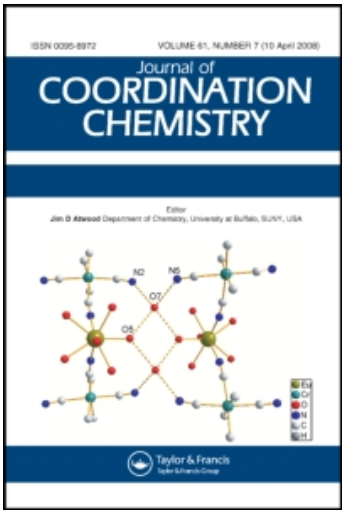

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Crystal and Molecular Structure of A Uranyl Nitrate Dihydrate-Dibenzo-18-Crown-6 Compound: $[UO_2(NO_3)_2(H_2O)_2](Db\text{-}18\text{-}Crown\text{-}6)_2$

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NOTE

CRYSTAL AND MOLECULAR STRUCTURE OF A URANYL NITRATE DIHYDRATE-DIBENZO-18-CROWN-6 COMPOUND: $[UO_2(NO_3)_2(H_2O)_2]\cdot(DB\text{-}18\text{-}CROWN\text{-}6)_2$

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The title complex crystallizes with formula $C_{40}H_{52}N_2O_{22}U$, $M_r = 1150.9$, monoclinic, space group $P2_1/n$, $a = 11.782(2)$, $b = 8.584(2)$, $c = 22.631(2)$Å, $\beta = 98.29(2)°$, $V = 2265.1$ Å^3, $Z = 2$, $D_c = 1.687$ g cm^{-3}, $D_o = 1.685$ g cm^{-3}, $\mu = 33.7$ cm^{-1} (Mo$K\alpha$), $F(000) = 1148$. The structure was solved and refined to $R = 0.066$, $R_w = 0.069$ for 3024 observed flections. The uranyl group is not located within the crown ether, but is bonded to two bidentate nitrate groups and to two water molecules. The structure consists of neutral $UO_2(NO_2)_2(H_2O)_2$ units and separate crown ether molecules connected by hydrogen bonding through intermediary water molecules.

Keywords: uranyl, nitrate, dibenzo-18-crown-6, X-ray, structure

INTRODUCTION

Among the crown ether complexes of actinide elements the most studied are complexes of the uranyl ion.[1,2] Previous works mainly concern the synthesis and characterization of the complexes, while crystal structures of these compounds are little investigated. The only structure reported is that of a complex of uranyl nitrate hydrate with a crown ether in a 1:1 ratio.[3] We have recently prepared single crystals of the title compound $[UO_2(NO_3)_2(H_2O)_2]\cdot(DB\text{-}18\text{-}crown\text{-}6)_2$ in an acetonitrile medium and have determined its crystal and molecular structure, the results of which are reported below.

EXPERIMENTAL

Preparation

Uranyl nitrate hexahydrate (0.251 g, 0.5 mmol) was added to a solution of DB-18-crown-6 (0.360 g, 1 mmol) in acetonitrile (60 cm^{-3}). The solution was placed in a desiccator over $CaCl_2$ at room temperature. The desiccator was left open a little.

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After about three weeks yellow crystals of the title compound were formed in the solution. Anal.; Calcd: C, 41.74; H, 4.55; N, 2.43; U, 20.68%. Found: C, 41.52; H, 4.67; N, 2.29; U, 20.87%.

X-ray Structure Determination

Crystal data

$C_{40}H_{52}N_2O_{22}U$, $M = 1150.9$, monoclinic, space group $P2_1/n$, $a = 11.782(2)$, $b = 8.584(2)$, $c = 22.631(2)$Å, $\beta = 98.29(2)°$, $V = 2265.1$Å^3, $Z = 2$, $D_c = 1.687\,g\,cm^{-3}$, D_o (flotation in CCl_4/CH_2I_2) $= 1.685\,g\,cm^{-3}$, λ(Mo$K\alpha$) $= 0.7109$Å, $\mu = 33.7\,cm^{-1}$, $F(000) = 1148$.

A single crystal of dimensions of $0.2 \times 0.2 \times 0.4$ mm was selected for data collection on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo$K\alpha$ radiation, $\omega/2\theta$ scan. Some 25 reflections were used for measuring lattice parameters and 4647 independent reflections were collected in the range $2° \leqslant 2\theta \leqslant 52°$. Of these, 3024 reflections with $I \geqslant 3\sigma(I)$ were used in the structure determination and refinement. LP and absorption corrections were applied. The structure was solved by the Patterson method and Fourier techniques and refined by full-matrix least-squares method with anisotropic thermal factors for all non-hydrogen atoms and isotropic thermal parameters for H atoms. Final $R = 0.066$, $R_w = 0.069$.

RESULTS AND DISCUSSION

The final atomic coordinates and equivalent thermal parameters are given in Table I, and selected bond lengths and bond angles in Tables II and III. Fig. 1 shows the sandwich structure and the numbering scheme for the complex. Fig. 2 shows the molecular packing arrangement in the unit cell.

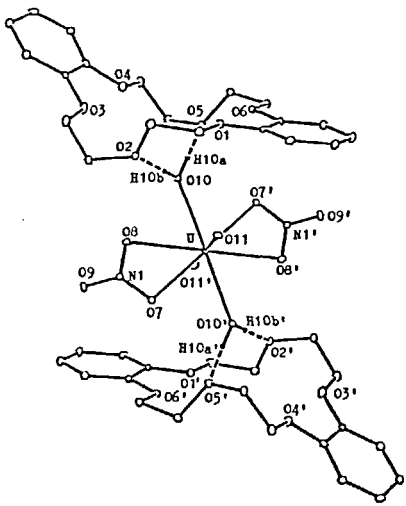

FIGURE 1 Sandwich structure and numbering scheme for the complex molecule. Note that atoms otherwise not indicated are carbon atoms.

TABLE I
Final atomic coordinates and equivalent thermal parameters.

Atom	x/a	y/b	z/c	Beq(Å²)
U	0.000	0.000	0.000	2.597(8)
O(1)	0.1957(5)	0.6423(7)	0.1132(3)	3.7(1)
O(2)	−0.0408(5)	0.5934(8)	0.0966(3)	4.2(1)
O(3)	−0.1241(7)	0.657(1)	0.2042(4)	6.2(2)
O(4)	−0.0226(6)	0.8803(9)	0.2629(3)	4.8(2)
O(5)	0.1213(5)	1.0804(8)	0.2038(3)	3.9(1)
O(6)	0.2787(5)	0.8858(7)	0.1659(3)	3.1(1)
O(7)	−0.1743(5)	−0.1023(8)	−0.0648(3)	3.9(1)
O(8)	0.1782(6)	0.1216(9)	−0.0285(3)	4.3(1)
O(9)	−0.3177(5)	−0.2175(8)	−0.0343(3)	4.5(1)
O(10)	−0.0147(5)	0.0848(7)	−0.1043(3)	3.4(1)
O(11)	0.0607(5)	−0.1806(7)	−0.0144(3)	3.7(1)
N(1)	−0.2262(6)	−0.1493(8)	−0.0240(3)	3.0(1)
C(1)	0.3397(7)	0.829(1)	0.1228(4)	3.1(2)
C(2)	0.2942(7)	0.6957(9)	0.0946(4)	2.9(2)
C(3)	0.1442(9)	0.503(1)	0.0855(5)	4.6(2)
C(4)	0.0384(9)	0.472(1)	0.1134(5)	4.7(2)
C(5)	−0.1563(8)	0.561(7)	0.1068(5)	5.0(2)
C(6)	−0.170(1)	0.531(2)	0.1703(6)	6.5(3)
C(7)	−0.1368(7)	0.658(1)	0.2636(4)	3.9(2)
C(8)	−0.0808(7)	0.783(1)	0.2958(4)	3.8(2)
C(9)	0.0168(9)	1.025(1)	0.2894(5)	4.9(2)
C(10)	0.0374(8)	1.135(1)	0.2384(5)	4.3(2)
C(11)	0.2337(8)	1.068(1)	0.2371(4)	3.5(2)
C(12)	0.3156(7)	1.034(1)	0.1939(4)	3.5(2)
C(13)	0.4398(8)	0.894(1)	0.1089(5)	4.3(2)
C(14)	0.4975(9)	0.827(1)	0.0655(5)	4.6(2)
C(15)	0.4531(8)	0.693(1)	0.0386(4)	4.8(2)
C(16)	0.3515(9)	0.622(1)	0.0523(4)	3.9(2)
C(17)	−0.2036(9)	0.557(1)	0.2916(5)	5.0(2)
C(18)	−0.2157(8)	0.573(1)	0.3507(5)	5.0(2)
C(19)	−0.1556(9)	0.693(1)	0.3829(5)	5.1(2)
C(20)	−0.0881(8)	0.796(1)	0.3560(4)	4.1(2)

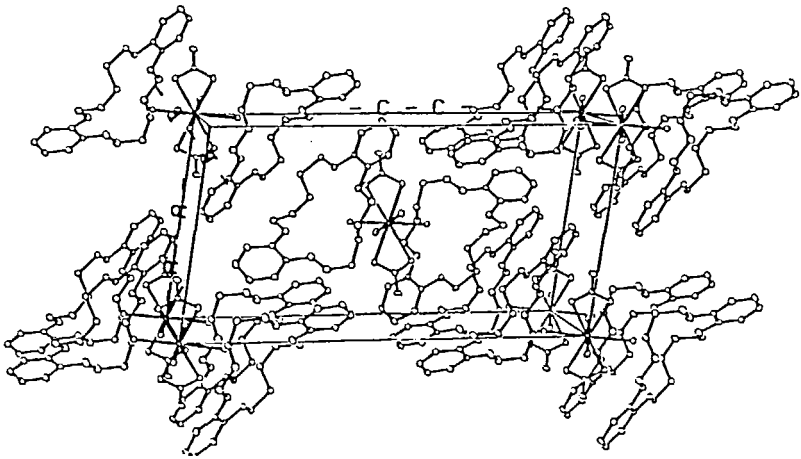

FIGURE 2 The packing of the molecules in the unit cell.

TABLE II
Selected bond lengths (Å) for the complex.

U-O(7)	2.505(3)	C(1) -C(2)	1.381(6)
U-O(8)	2.510(3)	C(1) -C(13)	1.381(7)
U-O(10)	2.453(4)	C(2) -C(16)	1.399(6)
U-O(11)	1.758(4)	C(3) -C(4)	1.501(8)
O(1)-C(2)	1.369(5)	C(5) -C(6)	1.493(8)
O(1)-C(3)	1.440(7)	C(7) -C(8)	1.402(7)
O(2)-C(4)	1.416(7)	C(7) -C(17)	1.397(7)
O(2)-C(5)	1.439(6)	C(8) -C(20)	1.384(7)
O(3)-C(6)	1.387(8)	C(9) -C(10)	1.538(8)
O(3)-C(7)	1.375(6)	C(11)-C(12)	1.498(6)
O(4)-C(8)	1.369(6)	C(13)-C(14)	1.399(8)
O(4)-C(9)	1.425(6)	C(14)-C(15)	1.370(9)
O(5)-C(10)	1.424(6)	C(15)-C(16)	1.414(7)
O(5)-C(11)	1.430(6)	C(17)-C(18)	1.372(8)
O(6)-C(1)	1.381(5)	C(18)-C(19)	1.396(9)
O(6)-C(12)	1.456(5)	C(19)-C(20)	1.387(9)
O(7)-N(1)	1.246(5)	O(10)-O(2)	2.840(5)
O(8)-N(1)	1.263(5)	O(10)-O(5)	2.800(4)
O(9)-N(1)	1.219(5)		

TABLE III
Selected bond angles (°) for the complex.

O(7)-U-O(7')	180.1(4)	O(6)-C(1)-C(2)	114.3(4)
O(7)-U-O(8)	50.1(2)	O(6)-C(1)-C(13)	124.5(4)
O(7)-U-O(8')	129.9(2)	C(2)-C(1)-C(13)	121.2(4)
O(7)-U-O(10)	113.4(2)	O(1)-C(2)-C(1)	115.2(4)
O(7)-U-O(10')	66.6(2)	O(1)-C(2)-C(16)	125.1(5)
O(7)-U-O(11)	84.5(1)	C(1)-C(2)-C(16)	119.8(4)
O(7)-U-O(11')	95.5(1)	O(1)-C(3)-C(4)	106.9(4)
O(8)-U-O(8')	180.1(4)	O(2)-C(4)-C(3)	108.1(4)
O(8)-U-O(10)	64.9(2)	O(2)-C(5)-C(6)	115.3(5)
O(8)-U-O(10')	115.1(2)	O(3)-C(6)-C(5)	108.0(5)
O(8)-U-O(11)	93.4(1)	O(3)-C(7)-C(8)	113.9(5)
O(8)-U-O(11')	86.7(1)	O(3)-C(7)-C(17)	126.2(5)
O(10)-U-O(10')	180.1(6)	C(8)-C(7)-C(17)	119.8(5)
O(10)-U-O(11)	93.3(1)	O(4)-C(8)-C(7)	114.8(4)
O(10)-U-O(11')	86.7(1)	O(4)-C(8)-C(20)	126.2(5)
O(11)-U-O(11')	180.1(2)	C(7)-C(8)-C(20)	118.9(6)
U-O(10)-O(2)	104.2(1)	O(4)-C(9)-C(10)	107.1(4)
U-O(10)-O(5)	125.8(1)	O(5)-C(10)-C(9)	114.2(5)
O(2)-O(10)-O(5)	127.9(2)	O(5)-C(11)-C(12)	107.9(4)
C(2)-O(1)-C(3)	117.8(4)	O(6)-C(12)-C(11)	105.9(4)
C(4)-O(2)-C(5)	114.7(4)	O(7)-N(1)-O(8)	115.8(4)
C(6)-O(3)-C(7)	117.3(5)	O(7)-N(1)-O(9)	121.9(4)
C(8)-O(4)-C(9)	117.4(4)	O(8)-N(1)-O(9)	122.4(4)
C(10)-O(5)-C(11)	113.5(4)		
C(1)-O(6)-C(12)	117.5(3)		

It can be seen from Fig. 1 that the uranyl group does not enter into the dibenzo-18-crown-6 cavity, but is hexacoordinated in the equatorial plane by two water molecules and two bidentate nitrate groups. The U atom lies at the inversion centre of the complex molecule and its coordinated configuration is a hexagonal bipyramid. The neutral $UO_2(NO_3)_2(H_2O)_2$ units and crown ether molecules are linked together by hydrogen bonding through intermediary water molecules. It can be seen clearly that the two hydrogen atoms in one coordinated water molecule are bonded to two oxygen atoms in the upper crown ether ring and two hydrogen atoms in another coordinated water molecule are bonded to two oxygen atoms in the lower crown ether ring (O(10)···O(2) 2.840Å, (O(10)–H···O(2) 179.9°; (O(10)···O(5) 2.800Å, (O(10)–H···O(5) 175.2°). Thus the compound $[UO_2(NO_3)_2(H_2O)_2]\cdot(DB\text{-}18\text{-}crown\text{-}6)_2$ forms a sandwich structure and has similar structural features as the 1:1 uranyl nitrate tetrahydrate 18-crown-6 compound,[3] in which the U atom is not located within the crown ether group and the neutral $UO_2(NO_3)_2(H_2O)_2$ units are also linked to crown ether molecules by hydrogen bonding through water molecules.

This study has served once again to emphasize that the uranyl ion displays a striking preference for polar oxygen ligands such as H_2O and NO_3^-. The presence of such ligands presents an unfavourable competition with respect to crown ether ligation.

SUPPLEMENTARY MATERIAL

Full lists of anisotropic thermal positions, H atom coordinates and observed and calculated structure factors are available from the authors upon request.

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