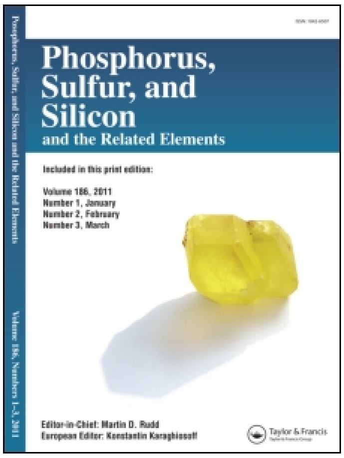

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Acidity and Complexation of (o -Hydroxyphenyl) Mono-Methylenephosphonic Acids Towards Lanthanide (III) Ions

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ACIDITY AND COMPLEXATION OF (*O*-HYDROXYPHENYL) MONO-METHYLENEPHOSPHONIC ACIDS TOWARDS LANTHANIDE (III) IONS

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pH-Metric and UV-visible spectrophotometry studies were performed in aqueous solution at 25°C and 0.1 mol dm^{-3} *ionic strength* ($NaClO_4$) *in order to determine the acidity and the complexing ability of five (*o*-hydroxyphenyl) mono-methylenephosphonic acids* (H_3L) *toward Ce(III), Pr(III), Nd(III), Sm(III), and Eu(III). The* pK_a *values of the ligand, the hydrolysis constants of the cations, the number, the nature of their metallic complexes present in solution, their stability constants, and their individual electronic spectra as restored by computation over a broad acidity range have been determined by potentiometry and UV-visible spectrophotometry between 200 and 550 nm and are reported. The formation of 1:1 species partially protonated* $[MLH_x]$ *and totally deprotonated [ML] as well as hydroxo species* $[ML(OH)_x]$ *has been established with lanthanides (III). Selectivity of complexation in the lanthanides and the complexing ability of the ligands are discussed.*

Keywords: Lanthanide (III) complexes; mono-methylenephosphonic acids; protonation constants; selectivity; stability constants

A large number of phosphonic compounds has been examined with respect to their complexing properties[1–4] and their suitability as extractants.[5] The chemistry of lanthanides (III) ($Ln^{3+} = Ce^{3+}$, Pr^{3+}, Nd^{3+}, Sm^{3+} et Eu^{3+}) has been the subject of many investigations as well, but few quantitative studies on the stability of cations Ln^{3+}

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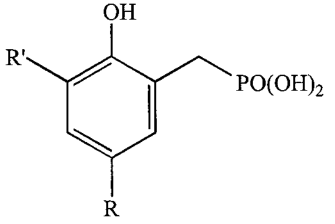
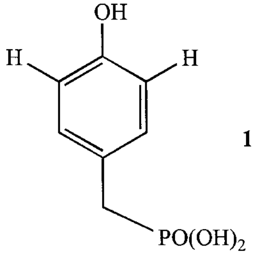
with polyphosphonate ligands have been carried out.[6] Very few results have been published concerning the species in solution. Sawada et al.[7] have determined the protonation constants of cyclic amines substituted by methylene-phosphonic group on the nitrogen atom. Geraldes and coworkers[8] have studied the acidity and the complexation properties of macrocyclic ligands using potentiometric and NMR techniques. Chafaa et al.[9,10] have reported previously on the acid-base properties of a series of (*o*-hydroxyphenyl) methylenephosphonic acids which were synthesized by Vogt and coworkers.[11] These studies were performed using potentiometric and spectrophotometric techniques.

In this article, we report the results of our studies on the acid-base and complexation properties of five mono-methylenephosphonic acids (triacids H_3L, compounds **1a–1e**) with a wide variety of lanthanide (III) cations, by potentiometric and UV-visible spectrophotometry methods.





1b

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

RESULTS

Potentiometry

Figure 1 shows, as an example, the protonation curve of ligand **1c**, and in the presence of different lanthanide cations, at $C_M = C_L = 10^{-2}$ mol dm^{-3}.

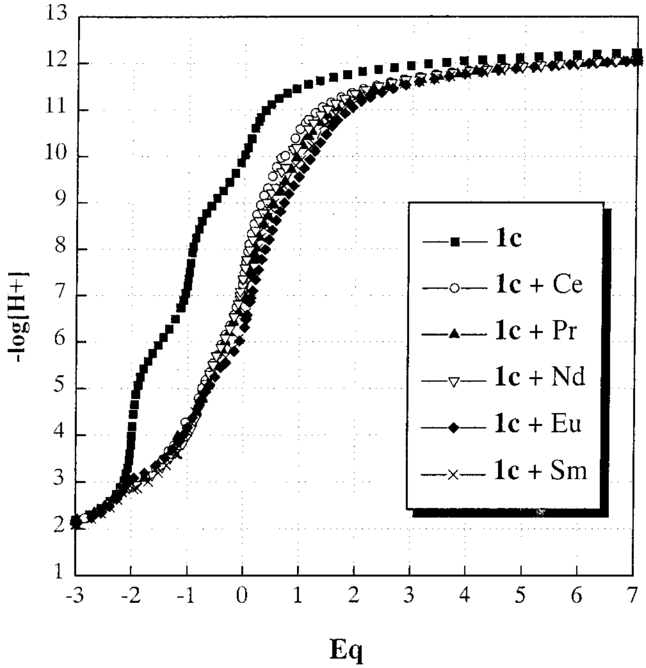


FIGURE 1 Titration curves of the ligand **1c** with the different lanthanide cations.

Acid-Base Equilibrium

In order to simplify the interpretation of the results, the pH is given versus the number of OH^- equivalents per ligand mol, calculated after neutralization. The titration curve of the ligand alone is characterized by three inflexion points clearly corresponding to one, two and three equivalents of base, i.e., the ionization of the two phosphonic $PO(OH)_2$ protons followed by that of the phenolic OH. The pK_a's of the different ligands, as determined in this work, are in good harmony with previous literature values (Table I).

Complexation Studies

The titration curves of the ligand in presence of metal cations show four equivalent points. The first point (pH = 3) situated slightly before 1 equiv OH^-, corresponds to the neutralization of the phosphonic function of the ligand and formation of the complex MLH_2. Before this first equivalent point, the curves are superimposed which means that no complexation occurs below pH = 2 in our experimental conditions. The second and third equivalent points (pH = 4.5, m = 2 and pH = 6.5,

TABLE I Dissociation Constants of Mono-Phosphonic Acids Determined by Potentiometric and Spectrophotometric Data

Ligand	pK_{a1}	pK_{a2}	pK_{a3}
1a	2.13 ± 0.85[a]	6.45 ± 0.84[a]	11.17 ± 0.36[a]
	2.23 ± 0.11[b]	6.53 ± 0.09[b]	11.43 ± 0.04[b]
	1.80[e]	6.35[e]	11.21[e]
1b	1.89 ± 0.03[a]	7.20 ± 0.02[a]	9.30 ± 0.01[a]
	1.91[e]	7.43[e]	10.05[e]
1c	1.94 ± 0.23[a]	6.03 ± 0.21[a]	9.10 ± 0.08[a]
	1.93 ± 0.04[b]	6.06 ± 0.02[b]	9.17 ± 0.01[b]
	1.80 ± 0.20[c]	6.22 ± 0.09[c]	9.09 ± 0.01[c]
	1.70 ± 0.02[d]	5.91 ± 0.02[d]	9.10 ± 0.01[d]
	1.68 ± 0.15[e]	6.00 ± 0.09[e]	9.10 ± 0.03[e]
	1.91 ± 0.25[f]	6.24 ± 0.15[f]	9.22 ± 0.06[f]
1d	1.82 ± 0.10[a]	6.61 ± 0.27[a]	9.04 ± 0.11[a]
	1.73 ± 0.04[c]	7.10 ± 0.11[c]	9.58 ± 0.01[c]
	1.98[e]	6.77[e]	9.93[e]
1e	1.91 ± 0.22[a]	5.98 ± 0.19[a]	9.59 ± 0.01[a]
	190 ± 0.13[b]	5.98 ± 0.08[b]	9.60 ± 0.04[b]
	2.02 ± 0.17[c]	5.89 ± 0.09[c]	9.56 ± 0.03[c]
	1.87 ± 0.02[d]	5.89 ± 0.02[d]	9.71 ± 0.01[d]
	1.51[e]	5.76[e]	9.56[e]
	1.91 ± 0.23[f]	6.62 ± 0.14[f]	9.93 ± 0.08[f]

[a] Potentiometric values determined by authors with Sirko_P program.
[b] Potentiometric values determined by authors with Superquad program.
[c] Potentiometric values determined by Vogt and coworkers.[11]
[d] Spectrophotometric values determined by authors with Letagrop_Spefo program.
[e] Spectrophotometric values determined by authors with Sirko_S program.
[f] Spectrophotometric values determined by Chafaa and coworkers.[9]

m = 3) can be attributed respectively, to the probable formation of the complexes MLH and ML. Finally, the position of the fourth equivalent point (pH = 9.5, m = 4) could correspond to the probable formation of the hydroxo species. It was shown, a posteriori, that neglection of the hydrolysis constant $\beta_{10\text{-}1}$ of the lanthanide cations was justified.

The complexation results for Ce (III), Pr (III), Nd (III), Sm (III), and Eu (III) with *o*-hydroxy phenyl mono-methylenephosphonic acids variously substituted were calculated. The β_{xyz} values computed by Sirko_P are given in Table II. They also were calculated by Superquad and, within the uncertainty limits, are in good agreement.

Spectrophotometry

All absorption variations were recorded as a function of pH. The quantitative interpretation was carried out for molecules containing the group

TABLE II Values of $\log\beta_{11z} \pm \sigma_{N-1}$[a] (N = 8) Determined by Sirko_P Program for the Complexes Formed with Ln^{3+} in Water (25°C, I = 0.1 mol dm^{-3} $NaClO_4$)

Ligand[b]	Cation	$\log\beta_{110}$	$\log\beta_{111}$	$\log\beta_{112}$	$\log\beta_{11\text{-}1}$	$\log\beta_{11\text{-}2}$	pH range	R_f %
1a	Ce(III)	10.03 ± 0.08	16.44 ± 0.08	20.56 ± 0.07	0.5 ± 0.1	−11.5 ± 0.2	2.12–10.22	1.6
$C_L = 10^{-2}$[b]	Pr(III)	9.9 ± 0.1	16.0 ± 0.1	19.9 ± 0.1	0.6 ± 0.2	−11.0 ± 0.1	2.22–10.93	2.7
$C_M = 10^{-2}$	Nd(III)	1 0.4 ± 0.2	16.9 ± 0.1	20.9 ± 0.1	0.9 ± 0.3	−11.1 ± 0.2	2.08–10.12	1.6
	Sm(III)	10.65 ± 0.07	17.0 ± 0.1	20.7 ± 0.1	1.49 ± 0.08	−10.92 ± 0.09	2.21–10.43	1.7
	Eu(III)	10.62 ± 0.08	16.87 ± 0.08	20.60 ± 0.09	1.53 ± 0.03	−10.78 ± 0.09	2.20–10.67	1.8
1b	Ce(III)	6.6 ± 0.1	12.4 ± 0.7		−1.7 ± 0.2	−12.0 ± 0.1	3.37–10.11	1.8
$C_L = 10^{-3}$	Pr(III)	7.5 ± 0.3	12.9 ± 1.1		−0.8 ± 0.3	−11.9 ± 0.1	3.02–10.21	2.3
$C_M = 10^{-3}$	Nd(III)	7.6 ± 0.2	12.9 ± 1.3		0.2 ± 0.3	−11.9 ± 0.1	3.02–10.07	1.9
	Sm(III)	7.68 ± 0.04	13.22 ± 0.09		0.21 ± 0.05	−10.63 ± 0.07	3.25–10.11	1.8
	Eu(III)	7.54 ± 0.03	13.23 ± 0.06		0.3 ± 0.3	−10.11 ± 0.07	3.30–10.20	2.2
1c	Ce(III)	8.67 ± 0.05	14.43 ± 0.05		−0.93 ± 0.06	−11.35 ± 0.09	2.12–10.71	2.7
$C_L = 10^{-2}$	Pr(III)	8.84 ± 0.06	14.35 ± 0.06		−0.11 ± 0.06	−11.6 ± 0.1	2.12–10.46	2.3
$C_M = 10^{-2}$	Nd(III)	8.96 ± 0.07	14.62 ± 0.07		−0.41 ± 0.08	−11.9 ± 0.1	2.10–10.32	2.8
	Sm(III)	9.28 ± 0.05	14.46 ± 0.05		0.49 ± 0.05	−10.63 ± 0.07	2.10–10.43	1.8
	Eu(III)	9.11 ± 0.05	14.10 ± 0.05		0.74 ± 0.05	−10.11 ± 0.07	2.11–10.38	1.8
1d	Ce(III)	9.55 ± 0.07	14.2 ± 0.2	19.92 ± 0.04	2.26 ± 0.04	−7.70 ± 0.04	3.36–10.21	1.8
$C_L = 10^{-3}$	Pr(III)	10.1 ± 0.6	15.7 ± 0.6	21.1 ± 0.5	3.2 ± 0.6	−7.2 ± 0.7	2.98–10.31	2.4
$C_M = 10^{-3}$	Nd(III)	10.4 ± 0.4	15.2 ± 0.3	20.4 ± 0.3	3.4 ± 0.5	−6.4 ± 0.5	3.14–10.47	2.3
	Sm(III)	11.0 ± 0.7	15.9 ± 0.6	20.8 ± 0.6	4.1 ± 0.7	−5.7 ± 0.7	3.01–10.46	2.4
	Eu(III)	10.30 ± 0.03	15.36 ± 0.07	20.11 ± 0.01	3.89 ± 0.03	−5.36 ± 0.03	3.22–10.56	1.5
1e	Ce(III)	9.72 ± 0.03	15.46 ± 0.03		0.89 ± 0.04	−10.32 ± 0.06	2.01–10.35	2.2
$C_L = 10^{-2}$	Pr(III)	9.36 ± 0.04	15.02 ± 0.04		0.01 ± 0.05	−11.8 ± 0.1	2.01–10.76	2.2
$C_M = 10^{-2}$	Nd(III)	10.72 ± 0.07	15.77 ± 0.07		1.46 ± 0.07	−9.81 ± 0.09	1.98–10.80	1.8
	Sm(III)	9.69 ± 0.04	14.94 ± 0.04		1.61 ± 0.04	−8.93 ± 0.05	2.10–10.09	2.3
	Eu(III)	10.07 ± 0.04	15.30 ± 0.04		2.14 ± 0.04	−8.20 ± 0.05	2.05–10.19	2.2

[a] Arithmetic mean of N (≥2) determinations; negative z values refer to hydroxo species.

[b] The concentration given in the first column are in mol dm^{-3}.

NO_2 on the aromatic ring: **1c**, **1d**, **1e**. The spectral variations of **1a** and **1b** are so feeble that they can not be exploited.

Acid-Base Equilibrium

The absorption spectra of **1c** and **1e** are quite similar and differ from that of **1d**. For **1c**, the principal absorption band corresponding to the totally protonated molecule is situated at 323 nm ($\varepsilon = 9270$ dm^3 mol^{-1} cm^{-1}). At higher pH values there is an intense maximum at 422 nm ($\varepsilon = 19500$ dm^3 mol^{-1} cm^{-1}) along with the presence of a small band at 270 nm. The acid solutions of **1d**, on the other hand, present three absorptions bands: 215 nm ($\varepsilon = 13500$ dm^3 mol^{-1} cm^{-1}), 295 nm ($\varepsilon = 6490$ dm^3 mol^{-1} cm^{-1}), and 379 nm ($\varepsilon = 3070$ dm^3 mol^{-1} cm^{-1}). In alkaline solutions all the three bands undergo a strong bathochromic shift which is of the same magnitude as that obtained for the deprotonated species.

The overall stability constants β_{01z} of the concerned species were determined. They agree well with the pK_a values obtained by potentiometry and by spectrophotometry as well as those reported in the literature. The electronic spectra of all these species were drawn from the calculated ε values. It is only due to the comparison between the experimental and the calculated spectra in highly acid or alkaline solutions that the identification of the completely protonated species H_xL and the completely deprotonated species L^{x-} was possible.

Complexation Studies

The ligands **1c**, **1d**, and **1e** were complexed with different lanthanides (Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, and Eu^{3+}) in a ratio of $[M]_0/[L]_0 = 1$. The UV-visible spectral variations, as a function of pH, of different solutions of **1c** and **1d** with Sm^{3+} is presented in Figure 2.

Whatever the system, the spectra is characterized by four principal absorption bands. The first band is situated between 200 and 280 nm; the bands between 280 and 350 nm clearly result from the deprotonation of the ligands. In the range of 350 and 410 nm, the formation of new complexes strongly modifies not only the intensity, but the lateral displacement of the bands as well. Finally, the high intensity absorption bands between 410 and 480 nm correspond to those of the totally deprotonated ligand: $\lambda_{max} = 421$ nm for **1c**, 461 nm for **1d** and 439 nm for **1e**.

The difference between these spectra and those of the ligands alone is localized between 330 and 420 nm. The absorption increases regularly ($5.96 < pH < 8.26$) and gives rise to a new maximum at 380 nm and then decreases as a function of pH with a slight bathochromic shift.

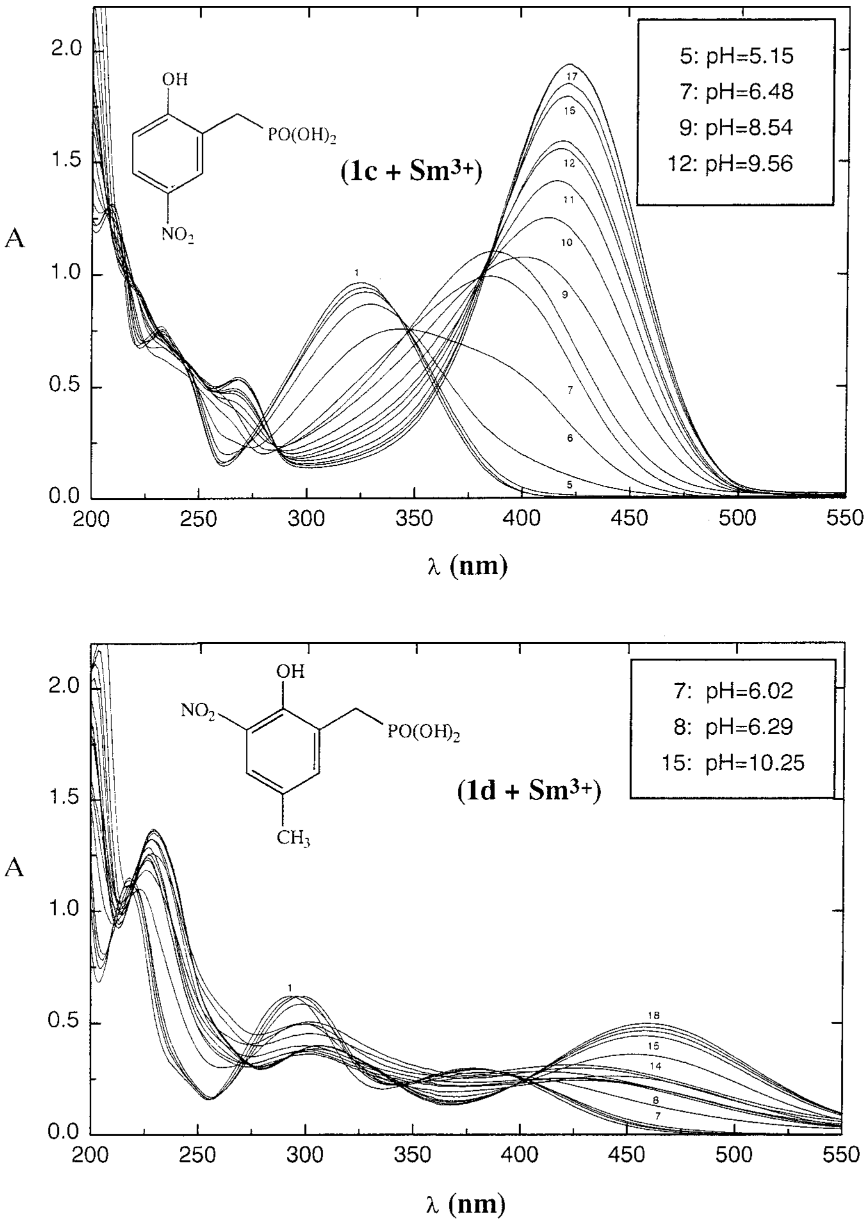


FIGURE 2 Experimental absorption spectra of **1c** and **1d** complexes with Sm^{3+}.

TABLE III Values of logβ_{11z} Determined by Letagrop and/or Sirko_S Programs for the Complexes Formed with Ln^{3+} (25°C, $I = 0.1$ mol dm^{-3} $NaClO_4$, $C_M = C_L = 10^{-4}$ mol dm^{-3})

Ligand	Cation	logβ_{110}	logβ_{111}	logβ_{112}	log$\beta_{11\text{-}1}$	log$\beta_{11\text{-}2}$	N × L	pH range	U ou Rf (*)
1c	Ce(III)	8.63 ± 0.05	15.0 ± 0.1	20.34 ± 0.08	−0.64 ± 0.08	−11.7 ± 0.3	15 × 10	1.62–10.58	0.1249E-03
	Pr(III)	8.84 ± 0.09	14.75 ± 0.08	20.62 ± 0.05	−0.4 ± 0.4	−9.5 ± 0.1	15 × 11	1.65–10.78	0.3481E-03
		7.9 ± 0.1*	15.05 ± 0.09*	19.95 ± 0.03*			8 × 7	1.65–7.41	0.4% (*)
	Nd(III)	8.9 ± 0.2	14.6 ± 0.4	22.04 ± 0.06	−0.3 ± 0.1	−9.6 ± 0.3	14 × 11	1.65–10.85	0.1202E-02
	Sm(III)	9.34 ± 0.06	15.41 ± 0.07	20.2 ± 0.1	0.34 ± 0.03	−9.77 ± 0.09	14 × 11	1.65–10.46	0.1781E-02
		9.3 ± 0.4*	16.0 ± 0.3*	18.08 ± 0.06*			8 × 6	1.65–8.54	0.7% (*)
	Eu(III)	8.15 ± 0.01	15.0 ± 0.2	20.82 ± 0.02	0.54 ± 0.02	−8.02 ± 0.01	15 × 11	1.70–10.30	0.3596E-02
		8.5 ± 0.4*	15.4 ± 0.3*	18.50 ± 0.03*			8 × 6	1.70–7.27	0.8% (*)
1d	Ce(III)	9.18 ± 0.05	14.44 ± 0.08	20.10 ± 0.06	1.87 ± 0.05	−7.88 ± 0.07	15 × 11	1.73–10.53	0.1800E-02
	Pr(III)	9.54 ± 0.05	14.98 ± 0.08	21.02 ± 0.05	2.6 ± 0.1	−7.3 ± 0.1	15 × 11	1.68–10.58	0.3501E-02
	Nd(III)	8.68 ± 0.07	14.42 ± 0.05	19.0 ± 0.1	3.6 ± 0.1	−6.3 ± 0.1	15 × 11	1.74–10.68	0.3001E-02
	Sm(III)	8.8 ± 0.1	15.38 ± 0.06	21.4 ± 0.3	3.71 ± 0.06	−5.39 ± 0.06	15 × 12	1.76–10.61	0.7002E-04
	Eu(III)	9.92 ± 0.08	14.9 ± 0.1	20.34 ± 0.09	3.20 ± 0.09	−5.08 ± 0.14	14 × 11	1.71–10.82	0.9001E-03
1e	Ce(III)	8.35 ± 0.04	15.45 ± 0.02	20.97 ± 0.02	1.67 ± 0.01	−8.15 ± 0.05	14 × 11	1.68–10.50	0.1603E-02
		9.0 ± 0.6*	15.0 ± 0.1*	19.02 ± 0.03*			8 × 7	1.68–7.38	1.0% (*)
	Pr(III)	9.08 ± 0.07	15.04 ± 0.09	21.05 ± 0.03	0.70 ± 0.08	−9.17 ± 0.24	14 × 12	1.69–10.54	0.2176E-03
		9.2 ± 0.6*	15.2 ± 0.1*	20.3 ± 0.1*			9 × 7	1.69–8.67	1.0% (*)
	Nd(III)	8.79 ± 0.06	15.70 ± 0.04	21.18 ± 0.07	1.43 ± 0.04	−7.98 ± 0.01	14 × 12	1.66–10.54	0.2933E-02
	Sm(III)	9.4 ± 0.1	15.87 ± 0.03	21.79 ± 0.03	1.85 ± 0.03	−8.17 ± 0.03	14 × 11	1.64–10.45	0.3362E-02
		9.0 ± 0.3*	15.74 ± 0.08*	20.0 ± 0.1*			7 × 7	1.64–6.81	1.1% (*)
	Eu(III)	9.25 ± 0.07	15.47 ± 0.05	21.53 ± 0.05	1.07 ± 0.09	−8.79 ± 0.07	14 × 12	1.51–10.41	0.1085E-02

*Values determined by Sirko_S.

Isosbestic points are observed, indicating equilibrium between at least two species. The coordinates of these points, compared to those obtained from the calculated electronic spectra is a major factor in choosing the best model.

The logarithm of the overall stability constants are given in Table III. These values are the arithmetic mean of three results. With the help of these values the specific extinction coefficients were calculated leading to the individual electronic spectra. As a representative example these spectra are given with the metal Sm^{3+} and the ligands **1c** and **1d** in Figure 3.

DISCUSSION

Nature of the Complexes Formed

For simplicity, the charges of the complexes will be omitted in the following discussion. Referring to global results, the complexes formed within the defined pH range (2–10) are, in all cases, ML, MLH, MLOH, and $ML(OH)_2$. The MLH_2 species, on the other hand, is only observed in the case of **1a** and **1d**.

Order of Magnitude of the Constants

The ML formation constants are of the order of 9–10 log units with the sole exception of the ligand **1b** where P is in the *para* position and the mean log β_{110} value is only 7.4. This result can be easily explained considering that the phosphonate group in the *para* position, is quite far removed from the phenolic OH and therefore any cooperation between the two groups is limited.[12] On the other hand, this cooperative interaction would be more effective for compounds of type **1a**, where the phosphonate group is in the *ortho* position. Likewise, the mean log β_{111} value is clearly weaker for **1b** (12.9) than for the **1a** type ligands (16.6). Nevertheless, the mean first stepwise protonation constant of ML into MLH, which for each ligand is equal to the ratio of the mean $\beta_{111}$to the mean β_{110} is not significantly different for **1b** (5.5 log units) than for **1c** (5.4), **1d** (5), and **1e** (5.4). However, it is higher for **1a** (6.3 log units). The average log β_{112} value for **1a** and **1d** is 20.5, and the mean second stepwise protonation constants of MLH into MLH_2 are equal to $20.5 - 16.6 = 3.9$ for **1a** and $20.5 - 15.2 = 5.2$ for **1d.** Eventually, the first stepwise protonation constant of the ML complexes of **1a** (6.3) is much higher than the second one (3.9), probably due to electrostatic and statistical reasons. But in the case of **1d**, both stepwise constants

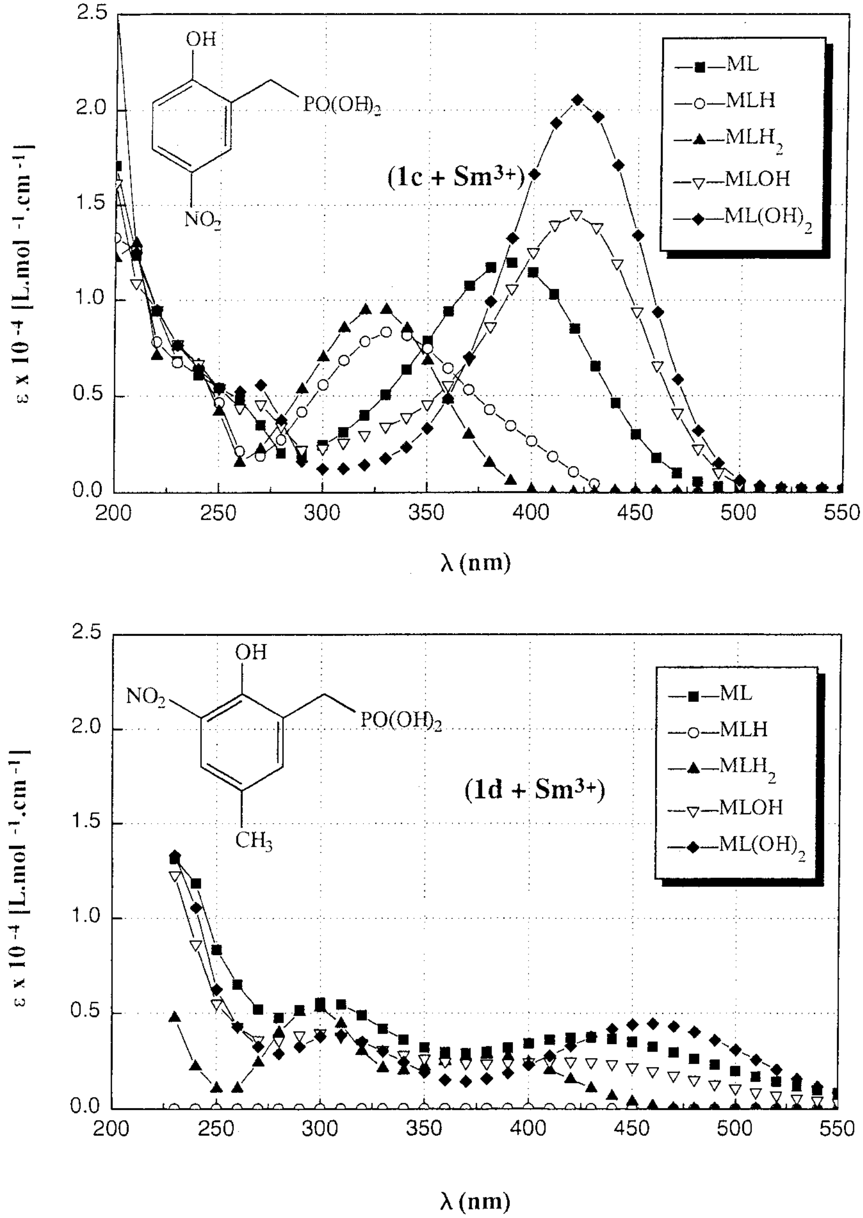


FIGURE 3 Calculated electronic spectra of **1c** and **1d** complexes with Sm^{3+}.

are alike (5 and 5.2). No clear reason for this difference in behavior of **1a** and **1d** can be advanced at this stage.

Distribution Curves of the Complexes

Using the log β_{11z} values determined earlier, and with the help of Haltafall program,[13] the percentage formation of the different species resulting from the complexation of the different ligands was calculated. For all of the ligands, the distribution of the complexes is quite well balanced within the pH range considered. One can nevertheless define selective pH ranges for which each of the complexes is predominant. With Sm^{3+} and with **1c** and **1d**, for example, these are shown in Figure 4.

- For **1c** instantaneous formation is observed with complete predominance of the MLH_2^{2+} species (98%) from pH 2 to pH 4, the species ML (96%) between pH 6.5 and 7.5, and finally, $MLOH^-$ (90%) at around pH 10. The $ML(OH)_2^{2-}$ species only begins to form at pH 10 and onward. A coexistent species with equal proportions is noted at pH 5.5 for the pairs MLH_2^{2+}, ML (40%) and also at pH 8.7 for ML, $MLOH^-$ (50%).
- For **1d**, the distribution curves show two important maxima corresponding respectively to the species ML, formed at pH 6 (80%) and $MLOH^-$, formed at about pH 8.3 (92%). The formation of a species MLH_2^{2+} is observed at pH 3 (80%). The $ML(OH)_2^{2-}$ species only begins to form at pH 9 and reaches a maximum 92% at pH 11. A coexistent species with equal 50% formation is observed for the pairs ML, $MLOH^-$ at around pH 7 and $MLOH^-$, $ML(OH)_2^{2-}$ close to pH 10.

Selectivity of Complexation in the Lanthanide Series (Z = 58–63)

A attempt was made to plot the selectivity profiles of the ligands studied, (logβ_{110}), as a function of the atomic number Z of the cations, and this is shown in Figure 5.

These profiles are relatively flat, demonstrating feeble selectivity, except for cerium, which has a formation constant slightly weaker than the others. Table IV represents the complexation selectivity S(M/M′) of a cation M with respect to another cation M′, as the logarithm of the ratio of the stability constants of the ML and M′L complexes. A good selectivity of 26 is observed for Sm^{3+}/Ce^{3+} with **1d**. It may be recalled that this ligand is characterized by a methyl group in the *para* position.

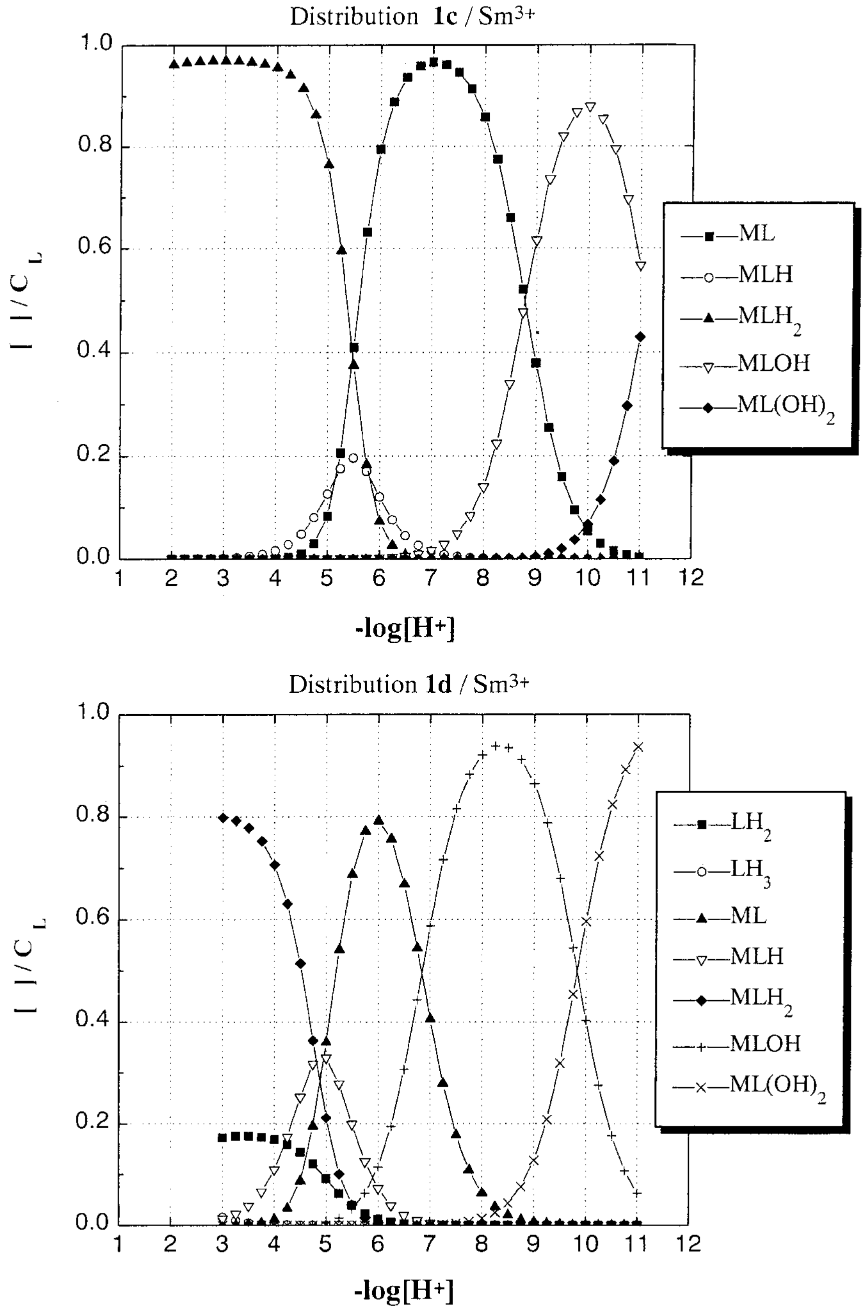


FIGURE 4 Distribution curves of **1c** and **1d** complexes with Sm^{3+}.

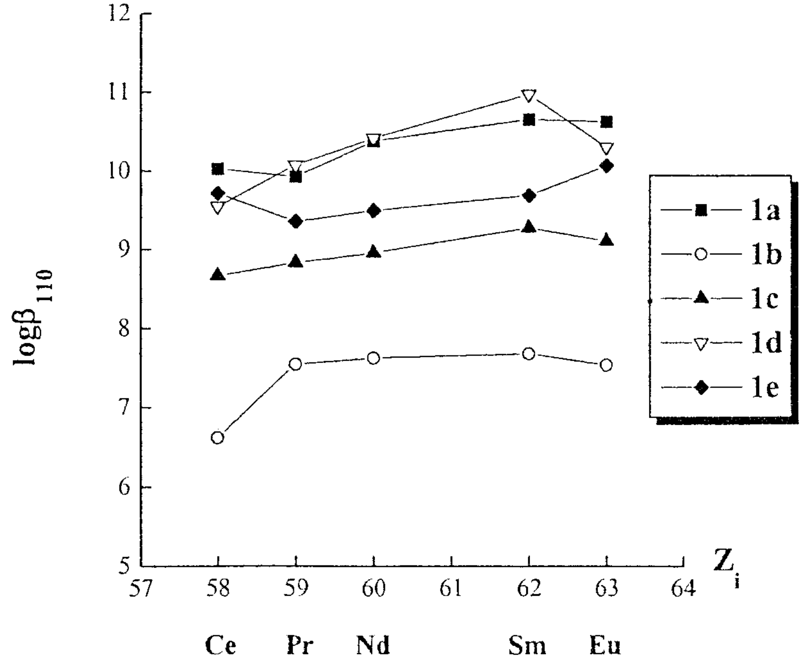


FIGURE 5 Variation of $\log \beta_{110}$ of complexes versus the atomic number of Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, and Eu^{3+}.

Scaling of the Complexing Ability of the Ligands

The complexing power (β_{110}) of the different ligands is presented in Figure 5. This power is the weakest for **1b** because of the *para* position of the methylenephosphonic group for which the cooperative interaction is the least with the OH phenolic group. As regards the ligands with the methylene-phosphonic in *ortho* position, those that have the substituent NO_2 in *para* position **1c** and **1e** are less complexing than those without the NO_2 group **1a** and this in turn has a complexing power

TABLE IV Selectivities of Complexation for the Ligands Studied $S(M/M') = \beta_{110}(M)/\beta_{110}(M')$

Ligand	S (Sm^{3+}/Ce^{3+})	S (Sm^{3+}/Pr^{3+})	S (Sm^{3+}/Nd^{3+})
1a	4.16	5.25	1.86
1b	11.48	1.35	1.12
1c	4.07	2.75	2.09
1d	26.30	7.76	3.55
1e	0.93	2.13	0.09

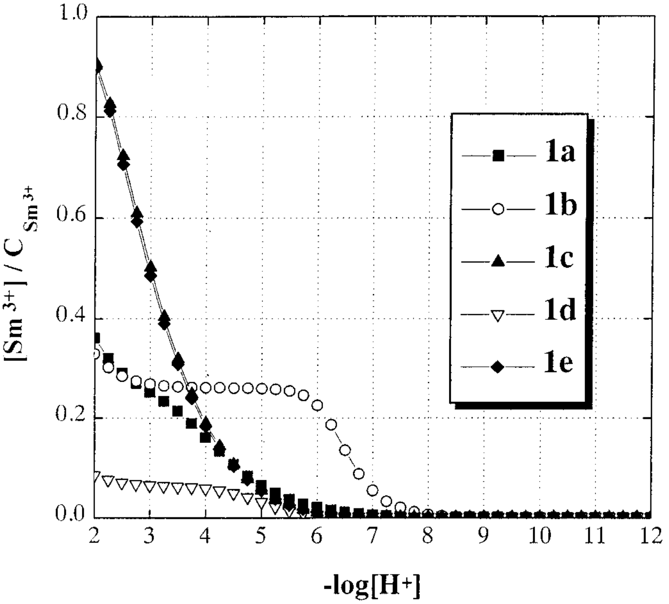


FIGURE 6 Fraction of calculated free Sm^{3+} concentration versus $-\log[H^+]$, for the five ligands studied ($C_M = C_L = 10^{-2}$ mol dm^{-3}).

even less than ligands with NO_2 in *ortho* position **1d**. This is readily ascertained by the vicinity of the NO_2 and OH groups favoring high cooperative interaction.

Figure 6 represents the percentages of free Sm^{3+} calculated as a function of—log[H^+] for the different ligands at $C_M = C_L = 10^{-2}$ mol dm^{-3}.

This equally shows that the complexing power (β_{110}), of the triacids is in the proposed relative order: **1b** < **1c** = **1e** < **1a** < **1d**.

The above properties, such as selectivity and the complexing ability of the mono-methylenephosphonic acids are compared to those of bis-methylenephosphonic acids and have been reported in our recent publication.[14]

EXPERIMENTAL

Reagents

All ligands were prepared according to the method previously described,[11] and their purity was further controlled by microanalysis:

Anal. Calc. For **1a** : C: 44.7; H: 4.82 Found C: 44.8; H: 4.80
Anal. Calc. For **1b** : C: 45.68; H: 4.82 Found C: 45.83; H: 4.70

Anal. Calc. For **1c** : C: 37.15; H: 3.76 Found C: 37.04; H: 3.53
Anal. Calc. For **1d** : C: 38.90; H: 4.08 Found C: 39.40; H: 4.01
Anal. Calc. For **1e** : C: 40.18; H: 4.32 Found C: 39.93; H: 4.11

They were used as free acids and their solutions were made by dissolution of a weighed quantity in bidistilled water. Sodium perchlorate, sodium hydroxide, and hydrochloric acid were obtained from E. Merck as analytical reagents grade materials and were used without any purification. The ionic strength, I, was kept constant at 10^{-1} mol dm^{-3} by addition of sodium perchlorate recrystallized twice from water. The titrant base used was sodium hydroxide made from an aqueous dilution of the commercial solution and its concentration was determined using a potassium hydrogen phthalate standard solution.

The metallic salts were the commercial p.a. lanthanide chlorides $MCl_3 \cdot xH_2O$ (M = Ce, Pr, Nd, Sm, and Eu). These salts were dried at room temperature under vacuum before use. Their stock solutions were titrated by complexometry with ethylenedinitrilotetraacetate at pH 6 (sodium acetate) using xylenol orange as indicator.[15]

Ligand solutions were prepared in the concentration range 10^{-2} or 10^{-3} mol dm^{-3}. A given amount of perchlorate acid was initially added to all ligand solutions in order to completely protonate the ligand. The solution was then neutralized by NaOH solution 0.1 or 1 mol dm^{-3} until $-\log [H^+] = 12$. In the following discussions, $-\log [H^+]$ will be abbreviated as pH.

The final analytical concentration of metal was 10^{-4} mol dm^{-3} for spectrophotometric measurements and $NaClO_4$ at 0.1 mol dm^{-3} was used as reference solution. The final solutions of metal and ligand were prepared just before the measurements.

Potentiometric Measurements

The potentiometric investigations of acid-base and metal-binding equilibria were carried out at 25.0 ± 0.1°C and at a fixed ionic strength of 0.1 mol dm^{-3} ($NaClO_4$).

The complexation was studied in aqueous solutions with equal analytical concentrations of the ligand C_L and the cation C_M (10^{-2} mol dm^{-3} with **1a**, **1c**, **1e** and 10^{-3} mol dm^{-3} with **1b**, **1d**). The titrating agent NaOH (1 or 0.1 mol dm^{-3}) used was stored in a polyethylene container equipped with a CO_2 trap. All experiments were performed in a thermoregulated double-wall glass cell (25 cm^3) at 25.0 ± 0.1°C under an argon stream. The stepwise addition of the base was carried out with a microburette (Dosimat E635, 1 cm^3) driven by an automatic titrator (Titroprocessor 636, Metrohm) able to deliver amounts of solution as small as 10^{-3} cm^3. The dynamic mode (variable addition of titrant, smaller in the steep equivalence regions) was used to establish the titration curve and its first derivative and to collect the numerical data. The logarithm of the concentration of H^+ was measured with a combined glass electrode (Ingold) in which the reference liquid was replaced by a NaCl (0.01 mol dm^{-3})—$NaClO_4$ (0.09 mol dm^{-3}) solution of the same ionic strength as the solution to be measured. The electrode was calibrated in concentration, using the experimental law[16] given in Eq. 1, with a and b being constants experimentally determined with the calibration solutions 10^{-2} and 10^{-3} mol dm^{-3} HCl in 0.1 mol dm^{-3} $NaClO_4$:

$$-\log{[H^+]_{true}} = -\log{[H^+]_{read}} + a + b\log{[H^+]_{read}} \tag{1}$$

The quantities within square brackets are the concentrations of the species.

Spectrophotometric Measurements

The UV-visible spectra between 200 and 550 nm were recorded using a Shimadzu UV 2101 PC spectrophotometer regulated at 25.0 ± 0.1°C and matched 10 mm quartz cell. 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 never exceeded 10^{-3} mol dm^{-3} to guarantee accurate and confident absorbance values between 0.2 and 2.0. All of the 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. The analytical concentration of the metal and ligand was fixed at 10^{-4} mol dm^{-3}. Under the experimental conditions only the formation of the mononuclear complexes was envisaged. The spectra were recorded immediately after mixing the reagents, and it took less than 1 min to obtain the absorption curve in the studied range of 200 to 550 nm.

Calculation of Equilibrium Constants

The overall apparent protonation constants β_i corresponding to the equilibrium:

$$L^{n-} + iH^+ \rightleftharpoons H_iL^{(n-i)-} (0 \le i \le n)$$

are defined by Eq. 2:

$$\beta_i = \frac{[H_iL^{(n-i)-}]}{[H^+]^i[L^{n-}]} \tag{2}$$

They are related to the stepwise protonation constants K_i by:

$$K_i = \beta_i/\beta_{i-1}, \tag{3}$$

which are themselves related to acidity constants pK_a by:

$$\log K_i = pK_{a(n-i+1)}(1 \leq i \leq n). \tag{4}$$

The hydrolysis constants $K_{1,z}$ (Eq. 5) corresponding to the following equilibrium:

$$M^{3+} + zH_2O \rightleftharpoons M(OH)_z^{(3-z)+} + zH^+$$

$$K_{1,z} = \frac{[M(OH)_z^{(3-z)+}][H^+]^z}{[M^{3+}]} \tag{5}$$

are related to overall stability constants by:

$$\beta_{10z} = K_w^z \cdot K_{1,z} \quad \text{or} \quad \log \beta_{10z} = \log K_{1,z} - zpK_w, \tag{6}$$

where K_w is the hydrolysis constant of water at 25°C ($K_w = 10^{-13.78}$).

The apparent overall stability constants β_{xyz} of the complexes, corresponding to the following equilibrium:

$$xM^{m+} + yL^{n-} + zH^+ \rightleftharpoons M_xL_yH_z^{(xm-yn+z)+}$$

are given by Eq. 7:

$$\beta_{xyz} = \frac{[M_xL_yH_z^{(xm-yn+z)+}]}{[M^{m+}]^x[L^{n-}]^y[H^+]^z}, \tag{7}$$

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.

Potentiometric Data

Approximate values of the stepwise protonation constants K_i (Eq. 3) were first obtained by analysis of the curve $\bar{p}$ versus pH,[17] with $\bar{p}$ defined as the average number of protons fixed per mol of L^{n-}. From these initial values, the overall protonation constants β_i (Eq. 2) as well as the hydrolysis constants β_{10z} (Eq. 6) were then refined with programs Sirko[18] and Superquad.[19] The hydrolysis constants were calculated with the help of Eq. 6. The overall stability constants β_{xyz} of the complexes (Eq. 7) were computed with the above programs. Several titrations, each including not less than 150 pairs of data, were simultaneously processed with Sirko and/or Superquad. The values reported in the tables are the mean values of the results of N independent runs, given with their 95% confidence interval $\pm 2\sigma_{N-1}$ where σ is the standard deviation. R-factor (R_f) is the result of a statistical test related to the fit between the experimental and calculated curves.

Spectrophotometric Data

The whole set of spectrophotometric data was analyzed using the multiwavelength program Letagrop-Spefo[20] and/or Sirko-S,[18] which refine the overall stability constant β_{xyz} of the complexes. The protonation constants β_{01z} of the deprotonated forms of the ligands were constant during the refinement procedure, as well as the formation constants β_{10z} of hydroxo species. The β_{01z} values were obtained by titration, which led simultaneously to two sets of optimized parameters: the dissociation constants or overall stability constants and the extinction coefficients ε of all species involved in the deprotonation sequence or in the metallic complexation. Using these data, the individual electronic spectra for each species could be constructed. The calculated pK_a values or β_{xyz} values are indicated here with the usual 99% confidence interval ($\pm 3\sigma$). In general, the deviations on the pK_a (or stability constants) are slightly larger for absorption data treated by Letagrop-Spefo than for potentiometric data treated by Sirko-P and/or Superquad or the pK_a computation method described by Vogt.[11]

For a given model, the quality of the fit is judged from the value of U, sum of the squares of the differences between experimental and calculated absorptions for N solutions at L wavelengths. If U is smaller than 0.02 for (N, L), it is considered a good fit for such rather complicated multiparameter systems. The minimum of U leads to the best values of pK_a which enable the physical chemist to better understand the phenomena and to place these acids in the pK_a scale.

The constants deviations are secondary factors which do not really improve the goodness of the fit; it is necessary in all existing programs treating multicomponent systems to postulate supplementary approximations in the vicinity of the minimum of the least squares function and complementary statistical criteria to obtain satisfactory values of the constants deviations.[21]

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