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A comparison of the acidity and the complexing ability of (*o*-hydroxyphenyl) bis- and (*o*-hydroxyphenyl) mono-methylenephosphonic acids towards lanthanide(III) ions

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Abstract

The characterization of the acid–base properties of a family of three phenoldimethylenephosphonic acids differently substituted by auxo- or chromophoric groups was studied. These ligands may be considered as pentaacids. Their pK_a were determined in aqueous solution at 25 °C and constant ionic strength 0.1 mol dm^{-3} by potentiometry and UV–visible spectrophotometry. Eventually, the complexing power of these molecules with lanthanide cations, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+}, was studied keeping in view the possible application to the treatment of radioactive liquid waste. The number, the nature of the species in solution, their stability constants and their individual electronic spectra as restored by computation have been determined. In all cases, complexes of 1:1 stoichiometry accompanied by hydroxy and protonated species are postulated. The comparison of tri- and pentaacids confirms that the acids having the methyl group at the *para* position with respect to the phenolic OH, have the highest complexing power. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lanthanide(III) complexes; Phenol methylenephosphonic acids; Protonation constants; Stability constants

1. Introduction

A large number of phosphonic compounds have already been examined with respect to their complexing properties and their suitability as extractants in industrial applications [1–3].

The stability constants of the complexes of Ln^{3+} with some ligands have been reported. Tikhinova studied the system *N*,*N*′-di-(carboxymethyl) ethylenediamine bis-methylphosphonic acid (EDPA) towards Y^{3+},Yb^{3+} and Ce^{3+} [4]. The author reported higher stability of the complexes with respect to carboxylic homologues. Tereshin et al. [5] studied the complexation of Y^{3+} with nitrilotrimethylphosphonic acid and postulated two types of complexes, viz. YHL^{2-} and YH_2L^{-}. Suran et al. [6], on the other hand,

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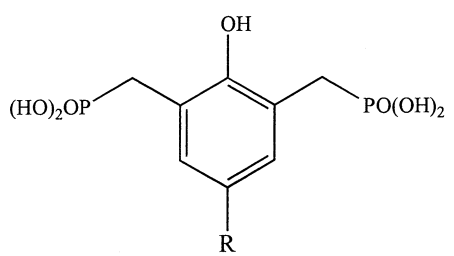
retained a model with four complexes, MLOH, ML, MLH and MLH_2. Sujatha and co-workers [7] have also reported the extraction of Ce(III) and Nd(III) by 2-ethylhexyl mono-2 ethylhexylester phosphonic acid (EHEHPA) in the presence of a second complexing agent which improves the separation factor amongst the lanthanides. Wagener et al. [8] have presented an interesting graph relative to complexes of lanthanides with diaminetetramethylene phosphonate (EDTMP). This graph of stability constants shows a maximum for Gd(III). Recently, Benghanem et al. [9] have reported the acid-base properties of a series of phenol methylenephosphonic acids. A recent pH-metric and spectrophotometric studies on the acidity of a family of (*o*-hydroxyphenyl) mono-methylenephosphonic acids (triacid series LH_3) and the stability of their lanthanide (III) complexes has been submitted by our laboratory [10] and the work has now been extended to pentaacids.

The present paper describes a detailed potentiometric and UV–visible spectrophoto-metric study of the proton dissociation of the bis-methylenephosphonic acids (pentaacid series LH_5) **2a**–**c**, as given in the scheme below, and of their lanthanide (III) complexes. The calculations were done with a method using numerical and chemical criteria for the representation of the model under investigation 1.

(1)



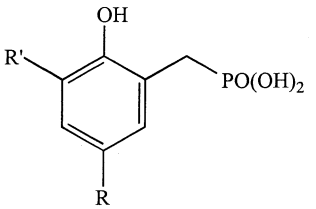
2a: R = CH_3

2b: R = NO_2

2c: R = Cl

As comparison has been made with (*o*-hydroxyphenyl) mono-methylenephosphonic acids in the discussion section, their structure scheme (**1a**–**e**) is presented here as well 2.

(2)



1a: R = H and R' = H

1b: $PO(OH)_2$ in *para*, R and R' in *ortho* = H

1c: R = NO_2 and R' = H

1d: R = CH_3 and R' = NO_2

1e: R = NO_2 and R' = CH_3

2. Experimental section

2.1. Reagents

All the compounds were synthesized as described by Böhmer et al. [11] and their purity was controlled by microanalysis: Anal. Calc. for **2a**: C, 34.12; H, 5.82. Found: C, 34.37; H, 5.58%. Anal. Calc. for **2b**: C, 29.40; H, 3.39; N, 4.28. Found: C, 28.50; H, 3.73; N, 3.99%. Anal. Calc. for **2c**: C, 28.91; H, 4.69. Found: C, 29.08; H, 4.40%.

Ligand solutions were kept away from light, in order to avoid degradation, and were used, at the latest, 5 days after their preparation. The lanthanide (III) chlorides were commercial products p.a. (Janssen for Ce, Pr and Eu, Aldrich for Nd and Ventron for Sm). Solutions of 0.1 mol dm^{-3} $Na(ClO_4) \cdot 6H_2O$ (Fluka p.a.) and 1 mol dm^{-3} NaOH (Merck) were prepared with doubly distilled and boiled water. The pH values of the solutions were adjusted by simple addition of acid ($HClO_4$) or of base (NaOH) and controlled with a precision pH-meter. The solution of $Na(ClO_4)$ was added to the medium so that the ionic strength remains constant and equal to 0.1 mol dm^{-3}. Stock solutions of metals, 10^{-2} mol

dm^{-3}, were prepared by mixing the solid metal (III) chlorides with the solvent; these solutions were standardized with EDTA [12] at pH 6, using xylenol orange as indicator. The final analytical concentration of metal was 10^{-2} or 10^{-3} mol dm^{-3} for potentiometric study and 10^{-4} mol dm^{-3} for measurements in UV–visible. $NaClO_4$, 0.1 mol dm^{-3} was the spectrophotometric reference solution. The final solutions of metal and ligand were prepared just before the measurements.

2.2. Potentiometric measurements

The potentiometric investigations of acid–base and metal-binding equilibria were carried out at 25.0 ± 0.1 °C and ionic strength 0.1 mol dm^{-3} ($NaClO_4$). The complexation was studied in aqueous solution with equal analytical concentrations of the ligand C_L and the cation C_M (10^{-2} mol dm^{-3} with **2a** and **2b** and 10^{-3} mol dm^{-3} with **2c**). All experiments were performed according to the method previously described [10].

2.3. Spectrophotometric measurements

The spectra, in the range of 200–550 nm, were recorded on a Shimadzu UV 2101 PC spectrophotometer equipped with a thermostat and matched 10 mm quartz cell. The absorption variations of acid-base and metal-binding equilibria were carried out at 25.0 ± 0.1 °C and the ionic strength of solutions was maintained constant, fixed at 0.1 mol dm^{-3}, with the help of the supporting electrolyte $NaClO_4$. The concentration of the ligands should not exceed 10^{-3} mol dm^{-3} to guarantee accurate and confident absorbance values between 0.2 and 2.0. All investigations in the presence of metal ions were carried out at a 1:1 molar ratio of metal ion to ligand. No determination could be done with higher molar ratios due to precipitation phenomena. Therefore, the analytical concentration of the metal and ligand was fixed at 10^{-4} mol dm^{-3}. Under these experimental conditions, only the formation of the mononuclear complexes was envisaged. The ligand solutions are stable for a few days, however, the spectra were run immediately after mixing the reagents.

2.4. Calculation of equilibrium constants

All the constants and their equations corresponding to the different equilibria involved in this study are described in our publication [10].

2.4.1. Potentiometric data

Approximate values of the stepwise protonation constants K_i, the overall protonation constants β_{01z}, and the overall stability constants β_{xyz} of the complexes were computed. The treatment of the potentiometric data was done using several titrations, each including not less than 150 points, by fitting to the Sirko [13] and/or Superquad [14] programs.

2.4.2. Spectrophotometric data

Computational treatment of the set of spectra, obtained for different pH values, results in the dissociation constants of the ligands (pK_a values) and overall stability constants of the complexes (β_{xyz}) and in the individual electronic spectra for all species involved. These pK_a values are compared with the potentiometric results reported previously [11,15]. The numerical treatment concerns a large set of absorbance values covering the whole investigated wavelength range (21 solutions, 32 wavelengths). The whole set of spectrophotometric data was analyzed using the multiwavelength program Sirko S [13] and/or Letagrop–Spefo [16] which refines the overall stability constant β_{xyz} of the complexes. The apparent overall stability constants β_{xyz} of the complexes, correspond to the following equilibrium:

$$x\mathrm{M}^{m+} + y\mathrm{L}^{n-} + z\mathrm{H}^{+} \rightleftharpoons \mathrm{M}_x\mathrm{L}_y\mathrm{H}_z^{(xm-yn+z)+}$$

$$\beta_{xyz} = \frac{[\mathrm{M}_x\mathrm{L}_y\mathrm{H}_z^{(xm-yn+z)+}]}{[\mathrm{M}^{m+}]^x[\mathrm{L}^{n-}]^y[\mathrm{H}^{+}]^z}$$

where x pertains to metal (M), y is for ligand (L) and z for proton (H). In the case of hydroxo species, z is negative.

The calculated values are indicated with 99% confidence interval ($\pm 3\sigma$). The protonation constants β_{01z} of the ligands were kept constant during the refinement procedure of the stability constants, as well as the formation constants or β_{01z} of hydroxo species, in this case z is negative.

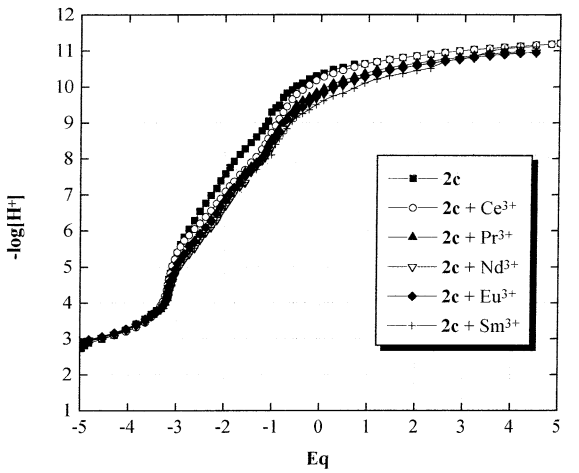


Fig. 1. Titration curves for **2c** and Ln(III)–**2c** complexes in aqueous solution ($C_L = C_M = 10^{-3}$ mol dm^{-3}, 25 °C, $I = 0.1$ mol dm^{-3} $NaClO_4$).

3. Results

The quantitative interpretation of potentiometric and spectrophotometric data was carried out on molecules **2a**, **2b**, **2c**. The results of ligand **2b**, which contains the chromophore group NO_2 on the aromatic ring were exploited spectrophotometrically. This was not possible with molecules **2a** and **2c** because of their feeble spectral variation with respect to pH.

3.1. Potentiometry

Fig. 1 shows, as an example, the protonation curve of ligand **2c** and the titration curves in the presence of various lanthanides (**2c** + Ln^{3+}, $C_M = C_L = 10^{-3}$ mol dm^{-3}).

3.1.1. Acid–base equilibrium

The five pK_a values determined are in good agreement with those previously obtained by Vogt et al. [1], and Ameziane and co-workers [15], especially if we take into account the differences in experimental conditions such as ionic strength and temperature (Table 1). For the three ligands the weaker acidity is attributed to the phenolic OH group and the corresponding higher values of pK_a can, as already pointed out, be explained by intramolecular H bonds between the POH groups and the phenolic OH.

3.1.2. Complexation studies

The titration curves of the ligand **2c** in the presence of metal cations (Fig. 1) show that before the first equivalent point, all the curves are superimposed which means that no complexation occurs below pH 3.5 under present experimental

Table 1
The five pK_a values determined by Sirko-P program and a comparison with values reported by other authors

Ligand	pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}	pK_{a5}
2a	1.4 ± 0.4	2.8 ± 0.5	6.6 ± 0.4	8.1 ± 0.4	11.4 ± 0.2
		2.8 ± 0.2[a]	6.6 ± 0.2[a]	8.2 ± 0.1[a]	11.6 ± 0.1[a]
	1.5[b]	2.5[b]	6.5[b]	8.3[b]	11.8[b]
	1.6[c]	2.3[c]	6.4[c]	8.1[c]	11.8[c]
	1.2 ± 0.1[d]	2.2 ± 0.1[d]	6.2 ± 0.1[d]	9.0 ± .0.1[d]	12.8 ± 0.1[d]
2b	1.7 ± 0.8	2.2 ± 0.6	5.9 ± 0.4	7.8 ± 0.5	10.2 ± 0.4
	1.01[b]	2.2[b]	5.9[b]	7.90[b]	10.5[b]
	1.6[c]	2.0[c]	5.8[c]	7.8[c]	10.3[c]
2c	1.2 ± 0.8	2.4 ± 0.8	5.93 ± 0.52	7.84 ± 0.35	11.74 ± 0.28
		2.5 ± 0.1[a]	6.0 ± 0.1[a]	7.9 ± 0.1[a]	11.7 ± 0.1[a]
	1.5[b]	2.3[b]	6.3[b]	8.1[b]	11.9[b]
	1.7[c]	2.1[c]	6.1[c]	7.9[c]	11.7[c]

[a] Values determined by authors with Superquad program.
[b] Values determined by Vogt and co-workers, method 1, [11].
[c] Values determined by Vogt and co-workers, method 2, [11].
[d] Values determined by Ameziane and co-workers, [15].

Table 2
Values of $\log \beta_{11z} \pm \sigma_{N-1}$ ($N = 8$) determined by Sirko P program for the complexes formed with Ln^{3+} in water from potentiometric data (25 °C, $I = 0.1$ mol dm^{-3} $NaClO_4$)

Ligand	Cation	$\log \beta_{110}$	$\log \beta_{111}$	$\log \beta_{112}$	$\log \beta_{113}$	$\log \beta_{11-1}$	$\log \beta_{11-2}$	pH range	R_f
2a	Ce(III)	11.36 ± 0.09	20.16 ± 0.08	26.54 ± 0.08	29.4 ± 0.9	0.5 ± 0.1	-12.0 ± 0.4	1.89–10.95	2.0
$C_L = 10^{-2a}$	Pr(III)	12.0 ± 0.3	20.7 ± 0.3	26.9 ± 0.3	29.6 ± 0.5	1.2 ± 0.3	-11.9 ± 0.4	1.83–10.93	2.1
$C_M = 10^{-2}$	Nd(III)	12.0 ± 0.3	20.9 ± 0.3	27.3 ± 0.3	30.1 ± 0.4	1.2 ± 0.3	-11.3 ± 0.4	1.88–10.58	2.1
	Sm(III)	12.8 ± 0.4	21.3 ± 0.4	27.3 ± 0.4	30.1 ± 0.5	2.2 ± 0.4	-9.7 ± 0.5	1.79–10.91	2.8
	Eu(III)	11.97 ± 0.08	20.84 ± 0.07	26.98 ± 0.07	29.9 ± 0.9	1.18 ± 0.09	-11.5 ± 0.4	1.85–10.39	2.9
2b	Ce(III)	12.1 ± 0.1	19.89 ± 0.09	24.7 ± 0.1	26.5 ± 0.8	1.3 ± 0.1	-10.2 ± 0.1	1.85–10.76	2.0
$C_L = 10^{-2}$	Pr(III)	12.5 ± 0.1	20.0 ± 0.1	24.8 ± 0.1	27.0 ± 0.9	2.2 ± 0.1	-9.2 ± 0.2	1.85–10.52	2.1
$C_M = 10^{-2}$	Nd(III)	12.56 ± 0.04	20.19 ± 0.02	24.95 ± 0.01	27.3 ± 0.7	1.98 ± 0.09	-9.5 ± 0.1	1.84–10.63	2.5
	Sm(III)	12.7 ± 0.1	20.3 ± 0.1	25.17 ± 0.04	27.6 ± 0.9	1.8 ± 0.2	10.2 ± 0.1	1.97–11.02	2.5
	Eu(III)	11.9 ± 0.1	19.7 ± 0.1	24.7 ± 0.1	27.4 ± 0.6	1.9 ± 0.1	-9.5 ± 0.1	1.81–10.53	2.2
2c	Ce(III)	12.04 ± 0.01	19.8 ± 0.1	24.81 ± 0.02		3.2 ± 0.3	-7.6 ± 0.1	2.83–10.08	2.2
$C_L = 10^{-3}$	Pr(III)	11.4 ± 0.2	19.48 ± 0.08	24.82 ± 0.04		2.9 ± 0.3	-8.1 ± 0.2	2.85–10.15	2.6
$C_M = 10^{-3}$	Nd(III)	12.41 ± 0.05	19.98 ± 0.05	24.47 ± 0.09		3.60 ± 0.06	-6.5 ± 0.1	2.88–10.05	1.9
	Sm(III)	12.62 ± 0.04	20.11 ± 0.03	24.42 ± 0.04		3.91 ± 0.04	-6.8 ± 0.1	3.04–10.29	0.6
	Eu(III)	12.2 ± 0.5	20.0 ± 0.2	24.4 ± 0.3		3.6 ± 0.6	-6.8 ± 0.1	2.73–10.09	1.0

Arithmetic mean of N (≥ 2) determinations; negative z values refer to hydroxo species. In Sirko program R_f is the result of a statistical test related to the fit between the experimental and calculated curves.
[a] The concentration given in the first column are in mol dm^{-3}.

conditions. At higher pH, the curves of the metal–ligand solutions show a decrease in pH and a displacement of the equivalent points compared with those of the free ligand, at the same concentrations, which is substantial proof of complexation.

The logarithms of the overall stability constants of the complexes are reported in Table 2. Each value is an average of at least three independent determinations with cation to ligand molar ratio equal to 1. Higher molar ratio could not be investigated due to precipitation phenomena.

3.2. Spectrophotometry

For the ligand substituted by the chromophore NO_2, the spectral variation is significantly higher and, therefore, in this section, the variations of especially the ligand **2b** will be studied.

3.2.1. Acid–base equilibrium

The principal absorption band of the totally protonated molecule is situated at 325 nm ($\varepsilon = 8070$ dm^{-3} mol^{-1} cm^{-1}). From pH 8 onward this maximum, which undergoes a shift to 351 nm diminishes and then splits into two new bands, a low intensity band at 275 nm and another of high intensity at 446 nm. At higher pH values, pH > 10, the pentaanion band corresponding to the totally deprotonated ligand is located at 446 nm ($\varepsilon = 21210$ dm^{-3} mol^{-1} cm^{-1}).

The numerical interpretation of (N, L) experimental data was done with Sirko S and/or Letagrop–Spefo programs, where N is the number of solutions studied and L, the number of wavelengths. The results obtained for the constants corresponding to the H_xL species, ($0 \leq x \leq n$, where $n = 5$ for pentaacids) using the two techniques are in good agreement.

3.2.2. Complexation studies

The spectral variation with respect to pH of solutions of ligand **2b** and different lanthanides (Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+} and Eu^{3+}) were recorded. The concentration ratio of metal and ligand was maintained at 1, i.e. $[M]_0/[L]_0 = 1$. A representative spectra of **2b** with Eu^{3+} is shown in Fig. 2.

This is characterized by four principal zones of absorption. The first zone is situated between 200 and 280 nm which is difficult to assign to either ligand or complexes. The region between 280 and 380 results from the deprotonation of the ligand. The variations between 360 and 430 nm correspond to the formation of complexes. Finally, the intense absorbance between 430 and 500 nm is due to the totally deprotonated ligand.

Isosbestic points are observed (275, 350, 383, and 408 nm), indicating an equilibrium between at least two species. A comparison of these coordinates to those present in the calculated electronic spectra is an additional argument for the choice of the best model.

The logarithm of the overall stability constants calculated with the help of programmes Letagrop and Sirko S are given in Table 3. The values are the arithmetic mean of three results.

The program Sirko S was used in the zone of $pH < 7.5$. It is not surprising, therefore, that in this case the species MLOH and $ML(OH)_2$ are not detected. This also explains the relatively lower number of solutions N and wavelengths L used for calculation with Sirko S. The constants were used to calculate the specific extinction coefficients which in turn were used to draw the individual electronic spectra. The electronic spectra of complexes of ligand **2b** with Eu^{3+} are given in Fig. 3.

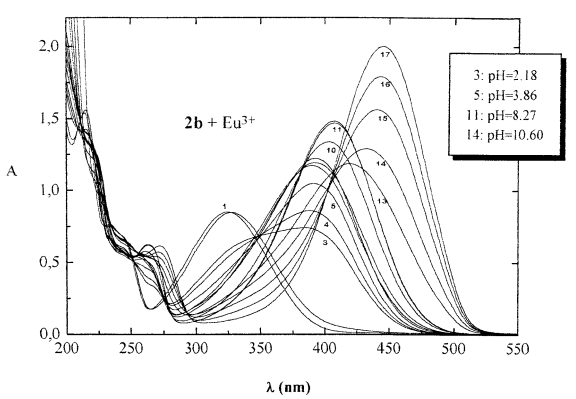


Fig. 2. Experimental UV–visible spectra of the ligand **2b** complexes with Eu^{3+}.

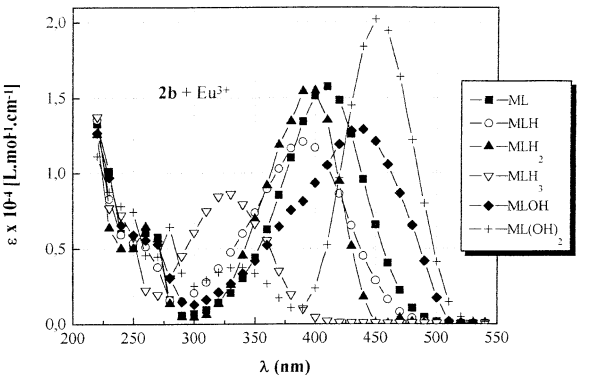


Fig. 3. Calculated electronic spectra of the ligand **2b** complexes with Eu^{3+}.

4. Discussion

Under this heading, a comparison will be made with the series of triacids: mono-methylenephosphonic acids (**1a**, **1b**, **1c**, **1d** and **1e**) studied earlier [10].

4.1. Nature of the complexes formed

For simplicity, the charges of the complexes will be omitted in the following discussion. If one refers to Table 2, which presents all the results, within the defined pH range (2–10), several complexes are observed for the pentaacids. An ML complex, a mono-protonated complex MLH a bi-protonated complex MLH_2, two anionic complexes MLOH and $ML(OH)_2$ and a tri-protonated complex MLH_3 in the case of **2a** and **2b** but absent with **2c**.

4.2. Order of magnitude of the constants

The ML complexes of the pentaacids have formation constants of the order of 12 log, 2 to 3 log

Table 3
Values of log β_{11z} determined by Letagrop and/or Sirko S programs for the complexes formed with Ln^{3+} by ligand **2b** from spectrophotometric data (25 °C, $I = 0.1$ mol dm^{-3} $NaClO_4$, $C_M = C_L = 10^{-4}$ mol dm^{-3})

Cation	log β_{110}	log β_{111}	log β_{112}	log β_{113}	log β_{11-1}	log β_{11-2}	$N \times L$	pH range	U or R_f [a]
Ce(III)	12.04 ± 0.08	20.22 ± 0.05	24.52 ± 0.06	27.99 ± 0.09	2.38 ± 0.07	-7.72 ± 0.07	15×11	1.63–11.09	0.6571E−02
Pr(III)	11.89 ± 0.06	19.88 ± 0.07	24.19 ± 0.09	28.6 ± 0.1	2.2 ± 0.1	-8.8 ± 0.2	15×12	1.68–11.10	0.3987E−02
Nd(III)	11.98 ± 0.09	20.26 ± 0.08	24.33 ± 0.06	29.39 ± 0.04	3.1 ± 0.1	-8.0 ± 0.2	15×12	1.64–11.08	0.1202E−02
	12.5 ± 0.6[a]	19.6 ± 0.4[a]	25.48 ± 0.08[a]	28.66 ± 0.05[a]			10×9	1.64–7.37	2.3% [a]
Sm(III)	12.07 ± 0.05	19.84 ± 0.07	24.03 ± 0.07	28.01 ± 0.06	1.24 ± 0.09	-7.2 ± 0.3	15×12	1.66–10.64	0.2511E−01
Eu(III)	11.89 ± 0.06	19.88 ± 0.07	2419 ± 0.09	28.6 ± 0.1	2.2 ± 0.1	-8.8 ± 0.2	15×12	1.63–10.94	0.3987E−02
	12.5 ± 0.6[a]	19.7 ± 0.5[a]	25.28 ± 0.07[a]	28.38 ± 0.04[a]			10×8	1.63–7.63	2.1% [a]

U is the sum of the squares of the differences between experimental and calculated absorption for N solutions at L wavelengths. R_f is the statistical factor in Sirko program.

[a] Values determined by Sirko S.

Table 4
Means of stability constants of trivalent lanthanide complexes

Ligand	log β_{113}	log β_{112}	log β_{111}	log β_{110}	log β_{11-1}	log β_{11-2}
2a	29.8[P]	27.0[P]	20.8[P]	12.0[P]	1.2[P]	−11.3[P]
2b	27.1[P]	24.9[P]	20.0[P]	12.3[P]	1.8[P]	−9.7[P]
	28.5[s]	24.5[s]	19.9[s]	12.1[s]	2.2[s]	−8.1[s]
2c		24.6[P]	19.9[P]	12.2[P]	3.4[P]	−7.2[P]

[P], Potentiometric values; [s], spectrophotometric values.

U higher than for the corresponding triacid complexes [10]. This fact may perhaps be attributed to a charge effect, as ML is a neutral complex for the triacids and a dianionic one for the pentaacids. A similar effect has been observed by P. Schwinte [17] concerning the lanthanide complexes of calixarenes substituted at the –OH position by carboxylic acid groups. Table 4 gives the average log β_{111} for the pentaacids as 20.2, and the average values of the first stepwise protonation constants are equal to 8.8 log U for **2a**, 7.6 for **2b** and 7.8 for **2c**. The average log β_{112} value is 25.5, and the average second stepwise protonation constants for MLH to MLH_2 is 6.2 log U for **2a**, 4.9 for **2b** and 4.7 for **2c**. These values are similar to those of the first protonation constants of the triacid complexes, therefore, it is likely that this second protonation of the pentaacids complexes occurs at the second phosphonate group, and that the complex MLH_2 is protonated once on each of the phosphonate sites. Finally, the average log β_{113} value is 28.5, and the third stepwise protonation constant of MLH_2 to MLH_3 is 2.8 for the complexes of **2a** and 2.3 for those of **2b** (in log U). These values are clearly weaker than the second protonation constants of the triacid complexes. The stepwise protonation constants of the complexes of **2a** are all greater than those of **2b** or **2c**, which is due to the donor inductive effect of the methyl substituent which favors the liberation of the proton.

4.3. Distribution curves of the complexes

With the values of log β_{11z} and with the aid of the Haltafall program, the extent of formation of each species in the chosen model is calculated. The distribution of europium(III) complexes with ligand **2b** is represented in Fig. 4. For all other ligands, the distribution of the complexes is quite well balanced within the pH range considered.

4.4. Selectivity of complexation in the lanthanide series

The complexing selectivity $S(M/M')$ of a cation M with respect to another cation M′, is defined, as the logarithm of the ratio of the stability constants of the ML and M′L complexes. A good selectivity of 26 and 25 is observed for Sm^{3+}/Ce^{3+} with, respectively, **1d** and **2a**. These ligands are characterized by a methyl group in the *para* position.

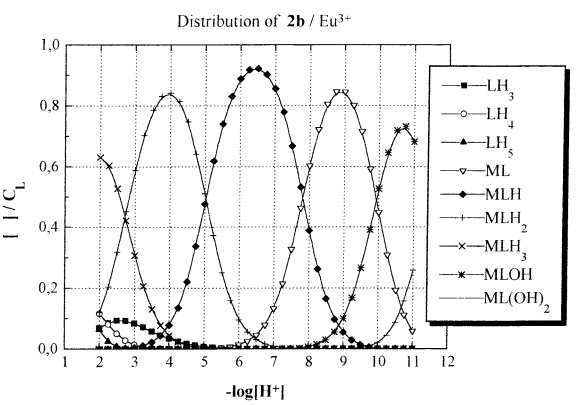


Fig. 4. Distribution curves of the complexes of the ligand **2b** with Eu^{3+}.

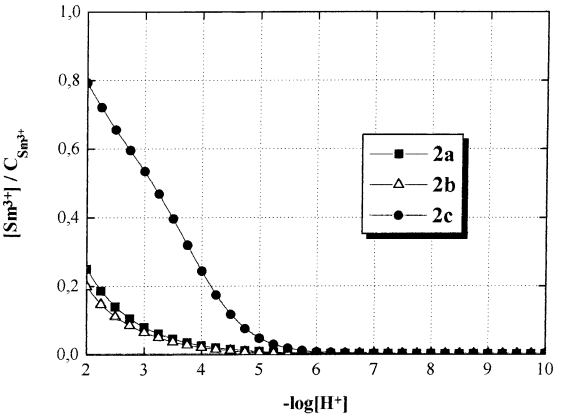


Fig. 5. Fraction of calculated free Sm^{3+} concentration vs. $-\log[H^+]$, for the ligands studied ($C_M = C_L = 10^{-2}$ mol dm^{-3}).

4.5. Scaling of the complexing ability of the ligands

The percentages of free Sm^{3+} are calculated as a function of-log[H^+] for the different ligands at $C_M = C_L = 10^{-2}$ mol dm^{-3}. This is illustrated in Fig. 5. An examination of the figure clearly shows that the complexing power (β_{110}) of the pentaacids is in the proposed relative order, **2c** < **2b** = **2a**. Hence, for both sequences, triacids as reported earlier, and pentaacids as in this work, the acid having the methyl group at the *para* position with respect to the phenolic OH has the greatest complexing power.

4.6. Comparison with the complexation of alkaline-earth cations

The alkaline-earth and lanthanide cations have in common the property of forming essentially electrostatic interactions with their ligands and it is interesting to compare the Ca^{2+} and Eu^{3+} complexes, as these cations have the same ionic radius [18]. It is, therefore, possible to examine the influence of the cationic charge.

S. Chafaâ [19] studied, the complexes of **1a**, **1c** and **2b** with calcium under similar experimental conditions as in this work. With that ligands, he identified, respectively, the ML and MLH complexes, the ML, MLH and MLH_2 complexes, the ML, MLH, MLH_2 and MLH_3 complexes. The hydroxide complexes were not taken into account in his study. The log β_{xyz} constants of the calcium complexes are reported in Table 5 together with the values for the europium.

If one takes into account the fact that there is no evidence of any sodium complex formation under the same experimental conditions even though Na^+ has the same ionic radius as Ca^{2+} and Eu^{3+}, it can be concluded that for equally sized cations, the stability of the ML complexes increases strongly as a function of cation charge (6–7 log U). The same conclusion is reached for the protonated complexes. It is for this reason that the most protonated complexes can be observed with europium, but never with calcium.

4.7. Comparison with the complexation of 3d metal cations

The values for the log β_{110} constants of the 3d metals cations Ni^{2+}, Cu^{2+} and Zn^{2+} have also been determined by Chafaa et al. [20], and again the eventual presence of hydroxide species within the pH range studied was not taken into account.

Table 5
Values of log β_{11z} of calcium(II) and europium(III) complexes

Ligand	log β_{110}		log β_{111}		log β_{112}		log β_{113}	
	Ca^{2+}	Eu^{3+}	Ca^{2+}	Eu^{3+}	Ca^{2+}	Eu^{3+}	Ca^{2+}	Eu^{3+}
1a	2.9	10.6	13.4	16.9		20.6		
1c	3.4	9.1	12.0	14.1	17.8			
2b	5.9	11.9	14.0	19.7	20.9	24.7	25.7	27.4

The columns of Eu^{3+} with **2b** is this work while with **1a** and **1c** is our work to be submitted ([10]). The other values are from [9].

Table 6
Values of log β_{110} of transition cations Ni^{2+}, Cu^{2+}, Zn^{2+} and Eu^{3+}

Ligand	Ni^{2+}	Cu^{2+}	Zn^{2+}	Eu^{3+}
1a	5.2[9]	11.5[9]		10.6[10]
1c	5.9[9]	10.4[9]		9.11[10]
2b	6.5	11.8	9.8	11.9

The results are reported in Table 6 and compared with those for Eu^{3+} determined in this study.

It is evident that the Cu^{2+} complexes are slightly stronger than those of Eu^{3+}, whereas the Ni^{2+} complexes are clearly weaker than those of Eu^{3+} (a difference of 5 log U). This is regardless of the ligand considered and is not surprising as this agrees with the Irving-Williams order of stabilities, recently confirmed for different systems with the 3d transition metals [21].

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