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COORDINATION OF URANYL(VI) CARBONATE SPECIES IN AQUEOUS SOLUTIONS

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There are very few examples in nature for U(VI) compounds with carbonate ligands other than the well known tricarbonates. Especially examples of U(VI) dicarbonato compounds are nearly completely missing. Even in aqueous solutions, the dicarbonato complex was found as a species of minor importance only. On the basis of structural data on the ligands H_2O and carbonate as well as the available data on U(VI) coordination compounds, steric requirements of equatorial coordination are studied for aqueous solution species. A pentagonally coordinated monocarbonato species $[\text{UO}_2\text{CO}_3(\text{H}_2\text{O})_3]$ is found as the most likely coordination. For the dicarbonato species, hexagonally coordinated $[\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2]$ with D_{2h} symmetry is found as most probable structure. Possible causes of the instability of U(VI) dicarbonato species are discussed.

Carbonate complexation of uranium (VI) is among the most important reactions of uranium under natural conditions. However, in the overwhelming amount of uranium(VI) carbonate minerals, a CO_3^{2-} : U(VI) ratio of 3 is observed, while lower ratios are very rare with the mineral rutherfordine UO_2CO_3 as a prominent example. The lack especially of verified U(VI) dicarbonato compounds is surprising, because uranium(VI) is known to have a various mineralogy and carbonate is a readily available ligand in natural systems. Both mineralogy and coordination chemistry of uranium(VI) are intensively investigated.

Uranium(VI) has a rich coordination chemistry dominated by the properties of the uranyl(VI) entity UO_2^{2+} . This entity is almost always linear and both thermodynamically and kinetically quite stable.¹ The bond length of axial uranyl oxygens with the central uranium atom is usually about 170 pm with some variation.^{2,3} The uncoordinated UO_2^{2+} group has apparently not been observed but entity is always found coordinated in the plane equatorial to the axial uranyl oxygens by four, five or six neighbors.^{2–4} The distance to equatorial ligands is in general significantly larger than to the axial uranyl(VI) oxygens, indicating strong covalent interaction of central uranium and axial oxygen.^{1–3} The uranyl(VI) ion is understood as a “hard” Lewis acid forming coordination compounds preferentially with “hard” donors, e.g., water, carbonate and nitrate.² The coordination given in the following will refer to equatorial coordination.

An intention of this work is to summarize the considerable amount of knowledge available on the structural properties of uranium(VI) and H_2O , CO_3^{2-} and NO_3^- for the analysis of steric constraints in uranium(VI) coordination compounds. Even though instrumental techniques, e.g., X-ray diffraction^{5,6} or EXAFS⁷ of concentrated U(VI) solutions, are able to provide structural informations on solution species. These techniques currently need the species concentrations to be above 10^{-4} M and almost a single species solutions. Both conditions are difficult to establish for aqueous mono- and dicarbonato species in the U(VI)– H_2O – CO_2 system.^{8,9} Structural data of U(VI) solution species, however, are found helpful in interpretation of UV–Vis spectra for U(VI) solution species.¹⁰ Spectrum structure correlations have been discussed in detail in References 11–13.

Results and discussion

Properties of water and carbonate coordinated to the uranyl(VI) group

Available reviews^{2–4} direct to structural data of more than 200 well known U(VI) coordination compounds. To illustrate the coordination characteristics of U(VI), typical data for selected compounds have been summarized in Table 1, where some emphasis is put on bond lengths between the central uranium atom and equatorial water molecules. From Table 1, the average bond distance between central uranium and equatorial water is found to be quite constant with $\text{U–O}=(243 \pm 3)$ pm.

The average $\text{U–O}(\text{H}_2\text{O})$ distance is quite insensitive to the coordination number, the structure and the phase of the compound and found to vary within only 1–2% of the total distance. The interatomic distances of uranium and oxygen donor atoms of other ligand molecules, e.g., carbonate, nitrate, oxalate or TEP (triethyle phosphate) are similar to those of water oxygen atoms. Chloride however is sterically more demanding by its larger interatomic distance to uranium(VI) of about 280 pm.

In aqueous solutions, the hydrated uranyl(VI) entity $\text{UO}_2^{2+}(\text{aq})$ is equatorially pentacoordinated by five water molecules^{5,14,25–27} as $[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$. A detailed structural analysis of this coordination geometry is available in $[\text{UO}_2(\text{H}_2\text{O})_5](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$.¹⁴ It may serve as a characteristic example for the coordinative properties of water molecules in uranyl(VI) compounds. Water oxygen atoms in uranyl coordination compounds are not approaching each other significantly closer than 260 pm in the absence of other strong forces, e.g., covalent bonds within, e.g., carbonate or nitrate groups.^{3,4} The limit of 260 pm is also kept in the approach of equatorially coordinated oxygen to the axial uranyl oxygens. In the following, the diameter of 260 pm will be referred to as the Van der Waals diameter of oxygen. However, it is to emphasize that this term is used operationally only for reasons outlined in Reference 28 and references cited therein.

Table 1
U–O(equatorial) bond lengths for coordinated water and ligands for some selected U(VI) compounds
with mono-, di- and tetrabasic ligands in solids and solution

Compound	C. N. (eq.)	U–O distance towards H ₂ O, ppm	U–O distance towards other ligands, ppm	Refer- ence
Monomeric				
[UO ₂ (H ₂ O) ₅](ClO ₄) ₂ · 2H ₂ O	5	245.4 ± 7.7	–	14
[UO ₂ (C ₂ O ₄) ₂ (H ₂ O)] · 2H ₂ O	5	244 (3)	233 (6)–256 (4) (oxalate)	15
[UO ₂ (CH ₃ COO) ₂ · H ₂ O]	5	234	237, 245 (acetate)	16
K ₂ [UO ₂ (SO ₄) ₂ (H ₂ O)] · H ₂ O	5	251.7 (18)	234.0 (11), 237.4 (11) (sulfate)	17
[UO ₂ (C ₄ H ₂ O ₄)(H ₂ O) ₂]	6	246.6 (8)	243.6 (7), 256.7 (7) (fumarate)	18
[UO ₂ (NO ₃) ₂ (H ₂ O) ₂] · 4H ₂ O	6	239.7 (3)	250.4 (5), 254.7 (6) (nitrate)	19
Ca ₂ [UO ₂ (CO ₃) ₃]	6	–	242.9 ± 1.6 (carbonate)	20
[UO ₂ (TEP) ₂ (NO ₃) ₂]	6	–	2.518 (5), 254.0 (5) (nitrate) 237.2 (3) (TEP)	21
Oligomeric				
[(UO ₂) ₂ (OH) ₂ Cl ₂ (H ₂ O) ₄]	5	244.2 ± 6.3	236.4 ± 3.1 (μ-OH) 275.4 (8), 274.8 (8) (chloride)	22
[(UO ₂) ₂ (OH) ₂ (NO ₃) ₂ (H ₂ O) ₃] · H ₂ O	5, 6	242.4 ± 1.2	254.1 ± 2.5 (nitrate)	23
K ₂ [(UO ₂) ₄ O ₂ (OH) ₂ Cl ₄ (H ₂ O) ₄] · 2H ₂ O	5	245.0 (24), 241.1 (14)	223.6 ± 2.3 (η-O) 287.5 (5), 287.3 (9) (chloride)	24
[Gua] ₆ [(UO ₂) ₃ (CO ₃) ₆ · 6.5H ₂ O]	6	–	243.6 ± 2.6 (bond to one U)	7
Solution species				
[UO ₂ (H ₂ O) ₅] ²⁺	5	246	–	5
[(UO ₂) ₂ (OH) ₂ Cl ₂ (H ₂ O) ₄]	5	240	240 (μ-OH) 275 (chloride)	6
[(UO ₂) ₃ (CO ₃) ₆] ^{6–}	6	–	248 (carbonate)	7

C. N. (eq.): equatorial coordination number; TEP: triethyle phosphate; Gua: guanidine.

(): measurement uncertainty given in the Reference.

± : calculated in this work from multiple data given for several bonds of the same kind.

Table 2
Calculated interatomic distances between water
oxygen coordinated to a central uranyl(VI) group
in hydrated uranium(VI)

Equatorial coordination	Interatomic distance $d(\text{H}_2\text{O})$, pm
Square (4 water ligands)	344
Pentagonal (5 water ligands)	285
Hexagonal (6 water ligands)	243

In Table 2, the calculated intermolecular distances $d(\text{H}_2\text{O})$ of water for square, pentagonal and hexagonal coordination in $\text{UO}_2^{2+}(\text{aq})$ are calculated on basis of an uranium–oxygen distance of 243 pm. The distances $d(\text{H}_2\text{O})$ within neighbouring water oxygen atoms are comfortable for pentagonal coordination with 285 pm, but hexagonal coordination requires $d(\text{H}_2\text{O})$ distances far below the observed limiting approach of about 260 pm. This observation agrees well with the experimental findings of pentagonally coordinated water in the hydrated uranyl(VI) ion in both crystalline¹⁴ and solution^{5,25,26} state.

To illustrate further the coordination characteristics of uranium(VI), reference is made to the compound $[(\text{UO}_2)_2(\text{OH})_2(\text{NO}_3)_2(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$. Single crystal analysis²³ of this compound shows that uranyl groups are arranged in dimeric structures as shown in Fig. 1.

One uranyl group in the hydroxy-bridged dimer is coordinated hexagonally (with slight distortions) by two bidentate nitrate ligands and two bridging hydroxides, while the second uranyl(VI) group is coordinated pentagonally by three water molecules and two hydroxo bridges.

Interatomic distances between neighboring oxygen donor atoms are calculated from crystallographic data given in Reference 23 and indicated in Fig. 1. Interatomic distances within oxygen atoms of different ligands are always larger than 260 nm with the exception of the approach of the two nitrate ligands in the hexagonal ring. Oxygen interatomic distances within nitrate ligands however are much closer than 260 nm and can be understood due to the strong covalent bonding within the nitrate molecule. For the uranyl(VI) group, hexagonal coordination is always associated with the presence of at least two bidentate "short-bite" ligands, for which the bond angle of the "bite" with the central uranyl(VI) is $< 60^\circ$, like in chelating carbonate, carboxylate or nitrate groups. Hexagonal coordination of the uranyl(VI) group by two bidentate ligands, where the bidentate ligands are in cis position, is only observed in oligomeric structures.

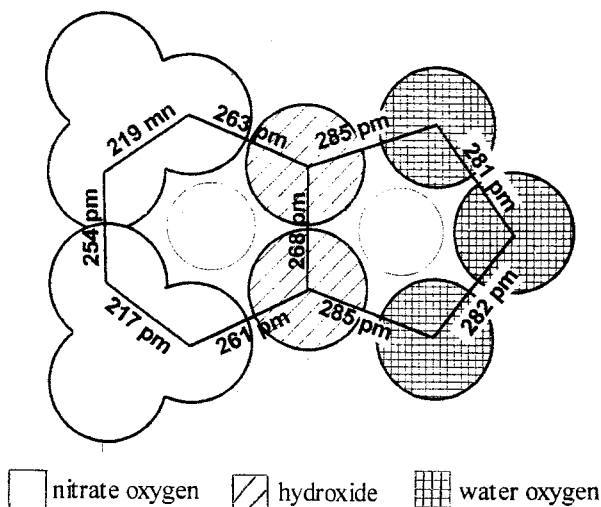


Fig. 1. Equatorial coordination of U(VI) in $[(\text{UO}_2)_2(\text{OH})_2(\text{NO}_3)_2(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$.²³ Coordinating oxygen atoms are represented by circles corresponding to 260 pm. Open circles represent the uranyl group with uranyl oxygens below and beyond the drawing plane

The two non-bidentate coordination sites in oligomers are always filled by bridging ligands, e.g., hydroxide as in Fig. 1.

Carbonate is an important constituent of natural waters and a strong complexant towards uranium(VI). A considerable number of single crystal structure determinations of uranium(VI) coordination compounds containing the $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ group have been reported with different degree of precision. Some structural data for coordinated carbonate in selected tricarbonato compounds are summarized in Table 3. Single crystal structure determinations with CO_3^{2-} : U(VI) ratios of 1 or 2, respectively, are apparently not available.

From Table 3, U–O interatomic distance between uranium and coordinating oxygen atoms are independent of the compound with very little variation and an unweighted mean of (243 ± 3) pm is calculated from the U–O distances given in Table 3. The same is found for the C–O bond lengths within carbonate ligands. The values given in Table 3 for the C–O interatomic distances are averaged over all three C–O distances of all three carbonate ligands reported in the reference.

All carbonate groups in the $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ units are distorted with respect to the D_{3h} symmetry of the free carbonate ion.^{20,32} C–O bonds to oxygens which also coordinate uranium are significantly longer than bonds to the terminal oxygens, while bond angles between coordinating oxygens are smaller than angles including terminal oxygen. Some selected data is given in Table 4.

Table 3
Structural parameters of carbonate groups in selected uranium(VI) tricarbonato compounds.
Mineralogical names of naturally occurring compounds are included

Compound (mineral name)	Interatomic distances				Reference
	U–O, pm	C–O, pm	O–O, pm	–O–O–, pm	
Na ₂ Ca[UO ₂ (CO ₃) ₃] · ~5.6 H ₂ O (Andersonite)	244 ± 2	128 ± 1	225 ± 2	267 ± 8	29
Mg ₂ [UO ₂ (CO ₃) ₃] · 18H ₂ O (Bayleyite)	242.9 ± 1.6	128.1 ± 2.5	217.3 ± 1.5	267.8 ± 3.0	30
K ₃ Na[UO ₂ (CO ₃) ₃] (Grimselite)	242 ± 1	128 ± 1	a	a	31
Ca ₂ [UO ₂ (CO ₃) ₃] · ~11H ₂ O (Liebigite)	242.7 ± 2.1	128.0 ± 2.2	218.0 ± 1.0	266.5 ± 8.8	20
NaCa ₃ [UO ₂ (CO ₃) ₃](SO ₄)F · 10H ₂ O (Schröckingerite)	242.4 ± 1.9	128.3 ± 2.1	217.6 ± 0.6	266.4 ± 1.1	32
CaMg[UO ₂ (CO ₃) ₃] · 12H ₂ O (Swarzite)	243.7 ± 2.1	128.2 ± 1.0	217.1 ± 0.4	269 ± 8	33
(NH ₄) ₄ [UO ₂ (CO ₃) ₃]	245.3 ± 2.2	128.0 ± 4.4	223 ± 1	270 ^b	34
K ₄ [UO ₂ (CO ₃) ₃]	243.0 ± 2.5	128.8 ± 4.0	220.8 ± 1.7	266.5 ± 1.5	35

^aNecessary data not available.

^bMean value taken from the Reference.

O–O: interatomic distance of coordinating oxygen atoms within a carbonate ligand.

–O–O–: interatomic distance of coordinating oxygen atoms of neighboring carbonate ligands.

Table 4
Comparison of bond angles and interatomic distances in carbonate groups
of selected uranyl(VI) tricarbonato compounds

Compound	<O _c –C–O _c , deg.	<O _c –C–O _t , deg.	C–O _c , pm	C–O _t , pm	O–O, pm	Reference
Liebigite	114.7 ± 0.6	122.6 ± 1.2	129.4 ± 1.0	125.3 ± 0.9	217.9	20
Schröckingerite	114.1 ± 0.3	123.0 ± 0.5	129.7 ± 0.2	125.2 ± 0.4	217.7	32
Swarzite	114.1 ± 0.3	123.0 ± 0.3	129.4 ± 0.4	125.4 ± 0.2	217.2	33

O_c: coordinated oxygen.

O_t: terminal oxygen.

In [UO₂(CO₃)₃]^{4–} groups the uranyl(VI) entity is coordinated distorted hexagonally as shown in Fig. 2. This distortion is partly due to the significantly smaller O–U–O bond angles to oxygen atoms of the same carbonate group compared to bond angles to neighboring oxygens of different carbonate groups. These data are also given in Table 3.

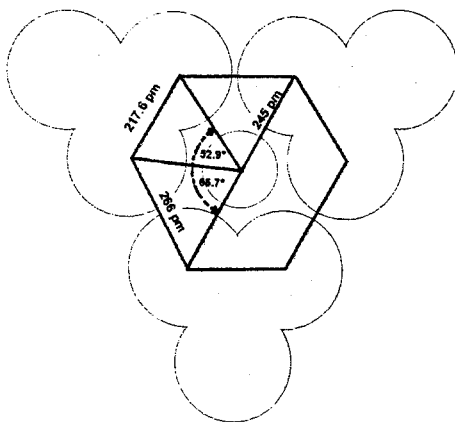


Fig. 2. Equatorial coordination of U(VI) in the $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ complex. The coordination hexagon is distorted due to an O-U-O angle $< 60^\circ$ to oxygen atoms of a carbonate ligand

The interatomic distances between neighboring oxygens from neighboring carbonate ligands in some compounds show considerable variation. In most compounds of Table 3, carbonate groups are slightly twisted and the coordinating oxygens of a carbonate group are lying some few pm above and below the calculated least square plane through the equatorial coordination hexagon. An exemption is grimselite where planarity is required by symmetry.²⁰ The effects due to this twisting are, however, negligible for the current discussion.

Structural parameters of carbonate ligands in the $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ group do not show any characteristic structural deviation from those in non-uranyl compounds. A concise review of the stereochemistry of carbonate ligands is available for 34 well known non-uranyl(VI) compounds.³⁶ The mean value of 102 C-O distances is found to be (128.4 ± 1.8) pm.³⁶ In all the 34 cases, a distortion of the carbonate group from D_{3h} symmetry due to coordination is observed: interatomic distances are reduced along edges shared with the coordination polyeder of the cation. The C-O distance to a non-coordinating oxygen is somewhat smaller compared to the coordinating oxygens of a carbonate molecule.^{20,36} Furthermore, comparison of structural data obtained from crystalline compounds with data given in the literature for uranyl(VI) carbonate species in solution (cf. Table 1) do not indicate differences between structures in solid phase and aqueous phase.

The following discussion of steric constraints on the coordination of carbonate to uranium(VI) in aqueous solution will be based on the mean values derived from the above discussion: an U-O bond length of 243 pm, a minimum interatomic distance of

260 pm between neighboring oxygens of different carbonate groups and an interatomic distance between coordinating oxygens of the same carbonate ligand 217 pm. These distances translate into an O–U–O angle of 53.0° to donor oxygens of the same carbonate ligand and a minimum O–U–O angle of 64.7° to neighboring oxygens of different carbonate ligands. Coordination of water will be considered by a Van der Waals diameter of 260 pm.

Table 5
Calculated mean interatomic distances –O O–
for different amount x of water
ligands in the coordination of $[\text{UO}_2(\text{CO}_3)(\text{H}_2\text{O})_x]$

x	2	3	4
–O O–, pm	378	300	246

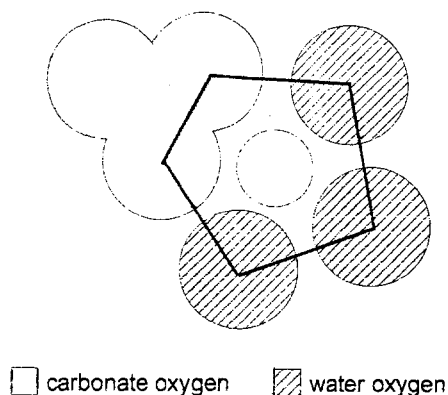
–O O–: distance between neighboring coordinating oxygen atoms.

Aqueous species $\text{UO}_2\text{CO}_3^\circ$

The uranium(VI) monocarbonato species is well known from solubility measurements and spectroscopic speciation.¹⁰ Its coordination geometry can be derived by filling the coordination sites by a carbonate group and various water ligands. An analysis will be made by analysing the steric situation by addition of two, three and four water molecules. the results are given in Table 5.

With two coordinated water molecules, one further coordination site can be filled without steric repulsion. The distance between coordinating oxygens is about 300 pm for three water ligands, still comfortably larger than the van der Waals diameter of 260 pm. Adding one further water ligand however reduces the interatomic distance to 247 pm, clearly smaller than 260 pm.

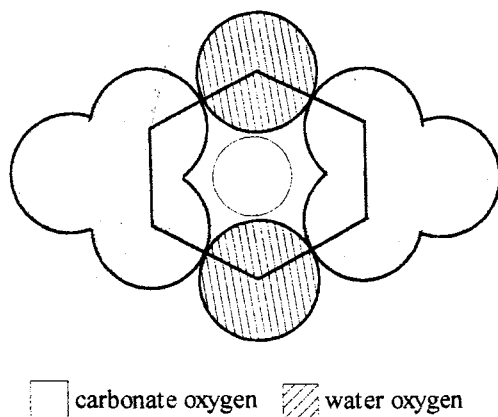
Therefore, an $\text{UO}_2(\text{CO}_3)(\text{H}_2\text{O})_3$ species with pentagonal coordination of uranium as given in Fig. 3 is the only possible structure. A model compound is found in $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$,¹⁶ where uranium is coordinated by one chelating CH_3COO group, two monodentate acetate oxygens and a water ligand. The uranium–oxygen(chelate) distance is 245 pm and the distance between chelating oxygens in the acetate ligand is 218 pm. Interatomic distances between neighboring monodentate oxygens are 294 pm.

Fig. 3. Equatorial coordination in $[\text{UO}_2(\text{CO}_3)(\text{H}_2\text{O})_3]$ *Aqueous species $\text{UO}_2(\text{CO}_3)_2^{2-}$*

In $\text{UO}_2(\text{CO}_3)_2^{2-}$, two carbonate groups are coordinated to a uranyl(VI) group. One or two water ligands may be coordinated to give either a pentagonal or a hexagonal coordination, respectively. Assuming pentagonal coordination, two neighboring carbonate ligands occur. Using an O–U–O angle of 65.7° between neighboring oxygen ligands from different carbonate groups and an O–U–O angle of 53.0° within each carbonate group, the added water ligand would have a distance of 364 pm from the closest carbonate oxygen. Under those conditions, any steric limitations are likely to occur and such a species may even be considered to be coordinatively unsaturated.²⁸

Addition of one further water ligand, however, may decide between two sites: either water ligands in cis position or in trans position. As mentioned above, a mononuclear hexagonally coordinated uranyl(VI) group with two bidentate “short-bite” ligands in cis geometry have obviously not yet been observed. On the basis of symmetry arguments too, trans coordination may be more likely. Cis geometry would be of symmetry C_{2v} only, while trans geometry has higher symmetry D_{2h} . For trans geometry, however, an oxygen(H_2O)–oxygen(CO_3) distance of 256 pm is calculated. Comparison with data summarized for –O– distances in Table 3 shows that such a distance is not completely excluded but, nevertheless, indicates that hexagonal coordination is quite demanding. A schematic representation of hexagonal $[\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2]^{2-}$ coordination is given in Fig. 4.

The U(VI) dicarbonato species seems to be confronted with a dilemma: pentagonal $[\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})]^{2-}$ is not optimally coordinated, hexagonal $[\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2]^{2-}$, however, experiences considerable steric strain. A conclusion, whether pentagonal

Fig. 4. Equatorial coordination in $[\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2]$

coordination or hexagonal coordination is more plausible for the uranyl(VI) dicarbonato species in aqueous solution, is not as straightforward as in case of the monocarbonato species.

It is to keep in mind that calculated interatomic distances are based on rigid inter- and intramolecular distances and bond angles. However, the involved bond angles and interatomic distances are flexible to a certain extent. The interaction of molecules and ions in the absence of covalent forces is often described by the so-called Lennard-Jones (12,6) potential

$$V_{LJ} = (C_{12}/r^{12}) - (C_6/r^6)$$

where C_{12} and C_6 are empirical constants and r is the interatomic distance. From the definition of the potential V_{LJ} it is understood that the approach of two atoms is limited by the steep increase of the repulsive forces with a power of 12. If a given approach falls below a limit, which is, e.g., expressed in this work by a Van der Waals diameter, this observation indicates considerable strain to work against the increasing repulsive forces.

An example for hexagonal D_{2h} symmetry is found in $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$,¹⁹ which will be compared to $[\text{UO}_2(\text{NO}_3)_3]^-$.³⁷ In these structures, nitrate is a common ligand. The coordination of the trinitrato complex is analogous to the tricarbonato complex Fig. 2, while the arrangement in the dinitrato complex is analogous to the schematic representation of the dicarbonato species shown in Fig. 4. In Table 6, relevant data for $-\text{O}-\text{O}-$ distances between water oxygens and nitrate oxygens, $\text{O}-\text{N}-\text{O}$ bond angles and $\text{O}-\text{O}$ distances between nitrate groups within a nitrate molecule are given. It is evident from the $-\text{O}-\text{O}-$ distances that hexagonal coordination is more comfortable for the

Table 6
Interatomic distances in some selected U(VI) nitrate and oxalate compounds

Compound	Rb[UO ₂ (NO ₃) ₃] Ref. 37.	[UO ₂ (NO ₃) ₂ (H ₂ O) ₂] · 4H ₂ O Ref. 19.	(NH ₄) ₄ [UO ₂ (C ₂ O ₄) ₃] (six-coordinated unit) ³⁸	
			Side-on	End-on
<) O–N–O	117.5 (4)°	114.6°, 115.6°		
–O O–	278.9 pm	262.4 pm		
O–O (nitrate)	216.1 pm	213.3 (8) pm, 213.9 (8) pm		
U–O	247.6 pm	250.4 pm, 254.7 pm		
<) O–C–O			127°, 129°	125°
U–O			241 pm, 244 pm	257 pm
<) O _c –U–O _c	51.8°	49.5°	62°	49.4°
minimum –O O– between neighboring oxalate oxygens in five-coordinate unit:			272 pm ¹⁵	
minimum –O O– between neighboring oxalate oxygens in six-coordinate unit:			252 pm ³⁸	

trinitrate, while the approaches of neighboring ligands are much closer in case of the dinitrate compound. The two nitrate ligands approach each other even closer than 260 pm. Furthermore, the coordinating O–N–O bond angles are reduced as also evident from internal O–O distances. In addition, the distances between coordinating nitrate oxygens and the central uranium are considerably larger for the dinitrate. These differences indicate considerable strain in the coordinative ring.

As a further example, the oxalate compounds of uranium(VI) are discussed. Oxalate (O₂C–CO₂) is usually coordinated to an uranyl(VI) group side-on by oxygen atoms bound to different C-atoms of an oxalate ligand thus forming five-membered chelate rings. Bond angles O–U–O are typically larger than 60° and therefore, oxalate is not a "short-bite" ligand. In oxalate compounds, U(VI) is usually pentagonally coordinated.^{15,38,39} In (NH₄)₄[UO₂(C₂O₄)₃], however, hexagonal coordination is observed.³⁸ It is obvious from the foregoing discussion that coordination by three oxalate ligands side-on is impossible by steric reasons. In the hexagonal trioxalate, one of the three oxalates is coordinated end-on, while two oxalate ligands are coordinated side-on (Fig. 5). Some structural data for side-on and end-on coordinated oxalate ligands in the hexagonal ring are included in Table 6. As outlined in more detail in Reference 38 the hexagonal ring experiences considerable strain. The bond angle within the end-on coordinated oxalate is smaller and the U–O bond length is considerably larger. When comparing the minimum –O O– distances (Table 6) within hexagonal³⁸ and pentagonal^{15,39} units, this strain becomes evident too.

Both nitrate and oxalate complexes of uranium(VI) indicate that hexagonal coordination is obtained even on the expense of considerable strain in the coordinating

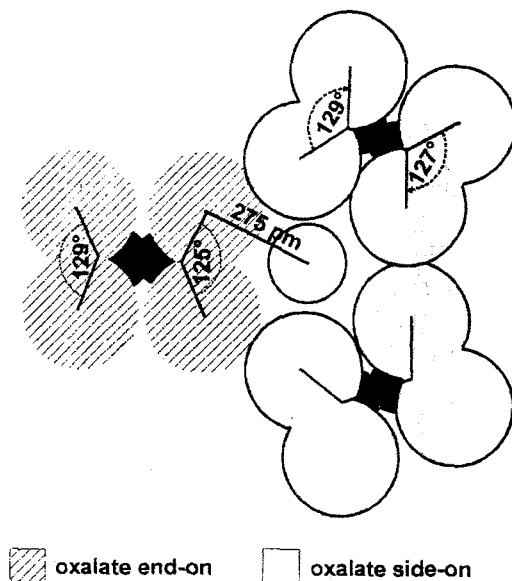


Fig. 5. Equatorial coordination in $[\text{UO}_2(\text{C}_2\text{O}_4)_3]^{4-}$ (from Ref. 38)

ring. On the basis of these observations, the uranyl dicarbonato species will most probably occur as a hexagonally coordinated $[\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2]^{2-}$ species with trans position of both bidentate carbonate and monodentate water ligands. The reader is further directed to the fumarate compound $[\text{UO}_2(\text{C}_4\text{H}_2\text{O}_4)(\text{H}_2\text{O})_2]$ with trans geometry of both the fumarate carboxyl groups and the water ligands, experiencing similar strain¹⁸ as indicated, e.g., by a maximum U–O distance of the carboxyl group 256.7 pm, considerably longer than 237 pm and 245 pm found for carboxylate, e.g., in $[\text{UO}_2(\text{CH}_3\text{COO})_2] \cdot 2\text{H}_2\text{O}$.¹⁶

Nevertheless, the steric strain in hexagonally coordinated $[\text{UO}_2(\text{CO}_3)(\text{H}_2\text{O})_2]^{2-}$ is more severe than in $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ due to the usually longer U–O distances found for nitrate ligands (cf. Tables 1 and 3). Therefore, it is not surprising that the dinitrate complex is well known from the $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$,^{19,40} while the dicarbonate complex is only suspected to occur in zellerite $\text{Ca}[\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ and metazellerite $\text{Ca}[\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$,^{41,42} two extremely rare uranium(VI) minerals. Despite intense study of the U(VI)–H₂O–CO₂ system during the past decade,⁹ structural data of phases containing complexes with an $\text{CO}_3^{2-} : \text{U}$ ratio of 2 have not been reported. Also from study of solid–aqueous phase equilibria of the U(VI)–H₂O–CO₂ system, a minor stability field of the dicarbonato species has been observed from both solubility⁴³ and

spectroscopic investigation.¹⁰ These observations can readily be understood in terms of the preceeding discussion by the steric strain that reduces the stability of the dicarbonato species with respect to either the monocarbonato and the tricarbonato species.

Conclusions

Based on analysis of structural data from available crystallographic studies of U(VI) coordination compounds, the steric situation in the equatorial sphere of the uranyl(VI) group has been analysed for different coordination geometries involving carbonate and water ligands. This analysis was motivated first by the lack of information concerning coordination of the species $\text{UO}_2\text{CO}_3^\circ$ and $\text{UO}_2(\text{CO}_3)_2^{2-}$ in aqueous solutions and second to find possible reasons for obvious instability of uranyl(VI) structures with an $\text{CO}_3^{2-} : \text{U}$ ratio of 2 in nature.

Pentagonally coordinated $[\text{UO}_2(\text{CO}_3)(\text{H}_2\text{O})_3]$ is found as most probable composition. Steric limitations for entrance of a fourth water molecule to form $[\text{UO}_2(\text{CO}_3)(\text{H}_2\text{O})_4]$ species requires interatomic approaches of 242 pm between neighboring oxygen atom. Such close approach has not been observed in equatorial coordination of U(VI).^{16,38}

The dicarbonato species will most likely occur as hexagonal $[\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})_2]^{2-}$ with D_{2h} symmetry. A demanding steric situation is found for this species. Assuming pentagonal coordination $[\text{UO}_2(\text{CO}_3)_2\text{H}_2\text{O}]^{2-}$, there remains generous space within the ligands in a possible structure $[\text{UO}_2(\text{CO}_3)_2(\text{H}_2\text{O})]$ due to the presence of two "short bite" carbonate ligands. Such coordinations, however, have not yet been observed. Furthermore, this situation also means considerable coordinative unsaturation. In hexagonal coordination, however, the coordinative ring faces considerable steric strain. Due to the lack of characterized uranyl(VI) structures with $\text{CO}_3^{2-} : \text{U}=2$, the question of the most likely structure could not be resolved by analogy with existing U(VI) carbonate structures. Two examples were given to show that hexagonal coordination is achieved even under considerable steric strain. Nevertheless, the rareness of uranyl(VI) dicarbonato structures in nature may well occur due to the discussed steric effects.

This paper adds some understanding of the uranium(VI)– H_2O – CO_2 system, especially concerning the rather limited stability of uranyl(VI) dicarbonate species in both solid and aqueous phase. This system is of importance, e.g., in the performance assessment of disposal concepts of nuclear wastes as well as in remediation of former uranium mining areas, where remediation of environmental damage due to irresponsible uranium exploitation procedures is of urgent necessity. In many uranium mining countries of the world, e.g., Canada, Czech Republic, Germany and South Africa, subsurface uranium shafts, uranium mill tailings and rock piles impose an eminent short term and long term risk to the health of populations.

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