Thermodynamics of Lanthanide(III) Complex Formation with Nitrogen-donor Ligands in Dimethyl Sulfoxide

Alberto Cassol,[a] Gregory R. Choppin,[b] Plinio Di Bernardo,[a] Roberto Portanova,*[,c] Marilena Tolazzi,[c] Giuliana Tomat[d] and Pier Luigi Zanonato[a]

[a] *Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Universita' di Padova, Via Marzolo 1, 35131 Padova, Italy*

[b] *Department of Chemistry, Florida State University, Tallahassee, FL 32306, USA*

[c] *Dipartimento di Scienze e Tecnologie Chimiche, Universita' di Udine, Via del Cotonificio 108, 33100 Udine, Italy*

[d] *Istituto di Chimica e Tecnologia dei Radioelementi del CNR, C.so Stati Uniti, 35100 Padova, Italy*

Potentiometric and calorimetric data for the complexation of lanthanide(III) cations by the neutral nitrogen-donor ligands diethylenetriamine or triethylenetetramine in anhydrous dimethyl sulfoxide at 25 °C and in an ionic medium of 0.1 mol dm^{-3} NEt_4ClO_4 have been obtained. All the complexes are strongly enthalpy stabilized while the entropy changes are unfavourable. The results are discussed in terms of the charge density of the metal ions, the solvation changes along the lanthanide(III) series and the structural and conformational characteristics of the ligands.

As discussed in a recent paper,[1] the lanthanide(III) ions have a strong affinity for nitrogen-donor ligands. This was evidenced by a thermodynamic and spectroscopic study of lanthanide(III) complexation by ethylenediamine (en) in the anhydrous aprotic solvent dimethyl sulfoxide (dmso). Studies on the complex formation of lanthanide(III) ions with strongly basic nitrogen-donor ligands, such as amines and polyamines, can be performed only in non-aqueous solvents, as in aqueous solution these ligands are protonated in the pH range where hydrolysis of the metal ions is negligible. The investigation in dmso has shown that the formation constants of $Ln(en)_j^{3+}$ (where $j = 1–3$ and Ln denotes lanthanides) increase almost linearly with increasing atomic number of the metal ions and, further, that both the enthalpy and entropy changes accompanying the complex formation are negative. These latter findings are opposite to the general observation for lanthanide(III) complexation in aqueous solution.[2–4] In particular, the negative values of ΔH_j° and ΔS_j° were interpreted as due to a less decisive role of the cation desolvation in this medium as compared with that in aqueous solution.

The present paper reports an extension of this study to other polyamines containing three- or four-co-ordinating nitrogen atoms. The ligands considered were the triamine diethylenetriamine, $NH(CH_2CH_2NH_2)_2$, and the tetraamine triethylenetetramine, $(CH_2NHCH_2CH_2NH_2)_2$. Our main aim in investigating these systems was to study the influence of the structural and conformational characteristics of the ligands on the stabilization of the complexes with the lanthanide(III) ions.

The stability constants of the complexes were determined by potentiometric titrations and the enthalpy values by titration calorimetry. All measurements were carried out at 25 °C in a constant ionic medium of 0.1 mol dm^{-3} NEt_4ClO_4.

Experimental

Reagents.—Adducts of the lanthanide perchlorates, $Ln(ClO_4)_3 \cdot n$dmso (where *n* decreases almost regularly from 7.9 for La to 7.1 for Lu), were prepared and characterized as reported previously.[1] The salt $AgClO_4 \cdot H_2O$ (Fluka) was dried under vacuum at 50 °C for several days and used without further purification. Dimethyl sulfoxide and tetraethylammonium perchlorate were purified according to ref. 5. The amines were preliminarily dried with metallic sodium and then purified by distillation under reduced pressure.[6] Metal-ion and ligand stock solutions were prepared and standardized as before.[1] All solutions were prepared and stored in a glove-box under a controlled atmosphere with less than 10 ppm of water. The water content in the stock solutions (10–30 ppm) was determined by a modified Karl Fischer method.[7]

Potentiometric Measurements.—Data for the calculation of the stability constants were obtained by potentiometric measurements using the method of competitive reactions.[8] Silver(I) was used as auxiliary central group and a Ag^+–Ag electrode as a titration electrode. The galvanic cell and the titration procedure have been described previously.[1] The electromotive force (e.m.f.) values were obtained with a Radiometer PHM 84 pH meter equipped with a Metrohm 6.0328.000 silver electrode as a working electrode and a Metrohm 6.0718.000 silver electrode as a reference. Each titration series was carried out with at least three different initial lanthanide concentrations, c^0_{Ln}, in the range 9–33 mmol dm^{-3}. All titrations were performed with at least two different initial silver(I) concentrations, c^0_{Ag}, to check that no mixed complexes, Ag–L–Ln, were formed in solution. The silver(I) concentration was in the range 1–10 mmol dm^{-3}. The e.m.f. values of cells containing Ln^{3+} and Ag^+ ions in the range $10^{-5} < [Ag^+] < 10^{-2}$ mol dm^{-3} proved that the silver(I) electrode behaved according to Nernst's law. To exclude moisture, all titrations were performed in a glove-box.

The stability constants were calculated from the experimental data by the computer program SUPERQUAD.[9]

Calorimetric Measurements.—Calorimetric titrations were carried out using a Tronac model 87-558 precision-titration calorimeter according to a basic procedure that has been previously described in detail.[1] Each system was investigated by performing at least three calorimetric titrations in which a ligand solution of concentration c^0_L was added at a constant rate to a known volume of a solution containing c^0_{Ln} mmol dm^{-3} of lanthanide(III) ions. The initial concentration of the lanthanide was in the range $9 \leqslant c^0_{Ln} \leqslant 33$ mmol dm^{-3}. Some of the titrations were repeated twice: the agreement between different

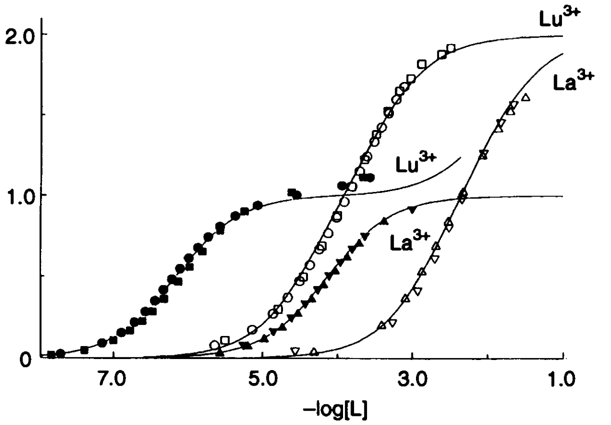

Fig. 1 Complex-formation functions for the lanthanum(III)–trien (▼) c^0_{La} 9.09, c^0_{Ag} 1.50; (▲) c^0_{La} 26.38, c^0_{Ag} 2.09; lutetium(III)–trien (■) c^0_{Lu} 9.80, c^0_{Ag} 1.00; (●) c^0_{Lu} 18.02, c^0_{Ag} 1.00; lanthanum(III)–dien (▽) c^0_{La} 22.17, c^0_{Ag} 10.00; (△) c^0_{La} 33.25, c^0_{Ag} 5.01; and lutetium(III)–dien (□) c^0_{Lu} 10.61, c^0_{Ag} 10.00; (○) c^0_{Lu} 21.95, c^0_{Ag} 5.01 mmol dm^{-3} systems. Only some of the experimental points, chosen at random, have been plotted. The full curves were calculated from the stability constants in Table 1

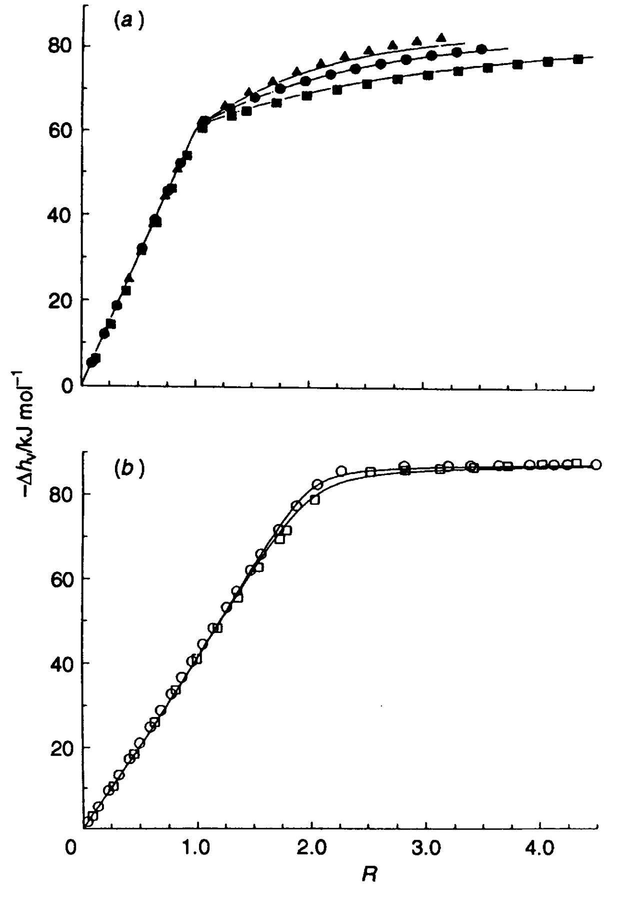

Fig. 2 Total molar enthalpy changes, Δh_v, as a function of $R = c_L/c_M$ for the lutetium–trien (*a*) and lutetium–dien (*b*) systems. Total lutetium(III) concentrations: (*a*) (■) 9.01, (●) 18.02, (▲) 30.34; (*b*) (□) 10.20, (○) 20.22 mmol dm^{-3}. Only some of the experimental points, chosen at random, have been plotted. The full curves were calculated from the stability constants and enthalpy changes in Table 1

runs was quite satisfactory. The corrections for the heats of dilution of the metal perchlorates and the ligands were determined in separate runs. They were negligible for the Ln^{3+} solutions in the concentration range investigated.

All measurements were performed at 25.000 ± 0.001 °C. The least-squares program LETAGROP KALLE[10] of the Letagrop series was used for the calculation of the enthalpy changes.

Results

The experimental results of the potentiometric titrations were qualitatively analogous for the various lanthanide ions. Hence, only the results obtained with lanthanum and lutetium, taken as representative of the light and heavy elements, are reported in detail.

Fig. 1 shows plots of $\bar{n}$, the average number of ligands per metal ion, *vs.* −log[L], where [L] is the free-ligand concentration, for the formation of diethylenetriamine (dien) and triethylenetetramine (trien) complexes of La^{3+} and Lu^{3+}. The relationship (1) was used to calculate $\bar{n}$ where $\bar{n}'$ denotes the

$$\bar{n} = (c_L - \bar{n}'c_{Ag} - [L])/c_M \qquad (1)$$

average number of ligands bound to silver(I) ion and c_L the analytical ligand concentration. The values of $\bar{n}'$ and [L] were obtained from the measured free silver(I) concentration calculated from the electromotive force data and the stability constants of the silver(I) complexes, determined previously[11,12] for the same experimental conditions, with these ligands. The complex-formation curves in Fig. 1 show that for all the systems neither polynuclear nor mixed complexes are formed in appreciable amounts and that the 1 : 1 complexes of the lanthanides with trien are much more stable than the corresponding complexes formed with dien. The shape of the dien curves with decreased slope at $\bar{n} \simeq 2$ is characteristic of the formation of successive complexes in stepwise equilibrium; the plateau at $\bar{n} \simeq 1$ followed by the values of $\bar{n}$ slightly exceeding 1 at higher free-ligand concentrations for the trien systems indicate the formation of two complexes for which the successive stepwise formation constants differ by at least 10^3.[8] Due to the large difference between the silver(I)–trien formation constant and the stepwise formation constant, K_2, of the lanthanide(III) bis(trien) complexes it was impossible to obtain accurate values of β_2 by the method of competitive reactions for these systems. On the other hand, the relatively low K_2 value and the relatively high stepwise complexation enthalpy, ΔH_2°, allowed us to obtain a sufficiently accurate estimate of β_2 and $\Delta H_{\beta 2}^{\circ}$ from the processing of the enthalpy values (see below).

The experimental data obtained from the calorimetric measurements for the lutetium(III)–dien and –trien systems are reported in Fig. 2 as Δh_v, the heat evolved per mole of metal ion, as a function of $R = c_L/c_M$, the ratio between the moles of ligand and the moles of lanthanide in the calorimeter vessel. The enthalpy curves are fully consistent with the information obtained from the analysis of the potentiometric data. In fact, the curves representing the complexation of lutetium by trien [Fig. 2(*a*)], which superimpose up to $R = 1$ and diverge at higher R values, reflect the formation of a 1 : 1 lutetium : trien complex of very high stability and of one (or more) successive and much weaker complex(es). The enthalpy data for the dien system coincide up to $R = 1$, slightly diverge at the inflection point ($R = 2$) and superimpose at higher R values. This trend can be easily explained by the formation of only two successive, almost equally stable, mononuclear lutetium(III)–dien complexes. The results obtained for the other lanthanides are quite similar and so they are not reported here.

The enthalpy changes for the formation of the lanthanide(III)–dien complexes were determined by using the stability constants obtained from the potentiometric-data-minimization process. For the lanthanide(III)–trien systems a different procedure had to be adopted. First, we obtained the enthalpy change for the formation of the 1 : 1 complex by refining the experimental data having $R < 1$ in the 'classical' way (β_1 from potentiometry). Successively, the stability constants and the enthalpy changes for the formation of the higher complexes were obtained from processing the whole of the calorimetric data keeping β_1 and ΔH_1° constant and varying simultaneously both the enthalpies and the stability constants of the complexes higher than ML. Both ML_2 and ML_3 were initially assumed to be present in the solutions of all the lanthanides studied, but the minimization computer program always ruled out the presence of any ML_3 complex. For the lanthanum(III)–trien system the stability constant of the second complex ML_2 was so small and the precision of the constant calculated so poor that no reliable value of log β_2, and hence ΔH_2° and ΔS_2°, could be obtained.

The full curves in Fig. 2 were calculated from the stability constants and enthalpy changes obtained from the minimization programs. The agreement between experimental and calculated values is satisfactory.

The overall stability constants and the free energy, enthalpy and entropy changes for the lanthanide(III) complexes ML_j (j = 1 or 2) with dien and trien are listed in Table 1 with the error limits indicated. The trends in the stability constants and in the thermodynamic quantities relative to the formation of the complexes are plotted in Figs. 3 and 4, respectively, *vs.* the lanthanide ionic radius.[13] The data in Table 1 and Fig. 3 show that for each ligand the overall free energy changes, $-\Delta G_{\beta_j}^{\circ}$, of the complex formation increase from La to Lu, following a similar trend to that previously found for the interaction of the lanthanides with ethylenediamine in the same solvent.[1] The general stability constant increase with a decrease in the cation ionic radius reflects the ionic nature of the bonding in these complexes while the similarity in the pattern of the curves indicates that complexation by the three ligands occurs *via* similar thermodynamic factors.

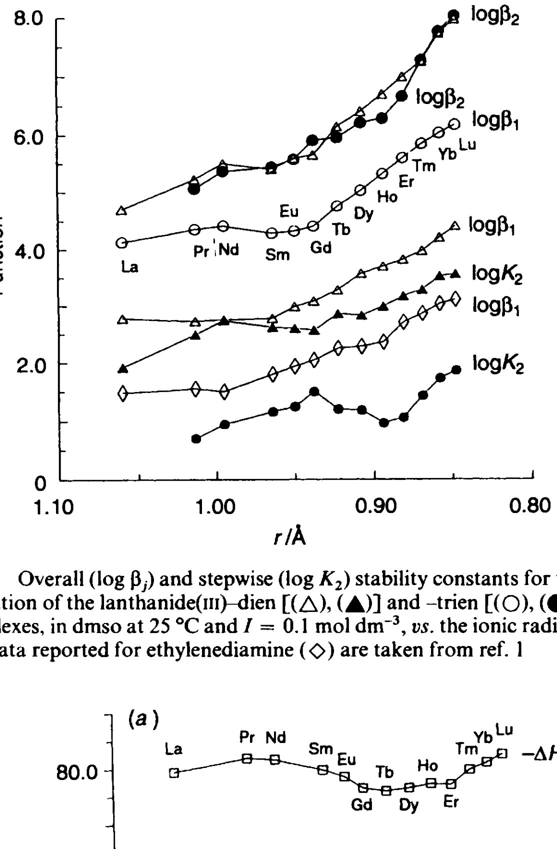

Fig. 3 Overall (log β_j) and stepwise (log K_2) stability constants for the formation of the lanthanide(III)–dien [(△), (▲)] and -trien [(○), (●)] complexes, in dmso at 25 °C and I = 0.1 mol dm^{-3}, *vs.* the ionic radius. The data reported for ethylenediamine (◇) are taken from ref. 1

Discussion

The values of log β_1 for the formation of the lanthanide(III)–trien complexes are 1.3–1.7 orders of magnitude higher than those for the formation of the dien complexes which in turn are 0.9–1.3 greater than those for the en complexes,[1] whereas the stability constants of the complexes formed by trien are almost constant from La to Gd and steadily increase for the heavier elements. For dien, the increase begins after Sm and for en after Nd. If the log β_j values depended only on the cation radius, there should be a steady increase from La to Lu. The stability of such complexes has been described as the result of interplay between electrostatic and steric effects.[14,15] The effect of three contributions on the complex stability has to be considered: (*i*) the regular increase in the charge density with the atomic number in the lanthanide series; (*ii*) the parallel increase in the desolvation energy of the cations with Z[16]; and (*iii*) the increase in the intramolecular strains associated with the greater difficulty of bringing the donor sites of the ligand close to the central metal ion as the molecular complexity of the ligand increases. The latter two effects decrease the stability of the complexes on increasing atomic number while the first increases it. Evidently there is almost a balance of these opposing effects in the early lanthanide complexes with the charge-density effect becoming strongest later. The occurrence of the break at different elements for different ligands most likely reflects a ligand effect as the first two are ligand independent.

In a previous paper we suggested that the lanthanide complexation with en in dmso involves chelation.[1] The increasing values of log β_1 from en to dien to trien support this model. Moreover, the sequence of $-\Delta H_1^{\circ}$ (en < dien < trien) indicates that the solvation interaction (disrupted by complexation) is weaker than the ligand bonding. The data indicate that in the first complex dien and trien act as ter- and tetra-dentate ligands forming two and three five-membered chelate rings, respectively. The low value of the ratio K_1/K_2 as well as the similarity of the thermodynamic functions for the 1:1 and 1:2 complexes is consistent with the second ligand in Ln(dien)$_2^{3+}$ being terdentate also. For the lanthanide(III)–trien system, however, the large values of the ratio K_1/K_2 (10^4–10^6), together with the much lower values of the stepwise enthalpy change $-\Delta H_2^{\circ}$ as compared with $-\Delta H_1^{\circ}$, suggests either that the second ligand brings about a rearrangement of the first so that both ligands

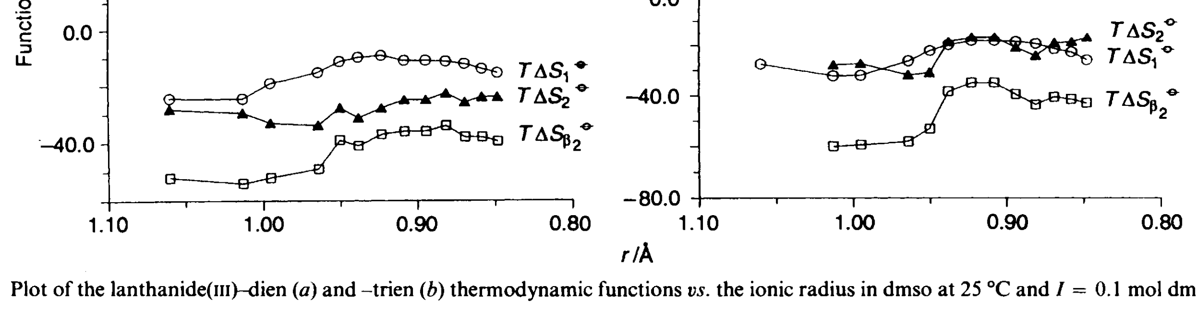

Fig. 4 Plot of the lanthanide(III)–dien (*a*) and -trien (*b*) thermodynamic functions *vs.* the ionic radius in dmso at 25 °C and I = 0.1 mol dm^{-3}

Table 1 Overall stability constants and thermodynamic functions of the lanthanide(III)–dien and –trien complexes in dmso at 25 °C and $I = 0.1$ mol dm^{-3}; $\Delta G_{\beta_j}^{\circ}$ and $\Delta H_{\beta_j}^{\circ}$ in kJ mol^{-1}; $\Delta S_{\beta_j}^{\circ}$ in J K^{-1} mol^{-1}. Estimated standard deviations in parentheses

Ln^{III}		Ln^{III}–dien				Ln^{III}–trien			
(Ionic radius*/Å)	ML$_j$	log β_j	$-\Delta G_{\beta_j}^{\circ}$	$-\Delta H_{\beta_j}^{\circ}$	$-\Delta S_{\beta_j}^{\circ}$	log β_j	$-\Delta G_{\beta_j}^{\circ}$	$-\Delta H_{B_j}^{\circ}$	$-\Delta S_{\beta_j}^{\circ}$
La	$j = 1$	2.78(1)	15.87(6)	40.2(6)	82	4.13(1)	23.57(6)	50.9(3)	92
(1.061)	2	4.70(2)	26.8(1)	79.0(7)	175	—	—	—	—
Pr	$j = 1$	2.73(2)	15.6(1)	40.4(5)	83	4.35(1)	24.83(6)	56.9(2)	108
(1.013)	2	5.22(3)	29.8(2)	83.9(4)	181	5.06(9)	28.9(5)	89(1)	202
Nd	$j = 1$	2.76(2)	15.8(1)	34.8(5)	64	4.41(1)	25.17(6)	57.3(1)	108
(0.995)	2	5.50(4)	31.4(2)	83.4(5)	174	5.36(9)	30.6(5)	90(1)	199
Sm	$j = 1$	2.78(1)	15.87(6)	31.1(7)	51	4.28(1)	24.43(6)	50.7(1)	88
(0.964)	2	5.40(2)	30.8(1)	79.6(6)	164	5.44(9)	31.0(5)	89(1)	194
Eu	$j = 1$	2.99(2)	17.1(1)	28.3(4)	38	4.32(1)	24.66(6)	46.8(3)	74
(0.950)	2	5.59(3)	31.9(2)	77.1(4)	152	5.57(9)	31.8(5)	85(1)	178
Gd	$j = 1$	3.08(1)	17.58(6)	27.5(5)	33	4.40(1)	25.11(6)	44.9(1)	66
(0.938)	2	5.65(2)	32.2(1)	73.0(6)	137	5.90(9)	33.7(5)	72(1)	129
Tb	$j = 1$	3.32(2)	18.95(6)	28.3(7)	31	4.75(1)	27.11(6)	45.2(1)	61
(0.923)	2	6.07(5)	34.6(3)	71.9(9)	125	5.95(9)	34.0(5)	69.0(5)	118
Dy	$j = 1$	3.57(2)	20.4(1)	31.5(3)	37	5.02(1)	28.65(6)	46.8(1)	61
(0.908)	2	6.40(3)	36.5(2)	73.0(4)	122	6.20(9)	35.4(5)	70.3(4)	117
Ho	$j = 1$	3.70(2)	21.1(1)	32.2(4)	37	5.31(1)	30.31(5)	48.8(1)	62
(0.894)	2	6.69(3)	38.2(2)	74.5(7)	122	6.28(9)	35.8(5)	75.3(4)	132
Er	$j = 1$	3.82(2)	21.8(1)	33.2(4)	38	5.59(1)	31.91(6)	51.2(1)	65
(0.881)	2	6.99(3)	39.9(2)	74.1(7)	115	6.65(9)	38.0(5)	81.6(4)	146
Tm	$j = 1$	3.97(2)	22.7(1)	34.8(3)	41	5.84(1)	33.33(6)	54.8(1)	72
(0.869)	2	7.25(3)	41.4(2)	79.5(4)	128	7.27(9)	41.5(5)	82.0(3)	136
Yb	$j = 1$	4.20(2)	24.0(1)	38.1(4)	47	6.02(1)	34.36(6)	58.2(1)	80
(0.858)	2	7.72(3)	44.1(2)	82.0(7)	127	7.75(9)	44.2(5)	85.8(3)	139
Lu	$j = 1$	4.40(2)	25.1(1)	40.5(7)	52	6.16(2)	35.2(1)	61.1(1)	87
(0.848)	2	7.83(3)	44.7(2)	84.9(6)	135	8.02(9)	45.8(5)	88.7(3)	144

* From ref. 13.

might be bound in a terdentate manner or that the second ligand exhibits bidentate co-ordination. For each lanthanide ion, the overall enthalpies of complexation for the formation of the tris(en),[1] bis(dien) and bis(trien) complexes are of the same order of magnitude. Since the nitrogen atoms in each of these ligands are expected to be of comparable donor strength, it is reasonable to conclude that the complexation of the lanthanides with all the ligands involves six metal–nitrogen bonds with an average value of the enthalpy contribution per amino group of about 13 kJ mol^{-1}.

Some years ago Forsberg[17] reported enthalpy data on the interaction between the ligands studied here and lanthanide(III) perchlorates in acetonitrile. These calorimetric measurements gave quantitative evidence for the existence in solution of the species $\mathrm{Ln(en)}_j^{3+}$ (j = 1–4), $\mathrm{Ln(dien)}_j^{3+}$ (j = 1–3) and $\mathrm{Ln(trien)}_j^{3+}$ (j = 1–2). The enthalpy changes were more negative than in dmso and the trends of $-\Delta H_j^{\circ}$ in acetonitrile had a quasi-regular increase from lanthanum(III) to lutetium(III). Apart from the substantially different donor properties of the two solvents,[18,19] reflected in the higher number of ligands co-ordinated to the lanthanides in acetonitrile together with the more negative enthalpies of complexation, the different $-\Delta H_j^{\circ}$ trends in the two solvents might be explained considering that, as shown recently,[20] the average number of co-ordinated acetonitrile molecules does not vary substantially from La to Yb and that while the lanthanide(III) perchlorates are completely dissociated in dmso[15] they are not in acetonitrile where they exist as $\mathrm{Ln(ClO_4)}^{2+}$ and $\mathrm{Ln(ClO_4)_2}^{+}$ complexes.[20]

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