Inorganica Chimica Acta, 29 (1978) 171–176
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Polarographic Investigations on Uranyl(VI) Complexes in Dimethylsulfoxide. IV. Ammonia and Polyamines

P. ZANELLO, A. CINQUANTINI, R. SEEBER and G. PIERI
Institute of General Chemistry, University of Siena, Italy

Received October 10, 1977

Complex formation of uranyl(VI) ion with ammonia and some polyamines has been studied by the polarographic technique at 25 °C in 0.1 M *TBAP–DMSO solutions. The polarographic data could be explained in terms of the formation of the following complexes:* $[UO_2(L)_n]^{2+}$ *where* $L = NH_3$*, en, dmen and* $n = 2, 3$*;* L = *tn, hexn and* $n = 1, 2$*;* L = *tmen and* $n = 3$*;* L = *trien and* $n = 2$*. The relative coordinating abilities of the ligands have been discussed on the basis of the calculated* β_{Ox}/β_{Red} *values.*

Introduction

In previous papers we studied the formation of complexes between uranium(VI) and diethyldithiocarbamate [1], carboxylic acids [2], aliphatic amines [3] and halides and pseudohalides [4] in dimethylsulfoxide. The present paper is devoted to the polarographic investigation of the complex species formed by uranium(VI) ion with ammonia and polyamine ligands.

Ammonia is a very common ligand for several metal ions of d-block in aqueous media [5–8], while for uranium(VI), as well as for other f-type transition metal ions, ammonia acts mainly as a precipitating agent of their hydroxides [9]; up today no investigations have been reported in nonaqueous solvents.

Polyamines also constitute a class of widely studied metal-ligands and the relative literature data up to 1972 have been reviewed by Paoletti *et al.* [10]. Like previous papers also the more recent ones deal with equilibria in aqueous media [11–15] or with structure/property relationships of some adducts [16–20]; only Forsberg and Moeller [21] have studied some polyamines complexes of lanthanide ions in acetonitrile medium, but no data are available on uranium(VI)–polyamine complexes in aqueous and in nonaqueous solvents.

Experimental

The apparatus and the methods as well as the preparation and the purification of dimethylsulfoxide (DMSO), the DMSO–uranyl(VI) solvate $[UO_2(NO_3)_2 \cdot 5DMSO]$ and tetrabutylammonium perchlorate supporting electrolyte (TBAP) have been already described [1, 2].

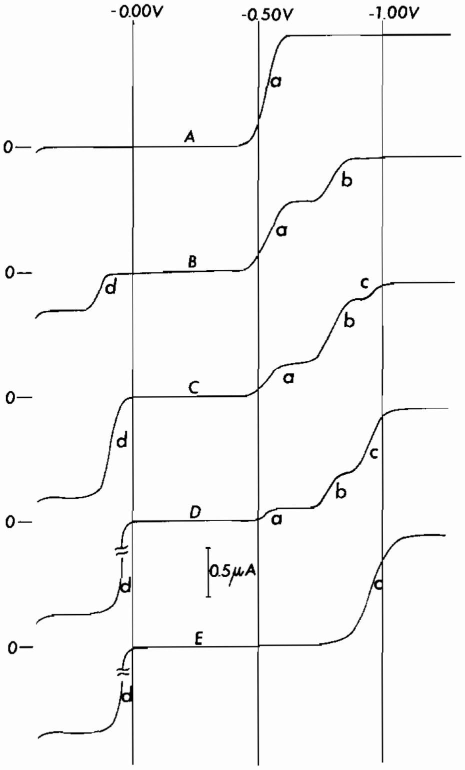


Figure 1. Polarographic profiles recorded on a 0.1 *M* TBAP, 1.02×10^{-3} *M* UO_2^{2+}, DMSO solution (curve A); the same at mol ratios $[NH_3]/[UO_2^{2+}]$ 1 (curve B), 2 (curve C), 3 (curve D) and 4 (curve E).

Reagent grade ethylenediamine (en), 1,3-diaminopropane (tn), 1,6-hexanediamine (hexn), sym-dimethylethylenediamine (dmen), N,N,N′,N′-tetramethylethylenediamine (tmen), triethylenetetramine (trien) and hexamethylenetetramine were used as received (Aldrich) without further purification.

The stock ammonia–DMSO solution was prepared by bubbling gaseous ammonia through the solvent. It was every time standardized immediately before

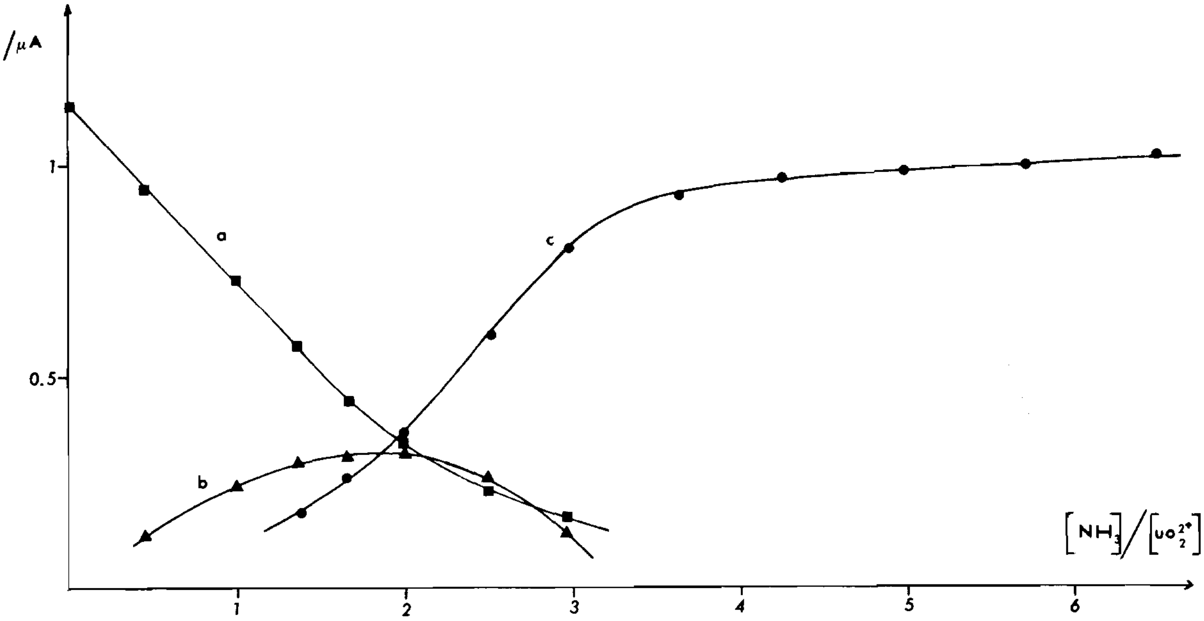


Figure 2. Current trend of the polarographic reduction processes as a function of the mol ratio NH_3/UO_2^{2+}. Uranium(VI) concentration: 1.02×10^{-3} *M.*

use by titration with aqueous hydrochloric acid. 0.1 *M* TBAP was used as supporting electrolyte.

All experiments were carried out at 25 °C.

Results

The voltammetric behaviour of uranyl(VI) ion in DMSO has been previously reported [1]. Some tests at different uranyl concentrations indicated that no formation of polynuclear species occurred [2].

Ammonia

The addition of increasing amounts of ammonia to uranyl(VI) solutions gave the polarographic pictures outlined in Fig. 1. As can be noted the limiting current of the free uranium(VI) cathodic wave (a) ($E_{1/2} = -0.53V$) decreases and a second reduction process (b) appears, followed in turn by a well defined third one (c). The $E_{1/2}$ value of the reduction wave of free uranyl ion was unaffected by the additions of ammonia. Also a well formed anodic wave took place (d), related to the formation of stable ammonia–mercury complexes [22]. In Fig. 2 the trend of the limiting current of the reduction processes a, b, c, against the mol ratio ammonia/UO_2^{2+} is plotted.

The half-wave potentials of the cathodic waves "b" and "c" remained constant at –0.78V and –0.95V respectively.

Logarithmic analysis [E *vs.* log $(i_d - i)/i$] of the waves "b" and "c" gave a straight line with a slope of 0.067 and 0.065V respectively, indicating in both cases an almost reversible one-electron reduction process.

The trend of Fig. 2 indicates that under our experimental conditions the existence of two complex species, $[UO_2(NH_3)_2]^{2+}$ and $[UO_2(NH_3)_3]^{2+}$, can be evidentiated. The 2:1 ammonia–uranyl complex is however less stable than the 3:1 one, as evidentiated by the higher value of the limiting current of the process "c".

On the basis of the $E_{1/2}$ values relative to the reduction waves of the 2:1 and 3:1 species in respect to that of the free uranyl ion, it is possible to calculate the order of magnitude of the corresponding stability constants ratios [23], $\beta_{Ox}/\beta_{Red} = 1 \times 10^4$, where β_{Ox} refers to the 2:1 ammonia–uranium(VI) complex, β_{Red} refers to the 2:1 ammonia–uranium(V) complex and $\beta_{Ox}/\beta_{Red} = 1 \times 10^7$, where β_{Ox} and β_{Red} refer now to the 3:1 complexes.

Ethylenediamine

Uranyl(VI) solutions containing increasing amounts of ethylenediamine (en) gave a polarographic cathodic picture very similar to that reported in Fig. 1 for ammonia, giving rise to a current plot analogous to Fig. 2; in this case the half-wave potentials of the free uranyl ion and of the second and third cathodic waves were constant at –0.53V, –0.79V and –0.99V respectively.

Logarithmic analysis indicated again an almost reversible behaviour for both reduction steps "b" and "c".

The trend of the plot of reduction currents as a function of the mol ratio en/UO_2^{2+} allows to evidentiate the presence of the species $[UO_2(en)_2]^{2+}$ and $[UO_2(en)_3]^{2+}$ and suggests that the 3:1 complex is more stable.

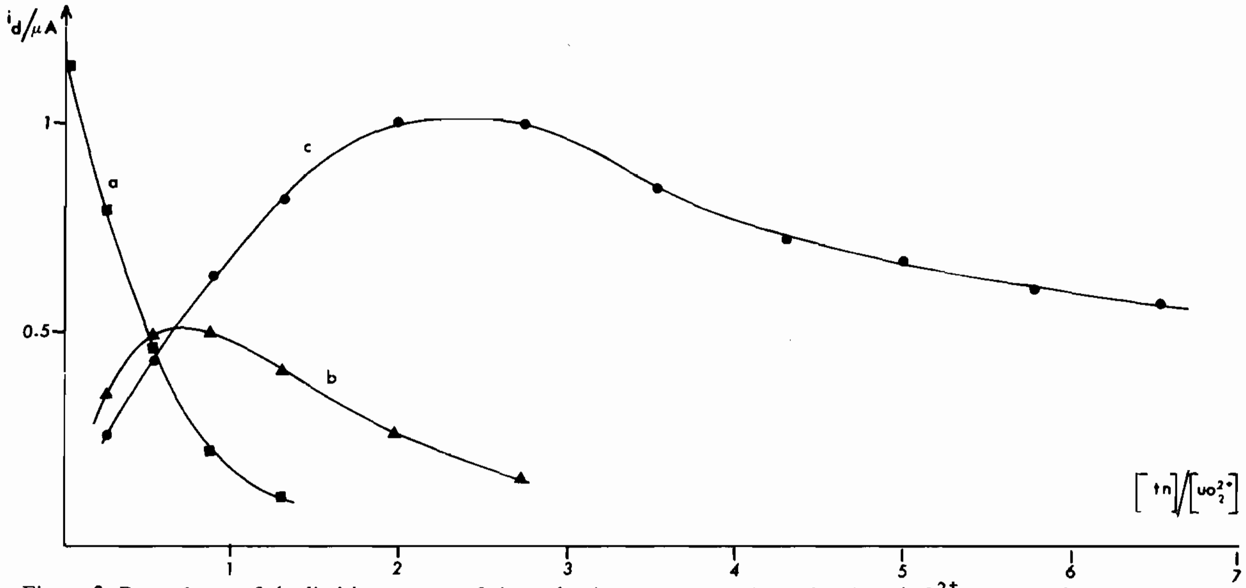


Figure 3. Dependence of the limiting current of the cathodic processes on the mol ratio tn/UO_2^{2+}. Uranium(VI) concentration: 1.01×10^{-3} *M*.

The ratio of stability constants for the 2:1 and 3:1 complexes is $\beta_{Ox}/\beta_{Red} = 2 \times 10^4$ and $\beta_{Ox}/\beta_{Red} = 6 \times 10^7$ respectively.

1,3-Diaminopropane

The polarographic cathodic behaviour exhibited by uranyl(VI) solutions containing increasing amounts of 1,3-diaminopropane (tn) was qualitatively similar to that reported in Fig. 1.

In Fig. 3 the dependence of the limiting currents of the polarographic processes occurring up to −1.35V (beyond these potential values the interference of traces of water arises [1]) on the mol ratio tn/UO_2^{2+} is reported.

Also in this case two complexes are evidentiated, but the first, corresponding to the process "b" ($E_{1/2}$ = −0.78V), is attributable to the reduction of the complex $[UO_2(tn)]^{2+}$ and the second, corresponding to the process "c" ($E_{1/2}$ = −0.99V), to the species $[UO_2(tn)_2]^{2+}$.

The curve "c", Fig, 3, reaches its maximum value at a mol ratio between 2 and 3 and then slowly decreases, suggesting the formation of further higher complexes reducible at potential values more negative than −1.35V.

Logarithmic analysis of the waves corresponding to "b" and "c" of Fig. 1 indicated almost reversible reduction processes.

The stability constant ratios for the 1:1 and 2:1 complexes are $\beta_{Ox}/\beta_{Red} = 1 \times 10^4$ and $\beta_{Ox}/\beta_{Red} = 6 \times 10^7$ respectively.

1,6-Hexanediamine

Additions of 1,6-hexanediamine (hexn) to the uranyl gave a polarographic picture very similar to that described above as the cathodic wave of uranium(VI) progressively decreased and two successive cathodic waves appeared at constant half-wave potential values of −0.81V and −0.99V respectively. The current plot is analogous to that reported in Fig. 3 indicating the existence of the two complexes $[UO_2(hexn)]^{2+}$ and $[UO_2(hexn)_2]^{2+}$ and furthermore suggesting the probable formation of successive higher complexes.

Taking into account the $E_{1/2}$ values relative to the reduction of the 1:1 and 2:1 diamine–uranyl complexes the stability constants ratios are respectively $\beta_{Ox}/\beta_{Red} = 5 \times 10^4$ and $\beta_{Ox}/\beta_{Red} = 6 \times 10^7$.

sym-Dimethylethylenediamine

Uranium(VI) solutions containing increasing amounts of *sym*-dimethylethylenediamine (dmen) gave rise to polarographic cathodic waves similar to those reported for ammonia; in fact the decrease of the free uranium(VI) limiting current was compensated by the appearance of two successive distinct cathodic processes ($E_{1/2}$ = −0.77V and −0.98V, respectively). The $E_{1/2}$ values of these reduction waves and that of free UO_2^{2+} were unaffected by ligand successive additions. The usual current *vs.* mol ratio $dmen/UO_2^{2+}$ plot is very similar to that reported in Fig. 2. This trend evidentiates the existence of the two stable complexes $[UO_2(dmen)_2]^{2+}$ and $[UO_2(dmen)_3]^{2+}$.

The almost reversible polarographic behaviour allows to calculate the stability constant ratios for the 2:1 and 3:1 diamine-uranyl complexes; these ratios are $\beta_{Ox}/\beta_{Red} = 1 \times 10^4$ and $\beta_{Ox}/\beta_{Red} = 4 \times 10^7$.

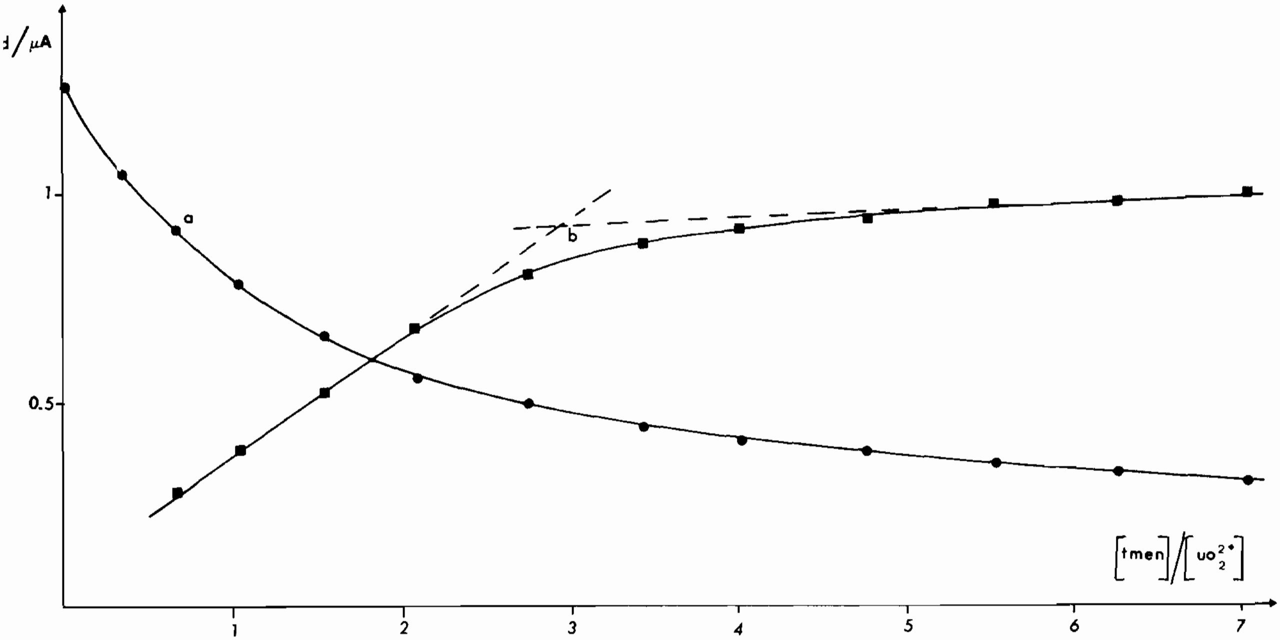


Figure 4. Current trend of the cathodic processes as a function of the mol ratio tmen/UO_2^{2+}. Uranium(VI) concentration: 1.02 × 10^{-3} *M*.

N,N,N′,N′-Tetramethylethylenediamine

By adding increasing amounts of N,N,N′,N′-tetramethyletylenediamine (tmen) to uranyl(VI) solutions a polarographic picture somewhat different from that reported in Fig. 1 was obtained; in fact as the free uranium(VI) wave decreased only one successive cathodic wave appeared ($E_{1/2}$ = –0.84V).

In Fig. 4 the dependence of the limiting currents of the observed cathodic processes on the mol ratio tmen/UO_2^{2+} is reported. As can be observed the limiting current of the free uranium(VI) wave (curve "a") decreases much more slowly than in the previous cases; correspondingly, also curve "b" increases very slowly. However, the formation of the 3:1 complex can be deduced from the intersection of the straight line portions drawn through the experimental points away from the 3:1 ratio. The curvature exhibited by curve "b" around this value indicates a rather small β_{Ox} value.

Moreover the constant $E_{1/2}$ value of the free UO_2^{2+} reduction wave allows to disregard the occurrence of the formation of stable 1:1 and 2:1 complexes.

From the $E_{1/2}$ value a β_{Ox}/β_{Red} ratio of 2 × 10^5 was calculated for this complex.

Triethylenetetramine

The addition of increasing amounts of triethylenetetramine (trien) to uranyl(VI) solutions gave a polarographic picture qualitatively similar to that reported for N,N,N′,N′-tetramethylethylenediamine, as only one successive cathodic wave compensated the decrease of the limiting current of free uranyl(VI) ion. The half-wave potential of this second cathodic wave was constant at –0.81V up to ligand concentrations of about 2 × 10^{-3} *M*; at higher concentrations the wave is distorted by a maximum of the first kind, preventing any reliable measurement of the half-wave potential.

In Fig. 5 the current *vs.* mol ratio trien/UO_2^{2+} plot is reported. The trend clearly evidentiates the formation of the $[UO_2(trien)_2]^{2+}$ species; the existence of higher complexes cannot be however excluded owing to the poor reliability of $E_{1/2}$ measurements at higher ligand concentrations.

In the hypothesis of an almost reversible reduction process, the stability constant ratio for the 2:1 complex is β_{Ox}/β_{Red} = 5 × 10^4.

Hexamethylenetetramine

The reduction wave of uranium(VI) was not affected by the addition of increasing amounts of hexamethylenetetramine, neither lowering of the limiting current nor $E_{1/2}$ shift were observed; hence no other cathodic wave could arise. This suggests that hexamethylenetetramine is not able to initiate the desolvation process, owing to its hindered structure.

Discussion

The polarographic behaviour of ammonia and diamine–uranyl(VI) solutions in DMSO indicates that these ligands form stable complexes in agreement with the hard character of uranyl(VI) ion; the

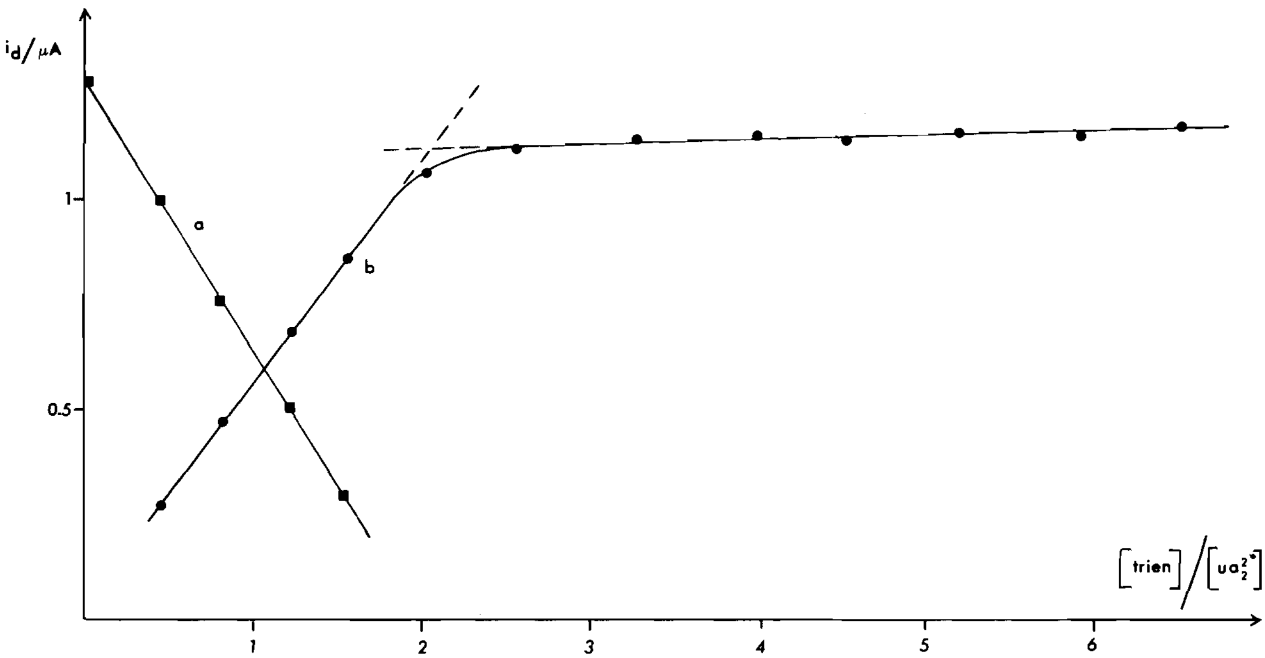


Figure 5. Current trend of the reduction processes as a function of the mol ratio trien/UO_2^{2+}. Uranium(VI) concentration: 1.14 × 10^{-3} *M*.

appearance of cathodic waves, distinct from that of free uranyl(VI) ion, points out that the rate of formation and dissociation of the involved complexes is lower than that of their diffusion towards the electrode.

By assuming a constant coordinating ability of uranium(V) ion in respect to every ligand tested, the obtained results, summarized in Table I, allow some correlations to be stated about the relative stability of the studied complexes. This assumption can be justified on the basis of the well-known poor coordinating tendency of uranium(V) ion.

The maximum number of ammonia molecules linked to the uranyl(VI) ion is three under the present experimental conditions. By comparing the β_{Ox}/β_{Red} value relative to the 3:1 ammonia complex with those of monoamine ligands–uranium(VI) complexes [3], it can be deduced that the coordinating ability of ammonia is of the same order of magnitude as that of primary amines; in addition the polarographic behaviour also evidentiates the distinct intermediate formation of the 2:1 complex. This fact is probably due to the low steric hindrance of ammonia in respect to the straight chain primary amines. The absence of the β_{Ox}/β_{Red} value for the 1:1 complex in the case of ammonia, as well as for other amines, does not mean that the 1:1 complex cannot exist. In fact the polarographic process involves a reduction of uranium(VI) to uranium(V), hence the absence of $E_{1/2}$ shifts of the uranyl(VI) wave and the absence of distinct cathodic waves, can be attributed either to small stability constants of the 1:1 complexes or to an unusual similarity between the stability constant values for the 1:1 complex of uranium(VI) and uranium(V).

As regards polyamine complexes it can be noted that ethylenediamine and its derivatives (en, dmen, tmen) form complexes of decreasing stability from primary to tertiary amino group, in agreement with the behaviour already described for monoamines [3]. The stoichiometry of the highest complex formed by uranium(VI) with these ligands is 1:3, as required by

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

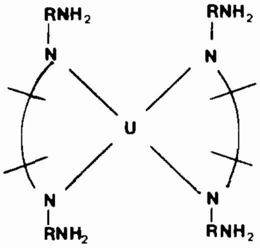
Ligand/UO_2^{2+} complex stoichiometry	Ligands											
	en	dmen	tmen	tn	hexn	trien	n-butNH$_2$	n-hexNH$_2$	tert-butNH$_2$	di-n-butNH	triethN	NH$_3$
1:1				1×10^4	5×10^4				*1×10^4			
2:1	2×10^4	1×10^4		6×10^7	6×10^7	5×10^4						1×10^4
3:1	6×10^7	4×10^7	2×10^5				*4×10^7	*2×10^7	*2×10^8	*4×10^6	*4×10^5	1×10^7

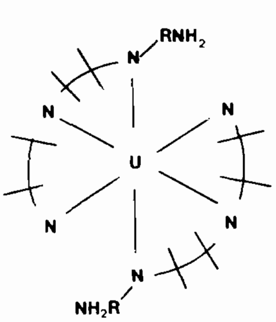
*Ref. 3.

the hexacoordination in the equatorial plane of UO_2^{2+} group, accomplished by three bidentate ligands able to give rise to five membered chelate rings.

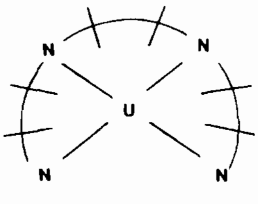
1:1 and 2:1 tn and hexn uranyl(VI) complexes show high stability constant ratios in respect to the known stability of five membered chelate rings. This behaviour can be explained by considering either the formation of stable puckered chelate rings [17], six or nine membered, respectively, or by assuming that these ligands, potentially bidentate, behave as monodentate [13]; the last hypothesis seems however in apparent disagreement with the constant ratios found for the corresponding monoamines.

The polarographic behaviour of trien–uranyl(VI) system allowed to evidentiate only the 2:1 complex. From the present measurements it is not possible to state the actual structure of this complex, however the two following possible structures can be proposed:





The first structure involves the formation of two stable five membered chelate rings, but does not complete the hexacoordination on the equatorial plane of urany(VI) ion. The second one, which satisfies the hexacoordination, involves however the formation of accumulated chelate rings of lower stability [10]. Our experimental data do not evidentiate the 1:1 complex formation of the type:



which is the accepted structure for aliphatic polyamine complexes with 3d metal ions [24].

Acknowledgements

The authors wish to thank Prof. G. A. Mazzocchin for his interest in this work and Mrs. G. Montomoli and Mr. M. Porcú for laboratory assistance. This work was supported by the Laboratorio di Chimica e Tecnologia dei Radioelementi, CNR (Padova)

References

1 P. Zanello, A. Cinquantini and G. A. Mazzocchin, *Inorg. Chim. Acta, 21,* 195 (1977).

2 P. Zanello, A. Cinquantini, P. Di Bernardo and L. Magon, *Inorg. Chim. Acta, 24,* 131 (1977).

3 A. Cinquantini, P. Zanello, G. A. Mazzocchin and O. Traverso, *Inorg. Chim. Acta, 25,* 141 (1977).

4 P. Zanello, A. Cinquantini, G. A. Mazzocchin and O. Traverso, *Inorg. Chim. Acta, 27,* 157 (1978).

5 L. G. Sillen and A. E. Martell, eds., "Stability Constants of Metal-Ion Complexes", *Spec. Publ. Nos. 17 and 25, The Chemical Society,* London (1964 and 1971).

6 M. C. Bonnet, R. A. Paris and R. P. Martin, *Bull. Soc. Chim. France, 3,* 903 (1972).

7 A. Szymaszek and J. Biernat, *Monatsch. Chem., 104,* 74 (1973).

8 J. Binstok and D. I. Levit, *An. Asoc. Quim. Argent., 61,* 101 (1973).

9 I. M. Kolthoff and P. J. Elving, "Treatise on Analytical Chemistry", Part II, Vol. 9, p. 76, Interscience, New York (1962).

10 P. Paoletti, L. Fabbrizzi and R. Barbucci, *Inorg. Chim. Acta Rev., 7,* 43 (1973).

11 E. Dazzi and M. T. Falqui, *Gazz. Chim. Ital., 104,* 589 (1974).

12 L. C. Van Poucke, *Talanta, 23,* 161 (1976).

13 E. CS. Porzsolt, M. T. Beck and A. Bitto, *Inorg. Chim. Acta, 19,* 173 (1976).

14 H. C. Nelson and D. E. Goldberg, *Inorg. Chim. Acta, 19,* L23 (1973).

15 M. Orama, R. Ahtola and P. Kuukka, *Finn. Chem. Lett.,* 161 (1976).

16 A. B. P. Lever and E. Mantovani, *Can. J. Chem., 51,* 1567 (1973).

17 S. Bagger and O. Bang, *Acta Chem. Scand., A30,* 765 (1976).

18 T. Duplancic, D. Grdemic, B. Kamenar, P. Matkovic and M. Sikirica, *J. Chem. Soc. Dalton Trans., 10,* 887 (1976).

19 J. Dwyer, W. Levason and C. A. McAuliffe, *J. Inorg. Nucl. Chem., 38,* 1919 (1976).

20 L. Fabbrizzi, P. Paoletti and A. B. P. Lever, *Inorg. Chem., 15,* 1502 (1976).

21 J. H. Forsberg and T. Moeller, *Inorg. Chem., 8,* 889 (1969).

22 Y. Matsui, Y. Kurosaki and Y. Date, *Bull. Chem. Soc. Japan, 46,* 147 (1973).

23 J. Heyrovsky and J. Kuta, "Principles of Polarography", Academic Press, New York (1966) p. 156.

24 L. Sacconi, P. Paoletti and M. Ciampolini, *J. Chem. Soc.,* 5115 (1961).