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Polarographic Investigations on Uranyl(VI) Complexes in Dimethylsulphoxide.
V. 14-Membered Tetra-aza Macrocycles

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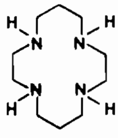
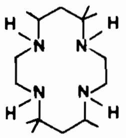
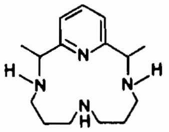
In previous investigations we have studied by polarographic techniques the complexes formation between uranyl(VI) ion and various classes of ligands, in dimethylsulfoxide [1–5]. We take into consideration here the following 14-membered tetra-aza macrocycles as ligands:



cyclam



CTH



CRH

Tetra-aza macrocycles form stable complexes with divalent transition metal cations, in which the metal ion is often coplanar with the four nitrogen atoms in a tetragonal stereochemical arrangement. Up until today no data are available on the ability of these ligands to form complexes with uranyl(VI) ions.

Experimental

The apparatus and the methods, as well as preparation and purification of dimethylsulfoxide (DMSO) and of the DMSO-uranyl(VI) solvate $[UO_2(NO_3)_2\cdot 5DMSO]$, have been already reported [1, 2]. Et_4NClO_4 (TEAP) (Carlo Erba) supporting electrolyte, previously dried in a vacuum oven at 50 °C, was used in a 0.1 *M* concentration.

Macrocyclic ligands used in this work have been prepared according to established procedures ([14]-aneN_4, cyclam, ref. 6; *meso*-Me_6[14]aneN_4 dihydrate, *ms*-CTH, ref. 7; *meso*-Me_2[14]py-ane N_4, *ms*-CRH, ref. 8).

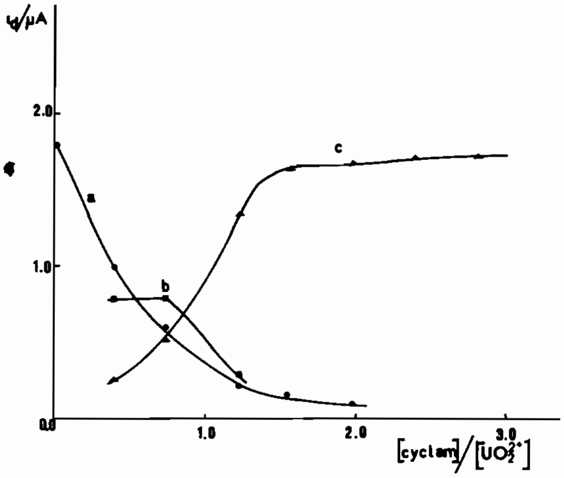


Fig. 1. Limiting currents trend of the polarographic reduction processes as a function of the mol ratio cyclam/UO_2^{2+}. Uranium(VI) concentration: 1.61×10^{-3} *M*.

All experiments were carried out at 25 °C. All reported potential values are referred to a saturated aqueous calomel electrode.

Results and Discussion

The electrochemical characteristics of uranyl(VI) ion in DMSO have been previously reported [1, 9] and the absence of polynuclear species in the tested experimental conditions has been checked [2].

From a qualitative viewpoint the addition of increasing amounts of the macrocyclic ligands here considered to uranyl(VI) DMSO solutions gave a polarographic picture in which the limiting current of the free uranium(VI) cathodic wave (a) ($E_{1/2}$ = –0.53 V) progressively decreases and a second reduction wave (b) appears and progressively increases in height. This is followed in turn by a well-defined third wave (c) [the polarographic profiles are qualitatively similar to those reported in the cathodic portions of Fig. 1, ref. 5].

The half-wave potentials of the cathodic waves 'a', 'b' and 'c' remained in all cases almost constant at increasing ligand concentration; in particular the $E_{1/2}$ values for the waves 'b' and 'c' are located at: –0.75 V and –0.93 V for cyclam, –0.74 V and –0.94 V for *ms*-CTH, –0.75 V and –0.91 V for *ms*-CRH, respectively.

Coulometric results, together with logarithmic analysis of the waves, indicated both the processes 'b' and 'c' to be almost reversible one-electron reduction processes.

The trends of the cathodic limiting currents relative to these processes against the mol ratio ligand/

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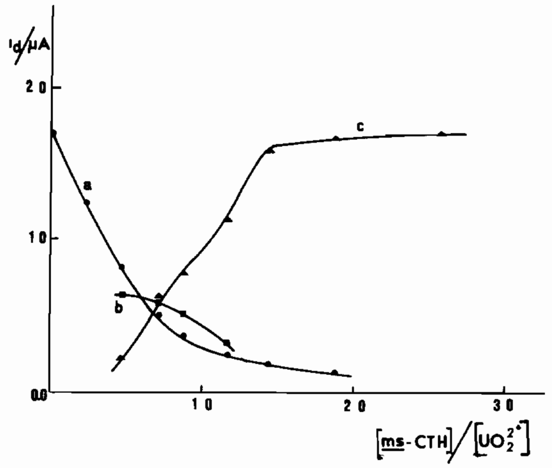

Fig. 2. Limiting currents trend of the polarographic reduction processes as a function of the mol ratio *ms*-CTH/UO_2^{2+}. Uranium(VI) concentration: 1.51 × 10^{-3} *M*.

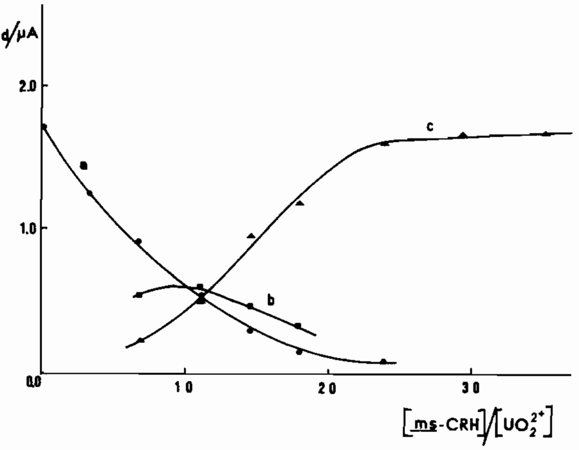

Fig. 3. Limiting currents trend of the polarographic reduction processes as a function of the mol ratio *ms*-CRH/UO_2^{2+}. Uranium(VI) concentration: 1.51 × 10^{-3} *M*

UO_2^{2+} are reported in Figs. 1, 2, 3 for cyclam, *ms*-CTH, and *ms*-CRH, respectively.

These plots show that under our experimental conditions (the concentration ranges are those allowed by the solubility of ligands in DMSO) cyclam and *ms*-CTH give rise to the 2:1 and 1:1 uranyl(VI) ligand complexes, while *ms*-CRH produces the 1:1 and 1:2 ones.

The constancy of the $E_{1/2}$ values for the processes 'b' and 'c' at increasing ligand concentrations indicates that uranium(VI) and uranium(V) form complexes of the same stoichiometry [2]. The ratios of the stability constants of the oxidized and reduced forms as well as the stoichiometry of the formed complexes are summarized in Table I.

By assuming a constant coordinating ability of uranium(V) ion in respect to every ligand tested,

TABLE I. β_{Ox}/β_{Red} values for the Different Ligands.

UO_2^{2+}/ligand complex stoichiometry	Ligands		
	cyclam	*ms*-CTH	*ms*-CRH
2:1	5 × 10^4	4 × 10^4	
1:1	6 × 10^6	9 × 10^6	5 × 10^4
1:2			3 × 10^6

the results in Table I disclose the relative stability of the uranyl(VI) complexes. The structurally analogues cyclam and *ms*-CTH ligands form complexes of the same stoichiometry and similar stability. The complex species containing two uranyl(VI) centers linked to one ligand molecule is very unusual, but if one considers that this species does not form with *ms*-CRH, it could be possible that in these experimental conditions the macrocycle acts through an exodentate coordination, each couple of nitrogen atoms linking one uranyl(VI) group; *ms*-CRH cannot assume this conformation because the required pseudo-rotation of the skeleton of the macrocycle is prevented by the pyridine ring.

Although the exodentate coordination is relatively usual with cyclic polythiaether [10–12], it has been proved that also tetra-aza macrocycles can assume this conformation [13].

At higher ligand concentrations, however, cyclam and *ms*-CTH probably behave, as usual, as endodentate conformers and encircle uranyl(VI) ion forming more stable complexes. *ms*-CRH, because of its lower flexibility, forms a 1:1 complex with UO_2^{2+} less stable than the preceding ones, which evolves to a more stable 2:1 ligand/UO_2^{2+} species.

The present measurements cannot help in the evaluation of the actual structure of this complex; however the existence of macrocyclic complexes in which one metal center is linked to more than one ligand molecule has been reported [12]. The large size of uranyl(VI) ion and the weakening of the metal–ligand interactions due to the substitution of a sp^3 amine nitrogen by a pyridine nitrogen may be responsible for such a behaviour.

Acknowledgements

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