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Crystal and Molecular Structure of $UO_2(NO_3)_2$-$(H_2O)_2 \cdot$(12-crown-4): Correction of the Reported Structure

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Introduction

Since crown ethers form inclusion complexes with a wide variety of ions, it was thought initially that the UO_2^{2+} ion might be complexed by its insertion into a crown of the appropriate size. However, as a number of structures containing this ion and various crown ethers were analyzed, it was found that none of them had this geometry [1–3]. One apparent exception was the compound formed with 12-crown-4 (1,4,7,10-tetraoxacyclododecane); in the structure reported [4] the UO_2^{2+} ion is in the crown and bonded to its four O atoms as well as to two H_2O molecules. Several features of this proposed molecule suggested to us that the structure determination was in error; among these were the nonplanar NO_3^- ions, C–O bond length ranging from 1.18 to 1.65 Å, and equatorial U–O lengths of 1.77 Å and 2.05 Å.

By analysis of the original Weissenberg data we (G.B.) showed that it was consistent with a structure having the crown ether out of the UO_2^{2+} coordination sphere and with the NO_3^- ions attached to the UO_2^{2+} ion, an arrangement similar to $UO_2(NO_3)_2$-$(H_2O)_2 \cdot$(18-crown-6) [2]. To establish the structure convincingly and obtain significantly greater precision, we (P.L.R. and J.H.B.) obtained diffractometric data and completed a new determination.

Experimental

To prepare $UO_2(NO_3)_2(H_2O)_2 \cdot$(12-crown-4) equimolar amounts of $UO_2(NO_3)_2 \cdot 6H_2O$ and 12-crown-4 (Parish Chem. Co.) were dissolved in warm acetonitrile, and the compound crystallized as the solution was evaporated. The crystals are pale yellow prisms, stable in air, and melt at 128 ± 1 °C.

TABLE I. Atomic Coordinates and Standard Deviations.[a]

Atom	10^4 x	10^4 y	10^4 z
U	0(0)	0(0)	0(0)
O(1)	3578(7)	5299(4)	1882(9)
O(2)	5613(5)	3723(4)	1678(8)
O(3)	45(7)	63(4)	2621(9)
O(4)	2685(6)	9765(4)	462(8)
O(5)	845(7)	8349(5)	442(13)
O(6)	9398(10)	7145(5)	307(15)
O(7)	8484(7)	8542(5)	–92(12)
C(1)	2872(10)	6124(6)	934(13)
C(2)	3189(9)	4457(6)	767(13)
C(3)	4073(8)	3667(5)	1875(13)
C(4)	5989(9)	3294(5)	–67(13)
N	9572(10)	7975(7)	201(14)

[a] Least-squares standard deviations of the last one or two digits are given in parentheses.

Crystal data for $UO_2(NO_3)_2(H_2O)_2(C_8H_{16}O_4)$: monoclinic; $P2_1/c$; a = 9.064(2) Å, b = 14.366(4) Å, c = 6.765(1) Å, β = 99.64(1)° at 23 °C; Z = 2; ρ_{obs} = 2.31 g cm^{-3}, ρ_{calc} = 2.32 g cm^{-3}. These data are in agreement with the previous report [4], ensuring that the same compound is studied.

Intensity data were collected with a Picker diffractometer using MoK_α X-rays (0.70926 Å) and a θ–2θ scanning method. A reference reflection measured hourly varied less than 2%. A total of 1888 unique reflections were measured up to 2θ = 60°. Calculated absorption corrections ranging from 3.7 to 12.5 were applied.

By use of the position of the UO_2^{2+} ion determined from a Patterson map, phases were calculated for electron-density maps which then revealed the rest of the structure. Least-squares refinement of all nonhydrogen atomic positions and anisotropic thermal parameters converged to yield an $R_F = 0.036$ and σ_1 = 1.60 for 1554 reflections larger than $3\sigma(F^2)$. After including all H atoms in idealized positions and assigning them a B = 5.0 Å^2, further refinement gave R_F = 0.034 and σ_1 = 1.46. Refined coordinates of nonhydrogen atoms are listed in Table I. Structure factors and anisotropic thermal parameters are deposited with the Editor. A list of significant bond distances and angles is given in Table II.

Results and Discussion

The structure of $UO_2(NO_3)_2(H_2O)_2 \cdot$(12-crown-4) consists of neutral $UO_2(NO_3)_2(H_2O)_2$ molecules and

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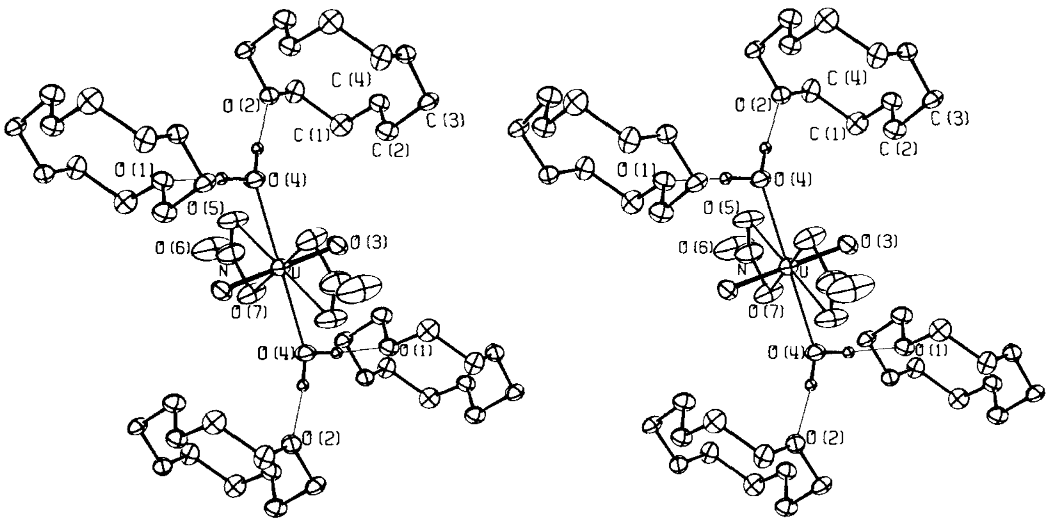

Fig. 1. A stereoscopic drawing of a single uranyl ion and its environment. The U atom is at a center of inversion as is the center of the 12-crown-4 ring.

TABLE II. Interatomic Distances and Bond Angles with Standard Deviations.

Interatomic Distances		Bond Angles	
Atoms	dist., Å	Atoms	angle, deg.
		O(3)–U–O(4)	91.4(2)
U–O(3)	1.769(6)	O(3)–U–O(4)′	88.6(2)
U–O(4)	2.425(6)	O(3)–U–O(5)	88.5(3)
U–O(5)	2.495(7)	O(3)–U–O(5)′	91.5(3)
U–O(7)	2.500(7)	O(3)–U–O(7)	89.3(3)
		O(3)–U–O(7)′	90.7(3)
N–O(5)	1.259(12)	O(7)–N–O(5)	114.7(8)
N–O(6)	1.206(11)	O(5)–N–O(6)	122.8(9)
N–O(7)	1.270(10)	O(6)–N–O(7)	122.5(9)
C(1)–C(4)	1.521(11)	C(2)–O(1)–C(1)	113.9(7)
C(2)–C(3)	1.513(12)	C(3)–O(2)–C(4)	115.3(6)
O(1)–C(1)	1.444(10)	O(1)–C(2)–C(3)	108.0(7)
O(1)–C(2)	1.439(10)	O(2)–C(3)–C(2)	110.9(6)
O(2)–C(3)	1.427(8)	O(1)–C(1)–C(4)′	110.1(7)
O(2)–C(4)	1.423(9)	O(2)–C(4)–C(1)′	110.7(7)
O(4)–O(1)	2.681(8)	U–O(4)–O(1)	109.7(2)
O(4)–O(2)	2.713(8)	U–O(4)–O(2)	127.4(3)
		O(1)–O(4)–O(2)	113.8(3)

12-crown-4 cyclomers connected in layers through a hydrogen-bond network. The crown does not complex the UO_2^{2+} ion as previously reported [4]; instead the structure is analogous to those in the compounds containing the UO_2^{2+} ion and 18-crown-6 [1, 2]. In all these compounds, the U atoms and the crowns are linked not by complexation but through hydrogen bonds involving water molecules.

The centrosymmetric $UO_2(NO_3)_2(H_2O)_2$ unit (Fig. 1) contains the linear O=U=O ion, with bond lengths of 1.769(6) Å, perpendicular to a nearly planar hexagon of O atoms around its equator. Four of these O atoms belong to two bidentate NO_3^- ions [at U–O(5) = 2.425(6) Å and U–O(7) = 2.500(7) Å] and two to water molecules [U–O(4) = 2.425(6) Å]. This configuration is the same as in $UO_2(NO_3)_2 \cdot 2H_2O$ [5] and in many other $UO_2(NO_3)_2L_2$ compounds where L is a neutral O donor. Each water molecule, containing O(4), is connected by moderately strong hydrogen bonds [2.681(8) Å, 2.713(8) Å] to 0 atoms of two 12-crown-4 rings. In this manner each $UO_2(NO_3)_2(H_2O)_2$ unit is linked to four separate crowns, each of which is linked to three additional U-containing units, forming layers perpendicular to the *b* axis (Fig. 2).

The $C_8H_{16}O_4$ crown has the same symmetry, C_i, as it has in crystals of the pure ether [6] and in $MgCl_2(H_2O)_6 \cdot (C_8H_{16}O_4)$ in which it is linked to the Mg^{2+} ion only by hydrogen bonds [7]. But in the several cases in which the crown actually complexes a metal ion, a different symmetry is adopted. In $NaCl(C_8H_{16}O_4)_2 \cdot 5H_2O$ [8], $NaOH(C_8H_{16}O_4)_2 \cdot 8H_2O$ [9], $NaClO_4(C_8H_{16}O_4)$ [10] and $CaCl_2(C_8H_{16}O_4) \cdot 8H_2O$ [11] its symmetry is approximately C_4, while in $CuCl_2(C_8H_{16}O_4)$ [12] approximately C_s.

The structure reported here is totally different from that assigned by Armagan [4], except for the location of the U atoms. The erroneous structure determination can be attributed mainly to three factors: (1) incorrect identification of Fourier maxima, (2) insufficient data of the type $k + l = 2n +$

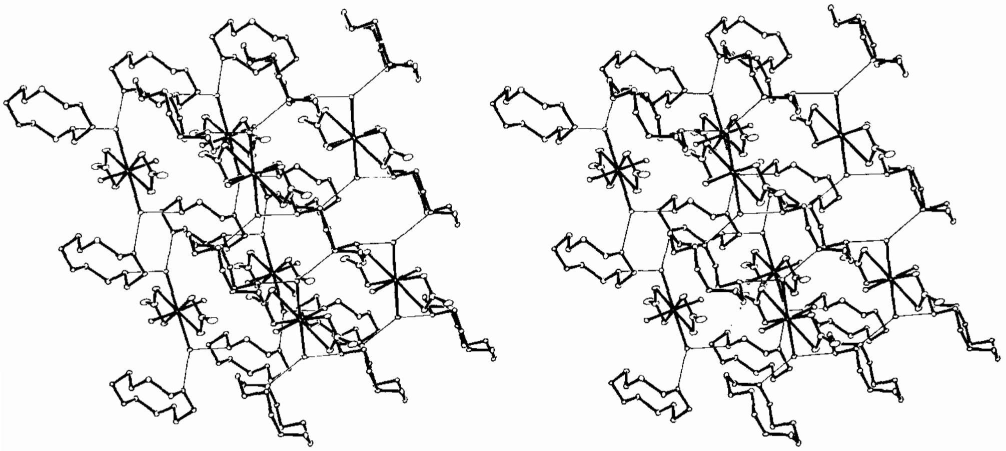

Fig. 2. A stereoscopic drawing showing two hydrogen-bonded layers of the structure.

1 (≈2% of Armagan's data *vs.* 30% here), and (3) reliance on an agreement factor based primarily on reflections dominated by the U atom contribution and not sensitive to the light atoms.

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