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Thermodynamic Parameters of the Complexation of Trivalent Lanthanides by Monocyclic and Bicyclic Cryptands and the Tripodal Ligand Tris(3,6-dioxaheptyl)amine in Propylene Carbonate

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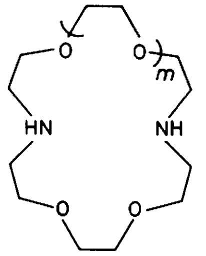
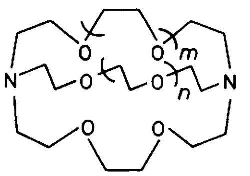
Complexation of lanthanide cations by the monocyclic trioxa (2.1) and tetraoxa (2.2) cryptands, the bicyclic tetraoxa (2.1.1), pentaoxa (2.2.1), and hexaoxa (2.2.2) cryptands, and the related tripodal ligand tris(3,6-dioxaheptyl)amine (tdoha) in propylene carbonate has been investigated at various temperatures by a competitive potentiometric method with Ag^+ as auxiliary cation. Values of the stability constants of the 1 : 1 cryptates and the 1 : 1 and 1 : 2 tdoha complexes are given for eight cations from La^{3+} to Yb^{3+}, as well as the complexation enthalpies and entropies for La^{3+}, Er^{3+}, Pr^{3+}, and Eu^{3+} complexes. The ligand tdoha is a weaker complexing agent than all cryptands but a stronger one than related crown ethers. For all nitrogen-containing ligands, the stabilities of the complexes increase with the atomic number of the lanthanides, whereas they decrease for the polyethers. All complexes are enthalpy stabilized, the entropic contributions being favourable to the complexation in some cases, and unfavourable in some others. The macrobicyclic effect is important if 2.2.1 is compared to 2.1, and entirely of enthalpic origin, but much weaker if 2.2.2 is compared to 2.2, due to unfavourable enthalpic contributions counterbalancing favourable entropic factors.

The sizes and chemical properties of trivalent lanthanides Ln^{3+} resemble to some extent those of alkali and alkaline-earth cations, in particular because of the ionic character of their interactions. Thus very stable complexes are expected to be formed between these cations and mono- or bi-cyclic cryptands. The results obtained by Burns and Baes[1] in water and by Anderegg[2] in a water–methanol (5:95) mixture evidenced the importance of hydrolysis phenomena, strongly competing with complexation. Our previous study of the complexation of Ln^{3+} cations by the cryptands 2.1 and 2.2.1 in the two anhydrous media methanol and propylene carbonate (pc)[3] showed that polyoxadiazamacrocycles are much stronger complexing agents for trivalent lanthanides than the macrocyclic polyethers 1,4,7,10,13-pentaoxacyclopentadecane (L^7) and 1,4,7,10,13,16-hexaoxacyclo-octadecane (L^8), and that the bicyclic 2.2.1 cryptates are more stable than the monocyclic 2.1 complexes. In both media the stability of the diazamacrocyclic complexes increases with the atomic number of the lanthanides whereas it decreases for complexes of the above crown ethers.

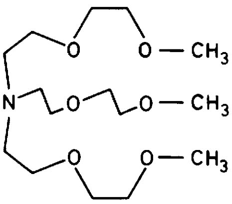
In extension of our earlier work, we report in the present paper our new results concerning the complexation in pc of some Ln^{3+} cations (Ln = La, Pr, Sm, Eu, Gd, Dy, Er, or Yb) by three cryptands L (L = 2.2.2, 2.1.1, and 2.2) and by a related tripodal ligand, tris(3,6-dioxaheptyl)amine (tdoha) which is a new phase-transfer catalyst of great industrial interest developed by Rhône-Poulenc Recherches (industrial name TDA-1).[4] The stoicheiometry and the stability constants β_{xy} of the M_xL_y complexes were first determined at 25 °C using a competitive potentiometric method with Ag^+ as auxiliary cation. The values of β_{xy} were also determined at 30, 40, and 50 °C in the case of Pr^{3+} and Er^{3+} with 2.2.2 (L^5), 2.2.1 (L^4), 2.1.1 (L^3), 2.2 (L^2), 2.1 (L^1), and tdoha (L^6), of Eu^{3+} with L^6, Pr^{3+} with L^8, and La^{3+} with L^5, in order to determine the enthalpic and entropic contributions to the stability of the complexes. In some cases where slow complexation kinetics were suspected, the value of β_{11} directly measured at 25 °C was compared to the value derived from the extrapolation at 25 °C of the plot $\log \beta_{11} = f(1/T)$. When the values disagreed, preference was given to the extrapolated one. When unavailable from the literature, the stability constants of the silver complexes, which are necessary for the calculations, were determined at each investigated temperature.



$m = 0$: 2.1 (L^1)
$m = 1$: 2.2 (L^2)



$m = n = 0$: 2.1.1 (L^3)
$m = 1, n = 0$: 2.2.1 (L^4)
$m = n = 1$: 2.2.2 (L^5)



tdoha (L^6)

Experimental

Solutions of the ligands in pc were added to mixtures of lanthanide trifluoromethanesulphonate and silver perchlorate in pc ($[Ln^{3+}]$ and $[Ag^+] \approx 10^{-3}$ mol dm^{-3}) in the presence of NEt_4ClO_4 (0.1 mol dm^{-3}) as supporting electrolyte. At the end of each experiment, the ligand was in excess with respect to the metal ions: $[L] \simeq 2([Ln^{3+}] + [Ag^+])$. The Ag^+ concentration was monitored by a silver electrode. The solutions were prepared and kept in a dry-box and the measurements were performed under dry nitrogen in order to minimize moisture effects. The water content of each solution was checked by the

Table 1. Stability constants (log $\beta_{11} \pm 2\sigma$) for the complexation of some lanthanides and silver by mono- and bi-cyclic cryptands and L^6 in pc, at 25 °C; $I = 0.1$ mol dm^{-3} (NEt_4ClO_4)

				L^6	
Cation	L^5	L^3	L^2		a
La^{3+}	16.1 ± 0.4 $(12.91)^b$	15.1 ± 0.1	16.5 ± 0.2	9.0 ± 0.1	16.3 ± 0.1
Pr^{3+}	15.9^c $(15.88)^b$	15.51^c	16.1 ± 0.1	8.8 ± 0.1	16.3 ± 0.1
Sm^{3+}	17.3 ± 0.1	15.3 ± 0.1	16.5 ± 0.1	9.5 ± 0.1	17.6 ± 0.1
$Eu^{3+\,d}$	17.2 ± 0.1	15.2 ± 0.1	16.5 ± 0.1	7.6 ± 0.1	14.0 ± 0.1
Gd^{3+}	16.8 ± 0.1	15.4 ± 0.1	16.5 ± 0.1	9.1 ± 0.1	16.7 ± 0.1
Dy^{3+}	17.1 ± 0.1	15.4 ± 0.1	16.9 ± 0.2	9.5 ± 0.1	17.5 ± 0.1
Er^{3+}	16.8^c	15.5 ± 0.1	16.9 ± 0.2	9.7 ± 0.1	17.7 ± 0.1
Yb^{3+}	18.0 ± 0.1 $(17.56)^b$	15.6 ± 0.2	16.9 ± 0.2	10.1 ± 0.2	18.3 ± 0.1
Ag^+	16.3^e	15.0^e	15.9 ± 0.1	8.5 ± 0.1	

[a] log β_{12} corresponding to $Ln^{3+} + 2L \rightleftharpoons LnL_2^{3+}$. [b] Ref. 7. [c] Extrapolated from higher temperatures. [d] log $\beta_{11}[Eu(L^7)^{3+}] = 5.6$ and log $\beta_{11}[Eu(L^8)^{3+}] = 8.5$ (this work). [e] From B. Spiess, F. Arnaud-Neu, and M. J. Schwing-Weill, *Inorg. Nucl. Chem. Lett.*, 1981, **17**, 253.

Karl-Fischer method, and was always found to be below 100 p.p.m. Purification of the solvent, preparation of the starting materials, and the experimental details have been previously described[3] as well as the interpretation of the data by the program MINIQUAD.[5]

Results

In pc, the cryptands L^3, L^5, and L^2 form only 1:1 complexes. In the case of L^6, the best-fit treatment was significantly improved (by a factor 100 to 1 000 on the minimized quantity U) when a second species of 1:2 stoicheiometry was taken into account. The logarithms of the overall stability constants β_{11} and β_{12} are reported in Table 1 with their 95% confidence interval $\pm 2\sigma$, corresponding to the simultaneous interpretation of generally two distinct experiments.

As already mentioned, our procedure generally leads to fast equilibria, except for the complexation of Pr^{3+} and Er^{3+} with L^5 where 15 min was necessary to reach stable readings of the silver electrode potential. The existence of a slow kinetics in these two cases was further confirmed by our determinations at higher temperatures, where the equilibria are supposed to be reached much faster: the linearity of log β_{11} with the reciprocal of T, expected in a small range of temperature, has been verified in each case and the values of log β_{11} extrapolated at 25 °C for the $Pr(L^5)^{3+}$ and $Er(L^5)^{3+}$ complexes (see Table 1) are fairly different from those directly determined at 25 °C. For the other systems, the experimental and extrapolated values are generally in good agreement. The stability constants at 30, 40, and 50 °C are given in Table 2. Values of log β_{11} for $Ag(L^5)^+$ were calculated for the three temperatures from the Van't Hoff equation using the value at 25 °C and the enthalpy of formation determined by Gutknecht *et al.*[6]

The thermodynamic parameters of the formation of some 1:1 complexes are reported in Table 3. Values of ΔH, the enthalpy of complexation, and ΔS, the corresponding entropy, have been obtained respectively from the slopes and the intercepts of the least-squares linear plots log $\beta_{11} = f(1/T)$. It is obvious that this technique should be employed when the reaction under investigation is not fast enough for a direct more precise calorimetric determination.

Results concerning the complexation of some lanthanide cations by L^5 which have recently appeared[7] are reported in parentheses in Table 1: these values of log β_{11} are generally lower than ours, especially for La^{3+} (3.2 log units). One might attribute these rather surprising differences to the fact that the procedure used in ref. 7 is different from ours: the addition of Ln^{3+} to $Ag(L^5)^+$ solutions could possibly result in slower exchange kinetics between Ag^+ and Ln^{3+}, particularly in the case of La^{3+}; however this difficulty should have been overcome by the authors extrapolation at 25 °C of their measurements at higher temperatures.

Table 2. Stability constants (log β_{11})[a] for the complexation of Pr^{3+}, Er^{3+}, and Ag^+ by mono- and bi-cyclic cryptands and related ligands in pc at several temperatures

Cation	Temperature	$L^{5\,b}$	L^4	L^3	L^2	L^1	$L^{6\,c}$	L^8
Pr^{3+}	30 °C	15.6	18.6	15.4	15.7	13.5	8.5	9.1
	40 °C	15.0	17.9	15.3	15.0	13.4	7.9	8.9
	50 °C	14.5	17.1	15.1	14.3	13.2	8.1	8.7
Er^{3+}	30 °C	16.5	18.9	15.4	16.5	14.2	9.7_5	
	40 °C	15.9	18.1	15.1	15.6	14.1	9.7	
	50 °C	15.3	17.3	14.9	14.8	13.9	9.6	
Ag^+	30 °C		18.5		15.6	13.0	8.5	6.9
	40 °C			14.9	14.8	12.8	7.8	6.7
	50 °C		17.0	14.8		12.7	7.4	6.6

[a] Precision: 95% confidence interval for ±0.1—0.2. [b] log β_{11}-$[La(L^5)^{3+}] = 15.4$ (at 40 °C) and 15.0 (at 50 °C). [c] log $\beta_{11}[Eu(L^6)^{3+}] =$ 7.7 (at 30 °C), 7.5 (at 40 °C) and 7.2 (at 50 °C).

Discussion

As for the previously studied L^4 and L^1 complexes the stability constants of L^3, L^2, and L^5 lanthanide complexes in pc are very high, ranging respectively around 15, between 16.1 and 16.9, and between 16.1 and 18.0. These values are much higher than in MeOH,[3] and, moreover, than in water[1] and Me_2SO,[8] as expected from the solvating properties of the solvents.[9]

Our new results confirm that polyoxadiazamacrocycles are better complexing agents for lanthanides than crown ethers, as already pointed out in methanol as well as in pc in the case of L^4, L^1, L^7, and L^8.[3] For instance, monocycles having the same cavity size and the same number of donor sites, such as L^1 and L^7 or L^2 and L^8 form complexes of very different stabilities. The substitution of two oxygen atoms in crown ethers by two NH groups leads to an important increase in stability (between 8 and 9.9 log units for the former and 7.5 and 9.2 log units for the latter) which could be ascribed, at least to some extent, to the higher polarizability of NH groups.

The stability of macrobicyclic cryptates follows the sequence: $Ln(L^4)^{3+} > Ln(L^5)^{3+} > Ln(L^3)^{3+}$, the difference in stability between L^4 and L^3 complexes averaging 3.5 log units. The better affinity of L^4 for lanthanide cations can be explained by favourable size considerations, as the internal cavity of this ligand (1.10 Å)[10] is well adapted to the metal ion. On the contrary, L^5 and L^3 are respectively too large and too small and the high stability of L^5 cryptates over L^3 homologues might be due to the greater flexibility and the greater number of donor sites of L^5. The reverse stability order was found in Me_2SO[8] on the basis of spectrophotometric measurements, the L^3 cryptates being the most stable complexes. This difference can be attributed to the strongly co-ordinating nature of Me_2SO, which is likely to interact with the lanthanide cations because of their high charges and co-ordination numbers. In water, pH-metric titration data led to no particular ligand selectivity[1] while other contradictory results, based on electrochemical measurements, indicated a higher stability for $Eu(L^4)^{3+}$ than for $Eu(L^5)^{3+}$.[11]

Table 3. Thermodynamic parameters[a] for the complexation of Ln^{3+} and Ag^{+} by mono- and bi-cyclic cryptands and related ligands

Cation		$L^{5\,b}$	L^{4}	L^{3}	L^{2}	L^{1}	L^{8}	$L^{6\,c}$
Pr^{3+}	$-\Delta G$	21.7^{d} $(20.6)^{f}$	25.9^{d}	21.1^{d}	21.9 ± 0.2	18.6^{d}	12.5^{e}	12.1 ± 0.2
	$-\Delta H$	25 ± 2 $(22.5)^{f}$	33 ± 5	6.9 ± 0.1	31 ± 1	6.7 ± 0.2	7 ± 2	12 ± 3
	ΔS	-10 ± 6 $(-7)^{f}$	-24 ± 15	48 ± 1	-31 ± 4	39.8 ± 0.2	19 ± 5	-2 ± 10
Er^{3+}	$-\Delta G$	23.0^{d}	26.3^{d}	21.1 ± 0.2	23.1 ± 0.3	19.4^{d}		13.2 ± 0.2
	$-\Delta H$	27 ± 1	35 ± 2	9 ± 2	37 ± 2	5 ± 1		0.7 ± 0.2
	ΔS	-12 ± 4	-28 ± 6	39 ± 1	-46 ± 8	47 ± 4		42 ± 1
Ag^{+}	$-\Delta G$	22.6^{g}	25.6^{h}	20.4^{h}	21.7 ± 0.2	17.9^{e}	9.6^{e}	11.6 ± 0.2
	$-\Delta H$	23.8^{g}	31 ± 2	3.1 ± 0.1	32 ± 2	8 ± 2	8 ± 2	22 ± 6
	ΔS	-4^{g}	-20 ± 7	58.0 ± 0.2	-35 ± 8	32 ± 7	4 ± 5	-33 ± 18

[a] ΔG and ΔH are in kcal mol^{-1} (cal = 4.184 J), ΔS in cal K^{-1} mol^{-1}. Precision: 95% confidence interval ($\pm 2\sigma$). [b] This work for $La(L^5)^{3+}$: $-\Delta G = 21.9 \pm 0.5$ (15.3), $-\Delta H = 18.5 \pm 0.1$ (13.0), $\Delta S = 11 \pm 1$ (15) (values from ref. 7 in parentheses). [c] This work for $Eu(L^6)^{3+}$: $-\Delta G = 10.7 \pm 0.2$, $-\Delta H = 12 \pm 2$, $\Delta S = -4 \pm 6$. [d] Corresponding to log β_{11} extrapolated from higher temperatures. [e] Ref. 3. [f] Ref. 7. [g] Ref. 6. [h] Footnote *e* Table 1.

1:1 Complexes of the tripodal ligand L^6 are much less stable than bicyclic or even monocyclic cryptates: for instance, the difference in stability between $La(L^5)^{3+}$ and $La(L^6)^{3+}$ is about 7 log units. On the other hand, L^6 is a better complexing agent than L^7 for all lanthanides, and better also than L^8, except for Eu^{3+}, which forms a 1:1 complex destabilized with respect to the Sm^{3+} and Gd^{3+} homologues (log β_{11} respectively 1.7 and 1.3 log units less). A small destabilization is also observed for the Eu^{3+} complexes of L^3, L^1, and L^7. An opposite Sm^{3+}/Eu^{3+} selectivity had been observed in MeOH with L^1 and L^4.[3] The successive stability constants of the 1:2 complexes of L^6 are about one log unit lower than those of the 1:1 complexes, with the same destabilization of the 1:2 chelates.

In pc the variation of the stability of the lanthanide cryptates with the atomic number *Z* of the cations is irregular (Figure). This is especially clear for the L^5 and L^1 complexes which display surprisingly parallel variations of log β_{11}, with stability minima and maxima for Pr^{3+}, Eu^{3+} (or Gd^{3+}), and Er^{3+} and for Sm^{3+}, Dy^{3+}, and Yb^{3+} respectively, which may be related at least to some extent to the 'tetrade effect.'* However, it can be concluded that the overall trend is a slight increase in stability of both mono- and bi-cyclic cryptates in pc along the lanthanide series, as already observed, even more pronounced in MeOH[3] but not in water or Me_2SO where polyoxadiazamacrocycles do not exhibit any particular Ln^{3+} selectivity.[1,8] These results contrast with the decrease in stability of the crown ethers (L^7 and L^8) complexes along the series, in pc as well in MeOH and CH_3CN.[3,12–14]

The stability of lanthanide cryptates results from a balance between various factors such as (*i*) the number of co-ordination sites of the ligands, (*ii*) the fit between the cation and the ligand cavity sizes in the case of macrocyclic type ligands, (*iii*) the ligand flexibility, (*iv*) the interactions with the solvent, and (*v*) the higher charge density of smaller lanthanides. The latter is generally thought to be responsible for the usual increasing stability with *Z* of the complexes with non-cyclic ligands such as aminopolycarboxylic acids.[15]

On the basis of (*ii*), the observed behaviour with L^7 and L^8 (interval cavity mean radii respectively 1.1 and 1.4 Å[10]) was foreseeable as the metal ion becomes less adapted to the ligand cavity as *Z* increases. Monocyclic cryptands L^1 and L^2, which have respectively the same cavity sizes as L^7 and L^8 should on this basis display the same behaviour. The fact that they do not must be related to the presence of N heteroatoms in the macrocycles leading to a behaviour intermediate between crown ether and nitrogen macrocyclic complexes. The same conclusions may be drawn for the bicyclic ligands.

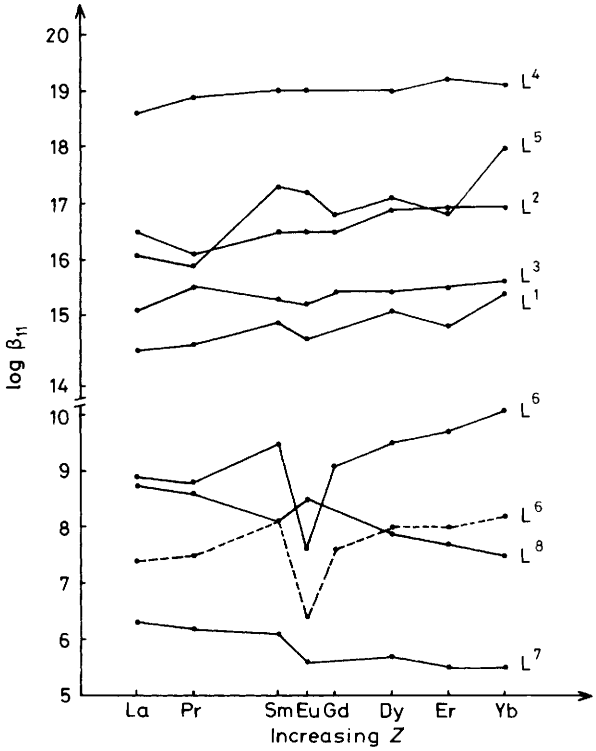


Figure. Variation of the stability (log β_{11}) of the lanthanide complexes of mono- and bi-cyclic cryptands and related ligands with the lanthanide atomic number, *Z*. Data for L^1 and L^4 are from ref. 3; those for L^7 and L^8, ref. 3 and this work. (— — —) Values for L^6 corresponding to log K_2 = log (β_{12}/β_{11})

From the results in Table 3 it appears that (*i*) mono- and bi-cyclic cryptates of Pr^{3+}, Er^{3+}, and Ag^{+}, as well as $La(L^5)^{3+}$, are enthalpy stabilized in pc, (*ii*) some of them [L^4 and L^1 cryptates, $La(L^5)^{3+}$] have also favourable entropies of complexation which are even dominant over the enthalpic terms. On the contrary, others (L^5, L^4, and L^2 cryptates of Pr^{3+}, Er^{3+}, and Ag^{+}) have negative unfavourable entropies. Thus two classes of lanthanide cryptates can be defined according to the nature of their stabilization: those which are both enthalpy and entropy stabilized ($\Delta H < 0$ and $\Delta S > 0$) and those which are only enthalpy stabilized ($\Delta H < 0$ and $\Delta S < 0$), the ΔH term over-

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* For more details see L. J. Jugendt, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3485 and S. P. Sinha, *Struct. Bonding (Berlin)*, 1981, 30.

coming unfavourable entropies. They will be referred to as belonging to 'type 1' and 'type 2' complexes respectively. In fact the stabilization of macrocyclic complexes is a combination of factors such as the difference in energy between cation–ligand bonds and cation–(co-ordinated solvent molecule) bonds, the ease of release of molecules of solvent from the cation during complexation, and the adaptability of the ligand to the cation size (namely its flexibility and its ability to undergo conformational changes). The first factor is measured by the enthalpy changes and the others are related to the entropy changes.[15]

For instance, it has been shown that alkali-cation cryptates belong to type 2 in water while alkaline-earth cryptates (Sr^{2+} and Ba^{2+}) in water and methanol, as well as $Li(L^3)^+$ and $Na(L^4)^+$ in water, belong to type 1.[16,17] The stabilizing positive entropy changes observed for the latter are interpreted by the release of the hydration shell of such greatly hydrated cations.

For type 2 lanthanide complexes in pc, the absolute values of the enthalpy are much higher than for type 1, indicating stronger cation–ligand interactions. Our results, combined with the previous ones obtained in various solvents, further demonstrate the importance of solvation upon the complexation of Ln^{3+} cations and especially its influence upon the enthalpic terms: the higher the solvating properties, the less negative the enthalpy. As already observed for most macrocyclic complexes in non-aqueous media (type 2 complexes),[18] we always find negative enthalpic contributions for Ln^{3+} cryptates or coronates in pc. It is noteworthy that the enthalpies of formation of $Eu(L^5)^{3+}$ and $Eu(L^4)^{3+}$ in water are positive, and that their stability is entirely due to a strongly positive entropic contribution.[11] In methanol, positive enthalpies of complexation have also been found for L^8 coronates of some pre-gadolinium lanthanides.[13] On the contrary, in acetonitrile which is, as pc, a poor co-ordinating solvent towards Ln^{3+} cations, these complexes are stabilized by enthalpic effects and destabilized by entropic ones.[14] The same trend has been observed for dibenzodecaoxacyclotriacontane complexes in pc.[19]

Concerning the stabilization of L^5 lanthanide cryptates we come to the same conclusions as Desreux and co-workers,[7] in spite of noticeable differences between their values of the thermodynamic parameters and ours, especially for the La^{3+} complex. Therefore we confirm the general trend observed by these authors for the ΔH and ΔS changes along the series, *i.e.* an increase of ΔH with Z and, at the same time, a decrease of ΔS, which is positive for the La^{3+} complex and becomes negative from Pr^{3+}. These observations can be generalized to the investigated cryptates. In general ΔH values become more negative (more favourable) from Pr^{3+} to Er^{3+}, as expected from the increased charge density on the cation and the subsequent increased electrostatic cation–ligand interactions. Accordingly, ΔH is generally less negative for the larger and less charged silver ion complexes. On the contrary, ΔS values decrease from Pr^{3+} to Er^{3+} (except for L^1), becoming less favourable or more unfavourable (respectively for type 1 and type 2 stabilizations) and probably indicating unfavourable conformational changes in the ligands induced by the smaller size of Er^{3+}. Thus the relative increase of stability observed for lanthanide cryptates along the series has rather an enthalpic origin. For a given cation, ΔH values for L^3 and L^1 cryptates are less negative than those for L^5, L^4, and L^2 cryptates. The larger number of heteroatoms and the larger flexibility of the latter might account for this difference. The maximum value of ΔH is reached for L^4 which is the best adapted ligand for lanthanide cations as well as for Ag^+, achieving the best arrangement between size, number of heteroatoms, and flexibility.

Complexes of Pr^{3+} and Eu^{3+} with L^6 have similar negative enthalpies which govern their stability, and negative entropies which should rather be considered as close to zero or even slightly positive because of the great inaccuracy of their determinations. It may be pointed out that both ΔH and ΔS have intermediate values between those corresponding to type 1 and type 2 complexes. The situation is completely reversed for the Er^{3+} complex which is entirely entropy stabilized, the enthalpic term being near to zero as in solvating media.[11,13,15]

The existence of a macrobicyclic effect has already been demonstrated for L^4 and L^1 lanthanide complexes in methanol and in pc.[3] Our results (Table 3) show that the extra stability of the L^4 cryptates over the L^1 homologues is entirely due to enthalpic effects, the entropic contribution being even unfavourable to the formation of the bicyclic complex. The same behaviour is displayed by alkali and alkaline-earth cations in water.[16] With L^5 and L^2 a similar but smaller effect is also observed, except for La^{3+}, Pr^{3+}, and Er^{3+}, which form complexes of about the same stability with both ligands, because of a favourable entropic contribution to the macrobicyclic effect counterbalanced by an enthalpic destabilization; as alkali and alkaline-earth L^5 cryptates display an important macrobicyclic effect, it is questionable whether the lanthanide L^5 cryptates are inclusive (*i.e.* the cation fits well in the ligand cavity) complexes in solution as they are in the solid state:[20–22] co-ordination may occur on one 'face' of the ligand L^5 with a similar environment to that in L^2 complexes.

Moreover, the remarkable higher stability of all lanthanide L^2 complexes compared with L^8 homologues may be the consequence of strongly more negative enthalpies despite unfavourable entropy changes, as we have observed here for Pr^{3+} and Ag^+.

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