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Complex Formation Reactions of Uranyl(VI) with Neutral N-Donors in Dimethyl Sulfoxide. Influence of Small Amounts of Water

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Quantitative information about the existence and thermodynamic stability of uranyl(VI) ion complexes based solely upon nitrogen coordination has been obtained in the solvent dimethyl sulfoxide. Calorimetric, potentiometric, and FT-IR investigations, under controlled anhydrous conditions, show that the uranyl(VI) ion can form both mono and bis chelates with the ethylenediamine ligand and only a mono chelate of rather low stability with propylenediamine. With the monodentate ligand *n*-butylamine only a very weak metal–ligand interaction has been detected. The stability constants and the enthalpy and entropy changes have been calculated for the identified coordinated species. All data refer to 25.0 °C and a tetraethylammonium perchlorate medium of ionic strength 0.1 M. All the complexes are enthalpy stabilized whereas the entropy contributions oppose the complex formation. Calorimetric and FT-IR measurements carried out to investigate the effects of small amounts of water present show that a very low water concentration, comparable to that of the coordinating metal ion, can give rise to hydrolysis reactions that may compete with complex formation. This is due to the combined action of different factors that are discussed.

Introduction

To date, studies concerning the complex formation equilibria of actinide ions have been predominantly carried out in aqueous solution. In this medium, the actinide ions (in all their oxidation states) typically behave as "a" or "hard" cations, which prefer to form complexes with charged "hard" bases such as fluoride ion or other ions coordinating via oxygen.[2,3]

Nitrogen was also proved to interact with actinide ions in water. However, this occurs almost exclusively when one or more charged oxygen atoms are present in the ligand. For instance, the higher stability of the uranyl(VI) and thorium(IV) iminodiacetate complexes when compared to the oxy diacetate complexes indicates that the amino group inserted in a suitable position on the aliphatic chain exhibits a greater affinity toward these metal ions than the ether group.[4,5] This behavior parallels the different basicity of the two coordinating groups.[2]

Most ligands coordinating only via nitrogen are so basic that in aqueous solution they coordinate the protons of the water instead of the actinide ion, thus causing the formation of metal–hydroxo or mixed complexes. This behavior makes it impossible to carry out quantitative studies on the metal–nitrogen interactions in aqueous solutions.

On the other hand, several neutral N-donors are considered to be important reagents in the coordination chemistry of a number of metals.[6,7] As a rule, the interactions between molecules belonging to this interesting series of ligands and hard acceptors, such as actinide ions, may be studied in nonaqueous solvents in order to avoid the difficulties caused by hydrolysis reactions.

Although a number of coordination compounds of actinide elements with ligands containing N-atoms have been isolated (see the two volumes cited in ref 2), experimental data regarding the nature and stability of complex species with neutral N-donors in solution are almost nonexistent in the literature, irrespective of the solvent. To our knowledge, only for the uranyl(VI) ion have some rather qualitative investigations been performed on the complexation equilibria with amines in dimethyl sulfoxide.[8-10] Very few studies are reported also for the lanthanide(III)–amine systems in solution.[11-13]

The purpose of the present investigation was to provide quantitative information about the existence and thermodynamic stability of complexes of an actinide ion in nonaqueous solution based solely on nitrogen coordination.

Dimethyl sulfoxide (DMSO) was selected as a suitable medium for complex formation studies for the general reasons reported by Ahrland and Bjork.[14] Furthermore, our recent investigations on the complex formation of silver(I) with amines in DMSO enable us to use the Ag/Ag^+ electrode for potentiometric measurements in the same solvent using the competition reactions method.[15,16]

The coordination systems investigated here are the uranyl(VI) ion with the ligands *n*-butylamine, 1,2-diaminoethane (ethylenediamine), and 1,3-diaminopropane (propylenediamine). Since the primary aim of this study was to ascertain the possible interactions between metal ion and ligand both solvated by DMSO, it appeared to be quite important to first consider all available information regarding the actual nature of the reagents in such a system.

As for the metal ion, on the grounds of some available data, it appears reasonable to assume that all the metal introduced as $UO_2(DMSO)_5(ClO_4)_2$ in DMSO solution exists as UO_2^{2+} solvated ions, since the association or coordination equilibria with the perchlorate anion are negligible.[2,17]

The amines interact with the nonhydroxylic solvent DMSO in the solvation process only, and no other interaction of practical importance needs to be considered.[18]

Furthermore, it is important to take into consideration the fact that it is experimentally impossible to obtain completely anhydrous DMSO solutions. The hygroscopic properties of this solvent bring about the presence of small amounts of water even though the

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most effective methods and precautions are used during purification, storage, and measurements. A number of studies,[14,19-22] chosen at random, indicate that most of the experimental investigations in DMSO solutions refer to systems in which the water content is in the concentration range 10^{-3}–10^{-1} M. It should be mentioned that several experimental methods widely applied in coordination chemistry frequently make use of reagent concentrations in the same range and sometimes even smaller.

Now, can water interfere with the complex formation equilibria when a water concentration comparable to that of the reagents' is present? Considering the basic nature of the amines, this question is quite legitimate. An indicative answer may be drawn from the available data referring to the acid–base behavior in DMSO of the reagents involved.

The basic properties of alkylamines in DMSO have been investigated by means of thermodynamic[20] and kinetic[22] studies. The values reported for the ionization constants of some protonated alkylamines show only minor changes when the solvent is changed from water to DMSO. In particular, for the *n*-butylammonium ion in DMSO a $\mathrm{p}K_\mathrm{a}$ of 11.1 was reported, which may be compared with the corresponding value of 10.6 in water.[22]

As for the acidity of water in DMSO, among other values reported, the most reliable seems to be the $\mathrm{p}K_\mathrm{a}$ of 31.4.[23]

The very low degree of autoprotolysis of the DMSO is well emphasized by the value of 35.1 determined for the corresponding $\mathrm{p}K_\mathrm{a}$.[23]

For a system consisting of a monoamine, RNH_2, and water in DMSO the following three equilibria may be written (K_n values are the corresponding equilibrium constants):

$$RNH_2 + CH_3SOCH_3 \rightleftharpoons RNH_3^+ + CH_3SOCH_2^- \quad K_1 \qquad (1)$$

$$H_2O + CH_3SOCH_3 \rightleftharpoons CH_3SOHCH_3^+ + OH^- \quad K_2 \qquad (2)$$

$$CH_3SOHCH_3^+ + CH_3SOCH_2^- \rightleftharpoons 2CH_3SOCH_3 \quad K_3 \qquad (3)$$

Combining these three reactions, we obtain the following acid–base equilibrium of the amine with water in DMSO:

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^- \quad K_4 \qquad (4)$$

Using the values of $\mathrm{p}K_\mathrm{a}$'s quoted above (with *n*-$BuNH_2$ as monoamine), we have computed following values for the equilibrium constants: $\log K_1 = -24.0$, $\log K_2 = -32.55$, $\log K_3 = 36.25$. From these, $\log K_4 = -20.3$.

The very small value of K_4 indicates that the corresponding equilibrium is quite negligible by itself in that it cannot cause any appreciable change in the amine concentration.

As for the metal ion solvates, we think that small amounts of water have no effect on them, since hydrated metal ions cannot be formed. In fact, it is well-known that DMSO is better than water at solvating cations. Accordingly, the enthalpies of transfer, $\Delta H_{tr}(H_2O \rightarrow DMSO)$, measured for a number of metal ions are generally large and negative.[24,25] On the other hand, it should be remembered that the anhydrous solvate $UO_2(DMSO)_5(ClO_4)_2$ is obtained by dissolving hydrated uranyl(VI) prechlorate in DMSO. If the uranyl(VI) ion is not coordinated with water, we can ignore the hydrolysis reactions in which the hydrated metal ion behaves as a Brønsted acid.

However, the UO_2^{2+} ion retains its intrinsic character of a Lewis acid in DMSO as well and, as such, can react with the hydroxide ions produced by the reaction (4) above, according to the following general equilibrium:

$$xUO_2^{2+} + yOH^- \rightleftharpoons (UO_2)_x(OH)_y^{(2x-y)+} \quad \beta_{5\,x,y} \qquad (5)$$

Whether or not hydrolytic reactions of the type

$$xUO_2^{2+} + yRNH_2 + yH_2O \rightleftharpoons (UO_2)_x(OH)_y^{(2x-y)+} + yRNH_3^+ \quad \beta_{6\,x,y} \qquad (6)$$

take place in a DMSO solution containing UO_2^{2+}, RNH_2, and H_2O depends on the relative values of the equilibrium constants $\beta_{5\,x,y}$ and K_4.

Unfortunately, there is no published information regarding the interactions of OH^- with metal ions in DMSO. Nevertheless, the strong basic character of the OH^- ion in DMSO, which is stronger than that in water, has been pointed out and attributed to the fact that the weak hydrogen bond donor properties of this solvent make it relatively poor at stabilizing anions wherein the charge is localized.[25-27]

In relation with this point it may be useful to consider the reactions (2) and (4) above. Since both these equilibrium involve OH^- as a base, we can compare the values of the corresponding constants obtained for the two different solvents, DMSO and water. As far as the equilibrium (2) in water is concerned, a value of $\log K_2 = -17.3$ was computed by using the reported $\mathrm{p}K_\mathrm{a} = -1.54$ for the dissociation of the protonated species $CH_3SOHCH_3^+$ in water.[28] For the equilibrium (4) in water, when the monoamine is *n*-$BuNH_2$, we obtained $\log K_4 = -5.14$ using the $\mathrm{p}K_\mathrm{a}$ value of 10.6 mentioned above for the amine in water. Now we can compare these values of K_2 and K_4 with the corresponding value in DMSO given above:

$$^{DMSO}\Delta^{H_2O} \log K_2 = -17.3 - (-32.55) = 15.25$$

$$^{DMSO}\Delta^{H_2O} \log K_4 = -5.14 - (-20.3) = 15.16$$

As can be seen, quite the same value of $\Delta \log K$ is obtained for the two equilibria, taking into account some inaccuracy in the values used.

In order to assume this Δ as a measure of how much stronger the base OH^- is in DMSO than in water, it is necessary to take into consideration the possible change in the acid strength, when the solvent is changed from DMSO to water, of the two species involved in the equilibria (2) and (4) as reagents for OH^-, i.e. the ions $CH_3SOHCH_3^+$ and RNH_3^+. This can be done by comparing the $\mathrm{p}K_\mathrm{a}$ of the two species in both of the solvents. We have already mentioned that for *n*-$BuNH_3^+$ the two values of $\mathrm{p}K_\mathrm{a}$ show only a minor change ($^{H_2O}\Delta^{DMSO}\mathrm{p}K_\mathrm{a} = 0.5$). As for the protonated DMSO, its standard $\mathrm{p}K_\mathrm{a}$ in DMSO is computed as follows:[29]

$$K_\mathrm{a} = \frac{[CH_3SOCH_3][CH_3SOHCH_3^+]}{[CH_3SOHCH_3^+]} = [CH_3SOCH_3] = 14$$

$$\mathrm{p}K_\mathrm{a} = -1.15$$

A comparison of this value with the corresponding value in aqueous solution mentioned above, $\mathrm{p}K_\mathrm{a} = -1.54$, indicates a minor change as well ($^{H_2O}\Delta^{DMSO}\mathrm{p}K_\mathrm{a} = 0.4$).

Therefore, it appears reasonable to consider the $\Delta \log K \simeq 15$ as a rough measure of increasing basicity for OH^- ion when the solvent is changed from water to DMSO. This agrees with a difference in acidity of 15 $\mathrm{p}K_\mathrm{a}$ units for the weakest oxygen acids, MeOH and H_2O, in water vs DMSO, reported by Bordwell.[27]

Let us consider the equilibrium (5) again. Several detailed studies of the hydrolysis of uranyl(VI) ions have been carried out in various aqueous media,[2,30] and although a strong tendency for dimerization has been pointed out, only the 1/1 hydroxo complex formation will be taken into consideration here. In this case a value of $\log \beta_{1,1} = 8.5$ can be used.[30]

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If, when changing from water to DMSO, it were reasonable to increase the Lewis basicity of the OH^- ion with respect to UO_2^{2+} by a quantity equal to $\Delta \log \beta = 15$, then a value of $\log \beta_{5\,1,1} = 23.5$ for the equilibrium (5) should be obtained. By combining this hypothetic value with the value found for K_4, we obtain the equilibrium constant $\log \beta_{6\,1,1} = 3.5$ for the hydrolytic reaction (6) when $x = y = 1$.

If the hydrolytic reactions (6) occur in the system under investigation, they can interfere with the following complex formation equilibria to be studied in DMSO:

$$UO_2^{2+} + nRNH_2 \rightleftharpoons UO_2(RNH_2)_n^{2+} \qquad (7)$$

It is evident that the prevalence of one of the two reactions depends on the relative values of the corresponding equilibrium constants (note that $\log \beta_{6\,1,1} = 3.5$ might be in a range of values of complex formation constants) as well as on the amount of water present.

The hypothetical value that was found for $\beta_{6\,1,1}$ only suggests that some studies on the possible influence that small amounts of water can have on the coordination systems here examined should be conducted.

The experimental methods used in this work were calorimetric measurement of enthalpies of complexation, FT-IR spectroscopy in solution, and, when possible, potentiometric measurements. Calorimetric and potentiometric measurements were performed at 25 °C and in a medium of ionic strength 0.1 M with tetraethylammonium perchlorate.

Experimental Section

In order to obtain and keep the lowest possible water content in the systems throughout experimentation, extreme care was taken to work under an inert atmosphere of dry nitrogen. All solutions were prepared, handled, and stored in a stainless steel glovebox filled with dry nitrogen and connected to an apparatus for the automatic purification and recycling of the gas so that the water content in the inert atmosphere could be kept <1 ppm. Before being introduced into the glovebox, the equipment and nonvolatile samples were degassed in a connected vacuum chamber that was repeatedly evacuated and purged with dry nitrogen.

Chemicals. Dimethyl sulfoxide (Merck Pro Analysi, 0.03% water) was dried for several days over activated Linde 4A molecular sieves and then distilled following substantially the procedures described by Matthews et al.[26] The receiver containing the purified DMSO was introduced into the glovebox.

n-Butylamine (Fluka puriss) was refluxed for several hours with and fractionally distilled from CaH_2 under nitrogen.[31]

Ethylenediamine (Fluka puriss) was treated with a mixture of CaO and KOH, decanted, refluxed with sodium for 2 h, and distilled under nitrogen.[31]

Propylenediamine (Fluka puriss) was refluxed with sodium and then distilled under nitrogen.

The adduct $UO_2(DMSO)_5(ClO_4)_2$ was obtained by adding a sufficient amount of benzene to a DMSO solution of hydrated uranyl(VI) perchlorate (K&K product). The yellow solid was filtered off, washed with benzene, and dried under vacuum over P_2O_5 for 2 days (Anal. Calcd: U, 27.69; C, 13.97; H, 3.52. Found: U, 27.58; C, 14.05; H, 3.48).

Tetraethylammonium perchlorate and silver(I) perchlorate (Fluka puriss) were purified as described previously.[14]

Stock solutions of uranyl(VI) were prepared by dissolving weighed samples of the pentasolvate perchlorate in DMSO. The exact concentration of the metal ion in these solutions was checked by ion-exchange analysis on a cation resin in the hydrogen form.

Solutions of the ligands were prepared by dissolving appropriate amounts of the amines in DMSO and standardized by thermometric titration with standard perchloric acid solution.

Water content in the stock uranyl(VI) and ligand solutions was determined by a modified Karl Fischer method using the Model 652 Coulomètre KF (Metrohm). Repeated measurements showed less than 30 ppm water present in these solutions, and thus, we confidently assumed that the upper limit of water concentration in the most anhydrous solutions used was 2 mM.

Calorimetric Measurements. A Tronac precision titration calorimeter, Model 87-558, equipped with a 25-mL titration vessel, was used. The cover of the titration vessel and its connection to the calorimeter were modified in order to make a gasproof closure possible. The calorimetric titrations were performed by adding ligand solutions of concentration $C_L°$ at a constant rate of 0.2116 mL min^{-1} from a piston buret to an uranyl(VI) perchlorate solution of concentration $C_M°$. The solutions were kept at ionic strength 0.1 M with the required amounts of tetraethylammonium perchlorate. Both the vessel and the piston buret were filled inside the box, joined together, taken out of the box, and connected to the calorimeter for measurements. The experimental values of the heat changes were corrected for the heat of dilution of the ligand solutions, which were determined separately. The heat of dilution of uranyl(VI) perchlorate solutions was negligible in the metal concentration range used here. All the experiments were carried out at 25.0 °C. ΔH and ΔS values for the identified complexes were calculated by using the least-squares program LETAGROP KALLE.[32]

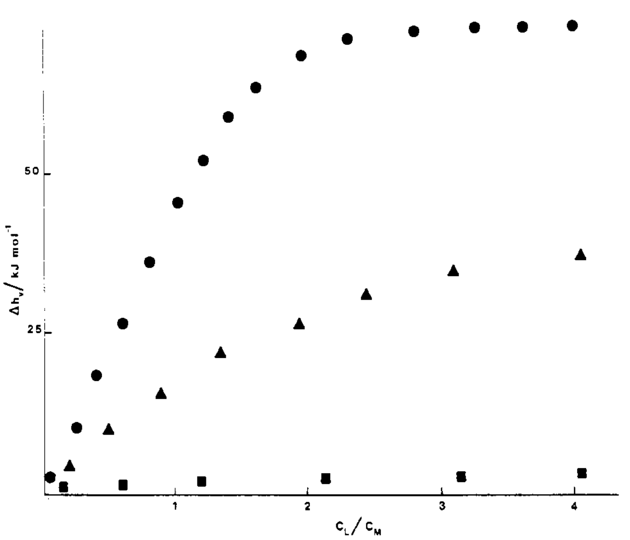

Figure 1. Uranyl(VI)–*n*-butylamine system. The total molar enthalpy change per mole of metal ion as a function of the ligand/metal concentration ratio is shown. $C_M° = 50$ mM. Water content: (■) <2 mM; (▲) ≃20 mM; (●) ≃0.2 M.

FT-IR Measurements. The spectra were recorded on a Nicolet 5SXC FT-IR spectrometer. Cells with barium fluoride windows and thickness of 0.1 or 0.4 mm were used. The cells were filled in the glovebox, accurately closed, and transferred into the spectrometer with a sealed container.

Potentiometric Measurements. The uranyl(VI)–ethylenediamine system was also investigated by the potentiometric method of competitive reactions[33] using the silver(I) ion as competitor and a Ag/Ag$^+$ electrode to determine its free concentration in anhydrous DMSO solutions containing both uranyl(VI) ion and ligand. The galvanic cell, potentiometric apparatus, and titration procedures were the same as previously described.[14] Some preliminary emf measurements showed that the silver electrode behaved according to Nernst's law in the presence of uranyl(VI) as well. The ionic strengths of all the solutions were kept at 0.1 M with tetraethylammonium perchlorate. Titrations were performed inside the glovebox.

The values of $\bar{n}$ (the average number of ligands bound to each uranyl(VI) ion) were obtained from the relationship $\bar{n} = (C_L - \bar{n}'C_{Ag} - [L])/C_M$, where C_L and [L] are the total and free ligand concentration, respectively, C_M is the total uranyl(VI) ion concentration, and $\bar{n}'$ and C_{Ag} refer to the silver(I) ion. [L] and $\bar{n}'$ were computed from the measured [Ag^+] and the known analytical concentrations with the formation constants previously determined for the silver(I)–ethylenediamine complexes.[15] Stability constants for the identified coordinated species were computed by using the program SUPERQUAD.[34]

Results and Discussion

Uranyl(VI)–*n*-Butylamine. The results of three calorimetric titrations, in the form of Δh_v, the total molar enthalpy change, as a function of the ratio C_L/C_M, are illustrated in Figure 1. The three titrations differed in water content only. As can be seen from the graph, the enthalpy changes are clearly dependent on the amount of water present. In particular, the data obtained when the concentration of water is greatly inferior to that of uranyl(VI)

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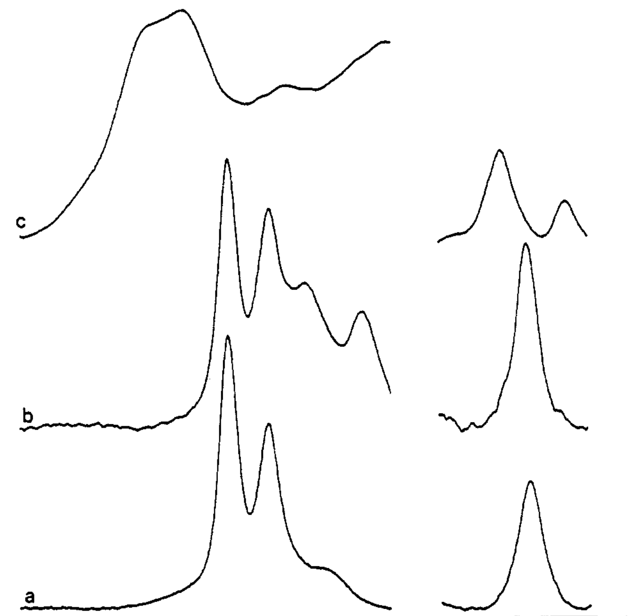

Figure 2. FT-IR spectra of 0.2 M *n*-butylamine in DMSO: (a) [water] < 2 mM; (b) [uranyl(VI) perchlorate] = 0.2 M, [water] < 2 mM; (c) [uranyl(VI) perchlorate] = 0.2 M, [water] = 0.2 M.

(■, Figure 1) indicate that only a very weak interaction, if any, takes place between the metal ion and the ligand, since very small heat changes are measured even at the higher values of C_L/C_M examined. Besides, these very small heat changes can hardly be attributed to complex formation reactions rather than to hydrolytic reactions due to traces of water present in the system. The experimental points of the titration carried out when the water concentration was of the same order of magnitude as that of the uranyl(VI) ion (▲, Figure 1) show that an exothermic reaction occurs, the heat released being a function of the total amounts of amine and water present. From the values obtained when water was in a large excess over the uranyl(VI) ion (●, Figure 1) one can notice that the total enthalpy changes per mole of metal ion point to a definite value for $C_L/C_M = 2$ ($\sim$70 kJ mol^{-1}) and then, on increasing C_L, it remains substantially unchanged.

These calorimetric results may be interpreted by assuming that in the system considered here in the presence of water the equilibria of the type (6) prevail over the complex formation equilibria (7). In particular the data referring to the system with an excess of water seem to be in accordance with the formation of hydroxo complexes having $x = 1$ and for $C_L/C_M > 2$ a maximum value of $y = 2$, that is the neutral species $UO_2(OH)_2$.

Useful information about the interactions of the amino group in these systems may be obtained from IR spectra. Part of the spectrum of *n*-butylamine in anhydrous DMSO is shown in Figure 2 along with the corresponding spectra obtained when uranyl(VI) and water are also present. The two absorption bands near 3360 and 3300 cm^{-1} and the band near 1600 cm^{-1} shown by the amine alone (spectrum a) can be attributed respectively to the asymmetrical and symmetrical NH stretching modes and to the NH bending (scissoring) vibration.[35] The same absorptions are found in the spectrum of an anhydrous DMSO solution containing equal concentrations of *n*-butylamine and uranyl(VI) ion (spectrum b). This indicates that no important metal–ligand interaction takes place in this system. Yet, a minor change due to the presence of uranyl(VI) is observed in the spectrum of *n*-butylamine as two weak bands near 3240 and 3150 cm^{-1}. These absorptions may be attributed to the NH stretching vibrations, which decrease their frequency, relative to that of the free amine, when coordination occurs (see below). If so, some tendency to complex formation, though weak, should be admitted for this system as well.

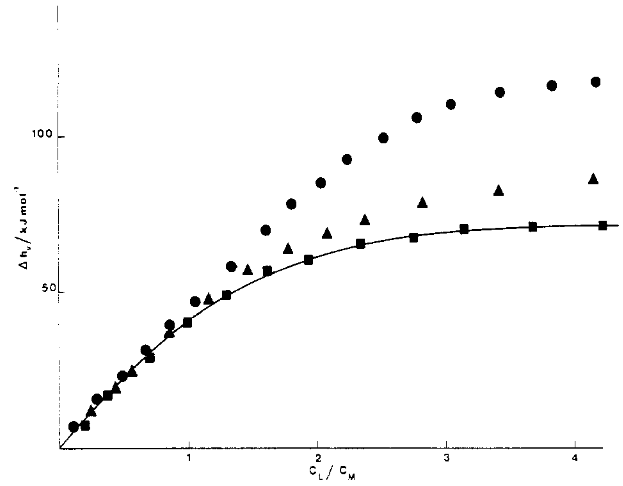

Figure 3. Uranyl(VI)–ethylenediamine system. The total molar enthalpy change per mole of metal ion as a function of the ligand/metal concentration ratio is shown. $C_M^\circ = 30$ mM. Water content: (■) <2 mM; (▲) $\simeq$20 mM; (●) $\simeq$0.2 M. The full-drawn curve was calculated from the values of β and ΔH reported in Table I.

It is apparent from Figure 2 (spectrum c) that when water is also present in the DMSO solution together with *n*-butylamine and uranyl(VI) ion (the three species having the same concentration), the NH spectrum undergoes quite evident alterations. These alterations consist of the disappearance of the two bands that are characteristic of the primary amines in the region of the NH stretching modes and the appearance of a new broad absorption between 3600 and 3200 cm^{-1} arising from OH stretching.[36] In addition, there are two bands near 1640 and 1540 cm^{-1}, instead of one, in the region of NH bending vibration. The protonation of a primary amine brings about a shift to a lower frequency of the absorptions due to NH stretching vibrations, so that the corresponding bands result superimposed on aliphatic CH stretchings in the region 3000–2800 cm^{-1}. The two bands around 1600 cm^{-1} were attributed to asymmetrical and symmetrical bending in the NH_3^+ group.[35] We interpreted the IR spectra obtained as a confirmation of what was deduced from the calorimetric measurements. In the system examined, if water is present even in small amounts, the hydrolytic reactions (6) prevail over complex formation reactions, which, in turn, must have very small equilibrium constants.

Assuming the small heat changes measured with the anhydrous solution as due to complex formation only, the rough value of 1 ± 0.5 was computed for the formation constant of the 1/1 complex (the corresponding rough ΔH was 22 ± 7 kJ mol^{-1}; see the Uranyl(VI)–Propylenediamine section below for the computational method). The value of the stability constant should be regarded as an upper limit.

Uranyl(VI)–Ethylenediamine. Figure 3 represents the results of calorimetric titrations which were carried out with a method similar to that used for *n*-butylamine. A comparison of the Δh_v values for titrations at different water contents clearly indicates that even with the most anhydrous system (■, Figure 3) there is a well-measured heat change that increases with the ratio C_L/C_M, and this may be attributed to metal–ligand exothermic interactions. The experimental values obtained with solutions containing different amounts of water show a fairly good overlap in the range $0 < C_L/C_M < 1$. This strongly suggests that even if water is present in the concentration limits here considered, the complex formation reaction (7), with $n = 1$, is prevalent over hydrolytic reactions. On the other hand, the increasing splitting of the three curves as a function of the ratio C_L/C_M above 1 can be interpreted by acknowledging that exothermic hydrolytic reactions occur involving the 1/1 complex UO_2L^{2+}, when C_L increases and water

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(35) Silverstein, R. M.; Bassler, C. G.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons: New York, 1974.

(36) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; John Wiley & Sons: New York, 1986.

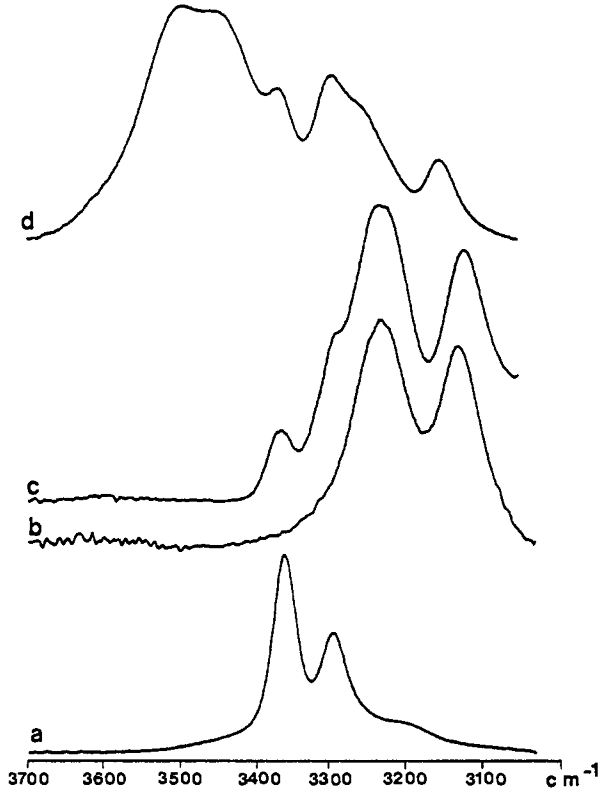

Figure 4. FT-IR spectra of 0.3 M ethylenediamine in DMSO: (a) [water] < 2 mM; (b) [uranyl(VI) perchlorate] = 0.4 M, [water] < 2 mM; (c) [uranyl(VI) perchlorate] = 0.1 M, [water] < 2 mM; (d) [uranyl(VI) perchlorate] = 50 mM, [water] = 0.3 M.

is present. Only in the case of the titration carried out when the water concentration is much smaller than the uranyl(VI) one (■, Figure 3) may the heat evolved at $C_L/C_M > 1$ be attributed to the formation of the successive complex with $n = 2$, $UO_2L_2^{2+}$. On the contrary, when the amount of water is comparable to that of the coordinating metal ion, hydrolytic reactions are expected to compete with the formation of the second successive complex. Indeed, the experimental points obtained when the concentration of water is much greater than that of uranyl(VI) with their inflexion around the value $C_L/C_M = 3$, even though not very sharp, might indicate formation of the neutral mixed complex $UO_2L(OH)_2$ as a result of competition between the two equilibria (6) and (7).

The IR spectra in Figure 4 clearly show that the two absorption bands at 3360 and 3300 cm^{-1}, due to the NH stretching in the free ethylenediamine in anhydrous DMSO solution (spectrum a), are shifted to 3230 and 3130 cm^{-1}, respectively, when uranyl(VI) perchlorate is also introduced into the solution (spectrum b). These alterations in the NH stretching frequency are generally considered an effect of the coordination of the amino group to a metal ion.[36,37] The spectrum c, which refers to a solution with $C_L/C_M = 3$, shows the characteristic absorption bands of both coordinated and free amino group. This should be expected if the third successive complex, $UO_2L_3^{2+}$, does not form or if its stability constant is very low. Spectrum d was found for a DMSO solution containing uranyl(VI) perchlorate and ethylenediamine in large excess ($C_L/C_M = 6$) and the water concentration equal to that of the ligand. The following absorptions are recognizable: OH stretching in the region 3550–3400 cm^{-1}, NH stretching of the free amino group (excess of amine), and two absorptions near 3250 and 3155 cm^{-1}. These two absorptions can be attributed to the NH stretching modes in the coordinated amino group. The smaller shift (by about 20 cm^{-1}) to a lower frequency of these bands, compared to the corresponding shifts when water is not present as in spectra b and c, may be due to a decrease in the positive charge of the metal ion acceptor as a consequence of the formation of mixed hydroxo complexes of the type $UO_2L(OH)^+$ and/or $UO_2L(OH)_2$ already considered in discussing the calorimetric results.

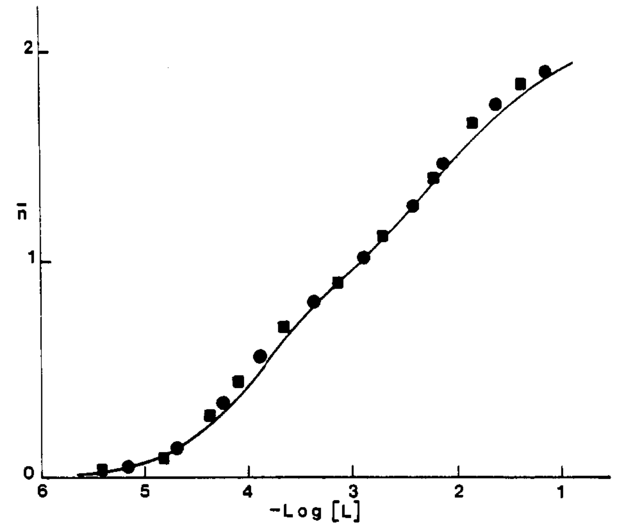

Figure 5. Complex formation functions for the uranyl(VI)–ethylenediamine system. C_M° = 41.7 (●) and 25.0 mM (—). Water content: <2 mM. The full-drawn curve was calculated from the values of β reported in Table I.

Table I. Stability Constants and Thermodynamic Functions of Uranyl(VI)–Diamine Complexes in DMSO at 25 °C and Ionic Strength 0.1 M[a]

ligand	reacn	log β	$-\Delta H$, kJ/mol^{-1}	$-\Delta S$, J K^{-1} mol^{-1}
ethylenediamine	$M + L \rightleftharpoons ML$	3.88 (2)	41.4 (6)	64 (3)
	$M + 2L \rightleftharpoons ML_2$	5.88 (5)	76.7 (9)	145 (4)
propylenediamine	$M + L \rightleftharpoons ML$	1.15 (4)	41 (2)	117 (8)

[a] The errors given correspond to three standard deviations.

Since a fairly strong metal–ligand interaction in this system was demonstrated by calorimetric and FT-IR measurements, it seemed worthwhile to provide further quantitative information about the nature and stability of the complexes formed by means of potentiometric measurements. Titrations were carried out with two different initial concentrations of uranyl(VI) and the most anhydrous solutions we could obtain. The experimental data, plotted as $\bar{n}$ vs $-\log$ [L], are shown in Figure 5. The complex formation curves obtained can be interpreted by the formation of two successive mononuclear complexes, according to the equilibrium (7), with $n = 1$ and 2.[33] The trend of the $\bar{n}$ values at the highest ligand concentration examined seems to indicate that a third complex is not formed or, at least, if it forms, it is of very low stability.

From the potentiometric data, the stability constants for the two ascertained complexes were computed, and by combining these values with the calorimetric data, we obtained the values for the corresponding enthalpy and entropy changes. All these results are listed in Table I, and their evaluation enables us to point out some properties of the system examined.

First of all, if we bear in mind the lack of appreciable interaction with n-butylamine, the comparatively high values of the two stability constants prove that a very strong chelate effect is associated with the formation of the uranyl(VI)–ethylenediamine complexes. The ΔH and ΔS values show that the complexes are enthalpy stabilized, whereas the entropy terms are negative and therefore oppose the complex formation.

It should be remembered that in aqueous solution the stabilities of complexes formed by "hard" acceptors, like the uranyl(VI) ion and other actinide ions, are essentially due to the favorable entropy terms, whereas the enthalpy changes are, as a rule, rather endothermic or quite small.[2,3] As mentioned above, only anionic ligands form complexes with hard cations in aqueous solution.

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(37) Forsberg, J. H.; Moeller, T. *Inorg. Chem.* **1969**, *8*, 883.

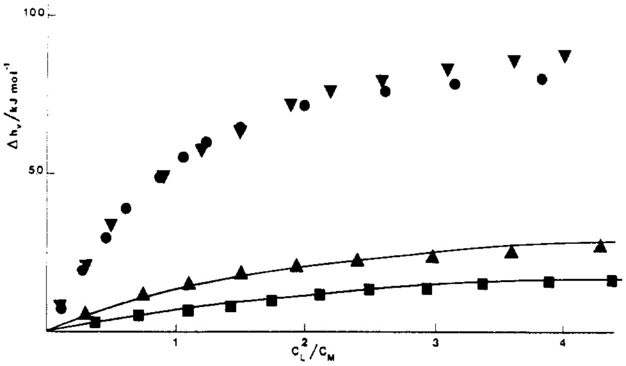

Figure 6. Uranyl(VI)–propylenediamine system. The total molar enthalpy change per mole of metal ion as a function of the ligand/metal concentration ratio is shown: (■) $C_M{}^\circ = 15$ mM, [water] < 2 mM; (▲) $C_M{}^\circ = 50$ mM, [water] < 2 mM; (●) $C_M{}^\circ = 15$ mM, [water] $\simeq$50 mM; (▼) $C_M{}^\circ = 50$ mM; [water] $\simeq$0.15 M. The full-drawn curves were calculated from the values of β and ΔH reported in Table I.

It may be of interest to notice that negative changes for both enthalpy and entropy terms were also found for ethylenediamine complexes in nonaqueous solvents with other metal ions, namely silver(I) in DMSO[38] and lanthanide(III) in acetonitrile.[11]

It is well-known that the observed net changes ΔH and ΔS reflect the relative extent of the opposed contributions of desolvation and cation–ligand combination. As far as the negative net change of entropy is concerned, at least two factors should be taken into account: the minor solvation of amines in aprotic solvents and the fact that uncharged ligands involve the loss of the positive entropic contribution connected with the compensation of charges. This contribution is caused by structural changes occurring within the solvent, since polar solvent molecules can be oriented by the field of force created by ionic charges and then set free when these charges are neutralized upon complexation.

Evidently, the entropy gain due to the desolvation processes does not compensate the negative entropy change associated with the joining of cation and ligand in the complex.

Given the relatively weak ligand–solvent interactions in the system here investigated, the enthalpy change associated with the complex formation is essentially a measure of the difference in bond energy toward the metal ion between the ligand and the coordinated molecules of the solvent. Thus, the enthalpy stabilization found emphasizes the importance of the metal–nitrogen interaction in these complexes.

Uranyl(VI)–Propylenediamine. Some results of the calorimetric measurements carried out for this system are plotted in Figure 6. The experimental data referring to two different metal ion concentrations and to the same anhydrous conditions (■ and ▲, Figure 6) show that an exothermic metal–ligand interaction occurs, even though the corresponding equilibrium constant must have a low value (compare with values (■) in Figure 3). The results obtained when excess water is present in respect to the metal ion (● and ▼, Figure 6) may be accounted for by admitting that the hydrolytic reactions (6) prevail over the complex formation reactions. The fact that the experimental values of Δh_v for the latter titrations at different C_M values are superimposed suggests that the hydrolysis equilibrium constant must have a rather high value ($\beta_{6\,1,1} > 10^3$).

FT-IR spectra obtained with anhydrous DMSO solutions containing uranyl(VI) perchlorate and propylenediamine in excess show absorptions like the ones in Figure 4, spectrum c, and are therefore consistent with the presence of both coordinated and free amino groups.

Although we attempted to perform a potentiometric investigation of this system using the Ag/Ag^+ electrode, no useful results were obtained due to the very low stability of the complexes studied with respect to those of the competitor silver(I).

On the other hand, given that the thermometric titration curves in this case are largely nonlinear ($\log K \ll 4$), stability constant and ΔH values can be calculated from calorimetric data only.[39] With use of the least-squares program LETAGROP KALLE, the available experimental data allowed the calculation of these parameters for the 1/1 complex only. The results are reported in Table I along with the entropy change. The full-drawn curves in Figure 6, calculated by using the values of log K and ΔH reported, closely fit the experimental points, and this indicates that no other species are necessary to adequately describe the reaction that occurs within the range of concentrations examined.

A consideration of the values in Table I shows that the uranyl(VI)–propylenediamine complex is enthalpy stabilized, its formation involving quite the same negative ΔH as the first ethylenediamine complex. Certainly both these bidentate ligands form chelate complexes with the uranyl(VI) ion and, as is generally found for saturated ligands, the five-membered chelate ring is the more stable. The difference in stability is particularly large in this case and entirely due to the entropic factor. This can be attributed to the conformational and rotational entropy loss, which becomes greater when the chain length increases.

Final Remarks. Although DMSO is a rather strong solvating agent for metal ions, in this nonaqueous solvent the uranyl(VI) ion does form complexes with bidentate neutral N-donors. The stability of such complexes is strongly dependent on the chelate formation with a marked preference for the five-membered ring.

Due to the concurrence of different factors such as the basic nature of the amines, the Lewis acidity of the uranyl(VI) ion, and the very strong basicity of OH^- in DMSO, even small amounts of water in these systems can give rise to hydrolysis reactions that compete with complex formation. Considering the effects of well-defined small concentrations of water on the complex formation equilibria here investigated, a rough value of $\log K = 23 \pm 2$ may be estimated for the formation constant of the 1/1 uranyl(VI)–hydroxo complex, UO_2OH^+, in DMSO. A comparison of this value with the corresponding value for the same equilibrium in water, $\log K = 8.5$, points out the very large increase in donor strength of the OH^- ligand when the solvent is changed from water to DMSO and suggests that investigations on the interactions between metal ions and the hydroxide ion in DMSO should be quite interesting.

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