Synthesis, Characterization and X-ray Structure of Hexahydrazinium Diuranyl Pentaoxalate Dihydrate, $(N_2H_5)_6(UO_2)_2(C_2O_4)_5\cdot 2H_2O$

SUBBIAH GOVINDARAJAN, KASHINATH C. PATIL*, M. DAMODARA POOJARY and HATTIKUDUR MANOHAR

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

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Abstract

A new hydrazinium uranyl oxalate complex, $(N_2H_5)_6[(UO_2)_2(C_2O_4)_5]\cdot 2H_2O$ has been prepared and characterized by chemical analysis, infrared, visible spectra and TG-DTA. The single crystal X-ray structure of the complex shows the presence of discrete $N_2H_5^+$ cations, water molecules and $[(UO_2)_2(C_2O_4)_5]^{6-}$ anions. In the anion, the linear uranyl groups are coordinated by two chelating bidentate oxalates and one bridging oxalate which lies on the center of symmetry between the two uranyl groups. The coordination polyhedron around each uranium atom is approximately a pentagonal bipyramid.

Introduction

A number of complexes containing the hydrazinium cation, $N_2H_5^+$ are known [1–5]. Of these, hydrazinium metal sulphates, $(N_2H_5)_2M(SO_4)_2$, where M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Mg [2–4, 6, 7] have been investigated in detail. Recently, we reported the synthesis and structure of hydrazinium rare earth sulphates, $N_2H_5Ln(SO_4)_2\cdot H_2O$ where Ln = La, Ce, Pr, Nd and Sm [8]. The interest in these complexes arises from the fact that $N_2H_5^+$ is coordinated to the metal [1–8] and the complexes exhibit one and three-dimensional magnetic interactions of a linear chain anti-ferromagnet [4]. Our studies on hydrazinium metal oxalates $(N_2H_5)_2M(C_2O_4)_2\cdot nH_2O$, where M = Co, Ni and Cu, n = 3, 2 and 1 respectively, showed that although $N_2H_5^+$ is coordinated to Co^{2+} and Ni^{2+} atoms, in the copper complex it is outside the coordination sphere [9]. It was therefore, considered interesting to extend these studies to the hydrazinium uranyl oxalate complexes. We now report the preparation, characterization and X-ray structure of the complex, $(N_2H_5)_6(UO_2)_2(C_2O_4)_5\cdot 2H_2O$. As far as we are aware, this represents the first X-ray crystallographic study on a uranyl hydrazinium complex.

Experimental

Hydrazinium uranyl oxalate was prepared by mixing aqueous solutions of uranyl nitrate hexahydrate (5.02 g, 10 mmol) and hydrazinium oxalate (6.16 g, 40 mmol) in the molar ratio of 1:4 and keeping the mixture at 5 °C for 2 days. Yellow tabular crystals were obtained and the composition of the crystals was fixed by the conventional analysis of hydrazine, oxalate and uranyl groups [10] to be $(N_2H_5)_6(UO_2)_2(C_2O_4)_5\cdot 2H_2O$. *Anal.* Calc. for $(N_2H_5)_6(UO_2)_2(C_2O_4)_5\cdot 2H_2O$: U, 39.21; N_2H_4, 15.81; C_2O_4, 36.24. Found: U, 38.83; N_2H_4, 15.83; C_2O_4, 35.72%. Infrared and visible spectra, TG-DTA analysis in air of the compound were recorded using instruments described earlier [8, 9].

X-ray Crystallography. Crystal Data

$(N_2H_5)_6(UO_2)_2(C_2O_4)_5\cdot 2H_2O$, $C_{10}H_{34}N_{12}O_{26}U_2$, M = 1214.1, orthorhombic, space group *Pbca*, a = 10.979(3), b = 26.708(5), c = 10.704(3) Å, V = 3138.7 Å^3, $F(000)$ = 2280, D_c = 2.56 g cm^{-3}, Z = 4, μ(Mo Kα) = 127 cm^{-1}, λ(Mo Kα) = 0.7107 Å.

A platelike crystal of dimensions 0.025 × 0.1 × 0.1 mm was used for intensity measurements on a CAD-4 automated diffractometer with graphite monochromated Mo Kα radiation. The unit cell dimensions and their associated standard deviations were derived from a least-squares fit to the setting angles for 20 carefully selected and centered reflections in the range $20° \leqslant 2\theta \leqslant 30°$. During data collection the intensities of two standard reflections measured after every 3000 s showed no systematic variations over the duration of the experiment.

Data were collected in the $\omega/2\theta$ scan mode with a constant scan speed of 1°/min. A total of 2932 reflections were measured up to a 2θ limit of 48° yielding 967 unique reflections with $|F| \geqslant 4.5\sigma(F)$. Intensities were corrected for Lorentz and polarization effects and for absorption from the ϕ-scan data.

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*Author to whom correspondence should be addressed.

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The structure was solved by the heavy atom method. SHELX-76 programs [11] were used for refinement, allowing anisotropic vibration for the uranium atom and individual isotropic vibration parameters for the other non-hydrogen atoms. Hydrogen atoms could not be located in the difference Fourier map. The weighting scheme employed was $w = 1.609/\sigma^2(F_o) + 0.00089\ (F_o)^2$ and refinement concluded with $R = 0.075, R_w = 0.068$.

A final Fourier difference map showed no significant feature, apart from some residual electron density around the uranium position. Scattering factors for U were from the International Tables for X-ray Crystallography, 1974; those for N, O and C were supplied internally by SHELX-76. A correction for the anomalous dispersion of U was applied. Computations were carried out on a DEC-1090 computer of our Institute. The diagram was drawn using the program ORTEP-II [12]. Positional and thermal parameters are given in Table I; distances and angles are given in Table II.

TABLE I. Final Positional Parameters ($\times 10^4$ for U and $\times 10^3$ for the Rest) and Temperature Factors ($\times 10^3$) with Estimated Standard Deviations in Parentheses

Atom	*x*	*y*	*z*	U_{iso}
U	447(1)	1049(1)	2310(1)	a
O(1)	172(2)	71(1)	172(2)	19(6)
O(2)	−80(2)	140(1)	295(2)	16(6)
O(3)	160(3)	138(1)	400(3)	28(7)
O(4)	141(2)	181(1)	187(2)	16(6)
O(5)	−9(3)	129(1)	23(3)	31(7)
O(6)	−93(3)	52(1)	130(2)	26(7)
O(7)	24(3)	37(1)	365(2)	32(7)
O(8)	261(2)	200(1)	486(2)	21(6)
O(9)	267(2)	242(1)	255(3)	32(7)
O(10)	−106(3)	109(1)	−153(2)	40(7)
O(11)	−210(3)	31(1)	−29(3)	37(8)
O(12)	−49(3)	56(1)	552(3)	47(8)
C(1)	210(4)	182(1)	401(4)	21(9)
C(2)	216(4)	205(1)	277(4)	24(10)
C(3)	−83(3)	101(2)	−42(3)	27(10)
C(4)	−138(3)	56(1)	22(3)	5(8)
C(5)	−13(4)	28(2)	481(4)	33(12)
N(1)	259(4)	473(1)	289(3)	41(11)
N(2)	170(4)	440(2)	329(4)	68(14)
N(3)	176(5)	340(2)	213(5)	86(17)
N(4)	67(5)	344(2)	170(4)	66(13)
N(5)	467(6)	253(3)	−59(6)	125(22)
N(6)	506(6)	268(2)	79(6)	125(25)
O(W)	293(3)	340(1)	457(3)	65(11)

^{a}For U: U_{11}, 28(1); U_{22}, 26(1); U_{33}, 14(1); U_{12}, 2(1); U_{13}, −2(1); U_{23}, −2(1).

TABLE II. Bond Lengths (Å) and Angles (°) with Estimated Standard Deviations in Parentheses

(a) Uranium environment			
U–O(1)	1.78(2)	O(2)–U–O(3)	86(1)
U–O(2)	1.79(2)	O(2)–U–O(4)	88(1)
U–O(3)	2.38(3)	O(2)–U–O(5)	92(1)
U–O(4)	2.35(2)	O(2)–U–O(6)	90(1)
U–O(5)	2.39(3)	O(2)–U–O(7)	95(1)
U–O(6)	2.34(3)	O(3)–U–O(4)	66(1)
U–O(7)	2.32(3)	O(3)–U–O(5)	137(1)
		O(3)–U–O(6)	157(1)
		O(3)–U–O(7)	83(1)
O(1)–U–O(2)	178(1)	O(4)–U–O(5)	72(1)
O(1)–U–O(3)	93(1)	O(4)–U–O(6)	137(1)
O(1)–U–O(4)	91(1)	O(4)–U–O(7)	148(1)
O(1)–U–O(5)	90(1)	O(5)–U–O(6)	65(1)
O(1)–U–O(6)	92(1)	O(5)–U–O(7)	140(1)
O(1)–U–O(7)	85(1)	O(6)–U–O(7)	75(1)
(b) Oxalate groups			
C(1)–O(3)	1.29(4)	O(3)–C(1)–C(2)	113(3)
C(1)–O(8)	1.18(4)	O(8)–C(1)–C(2)	120(4)
C(1)–C(2)	1.46(5)	O(3)–C(1)–O(8)	126(4)
C(2)–O(4)	1.41(4)	O(4)–C(2)–C(1)	114(3)
C(2)–O(9)	1.16(4)	O(9)–C(2)–C(1)	124(4)
C(3)–O(5)	1.31(4)	O(4)–C(2)–O(9)	122(4)
C(3)–O(10)	1.23(4)	O(5)–C(3)–C(4)	118(3)
C(3)–C(4)	1.50(5)	O(10)–C(3)–C(4)	119(4)
C(4)–O(6)	1.27(4)	O(5)–C(3)–O(10)	123(4)
C(4)–O(11)	1.17(4)	O(6)–C(4)–C(3)	110(3)
C(5)–O(7)	1.32(5)	O(11)–C(4)–C(3)	121(3)
C(5)–O(12)	1.15(4)	O(6)–C(4)–O(11)	129(3)
C(5)–C(5′)	1.59(6)	O(7)–C(5)–C(5′)	111(3)
		O(12)–C(5)–C(5′)	121(3)
		O(7)–C(5)–O(12)	127(4)
(c) Hydrazinium groups			
N(1)–N(2)	1.39(5)	N(5)–N(6)	1.59(8)
N(3)–N(4)	1.28(6)		

Results and Discussion

Metal oxalato complexes containing the coordinated oxalate ligand are quite well known [13]. A number of uranyl oxalate complexes are reported [14–17] and depending upon the mole ratio of uranyl:oxalate one can obtain $[(UO_2)_2(C_2O_4)_3]^{2-}$, $[UO_2(C_2O_4)_2]^{2-}$, or $[UO_2(C_2O_4)_3]^{4-}$ type complexes where the uranyl:oxalate mole ratio is 1:1.5, 1:2 and 1:3 respectively. When the reaction was carried out with a uranyl:oxalate mole ratio of 1:4 the product obtained has a uranyl:oxalate ratio of 1:2.5. The stoichiometry of the reaction could be written as:

$$2UO_2(NO_3)_2 6H_2O + 5(N_2H_5)_2C_2O_4 \longrightarrow (N_2H_5)_6(UO_2)_2(C_2O_4)_5 2H_2O + 4N_2H_5NO_3 + 4H_2O \quad (1)$$

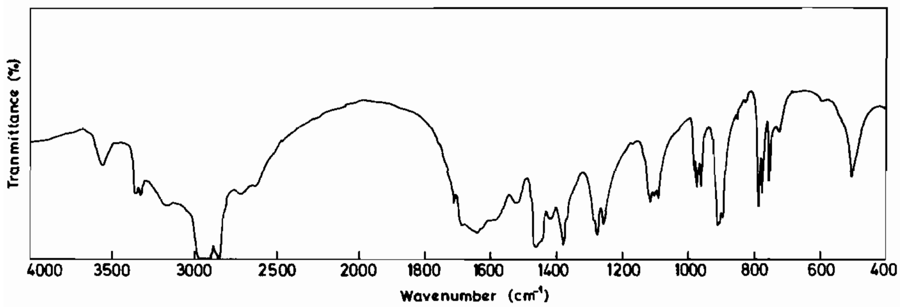

Fig. 1. Infrared spectrum of $(N_2H_5)_6(UO_2)_2(C_2O_4)_5\cdot 2H_2O$ in Nujol mull.

The 1:1.5 and 1:2 uranyl:oxalate complexes containing NH_4^+ have five-coordinated uranyl groups and the 1:3 complex is reported [15] to have six-coordinated uranyl ions. It would be interesting to know the nature of coordination of the uranyl ion in the 1:2.5 complex.

Infrared Spectra

A typical IR spectrum of $(N_2H_5)_6(UO_2)_2(C_2O_4)_5\cdot 2H_2O$ is shown in Fig. 1. Characteristic IR absorption of the uranyl ion [16], ν_3 (O=U=O) is seen at 910 cm^{-1}. The absorption at 960 cm^{-1} has been assigned to ν_{N-N} of ionic $N_2H_5^+$ [18]; ν_{N-N} of coordinated $N_2H_5^+$ is known [5] to occur in the region 990–1005 cm^{-1}. There are no absorptions in this region, indicating an absence of bonding of $N_2H_5^+$ groups to the uranyl ion. The splitting of the 960 cm^{-1} band may be due to the strongly H-bonded $N_2H_5^+$ groups. The absorption at 3530 cm^{-1} has been attributed to ν_{O-H} of free water molecule. The IR absorptions at 1710, 1420, 895 and 785 cm^{-1} are characteristic of bidentate oxalate [19]. The splitting of the 785 cm^{-1} band, δ(O–C–O) is probably indicative of non-equivalence of the oxalate groups within the complex.

Electronic Spectra

The visible absorption spectrum of the complex (Fig. 2) shows sharp absorption at 385, 395, 407, 418, 439, 453, 468 and 490 nm similar to that reported for $(NH_4)_4UO_2(C_2O_4)_3$ [15]. The absorption at 439 nm is assigned to the ${}^1\Sigma_g^+ \rightarrow {}^3\pi_u$ transition of the uranyl ion [20].

Thermal Analysis

The complex shows 3 steps of decomposition in TG and 4-peaks in DTA (Fig. 3). The TG steps correspond to the loss of water (% weight loss, observed –2.6, required –2.97); decomposition of the anhydrous complex to $UO_2C_2O_4\cdot 2N_2H_4$ (% weight loss, observed –30.0, required –30.40) and finally decomposition of the hydrazinate intermediate to U_3O_8 (% weight loss, observed –53.60, required –53.76). The DTA peaks are generally in agreement with the TG steps. The additional

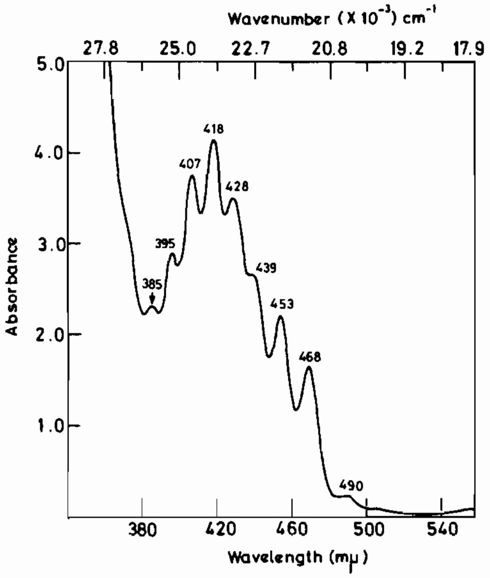

Fig. 2. Electronic spectrum of $(N_2H_5)_6(UO_2)_2(C_2O_4)_5\cdot 2H_2O$.

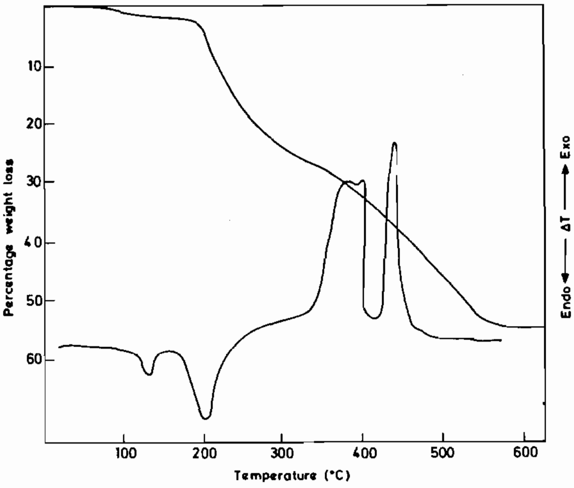

Fig. 3. DTA and TG curves of $(N_2H_5)_6(UO_2)_2(C_2O_4)_5\cdot 2H_2O$.

peak (350–390 °C) in DTA has been attributed to the exothermic decomposition of hydrazinate intermediate, $UO_2C_2O_4 \cdot 2N_2H_4$ to $UO_2C_2O_4$. The final exotherm at 430 °C corresponds to the decomposition of uranyl oxalate to U_3O_8 and is in agreement with the literature value [21]. Formation of the hydrazine intermediate was confirmed by interrupting the decomposition at ~200 °C and analysing the residue $UO_2C_2O_4 \cdot 2N_2H_4$ (U-observed, 57.50%; calculated, 56.4%; oxalate observed, 20.5%; calculated, 20.85%; hydrazine observed 15.0%; calculated, 15.16%).

The overall decomposition sequence can be summarised as follows:

$$(N_2H_5)_6(UO_2)_2(C_2O_4)_5 2H_2O \xrightarrow[endo]{148^\circ C} (N_2H_5)_6(UO_2)_2(C_2O_4)_5 + 2H_2O \tag{2}$$

$$(N_2H_5)_6(UO_2)_2(C_2O_4)_5 \xrightarrow[endo]{200^\circ C} 2UO_2C_2O_4 \cdot 2N_2H_4 + 4NH_3 + 6CO_2 + H_2 \tag{3}$$

$$UO_2C_2O_4 \cdot 2N_2H_4 \xrightarrow[exo]{350\text{–}390^\circ C} UO_2C_2O_4 + 2NH_3 + N_2 + H_2 \tag{4}$$

$$3UO_2C_2O_4 + O_2 \xrightarrow[exo]{430^\circ C} U_3O_8 + 6CO_2 \tag{5}$$

The slight discrepancy in the TG and DTA results is due to the dynamic nature of the former compared to the latter.

Coordination Geometry

The spectral and thermal results of $(N_2H_5)_6(UO_2)_2(C_2O_4)_5 \cdot 2H_2O$ indicate the presence of free $N_2H_5^+$ and H_2O groups in the complex. The IR spectral results clearly show the presence of bidentate coordination of oxalate groups to the uranyl ion. Based on earlier structural studies on the uranyl oxalato complexes [15], the anion $(UO_2)_2(C_2O_4)_5)^{6-}$ having a uranyl:oxalate ratio of 2:5 can be expected to have a shared oxalate group between the two uranyl ions. This common oxalate group may be present either as a bridging bidentate or tetradentate ligand. Therefore, the coordination geometry around the uranium atom may be either pentagonal or hexagonal bipyramidal assuming the other two oxalates as chelates. The X-ray structure described below confirms pentagonal bipyramidal geometry.

Description of the Structure

The crystal contains discrete $N_2H_5^+$, $(UO_2)_2(C_2O_4)_5^{6-}$ and water molecules. Uranyl groups are five-coordinated by oxygen atoms of three oxalate ions, resulting in an approximately pentagonal bipyramidal coordination for uranium. Two oxalate groups are chelating bidentate (1,4-coordination), while the third lying on a center of symmetry acts as a bridging bidentate (1,4-coordination) thus resulting in a dimeric structure as shown in Fig. 4.

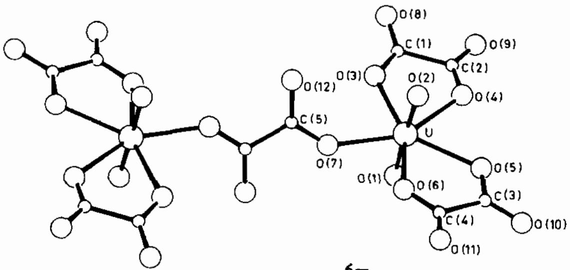

Fig. 4. Structure of $(UO_2)_2(C_2O_4)_5{}^{6-}$ anion. View down *a*.

The uranyl groups show the usual linear O–U–O geometry. The average U–O distance of 1.79 Å and the O–U–O angle of 178° compare well with the values observed in uranyl complexes of similar coordination [15(b–c), 22–25]. Five oxygen atoms, at an average U–O distance of 2.35 Å, form a puckered pentagon around the uranyl ion. The corresponding bond lengths are in the range of 2.37–2.48 Å for the other five-coordinated UO_2^{2+} complexes. The coordination around UO_2^{2+} is given in Table II.

While the chelating mode of oxalate coordination for the uranyl group is generally observed, as far as we are aware, the bridging bidentate (1,4-coordination) behaviour which leads to a dimeric structure is observed for the first time in the present case. The C(3)–C(4) oxalate and C(5)–C(5′) oxalate, which lies on a center of symmetry, are planar. However, the C(1)–C(2) oxalate group is not quite planar as reflected in the torsion angle, O(3)–C(1)–C(2)–O(4), which is 15°. The mean C–O (coordinated) distance of 1.32 Å is significantly longer than the free C–O bond (1.19 Å). It is possible that on coordination the free C–O bond acquires more of a double bond character [15(c)].

There are three independent $N_2H_5^+$ ions present in the structure, which are not coordinated to the metal ion, as in the case of $(N_2H_5)_2Cu(C_2O_4)_2 \cdot H_2O$ [9], $(N_2H_5)_3(CrF_6)$ [26] and $(N_2H_5)(InF_4H_2O)$ [27]. On the other hand, in the case of neodymium sulphate, transition metal double sulphate and copper chloride complexes, the hydrazinium coordinates the metal through one of the nitrogen atoms. The N(1)–N(2), N(3)–N(4) and N(5)–N(6) bond distances are 1.39(5), 1.28(6) and 1.59(8) Å respectively. These may be compared with values of 1.429(4), 1.43(3) and 1.451(4) Å observed in the earlier three complexes. The reasons for the wide variation in N–N bond lengths for the three $N_2H_5^+$ ions in the present case is not clear. However, it may be noted that N(5) and N(6) atoms have high e.s.d.s and large thermal parameters. This $N_2H_5^+$ group has two atoms O(5) and O(8) located on either side

TABLE III. Possible Hydrogen Bonds (A)[a]

$O(9)^1\cdots N(3)^1$	2.84	$O(8)^1\cdots N(3)^4$	2.82
$N(2)^1\cdots N(3)^1$	2.94	$O(10)^{1'}\cdots N(4)^{4'}$	2.97
$O(11)^{1'}\cdots N(1)^{2'}$	2.81	$N(4)^1\cdots N(5)^{2'}$	3.03
$O(12)^{1'}\cdots N(1)^{2'}$	2.82	$O(4)^{1'}\cdots N(5)^{2'}$	2.94
$O(6)^{1'}\cdots N(1)^{3'}$	2.90	$O(9)^{1'}\cdots N(5)^4$	2.97
$O(4)^1\cdots O(W)^{4'}$	3.03		

[a] Symmetry code: (1) x, y, z; (2) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (3) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (4) $x, \frac{1}{2} - y, \frac{1}{2} + z$. Primes denote the symmetry codes obtained by unit translation along the principal axes.

of the N(5)–N(6) bond at short contact distances (shortest being $N(5)\cdots O(8) = 2.63$ Å). As a result the two atoms are probably forced to vibrate along the length of the bond resulting in a longer N–N distance.

In the crystal the anions are stacked one above the other along the *a* axis. This stacking extends in a zig-zag fashion along *b*. The $N_2H_5^+$ ions and water molecules occupy the empty spaces between such chains. In the structure there is a network of hydrogen bonds involving the $N_2H_5^+$, lattice waters and the oxygen atoms of the oxalate anions (Table III).

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