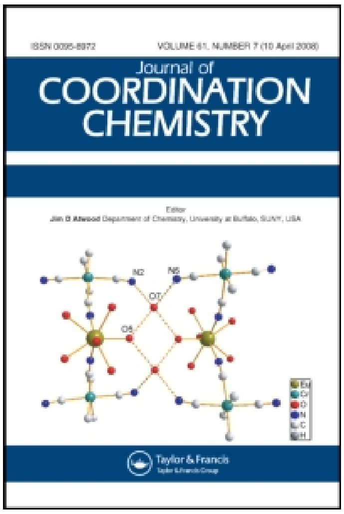

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METAL COMPLEXES OF BIOLOGICALLY OCCURRING AMINOPHOSPHONIC ACIDS

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METAL COMPLEXES OF BIOLOGICALLY OCCURRING AMINOPHOSPHONIC ACIDS

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The interaction of 1-aminoethylphosphonic acid, 2-aminoethylphosphonic acid and **2-amino-3-phosphomopropionic** acid with Cu(II), Ni(II), Zn(II), Co(II), Mn(II), Mg(II) and Ca(II) has been investigated potentiometrically. Stability constants for the protonated and normal 1:1 and 1:2 metal–ligand complexes are reported at 25.0° and $\mu = 0.2(KNO_3)$. The transition and alkaline earth metal ions show preferential binding to different sites on the ligands, the former interacting with carboxylate, phosphonate, and amine groups, while the latter show predominant interaction with the phosphonate moiety. The present study shows that compounds containing C–P bonds form more stable metal complexes than the corresponding compounds containing C–O–P bonds. This is partly due to the higher basicity of the phosphonate ligands and partly due to more favourable chelate ring formation. Structures are suggested for the various complexes.

INTRODUCTION

Derivatives of phosphoric acid play an important role in biological processes and considerable research has been carried out to understand the origin, nature, and metabolic transformations of these compounds. Prior to 1959, the biologically occurring organic phosphorus compounds were shown to have the carbon containing portion of the molecule usually attached to oxygen, or less commonly to nitrogen. The serendipitous discovery of 2-amino-ethylphosphonic acid[1] (2-AEP) marked the first member of a new class of naturally occurring biochemically active species containing direct carbon phosphorus bonds. Apart from 2-AEP which occurs free and as a major constituent of the phospholipids of ciliates, coelenterates, molluscs, and marine phytoplankton,[2] four aminophosphonic acids structurally related to 2-AEP have been discovered in coelenterates.[3] These are 2-amino-3-phosphonopropionic acid (2-A-3-PPA) and the three N-methyl derivatives of 2-AEP. Although more members of this class of compounds may be expected to be discovered, the functions of these compounds in living systems remain unclear. Since most of the organisms in which aminophosphonic acids have been found, live in an aquatic media, it has been proposed that such organisms might benefit from a greater selectivity in binding the cations present in natural waters by replacing their phosphoric acid groups (C–O–P) with phosphonic (C–P) groups.[3a] In order to determine whether any such selectivity difference exists between the phosphonate and phosphate groups in binding various metal ions, we have carried out a detailed equilibrium analysis of the interaction of 2-AEP and 2-A-3-PPA with Cu(II), Ni(II), Zn(II), Co(II), Mn(II), Mg(II) and Ca(II). A comparison of the stability constants of the metal complexes of 2-AEP and 2-A-3-PPA with those of such biological analogs as O-phosphoethanolamine (PEA) and O-phospho-DL-serine (PS) respectively, would reveal any patterns of selectivity in metal ion binding due to the presence of the C–P bond. In order to provide structural information, the metal complexes of 1-aminoethylphosphonic acid (1-AEP) have also been studied. Prior to our work, the only data available on metal binding by these ligands was a study on the interaction of 1-AEP with Cu(II).[4a] Schiff base formation between pyridoxal and 1-AEP, 2-AEP and 2-A-3-PPA, and the chelates of the schiff bases of 1-AEP and 2-AEP with Cu(II), Al(III) and Zn(II) have been recently reported.[4b]

EXPERIMENTAL

Materials

The ligands 1-aminoethylphosphonic acid, 2-amino-

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ethylphosphonic acid and 2-amino-3-phosphonopropionic acid were obtained from Calbiochem. The purity of these ligands was checked and their molecular weights determined by potentiometric titration with standard carbonate-free sodium hydroxide. The ligands dl 1-AEP and 2-AEP were used in the diprotonated form (H_2L) while the ligand dl 2-A-3-PPA was used in the triprotonated form (H_3L). Stock solutions of Cu(II), Ni(II), Zn(II), Co(II), Mn(II), Mg(II) and Ca(II) were prepared from analytical grade nitrates and standardized by titrating with the disodium salt of EDTA.[5] Carbonate-free sodium hydroxide was prepared and standardized by titrating with potassium hydrogen pthalate (B.D.H. Analar, dried at 120° for two hours). Glass distilled water was used for the preparation of all the solutions.

Methods

Dissociation constants for the free ligands and the association constants for the metal complexes were determined by potentiometric titration with standard carbonate-free sodium hydroxide in the absence and the presence of metal ions, respectively. In titrations involving Cu(II), Ni(II), Zn(II), and Co(II) the metal-ligand ratio was 1:2 while with Mn(II), Mg(II) and Ca(II) the metal-ligand ratio was 1:1. The concentration of each ligand was ca. 4.0×10^{-3} M. At least two titrations were carried out for each system.

Titrations were carried out in a 100 ml jacketed cell serviced by a constant temperature bath at 25.0° ± 0.1°. Carbon dioxide-free nitrogen was bubbled through the experimental solutions whose ionic strength was initially adjusted to 0.2 by addition of KNO_3. Standard NaOH was added to the titration cell with a Metrohm Dosimat microburette and the changes in the pH of the solution during the course of the titration were monitored with a digital Radiometer pH meter, PHM 52, in combination with a Radiometer combination electrode, GK2401C. The experimental data was obtained in homogeneous aqueous media and the titrations were terminated when either the pH meter readings became unstable (i.e. showed a continuous downward drift) or a solid phase appeared in the experimental solutions. The

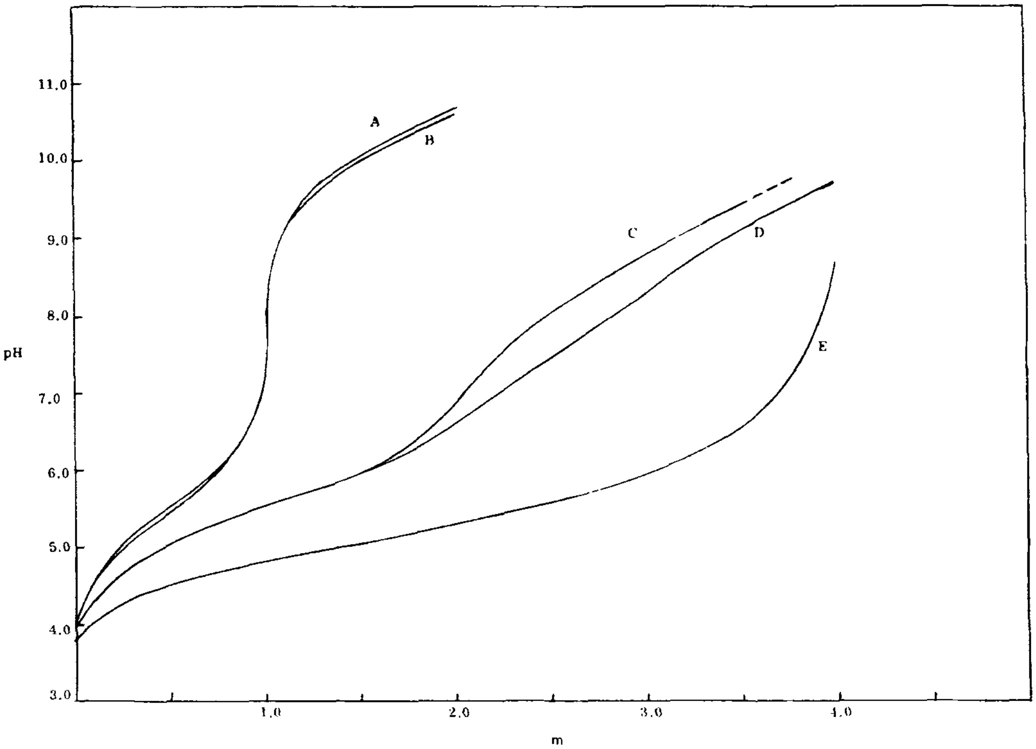


FIGURE 1 Potentiometric titration curves for 1-aminoethylphosphonic acid. A = Free ligand, B = 1:1 Mg(II) + ligand, C = 1:2 Co(II) + ligand, D = 1:2 Ni(II) + ligand, E = 1:2 Cu(II) + ligand. 'm' is the moles of base added per mole of metal ion. For curves A and B, the absicca represents 'a' the moles of base added per mole of ligand. The dotted lines represent unstable pH readings.

use of a digital pH meter accurate to the third decimal place was very helpful in detecting the onset of unstable pH values.

The electrode system was calibrated by direct titration of acetic acid, the observed pH meter readings being compared with the actual hydrogen ion concentration calculated from data tabulated by Harned and Owen.[6] The pH regions below 3.5 and above 10.5 were calibrated by measurements in the HCl and NaOH solutions, respectively.

Calculations

The various equilibrium constants reported in this study have been calculated from the potentiometric titration data using a corrected version of the computer program SCOGS.[7] The constants so obtained were further checked by processing the titration data with the computer programs Miniquad[8] and Miniquad 75.[9] All three programs gave essentially the same values for the various constants. An IBM 370/167 computer was used for executing the computer programs.

RESULTS

Acid Dissociation Constants

Potentiometric titration of the ligands 1-AEP and 2-AEP in the diprotonated form (Figures 1A, 2A) show that the two protons undergo dissociation in separate steps. Titration of the ligand 2-A-3-PPA in the triprotonated form (Figure 3A) indicates the stepwise dissociation of the three protons. The dissociation constants of the above three ligands are listed and assigned in Table I.

Interaction of 1-AEP and 2-AEP with Metal Ions

Titration curves for systems containing a 1:2 molar ratio of Cu(II) and 1-AEP or 2-AEP (Figures 1E, 2E) show that in the presence of Cu(II) ions the titration curves for both the ligands are substantially displaced to a lower pH region and all the protons on the ligands dissociate in a single step. The single steep inflection at about m=4 (m=moles of base added per mole of metal ion) probably indicates the overlapping

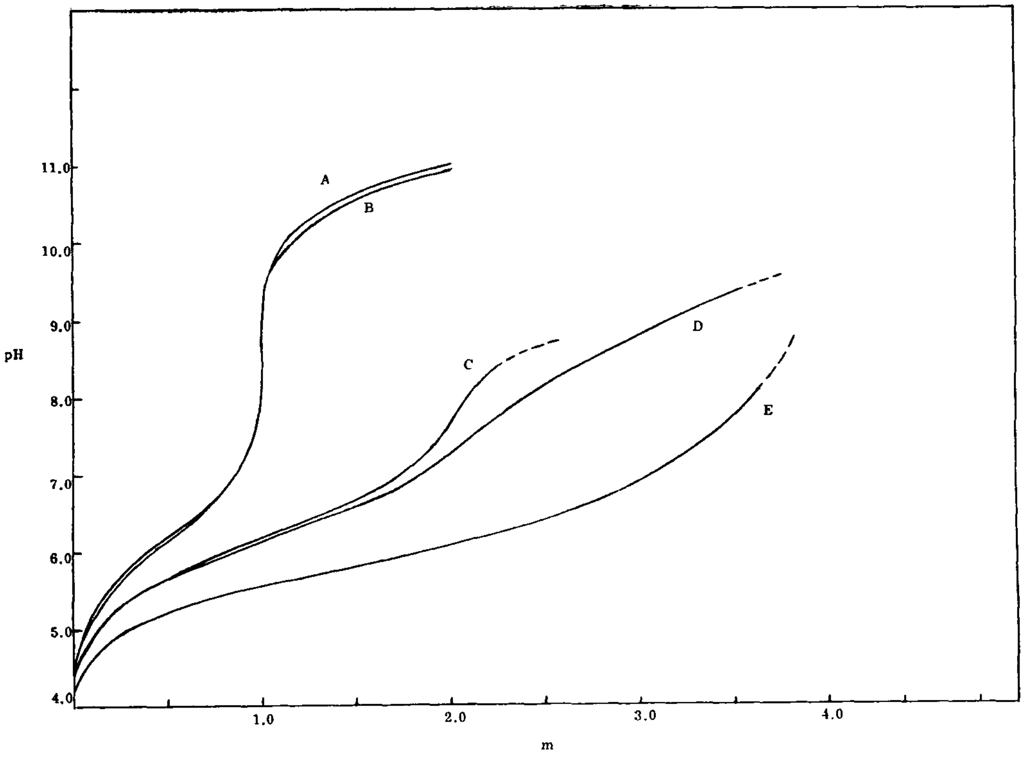


FIGURE 2 Potentiometric titration curves for 2-aminoethylphosphonic acid. A = Free ligand, B = 1:1 Ca(II) + ligand, C = 1:2 Co(II) + ligand, D = 1:2 Ni(II) + ligand, E = 1:2 Cu(II) + ligand. 'm' is the moles of base added per mole of metal ion. For curves A and B, the absicca represents 'a' the moles of base added per mole of ligand. The dotted lines represent unstable pH readings.

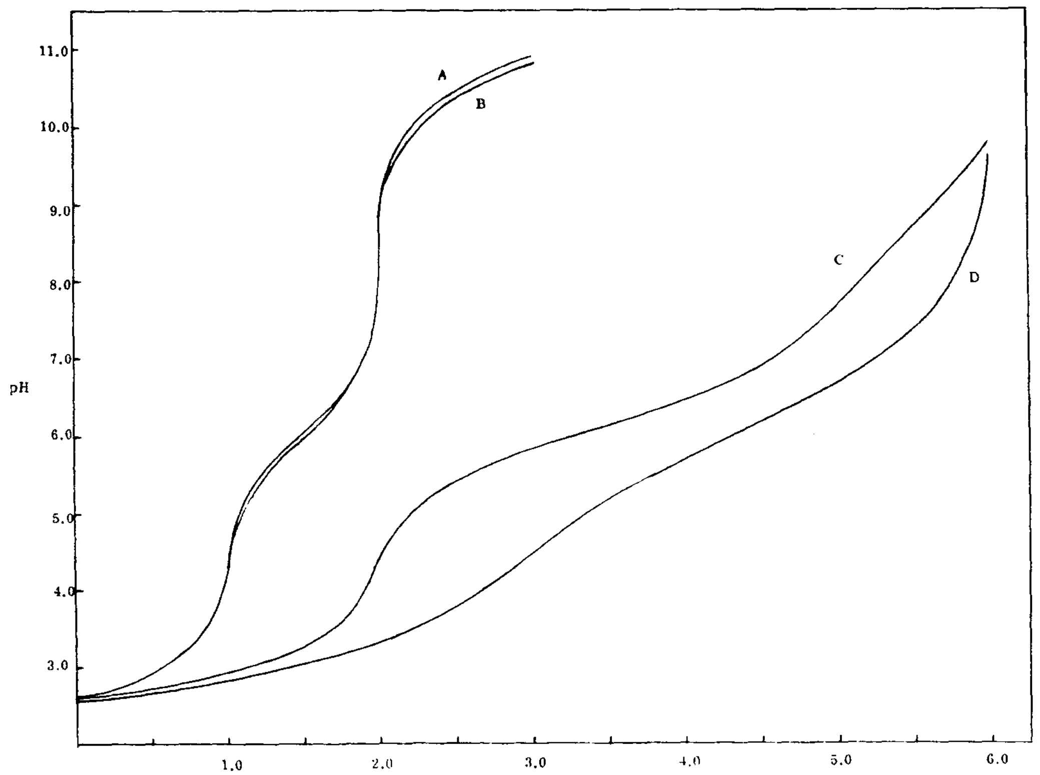


FIGURE 3 Potentiometric titration curves for 2-amino-3-phosphonopropionic acid. A = Free ligand, B = 1:1 Ca(II) + ligand, C = 1:2 Zn(II) + ligand, D = 1:2 Cu(II) + ligand. 'm' represents the moles of base added per mole of metal ion. For curves A and B the absicca represents 'a' the moles of base added per mole of ligand.

formation of protonated and normal 1:1 and 1:2 metal-ligand complexes according to the equilibria 1, 2, 3 and 4 respectively. Since 1-AEP and 2-A-3-PPA are dl mixtures, the 1:2 complexes of these ligands are diastereomeric. No attempt was made to evaluate seperate formation constants for the diastereomers and so the 1:2 constants are mixed constants reflecting the total formation of bis complex. Stability constants are listed in Table II.

$$M + HL \rightleftharpoons MHL \qquad (1)$$
$$M + L \rightleftharpoons ML \qquad (2)$$
$$ML + HL \rightleftharpoons MHL_2 \qquad (3)$$
$$ML + L \rightleftharpoons ML_2 \qquad (4)$$

Titration curves (Figures 1 and 2, B, C, D) for the 1:2 metal-ligand (metal = Ni(II), Zn(II) or Co(II)) and for the 1:1 metal-ligand systems (metal = Mn(II), Mg(II) or Ca(II)) show inflections at m=2 and a=1

TABLE I
Dissociation constants for free ligands
$t = 25.0°$, $\mu = 0.2$ (KNO_3)

Ligand	pK_1 (carboxylate)	pK_2 (phosphonate/ phosphate)	pK_3 (amine)
1-Aminoethylphosphonic acid		5.53 ± .01	10.12 ± .01
2-Aminoethylphosphonic acid		6.21 ± .01	10.98 ± .01
2-Amino-3-phosphonopropionic acid	2.34 ± .01	6.05 ± .01	10.68 ± .01
O-Phosphoethanolamine		5.52 ± .01	10.12 ± .01
O-Phospho-DL-Serine	2.11 ± .01	5.62 ± .01	9.72 ± .01

TABLE II
Stability constants for the complexation of DL-1-Aminoethylphosphonic acid and 2-Aminoethylphosphonic acid with bivalent metal ions
t = 25.0°, $\mu = 0.2$ (KNO_3)

	1-Aminoethylphosphonic acid				2-Aminoethylphosphonic acid			
Metal ion	Log K^{M}_{MHL}	Log K^{M}_{ML}	Log $K^{ML}_{ML_2}$	pK^{MHL}_{ML}	Log K^{M}_{MHL}	Log K^{M}_{ML}	Log $K^{ML}_{ML_2}$	pk^{MHL}_{ML}
Cu(II)[a]	2.55 ± .02	8.35 ± .01	6.76 ± .01	4.32	2.67 ± .02	8.34 ± .01	6.35 ± .01	5.31
Ni(II)	1.00 ± .10	5.18 ± .03	3.92 ± .03	5.94	1.76 ± .02	5.36 ± .02	4.43 ± .03	7.38
Zn(II)	1.70 ± .05	5.67 ± .05		6.15	1.96 ± .04			
Co(II)	1.45 ± .04	4.58 ± .01	3.37 ± .02	6.99	1.70 ± .01			
Mn(II)	1.97 ± .03	3.50 ± .03		8.59	2.12 ± .02			
Mg(II)	1.27 ± .04	1.84 ± .02		9.55	1.37 ± .03	2.24 ± .01		10.11
Ca(II)	1.02 ± .02	1.43 ± .01		9.76	1.09 ± .02	1.43 ± .01		10.64

[a] Log $K^{ML}_{MHL_2}$ are 1.36 ± .15 and 1.73 ± .10 with 1-AEP and 2-AEP, respectively.

respectively (a = moles of base added per mole of ligand). These inflections correspond to the neutralization of the phosphonate protons and calculations in the buffer region before m = 2 and a = 1 indicate the formation of protonated complexes according to equilibrium 1. The stability constants for these complexes are also listed in Table II.

Sufficient data for systems involving 2-AEP and Co(II) (Figure IIC), Zn(II) or Mn(II) could not be obtained beyond the inflection point due to unstable pH readings which continuously drift downwards. Therefqre, no constants were calculated for these systems. Systems involving 2-AEP and Ni(II), Mg(II) or Ca(II) (Figure 2B, D) and 1-AEP with Ni(II), Zn(II), Co(II), Mn(II), Mg(II) or Ca(II) (Figures 1B, C, D) were sufficiently stable to permit collection of data beyond the inflection point and to calculate the stability constants for the normal 1:1 and 1:2 metal-ligand complexes formed according to the equilibria 2 and 4. These values are listed in Table II.

Interaction of 2-A-3-PPA with Cu(II)

The titration curve for a system containing Cu(II) and 2-A-3-PPA in a 1:2 molor ratio exhibits inflections at m=3 and 6 (Figure 3D). Calculations indicate the formation of a protonated 1:1 complex in the region m=0 to m=3 and the normal 1:1 and 1:2 metal-ligand complexes in the region m=3 to m=6, according to the equilibria 1, 2 and 4 respectively. The corresponding stability constants are listed in Table III.

Interaction of 2-A-3-PPA with Ni(II), Zn(II) and Co(II)

Titration curves for systems containing 2-A-3-PPA and Ni(II), Zn(II), or Co(II) in a 2:1 molar ratio show inflections at m=2 and m=6 (Figure 3C). Calculations indicate the absence of complex formation in the region of m=0 to m=2 wherein the carboxylate protons are neutralized. If, for the 2:1 ligand-metal curves, the absicca is taken as 'a' rather than'm', the titration curves for 2-A-3-PPA in the absence and presence of Ni(II), Zn(II) or Co(II) overlap up to the first inflection point, confirming the lack of interaction between the carboxylate binding sites and the above metal ions. However, in the region of m=2 to m=6 calculations indicate the formation of protonated and normal 1:1 and 1:2 metal-ligand complexes according to the equilibria 1, 2, 3 and 4 respectively.

TABLE III
Stability constants for the complexation of DL-2-Amino-3-Phosphonopropionic acid with bivalent metal ions
t = 25.0°, $\mu = 0.2$ (KNO_3)

Metal ion	Log K^{M}_{MHL}	Log K^{M}_{ML}	Log $K^{ML}_{MHL_2}$	Log $K^{ML}_{ML_2}$	pK^{MHL}_{ML}
Cu(II)	5.11 ± .04	10.36 ± .05		6.34 ± .05	5.43
Ni(II)	2.80 ± .02	6.94 ± .06	2.90 ± .06	5.09 ± .02	6.54
Zn(II)	2.16 ± .04	6.63 ± .04	2.45 ± .07	5.16 ± .02	6.21
Co(II)	2.56 ± .02	6.52 ± .03	2.24 ± .10	4.29 ± .01	6.72
Mn(II)	2.60 ± .02	4.90 ± .01			8.38
Mg(II)	1.00 ± .20	2.59 ± .01			9.09
Ca(II)	1.01 ± .10	1.82 ± .03			9.87

Interaction of 2-A-3-PPA with Mn(II), Mg(II) and Ca(II)

Titration curves for systems containing a 1:1 molar ratio of 2-A-3-PPA and Mn(II), Mg(II) or Ca(II) show inflections at a=1 and 2 (Figure 3B). Absense of complexation in the region of a=0 to a=1 is indicated by the overlap of the metal free and metal-ligand curves. The depression of the metal-ligand curves in the region of a = 1 to a = 3 with an inflection at a = 2 indicates the stepwise formation of protonated and normal 1:1 complexes according to the equilibria 1 and 2. Stability constants for these complexes are listed in Table III.

In order to facilitate the comparison of the metal ion binding by 2-AEP and 2-A-3-PPA with the analogous compounds, O-phosphoethanolamine and O-phospho-DL-serine respectively, the dissociation constants for the latter two ligands and their association constants[10] with metal ions are listed in Tables I and IV.

DISCUSSION

1-AEP Metal Complexes

The low values for the formation constants of the MHL complexes are consistent with monodentate phosphonate binding, with the proton on the amine function. At high pH, the complexes ML and ML_2 constitute the major species. The magnitudes of their formation constants suggest bidentate coordination by the ligand for Cu(II), Ni(II), Zn(II), Co(II) and Mn(II). These constants are similar to those reported for glycine chelation of these metal ions.[14] The extent of bidentate coordination for a given metal ion is reflected in the relative decrease of the amine pK_a in the presence of that metal ion. In the case of Mg(II) and Ca(II), the very small decrease in the amine pK_a indicates that the metal binding is predominantly via the phosphonate group.

2-AEP Metal Complexes

The MHL complexes formed with 2-AEP and the various metal ions are relatively more stable than the corresponding complexes with 1-AEP. This is in accord with the higher basicity of the phosphonate moiety in 2-AEP. At high pH, stable ML complexes involving bidentate coordination are formed with Cu(II) and Ni(II) only. The metal ions Co(II), Zn(II) and Mn(II) have a greater tendency to hydrolyze than to form the normal 1:1 complexes. The alkaline earth metals, Mg(II) and Ca(II) with their low tendencies to hydrolyze, do form the ML complexes. As with 1-AEP, the low stabilities of these complexes along with the relatively small increase in the acidity of the amine pK_a indicates that once again the binding is predominantly through the phosphonate moiety.

2-A-3-PPA Metal Complexes

The stabilities of the MHL complexes in systems involving 2-A-3-PPA and the metal ions Ni(II), Zn(II), Co(II), Mn(II), Mg(II) and Ca(II) are of the same magnitude as those of the corresponding complexes of 1-AEP and 2-AEP, indicating that the metal ions are bound by the phosphonate group only. The MHL complex formed in the Cu(II)–2-A-3-PPA system is much more stable than the corresponding complexes with the other metal ions. This would indicate that the Cu(II) complex is a chelate with the metal ion bound by the carboxylate and phosphonate groups and the proton residing on the amine moiety.

The ML complexes with Cu(II), Ni(II), Zn(II),

TABLE IV

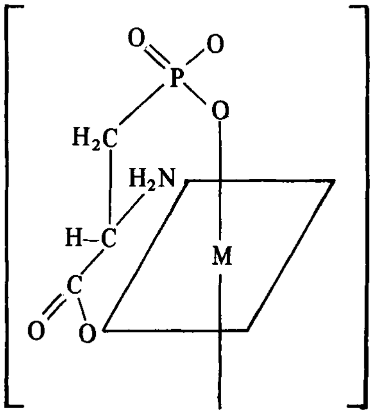
Stability constants for the complexation of O-Phosphoethanolamine and O-Phospho-DL-Serine with bivalent metal ions

t = 25.0°, μ = 0.2 (KNO_3)

Metal ion	O-Phosphoethanolamine			O-Phospho-DL-Serine				
	Log K^{M}_{MHL}	^{a}Log K^{M}_{ML}	pK^{MHL}_{ML}	Log K^{M}_{MHL}	Log K^{M}_{ML}	Log $K^{ML}_{MHL_2}$	Log $K^{ML}_{ML_2}$	pK^{MHL}_{ML}
Cu(II)	2.54 ± .10			4.72 ± .03	9.38 ± .03		6.00 ± .03	5.06
Ni(II)	1.87 ± .10			2.35 ± .02	6.29 ± .02	1.98 ± .11	4.58 ± .01	5.78
Zn(II)	1.77 ± .10			1.96 ± .04	5.80 ± .03	1.94 ± .17	4.25 ± .02	5.88
Co(II)	1.69 ± .09			2.21 ± .03	5.37 ± .02	1.95 ± .11	3.65 ± .01	6.56
Mn(II)	1.89 ± .03			2.33 ± .04	3.80 ± .03			8.25
Mg(II)	1.17 ± .10	1.56 ± .08	9.75	1.30 ± .06	2.00 ± .02			9.02
Ca(II)	1.16 ± .08	1.54 ± .05	9.74	1.00 ± .06	1.59 ± .02			9.13

[a] Due to unstable pH of the experimental solutions (which show a continuous downward drift) no constants could be obtained for Cu(II), Ni(II), Zn(II), Co(II) and Mn(II).

Co(II) and Mn(II) are significantly more stable than the corresponding complexes of 1-AEP and 2-AEP. This indicates tridentate coordination of the metal ion as in I. For Mg(II) and Ca(II) the formation constants are comparable to those for the AEP's and suggests predominant phosphonate binding.



I

With the metal ions, Ni(II), Zn(II) and Co(II), protonated 1:2 metal-ligand complexes (MHL_2) of low stability are formed. The higher stabilities of the ML_2 complexes of 2-A-3-PPA with the above three metal ions, as compared to the corresponding complexes with the AEP's would indicate that in the former complexes the two ligand molecules are still tridentate. However, the ML_2 complex of 2-A-3-PPA with Cu(II) has a stability comparable to that of 2-AEP. The similarity of these constants may indicate that the two 2-A-3-PPA molecules are bidentate in the ML_2 complex. Alternatively it may reflect the less effective coordination of the two tridentate 2-A-3-PPA molecules with Cu(II) which has typically four strong and two weak binding sites. With the data at hand it is not possible to distinguish between the above two possibilities.

Metal Complexation by the Phosphate and Phosphonate Ligands

In going from the phosphate to the phosphonate linkage two changes are expected to occur. First there may be a change in the basicity of the binding sites and second there will be a change in the size of the chelate rings involving the phosphorus donor.

Comparison of the dissociation constants in Table I shows that conversion of the phosphate type of linkage to phosphonate uniformly increases the basicity of the ligand binding sites. This is apparent in the comparison of the dissociation constants of PEA with 2-AEP and those of PS with 2-A-3-PPA.

Table IV presents equilibrium data for the metal binding of the ligands PEA and PS, for comparison with the data for the phosphonic acid derivatives reported in Tables II and III. The effect of the increased basicity of the phosphonate group is seen in the slightly higher values for the MHL complexes of 2-AEP and 2-A-3-PPA as compared to those of PEA and PS, respectively. At high pH a substantial difference between the two ligands, 2-AEP and PEA is found in their behavior towards Cu(II) and Ni(II). 2-AEP, but not PEA, forms stable ML and ML_2 complexes with the above metal ions. Similarly the formation constants of the ML and ML_2 complexes involving 2-A-3-PPA and the transition metal ions are considerably higher than those for PS. Although this enhanced stability associated with the metal complexes of the phosphonate ligands may be partially due to the increased ligand basicity, the major reason is most likely the fact that a six membered chelate ring can be formed by phosphonate coordination as opposed to the less stable seven membered ring that would be required if the phosphate group of PEA and PS coordinates with the metal ions.

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REFERENCES

1. (a) M. Horiguchi and M. Kandatsu, *Nature 184,* 901 (1959); *Bull. Agr. Chem. Soc. Japan,* **24**, 565 (1960).
   (b) J. S. Kittredge, E. Roberts, D. G. Simonsen, *Biochemistry,* **1**, 624 (1962).
2. (a) M. Horiguchi, *Tanpakushitu-Kakusan-Koso,* **12**, 315 (1967).
   (b) L. D. Quin, *Topics in Phosphorus Chemistry,* Ed. M. Grayson & E. J. Griffith, pp. 23–47, Interscience, New York, 1967.
   (c) J. S. Kittredge, M. Horiguchi and P. M. Williams, *Comp. Biochem. Physiol.,* **29**, 859 (1969).
3. (a) J. S. Kittredge and R. R. Hughes, *Biochemistry,* **3**, 991 (1964).
   (b) J. S. Kittredge, A. F. Isbell and R. R. Hughes, *Biochemistry,* **6**, 289 (1967).
4. (a) W. Wozniak, J. Nicole and G. Tridot, *Bull. Soc. Chim. France,* 4445 (1972).
   (b) M. F. Langohr and A. E. Martell, *J. Inorg. Nucl. Chem.,* **40**, 149 (1978).
5. H. A. Flaska, *EDTA Titrations,* 2nd ed. Pergamon Press, Oxford, 1964.
6. H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolyte Solutions,* 3rd ed., Reinhold, New York, N.Y., 1958.
7. I. G. Sayce, *Talanta,* **15**, 1397 (1968).
8. A. Sabatani, A. Vacca and P. Gans, *Talanta,* **21**, 53, (1974).
9. P. Gans, A. Vacca and A. Sabatani, *Inorganica. Chim. Acta,* **18**, 237 (1976).
10. M. S. Mohan and E. H. Abbott, *Inorganic Chemistry,* In press.
11. V. Chavane, *Ann. Chim.,* **4**, 383 (1949).
12. *Critical Stability Constants,* ed. R. M. Smith and A. E. Martell., Vol. II, Plenum Press, New York, 1975.
13. H. Irving and R. J. P. Williams, *Nature,* **162**, 746 (1948).
14. *Critical Stability Constants,* ed. A. E. Martell and R. M. Smith, Vol. I, Plenum Press, New York, 1974.