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Covalent and electrostatic contributions to the bonds involving lanthanoid(III) cations: a new look based on parametric correlation of complexation constants

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Abstract

The formation constants of 308 lanthanoid(III) complexes with (poly)aminopolycarboxylate ligands are correlated by the equation $\log K_1 = C_AC_B + E_AE_B$. The C and E parameters indicate the tendency of each cation A and anion B to undergo covalent or ionic bonding; the ratio $H = E/C$ indicates the charge control on the bond formation tendency of each species A or B. Steric effects are found to be negligible. A break in the H values occurs between the first (La–Gd) and the second half (Gd–Lu) of the lanthanoid series. This feature is interpreted in terms of the LUMO energy of the Ln^{3+} ions.

Introduction

During our studies on the lanthanoid(III) coordination chemistry and on the applications of the Ln^{3+} cations as reagents in organic chemistry [1], we observed significant differences between various lanthanoid(III) cations with regard to the complexation constants, the coordination numbers and the reactivity. These features agree quite well with the well known subperiodicity within the lanthanoid series [2] as well as with the known data concerning the organic reactivity of these cations [3]. However, particularly with regard to the organic reactivity of the Ln^{3+} ions, few papers deal with the reasons for the different behaviour between the various lanthanoid(III) cations. It can be assumed that most of these organic reactions occur through a coordination of the substrate to the metal. Thus, the different reactivity between the various Ln^{3+} cations can be ascribed, to a first approximation, to their different affinity for a given substrate. Consequently, a better knowledge of the lanthanoid(III) selectivity for the ligands can allow a deeper understanding of the different reactivities between the various Ln^{3+} cations.

At present, the concept of charge and frontier orbital control is widely applied in studies of the complexation selectivity [4, 5]. In order to apply it to the lanthanoid(III) complexes, it is worth noting that the Ln^{3+} coordinative bonds are generally considered as essentially electrostatic [6], but a considerable covalent character has been observed in some cases [7, 8]. A rather simplified approach to the frontier orbital concept is given by eqn. (1)

$$\log K_1 = C_AC_B + E_AE_B - D_AD_B \qquad (1)$$

where, as described by Drago and co-workers [4, 5], C_A and C_B are a measure of the strength of the covalent contribution to the metal–ligand bond for the acid A and the base B, E_A and E_B correspond to the ionic contribution to the metal–ligand bond, and D_A and D_B are a measure of the steric hindrance on formation of the metal–ligand bond [9]. The absolute values of the parameters C_i, E_i and D_i (i = A, B) are rather unimportant, because they depend on fixed reference values, but the ratios $E_A/C_A = H_A$ and $E_B/C_B = H_B$ are unique (i.e. independent of any fixed reference value). The parameters H_i (i = A, B) are a measure of the relative ionicity versus covalence in the metal–ligand bonds, and they can be considered as the charge control on the bond formation between the acid A and the base B.

In the present paper, we apply eqn. (1) to the experimental $\log K_1$ values corresponding to the complexation constants between the Ln^{3+} cations and some (poly)aminopolycarboxylic acids. Thus, we can evaluate the charge control of the various Ln^{3+} cations, as well as its dependence on the lanthanoid atomic number.

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Methods

Hancock and Marsicano used eqn. (1) to correlate the formation constants of complexes between Lewis acids and bases [9b]. This equation is undetermined and allows three parameters to be set arbitrarily for each metal ion. However, the steric term of eqn. (1) (i.e. D_AD_B) can be disregarded both in the case of small Lewis bases (such as fluoride, hydroxide and ammonia) and in the case of large metal ions (such as Ag^+, Hg^{2+}, Tl^{2+} and Ln^{3+}), where D_B or D_A are presumed to make no contribution. Therefore, only two parameters of eqn. (1) have to be arbitrarily defined for each metal ion. Hancock and Marsicano found it convenient to define the initial values of E_A and C_A as

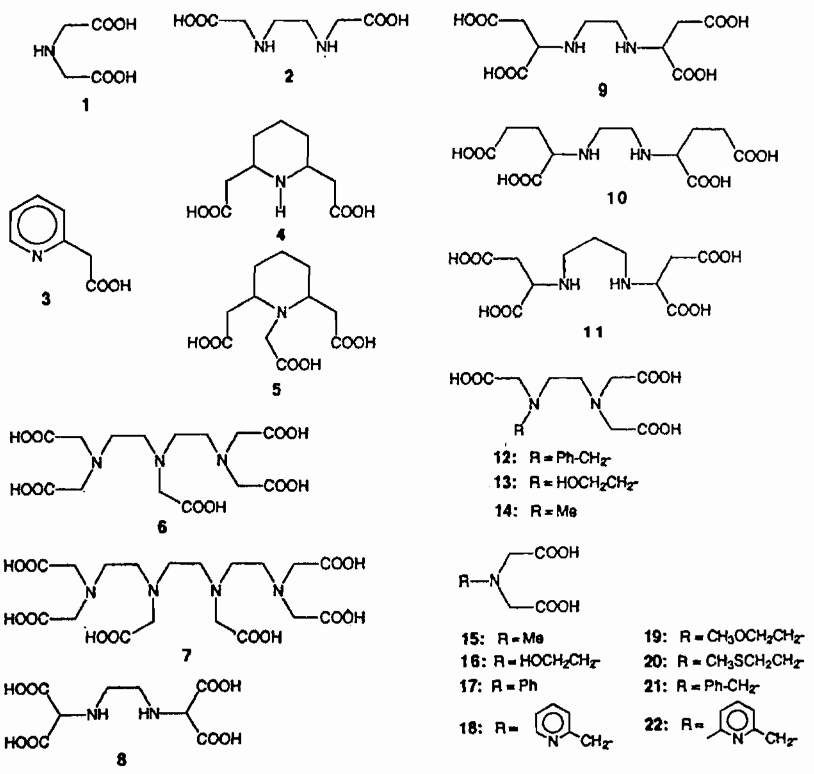
$$E_A = \log K_1(F^-) \tag{2}$$

$$C_A = \log K_1(OH^-)/14.00 \tag{3}$$

where $K_1(F^{-1})$ and $K_1(OH^-)$ are the formation constants of the fluoride and the hydroxide complexes of the Lewis acid A [9b, 9c]. In the present paper we followed a similar mathematical model.

C_A and E_A values for La^{3+} (0.379 and 3.904, respectively) and for Lu^{3+} (0.454 and 4.572, respectively) are reported in ref. 9a. Since the C_A and E_A values for the other lanthanoid(III) cations are unknown, a starting hypothesis has to be done in order to work out eqn. (1). Some different hypotheses seem reasonable: (i) on going from La^{3+} to Lu^{3+} both C_A and E_A change linearly with the atomic number; (ii) C_A and E_A do not depend linearly on the atomic number but their ratio $H_A = E_A/C_A$ does; (iii) C_A and E_A are the same for the Ln^{3+} (Ce^{3+}–Yb^{3+}) cations and equal to: (a) the La^{3+} value, (b) the Lu^{3+} value, (c) the mean value between La^{3+} and Lu^{3+}. We verified that the results we obtained are statistically independent of the starting hypothesis. Thereinafter, the hypothesis (i) (both C_A and E_A change linearly with the atomic number) will be considered.

We found in the literature the formation constants of the lanthanoid(III) complexes with the 22 (poly)aminopolycarboxylic acids reported in Scheme 1. No corrections were introduced but the complexation constant values were considered as they were published, as they were determined in identical experimental conditions (in water; at 25 °C; with $I = 0.1$ KNO_3) and because of the similarity between the various ligands. Although a number of ligands in Scheme 1 contains asymmetric carbons, the effects of the ligand asymmetry on the complexation constant values were considered statistically unimportant (note that all the experimental data were obtained on optically mixed compounds). Table S1 (see 'Supplementary material') reports the



Scheme 1.

complexation constants for each complex (together with a reference list).

Disregarding the steric term of eqn. (1), every complexation constant can be expressed as

$$\log K_1 = C_A C_B + E_A E_B \qquad (4)$$

Knowing the initial values of C_A and E_A, C_B and E_B can be calculated from eqn. (4) by a weighted least-squares procedure (weights $= \sigma(\log K_1)^{-2}$). Having obtained the values of C_B and E_B for each ligand, new values of C_A and E_A are obtained from eqn. (4) by a weighted least-squares procedure (weights $= \sigma(\log K_1)^{-2}$). The new C_A and E_A values can be used to refine the C_B and E_B values, and so on; such a refinement procedure converged after 14 full cycles (the convergence was considered reached when the third digit of C_A, E_A, C_B or E_B was unchanged by two successive cycles). The final C_A, E_A, H_A and C_B, E_B and H_B values are reported in Tables 1 and 2, respectively. Table S1 (see 'Supplementary material') shows the log K_1 values for each complex calculated using eqn. (4).

Results and discussion

C, E and H Parameters of the cations

The covalent (C_A) and ionic (E_A) parameters of La^{3+} and Lu^{3+} (see Table 1) are slightly different from those reported in refs. 9a and b. In the case of La^{3+}, C_A and E_A decrease rather significantly, passing from 0.379 and 3.904 (refs. 9a and b) to 0.364 and 3.741 (Table 1); in the case of Lu^{3+}, the differences are less significant, since C_A and E_A decrease from 0.454 and 4.572 (refs. 9a and b) to 0.452 and 4.540 (Table 1). Nevertheless, the C_A and E_A values reported in Table 1 are still suitable to predict the stability constants between La^{3+} or Lu^{3+} and ligands different from the (poly)aminopolycarboxylate considered in the present paper. In the case of the fluoride complexes, for example, Hancock and Marsicano predicted log K_1 of 3.9 (for La^{3+}) and 4.6 (for Lu^{3+}) [9b], we can predict values of 3.7 (for La^{3+}) and 4.5 (for Lu^{3+}), while the experimental values are 3.6 (for La^{3+}) and 4.5 (for Lu^{3+}). Contrary to C_A and E_A, the charge control parameters (H_A) of La^{3+} and Lu^{3+} reported in Table 1 are not significantly different from the corresponding values reported in refs. 9a and b. In the case of La^{3+}, H_A decreases only by 0.2%, from 10.300 (refs. 9a and b) to 10.277 (Table 1), and in the case of Lu^{3+} it decreases only by 0.3%, from 10.070 (refs. 9a and b) to 10.044 (Table 1). It appears that the actual values of the C and E parameters are easily (although slightly) affected by the number and the type of ligands employed to fit eqn. (4), while the ratio H between E and C is much more independent of the choice of these ligands.

TABLE 1. Covalent (C_A) and ionic (E_A) parameters and hardness (H_A) of the lanthanoid(III) cations (see eqn. (4))

Ln	C_A	E_A	H_A
La	0.364	3.741	10.277
Ce	0.385	3.954	10.270
Pr	0.397	4.058	10.222
Nd	0.403	4.130	10.248
Sm	0.413	4.234	10.252
Eu	0.413	4.222	10.223
Gd	0.409	4.181	10.222
Tb	0.416	4.237	10.185
Dy	0.424	4.308	10.160
Ho	0.426	4.313	10.124
Er	0.437	4.422	10.119
Tm	0.441	4.449	10.088
Yb	0.449	4.517	10.060
Lu	0.452	4.540	10.044

TABLE 2. Covalent (C_B) and ionic (E_B) parameters and hardness (H_B) for the ligands considered in the present paper (see Scheme 1 and eqn. (4))

Ligand	C_B	E_B	H_B
1	39.406	−2.271	−0.058
2	30.438	−1.047	−0.034
3	17.578	−0.762	−0.043
4	19.594	−0.473	−0.024
5	68.719	−4.223	−0.061
6	−104.188	15.445	−0.148
7	−520.375	55.211	−0.106
8	−80.563	10.480	−0.130
9	−33.688	6.477	−0.192
10	155.969	−13.371	−0.086
11	73.719	−4.836	−0.066
12	111.625	−7.992	−0.072
13	−46.375	8.109	−0.175
14	93.750	−6.090	−0.065
15	21.750	−0.480	−0.022
16	−28.438	4.918	−0.173
17	−18.859	2.507	−0.133
18	14.031	−0.727	−0.052
19	−26.719	4.504	−0.169
20	−6.031	2.080	−0.345
21	19.906	−0.492	−0.025
22	91.156	−7.338	−0.080

Figure 1 shows the dependence of the C_A, E_A and H_A parameters reported in Table 1 on the lanthanoid atomic number. It appears that both C_A and E_A (Fig. 1(a) and (b)) grow when going from La^{3+} to Lu^{3+}, but their dependence on the lanthanoid atomic number is not linear. An evident division is present, in Fig. 1(a) and (b), between the first half of the lanthanoid series (La–Gd) and the second one (Gd–Lu). Within the first half, the C_A and E_A distribution versus the atomic number can be fitted by a parabola with the maximum near Sm. Within the second half, the C_A and E_A dependence on the atomic number is linear.

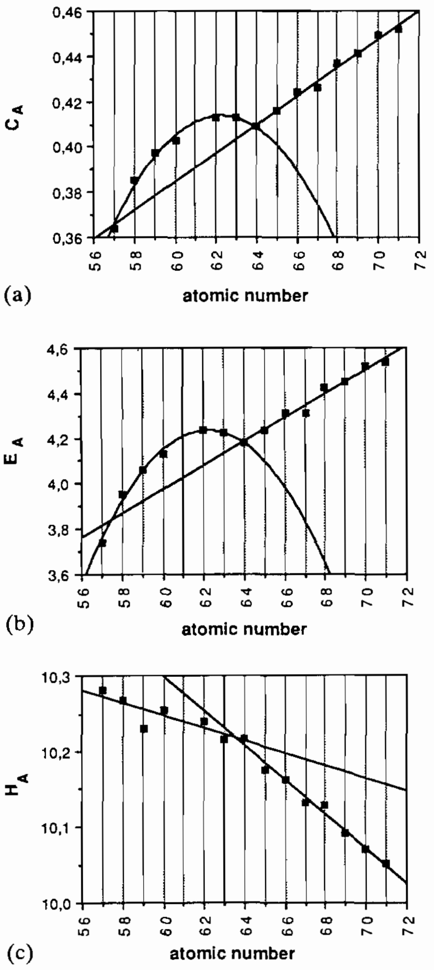


Fig. 1. Dependence on the lanthanoid atomic number of the C_A (a), E_A (b) and H_A (c) parameters (see eqn. (4)).

It is worth noting that the C_A and E_A points corresponding to La^{3+} are nearly lying on the straight line fitting the point distribution within the second half of the lanthanoid series. Thus, the cations ranging between Ce^{3+} and Eu^{3+} present a positive deviation from a hypothetical linear increase between La^{3+} and Lu^{3+}; that is, their tendency to form both ionic and covalent bonds increases more than could be foreseen by assuming a linear dependence of C_A and E_A on the atomic number between La^{3+} and Lu^{3+}. The break at the Gd level between the first and the second half of the lanthanoid series is a well known feature of these metals [2]. Nevertheless, the C_A and E_A values reported in Table 1 do not present any sound evidence of the tetrad effect [2], which often appears in the statistical studies concerning the lanthanoid complexation constants [10].

While the C_A and E_A values increase by increasing the Ln atomic number, the charge control parameter (H_A) values decrease (see Fig. 1(c)). Considering the definition of $H=E/C$, this means that going from La^{3+} to Lu^{3+} the ionic contribution of the metal–ligand bond increases less than the covalent one. As well as in the case of the plots of C_A and E_A versus the Ln atomic number (Fig. 1(a) and (b)), also in Fig. 1(c) a break at the Gd level is present, dividing the first and the second half of the lanthanoid series, but no sound evidence of tetrad effect is shown. The dependence of H_A on the Ln atomic number is linear both within the first and the second half, but with different slopes. H_A drops from 10.277 to 10.222 (difference = 0.055) between La^{3+} and Gd^{3+} and from 10.222 to 10.044 (difference = 0.178) between Gd^{3+} and Lu^{3+}. Therefore, in ranging between La^{3+} and Gd^{3+}, the charge control ratio H_A does not change drastically as it does in ranging between Gd^{3+} and Lu^{3+}.

It has been clearly pointed out that the charge control parameter H_A of an atom or of a molecule is related to the energy gap between its HOMO and its LUMO [5]. In the case of a Lewis acid, this can mean that the LUMO energy of a species having a high H_A is too high to accept electrons from a donor, whose HOMO energy is consequently too low. In the case of the Ln^{3+} cations, therefore, the fact that their H_A decreases by increasing the atomic number might mean that their LUMO energy decreases with increasing atomic number. This conclusion, however, cannot be as final as it could seem. Namely the lanthanoid(III)–ligand bonds can generally be considered as essentially electrostatic, with the consequence that the electron donor–acceptor model could be ignored [6]. Moreover, although a considerable covalent character has sometimes been observed in the lanthanoid(III)–ligand bonds, it is not clear which metal orbitals are involved in bonding. There is a strong evidence that the 4f electrons are not much affected by the ligands, while the higher lying orbitals interact with those of the ligands [7, 8], but some direct contribution of the 4f orbitals to the observed covalence cannot be always ruled out [11].

In order to understand better the reasons of the charge control parameter (H_A) variation among the lanthanoid series, we investigated the possibility that the H_A values reported in Table 1 are correlated with the first four ionization energies. The first ionization implies configuration changes of the type $5d^1 6s^2 \rightarrow 5d^2 6s^0$ in the case of La and Ce, $5d^1 6s^2 \rightarrow 5d^1 6s^1$ for Gd, $5d^1 \rightarrow 5d^0$ for Lu and $5d^0 6s^2 \rightarrow 5d^0 6s^1$ for all the other elements of the series [12]. In Fig. 2(a) it can be seen that a quite good linear relationship exists between H_A and the first ionization energy for all the lanthanoids except Lu. The second ionization implies a configuration change of the type $4f^n 6s^1 \rightarrow 4f^n 6s^0$ for all the Ln^+ cations except for La^+ ($5d^2 \rightarrow 5d^1$), Gd^+ ($4f^7 5d^1 6s^1 \rightarrow 4f^7 5d^1 6s^0$) and Lu^+ ($4f^{14} 6s^2 \rightarrow 4f^{14} 6s^1$) [12]; again a quite good linear correlation is found (see Fig. 2(b)) between H_A and the second ionization energy for all the Ln^+ cations,

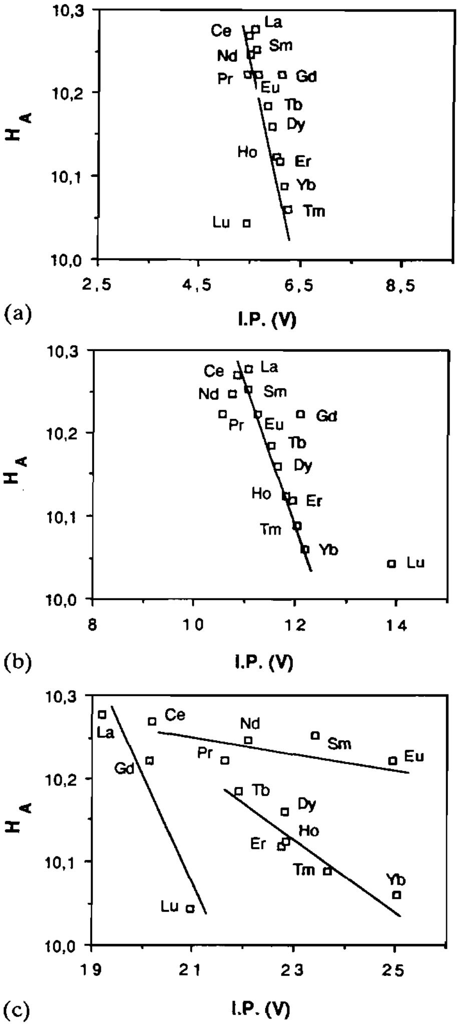


Fig. 2. Dependence on the lanthanoid H_A parameter of the first (a), second (b) and third (c) ionization potentials.

except Lu^+. The third ionization implies a configuration change in the 4f shell ($4f^n \rightarrow 4f^{n-1}$) for all the Ln^{2+} cations except La^{2+} ($6p^65d^1 \rightarrow 6p^65d^0$), Gd^{2+} ($4f^75d^1 \rightarrow 4f^75d^0$) and Lu^{2+} ($4f^{14}6s^1 \rightarrow 4f^{14}6s^0$) [12]. The plot of H_A versus the third ionization energy (see Fig. 2(c)) does not give a unique straight line from Ce^{2+} to Yb^{2+}, but two different straight lines with different slopes (Ce to Eu; Tb to Yb). The line Tb–Yb is steeper than the line Ce–Eu and analogous results are found plotting H_A versus the fourth ionization energy, which corresponds to configuration changes of the type $4f^n \rightarrow 4f^{n-1}$ for all the Ln^{3+} cations (except for La^{3+}). The slopes of Fig. 2(c) are much smaller than those of the Fig. 2(a) and (b), indicating that the H_A variations depend mainly on the energy of the 6s and 5d orbitals. However it appears that also the 4f orbitals, although to a lesser extent, determine the charge control variation through the lanthanoid series.

C, E and H Parameters of the ligands

The values of the C_B and E_B parameters of the ligands (see Table 2) are very variable (C_B ranges between -520.375 and 155.969; E_B between -13.371 and 55.211). On the contrary, the values of the H_B parameter are quite similar one to the other, ranging between -0.345 and -0.022. They can be compared with the corresponding values of the acetate ($H_B = 0.000$) and of ammonia ($H_B = -0.088$) [9a, b]. The H_B values of the (poly)aminopolycarboxylate ligands considered in the present paper are closer (the average is -0.103 ± 0.076) to that of ammonia than to the H_B value of acetate. This could mean that the bonding properties of these ligands are markedly influenced by donor groups other than the carboxylic ones.

The C_B and E_B values reported in Table 2 cannot be used to predict formation constants of complexes different from those considered to fit eqn. (4). For example, Fig. 3 reports the dependence between the experimental log K_1 values of ligand **1** (taken from ref. 13) and those calculated by inserting in eqn. (4) the C_B and E_B values of Table 2 and the C_A and E_A values reported in ref. 9a. It appears that the agreement between calculated and experimental log K_1 values is good only in the case of Mg^{2+} (experimental = 2.94, calculated = 2.79), not too bad in the case of Ca^{2+} (experimental = 2.59, calculated = 0.97), but very bad in all the other cases (for example, for Hg^{2+}, experimental = 11.76, calculated = 29.48). This 'prediction inability' could depend on the fact that the C_B and E_B parameters were obtained by fitting eqn. (4) only with log K_1 values of lanthanoid(III) complexes. Therefore they can be used to predict the log K_1 only for complexes of cations comparable with lanthanoids(III). It is well known that while the lanthanoids compare well with the second group cations, they are very different from d metals and this is the reason for the discrepancies shown in Fig. 3.

Steric hindrance

Table 3 reports the average value of the absolute values of the differences (Δ log K_1) between calculated

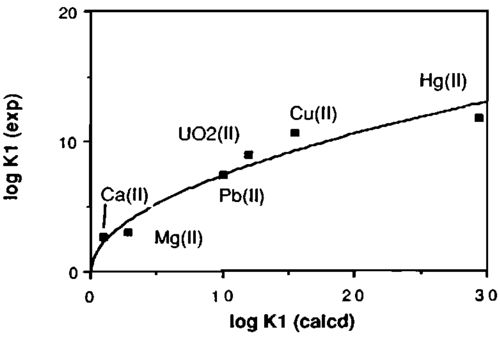


Fig. 3. Comparison between the experimental and the calculated log K_1 values of ligand **1**.

TABLE 3. Average of the absolute values of the differences between the experimental and calculated log K_1

Ln	Δ(log K_1)	Ligand	Δ(log K_1)
La	0.17	**1**	0.04
Ce	0.11	**2**	0.08
Pr	0.16	**3**	0.03
Nd	0.09	**4**	0.02
Sm	0.13	**5**	0.07
Eu	0.13	**6**	0.35
Gd	0.14	**7**	0.78
Tb	0.17	**8**	0.11
Dy	0.11	**9**	0.08
Ho	0.10	**10**	0.16
Er	0.10	**11**	0.14
Tm	0.04	**12**	0.13
Yb	0.10	**13**	0.14
Lu	0.15	**14**	0.12
		15	0.04
		16	0.06
		17	0.08
		18	0.04
		19	0.03
		20	0.03
		21	0.04
		22	0.12

and experimental log K_1 for each Ln^{3+} cation and for each ligand (see Table S1, 'Supplementary material'). It appears that the Δ log K_1 values are quite low for all the Ln^{3+} cations; the same goes for the ligands, with the exception of **6** and **7**. Therefore, the assumption to disregard the steric effects, that is the assumption to use eqn. (4) instead of eqn. (1), is justified.

The ligands **6** and **7**, which are the only ones that cannot be well fitted by eqn. (4), present the highest denticity among the various (poly)aminopolycarboxylates considered in the present paper. Therefore, it is likely that they present a certain steric interference between their donor groups (or with the water and/or the anion molecules bonded to the metal) when they complex a lanthanoid(III) cation. In this regard it is worth noting that the energy balance in the Gd^{3+} complexation by **6** is similar to those relative to the very rigid macrocyclic polyaminopolycarboxylates like DOTA, DO3A or OTTA [14]*. However, eqn. (4) can fit the log K_1 values of other extensively hindered ligands. It is therefore possible that the anomalous behaviour of ligand **6** and ligand **7** could depend only on a different accuracy in the determination of their complexation constants with Ln^{3+} cations.

Supplementary material

Listing of experimental and calculated log K_1 values are available from the authors on request.

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*DOTA = 1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid. DO3A = 1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″-triacetic acid. OTTA = 1-oxo-4,7,10-triazacyclododecane-*N*,*N*′,*N*″-triacetic acid.