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Crystal Structure of the Sodium Salt of the Uranyl–Oxyacetate–Fluoride Dimer, $Na_4(UO_2)_2(OCH_2COO)_2F_4 \cdot 6H_2O$

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The structure of the ternary uranyl–oxyacetate–fluoride dimer, $(UO_2)_2(OCH_2COO)_2F_4^{4-}$, was studied by single crystal X-ray diffraction. The space group is $P\bar{1}$, and the structure contains discrete dimers with a double pentagonal bipyramid geometry, linked by octahedrally coordinated sodium ions. The uranyl ion has a coordination number of five with two fluorides and three oxygens coordinated in a plane perpendicular to the linear UO_2 axis. The dimer is formed via bridging oxygen atoms from the deprotonated hydroxyl groups of the glycolate ligands.

Uranium(VI) exists in aqueous solution as the hydrated uranyl ion, $UO_2(H_2O)_5^{2+}$. Because of the linear structure of the uranyl ion the available coordination sites are located in the equatorial plane perpendicular to the linear O–U–O axis. The uranyl ion is known to form strong complexes, especially with hard ligands. Earlier potentiometric equilibrium studies[1–3] of the binary uranyl–glycolate system indicated that three complexes with the stoichiometry UO_2L^+, $UO_2L_2(aq)$ and $UO_2L_3^-$, where $L = HOCH_2COO^-$, were formed in aqueous solution. At low pH, the average number of coordinated ligands, $\bar{n}$ is a function of the free ligand concentration, [L] only. However, at higher pH, $\bar{n}$ at constant [L] turned out to be also a function of pH. This indicated that the simple model for complex formation given above is not entirely correct. Ahrland[1] suggested that the experimental observations could be explained by the hydrolysis of UO_2^{2+}. We have questioned this explanation and found that the experimental observations are a result of deprotonation of the OH group in the glycolate ligand.‡ This is remarkable, because deprotonation occurs at a pH around 3, indicating that coordination to UO_2^{2+} increases the acidity of the OH group by at least a factor of 10^{12}. Similar observations have been made previously by Grenthe on the Er^{3+}-glycolate system.[4] However, the increase in the dissociation constant of the OH-group is much smaller there, and complexes containing $^-OCH_2COO^-$ are only observed in strongly alkaline solutions. Using potentiometry and multinuclear NMR methods, complexes formed in the ternary uranyl–glycolate–fluoride system at different concentrations and pH were identified.[5] In these complexes the uranyl ion has a coordination number of five giving a pentagonal bipyramid structure which is known as the most common feature among uranyl complexes. At low pH the glycolate ion was coordinated through the carboxylate group only, while at higher pH a five-member chelate ring was formed via one carboxylate oxygen and the oxygen on the α-carbon atom, i.e. the deprotonated hydroxyl group. We decided to confirm the results of the solution studies with a solid-state structure determination on a complex that could be crystallized from solution. This complex is known to be dimeric and is dominant in the solution over a broad pH range. The solid phase had the composition $Na_4(UO_2)_2(OCH_2COO)_2F_4 \cdot 6H_2O$.

Experimental

Preparation. Chemicals of analytical grade were used. An aqueous solution of 10 mM $UO_2(ClO_4)_2$, 30 mM sodium glycolate and 20 mM NaF was prepared. The pH was adjusted to 7.5 with NaOH. The solution was evaporated in air protected from light. Yellow needle-like crystals were formed.

X-Ray crystallography. The data collection was carried out at room temperature using an Imaging Plate

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‡ Unpublished results by Szabó and Grenthe.

Diffraction System.[6] The measured intensities were corrected for background, Lorentz, polarization and absorption effects. The absorption correction was carried out numerically with the STOE-X-shape and X-red programs.[7] Table 1 summarizes the crystal data and selected experimental conditions. The structure was solved using the Patterson method (SHELXS-86[8]), and it was refined by full-matrix least-squares (LS) calculations based on F^2 values of all reflections (SHELXL-93).[9] The (C–)H atoms were added to the structure model at calculated positions, which were recalculated after each refinement cycle,[9] whereas the (O–)H atoms were located from the difference electron density ($\Delta\rho$) map and were held riding on their parent oxygens during the subsequent refinements. All non-hydrogen atoms were refined anisotropically, while isotropic vibrational parameters were refined for the hydrogens. Crystallographic R values and further details about the refinement calculations are listed in Table 1. The final $\Delta\rho$ map indicated relatively high residual electron densities (-3.3 e Å$^{-3}\geqslant$) in the proximity (≈ 1 Å) of the uranium positions, in all probability due to the very heavy uranium atom and small errors in the approximation applied for the description of its shape and its atomic vibrations in the crystal.

Table 1. Crystal data and details of data collection and structure refinement calculations for $Na_4(UO_2)_2(OCH_2COO)_2F_4 \cdot 6H_2O$.

Formula weight	964.19
Temperature	293(2) K
Wavelength	0.71073 Å (Mo Kα)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a=7.281(1)$ Å, $\alpha=95.68(2)°$ $b=7.606(1)$ Å, $\beta=105.21(2)°$ $c=10.436(2)$ Å, $\gamma=112.57(2)°$
Volume	501.88(14) Å^3
Z	1
Density (calculated)	3.190 Mg m^{-3}
Absorption coefficient	16.31 mm^{-1}
Minimum and maximum transmission	0.2248–0.3767
$F(000)$	432
Crystal size	$0.17\times0.1\times0.07$ mm^3
θ-Range for data collection	2.08–26.15°
Index ranges	$8\geqslant h\geqslant -9$, $9\geqslant k\geqslant -9$, $12\geqslant l\geqslant -12$
Reflections collected	3936
Independent reflections	1830 [R(int) = 0.047]
Refinement method	Full-matrix least-squares on F^2
Data[a]/restraints/parameters	1817/0/139
Goodness-of-fit on F^2	1.072
Final R-indices [$I>2\sigma(I)$]	$R_1=0.027$, $wR_2=0.068$[b]
R-indices (all data)	$R_1=0.028$, $wR_2=0.069$[b]
Largest difference peak and hole	3.30 and -2.50 e Å^{-3}

[a]Certain reflections with considerable differences between F_{obs} and F_{calc}, due to extinction effects, potential systematic errors, were excluded from the final refinement calculation. [b]$w=[\sigma^2F_o^2+(0.0575P)^2]^{-1}$, where $P=(F_o^2+2F_c^2)/3$.

Results and discussion

Crystal data, refined atomic coordinates, selected atomic distances and angles, and the geometry of possible hydrogen bond interactions are summarized in Tables 1–4. Standard deviations are given in parentheses. The

Table 2. Refined fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (in Å$^2\times10^3$) for non-hydrogen atoms in $Na_4(UO_2)_2(OCH_2COO)_2F_4 \cdot 6H_2O$.

	$x/10^{-4}$	$y/10^{-4}$	$z/10^{-4}$	U(eq)/Å^2 10^{-3}[a]
U	856(1)	1491(1)	1879(1)	10(1)
Na(1)	5000	0	5000	27(1)
Na(2)	0	5000	5000	22(1)
Na(3)	3918(5)	3762(4)	8251(3)	26(1)
F(1)	2244(7)	90(6)	3414(4)	24(1)
F(2)	1756(7)	3587(6)	3870(4)	24(1)
O(1)	3449(8)	2951(8)	1835(5)	24(1)
O(2)	−1700(8)	−4(8)	1977(5)	22(1)
O(3)	−853(7)	1089(7)	−493(4)	19(1)
O(4)	−509(8)	3838(7)	1356(4)	22(1)
O(5)	−3377(8)	4112(8)	141(5)	27(1)
C(1)	−2535(12)	1674(11)	−804(7)	25(2)
C(2)	−2142(11)	3349(10)	300(7)	18(1)
OW1	−3133(8)	2076(8)	3718(5)	28(1)
OW2	−681(8)	6499(8)	3205(5)	25(1)
OW3	5250(9)	7026(8)	3869(5)	31(1)

[a]U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond lengths (in Å) and angles (in °) for $Na_4(UO_2)_2(OCH_2COO)_2F_4 \cdot 6H_2O$.

Bond lengths			
U–O(2)	1.807(5)	Na(2)–OW1	2.420(5)
U–O(1)	1.802(5)	Na(2)–OW1#7	2.420(5)
U–F(1)	2.244(4)	Na(2)–F(2)	2.403(4)
U–F(2)	2.262(4)	Na(2)–F(2)#7	2.403(4)
U–O(3)#1	2.319(4)	Na(3)–O(5)#10	2.301(5)
U–O(4)	2.396(4)	Na(3)–OW2#7	2.368(6)
U–O(3)	2.390(4)	Na(3)–O(5)#7	2.426(5)
Na(1)–F(1)	2.271(4)	Na(3)–O(1)#6	2.528(6)
Na(1)–F(1)#2	2.271(4)	Na(3)–OW3#6	2.518(6)
Na(1)–OW1#3	2.420(6)	Na(3)–O(2)#4	2.637(6)
Na(1)–OW1#4	2.420(6)	O(3)–C(1)	1.429(8)
Na(1)–OW3#5	2.539(5)	O(4)–C(2)	1.288(8)
Na(1)–OW3#6	2.539(5)	O(5)–C(2)	1.231(8)
Na(2)–OW3#7	2.329(5)	C(1)–C(2)	1.513(9)
Na(2)–OW2	2.329(5)		
Bond angles			
O(2)–U–O(1)	177.9(2)	F(1)–U–O(4)	150.0(2)
O(1)–U–F(1)	89.6(2)	O(3)#1–U–O(4)	131.6(2)
O(1)–U–F(2)	86.7(2)	O(1)–U–O(3)	94.5(2)
F(1)–U–F(2)	77.70(14)	F(1)–U–O(3)	143.6(2)
O(1)–U–O(3)#1	87.6(2)	O(3)#1–U–O(3)	66.1(2)
F(1)–U–O(3)#1	78.1(2)	O(4)–U–O(3)	65.49(14)
O(1)–U–O(4)	95.5(2)		

Symmetry transformation used to generate equivalent atoms: (#1) $-x,-y,-z$; (#2) $-x+1,-y,-z+1$; (#3) $x+1,y,z$; (#4) $-x,-y,-z+1$; (#5) $x,y-1,z$; (#6) $-x+1,-y+1,-z+1$; (#7) $-x,-y+1,-z+1$; (#8) $x,y+1,z$; (#9) $x-1,y,z$; (#10) $x+1,y,z+1$; (#11) $-x+1,-y+1,-z+2$; (#12) $x-1,y,z-1$.

Table 4. Geometry of possible hydrogen-bonded interactions.[a]

Atoms involved/D–H···A	Symmetry of A	Distances/Å			D–H–A angle/°
		A···D	D–H	A···H	
OW1–HW11···O2	x, y, z	2.929	0.899	2.102	152.6
OW2–HW21···O4	x, y, z	2.717	1.068	1.762	146.5
OW3–HW32···F2	x, y, z	2.865	0.939	1.926	177.8
OW2–HW22···F1	$x, y+1, z$	2.687	0.952	2.095	118.9
OW3–HW34···F2	$-x+1, -y+1, -z+1$	2.972	1.072	1.900	178.7

[a]D and A denote donor and accepted atoms.

structure of the dimer anion is shown in Fig. 1, while Fig. 2 gives a view of the packing of the crystal.

Each uranyl ion is surrounded by five ligands, two fluorides and three oxygens coordinated in the plane perpendicular to the axis of the ion. Two of these oxygens, the deprotonated hydroxyl oxygens in the oxyacetate ligands, are bridging two uranium fragments forming a discrete dimer as a double pentagonal bipyramid con-

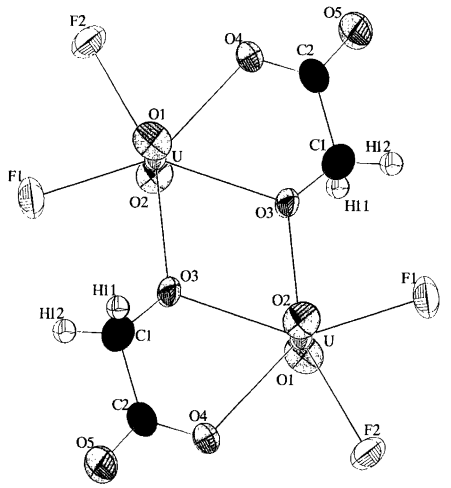

Fig. 1. Structure of the $(UO_2)_2(CH_2OCOO)_2F_4^{4-}$ dimer. Non-hydrogen atoms are represented with their displacement ellipsoids of 75% probability.

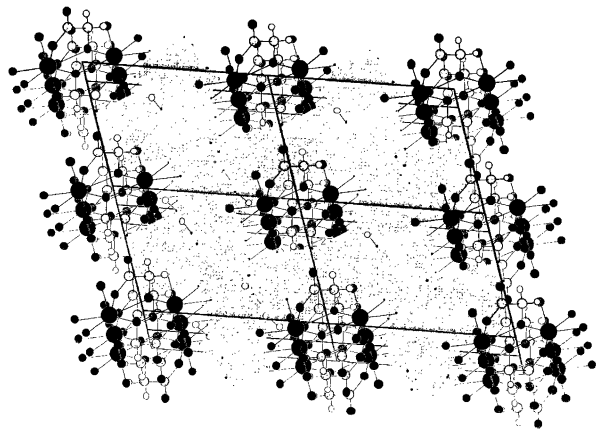

Fig. 2. Packing diagram with the octahedra around the sodium ions showing the channels of uranium dimers in the sodium ion net. The uranium ions are dark gray.

nected along one edge. Each oxyacetate has three potential ligand oxygens of which two, one carboxylic and the deprotonated α-hydroxy oxygen, are coordinated to the uranium. The length of the covalent bond between the uranium and the *yl* oxygens is 1.805(5) Å, which is similar to the one measured in the UO_2(picolinate)F_3^{2-} complex [1.792(5) Å][10] and is slightly longer than the average value, 1.77 Å, for this type of bond in uranyl complexes varying between 1.58 and 1.96 Å.[11] The U–O coordination distances in our complex are 2.319(4), 2.396(4) and 2.390(4) Å. They are slightly shorter than the corresponding one measured in UO_2(picolinate)F_3^{2-} [2.447(4) Å],[10] and within the range from 2.17 to 2.84 Å and near the mean value of 2.39 Å characteristic for U–O coordination bonds.[12] EXAFS measurements and theoretical calculations made on uranyl aqua and hydroxide complexes indicated that there is a correlation between the U–O coordination distances in the equatorial plane and the U–O distances in the uranyl ion.[13] Using the solid-phase structure determinations available in the database we found no correlation of this type. However, the uncertainty in the bond distances is often large, ±0.02 Å. U–F distances for uranyl complexes vary between 2.20 and 2.39 Å with an average of 2.28 Å.[14] Our values, 2.244(4) and 2.262(4) Å, are somewhat shorter than the mean value. Corresponding bond distances in the $K_3UO_2F_5$ complex [2.24(1) Å],[15] in the Na_2UO_2(oxalate)F_3 complex [2.24(3) Å][16] and in the Na_2UO_2(picolinate)F_3 complex [2.234(4), 2.237(4) and 2.260(4) Å][10] are nearly identical, which indicates that the additional ligand has little effect on the strength of bond between the fluoride and the uranyl ion. In the $UO_2(H_2O)F_4^{2-}$ formed with bulky cations the U–F distances are longer, 2.28(1) and 2.39(1) Å,[17] probably due to hydrogen bonds between the coordinated water molecule and the fluoride ions. Additional work is ongoing to confirm this. The C–C and C–O covalent bond lengths and bond angles in the oxyacetate ligand are reasonable.

The crystal structure consists of layers of sodium ions [Na(1) and Na(2)] located between layers containing dimers and Na(3) ions arranged in columns, cf. Fig. 2. The dimers are linked by Na(3) via bonds to the *yl* oxygens and to the carboxylic oxygen not coordinated to the uranyl ion (O5). The coordination polyhedra around all the sodiums exhibit distorted octahedral geo-

metry. Each of the two forming the sodium layer is located on the center of inversion and is coordinated to four crystal water oxygens and two fluorides. The third 'bridging' sodium ion is bonded to two water, two *yl* and two carboxylic oxygens. The octahedra are held together by shared water oxygens. An interesting feature in this structure, as in $Na_3UO_2(oxalate)F_3$[16] and $K_6(UO_2)_2(oxalate)_5$[18] is that the *yl* oxygens are coordinated to the counter ions, here to Na^+. Although these contacts are significantly longer [2.528(6) and 2.637(6) Å] than the ones between the sodium and the carboxylic oxygens [2.301(6) and 2.426(6) Å], they still give a clear indication that the *yl* oxygens have electron donor capacity. This is also supported by the fact that the *yl* oxygens are simultaneously involved in weak hydrogen bonds. There are possible hydrogen bonds between the water molecules and oxygens, both *yl* and organic, as well as the fluorides, judged by the distances between the water protons and the O and F acceptors. They also have an important role in stabilizing the structure. The carboxylic oxygens are involved in strong hydrogen bonds. The fluoride ions form bonds of medium strength. However, the H–O–H angles in the water are very uncertain (±40°), therefore the hydrogen positions and the angles of hydrogen bonds have a similar uncertainty.

Supplementary material, containing a list of the anisotropic temperature factors, a full list of bond lengths and angles and that of the observed and calculated structure factors, is available from the authors on request.

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