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A comparison of the acidity and the complexing ability of
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Abstract

The characterization of the acid–base properties of a family of three phenol dimethylene phosphonic acids differently substituted by auxo- or chromophoric groups was studied. These ligands may be considered as pentaacids. Their pKₐ 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, Ce³⁺, Pr³⁺, Nd³⁺, Sm³⁺ and Eu³⁺, 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 methylene phosphonic 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 Ln³⁺ with some ligands have been reported. Tikhinova studied the system N,N'-di-(carboxymethyl) ethylenediamine bis-methylphosphonic acid (EDPA) towards Y³⁺, Yb³⁺ and Ce³⁺ [4]. The author reported higher stability of the complexes with respect to carboxylic homologues. Tereshin et al. [5] studied the complexation of Y³⁺ with nitrilotrimethyl phosphonic acid and postulated two types of complexes, viz. YHL⁻ and YH₂L⁻. Suran et al. [6], on the other hand,
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 methylene phosphonic acids. A recent pH-metric and spectrophotometric studies on the acidity of a family of (o-hydroxyphenyl) mono-methylene phosphonic acids (triacid series LH₃) 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 spectrophotometric study of the proton dissociation of the bis-methylene phosphonic acids (pentaacid series LH₅) 2a–e, 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.

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

1a: R = H and R’ = H
1b: PO(OH)₂ in para, R and R’ in ortho = H
1c: R = NO₂ and R’ = H
1d: R = CH₃ and R’ = NO₂
1e: R = NO₂ and R’ = CH₃

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(ClO₄)·6H₂O (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 (HClO₄) or of base (NaOH) and controlled with a precision pH-meter. The solution of Na(ClO₄) 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
were prepared by mixing the solid metal (III) chlorides with the solvent; these solutions were standardized with EDTA [12] at pH 6, using xylentol 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\(_4\). 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 \(2\)a and \(2\)b and 10\(^{-3}\) mol dm\(^{-3}\) with \(2\)c). All experiments were performed according to the method previously described [10].

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 \(2\)a and \(2\)b and 10\(^{-3}\) mol dm\(^{-3}\) with \(2\)c). 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 the complexes, correspond to the following equilibrium:

\[
xM^{m+} + yL^n- + zH^+ \Leftrightarrow M_yL_xH_z^{(x+y-2m+z)}
\]

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 (±3σ). The protonation constants \(\beta_{01z}\) of the ligands were kept constant during the refinement procedure of the stability constants, as well as the formation constants or \(\beta_{01z}\) of hydroxo species, in this case \(z\) is negative.

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 \(K_a\), the overall protonation constants \(\beta_{01z}\), and the overall stability constants \(\beta_{xyz}\) 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 (p\(K_a\) values) and overall stability constants of the complexes (\(\beta_{xyz}\)) and in the individual electronic spectra for all species involved. These p\(K_a\) 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 \(\beta_{xyz}\) of the complexes. The apparent overall stability constants \(\beta_{xyz}\) of the complexes, correspond to the following equilibrium:

\[
xM^{m+} + yL^n- + zH^+ \Leftrightarrow M_yL_xH_z^{(x+y-2m+z)}
\]

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.
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 NO₂ 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 + Ln³⁺, C_M = C_L = 10⁻³ mol dm⁻³).

3.1.1. Acid–base equilibrium

The five pKₐ 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 pKₐ 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

![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 NaClO₄).](image-url)

Table 1

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

<table>
<thead>
<tr>
<th>Ligand</th>
<th>pKₐ₁</th>
<th>pKₐ₂</th>
<th>pKₐ₃</th>
<th>pKₐ₄</th>
<th>pKₐ₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>1.4 ± 0.4</td>
<td>2.8 ± 0.5</td>
<td>6.6 ± 0.4</td>
<td>8.1 ± 0.4</td>
<td>11.4 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>1.5b</td>
<td>2.5b</td>
<td>6.5b</td>
<td>8.3b</td>
<td>11.8b</td>
</tr>
<tr>
<td></td>
<td>1.6c</td>
<td>2.3c</td>
<td>6.4c</td>
<td>8.1c</td>
<td>11.8c</td>
</tr>
<tr>
<td></td>
<td>1.2 ± 0.1d</td>
<td>2.2 ± 0.1d</td>
<td>6.2 ± 0.1d</td>
<td>9.0 ± 0.1d</td>
<td>12.8 ± 0.1d</td>
</tr>
<tr>
<td>2b</td>
<td>1.7 ± 0.8</td>
<td>2.2 ± 0.6</td>
<td>5.9 ± 0.4</td>
<td>7.8 ± 0.5</td>
<td>10.2 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>1.01b</td>
<td>2.2b</td>
<td>5.9b</td>
<td>7.90b</td>
<td>10.5b</td>
</tr>
<tr>
<td></td>
<td>1.6c</td>
<td>2.0c</td>
<td>5.8c</td>
<td>7.8c</td>
<td>10.3c</td>
</tr>
<tr>
<td>2c</td>
<td>1.2 ± 0.8</td>
<td>2.4 ± 0.8</td>
<td>5.93 ± 0.52</td>
<td>7.84 ± 0.35</td>
<td>11.74 ± 0.28</td>
</tr>
<tr>
<td></td>
<td>1.5b</td>
<td>2.5 ± 0.1a</td>
<td>6.0 ± 0.1a</td>
<td>7.9 ± 0.1a</td>
<td>11.7 ± 0.1a</td>
</tr>
<tr>
<td></td>
<td>1.7c</td>
<td>2.3b</td>
<td>6.3b</td>
<td>8.1b</td>
<td>11.9b</td>
</tr>
<tr>
<td></td>
<td>1.2 ± 0.8</td>
<td>2.0c</td>
<td>6.1c</td>
<td>7.9c</td>
<td>11.7c</td>
</tr>
</tbody>
</table>

a Values determined by authors with Superquad program.
d Values determined by Ameziane and co-workers, [15].
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 NO₂, 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 (ε = 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 pentaaon band corresponding to the totally deprotonated ligand is located at 446 nm (ε = 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 H₂L species, (0 ≤ x ≤ n, where n = 5 for pentaaacids) using the two techniques are in good agreement.

Table 2

Values of \( \log \beta_{ij} \pm \sigma_{N-1} \) (N = 8) determined by Sirko P program for the complexes formed with Ln³⁺ in water from potentiometric data (25 °C, l = 0.1 mol dm⁻³ NaClO₄).

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Cation</th>
<th>log ( \beta_{110} )</th>
<th>log ( \beta_{111} )</th>
<th>log ( \beta_{112} )</th>
<th>log ( \beta_{113} )</th>
<th>log ( \beta_{11-2} )</th>
<th>pH range</th>
<th>( R_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>Ce(III)</td>
<td>11.36 ± 0.09</td>
<td>20.16 ± 0.08</td>
<td>26.54 ± 0.08</td>
<td>29.4 ± 0.9</td>
<td>0.5 ± 0.1</td>
<td>−12.0 ± 0.4</td>
<td>1.89–10.95</td>
</tr>
<tr>
<td></td>
<td>Pr(III)</td>
<td>12.0 ± 0.3</td>
<td>20.7 ± 0.3</td>
<td>26.9 ± 0.3</td>
<td>29.6 ± 0.5</td>
<td>1.2 ± 0.3</td>
<td>−11.9 ± 0.4</td>
<td>1.83–10.93</td>
</tr>
<tr>
<td>( C_M ) = 10⁻²</td>
<td>Nd(III)</td>
<td>12.0 ± 0.3</td>
<td>20.9 ± 0.3</td>
<td>27.3 ± 0.3</td>
<td>30.1 ± 0.4</td>
<td>1.2 ± 0.3</td>
<td>−11.3 ± 0.4</td>
<td>1.88–10.58</td>
</tr>
<tr>
<td>( C_M ) = 10⁻²</td>
<td>Sm(III)</td>
<td>12.8 ± 0.4</td>
<td>21.3 ± 0.4</td>
<td>27.3 ± 0.4</td>
<td>30.1 ± 0.5</td>
<td>2.2 ± 0.4</td>
<td>−9.7 ± 0.5</td>
<td>1.79–10.91</td>
</tr>
<tr>
<td></td>
<td>Eu(III)</td>
<td>11.97 ± 0.08</td>
<td>20.84 ± 0.07</td>
<td>26.98 ± 0.07</td>
<td>29.9 ± 0.9</td>
<td>1.18 ± 0.09</td>
<td>−11.5 ± 0.4</td>
<td>1.85–10.39</td>
</tr>
<tr>
<td>2b</td>
<td>Ce(III)</td>
<td>12.1 ± 0.1</td>
<td>19.89 ± 0.09</td>
<td>24.7 ± 0.1</td>
<td>26.5 ± 0.8</td>
<td>1.3 ± 0.1</td>
<td>−10.2 ± 0.1</td>
<td>1.85–10.76</td>
</tr>
<tr>
<td></td>
<td>Pr(III)</td>
<td>12.5 ± 0.1</td>
<td>20.0 ± 0.1</td>
<td>24.8 ± 0.1</td>
<td>27.0 ± 0.9</td>
<td>2.2 ± 0.1</td>
<td>−9.2 ± 0.2</td>
<td>1.85–10.52</td>
</tr>
<tr>
<td>( C_M ) = 10⁻²</td>
<td>Nd(III)</td>
<td>12.56 ± 0.04</td>
<td>20.19 ± 0.02</td>
<td>24.95 ± 0.01</td>
<td>27.3 ± 0.7</td>
<td>1.98 ± 0.09</td>
<td>−9.5 ± 0.1</td>
<td>1.84–10.63</td>
</tr>
<tr>
<td>( C_M ) = 10⁻²</td>
<td>Sm(III)</td>
<td>12.7 ± 0.1</td>
<td>20.3 ± 0.1</td>
<td>25.17 ± 0.04</td>
<td>27.6 ± 0.9</td>
<td>1.8 ± 0.2</td>
<td>−10.2 ± 0.1</td>
<td>1.97–11.02</td>
</tr>
<tr>
<td></td>
<td>Eu(III)</td>
<td>11.9 ± 0.1</td>
<td>19.7 ± 0.1</td>
<td>24.7 ± 0.1</td>
<td>27.4 ± 0.6</td>
<td>1.9 ± 0.1</td>
<td>−9.5 ± 0.1</td>
<td>1.81–10.53</td>
</tr>
<tr>
<td>2c</td>
<td>Ce(III)</td>
<td>12.04 ± 0.01</td>
<td>19.8 ± 0.1</td>
<td>24.81 ± 0.02</td>
<td>27.7 ± 0.7</td>
<td>1.1 ± 0.1</td>
<td>−10.2 ± 0.1</td>
<td>2.83–10.08</td>
</tr>
<tr>
<td></td>
<td>Pr(III)</td>
<td>11.4 ± 0.2</td>
<td>19.48 ± 0.08</td>
<td>24.82 ± 0.04</td>
<td>29.9 ± 0.8</td>
<td>2.9 ± 0.1</td>
<td>−8.1 ± 0.2</td>
<td>2.85–10.15</td>
</tr>
<tr>
<td>( C_M ) = 10⁻³</td>
<td>Nd(III)</td>
<td>12.41 ± 0.05</td>
<td>19.98 ± 0.05</td>
<td>24.47 ± 0.09</td>
<td>3.60 ± 0.06</td>
<td>−6.5 ± 0.1</td>
<td>2.88–10.05</td>
<td>1.9</td>
</tr>
<tr>
<td>( C_M ) = 10⁻³</td>
<td>Sm(III)</td>
<td>12.62 ± 0.04</td>
<td>20.11 ± 0.03</td>
<td>24.42 ± 0.04</td>
<td>3.91 ± 0.04</td>
<td>−6.8 ± 0.1</td>
<td>3.04–10.29</td>
<td>0.6</td>
</tr>
<tr>
<td></td>
<td>Eu(III)</td>
<td>12.2 ± 0.5</td>
<td>20.0 ± 0.2</td>
<td>24.4 ± 0.3</td>
<td>3.6 ± 0.6</td>
<td>−6.8 ± 0.2</td>
<td>2.73–10.09</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Arithmetic mean of \( N \) (≥2) determinations; negative \( z \) values refer to hydroxo species. In Sirko program \( R_i \) 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.
3.2.2. Complexation studies

The spectral variation with respect to pH of solutions of ligand 2b and different lanthanides (Ce³⁺, Pr³⁺, Nd³⁺, Sm³⁺ and Eu³⁺) 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 Eu³⁺ 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 Eu³⁺ are given in Fig. 3.

4. Discussion

Under this heading, a comparison will be made with the series of triacids: mono-methyleneephosphonic 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 pentaaicds. An ML complex, a mono-protonated complex MLH a bi-protonated complex MLH₂, two anionic complexes MLOH and ML(OH)₂ and a tri-protonated complex MLH₃ in the case of 2a and 2b but absent with 2c.

4.2. Order of magnitude of the constants

The ML complexes of the pentaaicds have formation constants of the order of 12 log, 2 to 3 log
Table 3
Values of log $\beta_{11}$ 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$^{-3}$)

<table>
<thead>
<tr>
<th>Cation</th>
<th>log $\beta_{110}$</th>
<th>log $\beta_{111}$</th>
<th>log $\beta_{112}$</th>
<th>log $\beta_{113}$</th>
<th>log $\beta_{11-1}$</th>
<th>log $\beta_{11-2}$</th>
<th>$N \times L$</th>
<th>pH range</th>
<th>$U$ or $R_f$ (*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(III)</td>
<td>12.04 ± 0.08</td>
<td>20.22 ± 0.05</td>
<td>24.52 ± 0.06</td>
<td>27.99 ± 0.09</td>
<td>2.38 ± 0.07</td>
<td>−7.72 ± 0.07</td>
<td>15 × 11</td>
<td>1.63–11.09</td>
<td>0.6571E–02</td>
</tr>
<tr>
<td>Pr(III)</td>
<td>11.89 ± 0.06</td>
<td>19.88 ± 0.07</td>
<td>24.19 ± 0.09</td>
<td>28.6 ± 0.1</td>
<td>2.2 ± 0.1</td>
<td>−8.8 ± 0.2</td>
<td>15 × 12</td>
<td>1.68–11.10</td>
<td>0.3987E–02</td>
</tr>
<tr>
<td>Nd(III)</td>
<td>11.98 ± 0.09</td>
<td>20.26 ± 0.08</td>
<td>24.33 ± 0.06</td>
<td>29.39 ± 0.04</td>
<td>3.1 ± 0.1</td>
<td>−8.0 ± 0.2</td>
<td>15 × 12</td>
<td>1.64–11.08</td>
<td>0.1202E–02</td>
</tr>
<tr>
<td>Sm(III)</td>
<td>12.5 ± 0.6a</td>
<td>19.6 ± 0.4a</td>
<td>25.48 ± 0.08a</td>
<td>28.6 ± 0.05a</td>
<td>2.4 ± 0.09</td>
<td>−7.2 ± 0.3</td>
<td>10 × 9</td>
<td>1.64–7.37</td>
<td>2.3% (*)</td>
</tr>
<tr>
<td>Eu(III)</td>
<td>12.07 ± 0.05</td>
<td>19.84 ± 0.07</td>
<td>24.03 ± 0.07</td>
<td>28.01 ± 0.06</td>
<td>1.24 ± 0.09</td>
<td>−7.2 ± 0.3</td>
<td>15 × 12</td>
<td>1.66–10.64</td>
<td>0.2511E–01</td>
</tr>
<tr>
<td>U</td>
<td>12.89 ± 0.06</td>
<td>19.88 ± 0.07</td>
<td>24.19 ± 0.09</td>
<td>28.6 ± 0.1</td>
<td>2.2 ± 0.1</td>
<td>−8.8 ± 0.2</td>
<td>15 × 12</td>
<td>1.63–10.94</td>
<td>0.3987E–02</td>
</tr>
</tbody>
</table>

$U$ 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.

* Values determined by Sirko S.
Table 4
Means of stability constants of trivalent lanthanide complexes

<table>
<thead>
<tr>
<th>Ligand</th>
<th>log $\beta_{113}$</th>
<th>log $\beta_{112}$</th>
<th>log $\beta_{111}$</th>
<th>log $\beta_{110}$</th>
<th>log $\beta_{11-1}$</th>
<th>log $\beta_{11-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>29.8p</td>
<td>27.0p</td>
<td>20.8p</td>
<td>12.0p</td>
<td>1.2p</td>
<td>$-11.3p$</td>
</tr>
<tr>
<td>2b</td>
<td>27.1p</td>
<td>24.9p</td>
<td>20.0p</td>
<td>12.3p</td>
<td>1.8p</td>
<td>$-9.7p$</td>
</tr>
<tr>
<td>2c</td>
<td>28.5p</td>
<td>24.5p</td>
<td>19.9p</td>
<td>12.1p</td>
<td>2.2p</td>
<td>$-8.1p$</td>
</tr>
</tbody>
</table>

$^p$: 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 $-\text{OH}$ position by carboxylic acid groups. Table 4 gives the average log $\beta_{111}$ 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 $\beta_{112}$ 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 $\beta_{113}$ 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 $\beta_{112}$ 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$^{3+}$.](image-url)
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. Chafaa [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 $\beta_{3yz}$ 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 $\beta_{110}$ 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>
<thead>
<tr>
<th>Ligand</th>
<th>log $\beta_{110}$ Ca$^{2+}$</th>
<th>log $\beta_{110}$ Eu$^{3+}$</th>
<th>log $\beta_{111}$ Ca$^{2+}$</th>
<th>log $\beta_{111}$ Eu$^{3+}$</th>
<th>log $\beta_{112}$ Ca$^{2+}$</th>
<th>log $\beta_{112}$ Eu$^{3+}$</th>
<th>log $\beta_{113}$ Ca$^{2+}$</th>
<th>log $\beta_{113}$ Eu$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>2.9</td>
<td>10.6</td>
<td>13.4</td>
<td>16.9</td>
<td>17.8</td>
<td>20.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>3.4</td>
<td>9.1</td>
<td>12.0</td>
<td>14.1</td>
<td>20.9</td>
<td>24.7</td>
<td>25.7</td>
<td>27.4</td>
</tr>
<tr>
<td>2b</td>
<td>5.9</td>
<td>11.9</td>
<td>14.0</td>
<td>19.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 $\beta_{110}$ of transition cations Ni$^{2+}$, Cu$^{2+}$, Zn$^{2+}$ and Eu$^{3+}$

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Ni$^{2+}$</th>
<th>Cu$^{2+}$</th>
<th>Zn$^{2+}$</th>
<th>Eu$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b</td>
<td>6.5</td>
<td>11.8</td>
<td>9.8</td>
<td>11.9</td>
</tr>
</tbody>
</table>

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].

References