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Photoreduction of UO_2 (18-Crown-6)$(ClO_4)_2$. Synthesis of a U^V Crown-ether Complex

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The photochemistry of uranyl complexes generally yields uranium(IV) derivatives even though the primary step is a reduction of a U^V intermediate. The latter species is unstable and disproportionates to U^{IV} and U^{VI}. However Sostero *et al.* [1] have shown that U compounds can be prepared by photochemical reduction of uranyl in the presence of radical scavengers and in an anhydrous medium. More recently similar studies [2, 3] have demonstrated that by irradiation of $UO_2(NO_3)_2L_2$ where L can be TBP, U^V could be formed in solution without a radical scavenger. We present here results showing that a macrocyclic complexation of the UO_2^{2+} ion also stabilises the U^V intermediate produced in the photoreduction process. In addition this paper describes the photochemical preparation and isolation of the first U^V macrocyclic complex.

Experimental

Synthesis

UO_2(18-crown-6)$(ClO_4)_2$ (I) was prepared as described in a previous paper [4]. A CH_3CN solution of (I) (1 to 5 × 10^{-2} *M*/l) was flushed with argon. Two sources of irradiation were used: with a mercury vapor lamp and ir filtration, U^V is formed followed by U^{IV}; when the 436 nm line is selected the process is slower and production of U^{IV} is considerably lower.

The photolysis of UO_2^{2+} was followed by electronic absorption spectroscopy and irradiation was stopped when only small amounts remained in solution. The solution was then concentrated and the complex crystallized at –2 °C as white solid. Elemental analysis: Found U, 30.2%; C, 18.5%; H, 3.9%; Cl, 13.5%; N, traces. Calculated for $UO(ClO_4)_3$(18-crown-6): U, 29.1%; C, 17.6%; H, 2.9%; Cl, 13.0%.

Visible-UV Spectroscopy

The photolytic reaction is followed by observing the 450 nm UO_2^{2+} (18-crown-6) band which decreases in intensity and two large bands at 1400 and 1030 nm which increase (Fig. 1). The same experiment with anhydrous $UO_2(ClO_4)_2$ leads to the formation of U^{IV} as witnessed by intense absorption bands at 650 and 1150 nm.

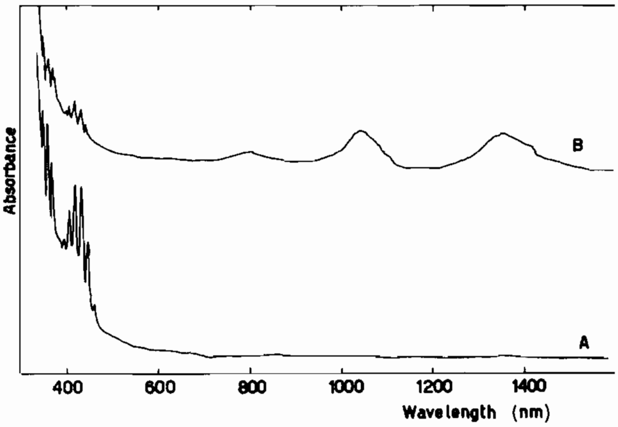

Fig. 1. Electronic absorption spectra of: A a 5 × 10^{-2} *M* solution of (I) in acetonitrile, B the same solution after irradiation.

The stability of the U^V compound in the dark can be investigated in the same cell. About 10% of the product undergoes a disproportionation in 24 hours. The U^{IV} form was not identified but complex (I) appeared.

The electronic spectrum of the solid product in a teflon mull is identical.

NMR Spectroscopy

A saturated solution of (I) in CD_3CN was successively exposed to a mercury vapor lamp as described above and analysed by PMR spectroscopy until no further evolution of the spectrum was observed. The sharp resonance of the uranyl complex [4] gradually diminishes to 40% of its initial intensity and a broad signal (*ca.* 100 Hz at 37 °C) grows at 13 ppm upfield from TMS.

The final spectrum is recorded at various temperatures between –50 °C and 90 °C. A Curie-type variation of the paramagnetic induced shift of the reduced species is observed. The magnetic susceptibilities $\Delta\chi$ were calculated using McConnel and Robertson's relation $\Delta H_i/H = 3\,N^{-1}\,\langle(3\cos^2\theta_i - 1)r_i^{-3}\rangle$, with the usual cylindrical coordinates of the crown-ether protons approximately equal to 90° (θ_i) and 4.2 Å (r_i). From these values, the Curie constant ($C = \Delta\chi\cdot T$) was found equal to 0.31 ± 0.03 $cm^3\ Kmol^{-1}$ and the effective magnetic moment equal to 1.6 ± 1 BM (compared to 2.5–2.8 for U^{IV}). This susceptibility value is typical of U^V compounds [5] (1.7 for spin only).

Intermolecular ligand exchange was found to be slow on an NMR time scale in the –50 °C to 90 °C temperature range as witnessed by the separate free

TABLE I. Infrared and Raman Data of UO^{3+}, 18-crown-6, $3ClO_4^-$ Assigned in D_{3d} Symmetry for 18-crown-6, T_d for ClO_4^-.

Infrared[a]			Raman Diffusion[b]		
Frequency	Assignments	Modes	Frequency	Assignments	Modes
1470 w	δ (CH_2)	Eu			
1382 vw	δ (CH_2)	Eu			
1355 w	ω (CH_2)	A_{2u}			
1287 w	t (CH_2)	Eu	1275 w	t (CH_2)	Eg
1250 vw	t (CH_2)	A_{2u}	1256 w	t (CH_2)	
1236 sh	t (CH_2)	A_{2u}			
1140 sh 1110 sh 1080 vs 1037 sh	ν_a (COC) vibrations of cycle COC, CC	Eu			
1110 sh 1080 vs	ν_3 (ClO_4^-)	F_2			
973 m	g (CH_2)	Eu			
941 vvw	ν_1 (ClO_4^-)	A_1	934 vs	ν_1 (ClO_4^-)	A_1
			870 vs	Macrocycle breathing	
840 sh 827 sh	ρ (CH_2)	Eu			
705 m	ν (UO)				
635 sh 624 m	ν_4 (ClO_4^-)	F_2	625 m	ν_4 (ClO_4^-)	F_2
			465 mb	ν_2 (ClO_4^-)	E
550 w	δ (cycle)	Eu			
345 w	δ (cycle)	Eu			

[a] Spectra in Nujol or KCl mulls. (Digilab spectrometer FTS20).

[b] Spectra of the powder compound in capillary (Raman spectrometer Coderg T800, Krypton Laser 6471 A).

and complexed crown-ether resonances in a solution containing an excess of ligand. On the contrary there is a fast conformational movement averaging all the proton chemical shifts for temperatures above −13 °C*. At low temperature two resonances are observed: they presumably correspond to pseudo axial and equatorial protons as in the analogous uranium(IV) chloride 18-crown-6 complex [6].

Ir Vibrational Spectroscopy

The observed absorption and diffusion lines in the ir and Raman spectra of the U^V complex are listed in Table I.

The ClO_4^- anions exhibit a strong Raman band at 934 cm^{-1} (ν_1) and two ir absorption bands at 1080 (ν_3) and 626 cm^{-1} (ν_4) in agreement with the expected T_d symmetry *i.e.* there is no bonding to the uranium. The other intense bands in the spectrum can be assigned to the macrocycle. The particularly simple spectrum observed between 1050 and 800 cm^{-1} is characteristic of 18-crown-6 bonded to a cation [7]. The strong absorption in the range 1000 cm^{-1} (mostly ν_a(C–O–C)) and the Raman diffusion band at 870 cm^{-1} (macrocycle breathing mode) support the D_{3d} symmetry for the 18-crown-6 moiety.

The broad absorption band at 705 cm^{-1} does not arise from the crown, either bonded or free. This band decreases when the compound is exposed to

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*At 60 MHz.

air and a broad absorption of UO_2^{2+} appears at 908 cm^{-1}. It is suggested to be the uranium–oxygen stretching. The stretching frequencies in oxo metal(V) complexes are generally found in the 900–950 cm^{-1} region [8]. In the case of uranium(V) two bands have been assigned to $\nu(U{=}O)$ in $[UOX_5]^{-2}$ where X = F, Cl Br, between 800 and 900 cm^{-1} [8–11] (760 cm^{-1} in $(Et_4N)_2UOF_5$ [11]). In the present U^V complex the metal–oxygen stretching occurs sensibly lower.

Discussion

The spectroscopic results establish that the new compound, prepared by photoreduction of UO_2(18-crown-6)$(ClO_4)_2$ is a U^V compound. The elemental analysis suggests the formula UO (18-crown-6)$(ClO_4)_3$ which is supported by the vibrational data.

The present photochemical reduction of the uranyl crown complex shows that there is a specific reaction involving the macrocyclic ligand. The U^V which is formed undergoes no disproportionation nor further photolysis to U^{IV} as in the case of other uranyl compounds [1, 2]. This presumably reflects an efficient shielding of the U^V or U^{VI} cations from the surrounding chemical reagents.

The proposed assignement of the UO^{3+} stretching frequency indicates a lowering of the uranium–oxygen force constant compared to that of the uranyl ion from 6.5 mdyne Å in $[UO_2(18\text{-crown-}6)]^{2+}$ to 4.4 mdyne $Å^{-1}$ in $[UO\ (18\text{-crown-}6)]^{3+}$, and the lengthening of the metal–oxygen distance from 1.747 in $[UO_2(18\text{-crown-}6)]^{2+}$ to 1.83 Å for U^V–O using Bagder–Jones [12] formula.

Another point of discussion is whether or not the uranium atom is inserted in the crown cavity. First of all, both optical and vibrational spectra of the solid and of the CD_3CN solution are very similar and provide an evidence that the structure of the molecules in the solid is retained in solution. From the nmr chemical shift it can be inferred that the protons from the crown are close to the uranium and from ir data the ClO_4^- anions are free. Moreover the 18-crown-6 in complex retains the 3-fold symmetry. This fact favors a structure where the uranium atom is located on the 3-fold axis. Finally the crown oxygen atoms are the only bonding atoms available in the compound. This leads to the hypothesis of the insertion of UO^{3+} in the crown cavity but only crystallographic determination will provide an unambiguous conclusion.

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