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Crystal and Molecular Structure of the Compound Formed between Diaquo Uranyl Nitrate and the Cyclic Polyether 18-Crown-6

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The reaction between the cyclic polyether 18-crown-6 (systematic name 1,4,7,10,13,16-hexaoxacyclooctadecane) and the $UO_2(NO_3)_2 \cdot 6H_2O$ in ethanol at 0 °C was reported[1] to yield the compound $UO_2(NO_3)_2(C_{12}H_{24}O_6) \cdot 4H_2O$; when tetrahydrofuran was used as a solvent the dihydrate was obtained.[2]

Following the method given in ref. 1 we obtained yellow crystals which analyse as $UO_2(NO_3)_2 \cdot 2H_2O(C_{12}H_{24}O_6)$: Calcd., C: 20.75, H: 4.03, N: 4.03%. Found, C: 20.78, H: 4.10, N: 3.93%. The melting point ranges between 148–154 °C.

The i.r. spectrum of the solid compound in KBr in the region between 4000–400 cm^{-1} is in agreement with the values found for the same compound by Costes *et al.*[2] who proposed that "uranyl ion is located in the center of the cyclic ligand".

However, the values of the i.r. stretching frequencies for the nitrate groups deviate from a D_{3h} symmetry indicating coordination by the anion. Further, considering that the uranyl ion has little tendency to give strong bonds with etheric oxygen[3] and the strong tendency for the nitrate group to be chelated to the uranyl ion, we decided to carry out an X-ray study on the title compound.

Crystal data: $UO_2(NO_3)_2 \cdot 2H_2O(C_{12}H_{24}O_6)$, M = 694.4, yellow prismatic crystals: triclinic, a = 9.072(3), b = 9.144(3), c = 8.323(3) Å, α = 64.53 (10)°, β = 104.23(10)°, γ = 110.72(10)°; U = 579.43 Å^3, D_c = 1.99 g cm^{-3}, Z = 1, F(000) = 334. (The structure at the present stage has been refined in the centrosymmetric $P\bar{1}$ space group; MoK_α radiation (λ = 0.7107 Å).)

Intensity data were collected by $\omega/2\theta$ scan method on an automated Philips PW 1100 four-circle diffractometer, using graphite-monochromatized MoK_α radiation. Scan width 1°, scan speed 2.4° per min and two 10 s background counts were chosen. The intensities of 1821 reflections between θ = 3° and θ = 24° were collected. 1820 reflections having a net intensity $> 3\sigma(I)$ were used in the structure refinement ($\sigma(I)$ based on counting statistics).

The structure was solved by Patterson and Fourier methods and refined by a full-matrix least-squares procedure using unitary weight factors to a conventional R factor of 0.045.

Anisotropic temperature factors have been introduced only for uranium, all other non hydrogen atoms have been refined isotropically. All the programs used throughout the structure determination were those written by Immirzi.[4,5] The calculations were performed with the Univac 1108 computer at the Politecnico di Milano.

In the figure is given the projection of the structure along [010] together with the labelling of the atoms.

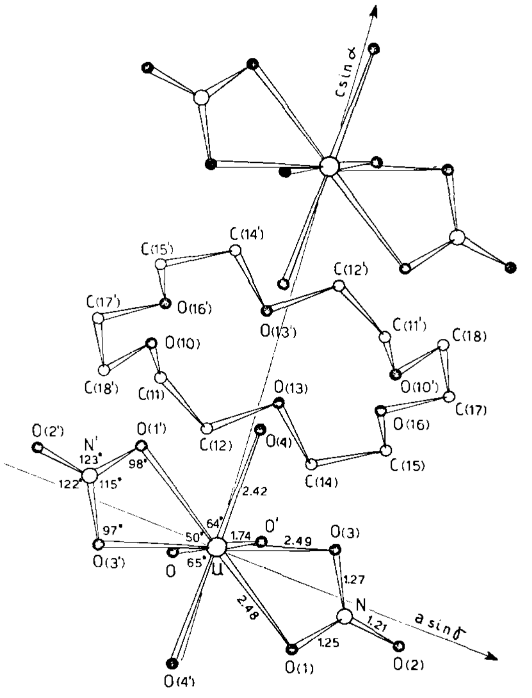

Figure. Projection of the structure along [010]. The primed atoms are related to the unprimed through inversion centers. The mean e.s.d's in the distances are 0.01 Å for that involving uranium and 0.03 Å for the others, for the angles 0.3° and 1° respectively.

The uranium atom is on the inversion center at 0,0,0 and the 18-crown-6 ligand lies about that at

0,0,1/2. The linear uranyl group has coordinated in its equatorial plane two equivalent nitrate groups and two oxygen atoms from the equivalent water molecules. The cyclic polyether which is uncomplexed is located midway between two uranium atoms as shown in the figure, and the plane passing through the etheric oxygen atoms is perpendicular to the equatorial uranium coordination plane (the two planes make an angle of 90°).

The bond distances and angles in the hexagonal bipyramid coordination polyhedron (reported in the figure) agree with the values found for example in $UO_2(NO_3)_2 \cdot 2H_2O$.[6] In the cyclic ether the three independent oxygen atoms O(10), O(13), O(16) are respectively at 2.97, 2.92 and 2.38 Å from their mass center, which is also an inversion center. This variety of distances has been observed in the uncomplexed dibenzo-18-crown-6 in the rubidium and sodium isothiocyanate complex with such a ligand.[7]

The bond lengths and angles are also similar to those reported for analogous ligands,[8,9] having C–C and C–O bond lengths with averaged values of 1.50 Å and 1.44 Å respectively. (In the averages the distances involving C(11) and C(12) are not considered because of some disorder in their positions.)

The six oxygen atoms are roughly on a plane to form a nearly planar hexagon of side approximately 2.78 Å. (The deviations from their mean plane are on average 0.016 Å.)

The torsion angles about the C–C bonds are all *gauche* at *ca.* 60 ° and those about angles of the type C–O–C–C are close to 180°.

The most interesting feature in this compound is that the hexaether adopts a conformation analogous to that found in the complexes with KNCS,[10] RbNCS,[11] CsNCS[12] rather than that of the free ligand[13] and this explains the variations observed by Costes *et al.*[1,2] in the i.r. spectra between the free ligand and the ligand in the present compound.

Contacts between the water molecules and the oxygen atoms from the cyclic ligands (O(4)···O(16) 2.98 Å, O(4)···O(10′) 2.87 Å, O(4)···O(13′) 2.87 Å, O(4)···O(16′) 3.03 Å) suggest the existence of some kind of hydrogen bonding. Therefore the whole structure could be described in terms of polymeric chains developing along [001] with alternance of $UO_2(NO_3)_2 \cdot 2H_2O$ group, 18-crown-6 molecule, $UO_2(NO_3)_2 \cdot 2H_2O$ *etc.* connected together through a hydrogen bonding system.

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