Thermodynamic and Spectroscopic Investigations on the Interaction of Uranyl(VI) with Neutral N- and O-Donors in Dimethyl Sulfoxide†

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The thermodynamic functions $\Delta G^\ominus$, $\Delta H^\ominus$ and $\Delta S^\ominus$ for the formation of uranyl(VI) complexes with the tridentate compound 4-azaheptane-1,7-diamine and with tetradentate 3,6-diazaoctane-1,8-diamine and 4,7-diazadecane-1,10-diamine have been determined in anhydrous dimethyl sulfoxide (dmso) by means of potentiometric, spectroscopic, and calorimetric measurements at 25 °C in a 0.1 mol dm^{-3} ionic medium. The data are discussed together with those for other polyamines previously investigated. Factors affecting the complexation of uranyl(VI) by these strongly basic ligands in anhydrous dmso are elucidated. Spectroscopic and calorimetric evidence has been obtained which demonstrates that polyglycols having molecular frameworks similar to those of some of the polyamines do not form complexes with uranyl(VI) in this solvent.

Over the past years several investigations on the complexation of uranyl(VI) in aqueous solution have been published.[1] Much less attention has been paid to the complexation in non-aqueous solution. Apart from some, rather qualitative, electrochemical investigations on the complexation of the couple UO_2^{2+}–UO_2^{+} by monocarboxylates,[2] halides and pseudohalides,[3] and amines[4,5] in dimethyl sulfoxide (dmso) and a series of spectrophotometric studies on the stability of the complexes of uranyl(VI) with macrocycles and cryptands in propylene carbonate and acetonitrile,[6,7] the only complete thermodynamic studies till now are those on the complexation of uranyl(VI) by *n*-butylamine, ethylenediamine (en), trimethylenediamine (tn) and diethylenetriamine (dien) in dmso.[8,9] In these studies it was shown that butylamine does not strongly interact with the uranyl(VI) ion, while the polyamines form chelate complexes the stability of which mainly depends upon the size of the chelate rings and, to a lesser extent, upon the number of donor atoms of the ligand. It was also found that the values of $\Delta H_j^\ominus$ are associated with the number of metal–nitrogen bonds formed between the amine and metal ion, while the entropy changes reflect mainly the loss in the translational and conformational entropy of the reagents as a consequence of the complexation.

As an accumulation of reliable data on the thermodynamics of complexation of uranyl(VI) in non-aqueous media should reveal some, not negligible, aspects of the co-ordination chemistry of this ion, we have extended the thermodynamic study to the complexation with some tri- and tetra-amines in dmso. The compounds investigated were 4-azaheptane-1,7-diamine (ahd), 3,6-diazaoctane-1,8-diamine (triethylenetetraamine, trien), and 4,7-diazadecane-1,10-diamine (dadd). The stability constants of the complexes formed in solution have been evaluated by potentiometric or spectroscopic measurements, the enthalpy terms by calorimetric titrations.

The relative affinity of N- and O-donors for the uranyl(VI) ion is a topic frequently treated and contrasting interpretations of the experimental data can be found in the literature.[10,11] In order to obtain experimental evidence on this point we carried out some calorimetric and spectroscopic measurements on solutions containing uranyl(VI) and polyglycols $HOCH_2(CH_2OCH_2)_nCH_2OH$ (n = 0–2) having molecular frameworks similar to that of some of the polyamines presently (trien) or previously (en[8] and dien[9]) considered.

Previous studies indicated that even small amounts of water gave rise to hydrolysis reactions which compete with the complex formation; for this reason we carried out some experiments in order to assess the effect of this on the equilibria in solution.

Experimental

Reagents.—The dmso pentasolvate of uranyl(VI) perchlorate was prepared by dissolution of the hydrate salt in dmso and then by repeated crystallizations from dmso–benzene mixtures. The yellow solid so obtained was dried under high vacuum at *ca.* 80 °C for several days. Stock solutions of uranyl(VI) were prepared with the dried adduct and analysed as described previously.[8] Anhydrous silver(I) perchlorate solutions were prepared following the procedure recently reported.[12] The amines and glycols (all of reagent-grade purity) were purified and dried according to the reported methods;[13] their solutions were prepared by weighing. The titre of the amines in solution was checked by acid–base thermometric titrations with standard $HClO_4$. No concentration check was made for the glycols. Particular care was devoted to the purification and dehydration of the solvent which, after the reported pretreatments,[8] was fractionally distilled at low pressure and stored over 4 Å molecular sieves in a dark bottle.

All the solutions used in the present study, prepared and stored in a glove-box assuring a moisture content less than 1 ppm, were made 0.1 mol dm^{-3} in ClO_4^- with tetraethylammonium perchlorate (Fluka purum, > 99%) recrystallized twice from water and dried *in vacuo* at 100 °C before use. The residual water content in the solutions, determined by a

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† To the memory of our dear friend and colleague Giuliana Tomat to whom we were bound by deep affection.

$$(+)\,\mathrm{Ag(s)}\;\left|\;\mathrm{AgClO_4}\ (100\ \mathrm{mmol\ dm^{-3}})\;\right\|\;\begin{array}{ll}\mathrm{AgClO_4} & (c_{\mathrm{Ag^+}})\\ \mathrm{UO_2(ClO_4)_2} & (c_{\mathrm{M}})\\ \mathrm{NEt_4ClO_4} & (100.0 - C_{\mathrm{Ag^+}} - 2c_{\mathrm{M}})\ \mathrm{mmol\ dm^{-3}}\\ \mathrm{Ligand} & (c_{\mathrm{L}})\end{array}\;\left|\;\mathrm{Ag(s)}(-)\right.$$

Scheme 1

Metrohm 684 KF Coulometer, ranged typically from 10 to 30 ppm.

Determination of the Stability Constants.—The UO_2^{2+}–trien and –dadd systems were investigated potentiometrically by the method of competitive reactions using silver(I) as auxiliary metal ion. A Metrohm massive silver electrode (cat. no. 6.038.000) and a Metrohm reference electrode (cat. no. 6.0718.000) were used to monitor the free silver(I) concentration. The titrations were carried out by adding, with a Metrohm 655 Multi-Dosimat burette, known volumes of an amine solution to the right-hand-side compartment of the galvanic cell shown in Scheme 1.

Two or three titrations of solutions containing different concentrations of the actinide (in the range 25–50 mmol dm^{-3}) were performed at various concentrations of silver(I) (2–10 mmol dm^{-3}). The equilibrium condition imposed on the automatic data-collection apparatus (ΔE = 0.0 mV for 2 min) was generally reached in 4–10 min. All titrations were carried out into a glove-box filled with dry nitrogen and containing silica gel and P_2O_5 as drying agents.

Stability constants of the silver(I)–amine complexes, needed for the calculation of $\bar{n}$ [the average number of ligands bound to uranyl(VI) ion] and [L] (the free amine concentration at the equilibrium condition) had been determined previously.[14,15]

The program SUPERQUAD[16] was employed to obtain the stability constants giving the best fit of the experimental data.

Owing to the large difference between the stability constants of the complexes formed by the metal ions and ahd, the method of competitive reactions was inapplicable to the UO_2^{2+}–Ag^+–ahd system. In a previous study on the complexation of uranyl(VI) by thiourea,[8] which also bonds preferentially silver(I), we could only obtain an estimate of β_{ML} and ΔH°_{ML} by simultaneous variation of these parameters in the minimization of the calorimetric data,[17] even though there were some limitations to the usage of this procedure, particularly in the case of fairly weak successive complexes.[18,19] As a recent study[20] indicated that Fourier-transform IR spectroscopy might be successfully used to obtain the formation constants of relatively weak complexes, we resorted to this technique in order to have an independent measure of the thermodynamic stability for both the uranyl(VI)–ahd and –tn systems.

Thus Fourier-transform IR spectra of solutions containing the amine and uranyl(VI) ion, in a 28 μm pathlength BaF_2 cell, were recorded at 25 ± 1 °C on a Nicolet 5 SX spectrometer with a 4 cm^{-1} resolution and 256 scans. The uranyl(VI) concentration in the solutions was maintained at 50 mmol dm^{-3} in all the experiments while the amine concentration varied from *ca.* 25 to *ca.* 150 mmol dm^{-3}. The preparation of the metal–amine solutions and the filling of the cell were performed in a glove-box. Numerical subtraction of the solvent spectrum from the solution spectra allowed us to obtain the difference spectra reported. The vibration $\nu_{asym}(NH_2)$ at 3360 cm^{-1} was chosen for quantitative measurements of the concentration of free amine in solution. It has a relatively high molar absorption coefficient and, due to the red shift of the stretching frequencies of the bonded amine, it appeared to be almost free from interferences. As a consequence, we constructed plots of A^{max}_{3360} *vs.* c_L, where L = amine, by measuring, with the baseline method,[21] the absorbances at the maximum of this band for a series of solutions containing increasing amine concentration (from 25 to 150 *ca.* mmol dm^{-3}). Successively, we calculated with the same method the free amine concentration in the solutions containing uranyl(VI). Simple mass-balance equations allowed calculation of the stability constants.

Determination of the Enthalpy Changes.—The reaction enthalpies were measured at 25.000 ± 0.001 °C with a Tronac titration calorimeter (model 87-558) modified in order to avoid contamination of the solutions by moisture.[9] Periodic checks of the accuracy and reproducibility of the apparatus gave an average heat of neutralization of tris(hydroxymethyl)methylamine with 0.1 mol dm^{-3} HCl ($\Delta H^\circ = -47.49 \pm 0.05$ kJ mol^{-1}) in agreement with the accepted value.[1]

Each uranyl(VI)–amine system was studied by carrying out two series of calorimetric titrations. The type (*a*) titrations were performed by adding an amine solution ($250 < c_L^0 < 500$ mmol dm^{-3}) to 20 cm^3 of a uranyl(VI) perchlorate solution ($25 < c_M^0 < 50$ mmol dm^{-3}). In the type (*b*) titrations the reagents were exchanged and a metal-ion solution (C_M^0 *ca.* 50 mmol dm^{-3}) was added to the amine solution (20 cm^3; $50 < c_L^0 < 1000$ mmol dm^{-3}) contained in the calorimeter reaction cell.

The experimental values of the heat changes were corrected for the heat of dilution of the titrant solution, which was determined in separate runs. The heats of dilution of the titrates were found to be negligible.

The quantity Δh_v, the total enthalpy change per mole of metal ion, was chosen to present the experimental results as it possesses some useful properties: (*i*) it allows normalization of the experimental heats of reaction, q_p, and makes it easier to check the agreement among experimental data concerning different titrations; (*ii*) it allows an immediate evaluation of ΔH_j° when highly stable mononuclear complexes, ML_j, are formed (see below); (*iii*) it is noticeably affected by the occurrence of side reactions (for example, hydrolyses due to the presence of traces of water in the solutions). When only mononuclear metal–ligand complexes are formed in solution the mathematical relationship between the experimental data (q_p, V_p, and c_M) and the equilibrium-defining parameters (β_j and ΔH_j°) in Δh_v is in equation (1) where n is the number of experimental measurements, q_p the pth experimental heat change, c_M is the metal concentration and V_p the volume of the test solution, m is the maximum number of ligands bound to the metal ion in the complexes ML_j, β_j and ΔH_j° are the thermodynamic parameters for the formation of the jth complex, and $[L]_p$ is the concentration of free amine at the pth point. One can deduce that the value of Δh_v at $c_L/c_M = j$ corresponds to ΔH_j°, if the β_j value is large enough. Similarly, when $c_L/c_M \gg m$ [type (*b*) titrations], the Δh_v values for titrations of solutions containing different metal-ion concentrations are equal to ΔH_m° if the mth complex is sufficiently stable, otherwise they differ.

$$\Delta h_v = \frac{\sum_{p=1}^{n} q_p}{c_M V_p} = \frac{\sum_{j=1}^{m} \beta_j [L]_p{}^j \Delta H_j^\circ}{1 + \sum_{j=1}^{m} \beta_j [L]_p{}^j} \qquad (1)$$

The program LETAGROP KALLE[22] was used to calculate the enthalpies of reaction.

Results and Discussion

Uranyl(VI) *with N-Donors.*—The plots in Fig. 1 represent the results of some selected potentiometric measurements on

Table 1 Overall stability constants and thermodynamic functions for uranyl(VI)–polyamine complexes in dmso at 25 °C and ionic strength 0.1 mol dm^{-3}. $\Delta\nu_{sym}$ corresponds to the shift toward lower frequencies of the symmetrical NH_2 stretching in the bonded amines. The errors given are three times the estimated standard deviations or, for log β_{1n}, three times the error calculated by the graphical extrapolation method

Amine	Complex	log β	$-\Delta G^\circ$/kJ mol^{-1}	$-\Delta H^\circ$/kJ mol^{-1}	$-\Delta S^\circ$/J K^{-1} mol^{-1}	$\Delta\nu_{sym}$/cm^{-1}
en[a]	ML	3.88	22.1	41.4	64	170
	ML_2	5.88	33.6	76.7	145	
dien[b]	ML	6.60	37.7	59.9	74	170
trien	ML	7.63 + 0.02	43.5 ± 0.2	70.0 ± 0.2	89	163
dadd	ML	3.75 ± 0.02	21.4 ± 0.1	47.3 ± 0.3	87	156
tn	ML	1.71 ± 0.15	9.8 ± 0.2	23.0 ± 1.2	44	153
	ML_2	2.14 ± 0.27	12.2 ± 1.5	40 ± 5		
ahd	ML	0.75 ± 0.19	4.3 ± 1.1	23.4 ± 1.6	64	137

[a] Ref. 8. [b] Ref. 9.

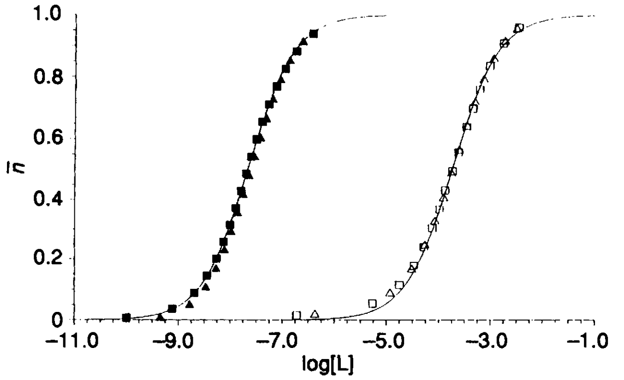

Fig. 1 Complex formation functions for the uranyl(VI)–trien (■, c^0_M, $c^0_{Ag^+}$ = 47.9, 4.95; ▲, 29.1, 8.75 mmol dm^{-3}) and –dadd (□, c^0_M $c^0_{Ag^+}$ = 45.9, 3.68; △, 37.5, 2.80 mmol dm^{-3}) systems. Water content < 2 mmol dm^{-3}. The full curves were obtained using the values of β reported in Table 2

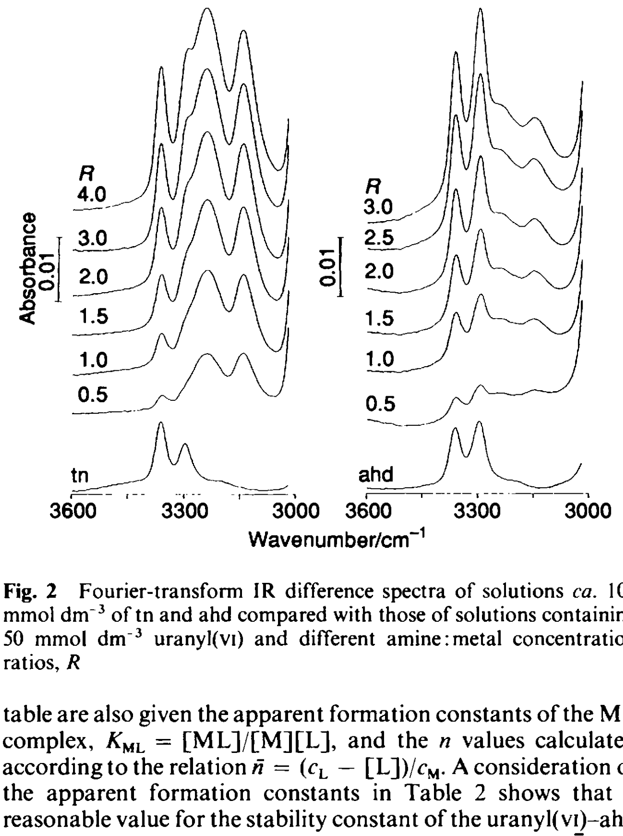

Fig. 2 Fourier-transform IR difference spectra of solutions *ca.* 100 mmol dm^{-3} of tn and ahd compared with those of solutions containing 50 mmol dm^{-3} uranyl(VI) and different amine:metal concentration ratios, *R*

UO_2^{2+}/Ag^+–trien and –dadd. For each system, in the range $\bar{n}$ 0–1, the formation curves for measurements taken at different c^0_M and at the lowest water concentration attainable overlap within the limits of experimental errors indicating that no polynuclear or hydrolysed complexes are formed in appreciable amount. The shape of the curves suggests that uranyl(VI) behaves in a qualitatively similar manner toward trien and dadd: in both cases only the 1 : 1 complex is formed. Evidently, due to its higher stability, the complex UO_2^{2+}–trien forms at lower amine concentrations. The stability constants of these complexes are reported in Table 1.

As anticipated in the Experimental section, stability constants of the uranyl(VI)–ahd and –tn complexes were evaluated by Fourier-transform IR measurements. In Fig. 2 are reported the spectra of solutions containing *ca.* 50 mmol dm^{-3} uranyl(VI) and different concentrations of the amines. In particular, the NH_2 stretching region, where absorptions arising from the primary nitrogen of the co-ordinated and unco-ordinated amine appear, is shown. In this spectral window the weak stretching band of the secondary amine group also occurs.[23,24] This, probably, causes the changes in the relative peak absorbances of the amines (see the spectra in the lower part of Figs. 2 and 3).

All the spectra in Fig. 2 show the presence both of free (ν_{asym} 3360, ν_{sym} 3294 cm^{-1}) and bonded (ν_{asym} 3255 and 3239, ν_{sym} 3157 and 3141 cm^{-1} for ahd and tn respectively) amine groups. This allowed the measure of reliable values of the absorbances at 3360 cm^{-1} from which the free amine concentrations, [ahd] or [tn], were calculated.

The analytical concentrations of the amines, c_L, and the corresponding values of A^{max}_{3360} and [L] at different amine to metal ratios, $R = c_L/c_M$, are reported in Table 2. In the same table are also given the apparent formation constants of the ML complex, $K_{ML} = [ML]/[M][L]$, and the *n* values calculated according to the relation $\bar{n} = (c_L - [L])/c_M$. A consideration of the apparent formation constants in Table 2 shows that a reasonable value for the stability constant of the uranyl(VI)–ahd complex can be obtained by averaging the K_{ML} values ($\bar{K}_{ML}$ = 5.6 ± 0.8 dm^3 mol^{-1}). For the UO_2^{2+} –tn system the regular increase of K_{ML} with c_L indicates formation of at least one complex besides the first one. In this case a plot of $(1 - \bar{n})[L]/\bar{n}$ *vs.* $(2 - \bar{n})[L]^2/\bar{n}$ should give a straight line with slope $-\beta_2/\beta_1$ and intercept $1/\beta_1$.[25] Indeed, elaboration of the experimental data gave related values which follow a linear trend from which the β_1 and β_2 values in Table 1 were obtained.

Above, we implicitly assumed that tn forms a chelate using both the terminal amine groups. This is the most immediate interpretation of the experimental evidence which suggests tn gives two (though weak) successive complexes, while butylamine does not significantly interact with uranyl(VI) at the concentrations adopted in the present study.[8]

In the case of the UO_2^{2+}–ahd complex, however, only one of the primary amine groups could be involved, with the secondary one, in the formation of a chelate ring without apparent changes in the shape of the spectra of the complex in Fig. 2. In this case, the absorption at 3360 cm^{-1} would account both for the free amine and for the non-bonded group. Therefore, the values of the effective free amine concentrations would be smaller than those in Table 2. This hypothesis has been tested.

Table 2 Analytical concentrations of the amines, c_L (L = ahd or tn), and the corresponding values of A^{max}_{3360} and [L] at different amine to metal concentration ratios, *R*; K_{ML} corresponds to the apparent formation constant of the ML complex and *n* is the average number of ligands bound to each metal atom

	UO_2^{2+}-ahd					UO_2^{2+}-tn				
R	c_L/ mmol dm^{-3}	A^{max}_{3360}	[ahd]/ mmol dm^{-3}	K_{ML}	$\bar{n}$	c_L/ mmol dm^{-3}	A^{max}_{3360}	[tn]/ mmol dm^{-3}	K_{ML}	$\bar{n}$
0.5	25.5	0.0026	20.8	5.0	0.094	25.3	0.0013	8.6	58.3	0.334
1.0	51.1	0.0054	42.6	4.8	0.170	50.5	0.0033	21.9	61.0	0.572
1.5	76.6	0.0079	62.4	6.4	0.285	75.8	0.0058	38.5	76.3	0.746
2.0	102.1	0.0109	86.1	5.5	0.321	101.0	0.0087	57.8	109.9	0.864
2.5	127.7	0.0135	106.5	6.9	0.425	126.3	0.0116	77.1	797.7	0.984
3.0	153.2	0.0169	133.0	5.1	0.404	151.5	0.0150	99.7	—	1.036
4.0	—	—	—	—	—	202.0	0.0216	143.5	—	1.170

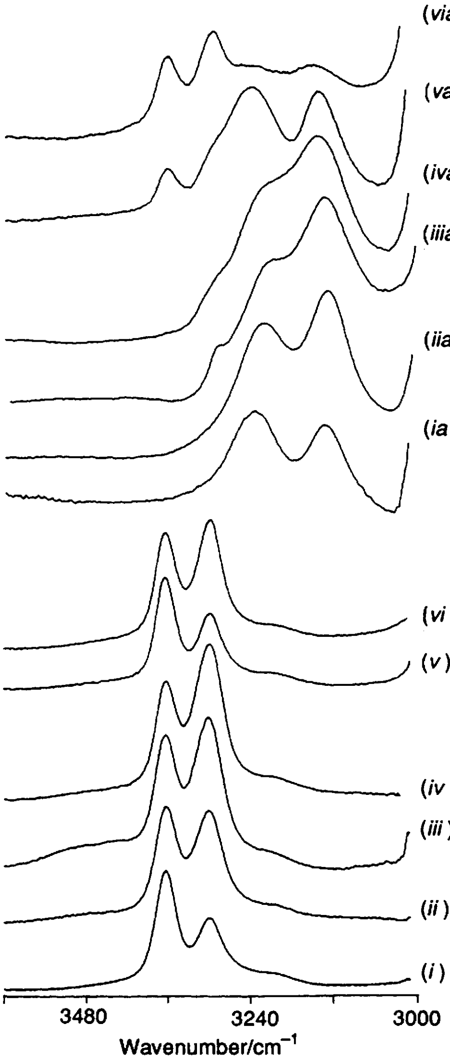

Fig. 3 Fourier-transform IR difference spectra of solutions of *ca.* 0.1 mol dm^{-3} of the amines in dmso [(*i*) en, (*ii*) dien, (*iii*) trien, (*iv*) daad, (*v*) tn, (*vi*) ahd]. Spectra (*ia*)–(*via*) refer to solutions containing uranyl(VI) perchlorate and the respective amine in equal concentrations (*ca.* 50 mmol dm^{-3}). Absorbances on arbitrary scale

New values of [L] were calculated for each of the spectra in Fig. 2 and the corresponding values of K_{ML} evaluated. The stability constants so obtained were randomly dispersed in a wider range ($14 < K_{ML} < 65$) than that in Table 2 with a standard deviation on $\bar{K}_{ML}$ ($\bar{K}_{ML} = 31 \pm 17$ dm^3 mol^{-1}) much greater than that obtained with the original assumption. Hence, this last hypothesis has been rejected.

In Fig. 3 part of the spectra in dmso of the polyamines considered is shown along with the corresponding spectra obtained when an equal concentration of uranyl(VI) is also present. As can be seen, in accordance with the lower stability of their complexes, only the spectra referring to uranyl(VI)–tn and –ahd [(*va*), (*via*)] show the characteristic absorption bands of both free and co-ordinated amine, whereas no evidence of unco-ordinated amine is seen for the other systems. Moreover, the spectral patterns show an approximately equal red shift ($\Delta\nu_{sym}$ in Table 1) of the NH_2 stretching bands for all the complexes formed, indicating similar metal–nitrogen interactions.

The results of some 'type (*a*)' calorimetric titrations with trien and dadd are reported in Fig. 4. Some of these titrations were carried out by minimizing the water content in the solutions (full symbols), in others the water content was increased to approximately 200 mmol dm^{-3}. In such a way it was possible to elucidate the effects of water on the equilibria in solution (see below for a detailed discussion). The dotted lines in Fig. 4 represent the average value of the heat per mole of uranyl(VI) added to a solution containing an excess of amine [type (*b*) titrations] once the thermal effects due to the formation of the mixed hydroxo complexes between amine, water, and uranyl(VI) ion have been accounted for following the procedure adopted in ref. 9. The good agreement between the results of the type (*a*) and (*b*) titrations unambiguously demonstrates that, at the lowest attainable water concentration in solution, trien and dadd do not show any tendency to form complexes higher than ML. This agrees with the conclusion drawn from the potentiometric measurements. The ΔH° and ΔS° values for these complexes are reported in Table 1.

The different paths taken by the Δh_v curves for type (*a*) titrations of uranyl(VI) perchlorate with ahd (Fig. 5) reflect the low stability of the ML complex. The fit between the experimental Δh_v values and those calculated with the enthalpy change and the stability constants reported in Table 1 (full lines in the figure) is considered very good taking into consideration the low net reaction heat and the possible errors in the evaluation of the thermal effects due to the hydrolysis reaction.

For the uranyl(VI)–tn complexes the values of ΔH_j° and ΔS_j° in Table 1 are those recalculated by using the new stability data, evaluated from Fourier-transform IR measurements, and the heat changes previously determined.[8] These results indicate that the description of this co-ordination system formerly given was a simplification of a more complex equilibrium involving the formation of two successive complexes contemporaneously present in the solution, the second one being particularly weak. The value of β_j for the UO_2^{2+}–tn complex found in this work confirms the previous findings on the large difference in affinity of en and tn towards the uranyl(VI) ion, but the recalculated thermodynamic parameters indicate that this difference is due

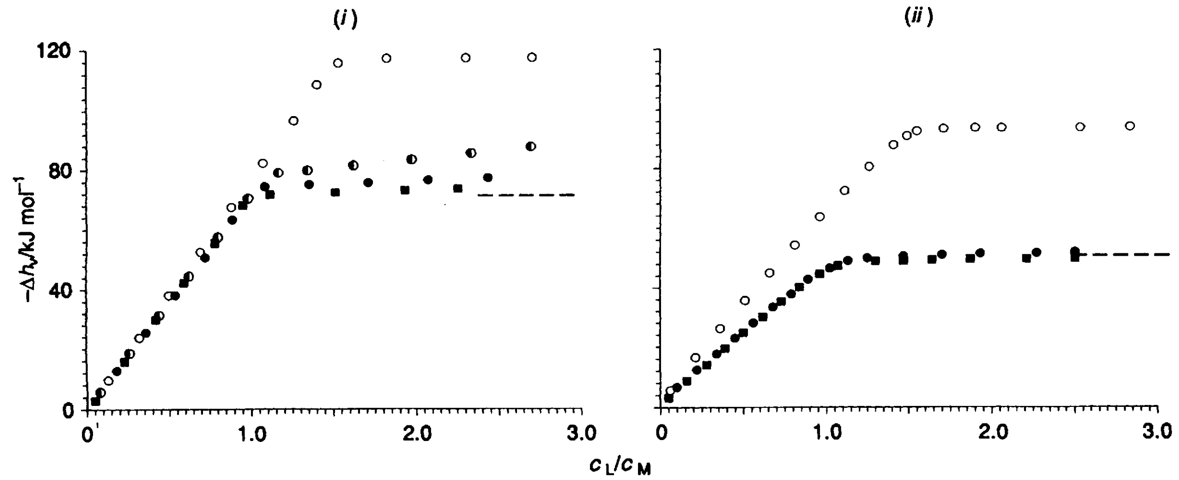

Fig. 4 Total enthalpy change per mole of metal ion (Δh_v) as a function of the amine:metal concentration ratio for uranyl(VI)–trien (*i*) and – dadd (*ii*) systems is shown; c^0_M and c^0_L represent the uranyl(VI) and amine concentrations in mmol dm^{-3}; $c^0{}_{H_2O(M)}$ and $c^0_{H_2O(L)}$ the estimated concentrations of water in the metal-ion and amine solutions. c^0_M, $c^0_{H_2O(M)}$, c^0_L, $c_{H_2O(L)}$; (*i*) 26.6, ≈1, 454, ≈1 (●); 49.8, ≈1, 454, ≈^{1} (■); 26.6, ≈, 454, ≈30 (◐); 25.1, ≈ 200, 454, ≈200 (○); (*ii*) 24.8, ≈1, 532, ≈1 (●); 49.6, ≈1, 532, ≈1 (■); 25.2, ≈200, 534, ≈200 (○)

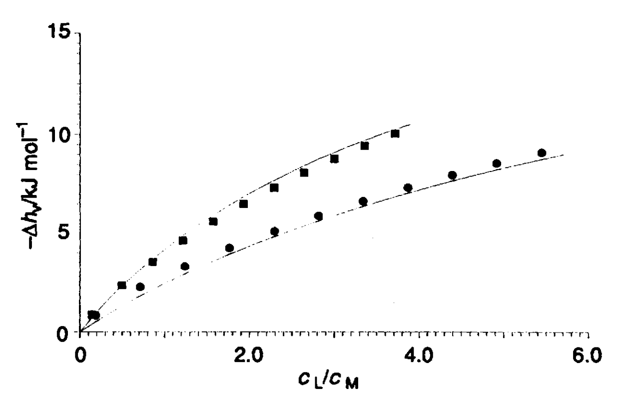

Fig. 5 Plots of Δh_v *vs.* the amine to metal concentration ratio for the uranyl(VI)–ahd system: c^0_M = 48.1 (■) or 22.9 mmol dm^{-3} (●); water content < 2 mmol dm^{-3}. The full curves were calculated from the values of β and ΔH° in Table 1

to the enthalpic factor rather than to the entropic one, as previously suggested. This last result emphasizes the importance of applying, whenever possible, independent methods to determine stability constants and enthalpy changes in complex-formation studies.[18,19]

A consideration of the values in Table 1 shows that all the uranyl(VI) complexes with polyamines are enthalpy stabilized whereas the entropy changes oppose the complex formation. Ethylenediamine and diethylenetriamine complexes, containing only five-membered chelate rings, are more stable than those of tn and ahd involving six-membered rings. Thermodynamic data show that the more negative free-energy change for the formation of en and dien complexes is exclusively due to a more negative enthalpy change. The entropies of reaction, all negative, increase in an order opposite to that of the relative stabilities; *i.e.* the less-stable complexes have the least unfavourable entropy changes. Recently Hancock and co-workers[26,27] demonstrated that, in metal complexes containing en and tn chelate rings, the five-membered rings have a minimum strain energy when the metal–nitrogen distance is 2.5 Å and the N–M–N angle is 69°, whilst the strain in a six-membered chelate is minimized when M–N is 1.6 Å and N–M–N 109°. Unfortunately, no structural data on the complexes of uranyl(VI) with chelating polyamines were available until now. However, the molecular structures of the complexes of $UO_2{}^{2+}$ with salen[28] [H_2salen = *N,N'*-bis(salicylidene)ethane-1,2-diamine] and saldien[29] [H_2saldien = *N,N'*-bis(salicylidene)-3-azapentane-1,5-diamine], forming respectively one and two five-membered chelate rings assimilable to those of en and dien, show that the mean U–N distance (2.56 Å) and the N–U–N angle (66–67°) fit very well the values required for the ideal non-strained geometry of the five-membered rings. On account of the rather large size of the uranyl(VI) ion, the formation of a six- instead of a five-membered chelate ring results in an increase in strain energy and thus a decrease in complex stability.[26,27] This is consistent with the data in Table 1.

Formation of complexes containing two or three fused chelate rings in planar co-ordination implies an increase in steric constraints[30–32] so a decrease in the average heat evolved per mole of bonded nitrogen is observed both for complexes containing five- (20.7, 20.0 and 17.5 kJ mol^{-1} for en, dien and trien complexes, respectively) and for those with six-membered rings (11.5 and 7.7 kJ mol^{-1} for tn and ahd). However, an important difference emerges between the two classes of compounds. For the complexes of en, dien and trien the heat of reaction increases much more than the reaction entropy decreases. Hence, the stability of the complexes with five-membered chelate rings is progressively favoured on going from en to trien. On the contrary, the formation of two relatively unstable six-membered chelate rings in $[UO_2(ahd)]^{2+}$ results in a reaction enthalpy that cannot compensate the decrease in entropy and consequently the complex is less stable than that of tn.

It is of interest that the average heat per mole of bonded nitrogen evolved when the 1 : 1 lanthanide(III)–en, –dien and –trien complexes are formed in dmso[33,34] increases, more or less regularly, on going from en to trien. Evidently, this trend indicates that the large number of co-ordination sites of the lanthanide(III) ions allows co-ordination of the amines in less strained configurations than those for the same ligands in the equatorial plane of the uranyl(VI) ion. In other words, the steric constraints of the ring system depend also on the geometric requirements of the central metal ion.

As for the $[UO_2(dadd)]^{2+}$ complex, its stability is close to that of the en complex, but there is no doubt that all the four nitrogen atoms of the ligand are co-ordinated to form chelate rings. The infrared spectrum (*iva*) in Fig. 3 does not show any band in the region 3000–3600 cm^{-1} which can be attributed to unco-ordinated amine groups when the $UO_2{}^{2+}$: dadd ratio is equal to 1 : 1. This clearly reflects a noticeable synergism between the en and tn subunits forming this complex. The value of $\Delta\nu_{sym}$, intermediate between that of trien and tn, confirms that, if one of the two atoms forming a six-membered chelate ring is firmly bonded to the metal ion, closure of the ring occurs easily and with a lower energy demand. Compare, for example,

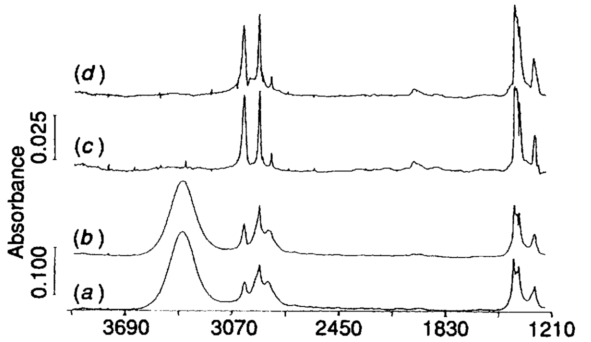

Fig. 6 Difference IR spectra for the uranyl(VI)–ethylene glycol system. See text for comments

$(\Delta H^\ominus_{1\,(\mathrm{dadd})} - \Delta H^\ominus_{1\,(\mathrm{trien})})/2 = 11.35$ kJ mol^{-1}, which might be taken as a rough measure of the steric strain counteracting the formation of a six-membered ring in the $[\mathrm{UO_2(dadd)}]^{2+}$ complex, with the values of $(\Delta H^\ominus_{1\,(\mathrm{tn})} - \Delta H^\ominus_{1\,(\mathrm{en})}) = 18.4$ kJ mol^{-1} and $(\Delta H^\ominus_{1(\mathrm{ahd})} - \Delta H^\ominus_{1(\mathrm{dien})})/2 = 18.2$ kJ mol^{-1} which are a measure of how much the steric constraints in the six-membered chelates 'freely formed' are larger than in the corresponding five-membered chelates.

The entropy values decrease with increase in the molecular complexity in both classes of ligands, those forming five- and those forming six-membered chelates. As is well known, the entropy change corresponding to a complexation reaction of a metal ion is mainly due to two contributions of opposite sign: one, negative, can be ascribed to the loss in total entropy of the metal–ligand system when co-ordination occurs; the other, positive, is due to the release of solvent molecules from the solvation spheres of the reagents. The former contribution becomes more and more negative with increase in the number of species involved in the reaction (translational entropy change) and with the molecular complexity of the ligand (conformational entropy change). The latter contribution, which also depends on possible ligand–solvent specific interactions (*e.g.* hydrogen bonding in water) primarily increases with the charge neutralization of the reacting species and, to a minor extent, with increase in dimensions of the ligand.[35]

In the co-ordination systems considered here, in which neither charge neutralization nor specific ligand–solvent interactions occur, the first contribution largely prevails over the second. Comparison of the data for the $[\mathrm{UO_2(en)_2}]^{2+}$ and $[\mathrm{UO_2(trien)}]^{2+}$ complexes shows the importance of the ligand translational entropy change: the more exothermic formation of the former complex is more than offset by the large loss in entropy due to the co-ordination of two en molecules and, consequently, the latter complex is the more stable. The incidence of the conformational entropy change can be seen in the following sequences of the negative $\Delta S^\ominus_1$ values, which parallel the molecular complexity of the ligands: en < dien < trien and tn < ahd.

The above observations, together with those previously reported and referring to polyamine complexes of lanthanide(III)[33,34] and silver(I)[14,15] in dmso, emphasize the generalization that in complex-formation reactions between a metal cation and uncharged ligands the contribution of the metal-ion desolvation to the total entropy change is of little importance.

Uranyl(VI) *with O-Donors.*—As the experimental results obtained for the various uranyl(VI)–glycol systems $\mathrm{HOCH_2(CH_2OCH_2)_nCH_2OH}$ (n = 0–2) were qualitatively analogous, only the results obtained with ethylene glycol (n = 0) are reported in detail in Fig. 6. Spectrum (*a*) refers to a solution of *ca.* 200 mmol dm^{-3} of the glycol, (*b*) to a solution containing *ca.* 50 mmol dm^{-3} $\mathrm{UO_2}^{2+}$ and *ca.* 200 mmol dm^{-3} glycol; (*c*) is the result of the numerical subtraction of (*a*) from (*b*) and (*d*) is the spectrum of a *ca.* 50 mmol dm^{-3} uranyl(VI) solution. For all systems the difference spectra (*c*) and the metal-ion spectra (*d*) were substantially identical in the range 4000–1200 cm^{-1} where the characteristic bands of the glycols ($\nu_{\mathrm{OH}} \approx 3360$, $\delta_{\mathrm{OH}} \approx 1440$ cm^{-1})[21] appear. Moreover, no heat effects were observed in performing either type (*a*) or (*b*) calorimetric titrations on the same systems. These findings give a clear indication that no interaction between the glycols and the uranyl(VI) ion takes place in dmso.

Effect of Water on the Equilibria in Solution.—In previous studies[8,9] we carefully elucidated the effects of the presence of water in the calorimetric titrations of uranyl(VI) by amines and polyamines in dmso. It was shown how to minimize and to account for the thermal effects due to the unavoidable presence of this reagent in solution. Also that hydrolysis reactions do not considerably influence the equilibria of formation of the very stable 1 : 1 complexes of uranyl(VI) with en[8] and dien[9] whereas they seriously affect measurement of the enthalpies of formation of the less-stable complexes with the monoamines and tn. A comparison between the curves in Fig. 4, obtained in the absence and presence of significant amounts of water, shows the effects of this reagent on the reaction enthalpies of the present systems. The experimental results can be explained in terms of three competing equilibria: (2), metal–ligand complex formation; (3) hydrolysis of the ligand; (4), generic hydroxo-complex formation.

$$\mathrm{UO_2}^{2+} + \mathrm{L} \rightleftharpoons [\mathrm{UO_2L}]^{2+} \tag{2}$$

$$\mathrm{L} + n\mathrm{H_2O} \rightleftharpoons \mathrm{H}_n\mathrm{L}^{n+} + n\mathrm{OH}^- \tag{3}$$

$$p\mathrm{UO_2}^{2+} + q\mathrm{L} + r\mathrm{OH}^- \rightleftharpoons [(\mathrm{UO_2})_p\mathrm{L}_q(\mathrm{OH})_r]^{(2p-r)+} \tag{4}$$

As already pointed out,[8] the prevalence of reaction (2) over (4) depends on the relative values of the corresponding equilibrium constants as well as on the amounts of water in solution. To simplify the discussion we will consider an equal concentration of water in all the solutions. In this case the extent of reaction (4) is strongly dependent on the relative value of the equilibrium constant for (3), *i.e.* on the basicity of the amines. Taking into account that the values reported for the ionization constants of some protonated alkylamines show only minor changes when the solvent is changed from water to dmso,[36,37] it seems reasonable to assume that the difference between the protonation constants K_n (n = 1–4) of trien and dadd is the same in water and in dmso. In water, dadd is slightly more basic than trien ($\Delta\log K_1 = 0.79$, $\Delta\log K_2 = 0.69$, $\Delta\log K_3 = 1.74$, $\Delta\log K_4 = 2.34$)[1] and reasonably this should be true also in dmso. Moreover, observation of equilibria (2)–(4) reveals that protonation of the ligand, reaction (3), should be easier the lower is the complex-formation constant. In this respect, formation of mixed-hydroxo complexes following reaction (4) in the dadd system is doubly favoured and for this reason it can take place contemporaneously to metal complex formation. On the other hand, due to the lower basicity of trien and especially to the higher stability of its uranyl(VI) complex, reactions (3) and (4) can only occur at $c_\mathrm{L}/c_\mathrm{M} > 1$ in the $\mathrm{UO_2}^{2+}$–trien system. This different behaviour of the two amines is clearly shown in Fig. 4 where the overlap of the data referring to the various concentrations of water in the range $0 < c_\mathrm{L}/c_\mathrm{M} < 1$ is good only for trien.

In the previous study on the complexation of uranyl(VI) with en,[8] which forms a 1 : 1 complex having stability comparable to that of the analogous complex with dadd, the hydrolysis reaction was observed only at $c_\mathrm{L}/c_\mathrm{M}$ values higher than 1. A convincing explanation of the different hydrolytic behaviours of these amines can be found in their different basicity. The more basic dadd (in water, $\log K_1 = 9.89$ and 10.53, $\log K_2 = 7.08$ and 9.77 for en and dadd, respectively)[1] can set free by hydrolysis [reaction (3)] a larger quantity of OH^- ions which, in turn, causes formation of hydroxo-complexes at a lower c_L/c_M value.

Conclusion

Uranyl(VI) forms stable complexes with polyamines in anhydrous dmso, but not with the structurally analogous polyglycols. The amines forming one or more five-membered chelate rings (en, dien, trien) give very stable uranyl(VI) complexes; tn and ahd, which are able to give only six-membered chelates, do not show such a marked affinity. All the complexes are enthalpy stabilized, the entropy terms counteracting the reactions. The lower stability of the tn and ahd complexes is mainly attributable to the steric strain disfavouring the formation of the six- in comparison with the five-membered chelate ring. The fact that polyglycols having the same molecular frameworks as the polyamines considered do not interact with the uranyl(VI) ion in dmso, shows that N donors exhibit a much higher affinity for uranyl(VI) than do O donors. The formation of hydroxo-complexes and/or mixed hydroxo-complexes due to the presence of water in solution mainly prevents formation of the less-stable uranyl(VI)–amine complexes.

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