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Thermodynamic and Spectroscopic Studies of Lanthanides(III) Complexation with Polyamines in Dimethyl Sulfoxide

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The thermodynamic parameters of complexation of Ln(III) cations with tris(2-aminoethyl)amine (tren) and tetraethylenepentamine (tetren) were determined in dimethyl sulfoxide (DMSO) by potentiometry and calorimetry. The excitation and emission spectra and luminescence decay constants of Eu^{3+} and Tb^{3+} complexed by tren and tetren, as well as those of the same lanthanides(III) complexed with diethylenetriamine (dien) and triethylenetetramine (trien), were also obtained in the same solvent. The combination of thermodynamic and spectroscopic data showed that, in the 1:1 complexes, all nitrogens of the ligands are bound to the lanthanides except in the case of tren, in which the pendant N is bound. For the larger ligands (trien, tren, tetren) in the higher complexes (ML_2), there was less complete binding by available donors, presumably due to steric crowding. FT-IR studies were carried out in an acetonitrile/DMSO mixture, suitably chosen to follow the changes in the primary solvation sphere of lanthanide(III) due to complexation of amine groups. Results show that the mean number of molecules of DMSO removed from the inner coordination sphere of lanthanides(III) is lower than ligand denticity and that the coordination number of the metal ions increases with amine complexation from ~8 to ~10. Independently of the number and structure of the amines, linear trends, similar for all lanthanides, were obtained by plotting the values of ΔG_j°, ΔH_j°, and $T\Delta S_j^\circ$ for the complexation of ethylenediamine (en), dien, trien, tren, and tetren as a function of the number of amine metal-coordinated nitrogen atoms. The main factors on which the thermodynamic functions of lanthanide(III) complexation reactions in DMSO depend are discussed.

Introduction

Lanthanide(III) ions have widespread applications in an impressive number of fields, such as materials science,[1] heterogeneous and homogeneous catalysis,[2] diagnosis and therapy in medicine,[3] and in the nuclear fuel cycle.[4] The technologies involving lanthanide compounds require extensive information on their physical and chemical properties. In this context, much work has been devoted to the coordination chemistry of these ions in aprotic solvents as, in nonaqueous media, it is possible to assess the affinity and selectivity of ligands which cannot be investigated in aqueous solutions. This, for example, is an important point in developing new extractants for the solvent/water separation of lanthanides from actinides in nuclear waste reprocessing.

Much effort has been put forth in the study of the physicochemical properties, in anhydrous solvents, of complexes with pyridines,[5] macrocycles,[6] ligands able to form supramolecular assemblies,[7] calixarenes,[8] and amides.[9] A

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(1) Stouwdam, J. W.; Hebbink, G. A.; Huskens, J.; vanVeggel, F. C. J. M. *Chem. Mater.* **2003**, *15*, 4604–4616.
(2) Shibasaki, M.; Yoshikawa, N. *Chem. Rev.* **2002**, *102*, 2187–2209.
(3) (a) Caravan, P. *Chem. Soc. Rev.* **2006**, *6*, 512–523. (b) Liu, S. *Chem. Soc. Rev.* **2004**, *33*, 445–461.
(4) Choppin, G. R. *Sep. Sci. Technol.* **2006**, *41*, 1955–1963.
(5) Hudson, M. J.; Boucher, C. E.; Braekers, D.; Desreux, J. F.; Drew, M. G. B.; Foreman, M. R. S.; Harwood, L. M.; Hill, C.; Madic, C.; Marken, F.; Youngs, T. G. A. *New J. Chem.* **2006**, *30*, 1171–1183.
(6) Arnaud-Neu, F. *Chem. Soc. Rev.* **1994**, *23*, 235–241.

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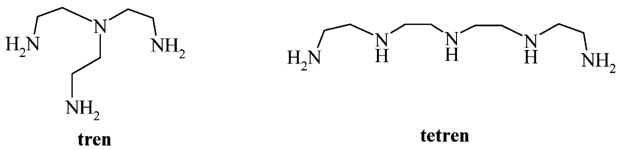
Scheme 1



variety of linear polyamines, such as ethylenediamine (en),[10] diethylenetriamine (dien), and triethylenetetramine (trien)[11] and mixed N−O donors[12] in dimethyl sulfoxide (DMSO) have also been studied by our group. These open-chain ligands are of renewed interest, as they can be used as models to assess the relative importance of factors connected with ligand structure on complexation reactions and also allow comparisons to be made with macrocyclic analogues.

The results of previous studies demonstrate that complexation in DMSO is essentially due to ion−dipole interactions between lanthanide cations and nitrogen donor atoms of amines. The inner-sphere nature of these complexes has also been confirmed by luminescence experiments for Ln(III)−ethylenediamine.[11] For all polyamine ligands, the enthalpies and entropies of complexation are negative, as also found for the complexation of transition metals with the same class of ligands,[13] unlike the situation in water and dimethyl formamide (DMF) with charged ligands.[14,15]

As an extension to previous works,[9−12] we report here the results of a thermodynamic study on the complexation in DMSO of Ln^{3+} cations with tris(2-aminoethyl)amine and tetraethylenepentamine (tren and tetren in Scheme 1).

Luminescence measurements on Eu^{3+} and Tb^{3+} complexes with dien, trien, tren, and tetren were performed to obtain complementary information on the nature of Ln(III)−N interactions in the previously studied systems. An in-depth FT-IR spectroscopic study was also carried out to evaluate the nature of the complexes forming in solution and changes in metal ion solvation upon complexation. The latter is an important point, as the solvation numbers of lanthanides play essential roles in their complexation behavior.[16]

The stability constants of lanthanide amino complexes were calculated from electromotive force (emf) values of potentiometric titrations, with Ag^+ as the competitive ion. Enthalpy values were determined by calorimetric titrations. All the experiments were conducted in DMSO, in a constant ionic medium of 0.10 mol dm^{-3} with NEt_4ClO_4. Spectroscopic studies were carried out in DMSO or acetonitrile (AN) solution containing small amounts of DMSO, with no added electrolyte.

Experimental Section

Chemicals. Adducts of lanthanide perchlorates $[Ln(DMSO)_n](ClO_4)_3$ (where *n* decreases from average values of 8.0 for La−Pr to 6.8 for Lu) were prepared and characterized as reported.[10]

Anhydrous perchlorates of lanthanum and europium were obtained following the procedure of ref 9. Anhydrous silver perchlorate was prepared by heating under vacuum at 50 °C for several days the solid crystallized from a solution of $AgClO_4{\cdot}H_2O$ (Fluka, puriss) in benzene after water removal.[12] DMSO and tetraethyl ammonium perchlorate were purified as described elsewhere.[17] Anhydrous AN (Aldrich, water content <0.005%) was used without further treatment. Tren (Aldrich, 96%) was purified by standing over metallic sodium prior to distillation under reduced pressure.[18] Crude tetren (Fluka, technical) was treated with HNO_3, and the precipitate of $H_2N(CH_2)_2(HNCH_2CH_2)_3NH_2{\cdot}5HNO_3$ was recrystallized several times from a 5% nitric acid solution. The free amine was obtained by percolation of an aqueous solution of the pentanitrate salt through a column of Amberlite-IRA-400 ion-exchange resin.[19] Anhydrous pentaamine was obtained by distillation of the eluate under reduced pressure. Dien and trien were purified as described earlier.[11]

Metal ion stock solutions in pure DMSO or AN were prepared as before.[10] Several stock solutions of Ln^{3+} (Ln = La, Pr, Eu, Tb, Er, Lu) in AN containing small amounts of DMSO were prepared by dissolving in a volumetric flask calculated amounts of lanthanide(III) adducts and DMSO in order to reach ratios of $[DMSO]/[Ln^{3+}] = 15{:}1$ or 30:1 in solution ($[DMSO]/[Ln^{3+}] = R_{DMSO}$). Lanthanide concentrations in the above solutions were determined by complexometry with EDTA and xylenol orange as indicator.[20]

Stock solutions of the ligands were prepared by dissolving weighed amounts of the anhydrous amines in anhydrous DMSO or AN, for FT-IR experiments. All solutions were prepared and stored in a glovebox under a controlled N_2 atmosphere with less than 1 ppm of water. The water content in the stock solutions (10−30 ppm) was determined on a Metrohm 684 KF coulometer.

Safety note: *Be careful. The use of lanthanide(III) perchlorates in AN can lead to serious accidents. A devasting explosion occurred using Nd(III) bis(TREN) perchlorate.*[21]

Potentiometry. The lanthanide−amine systems were investigated potentiometrically by the method of competitive reactions,[22] with silver(I) as auxiliary metal ion and with a Ag/Ag^+ electrode as the titration electrode. A pH meter (Radiometer PHM 84), equipped with a Metrohm 6.0328.000 silver electrode as working electrode and a Metrohm 6.0718.000 silver electrode as reference, was employed to obtain emf data. The galvanic cell and the procedure have been described before.[10]

Each titration series was carried out with at least three different initial lanthanide concentrations, $C°_{Ln}$, in the range of 9−33 mmol dm^{-3}. In order to ascertain that no formation of mixed complexes such as Ag−L−Ln occurred in solution, all titrations were performed with at least two different initial silver concentrations,

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(7) Piguet, C.; Bünzli, J-C. G. *Chem. Soc. Rev.* **1999**, *28*, 347−358.
(8) De Namor, A. F. D.; Baron, K.; Chahine, S.; Jafou, O. *J. Phys. Chem. A* **2004**, *108*, 1082−1089.
(9) Rao, L. F.; Zanonato, P. L.; Di Bernardo, P.; Bismondo, A. *Inorg. Chim. Acta* **2000**, *306*, 49−64.
(10) Cassol, A.; Di Bernardo, P.; Portanova, R.; Tolazzi, M.; Tomat, G.; Zanonato, P. L. *J. Chem. Soc., Dalton Trans.* **1992**, *3*, 469−474.
(11) Cassol, A.; Choppin, G. R.; Di Bernardo, P.; Portanova, R.; Tolazzi, M.; Tomat, G.; Zanonato, P. L. *J. Chem. Soc., Dalton Trans.* **1993**, *11*, 1695−1698.
(12) Comuzzi, C.; Di Bernardo, P.; Portanova, R.; Tolazzi, M.; Zanonato, P. L. *Polyhedron*, **2002**, *21*, 1385−1391.
(13) Comuzzi, C.; Melchior, A.; Portanova, R.; Polese, P.; Tolazzi, M. *Eur. J. Inorg. Chem.* **2003**, *10*, 1948−1955.
(14) Choppin, G. R. *J. Alloys Compd.* **1997**, *249*, 1−8.
(15) Ishiguro, S.; Takahshi, R. *Inorg. Chem.* **1991**, *30*, 1854−1858.
(16) Ishiguro, S.; Umebayashi, Y.; Komiya, M. *Coord. Chem. Rev.* **2002**, *226*, 103−111.
(17) Cassol, A.; Di Bernardo, P.; Zanonato, P. L.; Portanova, R.; Tolazzi, M. *J. Chem. Soc., Dalton Trans.* **1987**, *3*, 657−659.
(18) Perrin, D. D.; Armarego, W. L.; Perrin, D. R. *Purification of Laboratory Chemicals,* 2nd ed.*;* Pergamon Press: Oxford, 1980.
(19) Paoletti, P.; Vacca, A. *J. Chem. Soc.* **1964**, 5051−5057.
(20) Lyle, S. J.; Rahman, M. M. *Talanta* **1963**, *10*, 1177−1182.
(21) Raymond, K. N. *Chem. Eng. News* **1983**, *61*, 4.
(22) Rossotti F. J. C.; Rossotti, H. *The Determination of Stability Constants*; McGraw Hill: New York, 1961.

$C°_{Ag}$, in the range of 1−10 mmol dm^{-3}. The emf values of cells containing Ln^{3+} and Ag^+ ions in the range of $10^{-5} < [Ag^+] < 10^{-2}$ mol dm^{-3} proved that the Ag electrode behaved according to Nernst's law. To exclude moisture, all titrations were performed in a drybox under a nitrogen atmosphere. The stability constants were calculated from the experimental data by the *Hyperquad* program.[23]

Calorimetry. A model 87-558 Tronac precision titration calorimeter, equipped with a 25 cm^3 titration vessel, was used to measure reaction heats at 25.0 °C. The calorimeter was checked by the titration of tris(hydroxymethyl)amino-methane, tham, with a standard solution of HCl in water. The experimental value of the neutralization heat of tham was found to be $\Delta H° = -47.59$ kJ mol^{-1}, in good agreement with the accepted value ($\Delta H° =$ - 47.53 ± 0.13 kJ mol^{-1}).[24]

Titrations were performed by adding ligand solutions of concentration $C°_L$ (0.411 and 0.422 mol dm^{-3} for tren and tetren, respectively) at a constant rate to 20 cm^3 of lanthanide solution of concentration $\sim 10 < C°_M < \sim 33$ mmol dm^{-3}. Details about the treatment of calorimetric data are reported in ref 25. Some titrations were repeated twice; agreement between runs was quite satisfactory. The experimental values of the heat changes were corrected for the dilution heats of the ligand solutions determined in separate runs. The dilution heats of lanthanide perchlorate solutions were negligible in the metal concentration range used. Enthalpy changes for the studied systems were calculated with the *Letagrop Kalle* computer program.[26]

Luminescence Spectroscopy. Standard 1.00 cm quartz fluorimeter cells sealed with Teflon stoppers were used for spectroscopic studies of DMSO solutions. The excitation and emission spectra of the Eu^{3+} and Tb^{3+} complexes with the amines were recorded on a modified Perkin-Elmer MPF-2A spectrophotometer equipped with a Hamamatsu 928 photomultiplier and a temperature control unit. Excitation spectra were obtained by monitoring the intensity of the $^5D_0 \rightarrow {}^7F_2$ band at 616 nm for Eu^{3+} and the intensity of the $^5D_4 \rightarrow {}^7F_5$ band at 545 nm for Tb^{3+}. Emission spectra resulted from excitation of the $^7F_0 \rightarrow {}^5L_6$ band at 394 nm for Eu^{3+} and the $^7F_6 \rightarrow {}^5D_3$ band at 368 nm for Tb^{3+}.

The apparatus and procedures used to obtain selective excitation spectra of Eu^{3+} complexes and to measure the luminescence lifetimes of Eu^{3+} and Tb^{3+}samples have been described previously.[27]

The luminescence decay constant of each individual 1:1 complex was obtained from solutions in which the intensity of the complex was greater than 95%. The luminescence decay constants of the 1:2 complexes were obtained with solutions in which there was a large excess of ligand, leading to almost complete formation of the 1:2 complex. For each complex, excitation was applied at a wavelength corresponding to the maximum intensity of the complex in the excitation spectra of Tb^{3+} and Eu^{3+}.

FT-IR. A binary mixture of AN and small amounts of DMSO was selected as the solvent for FTIR studies, because this reaction medium can provide useful information on changes in the coordination sphere of lanthanide ions during the formation of metal−polyamine complexes. Three mixtures were prepared to measure the average number of DMSO molecules (NC_{DMSO}) coordinated to each lanthanide ion in these media. In two of the mixtures, the molar ratio of DMSO to Ln^{3+} (R_{DMSO}) was kept at 15.0, and the concentrations of Ln^{3+} were ≈33 mmol dm^{-3} and ≈50 mmol dm^{-3}, respectively. The third mixture was an AN solution in which R_{DMSO} was 30 and $[Ln^{3+}] \approx 33$ mmol dm^{-3}.

Preferential and quantitative solvation of lanthanides by DMSO in AN/DMSO mixtures is already well documented.[28] Due to this preferential solvation, solvated ions ($[Ln(DMSO)_x]^{3+}$) are discretely dispersed in AN and interaction with perchlorate inhibited. The low donor number (DN) of AN with respect to DMSO (DN = 14.1 and 29.8, respectively)[29] also enhances the metal−ligand interaction in the mixture and promotes quantitative formation of the complexes, which is the necessary prerequisite to quantify changes in the solvation sphere of lanthanides during complexation.

IR spectra were recorded under dry-air purge at room temperature on a Nicolet 5SXC FTIR spectrometer with a 2 cm^{-1} resolution and 256 scans. Cells with barium fluoride windows (optical path ∼33−35 μm) were used. Quantitative measurements were made with a single cell, the exact thickness of which was determined by the interference fringe method.[30] The cell was filled with sample solutions in the controlled atmosphere chamber, tightly closed, and quickly transferred into the spectrometer. The spectra of pure AN and the sample solutions were recorded separately, ratioed against the background, and converted to absorbance units. The AN spectrum was then numerically subtracted from the sample solution spectra, in order to obtain the difference spectra. For quantitative analysis, peak absorbance at 1060 cm^{-1}, characteristic of free DMSO,[31] was calculated by spectral deconvolution for each of the solutions analyzed. Calibration curves were obtained by plotting absorbance at 1060 cm^{-1} vs DMSO concentration for AN solutions containing various concentrations of DMSO (in the absence of Ln^{3+} and amines). Free DMSO concentrations in the Ln^{3+}/DMSO or Ln^{3+}/DMSO/amine systems were obtained with the calibration curves and values of absorbance at 1060 cm^{-1}, obtained after spectral deconvolution with a procedure similar to that described in ref 9. Stock solutions containing lanthanides(III) and DMSO in different ratios were prepared by adding calculated amounts of DMSO in the $[Ln(DMSO)_x](ClO_4)_3$ stock solutions in AN. A Marquardt nonlinear regression program was used to deconvolute the spectra into individual line bands, assuming Lorentzian line shapes.[9,32]

Results

The overall stability constants obtained from the potentiometric experiments are listed in Table 1, with error limits

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(23) Gans, P.; Sabatini, A.; Vacca, A. *Talanta* **1996**, *43*, 1739−1753.

(24) Smith, R. M., Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1986; Vol. 6, Second Supplement.

(25) (a) Rao, L.; Zanonato, P. L.; Di Bernardo, P.; Bismondo, A. *J. Chem. Soc., Dalton Trans.* **2001**, 1939−1944. (b) Srinivasan, T. G.; Zanonato P. L.; Di Bernardo, P.; Bismondo, A.; Rao, L. *J. Alloys Compd.* **2006**, *408−412*, 1252−1259.

(26) Arnek, R. *Ark. Kemi* **1970**, *32*, 81−88.

(27) Wang, Z.; Choppin, G. R.; Di Bernardo, P.; Zanonato, P. L.; Portanova, R.; Tolazzi, M. *J. Chem. Soc., Dalton Trans.* **1993**, *18*, 2791−2796.

(28) Milicic-Tang, A.; Bünzli, J.-C. G. *Inorg. Chim. Acta* **1992**, *192*, 201−209.

(29) a) Gutmann, V. *Chimia* **1977**, *31*, 431−442. (b) Persson, I. *Pure Appl. Chem.* **1986**, *8*, 1153−1161. (c) Marcus, Y. *Chem. Soc. Rev.* **1993**, *22*, 409−416.

(30) Nakanishi, K. *Infrared Absorption Spectroscopy*; Golden-Day: San Francisco, CA, 1964.

(31) Skripkin, I. M.; Yu Lundqvist-Reis, P.; Abbasi, A.; Mink, J.; Persson, I.; Sandstrom, M. *Dalton Trans.* **2004**, *23*, 4038−4049. In this paper the vibration at 1063 cm^{-1} in pure DMSO was assigned to an in-phase S−O stretching vibration of pairs of DMSO molecules held together by weak C−H···O interactions and electrostatic attraction between the negative oxygen and positive sulfur ends of adjacent dipoles. This strong dominating band is shifted at 1070 cm^{-1} in the IR spectra of the "monomeric" molecule of dimethyl sulfoxide in diluted solutions of DMSO in CCl_4. Possibly, intermolecular interactions similar to those observed in pure DMSO also take place in diluted solutions of DMSO in AN.

(32) Di Bernardo, P.; Choppin, G. R.; Portanova, R.; Zanonato, P. L. *Inorg. Chim. Acta* **1993**, *207*, 85−91.

Table 1. Stability Constants and Thermodynamic Parameters for Complexation of Ln^{3+} by tren and tetren in DMSO; $T = 25$ °C, $I = 0.1$ mol dm^{-3}, $\Delta G_j°$ and $\Delta H_j°$ in kJ mol^{-1}; $\Delta S_j°$ in J mol^{-1} K^{-1} [a]

	tren					tetren			
	j	log j	$-\Delta G_j°$	$-\Delta H_j°$	$-\Delta S_j°$	log j	$-\Delta G_j°$	$-\Delta H_j°$	$-\Delta S_j°$
La	1	2.88(1)	16.44(6)	40.5(2)	81	5.03(3)	28.7(2)	63(2)	115
1.356 Å	2	4.28(4)	24.4(2)	51(3)	89	6.36(15)	36.3(9)	72(2)	120
Pr	1	3.01(2)	17.2(1)	43.1(1)	87	5.51(3)	31.5(2)	66.7(9)	118
1.319 Å	2	4.32(6)	24.7(3)	52.4(7)	93	6.5(3)	37(1)	79(2)	141
Nd	1	3.07(2)	17.5(1)	42.8(2)	85	5.52(4)	31.5(2)	65(1)	112
1.303 Å	2	4.69(3)	26.8(1)	57(1)	101	7.03(3)	40.0(2)	73(1)	111
Sm	1	3.00(2)	17.1(1)	36.3(3)	64	5.47(3)	31.2(4)	64(1)	110
1.272 Å	2	4.79(3)	27.3(2)	60(1)	110	7.04(18)	40(1)	70(1)	101
Eu	1	3.08(2)	17.6(1)	32.8(4)	51	5.49(2)	31.3(1)	61.7(9)	102
1.260 Å	2	4.76(3)	27.2(2)	59(1)	107	7.44(7)	42.5(9)	65.4(9)	77
Gd	1	3.23(1)	18.44(5)	30.8(3)	41	5.49(4)	31.3(3)	54.7(5)	78
1.247 Å	2	4.77(3)	27.2(4)	58.7(7)	106	7.51(9)	42.9(5)	70.3(9)	92
Tb	1	3.52(2)	20.1(1)	31.5(4)	38	5.87(3)	33.5(2)	51.0(6)	59
1.235 Å	2	5.07(3)	28.9(2)	55(1)	88	7.92(9)	45.2(5)	69.4(9)	81
Dy	1	3.80(2)	21.7(1)	32.2(2)	35	5.90(2)	33.7(1)	50(2)	55
1.223 Å	2	5.39(3)	30.8(1)	48.9(4)	61	8.28(7)	47.3(3)	76(2)	96
Ho	1	3.97(1)	22.66(5)	33.3(1)	36	6.16(2)	35.1(2)	51.3(9)	54
1.212 Å	2	5.30(4)	30.3(3)	51.3(2)	71	9.06(10)	51.7(6)	75(1)	78
Er	1	4.23(3)	24.1(2)	35.3(1)	38	6.39(3)	36.5(1)	53.6(9)	57
1.202 Å	2	5.77(7)	32.9(4)	53.1(4)	68	9.18(6)	52.4(3)	77(3)	83
Tm	1	4.48(1)	25.57(6)	38.0(2)	42	6.66(3)	38.0(2)	58.8(8)	70
1.192 Å	2	6.09(3)	34.8(1)	62.0(7)	91	9.98(12)	57.0(6)	84.5(9)	92
Yb	1	4.69(1)	26.77(6)	41.5(2)	49	6.81(5)	38.9(2)	62.3(9)	78
1.182 Å	2	6.61(2)	37.7(1)	69.7(6)	107	10.07(9)	57.5(5)	91.8(8)	115
Lu	1	4.76(2)	27.2(1)	44.6(4)	58	6.90(4)	39.4(2)	66.2(9)	90
1.172 Å	2	6.76(3)	38.6(2)	71.9(6)	112	10.32(9)	58.9(5)	93.3(8)	11t

[a] The value in parentheses represents 3σ. Ionic radii of lanthanides are taken from ref 37.

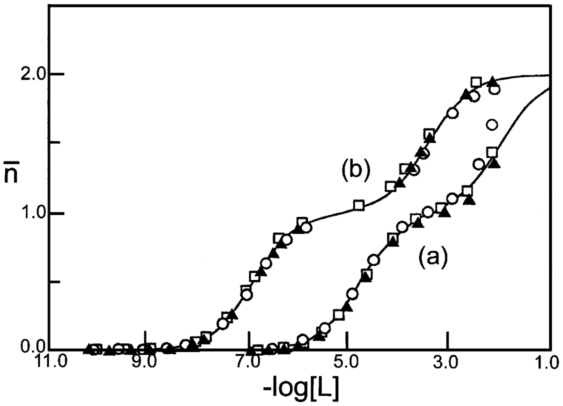

Figure 1. Complex formation functions for systems Lu^{3+}−tren (a): ○, $C°_{Lu}$ 9.05, $C°_{Ag}$ 1.77; ▲, $C°_{Lu}$ 17.80, $C°_{Ag}$ 4.78; □, $C°_{Lu}$ 26.60, $C°_{Ag}$ 1.77 mmol dm^{-3}; and Lu^{3+}−tetren (b): ○, $C°_{Lu}$ 10.00, $C°_{Ag}$ 4.23; ▲, $C°_{Lu}$ 18.60, $C°_{Ag}$ 4.14; □, $C°_{Lu}$ 32.70, $C°_{Ag}$ 7.91 mmol dm^{-3}. Only some experimental points, chosen at random, are plotted. Full curves: calculated with stability constants of Table 1.

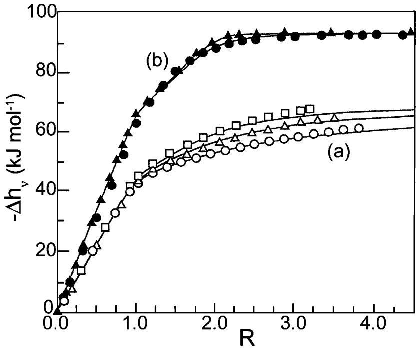

Figure 2. Total molar enthalpy changes, Δh_v, as a function of $R = C_L/C_M$ for Lu^{3+}−tren (a) and Lu^{3+}−tetren (b) systems. Total Lu^{3+} concentrations: (a) ○, 11.60; △, 23.20; □, 33.70 mmol dm^{-3}; (b) ●, 11.60; ▲, 32.70 mmol dm^{-3}. Only some experimental points, chosen at random, are plotted. Full curves: calculated with stability constants and enthalpy changes of Table 1.

indicated. Computer treatment of experimental data showed that the best fit was achieved when only LnL_j^{3+} ($j = 1, 2$) complexes were taken into account. No evidence of mononuclear complexes beyond LnL_2^{3+} was found.

Figure 1 shows the plots of $\bar{n} = (C_L - \bar{n}'C_{Ag} - [L])/C_M$, the average number of amines per metal ion, vs −log [L] for the formation of tren and tetren complexes of Lu(III), as representative of lanthanide elements. In the above equation, $\bar{n}'$ is the average number of ligands bound to the silver ion, C_{Ag}, C_M, and C_L are the total silver(I), lanthanide(III), and amine concentrations in solution, and [L] is the free ligand concentration. Values of $\bar{n}$ and $\bar{n}'$ were obtained from the measured free silver concentration, with the stability constants of silver complexes with tren[33] and tetren[34] previously determined in the same experimental conditions. The coincidence of the resulting complex formation curves shows that neither polynuclear nor mixed complexes had formed in appreciable amounts.[22]

Typical results of calorimetric titrations are shown in Figure 2, in which total enthalpy changes, Δh_v, are reported as a function of the ratio $R = C_L/C_M$ for the Lu−tren and Lu−tetren systems. Minimization of the differences between calculated and observed Δh_v values for each titration point gave the overall molar enthalpy changes for Ln(III) complex formation. These values, together with those of the corresponding free energy and entropy changes, are listed in Table 1.

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(33) Cassol, A.; Di Bernardo, P.; Zanonato, P. L.; Portanova, R.; Tolazzi, M.; Tomat, G. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 2841−2845.

(34) Di Bernardo, P.; Tolazzi, M.; Zanonato, P. L. *Inorg. Chim. Acta* **1997**, *255*, 199−202.

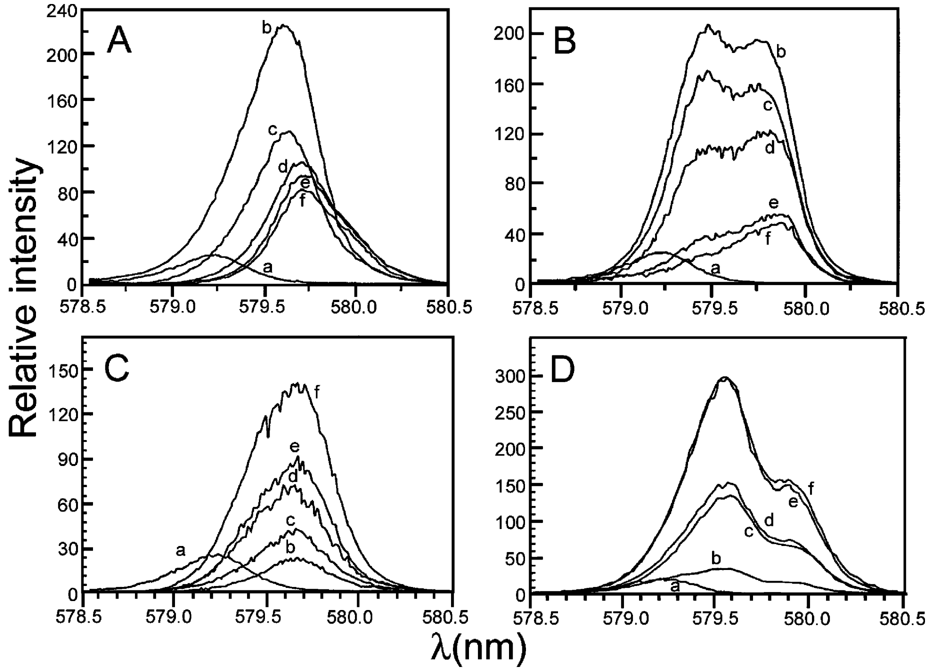

Figure 3. $^7F_0 \rightarrow {}^5D_0$ selective excitation spectra of Eu^{3+} complexes with dien (A), trien (B), tren (C), and tetren (D) in DMSO at different Eu^{3+}/amine ratios. $\lambda_{em} = 616.0$ nm. $[Eu^{3+}] = 0.02$ mol dm^{-3}. In A, $[Eu^{3+}]$/dien = 1:0 (a), 1:0.52 (b), 1:1.13 (c), 1:2.65 (d), 1:6.8 (e), and 1:20 (f). In B, $[Eu^{3+}]$/trien = 1:0 (a), 1:0.85 (b), 1:1.15 (c), 1:4.70 (d), 1:11.0 (e), and 1:25.0 (f). In C, $[Eu^{3+}]$/tren = 1:0 (a), 1:0.85 (b), 1:2.00 (c), 1:5.00 (d), 1:13.0 (e), and 1:20 (f). In D, $[Eu^{3+}]$/tetren = 1:0 (a), 1:0.07 (b), 1:0.30 (c), 1:0.60 (d), 1:2.00 (e), and 1:10.0 (f).

The excitation spectra of selected solutions, in which the 1:1 or 1:2 [Ln/amine] complex is almost completely formed, are shown in Figure S1 (Ln = Eu) and S2 (Ln = Tb) of the Supporting Information,[35] respectively. Figure 3 shows the $^7F_0 \rightarrow {}^5D_0$ selective excitation spectra of Eu^{3+} at different [Eu]/[amine] ratios for dien, trien, tren, and tetren.

It was previously found[27] that, in Ln(III)−ethylenediamine complexes in DMSO, each bound N−H vibrator unit acts independently in the luminescence quenching process, so that the observed decay constants of the amine complexes of Eu^{3+} and Tb^{3+} are related to the average number of bound vibrators, n_{N-H}, by eqs 1 and 2, respectively:

$$k_{obs} = 0.759 n_{N-H} + 0.416 \quad (1)$$

$$k_{obs} = 0.073 n_{N-H} + 0.299 \quad (2)$$

Table 2 lists the decay constants and number of NH vibrators of each amine bound to the lanthanide in 1:1 and 1:2 complexes as calculated from the decay constants with eqs 1 and 2.

As regards FT-IR study, most of the results fit those found in a previous study:[28] all DMSO molecules appear to be equivalent in the inner coordination sphere of the metal ions and in equilibrium with free DMSO, and none of the systems show any interaction with either perchlorate or AN. Also, the observed red shifts for the S−O stretching of coordinated DMSO with the increasing atomic number of Ln^{3+} ions are in excellent agreement with those reported. However, two important differences between the results of this study (carried out with $R_{DMSO} = 15$ and $[Ln^{3+}] \sim 33$ mmol dm^{-3}) and those of ref 28 ($R_{DMSO} = 15$ and $[Ln^{3+}] \sim 50$ mmol dm^{-3}) must be noted: (i) in this study, the decrease in the average number of molecules of DMSO (NC_{DMSO}) by almost 2 units, going from the lighter to the heavier cations, was not found; (ii) the value of NC_{DMSO} found was lower than that previously reported (Figure 4).

Table 2. Luminescence Decay Constants and Calculated Number of Bound N−H Vibrators

complex	decay constant (ms^{-1})[a]	M_{N-H} (±0.5)
$Eu(dien)^{3+}$	4.18 ± 0.05	5.0
$Eu(dien)_2^{3+}$	7.30 ± 0.08	9.1
$Tb(dien)^{3+}$	0.70 ± 0.03	5.5
$Tb(dien)_2^{3+}$	0.98 ± 0.03	9.3
$Eu(trien)^{3+}$	5.01 ± 0.05	6.1
$Eu(trien)_2^{3+}$	6.83 ± 0.08	8.5
$Tb(trien)^{3+}$	0.74 ± 0.03	6.0
$Tb(trien)_2^{3+}$	1.03 ± 0.03	10.0
$Eu(tren)^{3+}$	4.63 ± 0.13	5.6
$Eu(tren)_2^{3+}$	7.80 ± 0.14	9.7
$Tb(tren)^{3+}$	0.77 ± 0.05	6.5
$Tb(tren)_2^{3+}$	1.00 ± 0.05	9.6
$Eu(tetren)^{3+}$	5.82 ± 0.10	7.1
$Eu(tetren)_2^{3+}$	7.01 ± 0.11	8.7
$Tb(tetren)^{3+}$	0.78 ± 0.04	6.6
$Tb(tetren)_2^{3+}$	1.01 ± 0.04	9.7

[a] The errors are the statistical uncertainties of several experiments.

Several independent experiments were performed to confirm these results. First, the experiments were repeated in the same experimental conditions as in ref 28. Then study was extended to systems with $R_{DMSO} = 30$ to verify the effects of an increase in R_{DMSO} on the NC_{DMSO} value of lanthanides. Last, to rule out erroneous evaluation of the stoichiometry of the lanthanide/DMSO adducts, four series of experiments were carried out on solutions (~33 and ~50

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(35) In this and the following sections, figures and tables reported as Supporting Information are indicated with an S before their order number.

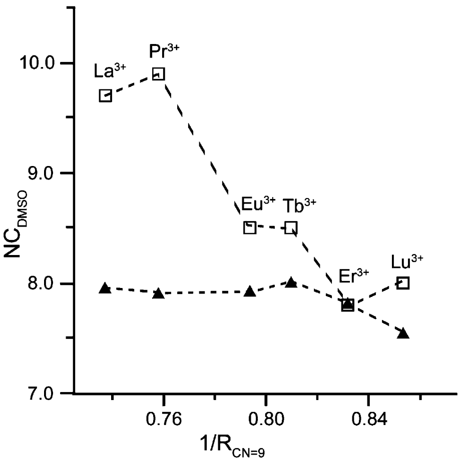

Figure 4. Average number of DMSO molecules coordinated to Ln^{3+} ions (NC_{DMSO}) vs the reciprocal of the ionic radius of Ln^{3+} ions in AN solutions containing small amounts of DMSO. Key: ▲, $[Ln^{3+}] \sim 33$ mmol dm^{-3}, $[DMSO]/[Ln^{3+}] = 15$, this work; □, $[Ln^{3+}] \sim 50$ mmol dm^{-3}, $[DMSO]/[Ln^{3+}] = 15$, ref 28.

mmol dm^{-3}) prepared with anhydrous perchlorates of La^{3+} and Eu^{3+} as starting materials and with R_{DMSO} values in the solutions varying from 2 to 30. All the results (Figures S3−S5, Supporting Information) confirm that the decrease in NC_{DMSO} in AN containing small amounts of DMSO going from La to Lu is modest (from ∼7.8 for La to ∼7.4 for Lu)[36] and that NC_{DMSO} slightly increases with both lanthanide concentration and R_{DMSO}. The above results fit the eight-coordination of lanthanum(III) observed in pure DMSO by Persson[37] by means of EXAFS and LAXS measurements. In addition, several solid-state studies report eight-coordination for DMSO adducts of lanthanide(III) ions, which becomes seven only in Yb and Lu.[38]

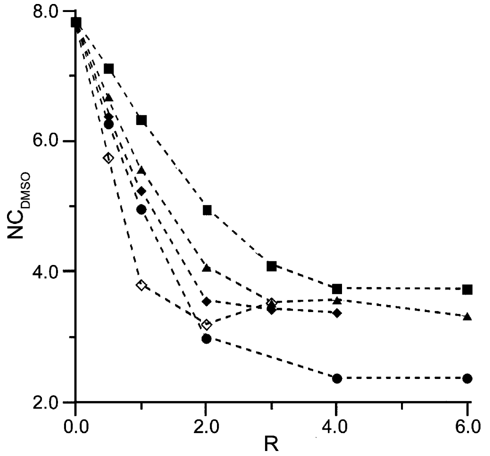

Figure 5. Decrease in NC_{DMSO} in the complexes formed by Eu^{3+} as a function of $R = [amine]/[Eu^{3+}]$ for different amines. $[Eu^{3+}] \sim 33$ mmol dm^{-3}; $[DMSO]/[Ln^{3+}] = 15$. Key: ■, en; ▲, dien; ◆, tren; ◇, tetren; ●, trien.

The NC_{DMSO} values, calculated for solutions containing $[Ln^{3+}] \approx 33$ mmol dm^{-3}, in the absence of amine and ratio $[DMSO]/Ln^{3+} = 15$, were used as references in order to follow the effects of the addition of increasing amounts of amine on NC_{DMSO} after complexation. The FT-IR spectra of solutions in which the ratio between total amine concentration and metal ion, R, varied from 0.5 to 6 were analyzed as described in the Experimental Section. The concentration of free DMSO in solution was calculated, and the difference $[DMSO]_{total} - [DMSO]_{free}$ allowed the calculation of NC_{DMSO}. The changes in NC_{DMSO} with R for the systems analyzed are listed in Table S1 and shown in Figures S6−S10 (Supporting Information). For each amine, NC_{DMSO} decreases almost regularly with R, reaching amine-dependent stationary values at $R > 3$ for en, $R > 2$ for dien, trien, and tren, and $R > 1$ for tetren. This is clearly shown in Figure 5, in which the data for Eu^{3+} are plotted.

Table 3 lists the differences between NC_{DMSO} at $R = 0$ and $R = j$, ΔNC_{DMSO}, for some of the amino complexes. These values give the number of molecules of DMSO removed from the primary coordination sphere of the metal ions for the formation of the $[Ln(amine)_j]^{3+}$ complex, if quantitative formation of the complex is assumed to occur, at $R < 3$ for Ln−en, $R < 2$ for dien, trien, and tren, and $R < 1$ for tetren, respectively. The FT-IR spectra in the region where N−H stretching occurs (3200−3400 cm^{-1}) provide experimental evidence for this assumption (Figures S11−S16, Supporting Information). The bands of coordinated amines appear much more intense and red-shifted (−40−50 cm^{-1}) with respect to those of the free ligands which, as expected for quantitative reactions, appear only for $R > 3$ (en), $R > 2$ (dien), and $R > 1$ (tren, trien, tetren).

Analysis of the 900−1200 cm^{-1} spectral region gives further interesting information about changes in the coordination sphere of the metal ions upon complexation. The spectral paths in Figures S11−S16 show that, as R increases, the intensity of the bands at 1009 and 965 cm^{-1} (S−O and C−S stretching of coordinated DMSO,[39] respectively) decreases, while band intensity at 1060 cm^{-1} (S−O stretching mode of free DMSO) gradually increases, indicating that DMSO is repelled from the coordination sphere of Ln^{3+} as Ln−polyamine complexes form. Simultaneously, the decreased intensity of the band at 1102 cm^{-1} (assigned to the vibrational mode of free perchlorate[40]) and the corresponding bandwidth increase, suggesting that perchlorate ions, orig-

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[36] For $R = 15$ and $[Ln^{3+}] \approx 33$ mmol dm^{-3}, $NC_{DMSO} = 7.81$ and 7.47 for La^{3+} and Lu^{3+}, respectively. For $R = 15$ and $[Ln^{3+}] \approx 50$ mmol dm^{-3}, $NC_{DMSO} = 7.85$ and 7.55 for La^{3+} and Lu^{3+}, respectively. For $R = 30$ and $[Ln^{3+}] \approx 33$ mmol dm^{-3}, $NC_{DMSO} = 8.50$ for both La^{3+} and Lu^{3+}.

[37] Näslund, J.; Lindqvist-Reis, P.; Persson, I.; Sandström, M. *Inorg. Chem.* **2000**, *39*, 4006−4011.

[38] (a) Cherkasova, T. G.; Anosova, Y. V.; Shevchenko, T. M. *Zh. Neorg. Khim.* **2004**, *49*, 22−24. (b) Chan, E. J.; Cox, B. G.; Harrowfield, J. M.; Ogden, M. I.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2004**, *357*, 2365−2373. (c) Plotnikova, T. E.; Grigoriev, M. S.; Fedoseev, A. M.; Antipin, M. Y. *Koord. Khim.* **2004**, *30*, 60−67. (d) Klinga, M.; Cuesta, R.; Moreno, J. M.; Dominguez-Vera, J. M.; Colacio, E.; Kivekas, R. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1998**, *54*, 1275−1277. (e) Huang Q.; Wu, X.; Lu, J. *Chem. Commun.* **1997**, 703−704. (f) Yu, H.; Zhang, W.; Wu, X.; Sheng, T.; Wang, Q.; Lin, P. *Angew. Chem.* **1998**, *37*, 2520−2521. (g) Fedorov, V. E., Geras'ko, O. A.; Mironov, Y. V.; Khegechvailer, K.; Stoop, R.; Gallus, Y.; Gramlikh, F.; *Zh. Strukt. Khim.* **1995**, *36*, 956−978. (h) Cherkasova, T. G. *Zh. Neorg. Khim.* **1994**, *39*, 1316−1319. (i) Wang, J. P.; Han Q. X.; Niu, J. Y. *J. Chem. Crystallogr.* **2005**, *35*, 629−634.

[39] Forel, M. R.; Tranquille, M. *Spectrochim. Acta, Part A* **1970**, *26*, 1023−1034.

[40] Bünzli, J. C. G.; Yersin, J. R.; Mabillard, C. *Inorg. Chem.* **1982**, *21*, 1471−1476.

Table 3. Decrease of the Number of DMSO Molecules Coordinated to the Metal Ions, ΔNC_{DMSO}, if Quantitative Formation of $[Ln(amine)_j]^{3+}$ Complexes in AN Containing Small Amounts of DMSO Is Admitted When the Stoichiometric Ratio $[amine]/[Ln^{3+}]$ in Solution, R, Corresponds to j

	en			dien		trien	tetren	tren
	ΔNC_{DMSO} $R_{0\to1}$	ΔNC_{DMSO} $R_{0\to2}$	ΔNC_{DMSO} $R_{0\to3}$	ΔNC_{DMSO} $R_{0\to1}$	ΔNC_{DMSO} $R_{0\to2}$	ΔNC_{DMSO} $R_{0\to1}$	ΔNC_{DMSO} $R_{0\to1}$	ΔNC_{DMSO} $R_{0\to1}$
La^{3+}	1.77	3.06	3.72	2.33	4.10	3.10	3.95	2.54
Pr^{3+}	1.46	2.64	3.39	2.14	3.83	2.82	4.04	2.52
Eu^{3+}	1.50	2.88	3.74	2.26	3.76	2.87	4.03	2.59
Tb^{3+}	1.87	3.18	4.06	3.18	4.58	3.44	3.98	2.75
Er^{3+}	1.39	2.73	3.31	2.16	3.81	2.55	3.94	2.49
Lu^{3+}	1.42	2.46	3.07	2.17	3.52	2.76	3.66	2.49
mean values	1.57 ± 0.18	2.82 ± 0.25	3.55 ± 0.33	2.37 ± 0.37	3.93 ± 0.33	2.92 ± 0.28	3.93 ± 0.13	2.56 ± 0.09

inally free in the solution of sole adducts, are somehow involved in the complexation reaction. Similar effects on the perchlorate band at 1102 cm^{-1} were not observed, in the same solvent mixture, for the formation of complexes of europium(III) with amides.[9] As the tetramethyl-substituted amides used in that study are much less prone to hydrogen bonding than the highly polarized N−H groups of the metal-coordinated amines of this study, it is reasonable to attribute the changes observed in the band at 1102 cm^{-1} to involvement of perchlorate in this kind of interaction. Moreover, as in pure DMSO perchlorate coordination is certainly inhibited,[10,12,28] the possibility of this interaction, which would render the solvation sphere of the metal complexes larger than that of octasolvated ions and the complexation entropies and enthalpies more negative, can easily be transferred to the solvent molecules.

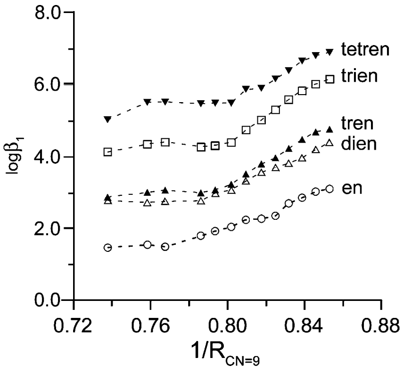

Figure 6. Log β_1 values for Ln^{3+}/amine = 1:1 complexation vs the reciprocal of the ionic radius of Ln^{3+} cations.

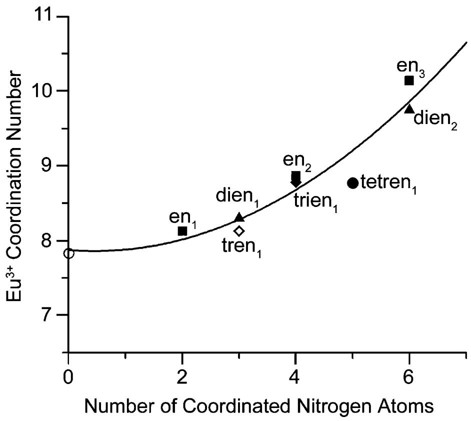

Figure 7. Increase in coordination number of Eu^{3+} for the formation of $[Eu(amine)_j]^{3+}$complexes. $j = 1-3$ for en; 1,2 for dien; 1 for tren, trien, and tetren. Full line: best fit of the plotted values obtained by a second-order polynomial.

Discussion

Figure 6 shows the values of log β_1 as a function of the reciprocal of the ionic radius of the Ln^{3+} cations for tren and tetren complexation and those of the previously studied en, dien, and trien. The data values for tren, close and almost parallel to those of terdentate dien, are quite far from those of tetradentate trien, plausibly indicating tercoordination for tren. In addition, the values of log β_1 for tetren are almost 1 order of magnitude larger than those for trien, which reflect pentadentation for tetren. The radii for the coordination number of 9 were chosen[41] to plot the data in Figure 6, according to the results of FT-IR spectra, showing that the calculated coordination numbers (CN_{LN}) of the metal ions increase with complexation from ~8 to ~10. Table 3 indicates that the origin of this increase lies in the difference between ligand denticity and the mean number of molecules of DMSO removed from the inner coordination sphere of metal ions. Figure 7 shows, for example, the increase in the CN_{LN} value of europium(III), due to the formation of metal−amine complexes. Similar trends were observed for all lanthanides.

The shapes of the curves in Figure 6 are similar for all ligands, with a small or no increase in log β_1 for the lighter lanthanides and a regular increase for the heavier ones. Closer inspection of Figure 6 reveals that this trend is ligand-denticity dependent, the break being shifted from Nd to Sm, Eu, and Gd for en, dien/tren, and trien and tetren, respectively.

An increase with the reciprocal of the ionic radius is expected, due to lanthanide contraction and the predominantly ion−dipole nature of Ln−N bonds. The lack of an increase in the log β_1 values in the earlier lanthanides in aqueous solutions has been associated with a change in the hydration number of lanthanides from 9 to 8.[42] The present study indicates that such a change in the CN_{LN} value does not occur in pure DMSO. Hence, changes in solvation number of metal ions should only have a small influence on the experimental paths shown in Figure 6.

The high stability of the lanthanide(III) complexes with tren and tetren (and also with other polyamines) is due to the large exothermic reaction which accompanies their

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(41) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751−767.

(42) Choppin, G. R. Chemical Properties of the Rare Earth Elements. In *Lanthanide Probes in Life, Chemical and Earth Sciences*; Bünzli J.-C. G., Choppin, G. R., Eds.; Elsevier: New York, 1989; Chapter 1.

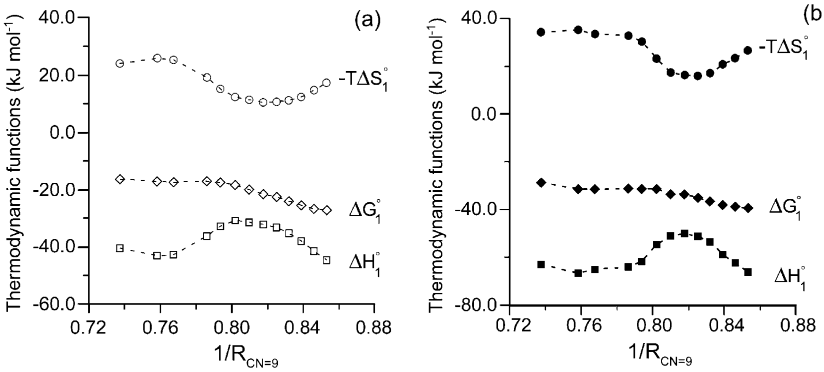

Figure 8. Thermodynamic functions for the formation of Eu^{3+}−tren (a) and Eu^{3+}−tetren (b) amine complexes.

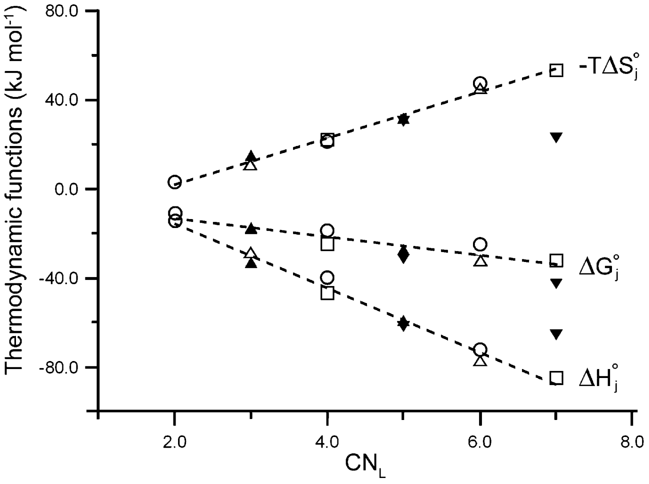

Figure 9. $\Delta G_j°$, $\Delta H_j°$, and $T\Delta S_j°$ values for the formation of 1:j complexes of Eu^{3+} (j = 1−3 for en and j = 1,2 for other amines) with en (○), dien (△), tren (▲), trien (□), and tetren (▼), as a function of CN_L.

formation. Reaction entropy, which is always negative, opposes the complexation reaction (Table 1 and Figure 8).

Linear trends, similar for all lanthanide(III) amine complexes, were observed by plotting the $\Delta G_j°$, $\Delta H_j°$, and $T\Delta S_j°$ values of complexation as a function of the total number of nitrogen donor groups of the ligands coordinated to the metal ion. For some of the complexes, to obtain the fit, a lower number of bound nitrogens, with respect to the total, must be assumed. Since luminescence measurements showed that the total number of bound nitrogens CN_L can easily be estimated, it is interesting to compare the results obtained with the two experimental techniques. Figure 9, for example, shows all the Eu(III) complexation data (including 1:1, 1:2, and 1:3 species). Linear relationships between thermodynamic parameters and CN_L are always observed for all lanthanide 1:1 complexes, with the exception of tren systems, when the CN_L value is set equal to the total nitrogens of the amine. The results of luminescence measurements in Table 2 support these findings.

Linear tends in Figure 9 show that the thermodynamics of these reactions mainly depend on CN_L being almost unaffected by the number and structure of coordinated ligands. As a matter of fact, both $\Delta H°$ and $T\Delta S°$ for the formation of $[Eu(en)_2]^{3+}$/$[Eu(trien)]^{3+}$ and $[Eu(en)_3]^{3+}$/$[Eu(dien)_2]^{3+}$ complexes are very close to each other. This reflects the prevailing importance of electrostatic interactions in these processes. It is instructive here to recall that charge neutralization in the formation of lanthanide chloride complexes in DMF, which has molecular properties similar to those of DMSO, implies completely opposite enthalpy and entropy contributions ($\Delta H° > 0$ and $T\Delta S° > 0$).[15,43] Schwarzenbach[44] attributed the positive values of $\Delta H°$ and $\Delta S°$ for the association of reactants having opposite charges to structural changes occurring within the solvent and compared this phenomenon "to the cooling effect which can be achieved by shutting off a magnetic field with which the elementary magnets of a paramagnetic substance were previously aligned". In reactions where no charge neutralization occurs, no bulk solvent structural changes are expected; hence, most of the energy released when a nitrogen atom of an amine comes into close contact with metal ions remains unused, and this causes the reaction enthalpies to be so exothermic. In addition, Table 3 shows that the number of DMSO molecules displaced from the first solvation sphere of the cations is almost equal for the couples $[Eu(en)_2]^{3+}$/$[Eu(trien)]^{3+}$ and $[Eu(en)_3]^{3+}$/$[Eu(dien)_2]^{3+}$ (ΔNC_{DMSO}: ∼2.9 and ∼3.7, respectively). Therefore, if the same is assumed to occur in pure DMSO, similar metal ion desolvation energies must be admitted. Considering the similarity of $\Delta H_j°$, it may be deduced that the enthalpy terms related to the different nature of the ligands (mainly connected with the removal of ligands from the bulk of the solvent and their inclusion in the coordination sphere of the metal ions) compensate each other or do not have a determining influence on the total reaction enthalpy which, as a consequence, depends only on CN_L.

The large negative entropy changes for the formation of Ln^{3+} complexes in DMSO indicate a consistent increase in the degree of order in solution. Among the several causes giving rise to negative entropy (losses of translational, rotational, and conformational entropies of reagents; incorporation into the highly ordered solvent structure[43,45] of molecules removed from the solvation sphere of metal ions

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(43) Marcus, Y. *J. Phys Chem. B* **2007**, *111*, 572−580.

(44) Schwarzenbach, G. Interpretation of Solution Stabilities of Metal Complexes. In *Proc. Summer Sch. Stab. Constants, 1st*; Paoletti, P., Barbucci, R., Fabbrizzi, L., Eds.; Edizioni Scientifiche Universitarie: Florence, Italy, 1977; pp 151−181.

(45) (a) Ahrland, S. Solvation and Complex Formation in Protic and Aprotic Solvents. In *The Chemistry of Non-aqueous Solvents*; Lagowsky, J. J., Ed.; Academic Press: New York, 1978; Vol. 5a, pp 1−62. (b) Ohtaki, H.; Ishiguro S. Complexation in Nonaqueous Solvents. In *Chemistry of Nonaqueous Solutions*—*Curr. Progr.*; Mamantov, G., Popov, A. I., Eds.; VCH: New York, 1994; pp 179−226.

and ligands), the combined thermodynamic and spectroscopic data of this work suggest that a further contribution, which may exert a significant influence on these equilibria, must be taken into account. In octasolvated cations, the oxygen atoms of the solvent fill the primary coordination sphere of the metal ions,[37] and the remaining parts of the molecules extend toward the bulk of the solvent, exercising a second sphere ordering effect, mainly by dipole−dipole interactions. When the nitrogen atoms of the amines replace DMSO in the primary coordination sphere of Ln^{3+} ions, the ordering ability of the complexes toward the solvent, which is a good hydrogen-bond acceptor,[42] may markedly increase, due to the hydrogen bonding ability of the coordinated amines. As a consequence, not only does this feature contribute toward making complexation entropy negative but the increased solvation of the complexes with respect to the solvated cations also renders reaction enthalpy more favorable. Similar effects have recently been invoked for silver(I),[46] comparing data for amine coordination with those for pyridines (unable to give H bonding), which have significantly fewer unfavorable entropic terms.

The decrease in $\Delta G_1°$ along the Ln(III) series is the result of compensation between larger changes in $\Delta H_1°$ and $T\Delta S_1°$ which operate in mutual opposition: the maximum value of $T\Delta S_1°$ corresponds to the lowest exothermic reaction enthalpies. Similar trends for other Ln(III)−polyamine systems have been explained[10,11] as due to the balance of several factors: (i) absence of charge neutralization during complexation, which does not change the long-range structuring effect of the metal ion and complexes on the bulk of the solvent; (ii) regular increase in charge density with atomic number in the lanthanide series; (iii) parallel increase in the desolvation energy of the cations with Z; (iv) 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 results of this work also show that the specific interactions via H bonding between coordinated amines and bulk solvent molecules should be considered, for a more complete description of these phenomena.

As the number and molecular complexity of ligands in complexes increase, differences between the values of the thermodynamic functions observed and those expected on the basis of the linear relationships shown in Figure 9 are found.

The luminescence data for the Eu^{3+} (and Tb^{3+}) tren complexes indicate that about 6 N−H vibrators are attached to the metal ion in the 1:1 complexes and 10 in the 1:2 complexes (Table 2). No direct information on the coordination of the fourth nitrogen atom can be obtained from luminescence data. In the solid state, tren has been shown to be tetracoordinated in the $[Nd(tren)_2(CH_3CN)](ClO_4)_3$ complex.[47] In AN solution, tren has been considered to be tetracoordinated, due to the close resemblance of the enthalpies of formation of bis-tren- and tetrakis-ethylenediamine chelates of Pr and Gd.[48] Our thermodynamic data fit linear relations such as that shown in Figure 9, when CN_L is 3 for complex $[Ln(tren)]^{3+}$ and 5 for complex $[Ln(tren)_2]^{3+}$. The combination of these results with those from luminescence measurements enables us to conclude that the tertiary nitrogen atoms are not coordinated to the metal ions in any lanthanide complex. The reason the podand does not behave as a tetradentate in DMSO is probably because, due to the higher donor number of this solvent as compared with that of AN, desolvation of cations, to allow coordination of the four nitrogen atoms of the amine, is energetically unfavored.

For the 1:2 trien complexes, Figure 9 indicates 7 Ln−N bonds, whereas the luminescence half-life corresponds to 8.5 NH units for Eu and 10 units for Tb. The latter fits linear correlations such as those of Figure 9, when one NH_2 group is not bound in one ligand. The disagreement between the luminescence results for Eu^{3+} and Tb^{3+} may reflect the presence of structural isomers in the solution of the former (see below).

The CN_L value of 7 reported for the $[Eu(tetren)_2]^{3+}$ complex is postulated on the basis of the number of NH vibrators (∼9 in Table 2), which implies two NH_2 and five NH groups involved in binding.

In all the amine systems, the effect of complexation is seen in the excitation spectra, as shown in Supporting Information Figures S1 (Eu^{3+}) and S2 (Tb^{3+}). For all the europium(III) complexes, a reduction in intensity with respect to the solvated ion is observed, reflecting the strong effect of quenching by the NH groups bound (via N) to the metal: the same does not occur for Tb^{3+}. Figure S2 shows a decrease in the relative intensities in the 300−400 nm excitation range and an increase in the 200−300 nm interval. Apparently, the field about the metal ion resulting from amine complexation increases the “allowedness” of the $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} to a greater extent than quenching of the bound NH vibrators. Similar effects on the $^7F_0 \rightarrow {}^5D_0$ transition may be responsible for the increase in the selective excitation spectra of europium(III) complexes with tren and tetren (Figure 3). Also, deconvolutions of the selective excitation spectra of Eu^{3+}−trien and Eu^{3+}−tetren complexes are consistent with the presence in solution of a pair of structural isomers. It is difficult to be definite about whether the pair of isomers has the same luminescent decay constants (i.e., the same number of bound NH groups) in each case, although the evidence does support such a model.

For all the amines studied, additional spectra show that complexation is decreased as temperature increases. This is consistent with the exothermic values for $\Delta H_j°$ of Table 1. In the selective ($^7F_0 \rightarrow {}^5D_0$) excitation spectra of the 1:1 complexes, while both isomers show decreased intensity with increased temperature, the decrease is not the same for both members of the isomer pair for both trien and tetren. In both amine systems, the isomer with a peak at 579.5 nm decreased more with temperature than that with a peak at 579.8 nm.

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(46) Del Piero, S.; Fedele, R.; Melchior, A.; Portanova, R.; Tolazzi, M.; Zangrando, Z. *Inorg. Chem.* **2007**, *46*, 4683−4691.

(47) Eingenbrot, C. W., Jr.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 2867−2870.

(48) Forsberg, J. H.; Kubik, T. M.; Moeller, T.; Gucwa, K. *Inorg. Chem.* **1971**, *11*, 2656−2660.

Conclusions

The thermodynamic parameters of complexation and luminescence measurements show that all the nitrogen donors of the polyamines, except tren, are bound to Ln^{3+} in the 1:1 complexes. In $[Ln(tren)]^{3+}$, the tertiary nitrogen is not bound. In $[LnL_2]^{3+}$ complexes (with L = trien, tetren), as ligand size increases, fewer amine groups can bind the cations.

FT-IR studies, carried out in AN/DMSO mixtures, show that the number of molecules of DMSO displaced is always lower than ligand denticity; as a consequence, the coordination numbers of the metal ions increase with complexation from ~8 to ~10.

Linear trends are obtained by plotting $\Delta G_j°$, $\Delta H_j°$, and $T\Delta S_j°$ of complexation vs the number of coordinated nitrogen atoms. The almost regular decrease in $\Delta G°$ along the lanthanide series is the result of compensation between $\Delta H°$ and $T\Delta S°$, which operate in mutual opposition. In general, the high stability of the amino complexes in DMSO is due only to the large exothermicity which accompanies their formation, whereas reaction entropy counteracts complexation. Several factors may lie at the origin of the order increase in solution: (i) the unchanged long−range structuring effect of the cation and complexation on the bulk of the solvent; (ii) loss of translational and conformational entropy of ligands; (iii) incorporation of solvent molecules displaced from the reacting species into the highly ordered solvent bulk structure; and (iv) formation of hydrogen bonds between solvent molecules and amino groups coordinated to the metal centers. The fact that the formation enthalpies of complexes with the same number of Ln−N bonds are close to each other reflects the prevalent importance of the (ion−dipole) electrostatic interactions with respect to the above-mentioned entropy-determining factors on the global reaction enthalpy. However, it is worth noting that a delicate balance between the energetic contributions connected to each of the above-mentioned entropy-determining factors may be the main cause of the trends of thermodynamic functions within the lanthanide group.

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Supporting Information Available: Figures S1−S16; Table S1, in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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