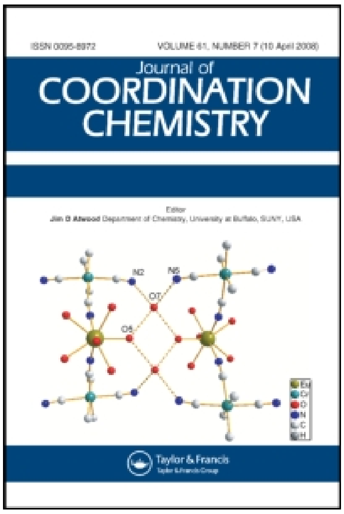

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METAL CHELATE FORMATION BY *N*-PHOSPHONOMETHYLGLYCINE AND RELATED LIGANDS

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Thirteen selected divalent and trivalent metal ions were equilibrated with *N*-phosphonomethylglycine (PMG) at 1:1 and 1:2 molar ratios of metal ion to ligand at 25.0° and ionic strength $\mu = 0.100$ M. Similarly, the same metal ions were also studied with iminobismethylenephosphonic acid (IDP), which has not been previously investigated, as well as the well known ligand, iminodiacetic acid (IDA) (to obtain equilibrium data for the latter not available in the literature). The complexes formed were studied as a function of $-\log[H^+]$. All of the appropriate equilibrium stability constants were calculated with the aid of the interactive computer program BEST. The constants obtained generally reproduce the entire experimental potentiometric equilibrium curves to within 0.01 $\log[H^+]$ units. The protonation constants 10.142, 5.460, 2.229 reproduce the potentiometric equilibrium curve of free PMG to within a σ value of 0.004 $\log[H^+]$ units while 10.79, 6.08, 5.04 and 0.86 are the protonation constants for IDP.

INTRODUCTION

Although *N*-phosphonomethylglycine (PMG) is used in large quantities as a phytotoxic agent, little is known about its affinities for the divalent and trivalent metal ions that occur in plants and in the environment, about the stoichiometries of the metal chelates formed, and the degree of formation of its metal chelates in solution. A single literature report[1] on PMG gives the stabilities of the 1:1 chelates of this ligand with five metal ions but does not address the possibility of the formation of 2:1 chelates. The latter is a distinct possibility, since the ligand possesses only three coordinating groups while most metal ions of interest have coordination numbers greater than or equal to 6. For example, iminodiacetic acid (IDA) has been found to form chelates with 2:1 molar ratios of ligand to metal ion. The 2:1 chelates of iminiodimethylenephosphonic acid (IDP) with divalent metal ions would be expected to be considerably weaker since the -4 charge of the two phosphonate groups of the ligand renders the initial 1:1 complex binegative. The tendency for the formation of the 2:1 chelate, ML_2^{6-}, would thus be relatively weak because of charge repulsion.

Furthermore, the literature also reveals that almost nothing is known about the chelating properties of IDP. Therefore, the series of ligands IDA, PMG and IDP forms an exceedingly interesting family of compounds whereby insight may be revealed about the chelating tendencies of the relatively poorly known phosphonate group. It is the purpose of this research to elucidate precisely and completely the solution equilibria of PMG and IDP with H^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Fe^{3+}, Al^{3+}, and La^{3+}, and to compare and contrast the results within this family of chelating agents to see what relationships can be found in their affinities for these metal ions.

EXPERIMENTAL

Reagents

All metal salts used were commercially available reagent grade nitrates. Stock solutions of the metal ions were standardized by the use of EDTA[2] titrations, or ion exchange with the hydrogen form of Dowex 50WX-8 ion exchange resin,[3] or both. The ligand *N*-phosphonomethylglycine was provided by the Stauffer Chemical Company and was found to be greater than 99.3% pure, with no detectable interferieng impurities. IDP was synthesized in these laboratories by a modification of literature methods.[4]

Procedure

Hydrogen ion concentrations were recorded at 25.0° with a 0.1000 M KNO_3 supporting electrolyte. A Corning Model 130 digital pH meter equipped with 5 inch extension electrodes was employed. This instrument was calibrated to read $-\log[H^+]$ directly by measuring accurately standardized nitric acid in dilute solution at ionic strength 0.1000 M maintained with KNO_3. The slope of the volt-p[H] response was found to be 0.05916 on each day of use. On this basis the alkaline $p[H^+]$ reading differed from that of the linear calibration line by less than 0.006 units, and the acid readings were exact. The concentrations of ligand and metal ion employed were generally 2.8×10^{-3} to 4.2×10^{-3} M for 1:1 molar ratios, and 5.6×10^{-3} M in ligand and 2.8×10^{-3} M in metal ion for 2:1 molar ratios. The value $-\log K_w$ ($\log [H^+][OH^-]$) was determined to be 13.795 (13.78 lit.).[5]

Computations

The potentiometric equilibrium data (~15–20 data points/a value where a = mole base/mole ligand) were processed with the use of the interactive Fortran program BEST[6] which basically solves for the dependent variable $-\log[H^+]$ at each equilibrium point. The program allows input for any number and kind of species and components so that approximations are avoided. This is advantageous for systems in which soluble polynuclear hydrolytic species are formed, or for complex systems involving combinations of many interacting components. The equilibrium constants are automatically refined so as to minimize the differences between calculated and observed $-\log[H^+]$ values, thus accurately reproducing the potentiometric equilibrium curves.

RESULTS AND DISCUSSION

The 1:1 and 2:1 potentiometric equilibrium curves obtained for PMG in this study are shown in Figures 1 and 2. Similar sets of curves were obtained for metal ions with iminodimethylenephosphonic acid and are shown in Figure 4. The stability constants obtained are listed in Tables I and II.

Ligands

The log protonation constants of PMG are 10.142, 5.460, and 2.229 ($\sigma = 0.004$). The "mixed" or Bronsted dissociation constants of PMG reported in the literature[1,7] are all ~0.1 log units higher, reflecting differences in calibration as well as differences in the definition of the dissociation constants measured. In this work $p[H] = -\log[H]$ and the constants are all concentration quotients.

Starting with totally deprotonated PMG the successive protonation sites are, in order, the amino nitrogen, the phosphonate oxygen, and finally the carboxylate oxygen

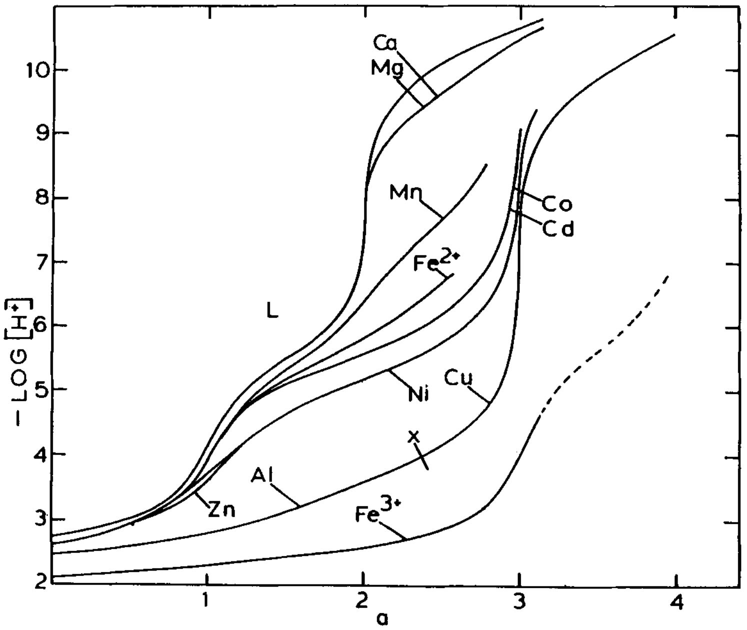

FIGURE 1 Potentiometric equilibrium curves for *N*-phosphonomethylglycine in the absence of complexing metal ions, and for a 1:1 molar ratio of ligand to metal ions. Concentrations are 3.000 × 10^{-3} M in metal ions and ligand. The ionic strength was maintained at 0.100 M (KNO_3); T = 25.0°; a = moles KOH added/mole ligand present. On the Al curve X indicates the pH at which an insoluble phase was formed.

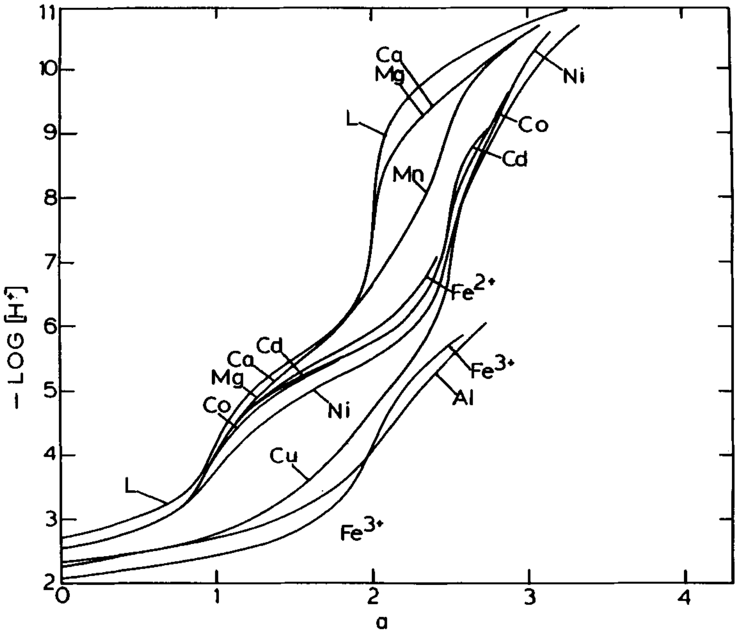

FIGURE 2 Potentiometric equilibrium curves for *N*-phosphonomethylglycine in the absence of complexing metal ions, and for a 2:1 molar ratio of ligand to metal ions. Concentrations are 3.000 × 10^{-3} M metal ion and 6.000 × 10^{-3} M ligand. The ionic strength was maintained at 0.100 M (KNO_3); T = 25.0°; a = moles 0.1000 M KOH added/mole ligand present.

atom. Thus, the neutral acid form (H_3L) is a dipolar ion possessing a positively charged protonated amino group and a negatively charged hydrogen phosphonate group. The relative basicities of the various donor groups will be of some importance in assigning the bonding sites for chelate formation between the ligands and the metal ions in the protonated chelates formed.

For IDP the successive protonation constants found are 10.79, 6.08, 5.04, and 0.86. The values in the literature for somewhat different conditions are 10.62, 5.82, and 4.83. Starting with totally deprotonated IDP, the successive protonation sites are the amino nitrogen, one of the six phosphonate oxygens, one of the three oxygens on the unprotonated phosphonate, and finally at very high acidity one more protonation occurs on a phosphonate oxygen atom to give a neutral ligand molecule which has a dipolar structure analogous to that of PMG. The remaining oxygen is too weakly basic to be protonated to any extent in strongly acid solution.

1:1 Metal Chelates of PMG

The chelates of calcium and magnesium are the least stable of those investigated, as can be inferred from the small depression that these metal ions produce in the corresponding potentiometric equilibrium curves shown in Figure 1. In addition to the 1:1 chelate (ML) that forms between "a" values 2–3 there is evidence for prior formation of a protonated species (MHL) for these and all of the other metal ions studied. In the presence of this ligand at the stoichiometric ratio employed, the metal hydroxides of Mn(II), Co(II), Fe(II), Al(III), and Fe(III) began to form either at or just above a = 3, indicating moderate degrees of chelation, with sufficient free metal ion present to exceed the solubility product constant of the corresponding metal hydroxides. The hydroxides of Mg(II) and Ca(II) are sufficiently soluble to overcome this problem, while the 1:1 Cu(II) chelate has sufficient stability to allow the formation of a high pH hydroxo species (M(OH)L, a soluble and stable complex that persists in alkaline solutions. With Al(III) it was not possible to continue measurements above pH 4 without encountering precipitation of the $Al(OH)_3$. With Fe(III) there was a continuous downward drift just beyond three equivalents of added base (a = 3). A break was observed at a = 3, and an indication of another at a = 4, but the system could not be precisely equilibrated in the p[H] range above 4 (beyond a = 3). Similar results were obtained for the 1:1 La(III)-PMG system.

TABLE I
Log Metal Chelate Stability Constants of PMG[a].

Metal Ion	$\frac{[M]}{[M][L]}$	$\frac{[MHL]}{[M][H][L]}$	$\frac{[ML_2]}{[M][L]^2}$	$\frac{[MLOH][H]}{[M][L]}$	σ 1:1	σ 2:1
Mg^{2+}	3.31	12.12	5.47		.003	.021
Ca^{2+}	3.25	11.48	5.87		.005	.039
Mn^{2+}	5.47	12.30	7.80		.006	.023
Fe^{2+}	6.87	12.79	11.18		.016	.009
Co^{2+}	7.23	12.59	11.12		.006	.009
Ni^{2+}	8.10	13.36	12.25		.003	.032
Cu^{2+}	11.93	15.85	16.02	2.06	.012	.001
Zn^{2+}	8.74	7.99	11.69	−0.99	.047	.072
Cd^{2+}	7.29	12.64	10.91	−3.46	.012	.027
Pb^{2+}	← Precipitate present throughout pH range →					
Fe^{3+}	16.09	17.63	23	10.31[b]	.019	.048
Al^{3+}	13.70	16.18	22.05[c]		.017	.002
La^{3+}	6.7	13.6	10.1			

[a] Log protonation constants of PMG (L^{3-}) are 10.142, 5.460, 2.229 (σ = 0.004); [b] For Fe(III), log $[ML(OH)_2][H]^2/[M][L]$ = 1.40; [c] For Al(III), log $[MHL_2]/[M][H][L]^2$ = 27.76.

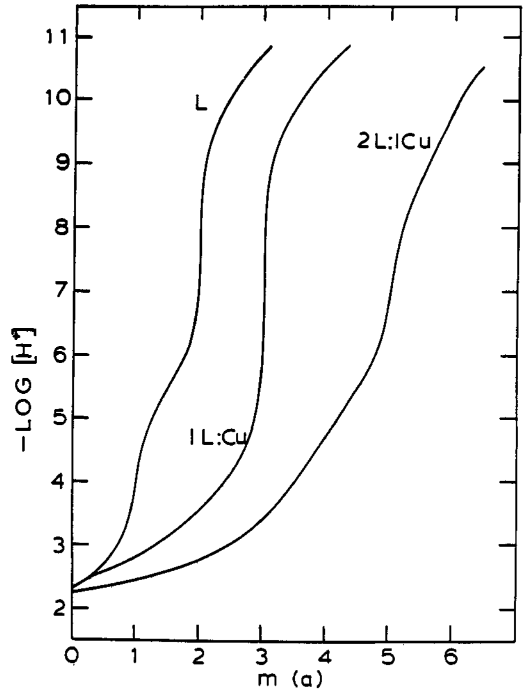

FIGURE 3 Potentiometric equilibrium curves for metal-free *N*-phosphonomethylglycine and for 1:1 and 1:2 molar ratios of Cu(II) ion to ligand; a = moles 0.100 M KOH added/mole ligand; m = moles 0.100 M KOH added/mole metal ion present; T = 25.0°; ionic strength = 0.100 M (KNO_3). Concentrations are 3.00×10^{-3} M for metal ion and 3.000 or 6.000×10^{-3} M for the ligand.

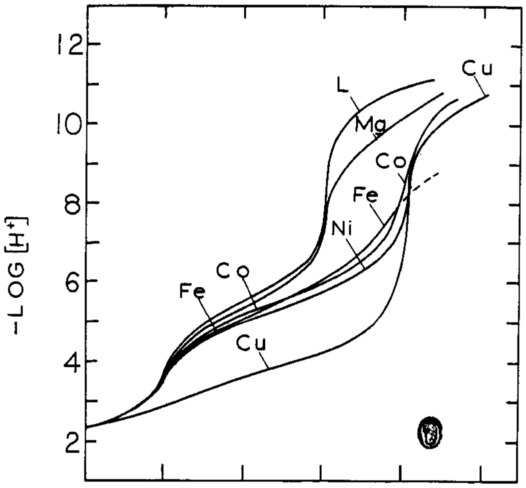

FIGURE 4 Potentiometric equilibrium curves for iminodimethylenephosphonic acid (IDP) in the absence of complexing metal ions, and for a 1:1 molar ratio of ligand to divalent metal ion. Ionic strength = 0.100 M (KNO_3); T = 25.0°; a = moles KOH added/mole ligand present. Concentrations of metal ions and ligand are 4.200×10^{-3} M.

TABLE II
Log Metal Chelate Stability Constants of IDP[a,b]

Metal Ion	$\frac{[ML]}{[M][L]}$	$\frac{[MHL]}{[M][H][L]}$	$\frac{[MH_2L]}{[M][H]^2[L]}$	$\frac{[MLOH][H]}{[M][L]}$	$\frac{[ML_2]}{[M][L]^2}$
Mg^{2+}	4.25	13.50	18.74	−7.1	
Ca^{2+}	3.84	13.22	18.58		
Mn^{2+}	6.26	14.42	19.28	−4.4	
Fe^{2+}	7.70	14.35	19.34		
Co^{2+}	7.75	14.07	18.89	−3.08	
Ni^{2+}	8.32	14.23	19.01	−2.48	9.84
Cu^{2+}	12.84	17.44	20.90	+2.55	
Zn^{2+}	9.03	15.52	18.9	−0.83	
Cd^{2+}	9.3	15.3	18.5		
Pb^{2+}	10.17	17.0	21.4	0.52	
Fe^{3+}[c]		3.90[d]		10.35	30.96
Al^{3+}[d]	>9			6.92	20.60
La^{3+}	9.24	18.43			7.04

[a] Iminodimethylenephosphonic acid. [b] 25.0. μ = 0.100 M (KNO_3). [c] 100% complex formation was present originally and formation constants cannot be obtained directly. [d] [MHL]/[ML][H].

2:1 Ligand: Metal Chelates of PMG

As seen above, 1:1 chelates form between a = 2 and 3 for most divalent metal ions. However, it is seen in Figure 2 that when the ligand concentration is doubled, most metal ions investigated also form 2:1 ligand to metal complexes in the range from a = 2.5 to 3.0. That the 2:1 complexes are only moderately more stable than the 1:1

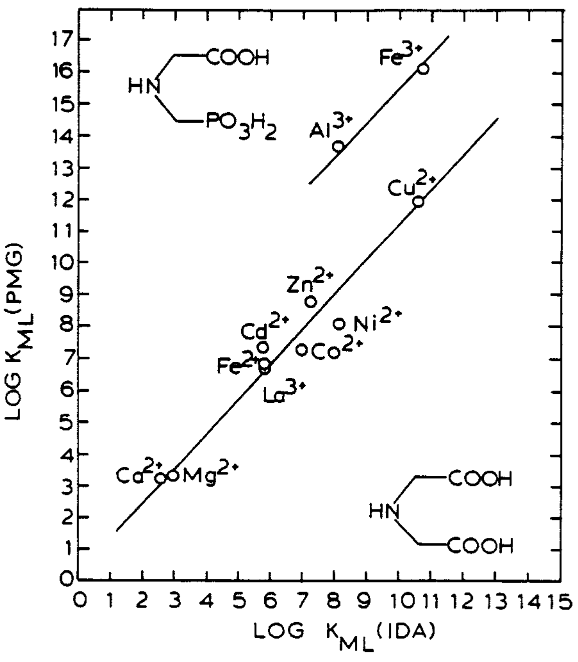

FIGURE 5 Log K_{ML} (*N*-phosphonomethylglycine) *vs* log K_{ML} (iminodiacetic acid) showing a correlation between stability constants of chelates of metal ions of like charge.

complexes is indicated by the inflection at a = 2.5 or m = 5.0 (mole base/mole metal present). Thus in 2:1 solution the first two protons must be completely dissociated before the 1:1 complex reacts with the additional ligand molecule.

The most dramatic comparison of 1:1 and 2:1 interactions is indicated in Figure 3, which shows the relative stoichiometric requirements of chelate formation with added base for the ligand alone, and for the 1:1 Cu:PMG and the 1:2 Cu:PMG systems. Although the same reactions occur with the other systems studied, the relative differences in behavior are not as obvious as is indicated by the copper(II) equilibrium curves.

The ligand curve reflects the stoichiometry of the three successive acid neutralization reactions. For the metal-containing 1:1 system, the buffer region through a = 3 represents the formation of complexes of the type MHL and ML. The formation of the latter overlaps significantly with the former since the protonated complex is considerably polarized by the Cu(II) ion and the proton is easily lost from the amino group as it becomes coordinated to the metal ion. The buffer region beyond m = 3 is influenced by the dissociation of CuL to form the hydroxo complex $Cu(OH)L^{2-}$. The equilibrium curve for two ligands per metal ion shows considerable shape distortion, rendering it different from that of the ligand along and from the 1:1 PMG curves. As before, the initial portion of the curve through m = 5 represents the formation of the chelate species CuHL and CuL. However, this time there is additional overlapping equilibrium derived from the protonation reactions of the free ligand, giving it a drawn-out appearance. Beyond m = 5, the 1:2 ML_2 chelate forms at first to the exclusion of the highly stable MOHL complex. Nevertheless, at pH 10.5 this latter chelate takes over as the major species in solution.

Figures 6, 7, and 8 represent the metal ion and metal chelate species distribution curves when PMG is present in fourfold excess. Calcium(II) (Figure 6) is representative of weak binding, nickel(II) (Figure 8) of strong binding and manganese(II) (Figure 7) of intermediate binding. Species distribution curves for the other metal ions studied are qualitively similar to those shown.

All three diagrams show an initial buildup of the MHL° species, which upon deprotonation, become ML^{-}. At yet higher pH values the 2:1 L:M chelates predominate. The latter effect is least prominent in the case of calcium(II).

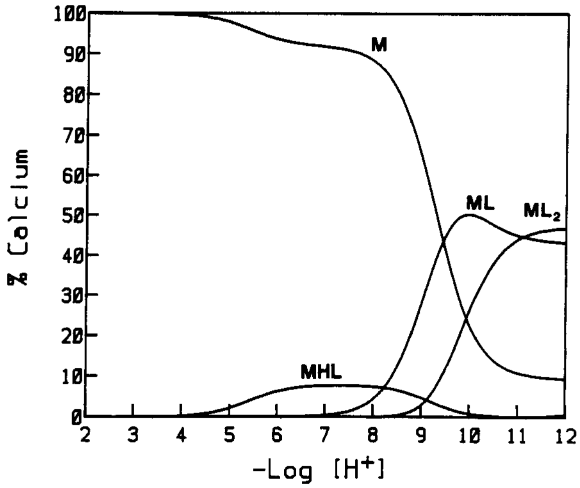

FIGURE 6 Distributions of metal ion and metal chelate species in a solution 0.00100 M in calcium(II) and 0.00400 M in PMG at 25°, $\mu = 0.100$ M.

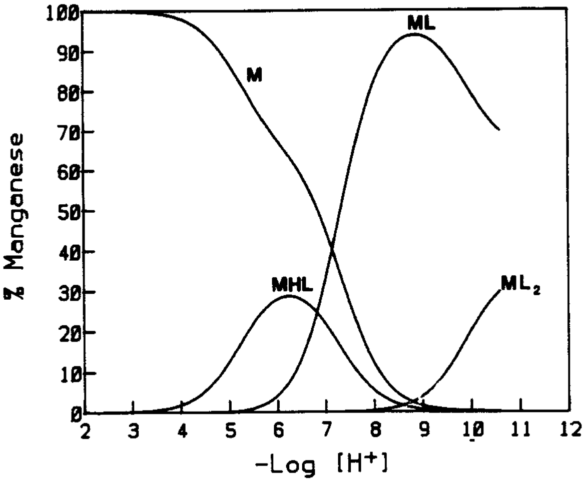

FIGURE 7 Distributions of metal and metal chelate species in a solution 0.00100 M in manganese(II) and 0.00400 M in PMG at 25°, μ = 0.100 M.

In addition Figures 7 and 8 show termination of the distribution curves at pH 10.6 and 11.4, respectively, since the solubility product of the $M(OH)_2$ becomes exceeded. The high pH ratio of $[ML_2]/[ML]$ is such that there is always some ML present under these conditions. In other words the second formation constant is not sufficiently large to effectively, even with fourfold excess of ligand, form exclusively 2:1 metal complexes.

Metal Chelates of IDP

Since IDP is a tetraprotonated ligand, H_4L, it requires four equivalents of base to completely neutralize the ligand, whereas only three protons were neutralized for each PMG molecule that combines with a metal ion. Examination of 1:1 M:L potentiometric

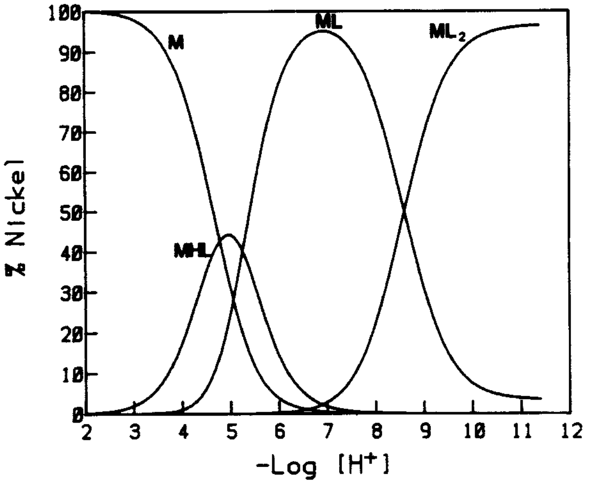

FIGURE 8 Distributions of metal ion and metal chelate species in a solution 0.00100 M in nickel(II) and 0.00400 M in PMG at 25°, μ = 0.100 M.

equilibrium curves showed that metal ions such as Mg^{2+} and Ca^{2+} possess the weakest chelating tendencies, Ni^{2+}, Fe^{2+} and Co^{2+} are intermediate, while Cu^{2+} reacts rather strongly with this chelating agent. Furthermore, it was found that all divalent metal ions form diprotonated and monoprotonated metal chelates in the neutralization range between a = 1 and a = 2, in addition to the normal chelate (ML) between a = 3 and a = 4.

Among the divalent ions Ni^{2+} was also investigated with a 2:1 ratio of ligand to metal to encourage the formation of 2:1 chelates. Visual inspection of the data indicates very low (if any) degree of 2:1 chelate formation. This contrast to the behaviour of PMG is not surprising in that the negative charge of IDP (-4) is higher than that of PMG (-3) and therefore divalent metal ions cannot support the burden of accommodating eight negative charges in their coordination spheres. For this reason the remaining divalent ions were not studied further for 2:1 metal chelate formation.

Only in the case of Mg^{2+} and Ca^{2+} is the formation of the deprotonated chelate ML separated from the low p[H] forms MH_2L and MHL. For all the ions investigated except Mg(II) and Ca(II), the three chelates are involved in overlapping equilibria over a range of about 2 p[H] units.

The more weakly coordinating metal ions for IDP, measured by the relative positions of the buffer region from a = 1 to a = 3 are Ca^{2+} and Mg^{2+}. The stronger coordinating metal ions are Cu^{2+} and the trivalent ions.

Copper(II) ion shows most clearly the presence of the MOHL species corresponding to the dissociation of a proton from a water molecule which is probably bound at the fourth position in the planar coordination sphere of the metal ion (the first three being occupied by the donor groups of the terdentate ligand).

It was also found that at 4×10^{-3} M concentration, the diprotonated chelate (MH_2L°) formed by some of the divalent metal ions, and the monoprotonated chelate (MHL°) formed by the trivalent ions, is rather insoluble and precipitates from solution. This tendency toward precipitation of metal-IDP chelates was first noticed as a slight cloudy suspension that forms in the p[H] range 5.3–8.0 in the Mn(II) system. Other metal ions which behave similarly are Zn(II) starting at pH 3.7, Cd(II) at pH 4.1, Pb(II) at pH 2.8 and all trivalent metal ions at the start of each potentiometric run (*i.e.*, at low pH). These systems were investigated potentiometrically by the technique of back-titration, wherein the soluble high-pH forms of the complexes were formed first by the addition of excess base, followed by the addition of increments of standard HNO_3. In this way quantitative information on the chelate equilibria was obtained from the potentiometric determinations.

Equilibrium Constants

The potentiometric equilibrium curves described were employed to calculate the equilibrium constants shown in Table I for PMG and in Table II for IDP. The values listed are overall stability constants (β values). The weakest complexing metal ion is Ca^{2+} ion while the strongest complexing divalent metal ion is Cu^{2+}. The trend for the relative stabilities, as indicated by the magnitudes of the stability constants, is in general parallel to the normal trends of the stabilities of the chelates of these metal ions with ligands containing nitrogen and oxygen donor groups. The PMG values of log K_{ML} are parallel to those reported[5,8] for IDA (Figure 5). A similar plot may be constructed for the IDP chelates. The numerical values of all the formation constants listed in Table I for PMG are larger than those of IDA, reflecting the larger negative charge of the PMG ligand.

In contrast, the numerical values for all the formation constants listed in Table II for IDP are only about one order of magnitude larger than those found for PMG, perhaps indicating coulombic repulsion between highly negative phosphonate groups coordinated to the same metal ion. The net effect of such repulsive forces would be to decrease the magnitudes of the stability constants of the IDP chelates, which would otherwise be expected to be considerably higher.

The probable coordinate bond arrangements of the 1:1 complexes of PMG may be deduced from the nature of the ligand and the metal ions. The low stabilities of the MHL type complexes, and the relatively high pK's for the dissociation of these protonation complexes, indicates that the proton resides on the nitrogen donor group. Thus the phosphonate oxygens seem to be the donor groups involved in the formation of these chelates. Carboxylate coordination may be dismissed since monodentate carboxylate donors have stability constants around 10 or less ($\log K \leq 1$). The normal complexes (ML type) probably chelate the metal ion in an approximately planar arrangement, thus minimizing charge repulsions between the *trans*-oriented negatively charged phosphonate and carboxylate groups.

Since all the metal ions investigated form mono- and diprotonated chelates of IDP, a comparison of the coordinating tendencies of the metal ions can be obtained by comparing the magnitudes of the phosphonate group protonation constants of the metal-free ligand and of the corresponding metal chelates. The two reference values of log K are 6.08 and 5.04 ($\log K_2$ and $\log K_3$ for IDP). The differences between $\log \beta_{MH_2L}$ and $\log \beta_{MHL}$ values in Table II represent reaction (*1*). The protonation reaction represented by (*1*) is considered to take place on the coordinated phosphonate group. A comparison of the differences between $\log \beta_{MHL}$ and $\log \beta_{ML}$ reveals that the metal ions can be grouped into two types based on whether this difference is <6 log units (Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}) or >> 6 log units (Mg^{2+}, Ca^{2+}, Mn^{2+}, Pb^{2+} and La^{2+}). The former group may be considered to represent normal behaviour whereby the first protonation occurs at one of the coordinated phosphonate groups. The latter set probably represents a situation wherein the metal ion in the monoprotonated species is bound to the two phosphonates, but the proton is on the amino nitrogen.

For 2:1 chelates, there is no problem orienting two terdentate ligands around essentially octahedral metal ions (e.g., Ni(II), Fe(II), Fe(III)), but it is a matter of speculation as to the exact orientation of the coordinate bonds in complex ions such as those of Cu(II), Zn(II) and Cd(II), which may require less than six coordination.

$$K^{H}_{MH_2L} = [MH_2L]/[MHL]\,[H] \tag{1}$$

Since the literature on iminodiacetic acid (IDA) is rather extensive, the only work carried out on this ligand in this research project was the determination of stability constants for the metal-IDA chelates not reported previously. The new results can be summarized as follows: Mg(II) ion forms a 1:2 complex (ML_2) with a value of $\log \beta_{ML_2} = 4.85$; Mn(II) forms both 1:1 and 1:2 complexes (ML and ML_2) with $\log \beta_{ML} = 4.72$; $\log \beta_{ML_2} = 7.82$; for Fe(III) the previously unreported second step in the formation of ML_2 is $\log K_{ML_2} = 9.42$; and the lead(II) formation constants are $\log \beta_{ML} = 7.31$, $\log \beta_{ML_2} = 9.30$ and $\log K_{MOHL} = -9.36$.

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