

X-ray structure of dihydrazinium uranyl dioxalate monohydrate

M D POOJARY and K C PATIL*

Department of Inorganic and Physical Chemistry, Indian Institute of Science,
Bangalore 560 012, India

MS received 8 July 1987; revised 19 November 1987

Abstract. The crystal structure of dihydrazinium uranyl dioxalate monohydrate, $(\text{N}_2\text{H}_5)_2[\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]$, has been determined by x-ray diffraction. The structure was solved by heavy-atom method and refined to an R value of 0.059 using 2312 reflections. The N_2H_5^+ ions are not coordinated to the metal. In the anion $[\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]^{2-}$, the linear UO_2^{2+} group is coordinated by two chelating bidentate oxalate oxygens and a water oxygen. The coordination polyhedron around the uranium atom is an approximate pentagonal bipyramid.

Keywords. Hydrazinium uranyl oxalate; crystal structure; uranyl complex.

1. Introduction

The uranyl ion, UO_2^{2+} , the most stable species among uranium compounds present in nature, has a linear structure. In uranyl complexes, the ligands coordinate to the metal centre in a plane nearly perpendicular to the O-U-O axis as shown by the structures of uranyl systems containing a variety of ligands. In the coordination chemistry of UO_2^{2+} , the chelating ligand oxalate, in particular, has drawn special attention due to the fact that complexes of different types are formed depending upon the $\text{UO}_2^{2+}:\text{C}_2\text{O}_4^{2-}$ mole ratio and the nature of oxalate coordination (Alcock 1973a, b, c; Jeyadevan and Chackraborty 1972; Jeyadevan *et al* 1975; Dalley *et al* 1972, Niinisto *et al* 1978, 1979). An additional interesting feature of the ligand is that it has an unusually large bite distance of $\approx 2.7 \text{ \AA}$.

We have been interested in the interaction of the hydrazinium ion, N_2H_5^+ , with metal complexes containing various anionic ligands like sulphate (Govindarajan *et al* 1986a), oxalate (Gajapathy *et al* 1983) and hydrazine carboxylate (Ravindranathan and Patil 1985). Recently the structures of a hydrazinium uranyl oxalate complex, $(\text{N}_2\text{H}_5)_6[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_5]\cdot 2\text{H}_2\text{O}$ was reported (Govindarajan *et al* 1986b). This paper describes the structure of a related complex, $(\text{N}_2\text{H}_5)_2[(\text{UO}_2)-(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]$ with a $\text{UO}_2^{2+}:\text{C}_2\text{O}_4^{2-}$ (1:2) mol ratio.

2. Experimental

The complex was prepared by mixing aqueous solutions of uranyl nitrate hexahydrate (5.02 g, 10 mmol) and hydrazinium oxalate (3.08 g, 20 mmol) in the

*To whom all correspondence should be addressed.

molar ratio of 1:2. Yellow acicular crystals appeared on slow evaporation. The composition of the crystals was fixed by the conventional analysis of hydrazine, oxalate and uranyl groups (Govindarajan *et al* 1986b) to be $(\text{H}_2\text{H}_5)_2\text{UO}_2(\text{C}_2\text{O}_4)_2\text{H}_2\text{O}$. Analysis: hydrazine—observed 12%, required 12.07%; oxalate—observed 33%, required 33.2%; and uranium—observed 45.0%, required 44.9%.

3. X-ray crystallography

Crystal data: $\text{C}_4\text{H}_{12}\text{N}_4\text{O}_{11}\text{U}$, $M = 530$, monoclinic, space group $P2_1/n$, $a = 7.850(2)$, $b = 10.893(3)$, $c = 15.051(4)$ Å, $\beta = 100.96(2)^\circ$, $V = 1263.5$ Å³, $Z = 4$, $D_c = 2.78$ g cm⁻³, $F(000) = 976$, MoK $_{\alpha}$ radiation, $\lambda = 0.7107$ Å, $\mu(\text{Mo-K}_{\alpha}) = 165.06$ cm⁻¹, specimen dimensions: $0.25 \times 0.18 \times 0.1$ mm, $2\theta_{\text{max}} = 55^\circ$.

Unit cell dimensions and their associated standard deviations were derived from a least-squares fit to the setting angles for 24 carefully selected and centred reflections on a CAD-4 automated diffractometer. Intensity data were collected in the $\omega/2\theta$ scan mode with a constant scan speed of 1°min^{-1} and scan width of $\theta = (0.75 + 0.45 \tan \theta)$. The intensities of three standards were monitored after every 3000 s and showed no systematic variations over the duration of the experiment. Of the 3512 reflections collected, 2312 were considered to be observed [$F_0 > 3 \sigma(F_0)$]. The data were corrected for Lorentz and polarization effects. An absorption correction was applied on the basis of the dimensions and face assignments (Sheldrik 1976).

The structure was solved by the heavy-atom method and refined using full-matrix least-squares method. Hydrogen atoms of the N_2H_5^+ groups could not be located. The final values of the discrepancy indices are:

$$R = \sum (|F_0| - |F_c|) / \sum F_0 = 0.059 \text{ and}$$

$$R^1 = [\sum w(|F_0| - |F_c|)^2 / \sum w|F_0|^2]^{1/2} = 0.057.$$

The weighting scheme used was $w = 2.32/\sigma^2(F) + 0.00047|F|^2$.

Computations were carried out on a DEC-10 computer. SHELX-76 (Sheldrik 1976) was used for structure solution and refinement. The curve for neutral scattering factors for U was taken from *International tables for x-ray crystallography* (1974). The scattering factors as available in SHELX-76 were used for all other atoms. Final atomic coordinates and equivalent isotropic temperature factors are listed in table 1, and bond parameters in table 2.

4. Results

The structure of $[\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]^{2-}$ anion is shown in figure 1. The uranyl group is coordinated by four oxygen atoms of two chelating bidentate oxalate groups and a water oxygen atom. The coordination polyhedron is an approximate pentagonal bipyramid, with the metal being virtually in the plane of the pentagon.

The uranyl ion is linear with an O-U-O angle of $178.0(4)^\circ$ with the two U-O distances of $1.770(8)$ and $1.773(8)$ Å. In the equatorial plane, the U-O (water) bond

Table 1. Final fractional coordinates ($\times 10^5$ for U; $\times 10^4$ for the rest) and equivalent isotropic temperature factors ($\times 10^3$) with estimated standard deviations (e.s.d.s) in parentheses.

$$U_{\text{iso}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

Atom	x	y	z	U_{iso}
U	73047(5)	28190(4)	57268(2)	17.3(1)
O(1)	8023(10)	1417(7)	5252(5)	20.0(2)
O(2)	6585(12)	4194(8)	6166(6)	28.0(3)
O(3)	4440(12)	2153(8)	5159(6)	27.0(3)
O(4)	6101(11)	1553(9)	6738(5)	28.0(3)
O(5)	9359(13)	2423(8)	7094(6)	29.0(3)
O(6)	9989(10)	3819(7)	5783(5)	21.0(3)
O(7)	1986(11)	1231(8)	5388(6)	29.0(3)
O(8)	3917(13)	421(10)	7040(6)	41.0(3)
O(9)	12039(13)	2651(8)	7890(7)	32.0(3)
O(10)	12789(11)	4051(8)	6449(6)	30.0(3)
O(w)	6696(12)	3740(8)	4255(5)	27.0(3)
C(1)	3511(15)	1512(11)	5617(7)	21.0(3)
C(2)	4578(16)	1142(11)	6556(8)	23.0(3)
C(3)	10880(16)	2844(10)	7215(8)	21.0(3)
C(4)	11284(15)	3651(11)	6421(8)	22.0(3)
N(1)	2397(17)	3197(11)	3625(8)	34.0(4)
N(2)	700(16)	3337(12)	3849(8)	35.0(4)
N(3)	793(16)	635(11)	3055(8)	35.0(4)
N(4)	-359(13)	674(11)	3711(7)	28.0(3)

Table 2. Bond lengths (Å) and angles (°) with e.s.d.s. in parentheses.

U-O(1)	1.770(8)	U-O(6)	2.359(8)	C(2)-O(4)	1.257(14)	C(4)-O(6)	1.271(14)
U-O(2)	1.773(8)	U-O(w)	2.395(8)	C(2)-O(8)	1.249(15)	C(4)-O(10)	1.253(14)
U-O(3)	2.363(9)	C(1)-O(3)	1.298(14)	C(3)-O(5)	1.260(15)	N(1)-N(2)	1.444(16)
U-O(4)	2.379(8)	C(1)-O(7)	1.220(14)	C(3)-O(9)	1.246(15)	N(3)-N(4)	1.461(16)
U-O(5)	2.400(9)	C(1)-C(2)	1.552(16)	C(3)-C(4)	1.564(17)		
O(1)-U-O(2)	178.0(4)	O(2)-U-O(5)	92.4(4)	O(4)-U-O(6)	134.9(3)	O(4)-C(2)-C(1)	116(1)
O(1)-U-O(3)	87.4(3)	O(2)-U-O(6)	86.7(4)	O(4)-U-O(w)	143.2(3)	O(8)-C(2)-C(1)	119(1)
O(1)-U-O(4)	88.5(4)	O(2)-U-O(w)	88.3(4)	O(5)-U-O(6)	66.6(3)	O(4)-C(2)-O(8)	125(1)
O(1)-U-O(5)	89.1(3)	O(3)-U-O(4)	65.6(3)	O(5)-U-O(w)	148.4(3)	O(5)-C(3)-C(4)	115(1)
O(1)-U-O(6)	92.6(3)	O(3)-U-O(5)	133.9(3)	O(6)-U-O(w)	81.9(3)	O(9)-C(3)-C(4)	120(1)
O(1)-U-O(w)	89.8(3)	O(3)-U-O(6)	159.5(3)	O(3)-C(1)-C(2)	111(1)	O(5)-C(3)-O(9)	126(1)
O(2)-U-O(3)	92.6(4)	O(3)-U-O(w)	77.6(3)	O(7)-C(1)-C(2)	122(1)	O(6)-C(4)-C(3)	114(1)
O(2)-U-O(4)	93.3(4)	O(4)-U-O(5)	68.3(3)	O(3)-C(1)-O(7)	127(1)	O(10)-C(4)-C(3)	120(1)
						O(6)-C(4)-O(10)	125(1)

length is 2.395(9) Å, and the U-O (oxalate) distances vary from 2.359(8) to 2.400(9) Å, with an average value of 2.375 Å. These values are in good agreement with those observed for other UO_2^{2+} complexes of similar coordination (Alcock 1973c; Dalley *et al* 1972; Niinisto *et al* 1978, 1979). Both the oxalate groups, which bind the metal through 1,4-coordination, are virtually planar.

The N-N distances of 1.44(2) and 1.46(2) Å in the two crystallographically independent N_2H_5^+ ions are comparable to those found in other complexes (Gajapathy *et al* 1983; Prodic *et al* 1972; Bukovec and Golic 1976).

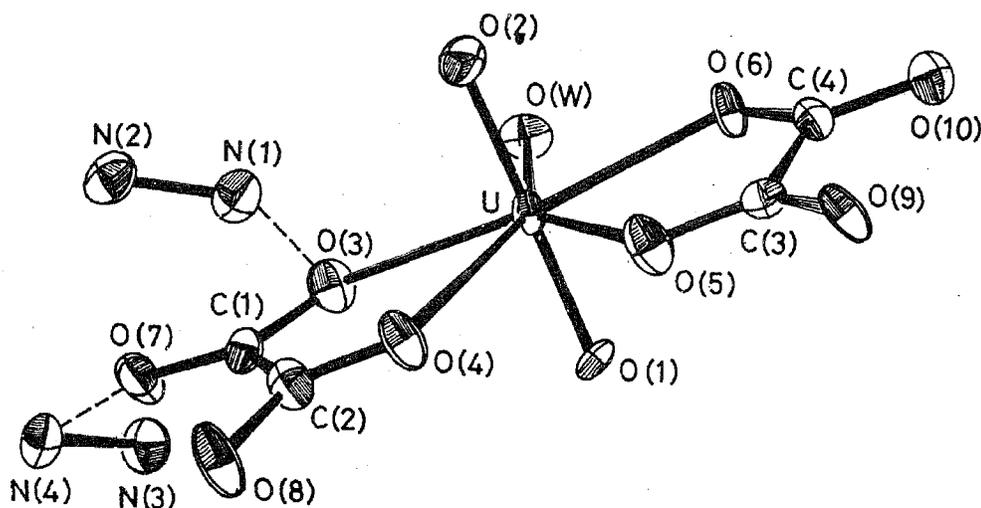


Figure 1. Structure of $(\text{N}_2\text{H}_5)_2[(\text{UO}_2)(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]$. Broken lines indicate hydrogen bonds.

In the crystal, the discrete $[\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]^{2-}$ ions are linked by hydrogen bonds. Both the free and coordinated oxygen atoms of $\text{C}_2\text{O}_4^{2-}$ act as acceptors. The coordinated water donates both its protons to the oxygen atoms of $\text{C}_2\text{O}_4^{2-}$ belonging to a neighbouring $[\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})]^{2-}$ moiety. The nitrogen atoms of the N_2H_5^+ ions are also involved in hydrogen bonds with the oxygen of oxalate groups.

5. Discussion

Depending upon the uranyl-oxalate ratio 1:1, 1:1.5, 1:2 or 1:3, complexes of the type: $\text{UO}_2\text{C}_2\text{O}_4$ (Jeyadevan and Chackraburthy 1972; $[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_3]^{2-}$ (Jayadevan *et al* 1975; Alcock 1973c); $[(\text{UO}_2)(\text{C}_2\text{O}_4)_2]^{2-}$ (Alcock 1973b); or $[(\text{UO}_2)(\text{C}_2\text{O}_4)_3]^{4-}$ (Alcock 1973a), respectively, are formed. The uranyl oxalate complexes with $\text{UO}_2^{2+}:\text{C}_2\text{O}_4^{2-}$ mol ratios of 1:1 (Jeyadevan and Chackraburthy 1972), 1:1.5 (Alcock 1973c) and 1:2 (Alcock 1973b) containing NH_4^+ cation have five coordinated uranyl groups. On the other hand, $\text{K}_2[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_3]$ (Jeyadevan *et al* 1975) and $(\text{NH}_4)_4[(\text{UO}_2)(\text{C}_2\text{O}_4)_3]$ (Alcock 1973a) complexes having $\text{UO}_2^{2+}:\text{C}_2\text{O}_4^{2-}$ ratios of 1:1.5 and 1:3 have six coordinated uranyl groups. The present structure may be compared with that of the related compound, $(\text{N}_2\text{H}_5)_6[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_5]\cdot 2\text{H}_2\text{O}$ (Govindarajan *et al* 1986b), a 1:2.5 uranyl oxalate complex, where the uranyl ions have similar pentagonal coordination of two bidentate chelating oxalate groups and one bridging oxalate oxygen replacing a water oxygen in the title compound. However, in the structure of the complex (Alcock 1973b) having the same mol ratio (1:2) as in the present case, but with a different cation, NH_4^+ , the uranyl ion is coordinated by the oxalate oxygens only and the bridging oxalate anions produce infinite chains of $[\text{UO}_2(\text{C}_2\text{O}_4)_2]_n^{2n-}$.

Unlike the cases of hydrazinium complexes of neodymium sulphate (Govindarajan *et al* 1986a) transition metal double sulphate and copper chloride, in both the hydrazinium uranyl oxalate complexes structurally characterised so far, the N_2H_5^+ remains uncoordinated. While this may be due to the availability of a sufficient

number of oxalate groups for coordination in the diuranyl pentaoxalate complex (Govindarajan *et al* 1986b), in the present case a water oxygen is preferred over N_2H_5^+ for completing the pentagonal coordination of UO_2^{2+} . The inability of N_2H_5^+ to bind the metal is, presumably, due to its poor ligating ability coupled with the geometrical restrictions in the uranyl coordination sphere arising from the chelation of rigid oxalate groups.

Acknowledgements

The authors are grateful to Dr. S Govindarajan for the preparation of the compound and Prof. H Manohar for useful suggestions.

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