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Anhydrous Uranyl Crown-Ether Complexes. ^{1}H Nuclear Magnetic Resonance and X-Ray Study

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The preparation of anhydrous uranyl perchlorate complexes with 18-crown-6 (I) and with dicyclohexyl-18-crown-6 (II) is described. Single crystals have been obtained and X-ray crystallographic data are discussed. Significant induced shift are observed in the ^{1}H nmr spectra of the complexes in acetonitrile solution. These arise from short interatomic distances between the crown-ether protons and the paramagnetic UO_2^{2+} cation as would be expected in insertion complexes. A visible spectroscopy study of the decomplexation of these compounds by DMSO or water is also presented.

Introduction

There has been a considerable interest in the complexation of the uranyl cation by macrocyclic polyethers. A number of compounds involving the UO_2^{2+} cation and 18-crown-6* or dicyclohexyl-18-crown-6 (dcc)** have been reported [1–5] but crystal structures of these compounds [6, 7] have revealed that the cation is bonded to the anions and water molecules rather than to the crown itself. The affinity of the solvents generally used and of the anions for the UO_2^{2+} cation appears to prevent its coordination to the polyether. The use of solvents with a high dielectric constant and a low solvating power has lead to the synthesis of Uranium(IV) crown-ether and cryptate derivatives [8]. The crystal structure of $[UCl_3\text{-}dcc^+]_2$, UCl_6^{2-} determined by X-ray diffraction, shows that the uranium atom is bonded directly to the crown oxygen atoms. The pmr spectra of these compounds all present large shifts induced by the paramagnetic U^{4+} cation.

We wish to report in this paper the synthesis of compounds involving uranyl perchlorate and crown-ethers with acetonitrile or nitromethane as solvent. Anhydrous compounds have been obtained, contrarily to those previously reported. The UO_2^{2+} cation is most likely directly bonded to the crown-ether oxygen atoms since these are the only donor atoms available in the solution[†].

TABLE I. Elemental Analysis.

Compound I		Compound II
Formula	$UO_2(ClO_4)_2\cdot C_{12}H_{24}O_6\cdot CH_3CN$	$UO_2(ClO_4)_2\cdot C_{20}H_{36}O_6\cdot CH_3CN$
C calcd	21.7	29.9
found	21.2	30.4
H calcd	3.4	
found	4.1	
N calcd	1.8	
found	1.1	
U calcd	30.7	27.0
found	30.2	27.2

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*(1,4,7,10,13,16-hexaoxacyclo-octadecane).

**(2,5,8,15,18,21-hexaoxatricyclo]20.4.0.0^{9,14}] hexacosane.

[†] The 18-crown-6 complex crystals which have been obtained are unfortunately twinned. A full X-ray crystallographic study has not been possible.

Results

Synthesis

$UO_2(ClO_4)_2$ was prepared by dissolving UO_3 in perchloric acid and by slowly crystallizing the resulting hydrated product. Dehydration was performed by using a method suggested by Desreux [9]. Uranyl perchlorate hydrate dissolved in acetonitrile was poured in a Kumagawa apparatus containing activated molecular sieve. The solution was refluxed for 10 hours; during that time, the water signals disappeared from the solution pmr spectrum. A stoichiometric quantity of crown-ether was then added to the solution and reflux was maintained for several minutes. The solution was concentrated under a stream of argon and crystals were obtained at room-temperature. This preparation proved to be successful with 18-crown-6 (complex I) and dicyclohexyl-18-crown-6 (complex II), but failed with dibenzo-18-crown-6, 15-crown-5 and cyclohexyl-15-crown-5 (Table I).

Crystallography

The two complexes form yellow needle-like crystals, suitable for a preliminary crystallographic study: unit-cell dimensions and space groups have been drawn from Weissenberg and precession photographs using nickel-filtered copper radiation.

Complex (I)

The cell is apparently monoclinic, with a C-centered face and the following parameters: a = 10.80 ± 0.03 Å, b = 18.54 ± 0.06 Å (b/a *ca.* $\sqrt{3}$), c = 5.72 ± 0.2 Å, β = 98 ± 0.5°, V = 1134 ± 10 Å^3. The calculated density with a probable value of $Z = 2$ is 2.15 g cm^{-3}. The structure shows a pseudo-hexagonal character owing to the C face-centered cell and to a b/a ratio close to $\sqrt{3}$. However, when starting the resolution of the structure – after collection of intensities on a computer-controlled four-circle diffractometer – it appeared that the cell was twinned and that the observed monoclinic cell was the average cell of two individuals. The evidence of a twinned crystal was provided by the necessity of fitting four uranium atoms into the cell which leads to an unrealistic density and to collisions between atoms.

A re-examination by photographic methods showed that all crystals are twinned with variable ratios of the two components. The X and Z (needle axis) axes are common to both twins, the (010) plane is the composition plane. Consequently, oscillation photographs with the Z axis as oscillation axis do not reveal the twins, neither do precession diagrams taken with b^* (b_1^* and b_2^* are practically parallel) along the X-ray beam, mimicking a binary axis.

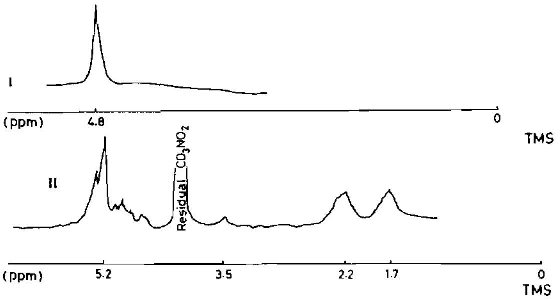

Fig. 1. ^{1}H nmr spectra at 60 MHz of $UO_2(ClO_4)_2$–18-crown-6 in CD_3CN (1) and $UO_2(ClO_4)_2$ –dicyclohexyl-18-crown-6 in CD_3CN (2).

Each twin cell is triclinic and the structural determination is made very difficult if not impossible. However important qualitative features can be obtained from clear relative positions in regions where no atomic super impositions occur:

- four nearly coplanar oxygen atoms are located approximately in the (001) plane in the immediate neighbourhood of the uranium atom,
- two others are on an axis perpendicular to this plane and on each side of it.

It is reasonable to identify the first four as crown oxygen atoms, the other two being the uranyl oxygens.

The two missing crown oxygens interfere with the ClO_4 anions from the other twin.

Complex II

This compound has also a monoclinic unit cell: a = 12.94 ± 0.02 Å, b = 12.90 ± 0.04 Å, c = 17.35 ± 0.10 Å, β = 91.5 ± 0.5°, V = 2895 Å^3.

With four [$UO_2(ClO_4)_2$dcc] units in the cell, a calculated density of 1.93 g cm^{-3} is obtained. The reflections limiting conditions are the following: hkl: no conditions; h0l:l = 2n; 0k0, k = 2n. These lead unambiguously to a P $2_1/c$ space group. In addition, hkl reflections with h = 2n + 1 and k + l = 2n + 1, are weak and diminish rapidly with increasing Bragg angle. Such an intensity pattern is obtained with uranium atoms forming an A face-centered cell with half a period (the a axis is the needle axis).

Spectroscopy Results

Characteristic UO_2^{2+} stretching frequencies are observed in the ir spectra of both compounds (I) and (II) [$\nu_{as}^{I}(UO_2^{++})$ = 960 cm^{-1} and $\nu_{as}^{II}(UO_2^{++})$ = 952 cm^{-1}].

Perchlorate: 930, 1100, 632 cm^{-1}, for (I) and 930, 1100, 628 cm^{-1} for (II).

The nmr spectra of (I) and (II) in CD_3NO_2 are displayed in Figure 1. The 18-crown-6 only resonance is shifted 1.7 ppm downfield, a similar result in acetonitrile solution has been mentioned by Klimes *et al.* [3]. This large shift induced by the UO_2^{2+} cation can

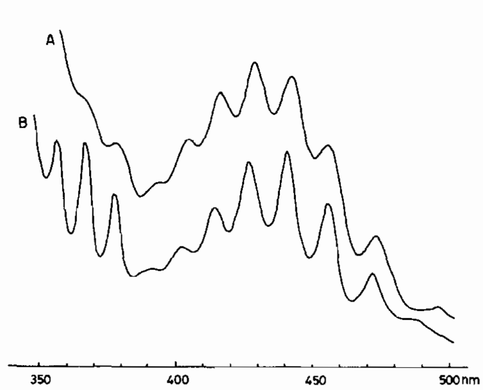

Fig. 2. Electronic absorption spectra of $UO_2(ClO_4)_2$–18-crown-6 in the solid phase (PTFE mull) (1) and in nitromethane solution (2).

be explained in terms of a short uranium–proton distance.

Studies on UO_2^{2+}-induced paramagnetic shifts have shown that there is a large contribution of the magnetic anisotropy to the observed shift [10].

The dipolar induced shift can be estimated from the geometric parameters (r, θ) of the proton [10] and from the value of the magnetic anisotropy estimated by Eisenstein and Pryce ($\chi_{\parallel} - \chi_{\perp} = -2.74 \times 10^{-28}$). Induced shifts greater than 1 ppm cannot be obtained for UO_2^{2+}–proton distances greater than 4 Å. Conversely, a shift of 1.7 ppm in the UO_2^{2+} equatorial plane ($\theta = 90°$) corresponds to a UO_2^{2+}–proton distance of 3.0 to 3.5 Å. This is approximately the predicted U–H distance in a UO_2-centered undistorted crown (4 Å). The nmr spectra of compounds where the UO_2^{2+} cation is not located inside the crown cavity display no resonances with measurable induced shift.

Significant shifts are also observed in the spectrum of compound (II). The overall symmetry of the crown-ether is reduced by the cyclohexyl groups. One signal can be attributed to the polyether protons (overall width 15 Hz; induced shift −1.50 ppm) and two other signals account for the cyclohexyl protons (induced shifts −0.8 and −0.3 ppm). These shifts correspond to the uranyl–proton distances expected in an insertion complex (5 and 7 Å).

Visible Spectroscopy

The transmission spectra of (I) and (II) were recorded in the solid phase (PTFE mull) and in nitromethane solution, as illustrated by Fig. 2. The immediate environment of the UO_2^{2+} cation is identical in both the solid phase and solution. The only definitive conclusion that can be drawn from these spectra is that the UO_2^{2+} environment has a symmetry which is higher than Cs as witnessed by the sharp absorption bands.

A study of the influence of the electron-donating power of various solvents on the stability of complex (I) was also undertaken. To a solution of (I) in acetonitrile were gradually added small quantities of DMSO. The effects of each addition are recorded by visible spectroscopy at a fixed frequency, characteristic of complex (I). The decrease of the concentration of I is thus followed and the corresponding absorbance is plotted against the ratio ρ = [DMSO]/[UO_2^{2+}] (Fig. 3). The absorbance decreases linearly for values of ρ comprised between 0 and 2 and becomes constant for $p > 2$.

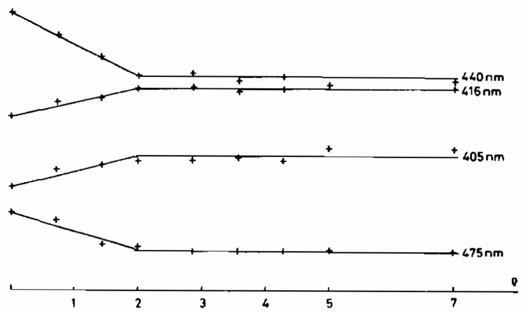

Fig. 3. Plot of the optical absorption *vs.* the concentration ratio [DMSO]/[UO_2^{2+}].

The following reaction: UO_2^{2+}-crown + 2 DMSO → UO_2^{2+}•2DMSO + crown appears thus to be complete. This process was also followed by nmr. As DMSO is gradually added to a solution of (I), the complexed ligand resonance disappears while the free ligand resonance reappears.

A similar decomplexation by water was studied in the same conditions. Water appears to be a far less efficient decomplexant than DMSO: half of the initial UO_2^{2+} complex remained in a solution of (I) after 40 equivalents of water had been added.

Discussion and Conclusions

Two novel uranyl compounds with crown-ethers have been synthesized. They differ from the previously reported uranyl–crown-ether compounds by the fact that the only atoms capable of bonding to the uranyl belong to the macrocyclic ligand. These compounds retain their solid-state structure when in solution in a high dielectric and low electron-donating medium. Their pmr spectra in solution exhibit large paramagnetic induced shifts. However the inclusion of UO_2^{2+} cation in the macrocyclic ligand can only be definitely proved by an X-ray crystal structure. There are two such structures concerning uranyl and macrocyclic ligands. One is the superphthalocyanin complex [11] where the donor atoms are nitrogen atoms. The other is the 12-crown-4 complex recently published by Armagan [12]. In the latter structure, the mean plane of the crown forms a surprisingly large angle with the uranyl equatorial plane and the distances between the uranium atom and the crown oxygen atoms are far shorter than those usually found in uranyl compounds. The UO_2^{2+} cation appears to be too large to fit into the 12-crown-4 cavity. Our unsuccessful attempts to obtain a 15-crown-5 complex by our method has led us to believe that even this ligand is too small to accept a uranyl guest.

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