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Uranyl Complexes with Cyclic Polyethers

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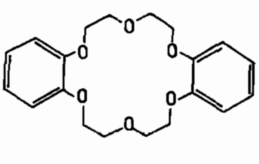
Uranyl(VI) nitrate, chloride, and perchlorate complexes with the cyclic polyethers dibenzo-18-crown-6 and benzo-15-crown-5 have been synthesized. The compounds have been characterized by elemental analyses, molar conductances, infrared and electronic spectra, and thermal analyses. The infrared and conductivity data, together with a consideration on the general coordination behaviour of the uranyl ion, suggest that the uranium is not located at the center of the cyclic ligand.

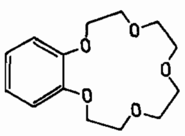
Introduction

The complexing ability of some cyclic polyethers has been widely shown [1 - 5]. Recently some uranyl complexes with the cyclic polyether 18-crown-6 have been prepared [6, 7]. On the basis of spectroscopic evidence the uranyl ion seems to be located at the center of the cyclic ligand.

We report here the synthesis and characterization of the complexes of the cyclic polyethers dibenzo-18-crown-6, L_I, and benzo-15-crown-5, L_{II}, with uranyl(VI) nitrate, chloride, and perchlorate:



L_I



L_{II}

Experimental

Uranyl nitrate hexahydrate and uranyl chloride trihydrate were reagent grade commercial products. Uranyl perchlorate was prepared according to the classical method. The ligands L_I and L_{II} were prepared following the methods described by Pedersen [1].

Preparation of the Complexes

One mmol of L_I or L_{II} ligand was added, under stirring, to the uranyl nitrate hexahydrate (one mmol) in acetonitrile solution (15 ml). The solution was refluxed for one hour. To the cooled solution, carbon tetrachloride was added until a first trace of turbidity remained. The solution was stored in the darkness and after four days a crystalline product was obtained. The crystals were filtered, washed with carbon tetrachloride and dried on diphosphorus pentaoxide *in vacuo* for a week. The same complexes were also obtained by concentrating the acetonitrile solutions containing the uranyl nitrate and the polyether. Minute crystals were obtained, which were filtered, washed with small portions of acetonitrile and dried *in vacuo.*

The uranyl perchlorate complexes with both the ligands were prepared by the same method starting from hydrated uranyl perchlorate. The addition of carbon tetrachloride to the clear acetonitrile solution (10 ml) containing the uranyl perchlorate (one mmol) and the polyether (one mmol) causes the separation of a viscous oil which crystallizes slowly in four days.

The analogous uranyl chloride complexes were prepared by concentrating slowly an ethanol–acetonitrile (1:5) solution containing the uranyl chloride trihydrate (one mmol) and the polyether (one mmol). Minute crystals were obtained, which were filtered, washed with ethanol–acetonitrile mixture and dried on diphosphorus pentaoxide *in vacuo*.

Analyses

Uranium was determined according to the classical method by precipitation as ammonium diuranate and weighed as U_3O_8. The water content was determined by the Karl–Fisher method and confirmed by the thermogravimetric analyses.

Measurements

The infrared spectra of the complexes in KBr pellets, nujol or hexachlorobutadiene mulls were obtained with a Perkin–Elmer 577 spectrophotometer.

TABLE I. Analytical and Conductivity Data for the Uranyl Complexes with Cyclic Polyethers.

Complex	% U		% C		% H		% N or Cl		Λ_M
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	(ohm^{-1} cm^2 M^{-1})
$UO_2(NO_3)_2L_I(H_2O)_2$	30.16	29.85	30.38	31.73	3.57	3.62	3.54	3.49	23
$UO_2(NO_3)_2L_{II}(H_2O)_5$	31.64	31.90	22.35	21.87	4.02	4.15	3.72	3.75	30
$UO_2(ClO_4)_2L_I(H_2O)_6$	25.40	26.05	25.62	25.90	3.87	3.96			203
$UO_2(ClO_4)_2L_{II}(H_2O)_7$	27.57	28.12	19.47	18.78	3.97	4.03			215
$UO_2Cl_2L_I(H_2O)_2$	32.29	32.76	32.57	32.02	3.83	3.90	9.61	9.82	12
$UO_2Cl_2L_{II}(H_2O)_2$	36.89	36.53	26.06	26.44	3.75	3.71	10.98	10.80	15

TABLE II. Uranyl Complexes with Cyclic Polyethers. IR Data for Nitrate and Perchlorate Groups.

Complex	$\nu_2+\nu_3$	$\nu_2+\nu_5$	ν_1	ν_4	ν_2	ν_6	ν_3	ν_5	(C_{2v})
$UO_2L_I(NO_3)_2(H_2O)_2$	1760w	[b]	1520s	1270s		818w	[a]	725w	
$UO_2L_{II}(NO_3)_2(H_2O)_5$	1770w	1740w	1530s	1280s	1030m	812w	[a]	710w	
	ν_3			ν_4	(T_d)				
$UO_2L_I(ClO_4)_2(H_2O)_6$	1150s, 1120s, 1080s			630s					
$UO_2L_{II}(ClO_4)_2(H_2O)_7$	1150sh, 1120s, 1080s			630s					

[a] Indistinguishable from ligand bands. [b] Not observed.

Ultraviolet and visible spectra were obtained from acetonitrile solutions with an Optica CF4NI double-beam spectrophotometer. The conductivity of acetonitrile solutions of the complexes was determined at 25 °C with a LKB type 3216-B conductivity bridge (concentration range = 1.8–2.3 × $10^{-3}M$). Thermoanalytical measurements were carried out with a Mettler thermoanalyzer in dynamic atmosphere of dry nitrogen.

Results and Discussion

The complexes obtained with both the polyethers are yellow solids. They are soluble in acetonitrile and light alcohols. Analytical results and conductivity data are reported in Table I.

The ultraviolet spectra of the complexes dissolved in acetonitrile show some spectral changes in the 280 nm region, where intraligand transition occurs, compared to the free ligand spectra. A similar behaviour observed for the corresponding complexes of alkali [1] and lanthanoid [3] cations was regarded as a sign of the metal–polyether interaction. The visible absorption spectra show the vibronic structure of the bands in the 350–500 nm range essentially determined by the triatomic UO_2^{2+} entity. The spectra are basically similar to those of the corresponding uranyl salts in the same solvent, but some peaks appear to be slightly shifted. No ligand → uranium charge-transfer band is observed.

The infrared spectra of all the complexes, compared with the spectra of the free ligands, clearly show some spectral changes indicating cation–polyether interactions. The bands which undergo significant changes are those exhibited by the free ligands in the region including CO stretching modes (1300–1200 cm^{-1}) and in the 800–700 cm^{-1} region which includes CH deformation modes. The shifts of the CO stretching mode to the lower frequencies and the disappearance of the medium band at 1000 cm^{-1} in the spectrum of the L_I ligand or the weak band at 980 cm^{-1} in the spectrum of the L_{II} ligand are some features of the spectra of the complexes. The observed changes are in agreement with those reported for the corresponding complexes of alkali and lanthanoid cations [1 - 4]. Some strong bands in the 3500–3200 and 1630 cm^{-1} regions of the spectra of the complexes are assigned to H_2O stretching and bending modes. The absence of bands in the 2200 cm^{-1} region excludes, on the other hand, the presence of acetonitrile molecules in the complexes.

Some infrared data for the nitrate and perchlorate groups in the uranyl complexes with the polyethers are reported in Table II.

Costes *et al.* find both the nitrate groups in the complex of uranyl nitrate with the polyether 18-crown-6 ionic in character, thus supporting their "inclusive" hypothesis. On the contrary, the infrared spectral data obtained from our nitrate complexes indicate that both the nitrate groups remain coordinated to the uranyl ion; in fact, assignments of the vibrational modes agree well with published values for the nitrate group with C_{2v} point-group symmetry [8, 9]. Unfortunately it is very difficult to distinguish between the mono and bidentate coordination of the nitrate group from infrared data only because it has C_{2v} symmetry and six infrared active vibrations when either a mono or a bidentation occurs [9, 10]. The absence of the ν_3 band (D_{3h} symmetry) at 1390–80 cm^{-1} confirms the coordination of both the nitrate groups.

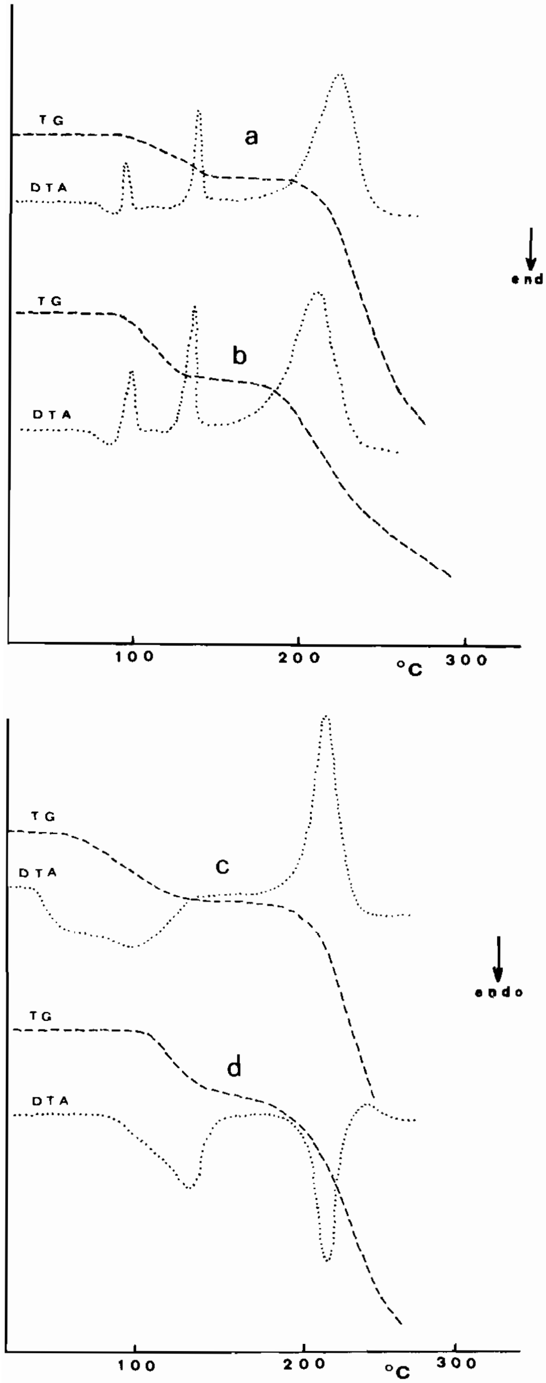


Fig. 1. Thermoanalytical curves at ϕ = 2 °C min^{-1} and in dynamic nitrogen atmosphere of: (a) $UO_2(NO_3)_2L_I(H_2O)_2$; (b) $UO_2(NO_3)_2L_{II}(H_2O)_5$; (c) $UO_2(ClO_4)_2L_I(H_2O)_6$; (d) $UO_2Cl_2L_{II}(H_2O)_2$.

The conductivity values are of about 25 ohm^{-1} cm^2 M^{-1} for the nitrate complexes in acetonitrile solutions; these values indicate the non-electrolytic behaviour of the complexes, yet confirming the coordination of both the nitrate groups.

In the infrared spectra of the solid perchlorate complexes the degeneracy of the ν_3 mode (T_d symmetry) of the perchlorate group appears removed and a resolved triplet is observed in the 1160–1080 cm^{-1} range. This indicates that distortion of the perchlorate group from T_d symmetry is occurring in the complex. The lack of any significant ν_3 splitting observed in the spectra of the complexes in acetonitrile solution and the conductivity values undoubtedly indicate that both the perchlorate groups are ionic in character. This is, however, the common trend shown by the uranyl perchlorate complexes and cannot support either the "inclusive" hypothesis or its contrary.

Some thermoanalytical data are reported in Figure 1. The thermogravimetric (TG) and differential thermal analysis (DTA) curves for the uranyl nitrate and chloride complexes with both the polyethers show some steps of mass-loss in the temperature range of 90–140 °C, corresponding to the loss of all the water molecules. For the analogous uranyl perchlorate complexes the loss of the water molecules takes place in the temperature range of 50–130 °C. The DTA curves of the chloride and perchlorate complexes with both the polyethers show that the dehydration processes occur with endothermic effects; also the dehydration of both the nitrate complexes begins endothermically, but two exothermic processes immediately follow before the first is completed (see Fig. 1). One reasonable explanation for these results is that structural rearrangements occur in these two complexes, probably with the contribution of the nitrate groups.

After the dehydration process, all the complexes are more or less stable in a temperature range of 30–50 °C, after which a thermal decomposition reaction begins.

The decomposition reactions of both the nitrate and perchlorate complexes are exothermic; this behaviour suggests the possibility of a ligand decomposition process with the contribution of the nitrate and perchlorate groups during the thermal dissociation.

In the TG curves of the chloride complexes a first thermal dissociation process is shown with a mass-loss corresponding to the loss of the cyclic polyether; the DTA curves indicate, moreover, that this process is endothermic. This behaviour is similar to that observed for some complexes of lanthanoid thiocyanates

[11, 12] and chlorides [13] with both the cyclic polyethers.

A significant difference between the uranyl chloride and lanthanoid chloride complexes with cyclic polyethers is the temperature at which the thermal dissociation reaction begins, being about 50–70 °C lower for the uranyl complexes.

Considering the data presented herein, particularly analytical, infrared, and conductivity data, and the ability of the uranyl ion to localize ligands in the equatorial plane displaying a maximum coordination number of six, it is probably appropriate to exclude the hypothesis that the uranyl ion is located at the center of the cyclic ligand, for the compounds described in this paper.

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