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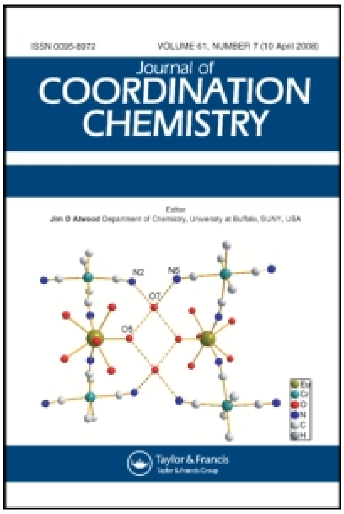

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SERINE AS A LIGAND: COMPLEX FORMATION WITH CADMIUM(II)

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The behaviour of serine as a ligand towards cadmium(II) has been studied at 25 °C in 3.00 M $NaClO_4$ by measuring the electromotive force of galvanic cells containing cadmium amalgam and glass electrodes. The experimental data can be explained by assuming the existence of the following species: CdL^+, $CdHL^{2+}$, CdL_2, $CdH_2L_2^{2+}$, CdL_3^-, $CdHL_3$ and $CdH_2L_3^+$. The stability constants have been determined. Good agreement between experimental and calculated values supports the validity of the model.

Keywords: Serine, cadmium, stability constants, complexes, amino acid

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INTRODUCTION

In the course of our studies on the behaviour of aminoacids as ligands we have had occasion to study the system involving cadmium(II) and serine(L). A survey of the literature[1-3] reveals only two reports on this subject. Perkins[4] explained measurements of e.m.f. of a cell containing a glass electrode by assuming only the formation of the complex CdL_2 where L^- is the serinate ion (log $\beta = 7.4$). Walker and Williams[5] explained their e.m.f. measurements carried out in a similar way but at 25°C and in 3.00 M $NaClO_4$, by assuming the presence of the species CdL^+ (log β = 4.154), CdL_2 (log β = 7.863) and CdL_3^- (log β = 10.221). As both studies were carried out over a limited range of concentraton of reagents, it was decided to investigate the cadmium(II)–serine system over a wide range of concentrations in order to ascertain whether protonated or polynuclear species are formed.

On this basis, it was necessary to use a medium of high ionic strength[6] in order to minimize the variations of activity coefficients. All measurements were performed in in 3.00 M $NaClO_4$ and at 25°C.

EXPERIMENTAL

Method

All solutions under investigation (S) were prepared by adding an excess of $NaClO_4$ with respect to the reagents, as according to Biedermann and Sillén,[6] and thus their general composition was the following: B M in Cd(II); H M in H^+; A M in L; (3–2B–H) M in Na^+; 3.00 M in ClO_4^-, where B and A represent the total concentration of cadmium(II) and serine, respectively, and H is the analytical excess of hydrogen ions.

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Because of the high ionic strength, activity coefficients could be assumed to be constant and concentrations could replace activities in the calculations.

At 25.00 ± 0.05°C, the e.m.f. of the galvanic cells

$$(-)\mathrm{Cd(Hg)} / \text{Solution S} / \mathrm{R.E.}(+) \tag{I}$$

$$(-)\mathrm{R.E.} / \text{Solution S} / \mathrm{G.E.}(+) \tag{II}$$

was measured. R.E. and G.E. are reference and glass electrodes, respectively. The e.m.f. of cells (*I*) and (*II*) at 25°C (mV units), can be expressed as a function of b (free concentration of cadmium(II)) and h (free concentration of H^+) as shown below.

$$E_I = E_I^\circ - 29.58 \log b - E_j$$

$$E_{II} = E_{II}^\circ + 59.16 \log h + E_j$$

E_I° and E_{II}° are two constants determined in the absence of the ligand. E_j is the liquid junction potential and, under the chosen experimental conditions, is equal to $-17\,h$. The values of b and h were obtained by a procedure similar to that described in ref. 7. For each measurement B and H were kept constant, whereas A and consequently $-\log h$ increased gradually. Titrations were terminated at $-\log h \sim 8$.

Materials and analysis

Cadmium(II) perchlorate, perchloric acid, sodium hydroxide, sodium perchlorate, cadmium amalgam (~0.01% weight) were prepared and analysed as described in ref. 8. Diluted amalgam allows a stable potential to $B = 5 \times 10^{-5}$ M and H = 0.200 M. *D,L*-serine (Fluka *puriss.* p.a.) was recrystallized twice from doubly-distilled water and then dried at 110°C. All solutions were freed from O_2 by bubbling purified N_2 as described in ref. 8. The apparatus was similar to that described in the same reference.

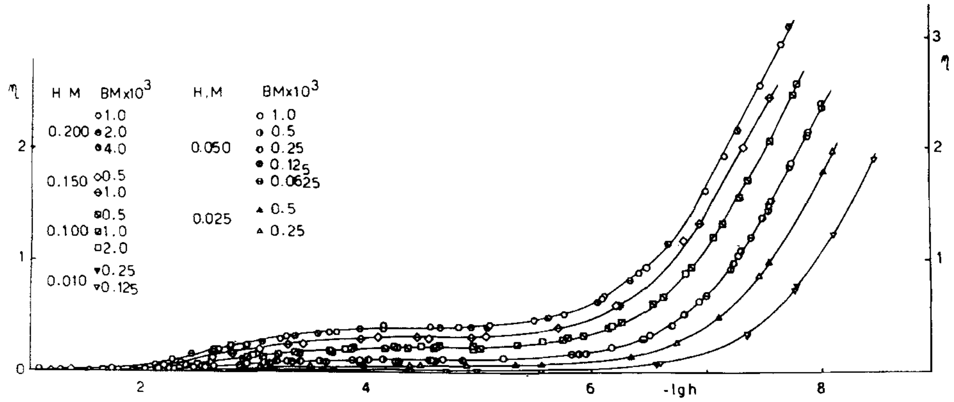

FIGURE 1 The experimental data in the form $\eta(-\log h)_{B,H}$. Curves are calculated using the values of Table II.

RESULTS AND DISCUSSION

Different series of e.m.f. measurements have been performed at several H values (0.010, 0.025; 0.050; 0.100; 0.150; and 0.200 M) and B values (0.0625; 0.125; 0.25; 0.50; 1.0; 2.0; 4.0 × 10^{-3}M) values. From the e.m.f. measurements of cells (*I*) and (*II*), b and h were obtained and, as B was known analytically, it was possible to calculate η (log (B/b)). The obtained η values were plotted as a function of $-\log h$. Fig. 1, where most of the experimental data are plotted in this form, shows that points at the same H, but at different B fall on the same curve; thus η is independent of B and therefore polynuclear species are not present in appreciable concentrations.

On the above basis the species formed can be indicated as M H_pL_r,with the relative stability constant $\beta_{1,p,r}$ where $p \geqslant 0$ and $r \geqslant 1$. To determine the prevailing values assumed by p and r and to obtain values for $\beta_{1,p,r}$, it is necessary to calculate the free concentration of the ligand, a. For each experimental point the a value was calculated, to a first approximation, from the mass balance for H. By taking into account the mass action law, (*1*) can be written

$$H=h + k_1ha + 2k_1k_2h^2a + \sum_p\sum_r p\beta_{1,p,r}bh^pa^r \qquad (1)$$

where $p \geqslant 0$ and $r \geqslant 1$. The terms k_1 and k_2 are the protonation constants of the serinate ion (L^-), determined as described in ref. 9, under the same experimental conditions and for which $\log k_1 = 9.72 \pm 0.03$; $\log k_1 k_2 = 12.20 \pm 0.05$.

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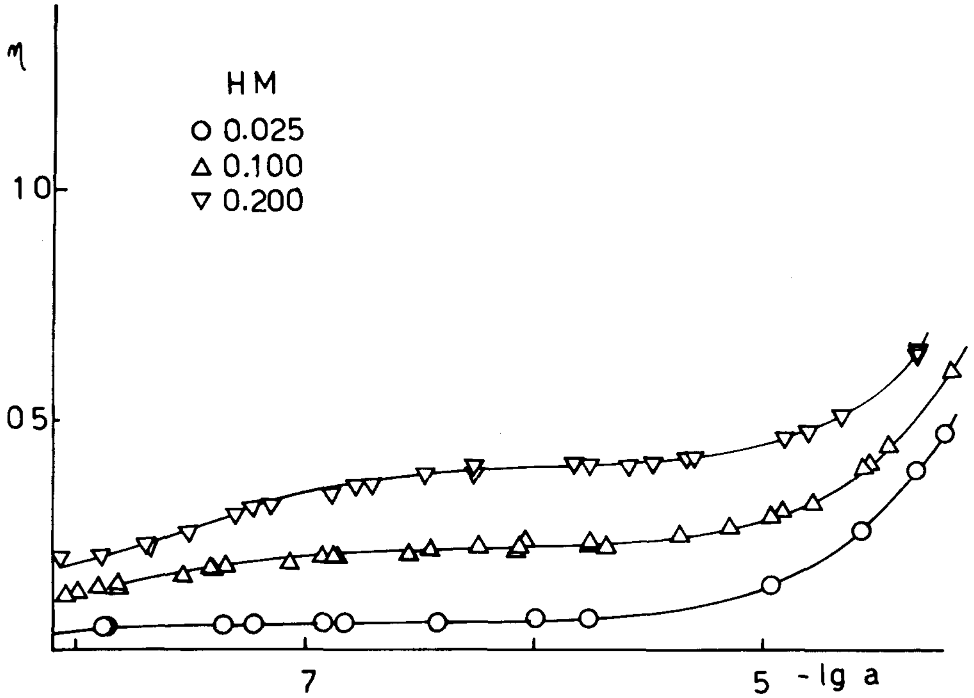

FIGURE 2 Some experimental data at three different H values, in the form $\eta(-\log a)_{B,H}$, reported as examples. Curves are calculated using the values of Table II.

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In equation (*1*) and in the following ones, hydrolytic species of cadmium(II) could be neglected on the basis of the results of Biedermann and Ciavatta[10] and because of the values obtained for b and h. From an inspection of the investigated range of B and H, it results that, for all points, $H \geqslant 0.02\ B$, so the last term of equation (*1*) can be neglected without significant loss of accuracy for the a values. Refined values, obtained by introducing the values of the constants in equation (*1*), practically coincide with those of the first approximation. First approximation values of a were used to study the dependence of η on a. An example of this kind of dependence is shown in Fig. 2, where η is plotted *versus* $-\log a$ for $H = 0.200$, 0.100 and 0.025 M. It can be seen that η is an increasing function of H, as points obtained at different H fall on different curves. The p and r values in the formula MH_pL_r as well as the corresponding values of the constants were obtained by starting with a preliminary inspection of the (log h, log a) data. It was found that the quantity $-\log$ (ha) remained constant within ± 0.01 for each H value in the range $4 \leqslant -\log h \leqslant 8$. By taking it into account and by considering the material balance of cadmium(II), equation (*2*) may be written.

$$B = b + \sum_p \sum_r \beta_{1,p,r} b h^p a^r \qquad (2)$$

In the range $4 \leqslant -\log h \leqslant 8$, and by setting $t = p - r$, equation (*2*) can be rewritten as (*3*)

$$\log (B/b - 1) = \log (\sum_t \gamma_t h) \qquad (3)$$

where $\gamma_t = \sum_r \beta_{1,p,r} (ha)^r$ is constant at constant log (ha). In equation (*3*), $\log (B/b - 1)$ is a function of h alone and the problem is reduced to finding the prevalling values of t and γ_t. Examination of the dependence of γ_t on ha gives the required p, r and $\beta_{1,p,r}$ values. It was found that the plot of $\log (B/b - 1)$ *versus* $-\log h$ could be fitted, according to Sillén,[11] with normalised curves of function (*4*)

$$y = \log (1 + \alpha u + u^2) \qquad (4)$$

indicating the predominance of species with $t = 0$, -1 and -2. From a comparison of equations (*3*) and (*4*), the following result: $y = \log (B/b - 1) - \log \gamma_0$, $\log u = (1/2)\log(\gamma_2/\gamma_0) - \log h$ and $\alpha = \gamma_1/\sqrt{\gamma_0\gamma_2}$.

The experimental points were superimposed on the family of normalised curves of equation (*4*) and the two plots were moved parallel to the two axes until the best fit was found. In this position from $y = 0$, $\log u = 0$ and from the value of α, the values of γ_t collected in Table I were obtained. As an example, Fig. 3 shows the agreement between points and normalised curves in the position of best fit for $H = 0.200$, 0.100 and 0.025 M.

From a study of the dependence of γ_t on (ha), values of p and r and the corresponding values of the constants were found. Although log(ha) was constant in the range $4 \leqslant -\log h \leqslant 8$, it was found that some points deviate from the normalised curve in the range $7.5 \leqslant -\log h \leqslant 8.5$, hence the values of $\beta_{1,p,r}$ refer to the range $4 \leqslant -\log h \leqslant 7.5$. To explain data obtained in the upper range the assumption was made that other species had to be present and the data were then treated as follows. The contribution of each found species could be calculated by means of the values of b, h, H, B and the found $\beta_{1,p,r}$. This contribution was subtracted from B, in order to obtain the quantity Bc. As $Bc > b$, the presence of other complexes was confirmed.

TABLE I
Survey of γ_r values.

H(M)	$-\log$ (ha)	$\log \gamma_0$	$-\log \gamma_{-1}$	$-\log \gamma_{-2}$
0.010	11.73 ± 0.01	−1.53 ± 0.03	7.40 ± 0.06	15.27 ± 0.05
0.025	11.33 ± 0.01	−0.85 ± 0.03	7.01 ± 0.06	14.37 ± 0.05
0.050	11.02 ± 0.01	−0.53 ± 0.03	6.68 ± 0.06	13.79 ± 0.05
0.100	10.72 ± 0.01	−0.17 ± 0.03	6.35 ± 0.06	13.13 ± 0.05
0.150	10.55 ± 0.01	0.20 ± 0.03	6.13 ± 0.06	12.80 ± 0.05
0.200	10.42 ± 0.01	0.20 ± 0.03	5.95 ± 0.06	12.46 ± 0.05

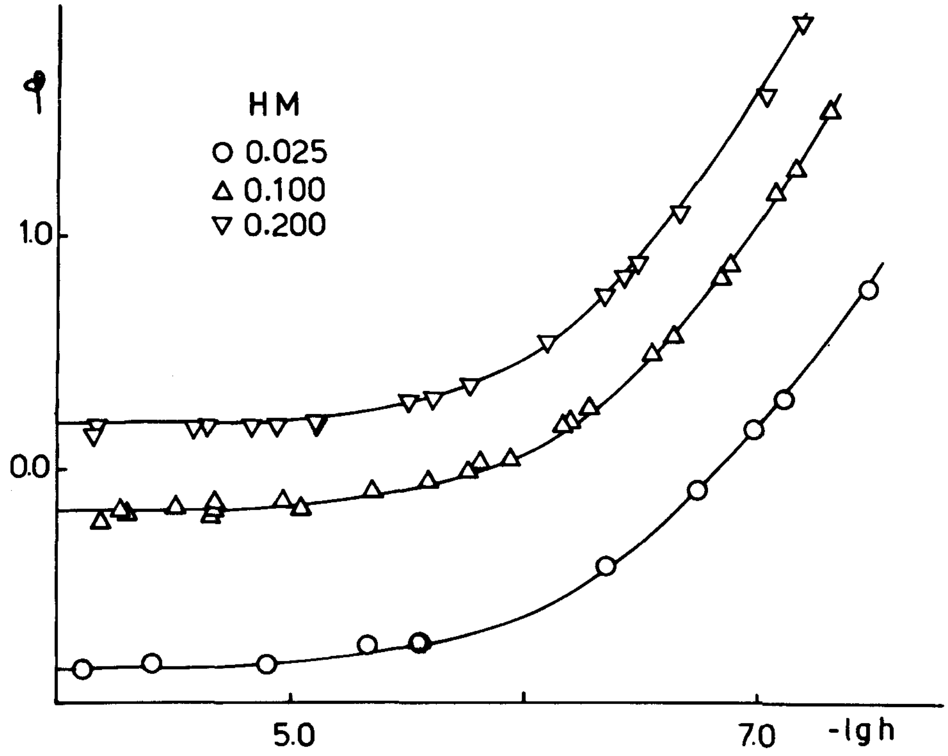

FIGURE 3 Dependence of log (B/b−1) on −log h at −log (ha) constant, in the range 4 ⩽ −log h ⩽ 7.5.

Since the product Bc $b^{-1}a^{-3}$ remained constant within experimental error for all points (independently of B and H), it was concluded that the presence of the additional complex CdL_3^- alone was sufficient to explain the experimental data in the investigated range. As a stability constant for CdL_3^-, $\beta_{1,0,3}$, the average value of the above calculated product was assumed.

The experimental data could be explained over the whole investigated range of reagent concentrations by assuming the formation of the complexes CdL^+, $CdHL^{2+}$,

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CdL_2, $CdH_2L_2^{2+}$, CdL_3^-, $CdHL_3$ and $CdH_2L_3^+$. The treatment applied to obtain species and relative constants has the advantage of using the experimental data directly. However, the values found for the constants are to be considered first approximation ones.

Refined values of $\beta_{1,p,r}$

In order to improve the accuracy of the stability constants and to verify if other species could be present, the experimental data found for b, h, H, A together with values for k_1 and k_2 were introduced in a computer program. By applying the treatment described in ref. 12, we found the values of $\beta_{1,p,r}$ collected in Table II. They can explain all data over the whole concentration range of reagents. No evidence was found for other species.

TABLE II
Proposed values for stability constants.

$\log \beta_{1,0,1} = 4.33 \pm 0.05$;	$\log \beta_{1,1,1} = 10.45 \pm 0.03$
$\log \beta_{1,0,2} = 8.19 \pm 0.05$;	$\log \beta_{1,2,2} = 20.56 \pm 0.1$
$\log \beta_{1,0,3} = 10.6 \pm 0.1$;	$\log \beta_{1,1,3} = 18.2 \pm 0.1$
	$\log \beta_{1,2,3} = 24.77 \pm 0.1$

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Furthermore, the program calculates values of $\eta(=\eta_c)$ by using refined $\beta_{1,p,r}$ constants. These values were compared with the experimental data (η_s) and the difference $|\eta_c - \eta_s|$ was obtained for each point. More than 250 experimental points were tested. The value $|\eta_c - \eta_s|$ was $\leqslant 0.01$ for nearly all points; for 15 points it lay between 0.02 and 0.05. Positive and negative deviations were comparable. By means of the values of Table II, theoretical curves for $\eta(-\log h)_{B,H}$ and $\eta(-\log a)_{B,H}$ were calculated. The good fit of the curves with the points shown in Figures 1 and 2 is good support for the validity of the existence of the assumed species with their calculated stability constants. The assumed species (with constants collected in Table II) explain the results of experiments performed at even higher B (B = 0.02 M).

CONCLUSION

The study of the equilibria between cadmium(II) and serine, carried out over a wide range of concentrations of the reagents has shown the presence of mixed complexes with participation of protons and the absence of polynuclear complexes. By changing B from 6.2×10^{-5} to 4.0×10^{-3} M no evidence of polynuclear complexes was found. A high ratio H/B was employed to bring to light the presence of protonated complexes. By using the values of Table II, distribution curves of complexes as a function of $-\log h$ were calculated for A = 0.025 and 0.100 M. They are plotted in Fig. 4. The quantity of formed complexes increases by increasing A as expected and the formation of complexes with $r > 1$ is favoured at higher values of A. In fact, at A = 0.100 M the CdL_2 and CdL_3^- predominate over CdL^+. The influence of protonated species is remarkable. Up to $-\log h = 5$, almost all bound cadmium(II) is present as a mixed complex ($CdHL^{2+}$ and $CdH_2L_2^{2+}$). Protonated species at A = 0.100 M are present even at $-\log h = 8$. At $-\log h = 6$, they represent about 35% of the total cadmium(II).

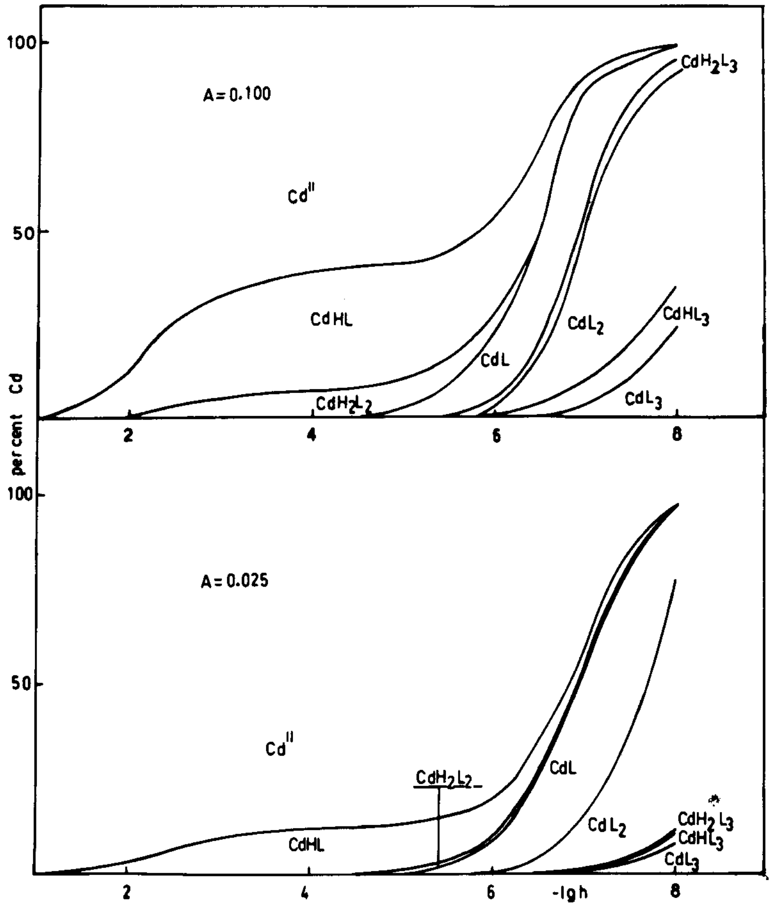

FIGURE 4 Distribution of complexes depending on $-\log h$, at A = 0.025 M and A = 0.100 M. Curves are calculated for $B = 0.125 \times 10^{-3}$ M. Curves calculated for all values of B coincide.

TABLE III

Comparisons between glycine and serine as ligands towards cadmium(II). Values of $\log \beta_{1,p,r}$ are listed.

Species	Glycine complex (1.00 M $NaClO_4$)	Serine complex (3.00 M $NaClO_4$)
CdL^+	4.36 ± 0.05	4.33 ± 0.05
$CdHL^{2+}$	10.52 ± 0.05	10.45 ± 0.03
CdL_2	7.99 ± 0.05	8.19 ± 0.05
$CdH_2L_2^{2+}$		20.56 ± 0.1
CdL_3^-	10.13 ± 0.15	10.6 ± 0.1
$CdHL_3$		18.2 ± 0.1
$CdH_2L_3^+$		24.77 ± 0.1

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To evaluate the behaviour of serine as ligand, only *D,L*-serine was used, because, according to Al-Ani and Olin,[13] no appreciable differences are noted in the behaviour of *D*-, *L*- and *D,L*- serine as ligands towards cations. In Table III a comparison between serine and glycine as ligand is reported. The stability of the species CdL^+ and $CdHL^{2+}$ for both ligands is the same within experimental error. However, serine seems to be a stronger ligand than glycine. It seems reasonable to attribute this effect to the presence of $-OH$ group in serine. Table IV collects together the stability constants of complexes formed by serine with several cations. Copper(II) forms the strongest complexes, but $CuHL^{2+}$ is the only protonated species and CuL_3^- is not reported. Cadmium(II) and lead(II) are able to form more than one protonated complex. Cadmium(II), cobalt(II) and nickel(II) also form complexes with a ratio of 1 : 3 while calcium(II) forms only CaL^+. From a comparison of the values reported in Table IV, it is seen that serine binds to cations according to the sequence $Ca < Mg < Co < Cd < Pb < Ni < Cu$. The difference $\log \beta_{1,0,2}- -\log \beta_{1,0,1}$ is very low for lead(II) with respect to the others, while cadmium(II) forms more protonated complexes than seems to be the case with other metallic cations.

TABLE IV
Behaviour of serine as ligand towards cations.[a]

Species	Ca(II)	Cd(II)	Co(II)	Cu(II)	Mg(II)	Ni(II)	Pb(II)
ML^+	1.00 ± 0.04	4.33 ± 0.05	4.32 ± 0.06	8.55 ± 0.05	1.03 ± 0.05	5.34 ± 0.05	5.25 ± 0.04
ML_2		8.19 ± 0.05	7.90 ± 0.06	16.02 ± 0.06	Evidence	9.94 ± 0.04	8.4 ± 0.07
ML_3^-		10.6 ± 0.1	10.2 ± 0.08			13.02 ± 0.06	
MHL^{2+}		10.45 ± 0.03		10.90 ± 0.10			10.88 ± 0.05
MHL_2^+							15.5 ± 0.1
$MH_2L_2^{2+}$		20.56 ± 0.10					21.2 ± 0.1
MHL_3		18.2 ± 0.1					
$MH_2L_3^+$		24.77 ± 0.1					

[a] Data relative to calcium(II), cobalt(II), magnesium(II) and nickel(II) were obtained at 25°C, but in 3.00 M NaCl.

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