

Interaction of MO_2^{2+} Ions ($M = \text{U, Np, and Pu}$) with Dicarboxylate Ligands Containing Other Donor Atoms

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A quantitative study of the interaction of uranyl(VI), neptunyl(VI), and plutonyl(VI) with oxydiacetate, iminodiacetate, thiodiacetate, and glutarate ligands has been carried out potentiometrically in aqueous solution with 1M (Na,H)ClO₄ at 20°C. Possible structures for the various species present in solution are indicated on the basis of an analysis of the potentiometric data. The behaviour of the four ligands towards the actinyl(VI) ions is discussed in terms of their different central groups and their basicities. The stability constants show that there are only minor differences among the tendencies of the three actinyl(VI) ions to form complexes with the ligands examined.

Introduction

In a previous paper¹ we showed that there is a linear relationship between complex stability and ligand basicity for a series of monocarboxylate complexes of a given MO_2^{2+} ion ($M = \text{U, Np, and Pu}$). The stability order of complexes of the various ligands examined is $\text{UO}_2^{2+} > \text{NpO}_2^{2+} > \text{PuO}_2^{2+}$. We also pointed out that these three oxocations in 1M perchlorate solution undergo hydrolysis following substantially the same scheme of reactions and exhibiting a decrease in acidity with increasing atomic number.²

As a part of our comparative studies of the equilibria involved in the interaction of the actinyl(VI) ions with various ligands in aqueous solution, we report here a potentiometric study of the complex formation equilibria of uranyl(VI), neptunyl(VI), and plutonyl(VI) with the ligands oxydiacetate, iminodiacetate, thiodiacetate, and glutarate. These molecules contain two carboxylic groups at the ends of a chain having the same number of atoms and differ from one another in the central group, this being -O-, -NH-, -S-, and -CH₂-, respectively. The ligands were chosen in order to determine the influence of the different central groups (three of which are potentially coordinating) and the ligand basicity, on structures and stabilities of the actinyl(VI) complexes in aqueous solution.

The only data available in the literature on the actinide(VI) complexes with the ligands herein consi-

dered concern the systems uranyl(VI)-iminodiacetate^{3,4} and uranyl(VI)-glutarate.⁵

Experimental Section

(i) *Chemicals.* Aqueous uranyl(VI) perchlorate solutions were prepared from uranyl(VI) nitrate.⁶ The concentration of uranium was determined by a lead reductor method⁷ and by ignition of suitable aliquots to U_3O_8 . The concentration of the free perchloric acid in the uranyl(VI) solution was determined by ionic exchange on a cationic resin in the hydrogen ion form (Dowex 50W-X4) and by potentiometric Gran's method.⁸

Aqueous neptunyl(VI) perchlorate solutions were prepared and standardized as described previously.¹

Aqueous plutonyl(VI) perchlorate solutions were prepared in the following way. A solution containing Pu^{IV} (isotopic composition: 99% ²³⁹Pu and 1% ²⁴⁰Pu) in HNO_3 (ca 1M) was treated with hydroxylamine hydrochloride until total reduction of the Pu^{IV} had been achieved. Plutonium(III) hydroxide was then precipitated with sodium hydroxide, washed with water and dissolved in 0.1 M perchloric acid. Plutonium(VI) solutions were prepared by electrolytic oxidation (electrodes of platinum wire; cathode and anode compartments separated by fine sintered glass discs; magnetic agitator in the anode compartment). The oxidation state of plutonium was checked spectrophotometrically. The concentration of plutonium in solution was determined by amperometric titration of a separate aliquot of the PuO_2^{2+} solution with Fe^{II} solution.⁹ The concentration of free perchloric acid in the plutonyl(VI) solution was determined as described above for uranyl(VI) solution.

Using standard solutions of NaOH and NaClO_4 , the solutions containing UO_2^{2+} or NpO_2^{2+} or PuO_2^{2+} , HClO_4 and NaClO_4 were adjusted to the concentrations required for the measurements.

(3) K.S. Rajan and A.E. Martell, *J. inorg. nucl. Chem.*, 26, 789 (1964).

(4) T.T. Lai and T.Y. Chen, *J. inorg. nucl. Chem.*, 29, 2975 (1967).

(5) A. Vanni, G. Ostacoli, and E. Roletti, *Ann. Chimica (Roma)*, 2, 847 (1969).

(6) R. Salvadori, *Chem. Ztg.*, 36, 513 (1912).

(7) W.D. Cooke, F. Hazel, and W.M. Mc Nabb, *Analyt. Chem.*, 22, 654 (1950).

(8) G. Gran, *Analyst*, 77, 661 (1952).

(9) I.M. Kolthoff and Ph. J. Elving, « Treatise on Analytical Chemistry », Part. II, Vol. 9, Interscience Publ. (1962).

(1) A. Cassol, L. Magon, G. Tomat, and R. Portanova, *Inorg. Chim. Acta*, 3, 639 (1969).

(2) A. Cassol, L. Magon, G. Tomat, and R. Portanova, *Inorg. Chem.*, 11, 515 (1972).

Aqueous solutions of the various ligands were prepared with analytical grade reagents. Oxydiacetic and thiodiacetic acids were purified by recrystallization: oxydiacetic acid from methyl acetate, and thiodiacetic acid from hot (1:2) mixture of benzene-glacial acetic acid. Disodium iminodiacetate (Fluka *purum*) was acidified with hydrochloric acid in order to crystallize out the pure acid. Glutaric acid was used without further purification. The equivalent weights were determined by alkalimetric titration and were all found to agree with the theoretical values within 0.2%.

Standard buffer solutions were obtained by exact neutralization of calculated amounts of acid with standard NaOH solution.

(ii) *Apparatus and Procedure.* The experimental method consisted of potentiometric measurements of the hydrogen ion concentrations of buffer solutions of the ligands in the presence of the actinyl(VI) ions by means of a galvanic cell of the type:

Ag—AgCl | 50 mM NaCl, 950 mM NaClO₄ (saturated with AgCl) || 1000 mM NaClO₄ || titration half-cell | glass electrode.

The details of the apparatus and the calibration of electrodes were described in previous papers.^{1,2} The behaviour of the cell was checked usually both before and after a series of measurements. The e.m.f. was described by the equation $E = E^{\circ} + 58.16 \log [H^+] - E_j$; where $E_j = 0.06 [H^+]$, with $[H^+]$ in mM.

All measurements were performed in an atmosphere of purified nitrogen at a temperature of $20.0 \pm 0.1^{\circ}\text{C}$ and in a medium containing 1M perchlorate ions using NaClO₄.

The solution in the titration half-cell was prepared by adding small amounts of a solution T from a burette, to a known volume of a starting solution S. These solutions had the following compositions:

S: C_M° mM MO₂(ClO₄)₂; C_H° mM HClO₄; $(1000 - 2C_M^{\circ} - C_H^{\circ})$ mM NaClO₄.

T: $C_{Na_2L}^{\circ}$ mM Na₂L; $C_{H_2L}^{\circ}$ mM H₂L; 1000 mM NaClO₄.

where Na₂L and H₂L represent the ligand as the sodium salt and the acid respectively.

For the uranyl(VI)-glutarate system other titrations were also carried out in which the total metal and ligand concentrations were held constant, by adding equal volumes of two solutions T' and T'' to a known volume of a starting solution S'. These solutions had the compositions:

S': C_M° mM UO₂(ClO₄)₂; C_H° mM HClO₄; $C_{H_2L}^{\circ}$ mM H₂L; $(1000 - 2C_M^{\circ} - C_H^{\circ})$ mM NaClO₄.

T': $2C_M^{\circ}$ mM UO₂(ClO₄)₂; $2C_H^{\circ}$ mM HClO₄; $2C_{H_2L}^{\circ}$ mM H₂L; $(1000 - 4C_M^{\circ} - 2C_H^{\circ})$ mM NaClO₄.

T'': C_{OH}° mM NaOH; 1000 mM NaClO₄.

To determine the stepwise protonation constants, K_1^H and K_2^H , of the four ligands in these ionic solutions, titrations were performed with the same cell at $C_M = 0$.

The actual oxidation state of neptunium and plutonium was checked both before and after each titration by recording the absorption spectrum of a sample in the wavelength range 360-1000 mμ.

All experiments with neptunium and plutonium were performed in special glove boxes.

Results

Stability constants for the proton-ligand complexes. For each of the four ligands considered, titrations were carried out at $C_M = 0$ with three different total concentrations of the ligand, $C_L = 10, 50, \text{ and } 100$ mM. From the e.m.f. values measured and the known analytical data, corresponding values of \bar{q}_H , (the average number of protons bound to one ligand), and $[H^+]$ were obtained.^{10a} The protonation constants, K_1^H and K_2^H , were calculated using Sillen's curve fitting procedure.^{10b} The constants were finally refined by a computerized least squares program. The refined values of the constants and their standard deviations are reported in Table I.

The MO₂²⁺-oxydiacetate systems. For each of the three ions, uranyl(VI), neptunyl(VI), and plutonyl(VI), measurements were carried out at different initial concentrations, C_M , and using ligand solutions, T, having different buffer ratio, $\delta = C_{H_2L}/C_{Na_2L}$. In all the titrations, except for the highest concentrations of ligand examined, equilibrium was obtained within few minutes after which the potentials measured were constant to ± 0.1 mV.

From the absorption spectra recorded after each titration no appreciable reduction of Np^{VI} or Pu^{VI} was detected.

The experimental data obtained were treated assuming the formation of only mononuclear chelate complexes of the type, MO₂L_n⁽²⁻²ⁿ⁾⁺. Corresponding values of \bar{n} , (the average number of ligand bound to each metal ion), and $[L^{2-}]$, (the free ligand concentration), were obtained from the $[H^+]$ measured, the analytical data of the solutions S and T, and the known values of K_1^H and K_2^H , by the following equations:

$$[L^{2-}] = \frac{C_L + 2C_{H_2L} - [H^+]}{K_1^H[H^+] + 2K_1^HK_2^H[H^+]^2} \quad (1)$$

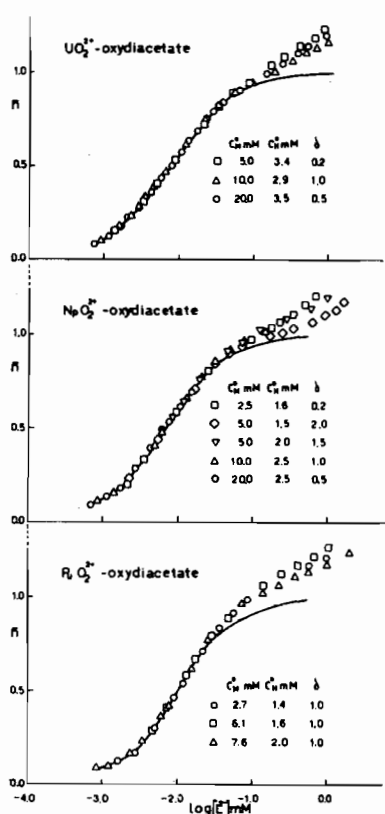
$$\bar{n} = \frac{C_L - [L^{2-}](7 + K_1^H[H^+] + K_1^HK_2^H[H^+]^2)}{C_M} \quad (2)$$

The data plotted in the form of \bar{n} as a function of $\log [L^{2-}]$ are reported in Figure 1. These curves show that the behaviour of the three systems investigated are qualitatively analogous. For each system in the range of \bar{n} values, 0 up to 1, the formation curves derived from measurements taken at different, C_M and buffer ratio, δ , overlap within the limits of experimental errors. This demonstrates that in the corresponding $[L^{2-}]$ range no polynuclear or acid or hydrolysed complexes were formed^{10c} and that only

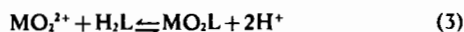
(10) F.J. Rossotti and H. Rossotti, « The determination of Stability Constants », (a) p. 155, (b) p. 87, (c) p. 391, (d) p. 108, Mc Graw-Hill Book Co. New York (1961).

Table I. Protonation constants of ligands and formation constants of the Uranyl(VI), Neptunyl(VI) and Plutonyl(VI) complexes in aqueous solution at (H₂Na)ClO₄, 1M and 20°C.

Ligand	Positive ion	Reaction	log of formation constant
Oxydiacetate	H ⁺	H ⁺ +L ²⁻ ⇌HL ⁻	3.75±0.02
		H ⁺ +HL ⁻ ⇌H ₂ L	2.82±0.02
	UO ₂ ²⁺	UO ₂ ²⁺ +L ²⁻ ⇌UO ₂ L	5.11±0.01
	NpO ₂ ²⁺	NpO ₂ ²⁺ +L ²⁻ ⇌NpO ₂ L	5.16±0.01
	PuO ₂ ²⁺	PuO ₂ ²⁺ +L ²⁻ ⇌PuO ₂ L	4.97±0.02
Iminodiacetate	H ⁺	H ⁺ +L ²⁻ ⇌HL ⁻	9.33±0.01
		H ⁺ +HL ⁻ ⇌H ₂ L	2.52±0.01
	UO ₂ ²⁺	UO ₂ ²⁺ +L ²⁻ ⇌UO ₂ L	8.66±0.02
	NpO ₂ ²⁺	NpO ₂ ²⁺ +L ²⁻ ⇌NpO ₂ L	8.72±0.02
	PuO ₂ ²⁺	PuO ₂ ²⁺ +L ²⁻ ⇌PuO ₂ L	8.50±0.02
Thiodiacetate	H ⁺	H ⁺ +L ²⁻ ⇌HL ⁻	4.04±0.02
		H ⁺ +HL ⁻ ⇌H ₂ L	3.14±0.02
	UO ₂ ²⁺	UO ₂ ²⁺ +L ²⁻ ⇌UO ₂ L	3.16±0.03
		UO ₂ ²⁺ +HL ⁻ +L ²⁻ ⇌UO ₂ (HL)L ⁻	4.38±0.06
Glutarate	H ⁺	H ⁺ +L ²⁻ ⇌HL ⁻	4.94±0.01
		H ⁺ +HL ⁻ ⇌H ₂ L	4.19±0.01
	UO ₂ ²⁺	UO ₂ ²⁺ +HL ⁻ ⇌UO ₂ (HL) ⁺	1.89±0.04
		UO ₂ ²⁺ +2HL ⁻ ⇌UO ₂ (HL) ₂	3.58±0.10
		UO ₂ ²⁺ +HL ⁻ +L ²⁻ ⇌UO ₂ (HL)L ⁻	4.01±0.20

**Figure 1.** The complex formation curves of the uranyl(VI)—, neptunyl(VI)—, and plutonyl(VI)—oxydiacetate systems. Full-drawn curves obtained from refined complexity constants (Table I).

reaction is metal chelate formation according to the following equation:



For the highest ligand concentrations examined

values of $\bar{n} > 1$ are obtained and, further, for a given value of $[\text{L}^{2-}]$ in this region, \bar{n} appears to be dependent on C_M and δ . This indicates that the first 1:1 complex formed exhibits some tendency to coordinate a second ligand, possibly to form polynuclear or acid complexes. Since the maximum pH values attained for all the titrations were below pH 3, the possibility of the coordinated water molecules of the actinyl(VI) ions undergoing hydrolytic dissociation may be considered less likely in view of the hydrolytic behaviour of the uranyl(VI),¹¹ neptunyl(VI)² and plutonyl(VI)¹² uncomplexed ions, none of which undergoes hydrolysis below pH 3.

The ligand concentration range examined was limited by an increasing drift of potentials and thus the experimental data collected for $\bar{n} > 1$ are not enough to determine the stoichiometry of the species formed.

By applying the graphical Sillen's method^{10b} to the corresponding \bar{n} , $[\text{L}^{2-}]$ values in the range $0 < \bar{n} > 1$, trial values of the formation constant β_1 for the three systems were obtained. These constants were then refined by a computerized least squares program and their values are reported in Table I.

The MO_2^{2+} -iminodiacetate systems. The equilibria of the three actinyl(VI) ions with the iminodiacetate ligand were investigated, and the data obtained were treated, as described above for the oxydiacetate. In this case, spectrophotometric check of the actual oxidation state of Np^{VI} and Pu^{VI} gave evidence that during the titrations Np^{VI} was progressively reduced to Np^{V} . The experimental data for this system are thus limited to $[\text{L}^{2-}]$ ranges in which the Np^{VI} reduction was negligible (below 1%).

The values of \bar{n} vs. $\log [\text{L}^{2-}]$ for the three systems are plotted in Figure 2. A consideration of the com-

(11) R.M. Rush, J.S. Johnson, and K.A. Kraus, *Inorg. Chem.*, **1**, 378 (1962).

(12) A. Cassol, L. Magon, R. Portanova, and E. Tondello, *Radiochim. Acta*, **17**, 28 (1972).

plex formation curves of uranyl(VI)- and plutonyl(VI)-iminodiacetate indicates that in both of these systems only 1:1 chelates are formed. The neptunyl(VI)-iminodiacetate system, apart from the mentioned reduction, seems to exhibit an analogous behaviour. The values obtained for the formation constants, β_1 , are reported in Table I.

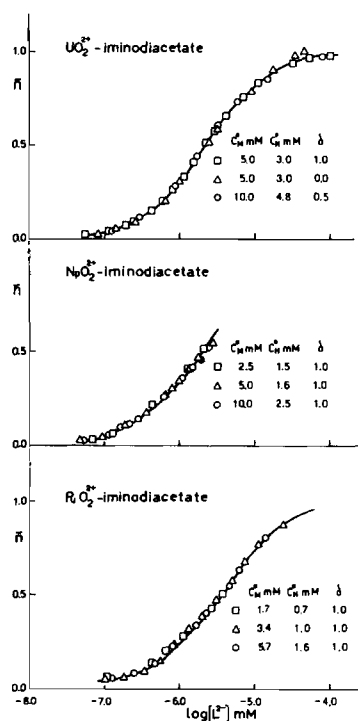


Figure 2. The complex formation curves of the uranyl(VI)-, neptunyl(VI)-, and plutonyl(VI)iminodiacetate systems. Full-drawn curves obtained from refined complexity constants (Table I).

The MO_2^{2+} -thiodiacetate systems. For the thiodiacetate ligand only the equilibria with uranyl(VI) and neptunyl(VI) were examined experimentally. Unfortunately, in the neptunyl(VI)-thiodiacetate system, Np^{VI} was rapidly reduced even at moderate ligand concentration and, thus, it was not possible to collect significant data for this system.

As for the uranyl(VI)-thiodiacetate system, the experimental data were at first treated as described above applying equations 1) and 2). The corresponding values of \bar{n} and $\log[L^{2-}]$ obtained for titrations carried out at different C_M and δ are shown in Figure 3. It is evident from the complex formation curves that this system has a different behaviour from that of oxydiacetate and iminodiacetate. The formation of some mixed complexes of the type $(MO_2)_p(HL)_qL_r$ must be postulated, since, for a given value of $[L^{2-}]$, \bar{n} varies with C_M and δ^{10c} .

In order to gain some information on the most important species present in this system and their stabilities, some calculations were carried out using a least squares program in the series «Letagrop Vrid». ¹³ The following schemes of different species were tried:

(13) N. Ingri and L.G. Sillén, *Arkiv Kemi*, 23, 97 (1965).

$ML - ML_2^{2-} - M(HL)^+$; $ML - ML_2^{2-} - M(ML)^+ - M(HL)L^-$; $ML - M(HL)^+ - M(HL)L^-$; $ML - M(HL)^+ - M(HL)L^- - M_2L^{2+}$. Starting values of the formation constants were obtained by assuming that the complexes formed between the uranyl(VI) ion and the non-protonated or monoprotated thiodiacetate ligand were of the same strength as that of uranyl(VI) oxydiacetate chelate or uranyl(VI) monocarboxylate complexes, respectively. ¹⁴ Of all the postulated species, the two ML and $M(HL)L^-$ resulted to be the most important ones; the refined values of their formation constants are reported in Table I.

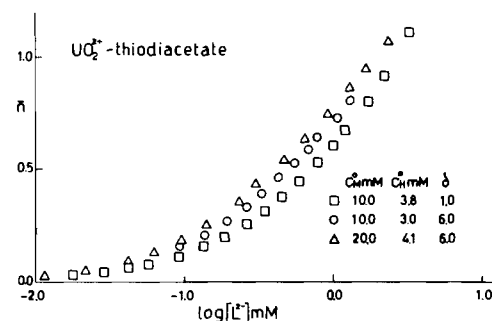


Figure 3. Experimental \bar{n} vs $-\log[L^{2-}]$ curves for the uranyl(VI)-thiodiacetate system.

The MO_2^{2+} -glutarate systems. For the glutarate ligand, potentiometric measurements were carried out with uranyl(VI) and neptunyl(VI) solutions at different C_M and buffer ratio. No appreciable reduction of Np^{VI} was detected during the titrations. The experimental data were treated using equations 1) and 2), and the results obtained indicated an analogous behaviour of the two systems examined. The values of \bar{n} vs. $\log[L^{2-}]$ for the neptunyl(VI)-glutarate system are plotted in Figure 4. As can be seen the complex formation curves are clearly dependent upon C_M and δ . This suggests that mixed complexes of the type $(MO_2)_p(HL)_qL_r$ should be taken into account.

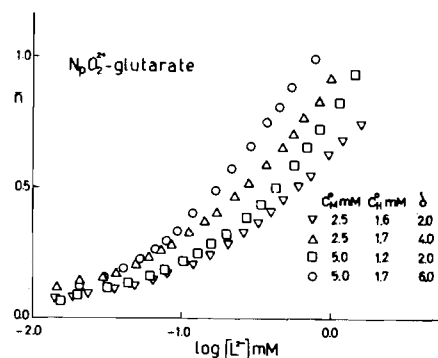


Figure 4. Experimental \bar{n} vs $-\log[L^{2-}]$ curves for the neptunyl(VI)-glutarate system.

In order to gain some information on the various

(14) L. Magon, R. Portanova, B. Zarli, and A. Bismondo, *J. inorg. nucl. Chem.*, 34, 1971 (1972).

species formed over a wide range of acidity, further investigations on the uranyl(VI)-glutarate system were carried out under suitable experimental conditions (see Experimental Section), as suggested by Österberg¹⁵ for the study of systems resulting in the formation of mixed complexes.

Titrations were performed for different constant total ligand concentrations $C_L = 1.0, 1.5, 2.0, 3.0,$ and 5.0 mM. The metal concentration was held constant, $C_M = 1.0$ mM. The experimental data so obtained are reported in Figure 5 as values of q vs. $-\log [H^+]$, where \bar{q} represents the average number of protons bound to one ligand, with $C_M \neq 0$ (q_H with $C_M = 0$).

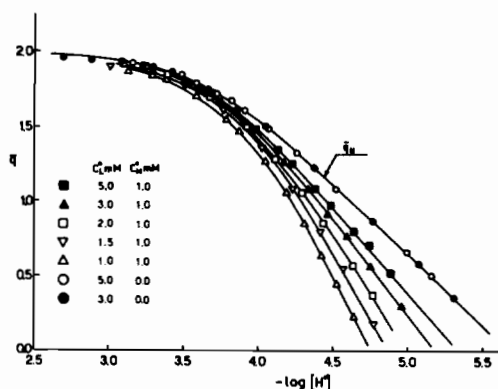


Figure 5. Uranyl(VI)-glutarate system. Experimental data \bar{q} vs $-\log[H^+]$ at constant C_M and C_L , and q_H vs $-\log[H^+]$ at constant C_L with $C_M = 0$.

The values of q for different C_L compared with those of \bar{q}_H clearly show complex formation in the pH range above $[H^+] = 10^{-3.1} = [H^+]_0$. At $[H^+]_0 = 10^{-3.1}$ \bar{q} differs only slightly from \bar{q}_H and complex formation is negligible. Therefore the free ligand concentration, $[L^{2-}]_0$, at $[H^+]_0$, is not affected by the metal ions, and it can be calculated from the equation:

$$[L^{2-}]_0 = C_L / (1 + K_1[H^+] + K_1K_2[H^+]^2) \quad (6)$$

The free ligand concentration in the region at $[H^+] < [H^+]_0$ i.e. in the presence of complex formation equilibria, can be computed without any special assumptions about the complexes formed by applying the Österberg's treatment,¹⁵ from which it follows that:

$$-\log[L^{2-}] = - \left[\int_{-\log[H^+]_0}^{-\log[H^+]} \left(-\frac{\partial C_H}{\partial C_L} \right)_{(H^+)} d(-\log[H^+]) \right]_{C_i} - \log[L^{2-}]_0 \quad (7)$$

The values of $\log [L^{2-}]_0/[L^{2-}]$ were obtained by graphical integration; \bar{n} values were then computed using equation 2). Since the values of \bar{n} obtained in this case, even at the highest C_L and pH, do not exceed unity, it is reasonable to assume that complexes are

formed in which the value of $(q+r)$ is not greater than 2. Further, taking into account the use of low values for C_M and C_L , with C_L in excess of C_M , in the measurements, occurrence of polynuclear complexes is assumed to be negligible ($p = 1$). Therefore, the complexes of $(MO_2)_p(HL)_qL_r$ type to be considered are UO_2L , $UO_2L_2^{2-}$, $UO_2(HL)^+$, $UO_2(HL)_2$, and $UO_2(HL)L^-$. On the basis of these assumptions, the average number n can be described by the following equation:

$$\frac{\bar{n}}{(1-\bar{n})[L^{2-}]} = {}^*\beta_{1,1,0}[H^+] + {}^*\beta_{1,0,1} + \frac{(2-\bar{n})[L^{2-}]}{1-\bar{n}} \quad (8)$$

$$({}^*\beta_{1,2,0}[H^+]^2 + {}^*\beta_{1,1,1}[H^+] + {}^*\beta_{1,0,2})$$

where ${}^*\beta_{p,q,r}$ represents the complex formation constants.

The quantity $\bar{n}(1-\bar{n})^{-1}[L^{2-}]^{-1}$ has been plotted against $(2-\bar{n})[L^{2-}](1-\bar{n})^{-1}$ for constant $[H^+]$ in Figure 6. As can be seen, data are best represented by a series of straight lines, indicating the true values of $(q+r)_{max}$ to be 2.

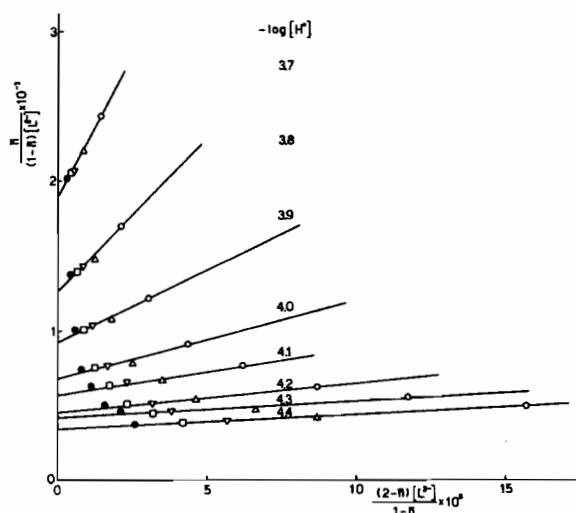


Figure 6. Uranyl(VI)-glutarate system. The quantity $\bar{n}(1-\bar{n})^{-1}[L^{2-}]^{-1}$ as a function of $(2-\bar{n})[L^{2-}](1-\bar{n})^{-1}$ with $[H^+]$ as parameter.

From subsequent treatment of the data, using Österberg's method,¹⁵ it follows that the species $UO_2(HL)^+$, $UO_2(HL)_2$, and $UO_2(HL)L^-$ are the most important complexes formed under the experimental conditions herein considered. Their stability constants are reported in Table I.

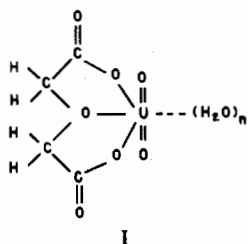
Discussion

The experimental results show that there are important differences among the four ligands examined in their interaction with actinide(VI) ions in aqueous solution.

In the MO_2^{2+} -oxydiacetate systems 1:1 chelate are formed. The relatively high values of the formation constants are in accordance with structure in which the ligand behaves as tridentate by coordinating

(15) R. Österberg, *Acta Chem. Scand.*, 14, 471 (1960).

through the two carboxylic groups and the central oxygen (I)



A consideration of the complex formation curves of these systems indicates that for high values of the ligand to metal ratio formation of other complexes, likely polynuclear, cannot be excluded. It may be worthwhile to notice that preliminary data from X-ray structural analysis on crystalline uranyl(VI)-oxydiacetate complexes indicate a polymeric structure in which the two oxygen of a carboxylic group are linked to two different uranyl(VI) ions.¹⁶

In the MO_2^{2+} -iminodiacetate systems 1:1 chelate are also formed. In these cases no evidence of other complexes is observed at the highest concentrations of ligand examined. A possible structure for these complexes in aqueous solution compatible with the values of the formation constants is one similar to structure (I), with the central group -NH- instead of -O- . The greater stabilities of the iminodiacetate complexes as compared to the oxydiacetate complexes may be explained by taking into account the difference in ligand basicities.

As far as the uranyl(VI)-iminodiacetate system is concerned, our results are in good agreement with those reported by Rajan and Martell,³ in an ionic media 1M using potassium nitrate at 25°C ($\log \beta_1 = 8.76 \pm 0.03$).

(16) G. Bombieri, E. Forsellini, R. Graziani, G. Tomat, and L. Magon, *Inorg. nucl. Chem. Letters*, 8, 1003 (1972).

Glutarate does not form stable chelate complexes with actinide(VI) ions in aqueous solution. This behaviour is consistent with the fact the possible chelation would result in a very unstable eight-membered ring.¹⁷ The stability constants obtained for the uranyl(VI)-glutarate complexes with the monoprotonated ligand acting as unidentate, (HL^-) , have values which would have been expected for a monocarboxylate ligand of the same basicity.¹

As for the thiodiacetate, its behaviour clearly indicates that the central group -S- exhibits a lower tendency, if any, to act as coordinating atom for actinyl(VI) ions in aqueous solution, when compared with -O- and -NH- in the oxydiacetate and iminodiacetate, respectively. Incidentally, this confirms the class "a"¹⁸ or "hard"¹⁹ character of the actinyl(VI) ions.

The formation constants for the oxydiacetate and iminodiacetate systems in Table I make possible some considerations on the relative tendency of the three actinyl(VI) ions to form complexes with these chelating ligands. It is evident that there are only minor differences among the stabilities of complexes with the same ligand. However, for both the ligands the complex stability order seems to be $\text{UO}_2^{2+} \leq \text{NpO}_2^{2+} > \text{PuO}_2^{2+}$.

This order reproduces only in part the more evident stability drift with atomic number pointed out for complexes with some unidentate ligands, such as fluoride²⁰ and monocarboxylic acids,¹ and also for hydroxo complexes,² that is $\text{UO}_2^{2+} > \text{NpO}_2^{2+} > \text{PuO}_2^{2+}$. Probably, in determining different complex stability sequence as a function of atomic number, an important factor is the dehydration thermodynamics of the reacting systems.

(17) F. Basolo and R.G. Pearson, « Mechanism of Inorganic Reactions », p. 29, J. Wiley, Ed., New York, London and Sidney (1967).

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