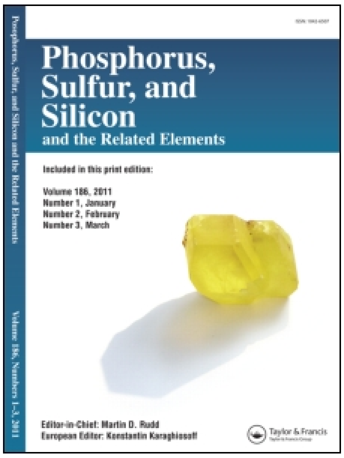

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POTENTIOMETRIC STUDIES OF 4-MONO(DIHYDROXYPHOSPHONYL) METHYL PHENOL AND 2,6-BIS(DIHYDROXYPHOSPHONYL) METHYL 4-METHYL PHENOL COMPLEXES WITH COBALT(II), NICKEL (II), COPPER (II), ZINC (II) AND CADMIUM (II)

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POTENTIOMETRIC STUDIES OF 4-MONO(DIHYDROXYPHOSPHONYL) METHYL PHENOL AND 2,6-BIS(DIHYDROXYPHOSPHONYL) METHYL 4-METHYL PHENOL COMPLEXES WITH COBALT(II), NICKEL (II), COPPER (II), ZINC (II) AND CADMIUM (II)

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The overall stability of the two acids: 4-mono(dihydroxy-phosphonyl) methyl phenol (L1) and 2,6-bis(dihydroxyphosphonyl)methyl 4-methyl phenol (L2) complexes with five divalent metal cations Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II} were determined potentiometrically at constant ionic strength of 0.1 $mol.L^{-1}$ and at 25.0 ± 0.1 °C (298.0 ± 0.1 K) in water. The values are as follows. For L1: Ni^{II}, 5.27; Co^{II}, 5.65; Cu^{II}, 7.69; Zn^{II}, 7.39 and Cd^{II}, 5.75. For L2: Ni^{II}, 7.24; Co^{II}, 7.47; Cu^{II}, 12.76; Zn^{II}, 11.39 and Cd^{II}, 7.94.

Keywords: hydroxyphenyl phosphonates; complexes; aqueous solution; stability

INTRODUCTION

The analytical, biologic and medical interest in complexes formed with metal cations and phosphonic acid and its derivatives is of great importance especially as they are widely used as antiviral drugs[1]. In addition, phosphonic acid derivatives are involved in hypothalamus metabolism [2]as well as in William's disease [3,4].

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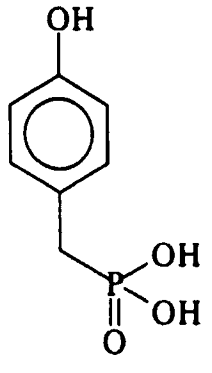
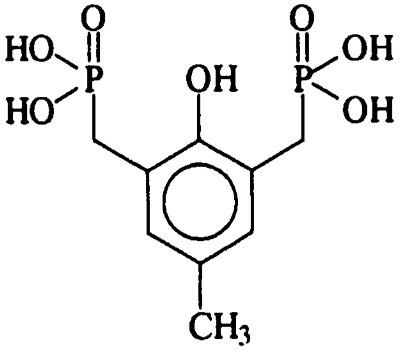
The substitution of a phosphonic group ($PO(OH)_2$) in carboxylic acids increases the stability of their metal complexes [5]. An earlier study has described the acid and complexing properties of ligands of the type $R\text{-}PO(OH)_2$ and $(HO)_2PO\text{-}(CH_2)_n\text{-}PO(OH)_2$ [6]. Schwarzenbach *et al.* have shown that, in aminopolycarboxylates, the phosphonic group plays a role of a donor site more efficiently than the carboxylic group in the formation of complexes [7]. For Plattenier and co-workers, the association of a phenolic group and phosphonic groups to the benzene ring increases the complexing power of the molecule [8].

Vogt *et al.* have synthesised a new series of phenol substituted with one or two methyl phosphonic groups [9,10]. The presence of these methyl substituent groups confers on these molecules a better flexibility as well as more favourable complexing sites. A study of the properties of these ligands allowed us to calculate the acidity constants of these molecules potentiometrically [9]and spectrophotometrically [10]. The stability constants of complexes obtained from four ligands with Ni(II) and Zn(II) have also been determined [11].

In this work, we have studied the complexes of two acids: 4-mono(dihydroxy-phosphonyl) methyl phenol (L1) and the 2,6-bis(dihydroxyphosphonyl)methyl 4-methyl phenol (L2) (Fig. 1) with bivalent metal cations of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).



L1



L2

FIGURE 1 Chemical structures of the ligands

EXPERIMENTAL

For all solutions, bi-distilled water was used. The ligands have been synthesized and characterized by Vogt and coll. as previously described [9,10]. The ligands parent solutions of the ligands were prepared by dissolving calculated amounts of L1 or L2.

Supporting electrolyte solution was made from sodium perchlorate $NaClO_4.H_2O$, 99 %. The stock solutions of metal cations were obtained from the hexahydrated perchlorates salts, except for zinc (II) where anhydrous chloride was used. They were first titrated by complexometric titration with EDTA for Co (II), Ni (II) and Cu (II)[11] and the results were verified by atomic absorption spectroscopy (Pye Unicam SP9). The concen-trations of Zn (II) and Cd (II) solutions were only determined by complexometry [12].

A stock solution of NaOH, used as titrant, was prepared and was calibrated by using potassium hydrogenophtalate standard solution. A 10^{-2} mol.L^{-1} working solution of the base was prepared by dilution.

The complexation was studied in aqueous solution with identical concentration for ligand and metal cations: 10^{-4} mol.L^{-1}. The ionic strength was maintained constant at and equal to 0.1 mol.L^{-1}) with the help of sodium perchlorate.

All measurements were made, under an atmosphere of argon, in a double-jacketed glass cell of 100 mL, thermoregulated at 25.0 ± 0.1 °C. The titrant solution was added with the help of a microburette (Metrohm, Dosimat E635, 1 mL) programmed with an automatic titrator, (Metrohm, Titroprocessor 636) injecting volume of solution as low as 1 µL. The added volumes of sodium hydroxyde solution varied automatically with the slope of the titration curve, which consists of 80 to 120 experimental points. The logarithm of $[H^+]$ was measured with an accuracy of 0.001 pH units (Metrohm, Titroprocessor 636) using a combined glass electrode in which the reference solution was made with NaCl (0.01 mol.L^{-1}), $NaClO_4$ (0.09 mol.L^{-1}) and saturated AgCl in order to obtain the same ionic strength as in the solution and thus minimise the junction potential.

The electrode was calibrated using the following experimental law:

$$pH_{true} = pH_{read} + a + b.10^{-pH_{read}}$$

where a and b are two constants (determined from the standard solutions: $[H^+] = 10^{-2}$ and 10^{-3} mol.L^{-1} respectively) and in our case, $a = -5.563.10^{-2}$ and $b = 5.563$.

Each result is the average of 6 measurements. These experimental conditions were chosen in order to avoid the formation of polynuclear species.

RESULTS AND DISCUSSION

For the interpretation of the experimental data, different theoretical models were tested, taking into consideration the existence of all species in solution and starting from the equilibrium:

$$M^{2+} + H_iL^{i-n} \rightleftharpoons MLH_i^{i-n+2}$$

For which overall constant is $\beta_j = \dfrac{[MLH_i^{i-n+2}]}{[M^{2+}][H_iL^{i-n}]}$

The methodology is based on the optimisation of parameters and modelization in solution. The pH values corresponding to the volume of added NaOH were interpreted with the help of the program "Superquad" [14,15]. In all the calculations, the water ionic product K_w was set at $1.66.10^{-14}$ as proposed by to Martell for solutions of same ionic strength [16].

The titration curves of ligands L1 and L2, in the absence and in the presence of metal cations in the ratio 1:1 against NaOH 10^{-2} mol.L^{-1} are given in figures 2 and 3 respectively. The curve for the ligand L1 (Fig. 2) shows two points of inflexion corresponding to the two acidities of $PO(OH)_2$ group. Though the third inflexion was not observed, the curve was sufficiently precise for its numerical determination. The ligand L2 (Fig. 3) presents three of the five theoretical inflexion points, corresponding to the 2nd, 3rd and 4th acidities of the $-PO(OH)_2$ groups as explained earlier [10]. The 2 other values of L2 were determined from the titration curves using SUPERQUAD program. The successive values of pK for L1 are 1.91, 7.43 and 10.05 and for L2: 1.60, 2.30, 6.36, 8.08 and 11.86.

Complexation of metal cations

The neutralisation curves of the ligand in presence of metal ions show a significative diminution of pH values in comparison to the values of the

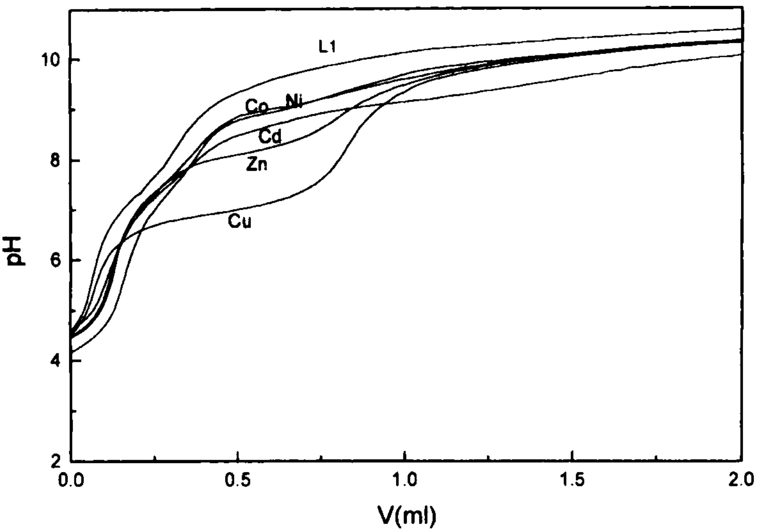


FIGURE 2 Neutralisation curves of L1 (10^{-4} mol.L^{-1}) by NaOH (10^{-2} mol.L^{-1}) in the absence and in presence of the metal cations (10^{-4} mol.L^{-1}) at 25 °C and with I = 0.1 mol.L^{-1}

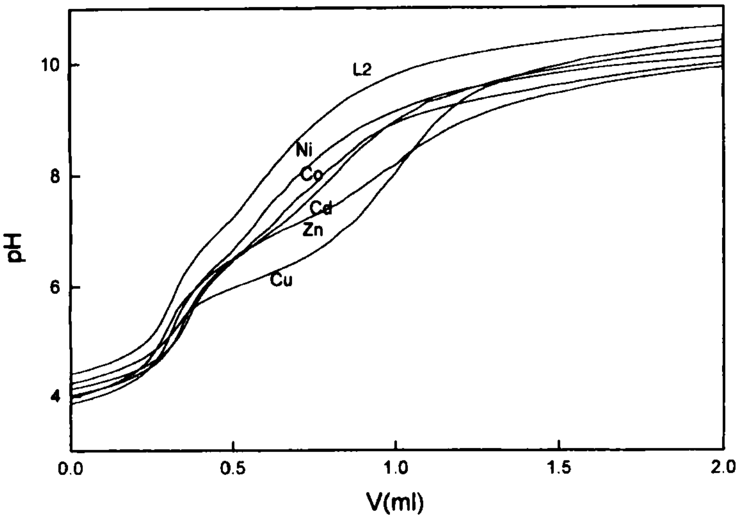


FIGURE 3 Neutralisation curves of L2 (10^{-4} mol.L^{-1}) by NaOH (10^{-2} mol.L^{-1}) in the absence and in presence of the metal cations (10^{-4} mol.L^{-1}) at 25°C and with I = 0.1 mol.L^{-1}

ligand alone. In the case of L1, the divergence between the curve plus the metal cation and that for the ligand alone begins at pH ≈ 4.2 for all the metal cations. This divergence is maximum between pH = 5.73 and 9.73 for Co(II); pH = 5.17 and 9.70 for Ni(II); pH = 4.73 and 9.63 for Cu(II); pH = 7.89 and 9.63 for Zn(II) and pH = 5.60 and 8.99 for Cd(II). On the other hand, for L2, the pH values are slightly more acidic than those pertaining to L1. The diminution begins at pH value of about 4.0. This divergence becomes more and more important between pH = 4.57 and 9.30 for Co(II); pH = 4.93 and 9.07 for Ni(II); pH = 5.07 and 9.50 for Cu(II); pH = 6.87 and 9.49 for Zn(II) and finally pH = 4.70 and 9.38 for Cd(II).

The decrease of the pH values is an indication of the eventual formation of one or more new species in solution. The most significant divergence is observed in the case of ligand and copper (II) which probably indicates the formation of cupric complexes in a medium more acidic than those of the other metal cations studied.

The mathematical analysis of the potentiometric data pH = f(V) of the different shows the evidence of the complexes formed in solution. The stability constants of these complexes have been determined and their values, expressed in log β_j, are grouped in Table I.

These values were used to calculate the degree of formation of all species in solution, which was done as a function of proton concentration, using the program "Haltafall"[17]. The corresponding distribution curves are given in Figures 5 and 6 respectively for L1 and L2 systems. The species $ML(OH)_2$ are presented here but we may remark that at higher pH values (e.g. for Cu^{2+} at pH ≈ 6.5 and pH ≈8.5 for L1 and L2 respectively) the $ML(OH)_2$ species are not soluble and hydrolysis leads to corresponding dihydroxydes.

The degree of formation of complexes of the type ML and MLH with the ligand L1 differs from one metal to the other and can be classified as follows:

- for ML: CuL > NiL > CdL > CoL > ZnL
- for MLH: ZnLH > NiLH > CoLH > CdLH > CuLH

The formation of the hydroxylated complex $ML(OH)_2$ is preponderant and to the extent of about 99 % at pH ≥ 10, but.this species precipitates at higher concentrations.

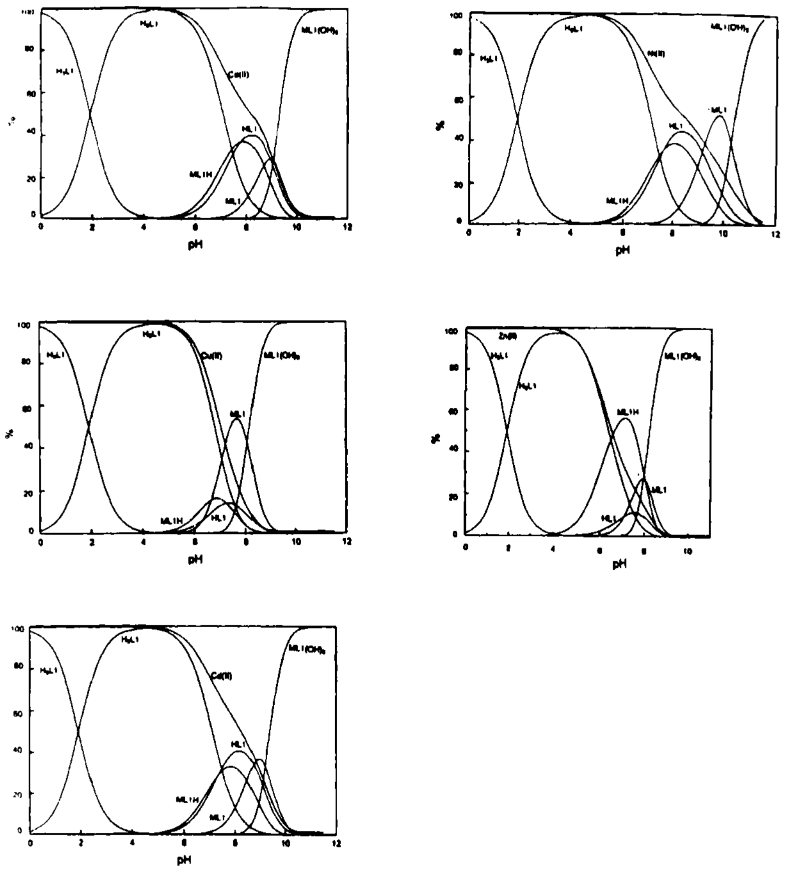


FIGURE 4 Distribution curves of the different species in solution for the system L1 and metal cations (at I = 0.1 mol.L^{-1}, $C_{metal} = C_{ligand} = 10^{-4}$ mol.L^{-1} and T = 298 K) a : Co(II); b : Ni(II); c : Cu(II); d : Zn(II); e : Cd(II)

With the ligand L2, the formation of ML and MLH complexes follows the order:

- for ML: CuL > ZnL > CdL > CoL > NiL
- for MLH : ZnLH > CuLH > CdLH > CoLH > NiLH

The stability constants of complexes CuL and ZnL are much higher than those of CdL, CoL and NiL. This indicates, in the cases of Cu(II) and Zn(II), that the metal is totally engaged in the formation of the complex.

TABLE I Stability constants of metal complexes in aqueous solutions, with interval of confidence of at least 95 % ($I = 0.1$ mol.L^{-1}, $C_{metal} = C_{ligand} = 10^{-4}$ mol.L^{-1} and $T = 298K$)

Ligand	*Metal*	*Complex*	*log β*
L1	Co (II)	ML	5.65 ± 0.05
		MLH	14.30 ± 0.04
	Ni (II)	ML	5.27 ± 0.09
		MLH	14.26 ± 0.05
	Cu (II)	ML	7.69 ± 0.07
		MLH	14.45 ± 0.08
	Zn (II)	ML	7.39 ± 0.03
		MLH	15.32 ± 0.02
	Cd (II)	ML	5.75 ± 0.04
		MLH	14.22 ± 0.03
L2	Co (II)	ML	7.46 ± 0.05
		MLH	16.19 ± 0.04
	Ni (II)	ML	7.24 ± 0.07
		MLH	15.95 ± 0.04
	Cu (II)	ML	12.76 ± 0.06
		MLH	20.48 ± 0.07
	Zn (II)	ML	11.39 ± 0.07
		MLH	20.51 ± 0.07
		MLH_2	26.05 ± 0.01
	Cd (II)	ML	7.95 ± 0.04
		MLH	16.49 ± 0.03

At higher concentrations for both ligand and metal (10^{-3} mol.L^{-1}), precipitation occurred with L1 and all the metals. However, when L2 is used as ligand, there was no precipitation and this indicated that the complexing ability of this series of ligands has increased with the presence of the second methyl phosphonic group in ortho position.

The numerical analysis of the experimental data pH = f(V) of the ligand L2 with the five cations at 10^{-3} mol.L^{-1} shows, in addition to ML and MLH, the presence of MLH_2.

As it could be expected, the stability of the complexes of the two ligands is in accordance with the Irving-Williams series [18,19]:

$$CuL > ZnL > CdL > NiL \approx CoL$$

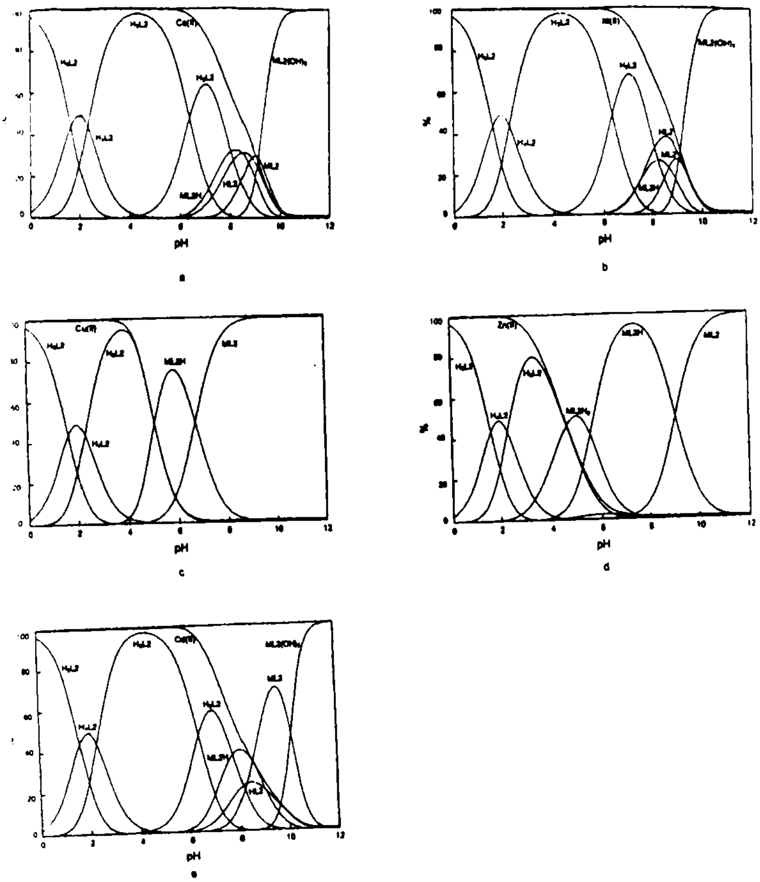


FIGURE 5 Distribution curves of the different species in solution for the system L2 and metal cations (at I = 0.1 mol.L^{-1}, $C_{metal} = C_{ligand} = 10^{-4}$ mol.L^{-1} and T = 298 K) a : Co(II); b : Ni(II); c : Cu(II); d : Zn(II); e : Cd(II)

The complexing ability of ligands studied has been compared with other ligands of the same family. The log β_{110} values of these complexes are assembled in Table II.

This table shows clearly that the complexes of L1 and L2 are weaker than those of EDTA* and EDTPO. The complexing ability of L2 is superior to that of EDDPI, EDTPI and EDTPO.

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* The explanations of abbreviations are given at the bottom of Table II.

TABLE II Comparison of stability constants (log β_{110}) of metal complexes with different ligands

Ligand[a]	*Ref.*	*Co (II)*	*Ni (II)*	*Cu (II)*	*Zn (II)*	*Cd (II)*
EDDPI	16	5.95	7.52	10.72	6.16	
EDTPI	16	7.29	8.44	9.75	7.60	
EDTPO	20	8.48	9.03	7.99	8.34	
HBEDPO	21	18.00	17.9	24		
NPDA	22				9.00	8.5
EDTA	23		18.50	18.70	16.1	16.4
Glyphosate	5			11.92	8.40	
P2	24		5.20	11.50		
P2N4	24		5.90	10.40		
P26	24		6.99	12.97	11.50	
P26N4	24		6.5	11.80	9.80	
L1		5.65	5.27	7.69	7.39	5.75
L2		7.46	7.24	12.76	11.39	7.95

a. EDTA: ethylenediamine tetraacetic acid; EDDPI: ethylene diamine N,N'-di(methyl phosphonic) acid; EDTPI: ethylene diamine N, N, N', N'-tetra(methyl phosphonic) acid; EDTPO: ethylene diamine (tetramethylene phosphonic) acid; HBEDPO: N,N'-bis(o-hydroxybenzyl)-ethylene diamine-N, N'-bis(methylene phosphonic) acid; Glyphosate: N- (phosphonomethyl) glycin; EDTPO:ethylene diamine N, N, N',N'-tetrakis (methylene phosphonic) acid; P2: 2- mono(dihydroxyphosphonyl)methyl phenol; P2N4: 2-mono(dihydroxyphosphonyl) methyl 4-nitrophenol; P26: 2,6- bis(dihydroxy-phosphonyl)methyl phenol; P26N4: 2,6-bis (dihydroxyphosphonyl) methyl 4-nitrophenol.

In the same series of chelating agents, it is observed that the ligands L1 and L2 have the same complexing property and it is diminished by the presence of NO_2 [24]. Finally, the complexes of this series are formed in a more acidic range than those for other nitrogen based ligands. This indicates that these ligands can be used as complexing agents for metals and as such this property may be used in the treatment of waste and as antiviral drugs.

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