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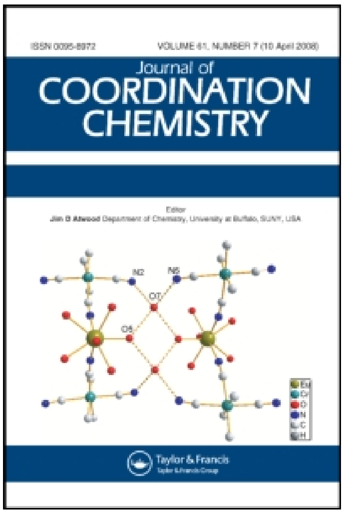

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ORGANOPHOSPHORUS HERBICIDES AND PLANT GROWTH REGULATORS, PART 2. EQUILIBRIUM STUDIES IN AQUEOUS SOLUTION OF THE COMPLEXATION OF TRANSITION METAL(II) IONS BY N-(PHOSPHONOMETHYL)IMINODIACETIC ACID AND RELATED COMPOUNDS

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ORGANOPHOSPHORUS HERBICIDES AND PLANT GROWTH REGULATORS, PART 2. EQUILIBRIUM STUDIES IN AQUEOUS SOLUTION OF THE COMPLEXATION OF TRANSITION METAL(II) IONS BY *N*-(PHOSPHONOMETHYL)IMINODIACETIC ACID AND RELATED COMPOUNDS

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(*Received May 29, 1992*)

Aqueous complex equilibria of nickel(II) ions with *N*-(phosphonomethyl)glycine, **1**, *N,N′* [phosphinicobis(methylene)]bis(glycine), **2**, *N,N*-bis(phosphonomethyl)glycine, **3**, and *N*-(phosphonomethyl)iminodiacetic acid, **4**, as well as of manganese(II), iron(II), cobalt(II) and zinc(II) ions with **4** have been investigated using glass electrode potentiometry. The conditions were: temperature, 25.0°C; and ionic strength, 0.10 mol dm^{-3} with respect to chloride ions. The complexation of **4** with copper(II) ions has been examined in the presence of a competing ligand, 4-nitrocatechol, **5**. The results indicate that there is strong binding between the plant growth regulators and the metal ions which could affect soil solution speciation and consequently, the bioavailability of these metal ions to plants. Plausible structures of the metal-ligand complexes formed are proposed.

Keywords: *N*-(phosphonomethyl)glycine, *N,N′* [phosphinicobis(methylene)]bis(glycine), *N,N*-bis(phosphonomethyl)glycine, *N*-(phosphonomethyl)iminodiacetic acid, complexes, stability constants

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INTRODUCTION

Plant growth regulators are natural or synthetic compounds which, when added in small amounts to plants, modify growth, development and the qualitative and quantitative yields of plants.[1–3] For example, they are used as controlling factors in the production of certain vegetables, maize, sugarcane and in the ripening of fruit. Synthetic as well as naturally occurring plant growth regulators produce their effects by changing endogenous levels of naturally occurring hormones in the required direction and to the desired extent.

Amongst the variety of plant growth regulators are ligands **1**, **2**, **3** and **4**; **1** and **3** have been used advantageously for the past twenty years in the United States of America and Southern Africa to control the ripening of sugarcane;[1] **3** and **4** have

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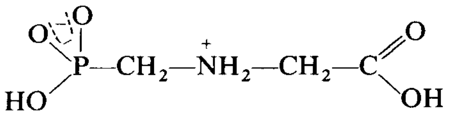
* Author for correspondence.

shown promising results in controlling the growth of Tall Fescue grass[4] and Kentucky Bluegrass[5] while **2** has been reported to exhibit growth retarding properties.[6]

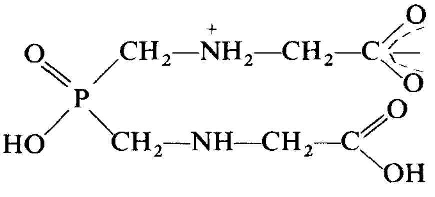
Plant growth regulators are chemically interesting in that they possess functional groups capable of binding to metal ions and could therefore alter speciation of the latter in soil solutions. Since the bioavailability of essential nutrient metals such as iron, copper, zinc and manganese is altered significantly by speciation,[7] such alteration of metal speciation by plant growth regulators could be beneficial or detrimental. Alternatively, the alteration of speciation may not be significant. Similarly, biotoxicity of poisonous metals such as lead and cadmium is dependent on speciation[8] and hence may be affected by plant growth regulators.

We are studying factors which affect metal speciation in soil solutions and plant nutrient solutions by computer simulation.[9–11] In order to conduct these studies, a thermodynamic database consisting of formation constants, solubility products, redox equilibria and selected atmospheric equilibria has been compiled. To facilitate studying the effects of **1**, **2**, **3** and **4** on metal ion speciation in soil solutions, formation constants for the complexes formed with a range of metal ions are required for incorporation into the thermodynamic database. Ligands **1**, **2**, **3** and **4** each contain multiple donor sites and form a potentially interesting series of compounds.

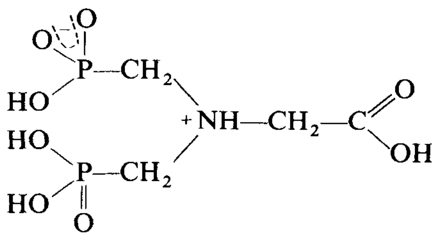
The protonation equilibria of **1**, **2**, **3** and **4** have been reported previously.[12] In



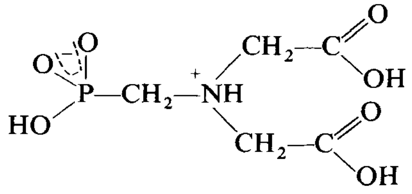
N-(phosphonomethyl) glycine (Ligand 1) **1**



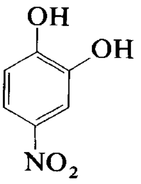
N,*N*′ [phosphinicobis(methylene)]bis (glycine) (Ligand 2) **2**



N,*N*-bis (phosphonomethyl) glycine (Ligand 3) **3**



N-(phosphonomethyl) iminodiacetic acid (Ligand 4) **4**



4-nitrocatechol **5**

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this study, the solution equilibria of **4** with manganese(II), cobalt(II), iron(II), nickel(II) and zinc(II) ions has been investigated. The equilibria between copper(II) ions and **4** also has been examined in the presence of a competing ligand, 4-nitrocatechol, **5**. Equilibria between **1**, **2** and **3** and nickel(II) ions also has been examined and the results give an indication of the order of stability of the plant growth regulators with various metal ions.

EXPERIMENTAL

Reagents

Ligands **1**, **2**, **3** and **4** have been synthesized.[12] 4-Nitrocatechol, **5**, (Merck, 97% pure), was twice recrystallized from water and analysed using ^1H nuclear magnetic resonance and microanalysis. Calcd. for $C_6H_5O_4N$: C, 46.46; H, 3.22; N, 9.03%. Found: C, 46.60; H, 3.10; N, 9.10%. The NMR spectrum (D_2O) yielded a doublet and a multiplet integrating for three protons which were assigned to the three aromatic protons. Metal chloride solutions were prepared using Merck chemicals (guaranteed reagents, GR) and standardized against EDTA solutions using known procedures and recommended indicators.[13–17]

Potentiometry

The potentiometric methods used have been described previously.[12] All titrations were conducted at a temperature of $25.0 \pm 0.1°C$ and an ionic strength of $0.1\ \text{mol dm}^{-3}$ (chloride) which was achieved by the addition of sodium chloride (BDH Aristar). Titrations were carried out by delivering the sodium hydroxide solution from a Radiometer ABU80 Autoburette controlled by a Bondwell computer, which also recorded the volume delivered and the e.m.f. of the cell as measured by a Radiometer PHM64 pH meter.

Analysis of Data

Potentiometric data were analyzed using the ESTA[18] suite of programs to obtain overall formation constants, β_{pqr}, for the complexes $M_pL_qH_r$ where

$$\beta_{pqr} = [M_pL_qH_r]/[M]^p[L]^q[H]^r$$

The appropriate metal ion hydrolyses[19] were accounted for in all of the computations.

Complexation titration data were processed initially by the BETA task and subsequently by the ZBAR and QBAR tasks of ESTA[18] in order to facilitate the identification of species. Refinement of the formation constants, β_{pqr}, was performed by running the complexation titration data on the ESTA optimization module with the weighted least-squares objective function based on e.m.f. residuals, OBJE. Once the final decision regarding the choice of species for a given metal-ligand system had been made, refinement computations were carried out with simultaneous optimization of formation constants and other titration parameters such as electrode intercept and concentration of components,[20] with a view to reducing the effects of systematic errors in the data. This procedure was carried out in a stepwise manner whereby the number of parameters refined, in addition to the formation constants, in each

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successive run was increased until the refinement process broke down or resulted in the computation of formation constants with correlation. In order that poor experimental points in the unbuffered region of the titrations may have less effect on the optimized values of parameters,[18] the following standard deviations, expressed as a percentage of the actual values, were specified; metal ion concentration, 0.2%; all other concentrations, 0.1%; initial volume, 0.1%; electrode intercept, 0.1 mV; electrode slope, 0.05 mV/pH; titre volume, 0.005 cm^3 and e.m.f. readings, 0.1 mV. The goodness of fit between the experimental and calculated curves is expressed by the Hamilton R factor, R_f, which has been tabulated in Table I for all the metal-ligand systems investigated. The validity of the chosen models and sets of best formation constants were checked by graphical comparisons of the observed formation and deprotonation curves with the corresponding calculated curves generated by ESTA.

RESULTS AND DISCUSSION

The overall stability constants calculated from the potentiometric data are presented in Table I together with the relevant statistical analyses. Literature constants available for some of the systems studied have also been tabulated for comparison.[21–25] In all cases the potentiometric studies were conducted over a wide pH range (1.7 to 11.4) but the actual ranges used for the refinement of the stability constants of the various equilibria have been tabulated. In all the metal-ligand systems, the titrations were carried out at 1:1 and 2:1 ligand:metal ratios. In addition to this, selected systems were studied at 1:2, 3:2, 5:2 and 3:1 ligand:metal ratios. The concentrations of the metal ions used were in the range of 2 to 6.6 mmol dm^{-3} and the ligands 2 to 10 mmol dm^{-3}.

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Protonations

Ligand **4** protonation constants reported in this study differ slightly from those reported previously.[12] The latter appear to be slightly in error owing to weighing errors arising from the hygroscopicity of ligand **4**. In the present study, this source of error was eliminated through utilizing stock solutions of ligand **4** which were standardized by titrating against sodium hydroxide solutions.

Metal Ion Complexations

Except for the nickel(II)-ligand **3** system, overlapping formation curves were observed in all cases for the various ligand:metal ratios indicating the dominance of mononuclear binary species.[26] Indeed, an ML species was found for all of the metal-ligand systems investigated and except for the nickel(II)-ligand **2** system, an MLH species was also found. In addition, an MLH_2 species was found for the nickel(II)-ligand **3** system. The latter finding is supported by a spectrophotometric study[22] where an MLH_3 species has also been found. The characteristic backfanning pattern of formation curves associated with the likely presence of hydroxy species[26] was found in all systems except for the nickel(II) systems with ligands **1**, **2**, **3** and **4**. ML_2 species were found for the nickel(II) and iron(II) ion systems with ligand **4**. An ML_2H_2 species was found only in the iron(II)-ligand **4** system. A commonly occurring phenomenon was that often it was possible to refine either of the stability constants for the complexes ML_2 or MLH_{-1} in addition to ML but not both simultaneously. In most cases the fit including MLH_{-1} as well as the statistical analysis was significantly better.

In the case of the copper(II)-ligand **4** system, the characteristics of the formation and deprotonation curves indicated the formation of the species MLH, ML and MLH_{-1}. The ESTA optimization resulted in correlation of the refined stability constants of these three species, however. When one of these three constants was fixed, the differences between the three constants remained the same irrespective of the value chosen for the fixed constant. The correlation was attributed to unusually strong binding of the copper(II) ions to ligand **4** which resulted in very low free ligand concentrations. In order to resolve this problem, the approach of using a competing ligand was adopted.[27] 4-Nitrocatechol, **5**, was found to be a suitable competing ligand in the present instance and led to the successful, correlation-free ESTA refinement of the three copper(II)-ligand **4** species mentioned above. Before the latter refinement procedures could be carried out, however, the protonation constants of 4-nitrocatechol and the stability constants of the copper(II)-4 nitrocatecholate complexes had to be determined. The results are included in Table I where 4-nitrocatecholate is referred to as "ligand **5**". Constants for the 4-nitrocatecholate–proton–copper(II) system found in the literature are also included in Table I. Titrations with copper(II):ligand **4**:4-nitrocatechol ratios of 1:1:1, 1:1:1.5, 1:1:2, 1:1:2.5 and 1:1:3 were performed. In the above titrations the metal ion and ligand **4** concentrations were 2.5 mmol dm^{-3} and that of 4-nitrocatechol in the range 2.5 mmol dm^{-3} to 7.5 mmol dm^{-3}. From the competing ligand titration data, stability constants for the ML and MLH complexes of the copper(II)-ligand **4** system were refined and no correlation was found. The results are presented in Table I. Log K for the quotient $[MLH]/[ML]\cdot[H] = 4.69$ (L = ligand **4**) and is in excellent agreement with the log K of 4.68 for the same reaction in the absence of the competing ligand. The MLH and ML constants of the copper(II)-ligand **4** system were refined from 7 titrations and 970 data points. The R factor of 0.00547 is highly satisfactory in view of the fact that there were four components (copper(II), ligand **4**, 4-nitrocatechol and H^+ ions) in solution. This competing ligand data set was also examined for ternary species but none was found. These two constants were then fixed in the original copper(II)-ligand **4** titration data set of 7 titrations and 753 data points and used to refine a stability constant for the MLH_{-1} species resulting in a log stability constant of 4.17. The R factor in this refinement was 0.00320 and the fit between the experimental and calculated formation (Figure 1) and deprotonation (Figure 2) curves is excellent. Speciation curves for the copper(II)-ligand **4** system are presented in Figure 3 and the most striking feature is the high percentage of copper(II) ions (100%) bound to ligand **4** at a pH of 2. This of course was the root cause of the correlation problem referred to above. Figure 4 represents a species distribution diagram of the copper(II)-ligand **4**–4-nitrocatechol system at a ratio of 1:1:2. The displacement of ligand **4** from copper(II) is clearly evident at higher pH where the formation of the copper(II)-ligand **4** MLH_{-1} complex is negligible.

Plausible Structures of Complexes

Ligand **1** has three functional groups and its metal ion complexes could potentially include two stable 5-membered chelate rings. The complexes found in the

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TABLE I

Logarithms of formation constants, β_{pqr}; n_t = number of titrations, n_0 = number of experimental observations, R_f = Hamilton R factor, T = temperature in °C and I = ionic strength in mol·dm^{-3}

Ligand	Cation	p	q	r	log β_{pqr}	std. dev.	n_t	n_0	pH range	R_f	T	I, ionic medium	exp. technique	Reference
1	Ni^{2+}	1	1	1	13.22	0.0042	4	125	2.8–10.1	0.0031	25	0.1 *M* NaCl	Potentiometry	This study
		1	1	0	7.90	0.0041								
		1	2	0	12.27	0.0098								
	Ni^{2+}	1	1	1	13.36						25	0.1 *M* KNO_3	Potentiometry	21
		1	1	0	8.10									
		1	2	0	12.25									
2	Ni^{2+}	1	1	0	12.24	0.0048	8	159	2.0–4.0	0.0029	25	0.1 *M* NaCl	Potentiometry	This study
3	Ni^{2+}	1	1	2	23.06	0.0080	5	308	1.9–10.5	0.0070	25	0.1 *M* NaCl	Potentiometry	This study
		1	1	1	18.24	0.0095								
		1	1	0	11.99	0.0102								
	Ni^{2+}	1	1	3	26.95						25	0.1 *M* KCl	Spectrophotometry	22
		1	1	2	24.28									
		1	1	1	18.73									
		1	1	0	11.69									
4	H^+	0	1	1	10.11	0.0016	4	348	1.7–11.4	0.0012	25	0.1 *M* NaCl	Potentiometry	This study
		0	1	2	15.66	0.0024								
		0	1	3	17.96	0.0036								
		0	1	4	19.44	0.0061								
	H^+	0	1	1	10.29						25	0.1 *M* KNO_3	Potentiometry	23
		0	1	2	15.86									
		0	1	3	18.30									
		0	1	4	19.50									

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	Mn^{2+}	1	1	1	13.81	0.0054	9	589	2.5–9.0	0.0045	25	0.1 *M* NaCl	Potentiometry	This study
		1	1	0	8.12	0.0052								
	Mn^{2+}	1	1	1	14.26						20	0.1 *M* KNO_3	Paper electrophoresis	24
	Fe^{2+}	1	1	1	15.27	0.0099	6	508	2.0–11.0	0.0067	25	0.1 *M* NaCl	Potentiometry	This study
		1	2	2	28.51	0.0145								
		1	1	0	9.86	0.0130								
		1	2	0	13.20	0.0177								
		1	1	−1	−0.97	0.0237								
	Co^{2+}	1	1	1	15.88	0.0044	6	547	2.5–9.0	0.0027	25	0.1 *M* NaCl	Potentiometry	This study
		1	1	0	10.82	0.0075								
	Co^{2+}	1	1	1	16.46						20	0.1 *M* KNO_3	Paper electrophoresis	24
	Ni^{2+}	1	1	1	16.82	0.0094	6	627	2.0–11.0	0.0035	25	0.1 *M* NaCl	Potentiometry	This study
		1	1	0	11.36	0.0110								
		1	2	0	14.48	0.0205								
	Cu^{2+}	1	1	1	18.77	0.0131	7	970	1.8–11.0	0.0054	25	0.1 *M* NaCl	Potentiometry	This study
		1	1	0	14.08	0.0084								
	Cu^{2+}	1	1	−1	4.17	0.0029	7	753	2.0–11.0	0.0032	25	0.1 *M* NaCl	Potentiometry	This study
	Zn^{2+}	1	1	1	16.28	0.0062	9	877	2.0–11.0	0.0061	25	0.1 *M* NaCl	Potentiometry	This study
		1	1	0	11.55	0.0068								
		1	1	−1	1.23	0.0079								
	Zn^{2+}	1	1	1	16.66						20	0.1 *M* KNO_3	Paper electrophoresis	24
5	H^+	0	1	1	10.54	0.0019	4	196	3.1–11.1	0.0040	25	0.1 *M* NaCl	Potentiometry	This study
		0	1	2	17.17	0.0027								
	H^+	0	1	1	10.85	0.05					25	0.1 *M* KCl	Potentiometry	25
		0	1	2	17.54	0.03								
	Cu^{2+}	1	1	0	11.37	0.0016	4	290	3.3–6.5	0.0042	25	0.1 *M* NaCl	Potentiometry	This study
		1	2	0	20.41	0.0041								
	Cu^{2+}	1	1	0	11.69	0.02					25	0.1 *M* KCl	Potentiometry	25
		1	2	0	20.10	0.10								

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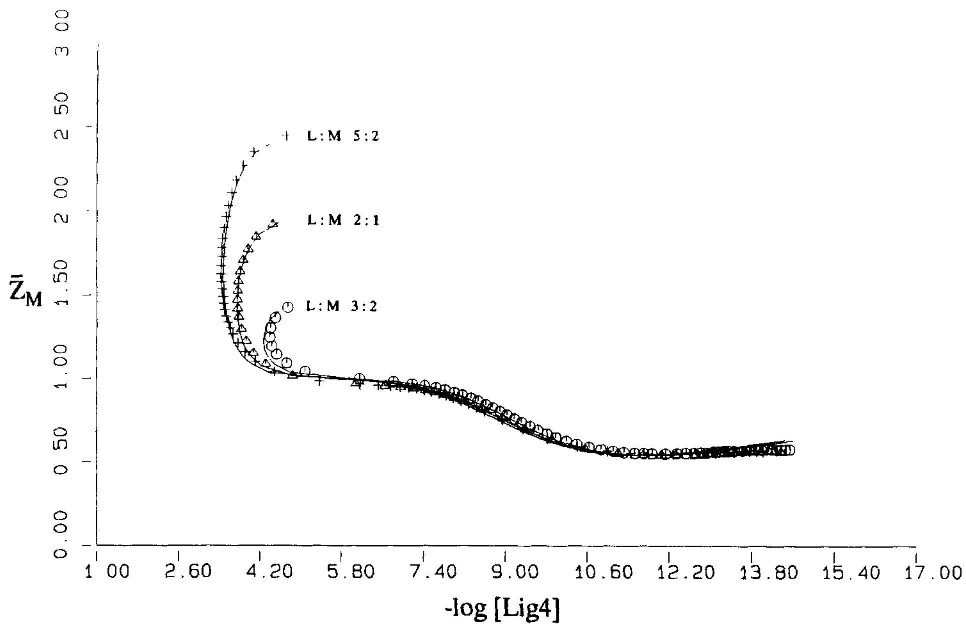

FIGURE 1 Experimental (symbols) and theoretical (solid line) metal formation curves for the copper(II)-ligand 4 system.

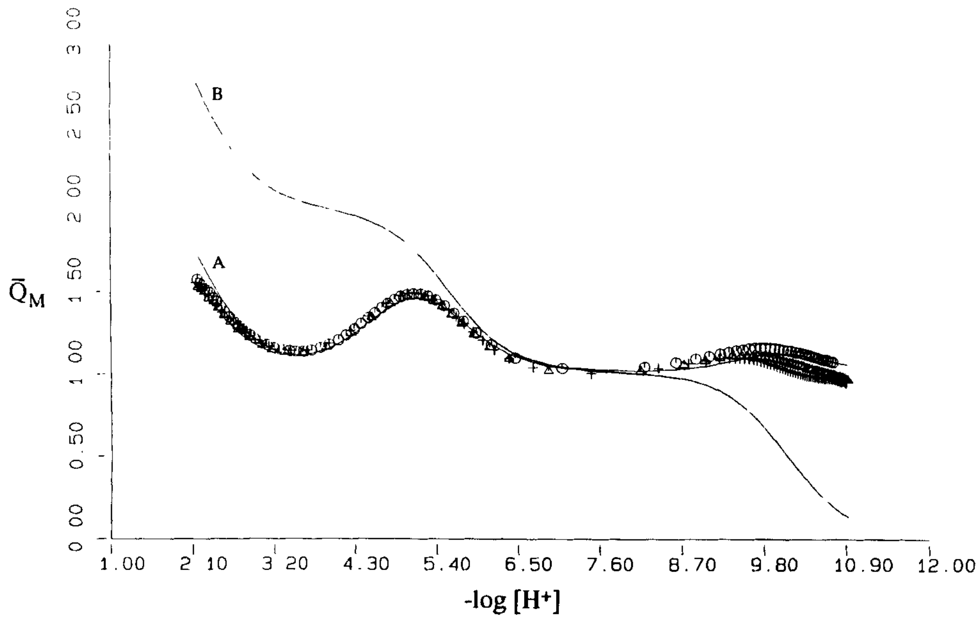

FIGURE 2 Experimental (symbols) and theoretical (solid line A) metal deprotonation curves for the copper(II)-ligand 4 system. Solid line B represents the average number of protons that would be bound to ligand 4 in the absence of metal.

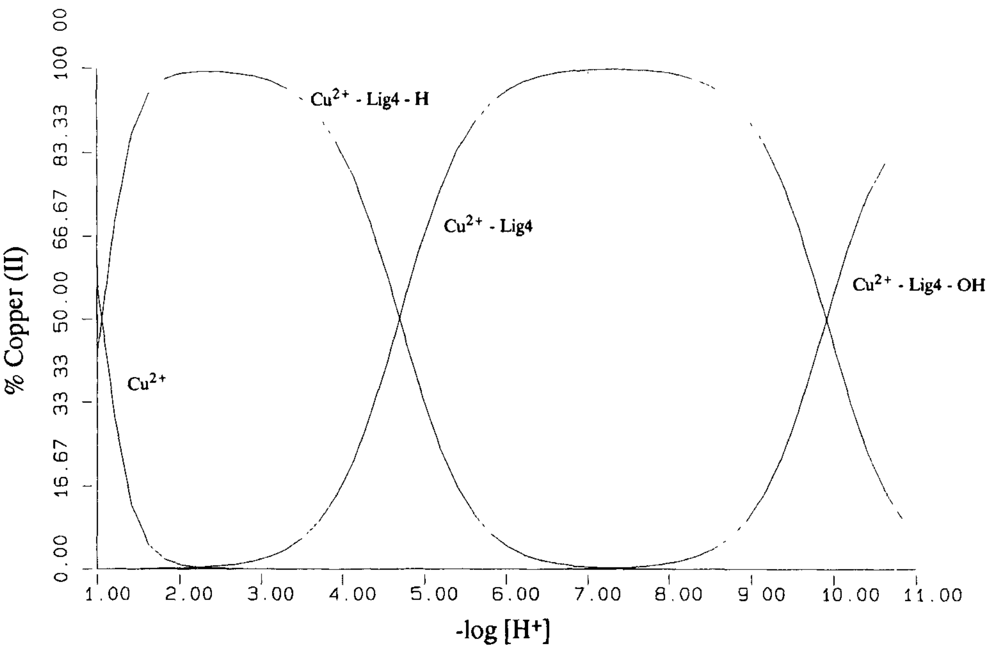

FIGURE 3 Species distribution curves for the copper(II)-ligand **4** system; Cu^{2+}:ligand **4**—2.5:5.0 mmol·dm^{-3}.

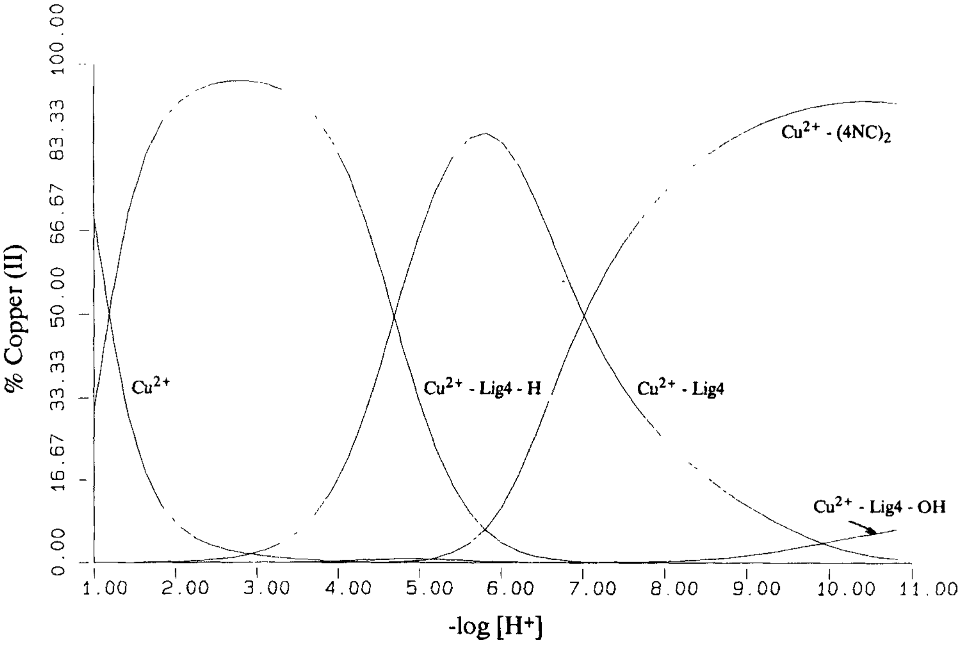

FIGURE 4 Species distribution curves for copper(II)-ligand **4**—4-nitrocatechol complexation; Cu^{2+}:ligand **4**: 4-nitocatechol—2.5:2.5:5.0 mmol·dm^{-3}.

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nickel(II)-ligand **1** system were MLH, ML and ML_2. The postulation of these three species can be rationalized as follows. Ligand **1** can be regarded as a combination of glycine (GLY) and aminomethylphosphonic acid (AMPA). The logarithms of the stability constants of the monocomplexes, ML, formed between these compounds with nickel(II) ions are 5.74[28] and 5.29[29] respectively. Since the logarithm of the ML constant for the nickel(II)-ligand **1** complex is 7.90, the latter is more stable than the former two. One possible source of the increased stability might be the formation of two chelate rings as indicated in Figure 5. In the MLH complex. the proton is probably bound to the phosphonic acid end of the molecule since log K for the reaction

$$ML + H \rightleftharpoons MLH$$

is 5.32, which is similar to the second protonation constant (5.42) for ligand **1**.[12] As the pH is increased, the proton dissociates resulting in the formation of the ML complex. The ML_2 complex could possibly have each ligand in a plane with the two planes perpendicular to each other. In this complex, all six functional groups would be bound to the metal ion. The only complex found in the nickel(II)-ligand **2** system was an ML complex. A likely structure for this complex is presented in Figure 6 and which consists of four 5-membered rings. The high stability of this structure is reflected in the log stability constant of 12.24 which is greater than that of the ligand **1**, ligand **3** and ligand **4** constants with nickel(II) ions. Figure 7 represents a possible structure for the ML complex of the nickel(II)-ligand **3** system. This three 5-membered chelate ring structure would be consistent with the fact that log β_{ML} for this system is 11.99, some 4 log units greater than log β_{ML} for the nickel(II)-ligand **1** system which we postulate as having two chelate rings. The logarithms of the stepwise formation constants (log K) for the MLH and MLH_2 species for the nickel(II)-ligand **3** system are 6.25 and 4.82, respectively. These values appear to correspond with the

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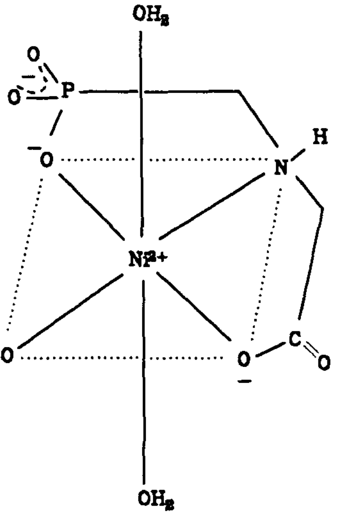

FIGURE 5 Proposed structure of the ML complex of the Ni^{2+}-ligand **1** system.

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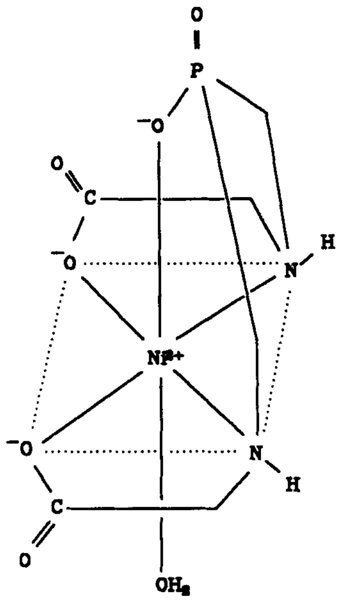

FIGURE 6 Proposed structure of the ML complex of the Ni^{2+}–ligand **2** system.

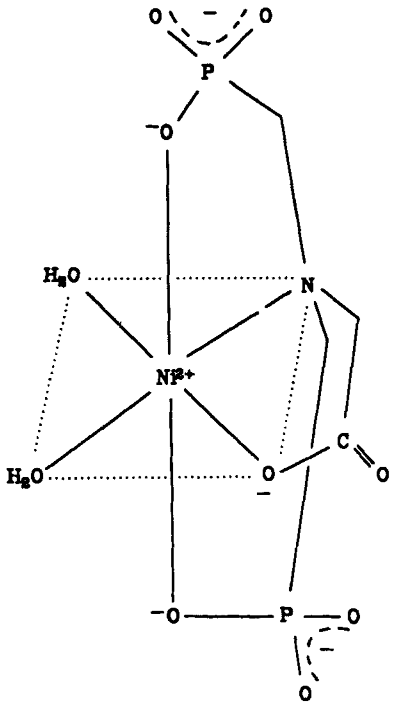

FIGURE 7 Proposed structure of the ML complex of the Ni^{2+}–ligand **3** system.

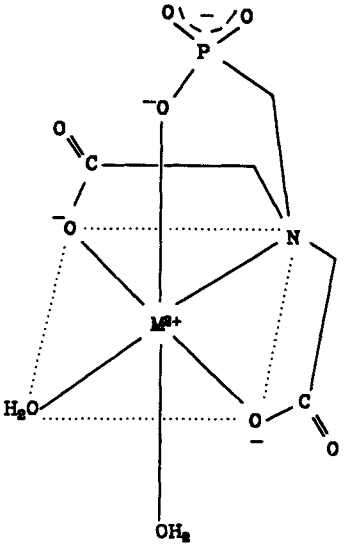

FIGURE 8 Postulated structure of the ML complex of ligand 4 with Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}.

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deprotonation of the phosphonic acid protons of ligand **3** which have the constants $\log K_2 = 6.40$ and $\log K_3 = 5.02$.[12] The protonated species could therefore have the same structure as that of the ML complex with the protons bound to the phosphonic acid functional groups. Like ligand **3**, ligand **4** is tetracoordinate and may form complexes with three stable 5-membered rings. Figure 8 represents a possible structure for the ML complexes of ligand **4** with manganese(II), iron (II), cobalt(II), nickel(II), copper(II) and zinc(II) ions. An MLH complex was found in all the ligand **4**–metal ion systems and since the stepwise formation constant log K for the MLH complex is similar to the second protonation constant of ligand **4** ($\log K_2 = 5.55$), a likely structure is one where the proton resides on the phosphonic acid functional group and dissociates at pH 5 to 6. An MLH_{-1} species was found for the iron(II), copper(II) and zinc(II) metal ions in their speciation with ligand **4**. The structures of these complexes are likely to be those of the ML species with the additional loss of a proton from one of the water molecules in the hydration sphere of the metal ion. An ML_2 species was found for nickel(II) and iron(II) with ligand **4**. There are many possibilities for such a structure since each ligand is four coordinate.

The structures proposed in Figures 5–8 are, of course, speculative because potentiometry, in general, yields stoichiometric and not structural information. Added data which could assist in structural determinations of the dissolved complexes could potentially be obtained from calorimetric measurements. Hence comparative interpretations could fruitfully be made of the derived enthalpy and entropy values.

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