solution (0.138 g, 1.04 mmol in 4 ml of water). CaO (0.020 g, 0.35 mmol) was added to H_2glt (0.046 g, 0.35 mmol in 2 ml of water) in a separate vial. These two solutions were combined (resulting pH ≈ 3.0) and evaporated at room temperature. After one week, crystals of **2** precipitated. Yield: 35% based on uranium. Chem. analysis, found (calculated): U 38.0% (38.2%).

*$Ba(UO_2)_2(glt)_2(Hglt)_2·7H_2O$ (**3**)*

The synthesis of **3** was carried out in the same way as for **1**, substituting $MgCl_2·6H_2O$ with $BaCl_2·2H_2O$. Yield: 41% based on uranium. Chem. analysis, found (calculated): U 35.5% (35.9%).

Our numerous attempts to obtain the Sr analogue of **1-3** led to poor quality crystals which were not appropriate for XRD experiments.

2.2 Single crystal XRD

X-ray diffraction experiments were carried out using a Bruker KAPPA APEX II automated four-circle diffractometer equipped with an area detector. The lattice parameters were refined from all the collected reflections [17]. The experimental reflection intensities were corrected for absorption using SADABS (for **1** and **3**) software [18] and the TWINABS (for **2**) program [19]. The structures were solved by direct methods (SHELXL97-2014 [20]) and refined by full-matrix least squares [21] calculations against F^2 in an anisotropic approximation for all non-hydrogen atoms. The crystal structure of $Ca(UO_2)_2(glt)_2(Hglt)_2 \cdot 8H_2O$ (**2**) was determined and refined from a twin crystal. The components of the twin are related by 180º rotation around the *a*-direction, and the contribution of the minor part is 0.2968(15).

The H atoms of the CH_2 groups were placed in geometrically calculated positions with the isotropic temperature factors being 1.2 Ueq of the C atom factors. The H atoms of the water molecules and -COOH groups were partially located from difference Fourier syntheses and refined isotropically with restrains on the O–H distances and H–O–H angles, and the isotropic temperature factors being 1.5 Ueq of the O atom factors. Relevant crystallographic data for **1-3** are summarized in Table 1. The coordination numbers (CN) of the atoms were calculated by the intersecting spheres method [22].

Table 1
Selected crystallographic data and parameters of the XRD experiments for $Mg(UO_2)_2(glt)_2(Hglt)_2 \cdot 12H_2O$ (**1**), $Ca(UO_2)_2(glt)_2(Hglt)_2 \cdot 8H_2O$ (**2**) and $Ba(UO_2)_2(glt)_2(Hglt)_2 \cdot 7H_2O$(**3**).

	1	**2**	**3**
Chemical formula	$C_{20}H_{50}MgO_{32}U_2$	$C_{20}H_{42}CaO_{28}U_2$	$C_{20}H_{40}BaO_{27}U_2$
Formula weight	1302.96	1246.68	1325.93
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a (Å)	8.6588(2)	8.2381(8)	7.8675(2)
b (Å)	9.9824(3)	17.6028(18)	23.9490(6)
c (Å)	11.9098(3)	12.8526(12)	19.3119(5)
α (°)	105.098(2)	90	90
β (°)	95.861(2)	97.184(6)	98.9550(10)
γ (°)	91.646(2)	90	90
V (Å^3)	987.06(5)	1849.2(3)	3594.37(16)
Z	2	2	4
ρ_{calc} (g/cm^3)	2.192	2.235	2.452
μ (mm^{-1})	8.314	8.983	10.170
θ_{max} (°)	29.995	27.499	35.000
h, k, l range	-12≤ h ≤12, -14≤ k ≤13, -16≤ l ≤16	-9≤ h ≤10, -22≤ k ≤22, -16≤ l ≤16	-12≤ h ≤12, -31≤ k ≤38, -27≤ l ≤31
Reflections collected / unique	12936/5684	17017/6653	81964/15801
R_{int}	0.0454	0.1000	0.0526
R_1 ($I > 2\sigma(I)$)	0.0336	0.0616	0.0354
S	1.018	1.082	1.098
Largest difference peak/hole (e/Å^3)	1.719/-1.496	1.887/-2.462	1.323/-1.701

3. Results and discussion

3.1. Description of the crystal structures

The structures of **1-3** contains four independent uranium atoms with CN = 8. The uranium coordination polyhedra have the shape of a hexagonal bipyramid with shorter axial uranyl U=O bonds, 1.761–1.785 Å, compared to the equatorial bonds, 2.426–2.513 Å, consistent with the literature data [23,24]. In **1** and **3**, the U=O distances within a single UO_2^{2+} cation differ by ≈ 0.01 Å, which is likely due to the formation of hydrogen bonds involving the uranyl oxygen atoms. The UO_2^{2+} ions in the discussed structures are nearly linear, with an average O=U=O angle equal to 178.7(6)°. Each UO_8 bipyramid shares two edges with two bis-bidentate glutarate anions and one edge with a single-bidentate hydroglutarate anion.

In the structures of **1-3**, the glt^{2-} and $Hglt^-$ anions adopt Q^{02} and B^{01} types of coordination with respect to the uranium atom (Fig. 1). Hereinafter the designation of coordination types and crystallochemical formulae are given according to the system in reference [25]. In this system, the general denticity of a ligand (i.e. the number of atoms involved in bonding with the metal centers) is indicated by the capital letter. For example, the glutarate ions in **1-3** form four bonds, which corresponds to the symbol “Q” (“quadri” = “four”). The superscript indices specify the number of corners, edges, faces, etc. shared by the uranium atom and the ligand, i.e. 02 in this case.

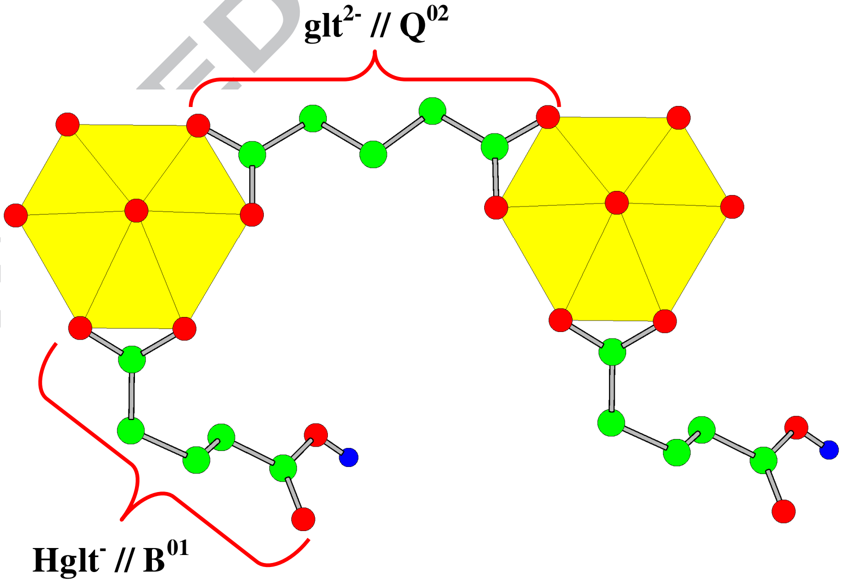

Fig. 1. The coordination of the glutaric acid anions to the uranyl cations in the glutaratouranylate structures **1-3**. Hereinafter, the uranium coordination polyhedra are yellow, carbon, oxygen and hydrogen atoms are green, red and blue respectively.

In the considered compounds each glutarate ion links two uranyl centers to form infinite chains enframed by bidentate hydroglutarate anions. These chains have the $[UO_2(glt)(Hglt)]^-$ composition, identical to the composition of the chains found earlier in the structures of alkali metals (R^+) glutaratouranylates [16,26]. There are two different types of $[UO_2(glt)(Hglt)]^-$ units in the glutaratouranylates structures with the R^+ and R^{2+} (**1-3**) cations. The most common type is characterized by one side placement of $Hglt^-$ anions, wherein the extent of chain distortion may differ (Fig. 2a). The second type of chain with alternate placement of hydroglutarate ions was revealed in the structure **2** for the first time (Fig. 2b).

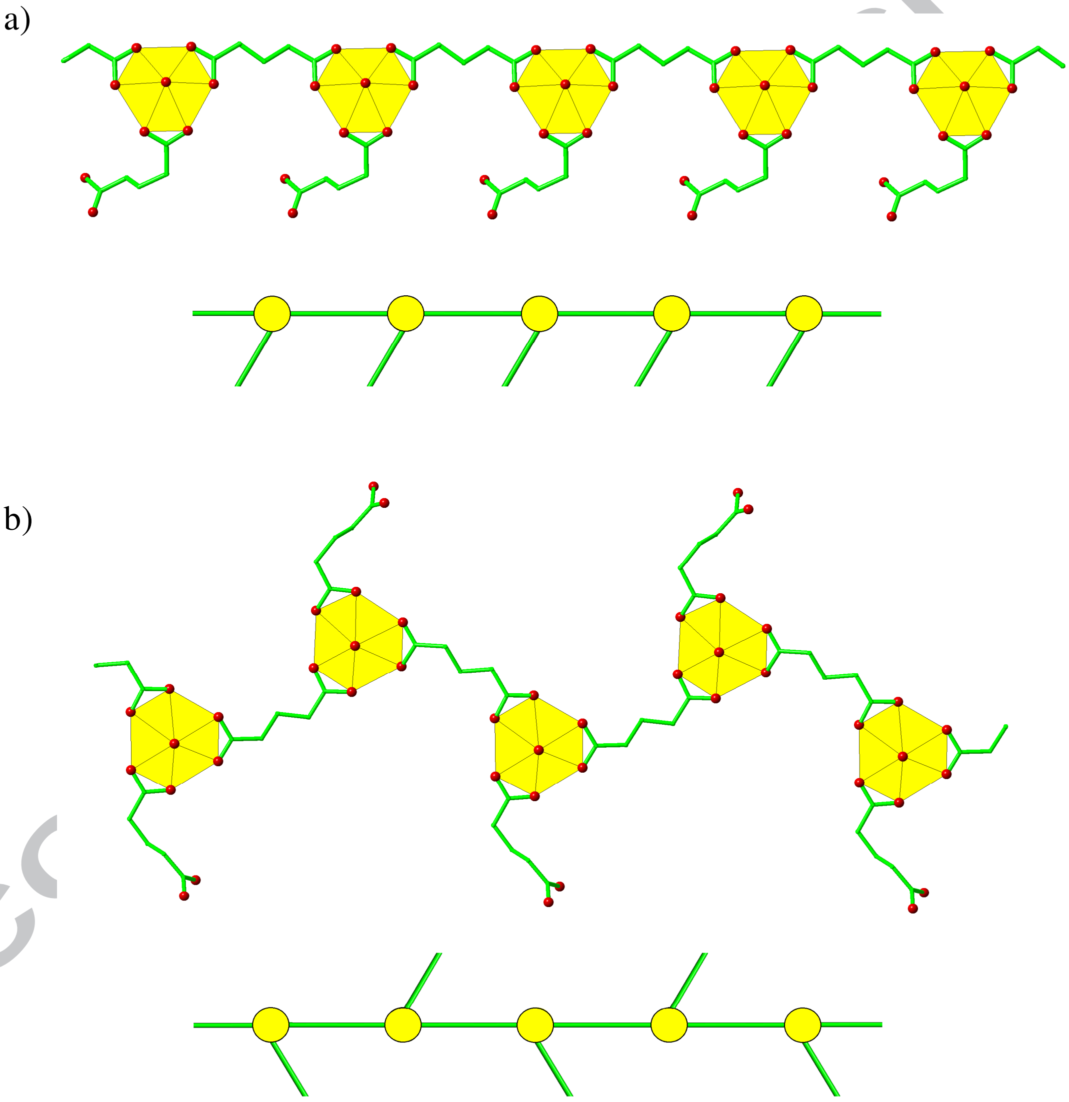

Fig. 2. A fragment of the $[UO_2(glt)(Hglt)]^-$ chain and its simplified representation in: a) $[Mg(H_2O)_6][UO_2(glt)(Hglt)]_2\cdot 6H_2O$ (**1**); b) $[Ca(H_2O)_4][UO_2(glt)(Hglt)]_2\cdot 4H_2O$ (**2**).

The magnesium cations in **1** form the typical hexaaqua complex $[Mg(H_2O)_6]^{2+}$. Electrostatic interactions and multiply hydrogen bonds betweenthe complex magnesium counter ion and uranyl-glutarate chains results in the formation of a 3D framework in **1**.

In the second structure, the Ca^{2+} ion has CN = 6 and coordinates to four water molecules and two oxygen atoms from two hydroglutarate ions, which display the M^1 type of coordination to the calcium center. Since the $Hglt^-$ anions belong to two neighboring $[UO_2(glt)(Hglt)]^-$chains, the calcium ions draw the uranyl-glutarate chains together, with the formation of infinite $[Ca(H_2O)_4][UO_2(glt)(Hglt)]_2$ layers in the *bc* plane (Fig. 3).

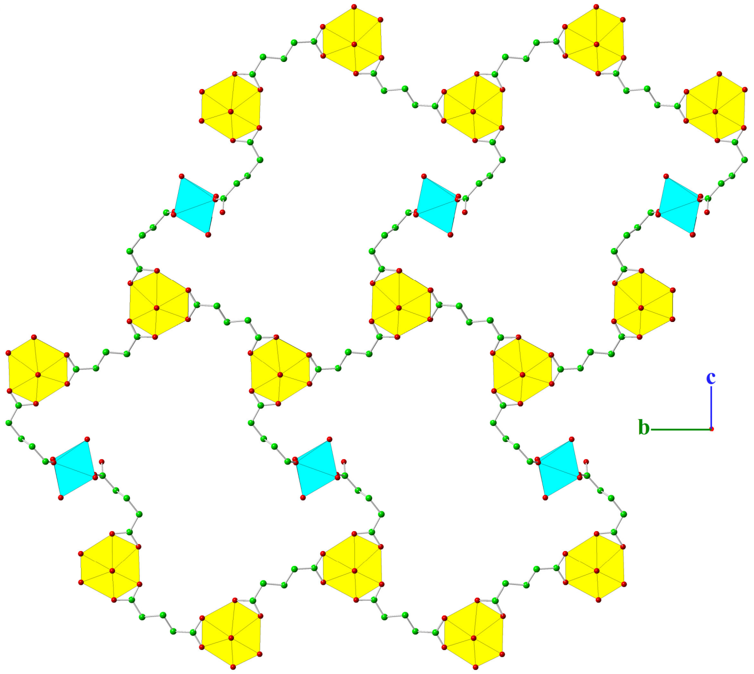

Fig. 3. A fragment of the $[Ca(H_2O)_4][UO_2(glt)(Hglt)]_2$ layer in the structure **2**. The calcium polyhedra are cyan.

The barium atoms in **3** have CN = 9 and form bonds with five water molecules, two glutarate ions (with M^1 coordination to the Ba atoms) and one hydroglutarate ion (with B^2 coordination). Here, the formation of infinite $[Ba(H_2O)_5][UO_2(glt)(Hglt)]_2$ layers in the *ac* plane takes place (Fig. 4). However, the increasing coordination number of R^{2+} leads to the formation of denser layers, compared to those in **2**.

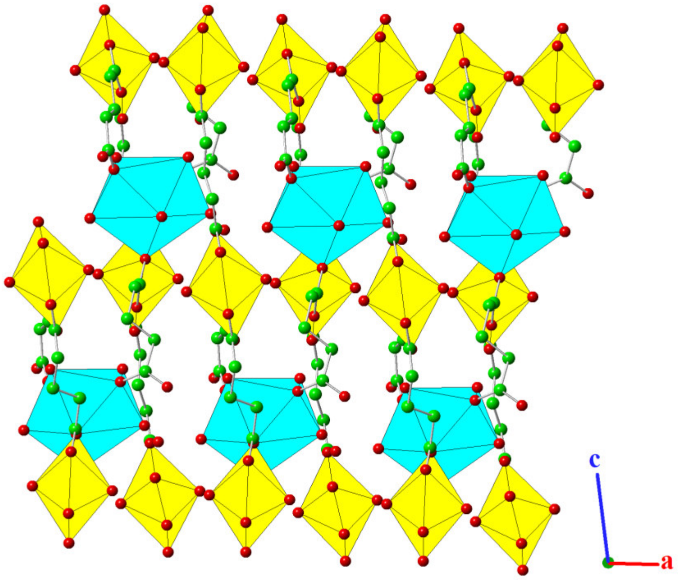

Fig. 4. A fragment of the $[Ba(H_2O)_5][UO_2(glt)(Hglt)]_2$ layer in **3**. The barium polyhedra are cyan.

Each uranyl glutarate layer in **2** and **3** participates in hydrogen bonding with the adjacent layers and water molecules to form 3D frameworks.

3.2. Structural features of the uranyl glutarate complexes with R^+ and R^{2+} cations

Including **1-3**, there are eight crystal structures with $[UO_2(glt)(Hglt)]^-$ chains and R^+ or R^{2+}counter ions reported to date (Table 2).

Table 2. Selected characteristics of uranyl glutarates with R^+ and R^{2+} cations*

R^+ / R^{2+}	φ_{UU}, deg.	d_{UU}, Å	d_{CC}(glt), Å	d_{CC}(Hglt), Å	Coordination type of the anions to the R atoms		Reference
					glt^{2-}	$Hglt^-$	
Li	0	9.14	4.52	5.09	-	M^1	[26]
Na	48.3	9.99	5.06	4.63	T^3	B^2	[16]
K	45.5	10.14	5.09	4.66	T^3	B^2	
Rb	0	8.13	3.79	4.54	T^{11}-8	T^3	
Cs	0	8.24	3.86	4.52	T^{11}-8	T^3	
Mg	0	9.98	5.04	4.53	-	-	This work
Ca	6.6	10.09	5.06	4.53	-	M^1	
Ba	13.9	9.89	5.05 4.67	5.02 4.52	- M^1	M^1 B^2	

*φ_{UU} – the angle between the equatorial planes of nearest uranyl ions in one $[UO_2(glt)(Hglt)]^-$ chain, d_{UU} – the distance between neighbor uranium atoms in the chain, d_{CC} – the distance between carbon atoms of the -COO group in the given glutarate or hydroglutarate ion. Digit to the right of the symbol of the chelate coordination type T^{11} shows the number of bonds in the metallocycle formed by the given ligand.

The structures of the compounds with the lithium, rubidium, cesium and magnesium cations contain uranyl glutarate chains in which the equatorial planes of the uranyl ions are parallel ($\varphi_{UU} = 0$). The compounds with the sodium, potassium, calcium and barium cations are built of uranyl glutarate zigzag chains. The angle between the equatorial planes of the uranyl ions is several times higher in the compounds with Na^+ and K^+ ($\varphi_{UU} \approx 45\text{-}48^o$) compared to the Ca^{2+} and Ba^{2+} compounds ($\varphi_{UU} \approx 6\text{-}14^o$).

Variations of the glutaric acid anions conformation in the crystal structures can be characterized by the d_{CC} value, which shows the distance between the carbon atoms of the opposite carboxylate groups in the anion. As can be seen from Table 2, d_{CC} fluctuates more for glutarate (3.79-5.09 Å), than for hydroglutarate (4.52-5.09 Å). The lowest d_{CC} values of the glt^{2-} anions are observed in the rubidium and cesium containing structures, where glutarate anions coordinate the R^+ cations in the T^{11}-8 mode, forming an eight-membered metallocycle (Fig. 5). In this type of coordination, the anion binds the single R^+ cation by both $–COO^-$ groups, leading to the significant distortion of the dicarboxylate ion and a strong decrease of the corresponding d_{CC} value.

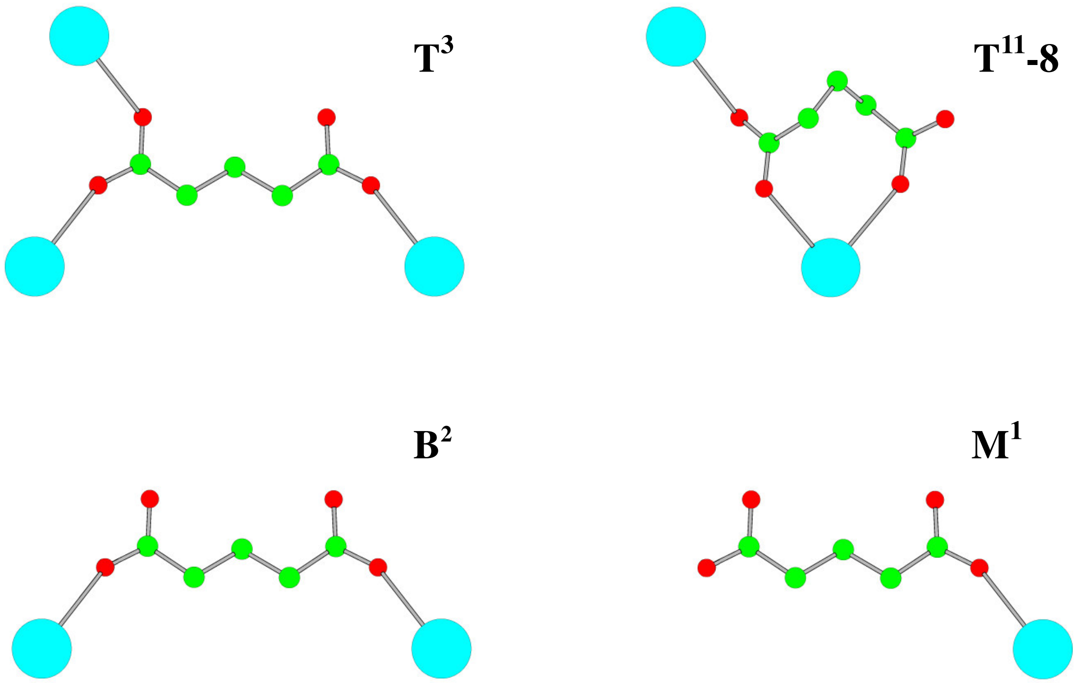

Fig. 5. The coordination types of the glutaric acid anions with respect to the R^+ or R^{2+}cations (represented by cyan circles) in the uranyl glutarate structures.

According to Table 2, the glutarate ions in the $[UO_2(glt)(Hglt)]^-$complexes play the role of a T^3 or T^{11} tridentate ligand to the majority of the R^+ cations (from Na to Cs). At the same time, the four oxygen atoms of the glutarate ion are coordinated to the uranium atoms, leading to edge sharing between RO_n and UO_8 polyhedra [16].

The structures of **1-3** differ completely from the R^+ structures. The R^{2+} cations form bonds with water molecules rather than glutarate anions. Thus, the magnesium cation exists as a hexaaqua complex, the Ca atom coordinates four water molecules and Ba - five water molecules. The magnesium ions obviously do not have any covalent bonds with the glutaric acid ions; calcium has bonds only with $Hglt^-$, and the barium atom coordinates to two $Hglt^-$ ions and one glt^{2-} ion. Therefore, $U(1)O_8$ and BaO_9 coordination polyhedra share one edge in **3**.

In spite of the similar synthetic conditions for the R^+ and R^{2+} uranyl glutarates and also the presence of the similar$[UO_2(glt)(Hglt)]^-$ chains in their structures, the nature and charge of the R ions significantly affect the content of water in their crystals. Thus, compounds with R^+ = Na, K, Rb and Cs are monohydrates, while the Li compound includes four water molecules per formula unit. Simultaneously, in **1-3** there are twelve, eight and seven water molecules per one R^{2+} ion for Mg, Ca, and Ba, respectively. These differences of R^+ and R^{2+} uranyl glutarates can be explained using Pauling's second rule [27]. Each oxygen atom of the glt^{2-} ion forms bonds with carbon and uranium atoms. The carbon atom of the carboxyl group forms one C-C bond, so that the remaining bond strength (s_C) for each of the oxygen atoms is 3/2 valence units (v.u). The uranyl ion forms bonds with six glutarate oxygen atoms so the bond strength of the uranyl ion is 2/6 v.u. for each equatorial bond. Eventually, the sum of the bond strengths on each glutarate oxygen atom (s_O) is equal to $s_C + s_U = 9/6 + 2/6 = 11/6$ v.u. In the R^+ compounds, where the oxygen atoms of the glutarate ions lack $\delta(s_O) = 1/6$ v.u., the balance for the majority (3/4) of the oxygen atoms is achieved by R-O coordination bonds. The value of $\delta(s_O)$ can be decreased to 0 (R^+ = Na or K with CN = 6) or to 0.056 v.u. (R^+ = Rb or Cs with CN = 9). If the oxygen atom has $\delta(s_O) \neq 0$ (for example, it has no bonding with R^+), it forms hydrogen bonds with water molecules or $Hglt^-$ ions.

In the studied $R^{2+}[UO_2(glt)(Hglt)]_2{\cdot}nH_2O$ compounds, the bond strength balance cannot be achieved easily for the two following reasons. First, in **1-3** there are two times more oxygen atoms with $\delta(s_O) = 1/6$ per one R^{2+} ion compared to the R^+ compounds. Moreover, the 2+ state of the cation changes its bond strength (s_R) on each R^{2+}-O bond to 2/6 v.u. in the case of Mg and Ca with CN 6. In this case, only the sign (+ or -) of the imbalance could be changed, but the absolute value would be the same. For these reasons, in **1**, **2**, and partially in **3**, the glutarate ions do not have bonds with the R^{2+}cations, which form aqua complexes instead. Only in **3** do the barium atoms with CN = 9 coordinate one glutarate-ion in a monodentate mode. As a consequence, only one of the eight oxygen atoms has $s_O = 2.055$ and its imbalance decreases from 0.167 to 0.055.

The other O atoms in **3**, similar to the oxygen atoms in **1** and **2**, participate in hydrogen bonding to reduce their bond strength imbalance.

*3.3. Cationic sublattice in **1-3***

The mutual arrangement of the metal atoms in a crystal structure can be described by the characteristics of their Voronoi-Dirichlet polyhedra (VDP) in the corresponding sublattice [28]. Selected parameters of the atomic VDPs in the U-sublattice of **1-3** are shown in Table 3.

Table 3. Selected parameters of atomic VDP in U-sublattice of **1-3***

Compound	N_f	d_{UU}, Å	V_{UU}, Å^3	CTT
1	18	5.65–14.28	493.5	$3^8 4^2 6^4 10^4$
2	16	6.77–13.07	462.3	$3^2 4^6 5^2 6^1 7^2 8^3$
3	14	7.11–11.66	469.2	$4^4 5^4 6^6$
	14	7.11–12.52	429.4	$4^4 5^4 6^6$

*N_f is the number of U atom VDP faces, d_{UU} is the range of distances between atoms sharing a common VDP face, V_{UU} is the volume of a VDP in U-sublattice, CTT is the combinatorial-topological type of VDP (the digits are the numbers of VDP face apices, and their superscripts are the total numbers of corresponding faces).

In the series **1-3**, the number of uranium neighbors in the U-sublattice, which is determined by the number of its VDP faces (N_f), decreases steadily from 18 to 14 simultaneously with the growth of the R^{2+} ionic radius. It is noteworthy that the R^+ compounds are characterized by the opposite trend [16]. For **1-3**, the shortest distance between neighbor atoms (d_{UU}) increases. At the same time, the V_{UU} value fluctuates because of the changing water content and different coordination of the R^{2+} cations.

According to [29], the VDP with $3^8 4^2 6^4 10^4$ CTT, found in structure **1**, appears to be quite rare for uranium compounds. Polyhedra with 14 faces and $4^4 5^4 6^6$CTT (typical of structure **3**) are widespread and were also revealed in the Li[UO_2(glt)(Hglt)]·4H_2O [26] structure. The VDP with the rarest CTT in the U-sublattice was found in **2**.

It should be noted that the VDPs of the alkaline earth metal cations in the R-sublattices have 14 faces and $4^6 6^8$ CTT, which is consistent with the maximum filling principle by soft (easily deformable or intersecting) spheres [29]. The VDP of the Li atom in the corresponding sublattice also has $4^6 6^8$ CTT in Li[UO_2(glt)(Hglt)]·4H_2O [26]. The alkali metal atoms have 16 neighbors in the R-sublattice and their VDPs relate to $3^4 4^2 5^4 7^4 8^2$ (Na and K) or $3^4 4^2 5^4 6^2 8^4$ (Rb and Cs) CTT.

3.5 IR spectra

The infrared spectra of **1-3** were recorded as KBr pellets on a Perkin Elmer Spectrum 100 Fourier-transform spectrometer within the region 400–4000 cm^{-1}. The spectra contain the characteristic bands corresponding to the vibration of the uranyl ions, glutarate and hydroglutarate ions, and water molecules. Assignment was done in accordance with the literature [30,31]: ν(C=O) vibrations of COOH groups lie in a range 1693-1707 cm^{-1}. Frequencies of ν_{asy}(COO) vibrations are in the range 1530-1535 cm^{-1}. Symmetrical vibrations ν_{sym}(COO) are found in the 1404-1424 and 1453-1462 cm^{-1} ranges. Valence ν_3 vibrations of the uranyl ions have the following frequencies: 925 (**1**), 923 (**2**) and 923 (**3**) cm^{-1}.

4. Conclusion

The crystal structures of three novel glutaratouranylates, namely $[Mg(H_2O)_6][UO_2(glt)(Hglt)]_2\cdot 6H_2O$ (**1**), $[Ca(H_2O)_4][UO_2(glt)(Hglt)]_2\cdot 4H_2O$ (**2**) and $[Ba(H_2O)_5][UO_2(glt)(Hglt)]_2\cdot 2H_2O$ (**3**) illustrate the different crystallochemical roles of the R^{2+} counter ions. In spite of the presence of similar $[UO_2(glt)(Hglt)]^-$ chains in **1-3**, their further connection with R^{2+} cations differ significantly among the reported compounds. The counter ions demonstrate only non-covalent interactions with the uranyl-glutarate chains in **1**, while in **2** and **3** coordination of the R^{2+} cation by hydroglutarate and glutarate (in **3**) ions appears. Moreover, the geometry of the $[UO_2(glt)(Hglt)]^-$ units in **1-3** fluctuates as a consequence of the significant organic ions flexibility. Compared to the previously studied alkali metal complexes with the same uranyl-glutarate structural units, compounds **1-3** contain many more water molecules per formula unit, which can be explained in bond strength terms.

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Appendix A. Supplementary data

CCDC 1577458-60 contain the supplementary crystallographic data for **1-3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.htm, or from the

Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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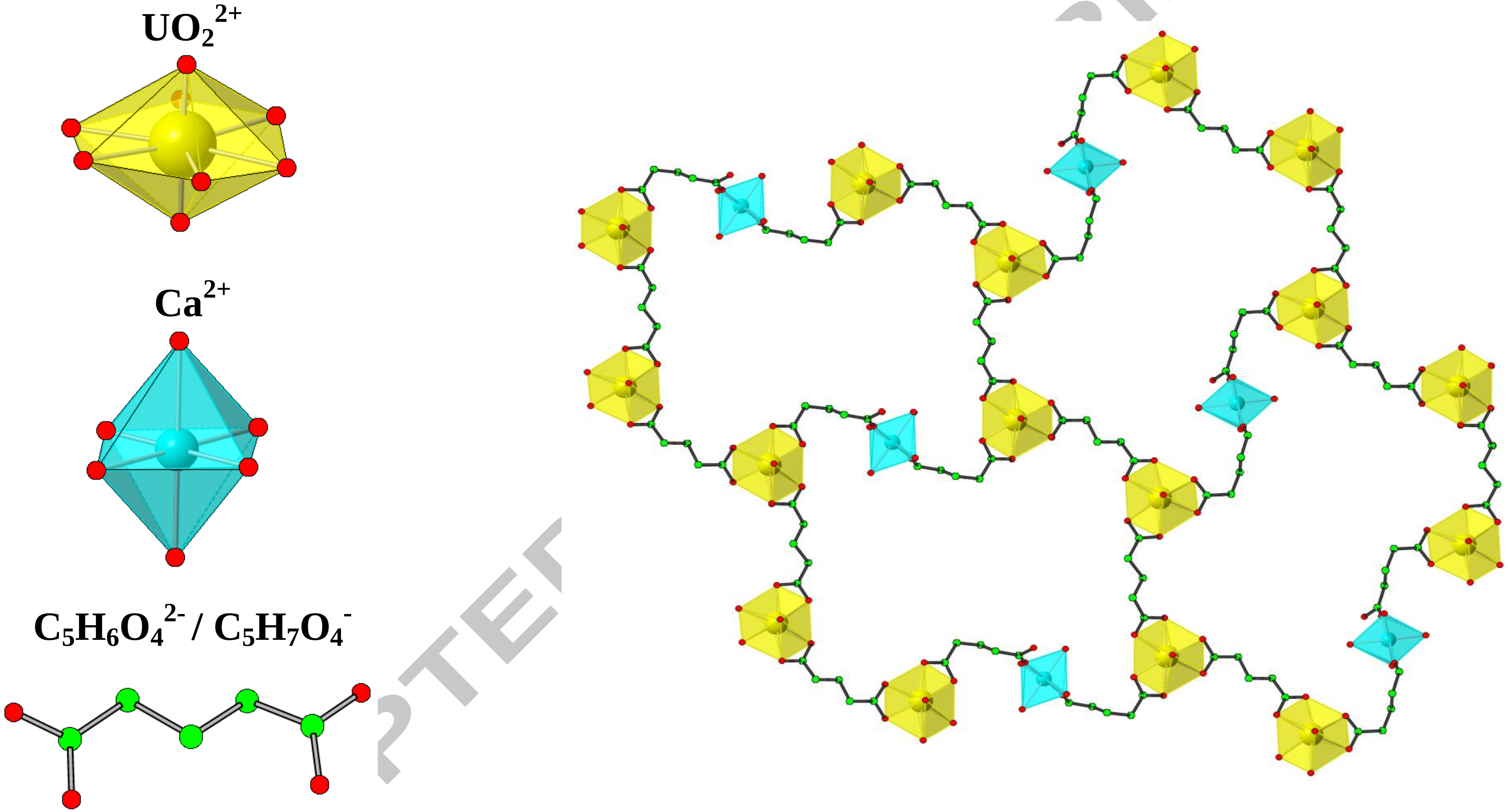

Abstract for content page

Single crystal X-ray diffraction was employed to characterize three novel uranyl coordination polymers with glutaric acid anions: $[Mg(H_2O)_6][UO_2(C_5H_6O_4)(C_5H_7O_4)]_2\cdot 6H_2O$ (**1**), $[Ca(H_2O)_4][UO_2(C_5H_6O_4)(C_5H_7O_4)]_2\cdot 4H_2O$ (**2**) and $[Ba(H_2O)_5][UO_2(C_5H_6O_4)(C_5H_7O_4)]_2\cdot 2H_2O$ (**3**). Crystals of **1-3** contain the same 1D $[UO_2(C_5H_6O_4)(C_5H_7O_4)]$ units, but the different roles of the alkaline earth cations significantly influence the overall structures.