Thermodynamics of Lanthanide(III) Complexation with Ethylenediamine in Dimethyl Sulfoxide

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The thermodynamics of complex formation of lanthanide(III) ions with the neutral nitrogen-donor ligand ethylenediamine has been studied in the anhydrous aprotic solvent dimethyl sulfoxide at 25 °C and in an ionic medium, 0.1 mol dm^{-3} NEt_4ClO_4. The stability constants of the complexes and hence the free-energy changes have been determined by potentiometry and the heats of formation by direct calorimetric measurements. All the complexes are formed in exothermic reactions whereas the entropy terms are unfavourable. Fourier-transform infrared spectroscopic measurements have also been carried out in order to obtain some information on the interaction between the ligand and the metal ions. The results are discussed in terms of the charge density of the metal ions and of solvation changes occurring along the series.

The solvation and complexation of the trivalent lanthanide cations are dominated by strong ion–dipole interactions. The number of ligand donor atoms and their arrangement in the primary co-ordination sphere of the metal are the result of the interplay between steric and electrostatic factors.[1] As a result of the ionic nature of the bonding, the lanthanide(III) ions do not display the restricted stereochemistry typical of d transition metals but are rather characterized by variable co-ordination numbers and geometries. Thus, for rare-earth metal ions, co-ordination numbers ranging from three to 14 have been observed in the solid state,[2,3] whereas in aqueous solution co-ordination numbers of nine for lighter lanthanide ions and eight for heavier ones have been reported.[4]

To date, most studies in solution on the complex formation of lanthanides(III) have been carried out in aqueous solution. In this medium the lanthanides(III) behave as typically 'hard' acid cations and appear to have a considerable affinity for oxygen, nitrogen and fluoride donor atoms.[5,6] Much less attention has been paid to non-aqueous solvents in which high co-ordination numbers are also common. Recent studies indicate that eight- and nine-co-ordinate species are present in anhydrous solvents[7–9] and for europium(III) and terbium(III) the co-ordination numbers are larger in organic solvents than in water.[9,10]

The numerous solution studies during the last decades have however not yet resolved certain aspects of the co-ordination chemistry of the lanthanides(III). For instance, the questions of a change in co-ordination number in the middle of the series, the bonding mode (inner or outer sphere) for specific ligands, and covalent effects which may be present in the bonds are still debated.[6] On the other hand, as these ions are being increasingly used as probes of chemical systems and scientific and technological interest in them has grown, a more complete understanding of their co-ordination chemistry would be very useful. In this respect the determination of thermodynamic functions such as the changes in free energy, enthalpy and entropy upon complexation in different solvent media are useful quantities.

As mentioned above, the lanthanides(III) bond preferentially to oxygen, nitrogen and fluoride donor atoms. In aqueous solution, the co-ordination properties of neutral nitrogen atoms toward the lanthanides are strongly enhanced when negatively charged oxygen donors are also present in the ligands. Studies of complexation by a variety of aminopolycarboxylates have provided evidence of the existence of strong Ln^{III}–N interactions.[1,11,12] On the other hand, ligands containing nitrogen donor atoms only, such as amines and polyamines, cannot be studied in aqueous solution as they are protonated in the pH region where the hydrolysis of the lanthanide(III) ions is negligible. Therefore, equilibrium measurements on the interactions between these species must be performed in aprotic media: the use of non-aqueous solvents eliminates problems associated with metal ion hydrolysis and protonation of the ligands.

We have chosen, therefore, the dipolar aprotic solvent dimethyl sulfoxide (dmso) to investigate the interactions in solution between lanthanides and ethylenediamine (en), a ligand co-ordinating only through nitrogen. The purpose of the present investigation was primarily to provide quantitative information on the thermodynamic stability of the cations with a neutral N-donor ligand in an aprotic solvent and then compare the data obtained in dmso with the corresponding values previously determined[13] for the same system in acetonitrile, a poorly co-ordinating solvent for the lanthanides(III).

In order to obtain qualitative information on the interaction between lanthanides and en in dmso, Fourier transform infrared (FTIR) spectra were recorded for some representative lanthanides. As stressed in a recent paper,[14] this technique gives useful and accurate information on the interaction, occurring in solution, between the ligand amino groups and metal ions. The stability constants of the complexes were obtained from potentiometric mesurements,[15] and the heats of formation determined by calorimetry.

Experimental

Reagents.—Lanthanide perchlorates were prepared by dissolving a slight excess of the 99.99% pure oxides (Aldrich) in

(−) Ag	c_{Ag} mmol dm^{-3} $AgClO_4$ c_M mmol dm^{-3} $Ln(ClO_4)_3 \cdot n$dmso c_L mmol dm^{-3} en I = 0.1 mol dm^{-3}	NEt_4ClO_4 0.1 mol dm^{-3}	$AgClO_4$ 0.1 mol dm^{-3}	Ag(+)	(1)

reagent grade perchloric acid. The mixtures were heated at 50–80 °C for 4–5 h and the excess of the oxides filtered off. An excess of dimethyl sulfoxide was then added to the solutions and water was removed by distillation under vacuum. Solids with a not well defined stoichiometry and general formula $Ln(ClO_4)_3 \cdot n$dmso (where n decreases almost regularly from 7.9 for La to 7.1 for Lu) were obtained by precipitation with benzene and/or acetone. After filtration they were dried under vacuum at 50 °C for several days. The lanthanide adducts were characterized by elemental carbon and hydrogen analyses and, for the lanthanide content, by titration with ethylenediaminetetraacetate (edta) using xylenol orange as an indicator.[16] The salt $AgClO_4 \cdot H_2O$ (Fluka) was dried under vacuum at 50 °C for several days and used as such. Ethylenediamine (Merck p.a.) was purified by fractional distillation.[17] The dmso was purified and stored as reported previously.[18] The salt NEt_4ClO_4 (Fluka) was recrystallized from methanol and dried at 110 °C.

Perchlorate stock solutions of the lanthanides were prepared by dissolving weighed amounts of the adducts in dmso. The lanthanide concentrations were checked by titration with edta (see above). Standard solutions of $AgClO_4$ in dmso were prepared and standardized as before.[18] Solutions of the ligand were prepared by dissolving the appropriate weights in dmso and standardized by thermometric titrations with standard $HClO_4$ solutions. All standard solutions were prepared and stored in a glove-box under a controlled atmosphere containing less than 10 ppm of water. The water content in the solutions (typically 10–30 ppm) was determined by a modified Karl Fischer method.[14]

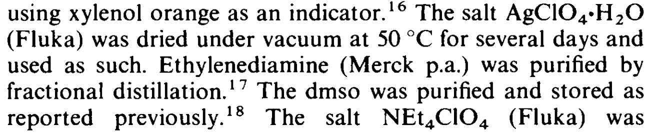

Fig. 1 The FTIR difference spectra (3600–3000 cm^{-1}) of 0.05 mol dm^{-3} $Pr(ClO_4)_3$ in anhydrous dmso in the presence of different amounts of ethylenediamine (R = $[en]_T/[Pr^{3+}]_T$)

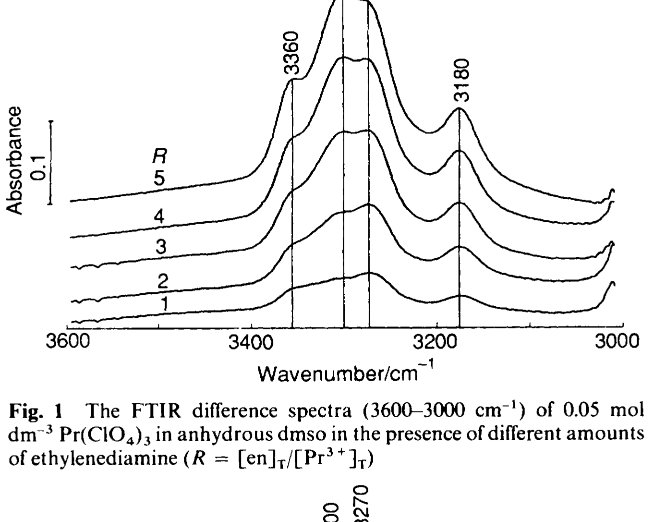

Fig. 2 The FTIR difference spectra (3600–3000 cm^{-1}) of 0.05 mol dm^{-3} $Yb(ClO_4)_3$ in anhydrous dmso in the presence of different amounts of ethylenediamine (R = $[en]_T/[Yb^{3+}]_T$)

Potentiometric Measurements.—Stability constants for the lanthanide(III)–en complexes were obtained *via* potentiometric titration measurements by the method of competititive reactions.[15] Silver(I) was used as auxiliary metal ion and a Ag–Ag^+ electrode as a titration electrode. The experimental data were obtained by measuring the emf of the cell (1).

A PHM 84 Radiometer pH meter, equipped with a Metrohm EA282/2 silver electrode as a working electrode and a Metrohm 440 silver electrode as a reference, was used for the electromotive force measurements. The titrations were conducted in jacketed vessels maintained at 25.0 ± 0.1 °C by circulating silicone oil from a constant-temperature bath. Aliquots of ligand solutions of known concentrations were added to the left-hand cell containing solutions of silver(I) and lanthanide(III) perchlorates of exactly known concentration and the free silver(I) concentration measured after each titrant addition. For each system, three different initial concentrations, c_M^0, of metal ion in the range 10–30 mmol dm^{-3} were used. In order to check that no formation of mixed complexes of the type Ag–L–Ln occurred in solution, all titrations were performed with at least two different initial silver(I) concentrations, ranging from 2 to 10 mmol dm^{-3}. All titrations were repeated two or three times: in all cases the replicate runs agreed quite satisfactorily. Stable readings were usually obtained within 5 min of addition of titrant. The electromotive force measured was usually reproducible within 0.3 mV. The electrode couple was periodically checked in the range $10^{-5} \leqslant [Ag^+] \leqslant 10^{-2}$ mol dm^{-3} in the presence of lanthanide(III) ions. No significant deviations from Nernst's law were observed. All titrations were performed in a glove-box.

Calorimetric Measurements.—A Tronac precision titration calorimeter model 87-588, equipped with a titration vessel (25 cm^3) and interfaced with a North Star-Horizon computer, was used to determine the heats of complexation of lanthanide(III) by en. The calorimetric calibration was checked by tris(hydroxymethyl)methylamine (tham) titrations with HCl and HNO_3 titrations with KOH.[19,20]

The calorimetric titrations were performed by adding ligand solutions of concentration c_L^0 at a constant rate of 0.2116 cm^3 min^{-1} to a known volume of lanthanide solution of concentration c_M^0. For each system investigated generally three titrations were performed with c_M^0 varying from 10 to 30 mmol dm^{-3}. In any case at least one titration was repeated two times: the agreement between different runs was always quite satisfactory. The experimental values of the heat changes were corrected for the heats of dilution of the ligand solutions determined in separate runs. The heats of dilution of lanthanide perchlorate solutions were negligible in the metal concentration ranges used here. All experiments were performed at 25.000 ± 0.001 °C.

The enthalpy changes for the systems investigated were calculated using the least-squares program LETAGROP KALLE.[21]

Spectroscopic Measurements.—The FTIR spectra were

Table 1 Stability constants and thermodynamic functions of lanthanide(III)–en complexes in dmso at 25 °C and $I = 0.1$ mol dm^{-3}; $\Delta G_j^\ominus$ and $\Delta H_j^\ominus$ in kJ mol^{-1}; $\Delta S_j^\ominus$ in J K^{-1} mol^{-1}. The errors given are three times the standard deviations as given by the computer

Ln^{III} (Ionic radius * Å)	Complex	log β	$-\Delta G_j^\ominus$	$-\Delta H_j^\ominus$	$-\Delta S_j^\ominus$
La	ML	1.48(4)	8.4(3)	23(3)	49
(1.061)	ML_2	2.77(5)	15.8(3)	51(4)	118
	ML_3	3.31(10)	18.9(6)	75(8)	188
Pr	ML	1.55(5)	8.8(3)	22.3(1.5)	45
(1.013)	ML_2	2.81(8)	16.0(5)	50.4(2.7)	115
	ML_3	3.50(11)	20.0(6)	82(5)	208
Nd	ML	1.50(6)	8.6(3)	22(3)	45
(0.995)	ML_2	2.89(5)	16.5(3)	52.6(2.8)	121
	ML_3	3.80(12)	21.7(7)	84(8)	209
Sm	ML	1.80(3)	10.3(1)	16.1(1.2)	19
(0.964)	ML_2	3.0(2)	17(1)	42(5)	84
	ML_3	4.3(2)	25(1)	78(5)	178
Eu	ML	1.94(4)	11.1(2)	14.4(1.5)	11
(0.950)	ML_2	3.27(16)	18.7(9)	40(4)	71
	ML_3	4.43(24)	25(1)	72.3(2.7)	159
Gd	ML	2.05(3)	11.7(2)	14.0(1.2)	8
(0.938)	ML_2	3.82(6)	21.8(3)	31.3(2.9)	32
	ML_3	4.98(12)	28.4(7)	72.1(2.7)	147
Tb	ML	2.25(1)	12.8(1)	16.8(1.2)	13
(0.923)	ML_2	3.89(6)	22.2(3)	35.4(2.4)	44
	ML_3	5.28(7)	30.1(4)	71.6(1.8)	139
Dy	ML	2.28(5)	13.0(3)	18.1(0.9)	17
(0.908)	ML_2	4.12(9)	23.5(5)	38.6(1.8)	51
	ML_3	5.49(14)	31.3(8)	77.8(1.8)	156
Ho	ML	2.36(3)	13.5(1)	19.7(1.8)	21
(0.894)	ML_2	4.38(6)	25.0(3)	40.2(2.1)	51
	ML_3	5.68(12)	32.4(7)	85.7(2.7)	179
Er	ML	2.71(6)	15.5(3)	21.1(1.2)	19
(0.881)	ML_2	5.15(6)	29.4(3)	40.8(1.5)	38
	ML_3	6.76(12)	38.6(7)	81.4(2.1)	144
Tm	ML	2.86(3)	16.3(2)	21.6(1.2)	18
(0.869)	ML_2	5.36(3)	30.6(2)	40.7(1.5)	34
	ML_3	7.04(6)	40.2(3)	84.0(1.9)	147
Yb	ML	3.03(3)	17.3(2)	21.7(1.4)	15
(0.858)	ML_2	5.70(6)	32.5(4)	42.6(2.1)	34
	ML_3	7.70(7)	43.9(4)	82.2(2.7)	128
Lu	ML	3.11(3)	17.8(1)	22.2(1.5)	15
(0.848)	ML_2	5.87(3)	33.5(2)	49.1(1.5)	52
	ML_3	7.76(6)	44.3(4)	82.2(1.5)	127

* From ref. 25.

obtained using a Nicolet 5SXC spectrometer, having a maximum resolution of 4 cm^{-1}. Cells with barium fluoride windows and thickness of 0.1 mm were used. The cells were filled in a glove-box and quickly transferred to the spectrometer. Difference spectra for the solvent and solution were recorded separately, ratioed against the background, and transformed into absorbance units. The solvent spectrum (reference) was then numerically subtracted from the solution spectra (sample) by adjusting the degree of subtraction until the peaks common to both sample and reference were nulled as completely as possible.

Results

As mentioned above, preliminary information on the interaction between en and lanthanide ions in dmso has been obtained by FTIR spectroscopy. The interaction of the amino groups with metal ions can be studied by observing the shift of the asymmetrical and symmetrical NH stretching modes of ethylenediamine in dmso, near 3360 and 3300 cm^{-1} respectively,[22] when lanthanide ions are added to the amine solution.

In Figs. 1 and 2 parts of the spectra of a series of solutions containing the same concentration (50 mmol dm^{-3}) of Pr^{3+} and Yb^{3+} and different ligand to metal ratios, R, are reported. Fig. 3 reports IR spectra of solutions containing 50 mmol dm^{-3} Ln^{3+} (Ln = Pr, Sm, Dy or Yb) and 150 mmol dm^{-3} en.

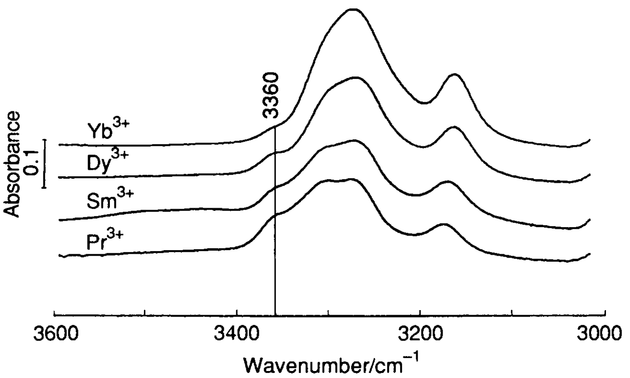

Fig. 3 The FTIR difference spectra (3600–3000 cm^{-1}) of lanthanides(III) 0.05 mol dm^{-3} in anhydrous dmso in the presence of 0.150 mol dm^{-3} ethylenediamine; $R = 3:1$

For all the systems studied a significant and similar bathocromic shift of the NH stretches was observed. Minor changes occurred in the position of the band near 1600 cm^{-1} attributable to the NH bending vibrations.[22] The almost regular bathocromic shift observed in going from praseodymium to ytterbium (ν_{asym} 3275, ν_{sym} 3180 cm^{-1} for Pr^{3+} and 3270 and 3165 cm^{-1} for Yb^{3+}) is expected and may be associated with the increase in charge density on the heavier ions.

A closer look at the spectra of solutions containing the same metal-ion concentration and increasing amounts of amine reveals some differences in the systems investigated. Those for en and praseodymium show that both the amount of bonded amine (band at 3180 cm^{-1}) and free amine (shoulder near 3360 cm^{-1}) increase with the concentration of the ligand, while the absorption of the free amine appears only when $R = 3$ in the Yb–en system. This indicates that Yb^{3+} can form in dmso at least three successive complexes and also that the third one is the weakest. No conclusion can be drawn about the stoichiometry of praseodymium complexes but certainly this metal forms less-stable complexes than those of the heavier lanthanides. It is evident from the spectra in Fig. 3 that the shoulder at 3360 cm^{-1}, proportional to the concentration of uncomplexed amine, decreases in the order Pr > Sm > Dy > Yb, indicating that the complex stabilities increase in the opposite order. On the basis of these results it seems reasonable that ethylenediamine is co-ordinated to the lanthanide ions as a chelate.

More accurate information about the composition of the species formed in solution has been obtained by calculating from electromotive force data the average number of ligands bound to lanthanide(III), $\bar{n}$, using the relationship (2) where [L]

$$\bar{n} = (c_L - \bar{n}'c_{Ag} - [L])/c_M \qquad (2)$$

is the free-ligand concentration and $\bar{n}'$ the average number of ligands bound to silver(I) ion. These values were obtained from the measured free silver(I) concentration and stability constants of complexes of silver(I) with ethylenediamine previously determined.[23]

The complex formation functions thus obtained show that in all cases neither polynuclear nor mixed complexes are formed in appreciable amounts and that all the systems can be described in terms of three mononuclear complexes. The overall stability constants of the co-ordinated species so identified were successively calculated by using the SUPERQUAD program.[24] Their values are reported in Table 1.

In Fig. 4 the average number of ligands bound per metal ion, $\bar{n}$, calculated from (2), is plotted *vs.* log[L] for the Pr–, Sm–, Dy– and Yb–en systems. The agreement between the experimental data and the curves calculated using the constants in Table 1 (solid lines in Fig. 4) is quite satisfactory. The complex

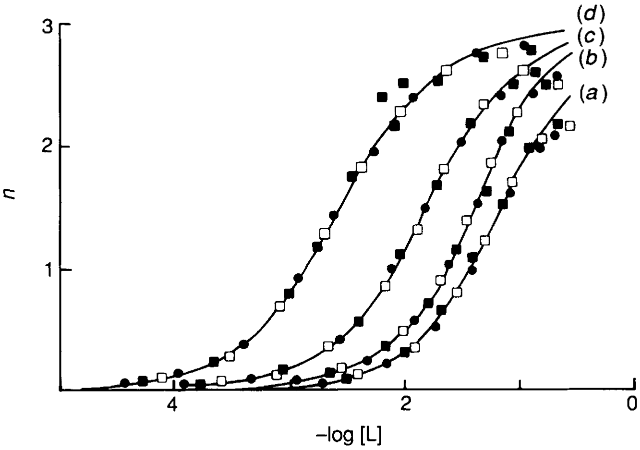

Fig. 4 Complex formation curves of en with (*a*) Pr, (*b*) Sm, (*c*) Dy and (*d*) Yb. Total initial concentrations: (□) $[Ag^+] = 2.01$, $[Ln^{3+}] = 10.20$; (■) $[Ag^+] = 10.07$; $[Ln^{3+}] = 20.40$; (●) $[Ag^+] = 10.07$, $[Ln^{3+}] = 30.60$ mmol dm^{-3}. Only one half of the experimental points, chosen at random, have been plotted. The full curves were calculated from the stability constants in Table 1

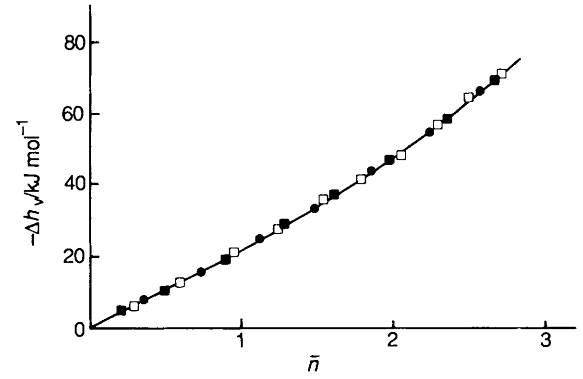

Fig. 5 The total molar enthalpy changes, Δh_v, as a function of $\bar{n}$ for the ytterbium–en system. Total lanthanide(III) concentrations: (●) 10.20; (□) 20.34; (■) 30.01 mmol dm^{-3}. Only one half of the experimental points, chosen at random, have been plotted. The full curve was calculated from constants and enthalpy changes in Table 1 for a total ytterbium(III) concentration of 20 mmol dm^{-3}

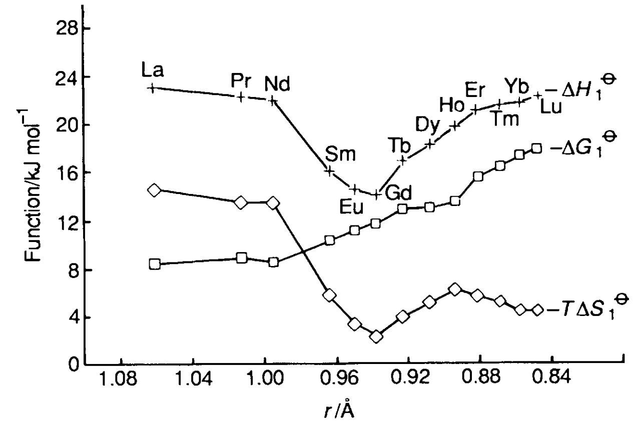

Fig. 6 Lanthanide(III)–en thermodynamic functions as a function of ionic radius at 25 °C and $I = 0.1$ mol dm^{-3}

formation curves for all the other systems are very similar and the set of data reported in Fig. 4 may be regarded as qualitatively representative.

The enthalpies of complexation were calculated from the observed heat changes, after correction for ligand heats of dilution. The complete set of thermodynamic functions for the complex formation of lanthanides with en is reported in Table 1. The fit between experimental and calculated values is quite good. For example, in Fig. 5 Δh_v, the heat evolved per mol of lanthanide(III), is plotted as a function of $\bar{n}$ for the Yb–en system. Similar fits were obtained for all the other systems investigated.

Discussion

The data reported in this paper represent the first consistent set of thermodynamic functions for complexation of lanthanide(III) with a ligand co-ordinating *via* neutral nitrogen atoms in dmso solution. All the complexes are formed in exothermic reactions, while the entropy terms are all negative and therefore unfavourable. Thus the stability of the species in solution is exclusively due to the enthalpy terms.

The data in Table 1 show that the stability constants of the complexes, and hence the ΔG_j° values, rise monotonously with increasing atomic number and with concomitant decrease in the ionic radius of the trivalent lanthanide ions. This trend reveals that the ionic character of the interactions is the most important feature of these complexes.

The enthalpies of formation of lanthanide complexes with en remain more or less constant between lanthanum and neodymium. For the three following elements, samarium, europium and gadolinium, the reactions gradually become less exothermic and then this trend reverses showing a nearly regular increase in enthalpy for the other elements of the series up to lutetium. The entropy values are all negative and far more unfavourable for La, Pr and Nd. A steep decrease occurs at samarium then there is only slight or no variation on going from this element to lutetium. Also in this case gadolinium has the lowest value. These features are well illustrated in Fig. 6 where the free energy, enthalpy and entropy changes for the formation of the first complex of the lanthanides with en are plotted *vs.* the ionic radius of the elements.

The trend in both ΔH_1° and ΔS_1° could be a consequence of some changes in the average co-ordination number along the lanthanide series: such changes are likely to occur after neodymium and extend to gadolinium. Evidence for such a co-ordination switch has recently been reported by Bünzli *et al.*[26] Studying the interaction between lanthanide trinitrates and dmso in anhydrous acetonitrile by FTIR spectroscopy, they concluded that, in the presence of a relatively high concentration of dmso ($R = [\text{dmso}]/[\text{Ln}^{\text{III}}] = 6:1$), the average co-ordination number decreases from 10.2 for La^{3+} to 8.4 for Lu^{3+}, with the main change occurring between samarium and gadolinium. In this context, it is interesting that a similar trend was observed[27,28] for the average co-ordination number of $Ln(ClO_4)_3 \cdot 6H_2O$ in CH_3CN–dmso mixtures: 9.9, 9.3 and 8.7 for Ln = Pr, Nd and Er, respectively, when $R = 20$.

These observations allow us to state that the average number of molecules of solvent present in the first co-ordination sphere of the lighter ions (La–Nd) is higher by one or two units than that of the heavier ones. This does not mean that on the whole the former are more solvated than the latter. Measurements of the heats of solution of several rare-earth-metal chlorides in dmso[29] showed that the negative enthalpy of solution of the solids regularly increases on going from La^{3+} to Yb^{3+}. All this confirms that, despite the fact that heavier ions (Sm–Lu) have a lower number of solvent molecules in the first solvation sphere, they are more strongly solvated.

The enthalpy change of a complexing reaction is the result of a compensation between the energy required for the desolvation (total or partial) of the reagents and the energy set free in the metal–ligand interaction. As is well known, lanthanides are strongly solvated in dmso.[9,10] The complexation reactions between lanthanides and en in this solvent are noticeably exothermic and the ΔS values are negative. This indicates that: (*i*) the interaction of the amino groups of the ligand with metal ions are quite strong, *i.e.* inner-sphere complexes are formed; (*ii*) the translational entropy gain due to the release of solvent molecules from the reacting species does not compensate the decrease in internal entropy of the ligand and the negative entropy change associated with the complex formation.

If we consider the above observations and that concerning the decrease in the average co-ordination number along the lanthanide series, we can tentatively interpret the trend of the thermodynamic functions in Fig. 6. The enthalpy of formation of the complexes of La–Nd with en is more exothermic than that of the subsequent elements (Sm–Lu) because of the lower energy required to remove a solvent molecule from the first co-ordination sphere of the former. The increasingly negative enthalpy change, on going from Gd to Lu, is expected because the higher charge density of the heavier lanthanides favours the electrostatic ligand–metal ion interaction.

The interpretation of the entropy changes is less immediate and requires some preliminary considerations. The negative sign of ΔH_j° and ΔS_j° for these reactions in dmso (see Table 1) is opposite to that generally found in aqueous solution for the complexation of lanthanides with a wide variety of charged ligands. In water, lanthanide ions are known to have a large hydration sphere and the enthalpy and entropy changes accompanying their complexation are largely determined by the desolvation of the ions and by the lowering of the effective charge on the metal.[30] Thus, the formation of lanthanide complexes in aqueous solution is generally characterized by a large gain in entropy whereas the enthalpy changes are very often positive or, if negative, they only slightly contribute to the complex stabilities.[1,11,31]

The same trend occurs in mixed solvents. The most striking result of an investigation concerning lanthanide complexation by *o*-aminophenolate ion in 50% aqueous dmso, ethanol and dioxane[32] was the difference in the ΔH_1° and ΔS_1° values for the water–dmso mixture relative to other less-solvating media. The positive ΔH_1° values for complex formation in the water–dmso solvent range from 25 to 46 kJ mol^{-1} more positive than the slightly negative ΔH_1° found for the other two solvent systems. However, this rather large destabilizing effect does not show up in the K_1 values because of the large positive entropy change for complex formation in the water–dmso system. Evidently, also in this case, the large gain in entropy accompanying the charge neutralization upon complexation is the driving force for the reaction.

Taking into account that no charge neutralization occurs in complex formation with neutral ligands, it is reasonable to presume that although in the lanthanide(III)–en systems in dmso the ligands penetrate in the first co-ordination sphere of the metal ions, this does not cause substantial modifications in the metal-charge ordering effect of the bulk solvent and thus no large positive entropy change takes place. Accordingly, as mentioned above, we obtain only negative ΔS_j° values. However, a minor entropy change associated with the disorder created in the solvation structure by the co-ordination of the ligand has to be considered, and this should be more marked for the heavier and more solvated ions than for the lighter ones. This may be the reason why the ΔS_j° for the formation of La–Nd ethylenediamine complexes is more unfavourable than that for the later elements.

The data in Table 1 show that the stepwise values of ΔS_1° and ΔS_2°, throughout the series, are not so negative as ΔS_3° and that the heats of complex formation for the first two steps are less exothermic than those for the successive one. This suggests that the solvent molecule rearrangement in the inner solvation sphere of the acceptors mainly takes place in the first step but extends over this step and is more or less complete in the second one. In accordance with this, the enthalpy values of these steps are less exothermic than those of the third one. Moreover, they are very close to each other.

On the other hand, our data seem to indicate that other factors play more than a minor role in the lanthanide complexation. As higher complexes are formed, the structural requirements and consequently the conformational entropies become more and more important. The conformational demands should become very severe when a third ligand is to be accommodated around the central ion. In line with that, the values of ΔS_3°, for all the systems, become extremely unfavourable.

As far as the solvent effect on these reactions is concerned, the only thermodynamic data available in literature on lanthanide(III) complexation with en are those reported by Forsberg and Moeller[13] in anhydrous acetonitrile. They report that, in this aprotic solvent, the lanthanides(III) form four mononuclear complexes with bidentate en. Moreover, the complexes are all formed in strongly exothermic reactions whereas the entropy changes heavily oppose their formation. All the stability constants in acetonitrile, determined by calorimetric measurements, are much higher than those determined in dmso and all the enthalpy and entropy terms are much more negative in the former solvent. These features reflect the reduced co-ordinating properties of acetonitrile for lanthanide(III) ions as compared with dmso[9,10] and consequently the predominance of co-ordination over desolvation effects.

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