

Structure of the Sodium Salt of the Ternary Uranyl–Picolinate–Fluoride Complex $[\text{UO}_2(\text{picolinate})\text{F}_3] \text{Na}_2(\text{H}_2\text{O})_4$

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The structure of a ternary U^{VI} –picolinate–fluoride complex has been investigated using single-crystal X-ray diffraction. The disodium tris(fluoro)(picolinate)dioxouranate(VI) tetrahydrate contains the discrete complexes $[\text{UO}_2(\text{picolinate})\text{F}_3]^{2-}$ with a pentagonal bipyramidal coordination geometry and belongs to the space group $P\bar{1}$. The picolinate ligand is slightly tilted out of the pentagonal plane owing to repulsion between fluoride and picolinate hydrogen. The complexes are linked to two hydrated sodium atoms, which both have a distorted octahedral geometry.

The linear dioxouranyl(VI) ion, UO_2^{2+} , has an unusual coordination geometry with two substitution-inert 'yl' oxygens and where the free coordination sites are situated in a plane perpendicular to this linear axis. Usually, there is five-coordination in this plane, forming a pentagonal bipyramidal symmetry, but there are examples of four-coordination with bulky ligands, e.g. HMPA,¹ or six-coordination for small bidentate ligands, e.g. CO_3^{2-} .² We have previously studied equilibria,³ coordination geometry, isomerism and ligand substitution mechanisms in various aqueous ternary U^{VI} –L–F systems, where L is acetate, oxalate, carbonate or picolinate.⁴ Uranyl forms strong complexes with these ligands, and we have been able to prepare solutions in which the dominant species are various ternary complexes. By using ^{19}F , ^{13}C and ^1H NMR and potentiometry we have shown that all complexes have a bipyramidal pentagonal coordination symmetry. To obtain a more detailed picture of the coordination geometry and to compare the solid-state structure with solution-chemical properties, we have synthesised single crystals of one of the ternary uranyl complexes, $\text{UO}_2(\text{picolinate})\text{F}_3 \text{Na}_2(\text{H}_2\text{O})_4$.

Experimental

Preparation. The chemicals were all of analytical grade. A mixture of 0.5 g of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) and 0.17 g of NaF (4 mmol) were dissolved in a small amount of water. A saturated solution of 0.12 g of picolinic acid

(1 mmol) was added. The pH was adjusted with NaOH to about 6. The solution was slowly evaporating in air, and small yellow needle-like crystals were formed.

X-Ray crystallography. The data collection was done on a Siemens SMART CCD diffractometer, and data reduction was carried out with SAINT. The structure factors were corrected for absorption using the SADABS program.⁵ Experimental conditions are summarised in Table 1. The structure solution was made using SHELXS⁶ and direct methods, and the refinement by using SHELXL.⁶ The H atoms on the picolinate ligand are constrained using a riding model, while the water hydrogen atoms were not included in the model. All the atoms, except hydrogen, were refined anisotropically. The residual electron density peaks are close to the uranium atom (0.8 Å). The negative peak has an absolute value higher than the positive one (2.48 and $-5.47 \text{ e } \text{Å}^{-3}$), indicating that the absorption correction is not perfect. The reason is that the crystal has very unequal dimensions, making it difficult to obtain a good absorption correction; however, this does not influence the structure model.

Results and discussion

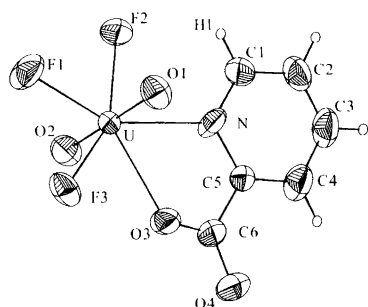
The uranyl has the expected five coordination in a plane perpendicular to the linear UO_2 group. One important observation is that the picolinate ligand is slightly tilted out of this plane. The distance between the C1 proton and F2 is 2.34 Å. This is too long for a hydrogen bond: a zero tilt angle would give a shorter hydrogen fluoride

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Table 1. Crystal data and summary of the data collection and structure refinement results.

Formula	[UO ₂ (C ₅ H ₄ NO ₂)F ₃]Na ₂ (H ₂ O) ₄
Formula weight/g mol ⁻¹	567.169
Cell setting	Triclinic
Space group	<i>P</i> 1
<i>a</i> /Å	7.1219(1)
<i>b</i> /Å	8.6926(2)
<i>c</i> /Å	12.8483(3)
α /°	106.260(1)
β /°	91.328(1)
γ /°	113.379(1)
<i>V</i> /Å ³	692.72(2)
<i>Z</i>	2
<i>D</i> _{calc} /mg m ⁻³	2.719
Radiation	Mo <i>K</i> α (λ = 0.71073 Å)
<i>F</i> (000)	520
No. of reflections for cell parameters	5401
Absorption coefficient/ mm ⁻¹	11.848
<i>T</i> /K	298
Colour and shape	Yellow needle
Crystal size/mm	0.33 × 0.17 × 0.06
Diffractometer	Siemens SMART CCD
Absorption correction	Empirical (SADABS)
<i>T</i> _{max}	0.308
<i>T</i> _{min}	0.145
Reflections collected	5809
Reflections unique	4040
<i>R</i> _{int}	0.0409
θ _{min} and θ _{max} /°	1.67 to 31.58
Index ranges	−9 ≤ <i>h</i> ≤ 10 −12 ≤ <i>k</i> ≤ 6 −17 ≤ <i>l</i> ≤ 18
Refinement on	<i>F</i> ²
Final <i>R</i> -indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0414, <i>wR</i> ₂ = 0.1030
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0432, <i>wR</i> ₂ = 0.1040
Goodness-of-fit	1.035
Residual electron density/ e Å ⁻³	2.48–5.47

distance. Hence the tilting is most likely the result of repulsion between the hydrogen and fluoride. Repulsion between F2 and H1 is also observed in aquatic solution. ¹⁹F and ¹H NMR spectra of the complex show highly shifted signals for both the F2 and H1 peaks.⁴ The structure of the binary uranyl picolinate has recently been determined.⁷ The uranium–nitrogen bond distance

**Fig. 1.** Molecular structure of UO₂(picolinate)F₃²⁻, represented with 75% probability ellipsoids (not for the hydrogen atoms).**Table 2.** Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
U	7443(1)	9732(1)	1906(1)	17(1)
Na(1)	7365(4)	4948(3)	−10(2)	29(1)
Na(2)	6486(5)	8115(4)	−1444(3)	41(1)
O(2)	10020(7)	9857(7)	1978(4)	29(1)
F(3)	6061(6)	6997(5)	713(3)	30(1)
O(1)	4937(7)	9749(7)	1924(4)	30(1)
F(2)	8916(6)	12709(5)	2357(3)	31(1)
F(1)	7599(9)	10151(6)	266(3)	43(1)
O(3)	6741(8)	7655(6)	2952(3)	31(1)
O(4)	6998(9)	6972(7)	4484(4)	36(1)
N	7771(9)	11003(7)	4020(4)	26(1)
C(6)	7084(9)	8043(8)	3995(5)	25(1)
C(5)	7557(9)	9902(7)	4642(4)	21(1)
C(2)	8127(11)	13278(9)	5698(6)	35(1)
C(1)	8051(10)	12667(8)	4557(5)	30(1)
C(4)	7661(12)	10457(10)	5769(5)	33(1)
C(3)	7958(11)	12198(10)	6293(5)	36(2)
O(7)	6949(9)	4400(7)	1695(4)	35(1)
O(8)	10976(8)	7039(6)	447(4)	33(1)
O(6)	7515(8)	5637(8)	−1647(4)	39(1)
O(5)	5900(10)	6536(8)	−3452(4)	47(1)

is comparable between this binary and our ternary structure, 2.58(1) and 2.596(5) Å, respectively, but the uranium oxygen distance has been lengthened, from 2.34(1) to 2.447(4) Å. The reason might be the effect of coordinated fluorides, which may result in a larger charge transfer between F and U than between O and U. All uranium fluoride bonds have approximately the same bond distance (2.24 Å). They are very similar to the bond distances in the corresponding UO₂(oxalate)F₃²⁻ complex⁸ (2.25 Å) as well as in the binary UO₂F₅³⁻ complex⁹ (2.24 Å), which indicates that the additional ligand has little effect on the strength of bonding fluoride. In our thermodynamic studies³ we observed a similar effect: the stepwise formation constant of binding a fluoride to the UO₂L complex is very similar to those in the binary uranium(VI)–fluoride complex.¹⁰

Both sodium atoms have a distorted octahedral geometry; one is coordinated with three water molecules

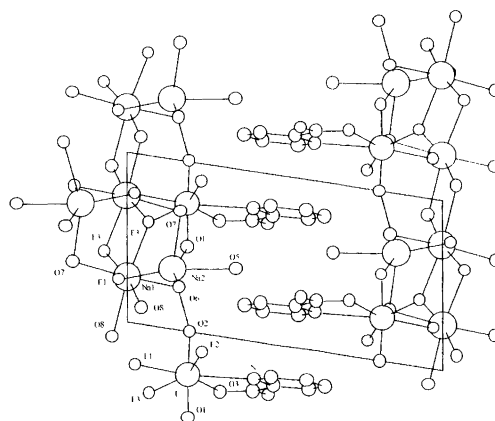
**Fig. 2.** Packing diagram viewed down the *b*-axis.

Table 3. Selected bond distances (in Å) and angles (in °).

U–O(1)	1.791(5)	C(2)–C(1)	1.405(9)
U–O(2)	1.793(5)	C(4)–C(3)	1.399(11)
U–F(1)	2.234(4)	Na(1)–F(3)	2.307(5)
U–F(3)	2.237(3)	Na(1)–F(3)#1	2.323(4)
U–F(2)	2.260(4)	Na(1)–O(6)	2.336(6)
U–O(3)	2.447(4)	Na(1)–O(7)	2.370(6)
U–N	2.596(5)	Na(1)–O(8)#2	2.409(6)
O(3)–C(6)	1.279(7)	Na(1)–O(8)	2.426(5)
O(4)–C(6)	1.244(8)	Na(2)–F(1)	2.284(5)
N–C(1)	1.346(8)	Na(2)–O(7)#1	2.489(7)
N–C(5)	1.377(7)	Na(2)–O(6)	2.489(7)
C(6)–C(5)	1.489(8)	Na(2)–O(5)	2.495(6)
C(5)–C(4)	1.382(8)	Na(2)–O(1)#3	2.638(6)
C(2)–C(3)	1.340(11)	Na(2)–O(2)#4	2.654(6)
O(1)–U–O(2)	175.75(17)	O(1)–U–O(3)	94.1(2)
O(1)–U–F(1)	90.9(2)	F(3)–U–O(3)	72.12(15)
O(1)–U–F(3)	90.44(19)	O(1)–U–N	83.4(2)
F(1)–U–F(3)	75.96(16)	F(2)–U–N	72.53(15)
F(1)–U–F(2)	77.57(16)	O(3)–U–N	62.75(15)

and the other with four. The additional coordination sites are with fluorides and the uranyl oxygen atoms. The water–hydrogen atoms could not be located in the refinement. There are several oxygen–oxygen and oxygen–fluoride distances at 2.6–3 Å indicating hydrogen bonding, but it is not possible to obtain an unambiguous location of all the hydrogen atoms using this information. The sodium atoms are linked with bridging water and fluoride forming a chain as indicated in Fig. 2. The packing geometry is very similar to the ternary uranyl–oxalate–fluoride complex,⁸ with the organic ligands

stacked above one another; in the picolinate case the stacking distance is 3.6 Å.

Supplementary material. The CIF file and a table giving the anisotropic temperature parameters are available from the authors on request.

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