A donor–acceptor model of Ln(III) complexation with terdentate nitrogen planar ligands

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The mechanism of the formation of a complex between several planar terdentate nitrogen ligands and trivalent lanthanides (Ln^{3+}) in mixed MeOH–H_2O solutions is studied and a model is proposed for the thermodynamic properties of the complexation reactions. The objective is not to cover all aspects of complexation between Ln^{3+} and planar terdendate nitrogen ligands, but rather to provide insight into the factors that govern the complexation mechanism. It is shown that the complexation of Ln^{3+} in solution with similar ligands does not follow the classical trends in change of thermodynamic properties across the Ln series, which have long been known. *Ab initio* calculations show that the stability of complexes increases with the increasing electron donor ability of the coordinating central nitrogen atom (N_c) of the ligand and the electron acceptor ability of the coordinating lateral ones (N_l). The effect of covalence for the stability of complexes is analysed. The complexes with high stability are characterised by distinct covalence of the bonds between Ln^{3+} and the lateral coordinating nitrogen atoms of the ligand. The thermodynamic properties of complexation of Ln^{3+} with 2,6-bis-(pyridin-2-yl)-4-amino-1,3,5-triazine (Adptz) and 2,6-bis-(1,2,4-triazin-yl)-pyridine (Btp) are compared. The central ring is negatively charged in the Adptz ligand, but positive in Btp. The strong donor–acceptor interaction and the net covalence result in an enthalpy mechanism of complexation of Ln^{3+} with Adptz. Owing to the repulsion between the cation and the central nitrogen atom in the $[Ln(Btp)]^{3+}{}_{solv}$ complexes, the cation is pushed away from the nitrogen cavity, the Ln–N_c interatomic distances become larger and the electron donor ability of N_c is weak. Entropy promotes the formation of the $[Ln(Btp)]^{3+}{}_{solv}$ complex.

Introduction

In the design of nitrogen polydendate ligands L, for application in the field of liquid–liquid extraction and separation of trivalent actinides An(III) from trivalent lanthanides Ln(III) for nuclear waste management, one important goal is to study the mechanism of complexation leading to LnL and AnL complex formation and the thermodynamic properties of these complexes in solution.[1]

The ability of polyaza ligands L to store charge in the excited state of their complexes and to take part in donor–acceptor interactions with metal ions has been noted in the literature for complexes with d-transition elements as well as for Lu^{3+} ion.[2–6] In the mechanism of LnL and AnL complex formation in the ground state, this type of interaction is also expected to be a significant factor. In an attempt to address this point in the case of planar terdendate ligands, three rather fundamental questions have to be answered: (i) Do the lateral and central rings of L in $[LnL]^{3+}$ complexes play the same role in the M $\leftrightarrow$ L donor–acceptor interaction? (ii) Do the lanthanide cation size and its donor–acceptor ability play significant roles in the complexation mechanism? (iii) Does the trend in thermodynamic properties of LnL complexes in aqueous solution differ from those with polyaminocarboxylate ligands, for which there exists an abundant literature?[7,8]

To the best of our knowledge, no systematic study has been carried out of the electronic complexation mechanism and thermodynamic properties of the LnL and AnL complexes across the Ln and An series, with L being planar N-terdendate ligands. The present work focuses on: (i) the study of the electronic mechanism of Ln^{3+} complexation with the ligands tpy, Tptz, Adptz, Btp, Me_4Btp, Pyr_2Pym and Bzimpy in solution (chemical formulas of these ligands are given in Table 1) and (ii) the establishment of a model for calculating enthalpy and entropy changes under complexation.

Quantum chemistry calculations

Quantum chemistry calculations were performed with the Gaussian 98 code[10] on a Silicon Graphics biprocessor workstation at CEA-Valrhô (Marcoule). The *ab initio* calculations were performed at the Hartree–Fock (HF) level of theory. The molecular geometry of all ligands L and corresponding $[LnL]^{3+}$ complexes was fully optimised and the Mulliken net atomic charges and bond overlap populations were computed. For Ln complexes, in order to reduce computational time, the calculations were performed by replacing the Ln core electrons with pseudo-potentials. The lanthanide atoms were calculated using quasi-relativistic pseudopotentials of the Stuttgart group,[11] where 46 + $4f^n$ electrons are included in the core so that lanthanides are modelled as 11-valence-electron systems. The contracted (7s6p5d)/[5s4p3d]-GTO valence basis sets were used for the lanthanides and the polarised all-electron 6-31G(d) basis sets for all other atoms.

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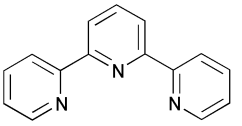
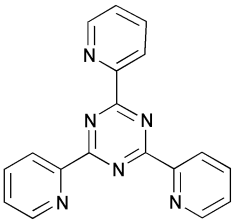
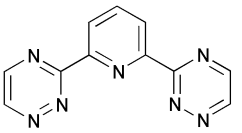
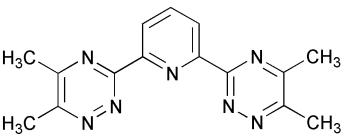
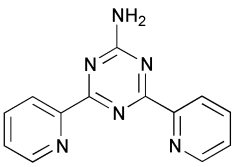
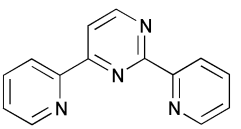
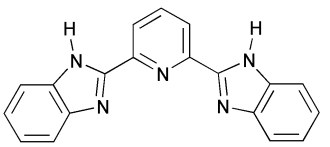
Table 1 Names, acronyms and developed formulas of studied ligands (in their coordinating conformation[a])

Name	Acronym	Formula
2,2′ : 6′,2″-Terpyridine	tpy	
2,4,6-Tri(pyridin-2yl)-1,3,5-triazine	Tptz	
2,6-Bis(1,2,4-triazin-3-yl)pyridine	Btp	
2,6-Bis(5,6-dimethyl-1,2,4-triazin-3-yl)pyridine	Me_4Btp	
2,6-Bis(pyridin-2-yl)4-amino-1,3,5-triazine	Adptz	
2,6-Bis(pyridin-2-yl)pyrimidine	Pyr_2Pym	
2,6-Bis(benzimidazol-2-yl)pyridine	Bzimpy	

[a] In the case of Btp ligands, this conformation was demonstrated recently by Drew *et al.*[9a] and Iveson *et al.*[9b]

Results and discussion

1 Crystal structural properties of the lanthanide complexes $Ln(tpy)Cl_3(H_2O)_m$

Only one isomorphous and isostructural series of single crystal compounds, $Ln(tpy)Cl_3(H_2O)_m$, has been studied to date for all lanthanide elements by X-ray diffraction.[12] In the crystal compounds $[Ln(tpy)Cl(H_2O)_m]\cdot Cl_2\cdot 3H_2O$, Ln^{3+} (=La–Nd) cations are coordinated to nine atoms: three nitrogen atoms (two lateral N_l and one central N_c atoms) from tpy, five oxygen atoms from water molecules and one Cl^- ion. In the middle of the series, in the complexes of Sm^{3+}, Eu^{3+} and Gd^{3+}, the change of coordination number (CN) results in a decrease of the average number of water molecules in the inner coordination sphere: $[Sm(tpy)Cl(H_2O)_{4.6}]\cdot Cl_2\cdot 3H_2O$, $[Eu(tpy)Cl(H_2O)_{4.45}]\cdot Cl_2\cdot 3H_2O$ and $[Gd(tpy)Cl(H_2O)_{4.1}]\cdot Cl_2\cdot 3H_2O$. In the complexes of the heavy elements (Tb–Lu), the number of water molecules was found to be exactly four.

The most intriguing result of the X-ray structural investigations is the inversion of the $R(Ln–N_c)$ and $R(Ln–N_l)$ distances between the cations and the central N_c and lateral N_l

coordinating nitrogen atoms, respectively: (i) for the light Ln compounds, $R(\mathrm{Ln–N_l}) < R(\mathrm{Ln–N_c})$, (ii) for the heavy Ln compounds, $R(\mathrm{Ln–N_l}) > R(\mathrm{Ln–N_c})$, (iii) in the middle of the series $R(\mathrm{Ln–N_l}) \approx R(\mathrm{Ln–N_c})$. These structural data may be interpreted as the occurrence of the strongest interaction between N_l and Ln^{3+} for the light elements and between N_c and Ln^{3+} for the heavy ones.

Another way to discuss these results is to study the trends in nitrogen radii, calculated as $R(N_l) = R(\mathrm{Ln–N_l}) - R(Ln^{3+})$ and $R(N_c) = R(\mathrm{Ln–N_c}) - R(Ln^{3+})$, across the series as shown in Fig. 1(a) [for the calculation of these differences, $R(Ln^{3+})$ were chosen according to the corresponding CN[13]]. These trends are the derivatives $dR(N_c)/dZ(\mathrm{Ln})$ and $dR(N_l)/dZ(\mathrm{Ln})$. Qualitatively, they are opposed: decreasing (increasing) $dR(N_c)/dZ(\mathrm{Ln})$ corresponds to increasing (decreasing) $dR(N_l)/dZ(\mathrm{Ln})$. Thus, the structural data can be interpreted as a manifestation of different effects in the interactions Ln^{3+}–N_c and Ln^{3+}–N_l.

In order to understand the nature of these effects, the trends in the change of $R(N_c)$ and $R(N_l)$ were compared with the trend of the potentials of the Ln(III/II) and Ln(IV/III) redox couples[14] across the series [Fig. 1(a) and 1(b)]. One can see a good qualitative correlation between the trends in $R(N_c)$ and $E^\circ_{3/2}$ redox potential across the series. It can be suggested that the central nitrogen atom of the tpy ligand takes part in a donor interaction with the Ln cation, that is, the cation is partly reduced. In contrast, the lateral nitrogen atoms can be expected to take part mainly in an acceptor interaction with the Ln cations. In other words, the $dR(N_l)/dZ(\mathrm{Ln})$ trend must be similar to the $dE^\circ_{4/3}/dZ(\mathrm{Ln})$ trend, as observed in Fig. 1.

If, in solution, the Ln–N_c and Ln–N_l interatomic distances for terdendate nitrogen ligands follow the same trends as observed in Ln(III)–tpy crystalline compounds, one can expect: (i) increasing stability of LnL complexes from Ln = La–Sm, (ii) maximal stability of complexes in the middle of the Ln series (Sm, Eu and Gd) and (iii) decreasing stability of LnL complexes from Ln = Gd to Lu. These predictions are in agreement with the measured $\log K(\mathrm{LnL})$ values for the complexes with Ln = La, Eu, Lu and L = Tptz, Adptz, Pyr_2Pym, Btp and Me_4Btp[15,16] and with $\log K(\mathrm{LnTptz})$.[17]

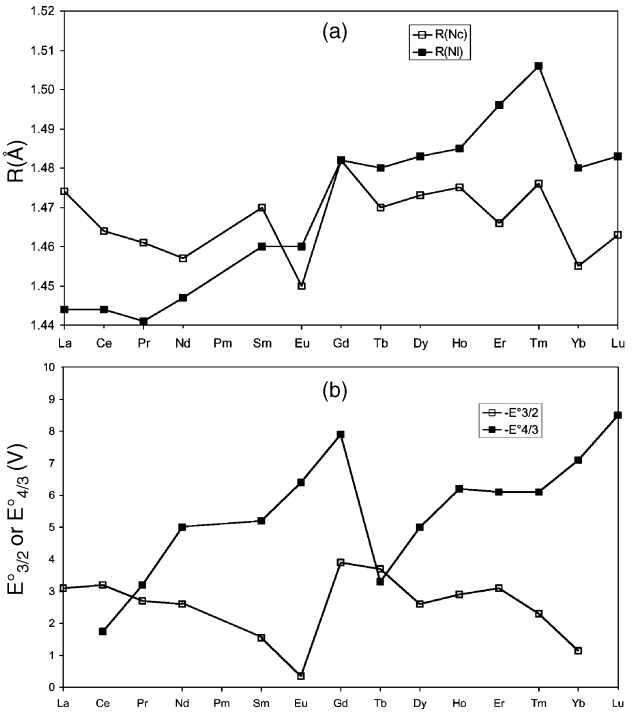


Fig. 1 (a) Lateral and central nitrogen radii in the crystal compounds $[\mathrm{Ln(tpy)Cl(H_2O)_y}]^{3+}$ along the Ln series. (b) Experimental and calculated $E^\circ_{3/2}$ and $E^\circ_{4/3}$ redox potentials along the Ln series.[14]

2 Results and interpretation of quantum chemical calculations

Quantum chemical ground state molecular orbital calculations of the free gas-phase ligands L = tpy, Tptz, Adptz, Btp, Pyr_2-Pym, Bzimpy and the complexes $[\mathrm{LnL}]^{3+}$ with Ln = La, Eu, Lu, were used to study the mechanism of Ln^{3+} complexation by planar terdendate nitrogen ligands in solution. *Ab initio* calculations determined the effective charges Q_c and Q_l on the central and lateral rings (including substituents),

Table 2 Calculated electronic parameters (atomic and group charges, bond overlap populations) related to the free ligand L and the corresponding $[\mathrm{LnL}]^{3+}$ complexes (Ln = La, Eu, Lu) in vacuum

						$[\mathrm{LnL}]^{3+}$						
	Free ligand charges					Charges					OP	
L	Q_c[a]	Q_l[a]	$q(N_c)$[b]	$q(N_l)$[b]	Ln	Q_c[a]	Q_l[a]	$q(N_c)$[b]	$q(N_l)$[b]	q(Ln)	Ln–N_c	Ln–N_l
					La	0.148	0.197	−1.067	−0.986	2.459	0.047	0.028
tpy	−0.004	0.002	−0.562	−0.521	Eu	0.149	0.211	−1.101	−1.002	2.429	0.059	0.055
					Lu	0.145	0.226	−1.141	−1.017	2.403	0.071	0.087
					La	0.113	0.227	−1.116	−0.958	2.434	0.039	0.048
Tptz[c]	−0.085	0.043	−0.558	−0.516	Eu	0.120	0.240	−1.152	−0.973	2.400	0.052	0.073
					Lu	0.123	0.253	−1.187	−0.986	2.371	0.066	0.102
					La	0.097	0.232	−1.132	−0.957	2.439	0.041	0.046
Adptz	−0.068	0.034	−0.586	−0.512	Eu	0.101	0.246	−1.165	−0.972	2.407	0.054	0.071
					Lu	0.100	0.261	−1.199	−0.986	2.378	0.067	0.100
					La	0.268	0.116	−0.986	−0.770	2.499	0.061	0.030
Btp	0.070	−0.035	−0.559	−0.312	Eu	0.274	0.129	−1.014	−0.792	2.468	0.074	0.027
					Lu	0.272	0.143	−1.051	−0.813	2.441	0.086	0.022
					La	0.084	0.228	−1.062	−0.975	2.460	0.044	0.039
Pyr_2Pym[c]	−0.040	0.020	−0.541	−0.509	Eu	0.086	0.243	−1.095	−0.991	2.428	0.056	0.064
					Lu	0.083	0.259	−1.131	−1.005	2.399	0.068	0.095
					La	0.188	0.182	−1.007	−1.083	2.447	0.047	0.024
Bzimpy	−0.003	0.001	−0.515	−0.554	Eu	0.195	0.195	−1.038	−1.101	2.416	0.058	0.047
					Lu	0.194	0.208	−1.078	−1.117	2.389	0.067	0.077

[a] Substituents borne by the central or/and lateral rings of L molecules are included in the Q_c and Q_l calculations. [b] N_c and N_l are nitrogen atoms involved in bonding with the Ln ion. [c] Since these molecules are not symmetric, the lateral rings are slightly different, thus only average Q_l and $q(N_l)$ values are included in the table.

respectively, $q(N_c)$ and $q(N_l)$ on the central and lateral nitrogen atoms, as well as the overlap populations (OP) in the Ln–N_c and Ln–N_l bonds. The results are presented in Table 2 (results are given with a large number of significant figures as the calculations do not allow an estimate of the errors). Of particular importance here is the role of the lateral and central nitrogen atoms in complex formation as well as the relative contributions of covalent and ionic interactions in the Ln–N_c and Ln–N_l bonds. Note that these bonds correspond mainly to ionic interactions with a small amount of covalence since the effective charge of the lanthanide atom in the complexes is close to +3 (from +2.37 to +2.50).

In all the free neutral ligands except Btp, the central coordinating nitrogen atom (N_c) is more negatively charged than the coordinating lateral ones (N_l), the sum of the effective charges on the central ring (Q_c) is negative and that on the lateral rings (Q_l) is positive (note that $Q_c = -2\,Q_l$ since the free ligands are electro-neutral). Btp, for which Q_c is positive (+0.070), appears to be an exception. The calculations suggest that N_c or, more exactly, the central ring including all substituents, may be the electron donor in the case of all ligands, except for Btp.

In order to shed further light on this matter, let us consider the electron density distribution in the $[LnL]^{3+}$ complexes in which the large positive +3 charge is shared by the cation and the ligand. For example, in the case of the $[Eu^{+2.407}(Adptz)^{+0.593}]$ complex, a charge fraction $\delta q = 0.593$ a.u. is transferred from the ligand to the Eu cation. In all calculated $[LnL]^{3+}$ complexes, the transferred electronic density varies as follows: $0.63 \geqslant \delta q \geqslant 0.50$ a.u. Thus, the Ln–N bonds tend to have a partly covalent character. The analysis of the global transferred electronic density shows that the bonding is due to electron donation from the N lone pairs of the ligand to the 5d (main contribution) and 6s (small contribution) empty orbitals of the Ln ion. However, all atoms in L = Adptz take part in the transfer of electron density onto the Ln cation: the coordinating nitrogen atoms N_c and N_l withdraw from the less electronegative C and H atoms a significant part of their electronic density and then transfer it to the cation. In the free Adptz ligand, $q(N_c + 2N_l) = -1.610$ but in the complex $[Eu(Adptz)]^{3+}$, the corresponding value is significantly more negative and equal to −3.109. In this complex, the Adptz ligand is positively charged: the sum of the charges of all atoms C, H and N* (N* meaning all N atoms except N_c and N_l) is positive and equal to +3.702 a.u. Thus, the formation of the $[Eu(Adptz)]^{3+}$ complex corresponds to a strong perturbation in the charge distribution within the ligand. Note that the trends observed in the charge distribution in the free ligands are strengthened in the complexes. The process of electron density redistribution is not so simple to interpret. On one hand, it promotes the formation of partly covalent bonds through the direct and back donation of electron density within the Eu^{3+} (or more generally Ln^{3+}) ⇔ Adptz system but, on the other hand, the large negative charge borne by the coordinating nitrogen atoms (−3.109 a.u.) also promotes a strong ionic interaction with the cation having a large positive charge (+2.407 a.u.). Again, only the $[Ln(Btp)]^{3+}$ complexes appear to be exceptions. For example, in the complex $[Eu(Btp)]^{3+}$, the central ring is more positive than the lateral ones: $Q_c = +0.274$, $Q_l = +0.129$ whereas in $[Eu(Adptz)]^{3+}$, which is representative of the rest of the other complexes, the lateral rings are charged more positively than the central one ($Q_c = +0.101$, $Q_l = +0.246$ a.u.) (*cf.* Fig. 2). In the same way, the calculated interatomic distances $R(Eu–N_c) > R(Eu–N_l)$ in the complex formed with Btp, whereas $R(Eu–N_c) < R(Eu–N_l)$ in the corresponding Adptz complex (*cf.* Table 3).

In order to estimate the covalent and ionic contributions for metal-ligand interactions in solution, correlations were established between the first stability constants $\log K(LnL)$ measured in MeOH–H_2O (75%/25% vol.) solution[15,16]

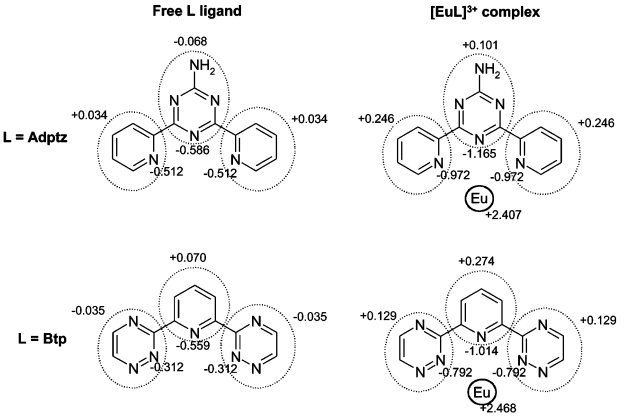


Fig. 2 Comparison of calculated atomic charges and ring group charges (in a.u.) for free L ligand and $[EuL]^{3+}$ complexes with L = Adptz and Btp.

(see Table 4) and: (i) the effective charges $q(N_c)$ and $q(N_l)$ on the central and lateral coordinating nitrogen atoms in the gas-phase complexes $[LnL]^{3+}$ (Fig. 3 for Eu^{3+} systems as an example) and (ii) the overlap population (OP) for Ln–N_c and Ln–N_l bonds (Fig. 4 for Eu^{3+} systems as an example). The effective charges on atoms are qualitative criteria of the ionic interaction in complex formation while the overlap populations in the bonds are criteria of the degree of covalent interaction.

First, Fig. 3 shows that the more negative the $q(N_c)$ values or the less negative the $q(N_l)$ ones in $[EuL]^{3+}$ complexes, the greater their stability in solution. This result demonstrates the opposing roles of N_c and N_l borne by the terdendate N ligand in the interaction with the lanthanide cation. The correlation with $q(N_c)$ is an indication that cation bonding with N_c is significantly electrostatic and that N_c is thus a good electron donor atom. However, it can be noted that the very low $q(N_l)$ charge in Btp (due to the presence of an adjacent nitrogen atom) means that the Btp molecule exhibits atypical behaviour compared to other studied ligands, and does not enter into the correlation between $\log K$ and $q(N_l)$.

Fig. 4 shows that the $[EuL]^{3+}$ complex stability increases from Btp to Adptz along with the covalent parameter OP for the Eu–N_l bonds; the OP parameter for Eu–N_c decreases slightly from $[Eu(Btp)]^{3+}$ to $[Eu(Adptz)]^{3+}$. There are thus significant differences in the variations of covalence for Ln–N_c and Ln–N_l bonds across the ligand series. One can note that the most stable complexes, $[Ln(Adptz)]^{3+}$ and $[Ln(Tptz)]^{3+}$, are characterised by the greatest covalence of the Ln–N bonds, due mainly to the interaction of the Ln cation with the two

Table 3 Calculated Ln–N_c and Ln–N_l bond distances (in Å) in $[LnL]^{3+}$ complexes (Ln = La, Eu, Lu) in vacuum

Ligand	Bond	La	Eu	Lu
tpy	Ln–N_c	2.49	2.36	2.23
	Ln–N_l	2.47	2.38	2.29
Tptz	Ln–N_c	2.41	2.29	2.17
	Ln–N_l	2.52	2.42	2.33
Adptz	Ln–N_c	2.42	2.29	2.17
	Ln–N_l	2.52	2.43	2.33
Btp	Ln–N_c	2.59	2.46	2.32
	Ln–N_l	2.45	2.36	2.27
Pyr_2Pym	Ln–N_c	2.47	2.35	2.22
	Ln–N_l	2.50	2.40	2.31
Bzimpy	Ln–N_c	2.57	2.44	2.30
	Ln–N_l	2.45	2.35	2.26

Table 4 Experimental thermodynamic data for LnL complexes with Ln = La–Lu and L = tpy, Tptz, Adptz, Btp, Me_4Btp, Pyr_2Pym and Bzimpy in aqueous or MeOH–H_2O solution (ΔH° in kJ mol^{-1}, ΔS° in J mol^{-1} K^{-1})

		tpy[b]	Tptz[a]	Tptz	Adptz[b]	Btp[b]	Me_4Btp	Pyr_2Pym[b]	Bzimpy[b]
La	log *K*	1.60 ± 0.05	2.23	2.80 ± 0.05[b]	3.90 ± 0.05	1.20 ± 0.05	2.2 ± 0.05[b]	1.90 ± 0.05	1.20 ± 0.05
				2.90 ± 0.05[c]			1.96 ± 0.05[c]		
				2.66 ± 0.05[d]			2.01 ± 0.05[d]		
	ΔH°			− 9.1 ± 0.2[e]			2.1 ± 0.2[e]		
	ΔS°			23.0 ± 0.5[e]			45.0 ± 0.5[e]		
Pr	log *K*		3.16						
Nd	log *K*		3.23				2.90 ± 0.05[c]		
							2.78 ± 0.05[d]		
	ΔH°						− 4.7 ± 0.1[e]		
	ΔS°						39.0 ± 0.4[e]		
Pm	log *K*		3.3						
Sm	log *K*		3.35						
Eu	log *K*	2.50 ± 0.05	3.11	3.60 ± 0.05[b]	4.60 ± 0.05	1.60 ± 0.05	2.90 ± 0.05[b]	2.60 ± 0.05	1.70 ± 0.05
				3.68 ± 0.05[c]			3.04 ± 0.05[c]		
				3.18 ± 0.05[d]			2.85 ± 0.05[d]		
	ΔH°			− 18.6 ± 0.2[e]			− 6.8 ± 0.3[e]		
	ΔS°			4.0 ± 0.4[e]			34 ± 1[e]		
Gd	log *K*		3						
Tb	log *K*		2.5						
Dy	log *K*		2.43						
Ho	log *K*		2.43				2.47 ± 0.05[c]		
							2.42 ± 0.05[d]		
	ΔH°						− 3.1 ± 0.2[e]		
	ΔS°						37.0 ± 0.7[e]		
Er	log *K*		2.03						
Tm	log *K*		2						
Yb	log *K*		2.09						
Lu	log *K*	2.90 ± 0.05	2.2	2.70 ± 0.05[b]	4.30 ± 0.05	1.50 ± 0.05	2.70 ± 0.05[b]	2.40 ± 0.05	2.00 ± 0.05
				2.76 ± 0.05[c]			2.51 ± 0.05[c]		
				2.67 ± 0.05[d]			2.60 ± 0.05[d]		
	ΔH°			− 3.4 ± 0.2[e]			3.2 ± 0.6[e]		
	ΔS°			41 ± 1[e]			59 ± 2[e]		

[a] Extraction measurements from aqueous solutions.[17] [b] UV/vis spectroscopy measurements [MeOH–H_2O (76%/24%) solution, T = 298 K].[15] [c] UV/vis spectroscopy measurements [MeOH–H_2O (75%/25%) solution, T = 278 K].[16] [d] UV/vis spectroscopy measurements [MeOH–H_2O (75%/25%) solution, T = 328 K].[16] [e] Determination using van't Hoff law.[16]

lateral coordinating nitrogen atoms of the ligand. Since the overlap integrals (calculated by us but not shown here) for the Am(III)–N bonds within Am(III) complexes with terdentate nitrogen ligands are larger than those corresponding to Eu(III)–N bonds, it is worthy noticing that Am(III)–N bonds are expected to be more covalent than Eu(III)–N ones.

The mechanism of complexation can thus be interpreted as the transfer of electronic density from the N_c atom to the Ln cation, and the acceptance of electronic density by N_l atoms to form bonds with a significant part of covalence. The Ln–N_l bonds are strengthened by partial π character owing to the donor properties of the cations.

More generally, if the effective charges q(N), q(Ln) and the overlap populations play a significant role in complexation, the enthalpy term ΔH°(LnL) must therefore contribute significantly to the free energy of complex formation ΔG°(LnL). In this case, the change of the Ln–N bond energy controls complex formation. But, if the geometry and conformation properties of the complexes appear to be the most significant factors, the role of entropy in complex formation should

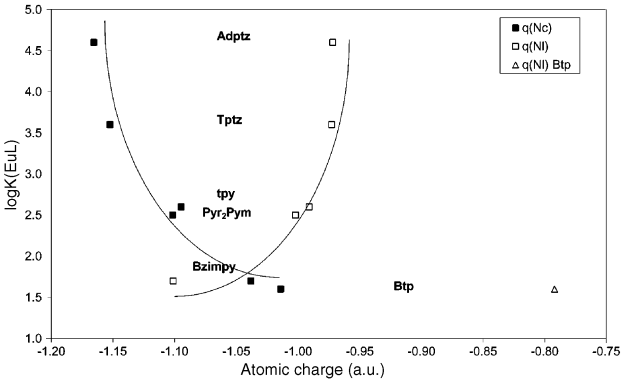


Fig. 3 Correlation between the atomic charges on N_l and N_c in $[EuL]^{3+}$ complexes calculated in the gas phase and the stability constants of $[EuLA_3]$ complexes (A = Cl^-, ClO_4^-) in MeOH–H_2O solution (room temperature).

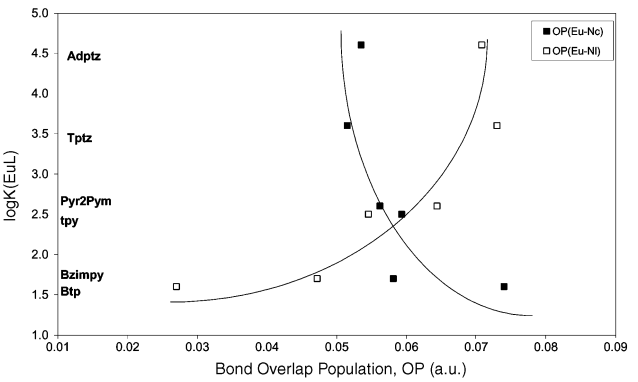


Fig. 4 Correlation between the Ln–N_l and Ln–N_c bond overlap populations in $[EuL]^{3+}$ complexes calculated in the gas phase and the stability constants of $[EuLA_3]$ complexes (A = Cl^-, ClO_4^-) in MeOH–H_2O solution (room temperature).

increase. It was noted above that the complexes with Btp do not follow the general complexation mechanism that was proposed; this can arise from a entropy contribution to ΔG°(LnBtp) that is more significant than the enthalpy.

3 Thermodynamics of Ln(III) chelation with planar terdendate nitrogen ligands

In the hypothetical reaction $[Ln(py)_3]^{3+} + tpy \rightleftharpoons [Ln(tpy)]^{3+} + 3$ py in aqueous solution, the driving force of complex formation is expected to be the positive entropy change; this corresponds to the well-known chelate effect.[18] Note that the two reactants $[Ln(py)_3]^{3+}$ and tpy form four products: $[Ln(tpy)]^{3+}$ and 3 py. In this case, the chelation increases the degree of freedom and the disorder of the system. These effects contribute to the positive entropy of the reaction. But, depending on the cation (La^{3+}, Eu^{3+} or Lu^{3+}) or ligand (Adptz or Btp), other factors must be taken into account that can not only change the entropy contribution over a wide range but also the entropy sign. These factors are: (i) the cation size, (ii) the chelate ring size, (iii) the effective charges of the nitrogen cavity and (iv) the donor–acceptor properties of the cations. The X-ray structural study[12] and the quantum-chemical data discussed above can serve to illustrate the thermodynamic aspects of Ln(III) complex formation.

It follows from the X-ray structural study that, in the complexes with a given ligand and various cations, the large light lanthanide cations (La–Nd) do not fit into the nitrogen cavity of L; this is why the main contribution to ΔG°(LnL) is due to the interaction between the Ln cation and N_I atoms; the effective number of nitrogen atoms n^* taking part in bonding is: $n^* \approx 2 < 3$. The entropy contribution, in this case, is expected to be significant. In the middle of the Ln series, with decreasing lanthanide ionic radii, the cations may better fit the ligand cavity and the n^* fraction of nitrogen atoms in bonding increases accordingly. Thus, the total bond energy Ln–N and the enthalpy contribution to the free energy of complexation increase whereas the entropy contribution decreases. With a further decrease in lanthanide ionic radii, the ligand cavity becomes too large and the Ln cations can sit closer to N_c, which has a more negative charge than N_I. Thus, the n^* fraction of nitrogen atoms in bonding decreases with decreasing $R(Ln^{3+})$, the enthalpy contribution to ΔG°(LnL) decreases but the entropy one increases.

As consequences of structural factors, the major contribution to the change in the free energy ΔG°(LnL) is the entropy for the light and heavy element complexes, those at the beginning and end of the lanthanide (and presumably the actinide) series, but the enthalpy in the middle of the series.

3.1 A chelating model predicting Ln(III) complex stability with terdendate nitrogen ligands.

The chelate effect theory was proposed in 1952 by Schwarzenbach[19] to interpret the formation of metal complexes with polyamines. A controversy exists in the literature about this theory,[18–20] but only the final equations of the theory will be considered here and applied to terpyridine-like planar ligands. Adamson[20] proposed to use the following equations for calculation of the free energy and chelate entropy changes under metal ion complexation by polyamine in aqueous solution:

$$\Delta G^\circ(\text{polyamine}) = \sum_n \Delta G_n^\circ - 2.303 \cdot RT \cdot \log 55.3 \cdot (n-1) \quad (1)$$

$$T\Delta S^\circ(\text{polyamine}) = T\sum_n \Delta S_n^\circ + 2.303 \cdot RT \cdot \log 55.3 \cdot (n-1) \quad (2)$$

where $R = 8.3143$ J mol^{-1} K^{-1}, T is the temperature in K, 55.3 is the molarity of water in pure water at 298 K and n is the denticity of the polyamine (number of bonding nitrogen atoms).

The first terms in the equations correspond to the thermodynamic parameters for the ammonia complexes of the metal ion. To apply these equations in the present case, for the simplest complexes $[Ln(tpy)]^{3+}$ one has to know $\Delta G_3^\circ[Ln(py)_3]$, the change of free energy upon complexation of Ln^{3+} with three pyridine ligands. According to Martell and Hancock,[18] the calculated $\log K_1$ values for the 1 : 1 complexes between La^{3+}, Lu^{3+} and pyridine are the same and equal to -0.2. For a series of ligands with the same n value, the $\sum_n \Delta G_n^\circ$ term in eqn. (1) is constant. But the second term in eqn. (1) is also constant. Thus, eqn. (1) cannot be used without modification for a series of polydendate nitrogen ligands to interpret the observed Ln(III) complex stability variation according to the type of ligand. The same reasoning can be applied to eqn. (2). In addition, for all the studied ligands except tpy, it is not clear what should be considered as the monodentate ligand. For example, for Pyr_2Pym, two kinds of monodentate ligands are involved: C_5H_5N (pyridine) and $C_4H_4N_2$ (pyrimidine). Finally, in eqn. (1) and (2), the second terms that determine the chelating effects are the same. This means that $\Delta G^\circ(\text{chelation}) = T\Delta S^\circ(\text{chelation})$ and therefore $\Delta H^\circ(\text{chelation}) = 0$, only the chelation entropy promotes complexation.

It will be shown below that the entropy and enthalpy contributions to the free energy of complexation depend to a significant extent on the type of terdendate nitrogen ligand and cation considered. These changes are related to the effective number of coordinating nitrogen atoms of the ligand. However, although the classical chelating model cannot be used without taking into account the exact characteristics of the ligands (*i.e.*, the moiety identities), the classical idea[19,20] of increasing stability of complexes with chelating ligands due to the chelate effect will be used. The only problem is to evaluate this effect quantitatively according to the complexes considered.

3.2 Calculation of the thermodynamic functions of $[LnL]^{3+}$ complex formation in MeOH–H_2O solutions.

The donor–acceptor model is used to calculate entropy ΔS°(LnL) and enthalpy ΔH°(LnL) changes where L = Adptz, Tptz, Btp, Me_4Btp and Pyr_2Pym, using the known $\log K$(LnL) values. Note that tpy and Bzimpy complexes are not considered here owing to their "atypical" behaviour.

The available experimental thermodynamic data base for complexation of some Ln^{3+} ions by various terdendate L ligands is listed in Table 4. This data base is unfortunately not as extensive as hoped, it was therefore undertaken to complete this table and obtain $\log K$, ΔH° and ΔS° values for all the ligands, except tpy and Bzimpy, in MeOH–H_2O solution. The method used to achieve this goal consisted in establishing correlations within the experimental data available.

Stability constants for $[LnL]^{3+}$ complexes. To determine the missing $\log K_1$ data for all the Ln^{3+} ions and all the ligands L considered in MeOH–H_2O medium, the following strategy was adopted. (i) The $\log K_1$ values corresponding to the Tptz ligand in aqueous solution determined experimentally by Vitorge[17] for almost all Ln ions were the starting data. (ii) Some experimental $\log K_1$ data corresponding to the Tptz ligand in MeOH–H_2O solution are available.[15,16] Comparing $\log K_1$(LnTptz) for given Ln ions in these two media shows an almost constant increase ($\Delta \log K_1 \approx 0.5$) in complex stability when passing from water to MeOH–H_2O solution. This constant value of $\Delta \log K_1$ was then used for calculating all $\log K_1$(LnTptz) for MeOH–H_2O solution. (iii) For ligands other than Tptz, experimental $\log K_1$(LnL) values for MeOH–H_2O solution were plotted *versus* the corresponding $\log K_1$(LnTptz) for the

Table 5 Calculated or *experimental* $\log K_1$(LnL) data for Ln = La–Lu and L = Tptz, Adptz, Btp, Me_4Btp and Pyr_2Pym in MeOH–H_2O solution

Ln	Tptz	Adptz	Btp	Me_4Btp	Pyr_2Pym
La	*2.80*	*3.90*	*1.20*	*1.98*	*1.90*
Ce	3.20	4.36	1.48	2.62	2.38
Pr	3.66	4.61	1.60	2.88	2.60
Nd	3.73	4.64	1.61	*2.86*	2.63
Pm	3.80	4.68	1.63	2.96	2.66
Sm	3.85	4.71	1.65	2.99	2.69
Eu	*3.60*	*4.60*	*1.60*	*2.96*	*2.60*
Gd	3.50	4.52	1.55	2.79	2.52
Tb	3.00	4.25	1.42	2.50	2.28
Dy	2.93	4.21	1.41	2.46	2.25
Ho	2.93	4.21	1.41	*2.45*	2.25
Er	2.53	3.99	1.30	2.24	2.06
Tm	2.50	3.98	1.29	2.22	2.05
Yb	2.59	4.03	1.32	2.27	2.09
Lu	*2.70*	*4.30*	*1.50*	*2.70*	*2.40*

same medium. Linear correlations were chosen for the calculation of all the missing $\log K_1$(LnL) data. The results of these calculations are presented in Table 5.

Proposed model for the entropy of complexation. From the discussion of the general trends in the variation of thermodynamic properties upon complexation of Ln^{3+} and An^{3+} with terdendate nitrogen ligands, it may be expected that the higher the number of nitrogen atoms (n^*) involved in the enthalpy changes during complexation, the smaller the corresponding entropy changes.

When $n^* \rightarrow 3$, the total bond energy (Ln–N) is expected to be large, thus the enthalpy contribution to ΔG°(LnL) is large but the entropy contribution is small. This is why the term $(3-n^*)$ has been included in the proposed formulas for calculating ΔS°(LnL):

$$\Delta S^\circ(\mathrm{LnL}) = 2.303 \cdot R \cdot \log 30 \cdot (3 - n^*) \cdot f(\mathrm{CN}) \qquad (3)$$

where 30 corresponds to the estimated molarity in (MeOH + H_2O) molecules for MeOH–H_2O medium (75/25% vol.) and the f(CN) function determines the entropy variation, depending on the change of coordination number (CN) in the LnL complexes.[16] This function can be expressed as follows:

$$f(\mathrm{CN}) = \frac{(\mathrm{CN})_{\mathrm{light}}}{2 \cdot (\mathrm{CN})_{\mathrm{Ln}} - (\mathrm{CN})_{\mathrm{light}}} \qquad (4)$$

where $(CN)_{Ln}$ for any lanthanide complex is normalised with respect to $(CN)_{light}$ for complexes of the light Ln ions. Thus, for the light Ln complexes, $f(CN) = 1$ since $(CN)_{Ln} = (CN)_{light}$.

The n^* value is the sum of two terms:

$$n^* = n(\mathrm{ionic}) + n(\mathrm{covalent}) \qquad (5)$$

where n(ionic) characterises the chelating ability of the ligand and n(covalent) depends on the interactions between the ligand and the cation, that is the charge transfer in the redox process discussed above (acceptor and donor abilities of the Ln cation). The n(ionic) term can be evaluated as follows:

$$n(\mathrm{ionic}) = \frac{\log K(\mathrm{LaL})}{\log 30} \qquad (6)$$

where $\log K$(LaL) is chosen as the reference since, for the LaL complex, the transfer of electron density from the cation to the lateral nitrogens tends to be minimal (La^{3+} is not oxidised). This term can be interpreted as the effective number of nitrogen atoms taking part in the purely electrostatic interaction with Ln cations. It depends on the charge $q(N) = q(N_c) + 2\,q(N_l)$ borne by the nitrogen cavity of the free ligand and the size of this cavity. In fact, a very good correlation exists between n(ionic) and the calculated q(N). The donor–acceptor interaction increases the effective number of nitrogen atoms taking part in the enthalpy changes owing to the direct $N_c \rightarrow Ln^{3+}$ and back $Ln^{3+} \rightarrow N_l$ electron transfers.

The term n(covalent) is the probability α_i ($i = 1$ or 2)[21] of increasing the effective number of nitrogen atoms taking part in bonding with the cation owing to the donor–acceptor covalent interaction. The probability α_1 for a cation to accept electron density from the central nitrogen atom of the ligand, defined for heavy Ln, can be expressed as:

$$\alpha_1 = \left(1 + \frac{\xi_q}{\xi_{q+1}}\right)^{-1} \qquad (7)$$

and the probability α_2 to donate electron density from the cation to the lateral nitrogen atoms of the ligand, defined for light Ln, as:

$$\alpha_2 = \left(1 + \frac{\xi_q}{\xi_{q-1}}\right)^{-1} \qquad (8)$$

where ξ are the configurational partition functions and q is the number of electrons in the ground state electronic configuration f^q of Ln^{3+} cations ($q = 0$–14 for La^{3+}–Lu^{3+}). In the approximation when only the ground level of the f ion is occupied, $\xi_q = 2L_q + 1$, where L_q is the orbital angular momentum quantum number for the ground state term.

3.3 Calculated results and discussion. Before discussing the results of ΔS° and ΔH° calculations for LnL complexes with Adptz and Btp ligands, the calculated values related to two Me_4Btp lanthanide (Ln = Nd and Eu) complexes, chosen as examples, were compared with the experimental data in order to check the model. First, a value for n(ionic) of 1.34 was calculated for the ligand Me_4Btp. In $[Nd(Me_4Btp)]^{3+}$ the electronic configuration of Nd^{3+} is $4f^3$, the ground state term is I, $L_q = 6$ and after electron transfer $L_{q-1} = 5$, then $\alpha_2 = n(\mathrm{covalent}) = 0.46$ and thus $n^* = 1.80$. With these data, $\Delta S^\circ(NdMe_4Btp)$ can be calculated using eqn (3) with $f(CN) = 1.0$: it is equal to 34.0 J mol^{-1} K^{-1}. With $\Delta G^\circ(NdMe_4Btp) = -16.3$ kJ mol^{-1}, $\Delta H^\circ(NdMe_4Btp) = -6.2$ kJ mol^{-1}. These calculated ΔS° and ΔH° values are close to the experimental values of 39 J mol^{-1} K^{-1} and -4.7 kJ mol^{-1}, respectively.[16]

In $[Eu(Me_4Btp)]^{3+}$ the electronic configuration of Eu^{3+} is $4f^6$ (F state), $L_q = 3$, $L_{q-1} = 2$ and $\alpha_2 = 0.61$. Unfortunately, the coordination number of Eu(III) in this complex is not known. A value of CN(Eu) = 8.45 as in $[Eu(tpy)Cl(H_2O)_{4.45}]Cl_2$[12] can be proposed, which leads to $f(CN) = 1.14$ and thus $\Delta S^\circ = 33.8$ J mol^{-1} K^{-1}, very close to the experimental value (34.0). The calculated and experimental[16] ΔH° values are also equal.

As shown by these examples, good agreement is obtained between calculated and experimental thermodynamic parameters. The uncertainty in these calculations was estimated to be a few kJ mol^{-1} (for ΔG°, ΔH° and $T\Delta S^\circ$).

Tables 6 and 7 present the ΔG°, ΔH° and ΔS° values for $[LnL]^{3+}$ complex formation with L = Adptz and Btp, respectively, calculated with the proposed model. According to the calculated data, the stability of the $[LnAdptz]^{3+}$ complexes in MeOH–H_2O solution is favoured by the enthalpy contribution in the free energy of complex formation whereas that of $[LnBtp]^{3+}$ is favoured by the entropy contribution. It is clear that the Adptz and Btp ligands are at the ends of the sequences of the enthalpy and entropy contributions to ΔG°(LnL): Adptz > Tptz > Me_4Btp > Pyr_2Pym > Btp for enthalpy, and the reverse for entropy.

The reason for the high stability of $[LnAdptz]^{3+}$ complexes lies in the high electrostatic capacity of the ligand [q(N) value] and in the strong donor–acceptor interaction resulting in an enthalpy mechanism of complexation. The central ring and the

Table 6 Thermodynamic data (calculated or *experimental*) for the complexation of Ln(III) with Adptz in MeOH–H_2O solution

Ln	log *K*	ΔG°/kJ mol^{-1}	*n**	ΔS°/J mol^{-1} K^{-1}	$-T\Delta S^\circ$/kJ mol^{-1}	ΔH°/kJ mol^{-1}
La	*3.90*	− 22.3	2.64	10.2	− 3.0	− 19.2
Ce	4.36	− 24.9	2.77	6.7	− 2.0	− 22.9
Pr	4.61	− 26.3	3.03	− 0.8	0.2	− 26.5
Nd	4.64	− 26.5	3.10	− 2.8	0.8	− 27.3
Pm	4.68	− 26.7	3.14	− 4.1	1.2	− 27.9
Sm	4.71	− 26.9	3.18	− 5.6	1.7	− 28.5
Eu	*4.60*	− 26.2	3.25	− 8.1	2.4	− 28.7
Gd	4.52	− 25.8	3.52	− 18.2	5.4	− 31.2
Tb	4.25	− 24.2	3.25	− 9.1	2.7	− 27.0
Dy	4.21	− 24.0	3.18	− 6.6	2.0	− 26.0
Ho	4.21	− 24.0	3.14	− 5.1	1.5	− 25.5
Er	3.99	− 22.8	3.10	− 3.6	1.1	− 23.9
Tm	3.98	− 22.7	3.03	− 1.1	0.3	− 23.0
Yb	4.03	− 23.0	2.77	8.6	− 2.6	− 20.4
Lu	*4.30*	− 24.5	2.64	13.1	− 3.9	− 20.6

Table 7 Thermodynamic data (calculated or *experimental*) for the complexation of Ln(III) with Btp in MeOH–H_2O solution

Ln	log *K*	ΔG°/kJ mol^{-1}	*n**	ΔS°/J mol^{-1} K^{-1}	$-T\Delta S^\circ$/kJ mol^{-1}	ΔH°/kJ mol^{-1}
La	*1.20*	− 6.9	0.82	61.7	− 18.4	11.5
Ce	1.48	− 8.4	0.94	58.2	− 17.3	8.9
Pr	1.60	− 9.1	1.21	50.7	− 15.1	6.0
Nd	1.61	− 9.2	1.28	48.7	− 14.5	5.3
Pm	1.63	− 9.3	1.32	49.8	− 14.8	5.5
Sm	1.65	− 9.4	1.36	50.9	− 15.2	5.8
Eu	*1.60*	− 9.1	1.43	50.6	− 15.1	5.9
Gd	1.55	− 8.9	1.69	46.2	− 13.8	4.9
Tb	1.42	− 8.1	1.43	57.1	− 17.0	8.9
Dy	1.41	− 8.0	1.36	59.6	− 17.8	9.8
Ho	1.41	− 8.0	1.32	61.1	− 18.2	10.2
Er	1.30	− 7.4	1.28	62.7	− 18.7	11.2
Tm	1.29	− 7.4	1.21	65.2	− 19.4	12.0
Yb	1.32	− 7.5	0.94	74.8	− 22.3	14.8
Lu	*1.50*	− 8.6	0.82	79.3	− 23.6	15.1

central coordinating nitrogen atom in the Adptz free ligand as well as in the complexes $[Ln(Adptz)]^{3+}$ are more negatively charged in comparison with the lateral ones. The high donor ability of the central ring and its coordinating nitrogen atom in the Adptz ligand results in the back donation of electron density from the cation and in a strengthening of the lateral bonds between the Ln cation and N_l. The covalent overlap populations (OP) shown in Fig. 4 clearly prove this effect. Moreover, the ligand Adptz is characterised by: (i) a large nitrogen cavity size, (ii) the most negative charge on the nitrogen cavity within the series of ligands considered and (iii) the largest difference $\delta q(N) = q(N_l) - q(N_c)$. From the comparison between *n*(ionic), $\delta q(N)$ and $q(N_c) + 2q(N_l)$ for Adptz, Tptz and Pyr_2Pym, we can conclude that a "good ligand" for Ln(III) complexation should have lateral and central nitrogen atoms with significantly different effective charges. Ligands of this type ensure a good donation from N_c to Ln^{3+} and a good back donation from Ln^{3+} to N_l.

A difference in the electronic structures was noted above between Btp and Adptz ligands and their corresponding Ln(III) complexes. The central ring in the Btp free ligand is charged positively, which pushes the cation away from the nitrogen cavity and, consequently, the interatomic distance Ln–N_c becomes larger and the electron donor ability of N_c is thus weaker. In this case, the lateral rings appear to be donors relative to the Ln cation. Moreover, the Btp ligand has a low electrostatic capacity *q*(N). This value for Adptz, Tptz and Pyr_2Pym ligands is about − 1.6 but only − 1.18 for Btp.

Other reason for the low stability of $[LnBtp]^{3+}$ is thought to be the size of the nitrogen cavity of the Btp ligand, which may be characterised by the N_c–Ln–N_l angle within the complex. From quantum-chemical calculations it appears that these angles in LnBtp complexes are smaller than those in the complexes with the other ligands. For example, in the $[EuL]^{3+}$ complexes with L = Adptz, Tptz and Pyr_2Pym, the calculated N_c–Ln–N_l angle is about 137° but only 130° for the Eu-Btp complex. The nitrogen cavity of the Btp ligand is thus too small to accommodate the Ln(III) cation. Without causing an important steric strain it is impossible to join the lateral and central nitrogen atoms together to form a 9-coordinated tricapped trigonal prism or an 8-coordinated square antiprism, which are characteristic of the lanthanide polyhedrons[7b] with

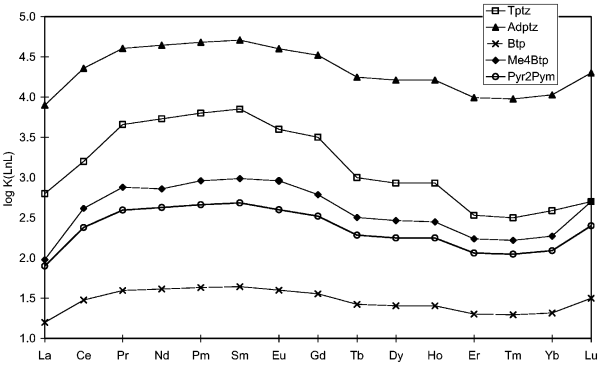


Fig. 5 Variation of calculated log *K*(LnL) values across the lanthanide series in MeOH–H_2O solution (76%/24% vol).

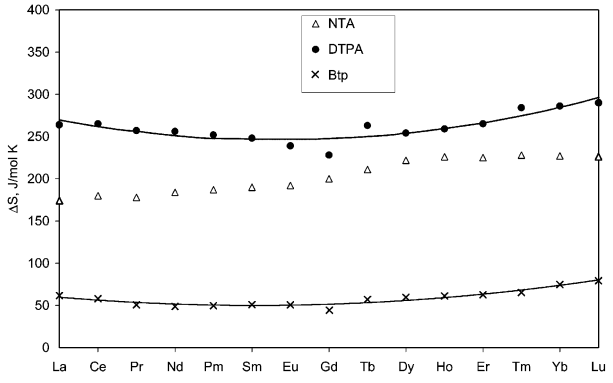


Fig. 6 Variation of ΔS° across the lanthanide series for the complexation of Ln(III) with NTA, DTPA in aqueous solution[22] and Btp in MeOH–H_2O solution (76%/24% vol).

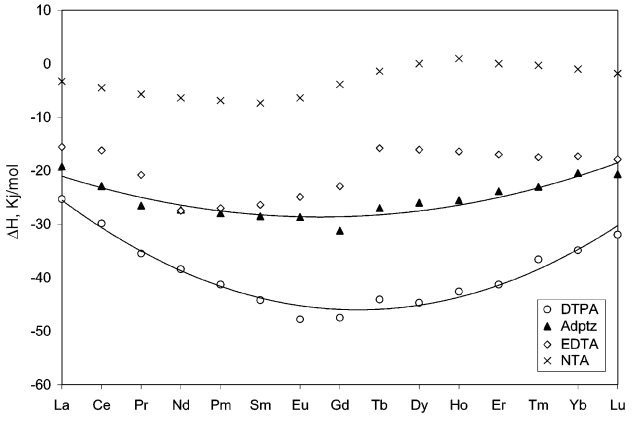


Fig. 7 Variation of ΔH° across the lanthanide series for the complexation of Ln(III) with NTA, DTPA, EDTA in aqueous solution[22] and Adptz in MeOH–H_2O solution (76%/24% vol).

planar nitrogen ligands. These factors are thought to be the main explanations for the low thermodynamic stability of the $[LnBtp]^{3+}$ complexes.

Finally, trends in the variations of $\log K_1$, ΔS° and ΔH° *vs.* atomic number across the Ln series, are presented in Fig. 5 to 7, respectively, for: (i) several planar terdendate-N ligands (Fig. 5), (ii) Btp ligand compared with nitrilotriacetic acid (NTA) and diethylenetriaminepentaacetic acid (DTPA)[22] (Fig. 6) and (iii) Adptz ligand, compared with NTA, EDTA and DTPA ligands[22] (Fig. 7). From these plots, one should note that the trends observed for Btp and/or Adptz ligands follow only that of the terdendate-N ligand DTPA, but not those of the other *n*-dendate-N ($n \neq 3$) ligands.

Conclusions

In an attempt to study the electronic mechanism of complexation of trivalent lanthanides with planar terdentate-N ligands, a donor–acceptor model has been developed to predict the thermodynamic properties of Ln(III) ion complexation in solution. The use of this model provides considerable insight into the factors affecting the thermodynamic stability of the lanthanide complexes.

It has been shown that: (i) the part of covalence in Ln–N_1 bonds, (ii) the relative sizes of the nitrogen cavity of the ligand and of the cation, (iii) the electrostatic capacity q(N) of the ligand and, (iv) the difference in the effective charges on the lateral and central nitrogen atoms are the main factors governing the formation of complexes between trivalent lanthanides and planar terdentate-N ligands. On the basis of the calculated overlap integrals, the covalence of An–N bonds in actinide(III) complexes with the same ligands is expected to be greater than for the Ln–N bonds in the corresponding Ln(III) complexes. The mechanism of complex formation between Ln^{3+} and the planar terdentate-N ligands may be interpreted in terms of the direct $N_c \Rightarrow Ln^{3+}$ and the back $Ln^{3+} \Rightarrow N_l$ electron donation, that is in terms of Ln(III) redox processes. This study shows that during complex formation in solution, partial reduction of the Ln cation is connected to the central ring of the terdentate nitrogen ligand whereas its partial oxidation is connected with the lateral nitrogen rings.

The difference in the thermodynamics of complex formation between trivalent lanthanide ions with planar terdentate-N ligands and polyaminocarboxylate ligands lies in the variation of the effective number of the chelating nitrogen atoms, depending on the donor–acceptor ability of the Ln cation.

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