Contribution from the Departments of Chemistry, City University of New York, Hunter College, New York, New York 10021, and Montana State University, Bozeman, Montana 59717

Metal Complexes of Amino Acid Phosphate Esters

M. S. MOHAN and E. H. ABBOTT*

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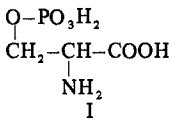
The interaction of *O*-phospho-DL-serine, *O*-phospho-DL-α-methylserine, *O*-phospho-DL-threonine, and *O*-phosphoethanolamine with Cu(II), Ni(II), Zn(II), Co(II), Mn(II), Mg(II), and Ca(II) has been investigated by potentiometry and by ^{31}P NMR. Stability constants for the protonated and normal 1:1 and 1:2 metal–ligand complexes are reported at 25.0 °C and μ = 0.2 (KNO_3). The normal 1:1 and 1:2 metal–ligand complexes are found to have interestingly different structures. Equilibrium data indicate that for the normal 1:1 complexes the phosphate moiety binds the transition-metal ion forming a seven-membered chelate ring. However, the ^{31}P NMR evidence shows that this ring is not formed in the normal 1:2 complexes. Reasons for this are discussed.

Introduction

A number of studies have shown a wide variety of reactivities in the metal ion catalyzed elimination of electronegative substituents from the β position of amino acid Schiff bases.[1] In particular, a recent kinetic study of the metal ion catalyzed elimination of phosphate ion from Schiff bases of *O*-phospho-DL-threonine (TP) reported that Cu(II) and vanadyl(IV) are effective catalysts for the reaction while Ni(II), Al(III), and Th(IV) are not.[1h] The ineffectiveness of the latter group of ions as catalysts was attributed to the possibility that TP can coordinate with them as a tridentate ligand with its phosphate group bound while with the former group phosphate does not bind and TP is bidentate. For phosphate to bind, a relatively uncommon seven-membered chelate ring must form. Potentially this has interesting consequences for the reactivity of such compounds as models for vitamin B-6 systems. Therefore, we have undertaken a detailed study of the interaction of the biologically occurring amino acid phosphate esters *O*-phospho-DL-serine (SP), I, and *O*-phospho-DL-threonine (TP), II, with the metal ions Cu(II), Ni(II), Zn(II),



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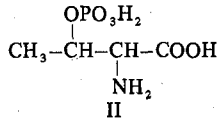


II

Co(II), Mn(II), Mg(II), and Ca(II) to determine the stability of the metal complexes and to decide whether the phosphate moiety is bound to the metal ion or not. Two structurally similar ligands, *O*-phospho-DL-α-methylserine (MSP) and *O*-phosphoethanolamine (PEA), have been included in the study to provide information regarding the structure of the metal complexes. Limited data on the interaction of a few metal ions with SP and PEA have been previously reported.[2]

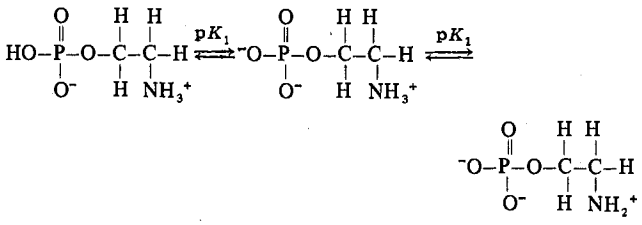
Experimental Section

Materials. The ligands *O*-phospho-DL-serine, *O*-phospho-DL-threonine, and *O*-phosphoethanolamine were obtained from Sigma Chemical Co. The ligand *O*-phospho-DL-α-methylserine was prepared by phosphorylating[3] DL-α-methylserine obtained from United States Biochemical Corp. The purity of all the ligands was checked, and their molecular weights were determined by potentiometric titration with standard carbonate-free sodium hydroxide. The amino acid phosphate esters were used in the triprotonated form (H_3L) while the ligand PEA was used in the diprotonated form (H_2L). Stock solutions of Cu(II), Ni(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 ethylenediaminetetraacetic acid.[4] Carbonate-free sodium hydroxide was prepared and standardized by titrating with potassium hydrogen pthalate (BDH AnalaR, dried for 2 h at 120 °C). Glass-distilled water was used for the preparation of all 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

* To whom correspondence should be addressed at Montana State University.

Scheme I



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 and 1:3, while with Mn(II), Mg(II), and Ca(II), the ratio was 1:1. The concentration of each ligand was approximately 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 °C. Carbon dioxide free nitrogen was bubbled through the solutions and their ionic strength was adjusted initially to be 0.2 by addition of KNO_3. Standard NaOH was added to the titration cell with a Metrohm Dosimat microburet, and changes in pH were monitored with a digital Radiometer pH meter PHM 52 (accurate to the third decimal place), in combination with a Radiometer combination electrode GK 2401C. All data were obtained from homogeneous aqueous media and the titrations were terminated when the pH meter readings became unstable (showed a continuous downward drift). In potentiometric titrations involving metal ions and ligands, pH instability is the first indication of hydrolysis and precipitation. This could be more easily detected with the digital pH meter used in the present study than could be observed with an analog or null type pH meter.

The electrode system was calibrated by direct titration of acetic acid, observed pH meter readings being compared with the actual hydrogen ion concentration calculated from data tabulated by Harned and Owen.[5] The pH regions below 3.5 and above 10.5 were calibrated by measurements in the HCl and NaOH solutions, respectively.

NMR Measurements. Line widths of the ^{31}P resonances were measured using an HA-100 NMR spectrometer operating in the HR mode. The probe temperature was 30 ± 1 °C and the scale was calibrated by the side-band method.

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.[6] The constants were further checked by comparing results with those obtained using the computer programs MINIQUAD[7] and MINIQUAD 75.[8] An IBM 370/168 computer was used for executing the computer programs.

Results

Potentiometric Measurements. Acid Dissociation Constants. Potentiometric titration of PEA in the diprotonated form (Figure 1A) shows that the two protons dissociate in individual steps, probably corresponding to the equilibria shown in Scheme I. Titration of the three amino acid phosphate esters in the triprotonated form shows three distinct buffer regions (Figure 2A) corresponding to the stepwise dissociation of the three protons and may be represented by the equilibria in Scheme II. The values of the various dissociation constants for the ligands PEA, SP, TP, and MSP are listed in Table I.

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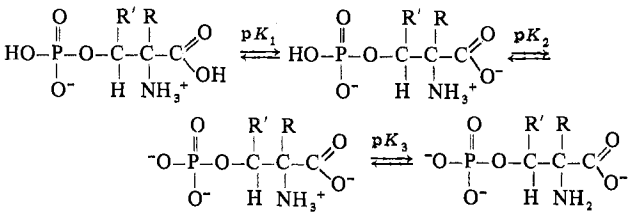
Scheme II[a]



[a] R and R′ = H for SP. R = H and R′ = CH_3 for TP. R = CH_3 and R′ = H for MSP.

Table I. Dissociation Constants for Free Ligands[a]

Ligand	pK_1 (carboxylate)	pK_2 (phosphate)	pK_3 (amine)
O-Phospho-DL-serine	2.11 ± 0.01	5.62 ± 0.01	9.72 ± 0.01
O-Phospho-DL-threonine	2.25 ± 0.01	5.83 ± 0.01	9.67 ± 0.01
O-Phospho-DL-α-methylserine	2.07 ± 0.01	5.68 ± 0.01	10.07 ± 0.01
O-Phosphoethanolamine		5.52 ± 0.01	10.12 ± 0.01

[a] $T = 25.0\,^{\circ}C$, $\mu = 0.2$ (KNO_3). Ranges indicate the standard deviation of the constants.

Table II. Stability Constants for the Complexation of *O*-Phosphoethanolamine with Bivalent Metal Ions[a]

Metal ion	$\log K_{MHL}{}^{M}$	$\log K_{ML}{}^{M}$	$pK_{ML}{}^{MHL}$
Cu(II)	2.54 ± 0.10		
Ni(II)	1.87 ± 0.10		
Zn(II)	1.77 ± 0.10		
Co(II)	1.69 ± 0.09		
Mn(II)	1.89 ± 0.03		
Mg(II)	1.17 ± 0.10	1.56 ± 0.08	9.73
Ca(II)	1.16 ± 0.08	1.54 ± 0.05	9.74

[a] $T = 25.0\,^{\circ}C$, $\mu = 0.2$ (KNO_3). Ranges indicate the standard deviation of the constants.

Interaction of PEA with Metal Ions. Titration curves obtained for systems containing PEA and metal ions are illustrated in Figure 1. With all seven metal ions the titration curves of the ligand in the presence of the metal ions are slightly depressed in the region of $a = 0$ to $a = 1$ (a = moles of base added per mole of ligand) indicating the formation of a protonated metal complex according to equilibrium 1.

$$M + HL \rightleftarrows MHL \quad (1)$$

Further addition of base to systems containing PEA and either Mg(II) or Ca(II) shows that the metal–PEA curves are lower than the metal-free PEA curve up to $a = 2$. This second buffer region corresponds to the formation of a 1:1 normal complex according to equilibrium 2. Data for systems involving PEA

$$M + L \rightleftarrows ML \quad (2)$$

and Cu(II), Ni(II), Zn(II), Co(II), or Mn(II) were obtained only up to $a = 1$. Beyond this point addition of base leads to unstable pH readings which drift downward. Stability constants were, therefore, not calculated for these systems beyond $a = 1$. The stability constants of the protonated complexes for the seven metal ions and the constants for the 1:1 PEA normal complexes with Mg(II) and Ca(II) are listed in Table II.

Interaction of Cu(II) with Amino Acid Phosphate Esters. The titration curve for a system containing Cu(II) and a representative amino acid phosphate ester in a 1:2 molar ratio appears as curve E in Figure 2. Comparison of this curve with the metal-free curve shows that in the presence of Cu(II) ions the entire titration curve is displaced to lower pH values with inflections at $m = 3$ and $m = 6$ (m = moles of base added per mole of metal ion). Calculations show that in the region m = 0 to $m = 3$ a protonated complex is formed according to equilibrium 1. In the region of $m = 3$ to $m = 6$, normal 1:1 and 1:2 metal–ligand complexes are formed according to equilibria 2 and 3. Analysis of the titration curve obtained

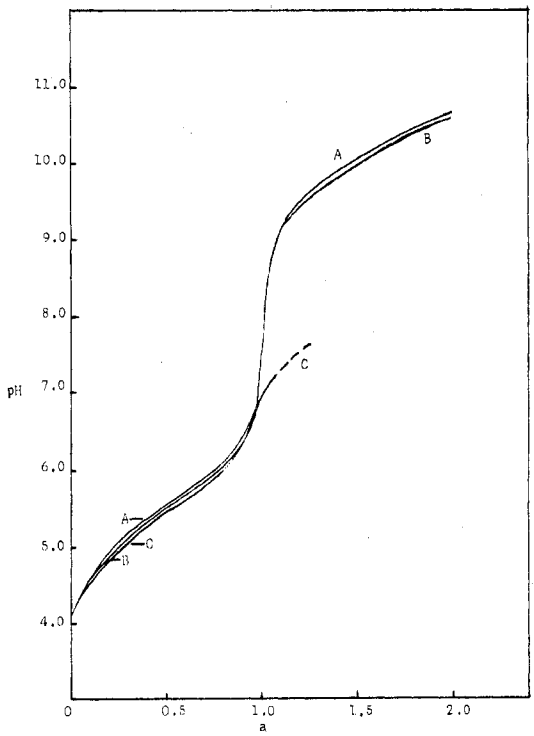


Figure 1. Titration curves for *O*-phosphoethanolamine with a = moles of base added per mole of ligand: A, free ligand; B, Mg(II) + ligand (1:1); C, Zn(II) + ligand (1:1). A titration curve similar to B was obtained with Ca(II), and similar titration curves to C were obtained with Cu(II), Ni(II), Co(II), and Mn(II).

$$ML + L \rightleftarrows ML_2 \quad (3)$$

for a system containing Cu(II) and SP in a 1:3 molar ratio indicates that ML_3 complexes are not formed.

Interaction of Ni(II), Zn(II), and Co(II) with Amino Acid Phosphate Esters. Titration curves for systems containing an amino acid phosphate ester and Ni(II), Zn(II), or Co(II) in a 2:1 molar ratio show inflections at $m = 2$ and $m = 6$, Figure 2C and 2D. Calculations indicate the absence of complex formation in the region of $m = 0$ to $m = 2$ wherein the carboxylate protons are dissociated off. With "a" as the abscissa, titration curves in the presence of the above metal ions overlap with the metal-free curves up to the first inflection point, confirming the lack of interaction between the carboxylate binding sites and the metal ions in the acidic pH range. 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 equilibria 1–4. For-

$$ML + HL \rightleftarrows MHL_2 \quad (4)$$

mation constants for the ML_3 complexes formed according to equilibrium 5 were calculated from titration curves obtained for systems containing Ni(II), Zn(II), or Co(II) and SP in a 1:3 molar ratio.

$$ML_2 + L \rightleftarrows ML_3 \quad (5)$$

Interaction of Mn(II), Mg(II), and Ca(II) with Amino Acid Phosphate Esters. Titration curves for systems containing a 1:1 molar ratio of the amino acid phosphate ester and Mn(II), Mg(II), or Ca(II) show inflections at $a = 1$ and $a = 2$ (Figure 2B). Overlap of the titration curves for the ligand and the metal–ligand solutions in the region of $a = 0$ to $a = 1$ indicates

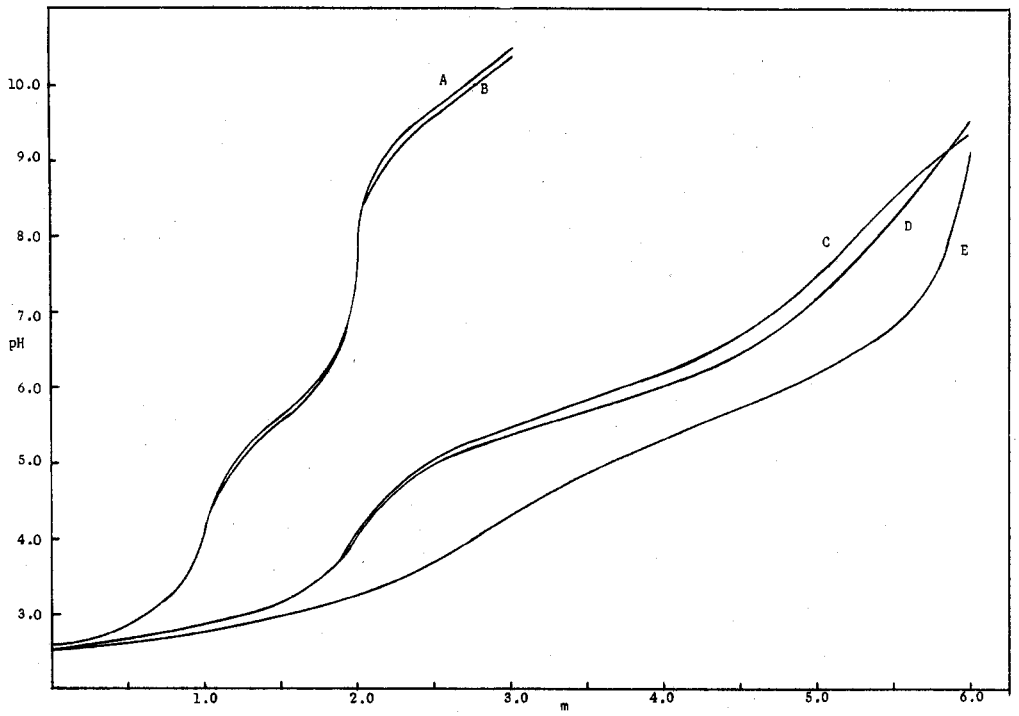


Figure 2. Titration curves for *O*-phospho-DL-serine: A, free ligand; B, Ca(II) + ligand (1:1); C, Zn(II) + ligand (1:2); D, Ni(II) + ligand (1:2); E, Cu(II) + ligand (1:2). Similar curves were obtained with TP and MSP. m = moles of base added per mole of metal ion. For curves A and B the abscissa represents a, the moles of base added per mole of ligand. A curve similar to B was obtained with Mg(II) and Mn(II), and a curve similar to C was obtained with Co(II).

Table III. Stability Constants for Complexation of *O*-Phospho-DL-serine with Bivalent Metal Ions[a]

Metal ion	$\log K_{MHL}^{M}$	$\log K_{ML}^{M}$	$\log K_{MHL_2}^{MHL}$	$\log K_{ML_2}^{ML}$	$\log K_{ML_3}^{ML_2}$	pK_{ML}^{MHL}
Cu(II)	4.72 ± 0.03	9.38 ± 0.03		6.00 ± 0.03		5.06
Ni(II)	2.35 ± 0.02	6.29 ± 0.02	1.98 ± 0.10	4.58 ± 0.01	2.84 ± 0.04	5.78
Zn(II)	1.96 ± 0.04	5.80 ± 0.03	1.94 ± 0.17	4.25 ± 0.02	2.20 ± 0.1	5.88
Co(II)	2.21 ± 0.03	5.37 ± 0.02	1.95 ± 0.11	3.65 ± 0.01	1.95 ± 0.2	6.56
Mn(II)	2.33 ± 0.04	3.80 ± 0.03				8.25
Mg(II)	1.30 ± 0.06	2.00 ± 0.02				9.02
Ca(II)	1.00 ± 0.06	1.59 ± 0.02				9.13

[a] T = 25.0 °C, μ = 0.2 (KNO_3). Ranges indicate the standard deviations of the constants.

Table IV. Stability Constants for the Complexation of *O*-Phospho-DL-α-methylserine with Bivalent Metal Ions[a]

Metal ion	$\log K_{MHL}^{M}$	$\log K_{ML}^{M}$	$\log K_{MHL_2}^{MHL}$	$\log K_{ML_2}^{ML}$	pK_{ML}^{MHL}
Cu(II)	4.58 ± 0.01	9.59 ± 0.02		6.29 ± 0.02	5.06
Ni(II)	1.98 ± 0.03	6.26 ± 0.02	1.93 ± 0.10	4.52 ± 0.01	5.79
Zn(II)	1.90 ± 0.09	5.93 ± 0.06	1.89 ± 0.30	4.45 ± 0.03	6.04
Co(II)	1.71 ± 0.09	5.28 ± 0.06	1.71 ± 0.40	3.68 ± 0.04	6.50
Mn(II)	1.92 ± 0.08	3.65 ± 0.03			8.34
Mg(II)	1.60 ± 0.05	2.36 ± 0.03			9.31
Ca(II)	1.09 ± 0.11	1.82 ± 0.04			9.34

[a] T = 25.0 °C, μ = 0.2 (KNO_3). Ranges indicate the standard deviations of the constants.

Table V. Stability Constants for the Complexation of *O*-Phospho-DL-threonine with Bivalent Metal Ions[a]

Metal ion	$\log K_{MHL}^{M}$	$\log K_{ML}^{M}$	$\log K_{ML_2}^{ML}$	pK_{ML}^{MHL}
Cu(II)	5.12 ± 0.04	9.61 ± 0.07	5.59 ± 0.08	5.18
Ni(II)	2.76 ± 0.02	6.57 ± 0.01	4.59 ± 0.08	5.86
Zn(II)	2.25 ± 0.03	6.00 ± 0.01	4.29 ± 0.02	5.92
Co(II)	2.03 ± 0.03	5.47 ± 0.01	3.58 ± 0.02	6.23
Mn(II)	2.20 ± 0.04	3.81 ± 0.03		8.06
Mg(II)	1.60 ± 0.07	2.27 ± 0.03		9.0
Ca(II)	1.53 ± 0.05	2.23 ± 0.02		8.97

[a] T = 25.0 °C, μ = 0.2 (KNO_3). Ranges indicate the standard deviations of the constants.

the absence of complexation. The lowering of the metal curves in the region of a = 1 to a = 3, with an inflection at a = 2, indicates the stepwise formation of a protonated complex in the region a = 1 to a = 2 and a normal 1:1 complex in the region a = 2 to a = 3, according to eq 1 and 2, respectively.

The stability constants of the various complexes formed in the metal–amino acid phosphate ester systems are tabulated in Tables III–V.

NMR Measurements. In order to determine the extent to which phosphate binds the metal ions in the protonated and

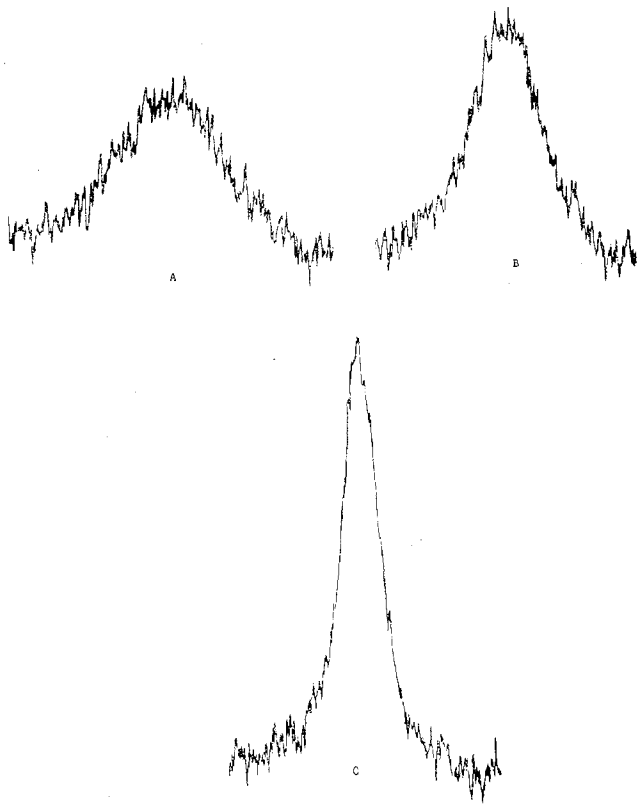


Figure 3. Phosphorus magnetic resonance spectra for *O*-phospho-DL-serine (1.0 M) in the presence of Cu(II) (1.0×10^{-3} M): A, pH 4.2, the percentages of MHL, ML, and ML_2 being 87, 12, and 1, respectively; B, pH 5.2, the percentage of MHL, ML, and ML_2 being 9, 10, and 81, respectively; C, pH 6.1, the percentage of ML_2 being 99.5.

normal 1:1 and 1:2 metal–ligand complexes, measurements of the ^{31}P resonance of SP (1.0 M) were made over a wide pH range in the presence of low concentrations (1.0×10^{-3} M) of Cu(II), Ni(II), or Co(II). Results for Cu(II) appear in Figure 3. The equilibrium constants determined potentiometrically were used to estimate the relative concentrations of the various complex species. At the lower pH, broadening of the ^{31}P resonance exceeding 20 Hz is observed. At high pH where ML_2 is largely formed, the ^{31}P resonance becomes quite sharp approaching the diamagnetic limit at these metal ion concentrations. The strong broadening observed at the lower pH where the MHL species for Cu(II) and the MHL_2 species of Ni(II) and Co(II) predominate is consistent with the phosphate binding the metal in these species. At high pH, where ML_2 predominates, little broadening is observed in the presence of Cu(II). For Ni(II) and Co(II), ML_3 species are important at high pH. Little broadening is observed in their ^{31}P resonances, and so their phosphate groups are not bound to the metal ion. Under the conditions of a large excess of ligand necessary to observe the resonance and in the pH region studied (which is limited by solubility restrictions), the concentration of the MHL species for Ni(II) and Co(II) and that of the ML species for Cu(II), Ni(II), and Co(II) do not predominate at any pH. Due to this, the broadening of the ^{31}P resonance at the lower pH may not be definite evidence for phosphate binding in these species. Zn(II) complexes could not be studied because of their insolubility.

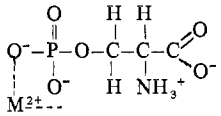
Discussion

Acid Dissociation Constants. Comparison of the acid dissociation constants listed in Table I with those of the amino acids serine, threonine,[9] and organic phosphates like adenosine tri-[10] and diphosphates[11] indicate that the pK_1, pK_2, and pK_3 for the amino acid phosphate esters correspond to the dissociation of protons from the carboxyl, secondary phosphate, and amine groups, respectively. Analogously the pK_1 and pK_2 of PEA would correspond to the dissociation of the protons from the secondary phosphate and amine groups, respectively. The pK of the primary phosphate dissociation is too low to be determined by the pH titration.

The dissociation constants listed in Table I are easily rationalized by the electron-withdrawing and electron-donating effects of the carboxylate and methyl groups, respectively. The presence of a carboxylate group in SP lowers the pK of the ammonium proton as compared to that of PEA by about 0.4 unit. The methyl group in MSP increases the pK of the amine proton by about the same magnitude when compared to SP. The methyl group in TP increases the basicity of the secondary phosphate moiety as compared to SP or MSP.

Metal–PEA Complexes. The formation constants of the MHL species are low and comparable to those reported for other organic phosphoryl compounds like adenosine monophosphate[11] where complexation has been shown to occur through the phosphate moiety alone.[12] Therefore, in the MHL species, PEA binds the metal ions through the phosphate, the proton being on the amine function. Previous studies have reported stability constants for ML complexes formed between PEA and transition-metal ions.[2] However, with the digital pH meter used in this study, the pH of these systems after $a = 1$ was found to be unstable with a continuous downward drift. This indicates metal ion hydrolysis rather than complex formation and hence no constants are reported. On the other hand, Mg(II) and Ca(II) with their low tendencies to hydrolyze do form ML complexes. The low stability of these complexes with the very small increase in the acidity of the amine pK indicates that metal binding is predominantly through the phosphate group.

Metal–Amino Acid Phosphate Ester Complexes. Protonated Metal Complexes. At low pH the carboxylate binding sites of SP, MSP, and TP do not interact with the metal ions Ni(II), Zn(II), Co(II), Mn(II), Mg(II), and Ca(II). The MHL complexes formed in the phosphate buffer region have small formation constants similar to that of PEA suggesting phosphate coordination with the proton on the amine group, as shown in structure III for SP. In systems containing SP



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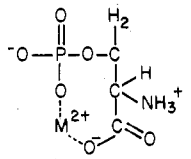
or MSP and Ni(II), Zn(II), and Co(II), MHL_2 complexes are also formed at a higher pH. The magnitude of their formation constants along with the ^{31}P NMR evidence indicates that the second ligand molecule is attached to the metal ion through the phosphate moiety, the proton again being on the amine function.

In the acidic pH region, the mode of interaction of Cu(II) with the amino acid phosphate esters differs from that of other metal ions. The inflection at $m = 3$ in the 1:2 Cu(II)–ligand titration curve and the relatively large formation constant (ca. 10^5) for the MHL complex formed in this region indicates bidentate coordination. The ^{31}P resonance shows intense broadening at a pH where the concentration of the MHL species predominates. Also, PEA does not form bidentate complexes with Cu(II) in the acidic region. Therefore, we conclude that with Cu(II) the MHL species has the structure shown in IV for SP.

ML, ML_2, and ML_3 Complexes. For Cu(II) the ^{31}P NMR data show that there is little broadening of phosphorus resonance for ML_2 under conditions where the phosphorus resonance of MHL is extensively broadened. This indicates



IV

that the phosphate moieties are not bound to the transition-metal ions for ML_2 and that the complexes are bis bidentate. Accordingly, the cumulative formation constants ($\beta = K_{ML}{}^{M}K_{ML_2}{}^{ML}$) of these complexes are quite similar to those where the ligand is alanine,[13] valine, or glycine.[2]

The analogous NMR experiment cannot be performed for ML with Cu(II), Ni(II), or Co(II) because this species is a minor component at ligand concentrations necessary to observe the phosphorus resonance. However, the equilibrium data show that ML complexes of SP are about 10 times more stable than those of alanine.[13] The most reasonable explanation for this difference is that the phosphate group is coordinated to the metal ion in ML and the ligand is tridentate.

For Co(II) and Ni(II) the structure of the ML_2 complex is less clear but appears to be analogous to that of Cu(II). For these metal ions, ML_3 species have appreciable formation constants and must be considered at high pH's and high ligand concentrations. It is clear that the phosphate groups do not bind the metal ions for ML_3, since broadening of the ^{31}P resonance is not observed for these species. Comparison of the change in ^{31}P line width to species concentration changes indicates that as in the Cu(II) case, the phosphate groups do not bind the metal ion in ML_2 for Co(II) or Ni(II); however, the fact that ML_2 does not predominate at any pH for these metals makes the determination more difficult.

It remains to offer an explanation for the difference in chelation by the amino acid phosphate esters in the ML and ML_2 complexes of transition-metal ions. This is most likely due to the high negative charge on the phosphate group. Evidently the charge repulsion of two phosphate groups bound to the same metal ion is so great as to prevent bis tridentate coordination. The large size of the chelate ring formed if phosphate coordinates in the ML_2 complex is unable to overcome the charge repulsion.

In the case of the alkaline earth metal ions the low stability of the ML complexes along with the relatively small increase in the acidity of the protonated amine group indicates that there is no significant binding by the nitrogen atom. Therefore, in these complexes, the amino acid phosphate esters bind Mg(II) and Ca(II) predominantly through their phosphate moieties.

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Registry No. SP, 17885-08-4; TP, 27530-80-9; MSP, 66515-29-5; PEA, 1071-23-4; Cu, 7440-50-8; Ni, 7440-02-0; Zn, 7440-66-6; Co, 7440-48-4; Mn, 7439-96-5; Mg, 7439-95-4; Ca, 7440-70-2.

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Contribution from the Chemistry Division,
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

Telluride Ion Chemistry in Molten Salts

L. M. TOTH* and B. F. HITCH

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The Te^- ion has been shown to be the dominant telluride ion present in molten LiCl–KCl (59–41 mol %) and LiF–BeF_2 (66–34 mol %). It is characterized by an intense band at 497 and 478 nm in the respective solvents, ϵ 3370 L mol^{-1} cm^{-1}, and has a solubility limit of 8×10^{-3} mol % at 550 °C in the chloride melt. Higher tellurides such as Te_3^- are also suggested in the chloride melts by the shift of the 497-nm band and the appearance of a second band at 650 nm. Prerequisites to reliable telluride ion control in molten salt solutions have been shown to be (1) the maintenance of Te_2 vapor in equilibrium with the melts and (2) the prevention of melt contact with oxidizing container materials such as silica.

Introduction

In contrast to the detailed studies[1] reported for tellurium cations, Te_m^{n+}, in high-temperature molten salts, little information is available for the corresponding tellurides in these media. Gruen et al.[2] have reported on the behavior of Li_2Te, Cs_2Te, and Te in molten chlorides at temperatures of 400–1000 °C and have suggested that the soluble telluride species giving rise to a weak band at 471 nm (ϵ 30 L mol^{-1} cm^{-1}) was the Te^{2-} ion. They further suggested that through solvation with the alkali metal ions, the net formal charge on the tellurium was reduced to 1.1– and 1.2– for the lithium and cesium telluride solutions, respectively. More recently, Bamberger et al.[3] examined various telluride species in molten LiF–BeF_2 (66–34 mol %) from 525 to 650 °C and observed a similar band at 478 nm. By prereduction of the melt with silicon to remove oxidizing impurities, they demonstrated that Te^{2-} either had no absorbance in the 200–2000-nm region or, if it did, was too insoluble in the molten fluoride solution to be detected. They therefore suggested that the species giving rise to the band at 478 nm was of higher oxidation state than Te^{2-} and was, most likely, Te_3^-.

Both of these groups used silica cells to contain the telluride solutions and they both noted chemical instability of the solutions due to a reaction with the container accompanied by vapor-phase transport of tellurium metal to colder regions of the cell. As a result of these experimental difficulties, the

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