ions. There are two $Rb^+FOSO_3^-$ molecules in each unit cell. Each Rb^+ ion is coordinated to nine oxygen atoms and two fluorine atoms, forming the distorted polyhedron shown in Figures 3 and 4. The individual Rb–O and Rb–F distances are all unique and range from 2.955 (10) to 3.303 (8) Å. These distances are all within the range expected for normal 11-coordinated Rb–O and Rb–F bonds. There is no evidence of further interactions within the structure.

Registry No. $RbFOSO_3$, 70631-32-2.

Supplementary Material Available: A listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

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Mixed-Ligand Complexes of *O*-Phospho-DL-serine

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The formation of mixed-ligand complexes MHAL and MAL has been studied for A = histamine, 1,10-phenanthroline, or α,α'-bipyridyl, L = *O*-phospho-DL-serine, and M = Cu(II), Ni(II), Co(II), or Zn(II). Equilibrium data and ^{31}P NMR studies show that in the MAL complexes *O*-phosphoserine is tridentate with Ni(II), Co(II), and Zn(II) but bidentate with Cu(II). Due to the square-planar configuration of Cu(II), the phosphate moiety is not bound in the MAL complexes. The mixed-ligand complex $ZnAL^-$ (A = histamine) is exceptionally stable when compared to either binary precursors. This is probably the result of a change in coordination geometry from tetrahedral in the binary complexes to idealized octahedral in the mixed-ligand complexes. With the other mixed-ligand complexes of Ni(II), Co(II), and Zn(II) the formation constants are consistent with the addition of ligands to an essentially octahedral coordination sphere.

Introduction

The final step in the biosynthesis of serine is the hydrolysis of *O*-phosphoserine according to the equation

$$\text{phosphoserine} + H_2O \rightarrow \text{serine} + \text{orthophosphate}$$

This reaction is catalyzed by the enzyme phosphoserine phosphohydrolyase, and a mechanism involving the formation of an enzyme–substrate complex has been suggested.[1] The presence of divalent metal ions is required for the activation of this enzyme.[2] A number of other metal ion activated enzymatic reactions have been shown to proceed via higher order complexes and to occur within the coordination sphere of the metal ion.[3] For a better understanding of these higher order complexes, information regarding the extent and the nature of interaction between the metal ion, the enzyme, and the substrate would be invaluable. As phosphoserine is potentially tridentate (i.e., binding through the carboxylate, phosphate, and amino moieties), it is expected to bind metal ions strongly. Further the nature and the geometry of the metal ion would determine the extent to which these three sites bind, thus giving rise to a variety of complexes with differing stability and structures. In the activation of phosphoserine phosphohydrolyase it was found that while Mg(II), Co(II), Fe(II), Mn(II), Ni(II), and Zn(II) activate the enzyme, other bivalent metal ions like Cu(II), Cd(II), and Ca(II) do not.[2] This raises the interesting question of whether in the ternary complexes involving the enzyme, metal ion, and phosphoserine the binding sites are different for the above two sets of metal ions. It was therefore considered important to undertake a detailed study of the interaction of bivalent metal ions with phosphoserine and to study the formation of ternary complexes in solutions containing a nitrogen donor, a bivalent metal ion, and phosphoserine. These ternary complexes could serve as models for the enzyme–metal ion–substrate complexes. in a previous study we have reported on the stabilities and structures of the binary metal complexes of phosphoserine with a number of bivalent metal ions.[4] In the present study we have investigated by potentiometry and ^{31}P NMR the stabilities and structures of ternary complexes formed in solutions containing phosphoserine and phenanthroline, bipyridyl, or histamine with the bivalent metal ions Cu(II), Ni(II), Co(II), and Zn(II).

Experimental Section

Materials. The ligands *O*-phospho-DL-serine, 1,10-phenanthroline, α,α'-bipyridyl, and histamine dihydrochloride were obtained from Sigma Chemical Co. The purity of these ligands and their molecular weights were determined by potentiometric titration with standard carbonate-free sodium hydroxide. The phosphoserine was used in the triprotonated form while the amines were employed in the diprotonated form. Stock solutions of Cu(II), Ni(II), Co(II), and Zn(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 phthalate (BDH AnalaR, dried for 2 h at 120 °C). Double-distilled water was used for the preparation of all stock and experimental solutions.

Potentiometric Measurements. Dissociation constants for the free ligands were determined by potentiometric titration of the ligands with standard carbonate-free sodium hydroxide. The stability constants for the binary complexes were computed from titrations in which the metal:ligand ratio was 1:2, while the constants for the ternary complexes were computed from titrations in which the total concentrations of the metal ion, the amine, and phosphoserine were in a 1:1:1 molar ratio. The concentration of the metal ions was approximately 2.0×10^{-3} M. Multiple titrations were carried out for each system.

All potentiometric titrations were carried out at 25.0 ± 0.1 °C with the apparatus and procedure described previously.[4] A constant ionic strength of 0.15 was maintained by the addition of potassium nitrate.

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Table I. Stability Constants for the Binary Complexes of *O*-Phospho-DL-serine, 1,10-Phenanthroline, and α,α′-Bipyridyl [t = 25.0 °C, μ = 0.15 (KNO_3)][a]

ligand	metal	log K^{M}_{MHL}	log K^{M}_{ML}	log $K^{ML}_{MHL_2}$	log $K^{ML}_{ML_2}$
O-phospho-DL-serine	Cu(II)	4.75 ± 0.01	9.40 ± 0.01		5.95 ± 0.02
	Ni(II)	2.45 ± 0.03	6.32 ± 0.06	2.29 ± 0.16	4.66 ± 0.03
	Co(II)	1.94 ± 0.10	5.31 ± 0.08	2.32 ± 0.2	3.85 ± 0.04
	Zn(II)	2.01 ± 0.06	5.82 ± 0.06	2.20 ± 0.2	4.29 ± 0.03
1,10-phenanthroline	Cu(II)		CF		7.11 ± 0.03
	Ni(II)		CF		8.82 ± 0.08
	Co(II)		CF		7.64 ± 0.06
	Zn(II)		CF		5.97 ± 0.04
α,α′-bipyridyl	Cu(II)		CF		5.30 ± 0.02
	Ni(II)		CF		CF
	Co(II)		CF		5.59 ± 0.03
	Zn(II)		4.95 ± 0.04		4.78 ± 0.01

[a] Ranges indicate the standard deviations of the constants. *O*-Phospho-DL-serine: pk_1 = 2.11 ± 0.01, pk_2 = 5.64 ± 0.01, pk_3 = 9.75 ± 0.01. 1,10-Phenanthroline: pk_2 = 4.96 ± 0.01. α,α′-Bipyridyl: pk_2 = 4.42 ± 0.01. For 1,10-phenanthroline and α,α′-bipyridyl the first proton is completely dissociated. CF: complexes are completely formed.

The equilibrium constants reported for the various systems are all concentration constants (concentration of H^+ and all other species).

Calculations. The dissociation constants for the free ligands and stability constants for the binary and ternary equilibria in eq 1–12 were calculated from the titration data by using a corrected version of the computer program SCOGS.[6] [A = phenanthroline, bipyridyl, or histamine; L = phosphoserine.]

$$M + HA \rightleftharpoons MHA \quad (1)$$

$$M + HL \rightleftharpoons MHL \quad (2)$$

$$M + A \rightleftharpoons MA \quad (3)$$

$$M + L \rightleftharpoons ML \quad (4)$$

$$MA + HA \rightleftharpoons MHA_2 \quad (5)$$

$$ML + HL \rightleftharpoons MHL_2 \quad (6)$$

$$MA + A \rightleftharpoons MA_2 \quad (7)$$

$$ML + L \rightleftharpoons ML_2 \quad (8)$$

$$M + H + A + L \rightleftharpoons MHAL \quad (9)$$

$$MA + HL \rightleftharpoons MHAL \quad (10)$$

$$M + A + L \rightleftharpoons MAL \quad (11)$$

$$MA + L \rightleftharpoons MAL \quad (12)$$

In the case of binary systems involving phosphoserine, the stability constants for equilibria 2, 4, 6, and 8 were calculated by taking into account the species H, H_3L, H_2L, HL, L, M, MHL, ML, MHL_2, and ML_2. In the case of binary systems involving histamine the stability constants for equilibria 1, 3, and 7 were calculated by taking into account the species H, H_2A, HA, A, M, MHA, MA, and MA_2. In the case of Cu(II), the species MHA_2 was also taken into consideration to obtain constants for equilibrium 5. Constants for equilibria 3 and 7 for the binary Zn–bipyridyl 1:2 system were obtained by taking into account the species H, HA, A, M, MA, and MA_2. Similar calculations for all other binary systems involving phenanthroline and bipyridyl show that the MA complexes are completely formed initially. In these cases the constants for equilibrium 7 were obtained by taking into account the species, H, HA, A, MA, and MA_2.

For ternary systems containing histamine–M^{2+}–phosphoserine in a 1:1:1 molar ratio, the constants for equilibria 9 and 11 were obtained by taking into account the species H, H_3L, H_2L, HL, L, H_2A, HA, A, M, MHL, ML, MHL_2, ML_2, MHA, MA, MA_2, MAHL, and MAL. In the case of Cu(II), the species MHA_2 was also included. In calculations of stability constants for ternary complexes containing phenanthroline or bipyridyl, the MA complexes were considered to be completely formed. Constants for equilibria 9 and 11 were therefore calculated by taking into account the species H, H_3L, H_2L, HL, L, MA, MHAL, and MAL. As found in a previous study for related systems,[7] these constants were in good agreement with the constants obtained by a more explicit calculation in which, in addition to the above species, the species HA, A, M, MA_2, MHL, ML, MHL_2, and ML_2 are also taken into account. Values for MA were taken from the work of Irving and Mellor.[8] In the case of the Zn–bipyridyl system, the values obtained in the present work were used. Constants for equilibria 10 and 12 were obtained from the constants for equilibria 3, 9 and 3, 11, respectively.

The program SCOGS is essentially a curve-fitting routine. To minimize the possibility of fitting the data to an incorrect model, we calculated all constants for binary complexes from the binary solutions. The constants obtained were held fixed while the constants for the ternary solutions were being obtained. Each time several constants were obtained simultaneously, separate test attempts were made to fit the data by using all but one of the constants. In each such test the obtained fit was beyond the bounds of experimental error.

NMR Measurements. Line widths of the ^{31}P resonances were measured with a Varian HA-100 NMR spectrometer operating in the HR mode. The probe temperature was 25 ± 1 °C and the scale was calibrated by the sideband method.

Results

Binary Systems. The acid dissociation constants for the free ligands and the stability constants for the binary systems involving *O*-phosphoserine,[4] phenanthroline and bipyridyl,[8] and histamine[9] have been reported earlier. We have redetermined these constants under the conditions used in this work for determining the ternary constants. The acid dissociation constants and the stability constants for the binary metal–ligand systems are reported in Tables I and III.

Analyses of the 1:2 metal–histamine titration curves show that protonated metal complexes (MHA) are first formed with all the metal ions studied. At a higher pH the proton dissociates and the normal complexes MA and MA_2 are formed. In the case of Cu(II) a protonated bis complex MHA_2 is also formed. In the protonated complexes the imidazole moiety is presumably bound to the metal and the proton resides on the amine group. In the normal complexes both the imidazole and the amine groups bind the metal ion.

The binary constants for *O*-phosphoserine determined in this work at 25.0 °C and μ = 0.15 (KNO_3) are in good agreement with those reported earlier[4] at 25.0 °C and μ = 0.2 (KNO_3). The small differences can be attributed to the change in the ionic strength.

Except in the case of Zn(II) and bipyridyl, analysis of the potentiometric titration curves for the 1:2 metal–phenanthroline or –bipyridyl system showed that the 1:1 metal–ligand complexes are completely formed initially. A partition method has been previously used to evaluate the formation constants for these complexes.[8] However, as discussed earlier, the ternary constants are not influenced to any appreciable degree

Table II. Stability Constants for the Ternary Complexes Involving 1,10-Phenanthroline and α,α′-Bipyridyl [t = 25.0 °C, μ = 0.15 (KNO_3)]

ligand	metal	log K^{MA}_{MHAL}	Δ log K^a	log K^{MA}_{MAL}	Δ log K^b
1,10-phenan-	Cu(II)	4.28	−0.47	8.30	−1.10
throline	Ni(II)	1.99	−0.46	5.87	−0.45
	Co(II)			4.85	−0.46
	Zn(II)			5.38	−0.44
	Cu(II)	4.38	−0.37	8.34	−1.06
α,α′-bipyridyl	Ni(II)	2.25	−0.20	5.93	−0.39
	Co(II)			4.90	−0.41
	Zn(II)			5.60	−0.22

[a] Δ log K = log K^{MA}_{MHAL} − log K^{M}_{MHL}. [b] Δ log K = log K^{MA}_{MAL} − log K^{M}_{ML}.

by whether the 1:1 metal–amine complexes are considered to be initially completely formed or not.

Ternary Systems. Potentiometric titration curves for ternary systems containing bipyridyl are similar to those obtained for ternary systems containing phenanthroline. When the metal ion present is Cu(II), the titration curves (Figure 1) exhibit a small inflection at m = 4 followed by a steep one at m = 5 (m = moles of base added per mole of metal ion). When the metal ion present is Ni(II), Co(II), or Zn(II), the titration curves (Figure 1) exhibit inflections at m = 3 and 5. Analysis of these titration curves for the ternary systems in terms of the species discussed earlier indicates that in the case of Cu(II) and Ni(II) both protonated (MHAL) and normal (MAL) ternary complexes are formed while with Co(II) and Zn(II) only the normal complexes are formed. In the case of Ni(II), Co(II), and Zn(II) the titration curve up to m = 3 represents the neutralization of the two protons of the amine and one proton from the carboxylate group of phosphoserine. The titration curve in the region of m = 3–5 represents the neutralization of the phosphate and amine protons of *O*-phosphoserine to form the ternary complexes. In the case of Cu(II) the appearance of the first inflection point at m = 4 instead of m = 3 indicates that the protonated and normal ternary complexes are formed in separate steps.

The titration curves (Figure 1) for the ternary systems involving histamine exhibit inflections at m = 1 and 5. Analysis of these curves in terms of the species discussed earlier indicates that protonated and normal ternary complexes are formed with all the metal ions. The titration curve up to m = 1 probably represents the neutralization of the carboxylate proton of phosphoserine. In the region of m = 1–5 binary and ternary complexes are formed simultaneously.

The stability constants for the various ternary complexes are listed in Tables II and III. The relative stability of the ternary complexes as compared to the corresponding binary complexes can be quantitatively expressed in different ways. We have tabulated the difference in stability, Δ log K, for the addition of phosphoserine to the aqueous metal ion and to the 1:1 metal–amine complex according to eq 13. The advantages

$$\Delta \log K = \log K^{M(amine)}_{M(amine)L} - \log K^{M}_{ML} \qquad (13)$$

of using Δ log K in comparing the stabilities of the binary and

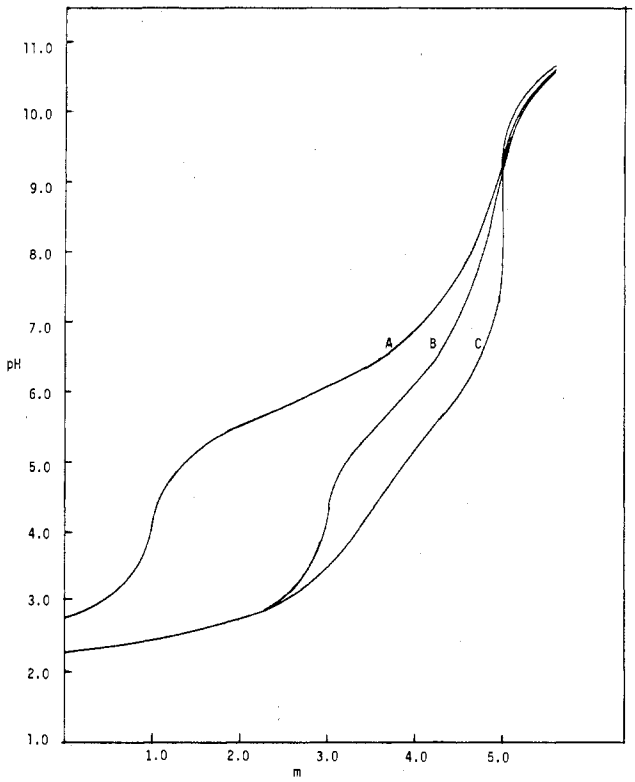

Figure 1. Titration curves for ternary systems. m = moles of base added per mole of metal ion. A = histamine + Ni(II) + phosphoserine (1:1:1). Similar curves were obtained with the other metal ions. B = bipyridyl + Ni(II) + phosphoserine (1:1:1). Similar curves were obtained for Co(II) and Zn(II). C = bipyridyl + Cu(II) + phosphoserine (1:1:1).

ternary complexes have been recently reviewed.[10]

NMR Measurements. For a determination of whether the phosphate moiety of phosphoserine binds Cu(II) in the protonated and normal ternary complexes, measurements of the ^{31}P resonance of *O*-phosphoserine (1.0 M) were made in the presence of low concentrations of Cu(II) (1.0×10^{-3} M) and phenanthroline (1.0×10^{-3} M) at a number of pH values. The results appear in Figure 2. At the lower pH strong broadening of the ^{31}P resonance is observed while at the higher pH the ^{31}P resonance becomes quite sharp. The computer program COGSNR[6] was used to calculate the relative concentrations of the various binary and ternary complex species. Under these conditions and in the pH range selected, the ternary complexes MHAL and MAL account for greater than 97% of all of the Cu(II). The remaining Cu(II) does not lead to substantial broadening of the ^{31}P resonance of 1 M phosphoserine even if it is predominantly bound to the phosphate group.[4] Therefore in Figure 2 the broadening observed is most likely due to differences in the proximity of the phosphate group to Cu(II) in MAL vs. MHAL. Comparison of ^{31}P line width to the percentages of MAL and MHAL given in the figure caption shows that MHAL has a line width in excess of 60 Hz while the line width of MAL is less than 7 Hz. This is

Table III. Stability Constants for the Binary and Ternary Complexes Involving Histamine [t = 25.0 °C, μ = 0.15 (KNO_3)][a]

metal	log K^{M}_{MHA}	log K^{M}_{MA}	log $K^{MA}_{MA_2}$	log K^{M}_{MHAL}	log K^{MA}_{MAL}	Δ log K^c
Cu(II)[b]	3.16 ± 0.03	9.58 ± 0.01	6.52 ± 0.01	23.49 ± 0.01	8.23	−1.17 (−0.63)
Ni(II)	1.89 ± 0.03	6.86 ± 0.01	5.15 ± 0.01	18.94 ± 0.05	5.55	−0.77 (−0.83)
Co(II)	1.63 ± 0.05	5.21 ± 0.01	3.77 ± 0.01	17.48 ± 0.10	4.70	−0.61 (−0.48)
Zn(II)	1.53 ± 0.04	5.27 ± 0.01	4.96 ± 0.01	18.26 ± 0.04	5.83	+0.01 (+0.17)

[a] Ranges indicate the standard deviations of the constants. Histamine: pK_1 = 6.14 ± 0.01, pK_2 = 9.87 ± 0.01. [b] log $K^{MA}_{MHA_2}$ for equilibrium 5 is 2.28 ± 0.02. [c] Δ log K = log K^{MA}_{MAL} − log K^{M}_{ML}. Values in parentheses refer to serine have been calculated from the data in ref 18.

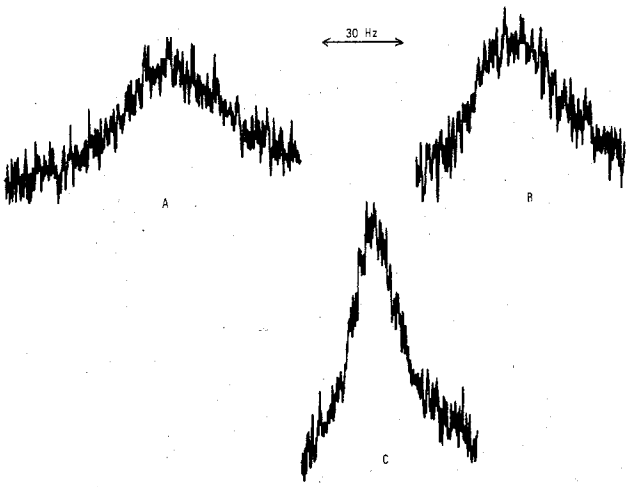

Figure 2. Phosphorus nuclear magnetic resonance spectra for phosphoserine (1.0 M) in the presence of Cu(II) and phenanthroline (1.0×10^{-3} M each): (A) pH 4.2, the ternary complexes MHAL and MAL comprising 96 and 3%, respectively, of the total metal; (B) pH 5.2, MHAL and MAL comprising 74 and 25%; (C) pH 6.0, MHAL and MAL comprising 34 and 63%. In the pH range 4.2–6.0 the total of the binary complexes of phenanthroline and phosphoserine is less than 3%.

consistent with phosphate–Cu(II) binding in MHAL and no phosphate–Cu(II) binding in MAL. Similar results were obtained for phosphoserine itself.[4]

Discussion

Ternary Systems Involving Bipyridyl and Phenanthroline. *O*-Phosphoserine should bind a 1:1 metal–amine complex with a smaller equilibrium constant than for the binding with a corresponding aqueous metal ion. This is due to possible interligand repulsions in the mixed-ligand complex as well as to the fewer number of sites left for the second ligand to bind. One can therefore expect negative values for $\Delta \log K$ as defined by eq 13. The data listed in Table II show that negative $\Delta \log K$ values are obtained for all systems involving bipyridyl and phenanthroline; they also show that ternary systems involving Cu(II) are destabilized the most. Values of $\Delta \log K$ for the addition of phosphoserine are −1.1 and −1.06 when the amine attached to Cu(II) is phenanthroline and bipyridyl, respectively. Similar results are observed for Cu(II) in other ternary systems like metal–ethylenediaminetetraacetic acid–imidazole,[12] metal–nitrilotriacetic acid–histidine[13] or –glycine.[14] To a degree, this behavior of Cu(II) can reasonably be attributed to its lower coordination number and fewer remaining binding sites for the second ligand.

In ternary complexes involving bipyridyl or phenanthroline and a second ligand, Cu(II) is expected to adopt a square-planar (or grossly distorted octahedral) structure.[15,16] Strong donor atoms are bound in the tetragonal plane, and coordination to the axial position is weak. Thus if, in the MAL complex, the bidentate amine occupies two of the four planar sites, the potentially tridentate phosphoserine can only bind to the remaining two strong planar sites and the phosphate moiety would be unbound or only weakly bound to an axial site, leading to the decrease stability. The ^{31}P NMR studies show that in the MAL complexes the phosphate moiety does not bind Cu(II). A previous study showed that the phosphate does bind Cu(II) in the binary ML complex.[4] Therefore the large negative value of $\Delta \log K$ is partially a reflection of the unbound phosphate group in the mixed-ligand complex. The probable structure of the MAL complex of Cu(II) is shown in Figure 3.

In the present study, ^{31}P NMR shows that for the protonated ternary Cu(II) complex MHAL (A = bipyridyl or phenanthroline) the phosphate group is bound to the Cu(II). Previously we showed that, for protonated binary MHL complexes of Cu(II) with phosphoserine, the metal binding sites are the phosphate and carboxylate groups.[4] Similar coordination is evidently the case in the protonated mixed-ligand case.

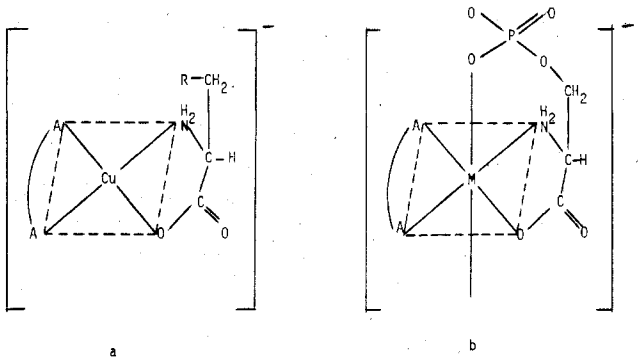

Figure 3. Probable structures for MAL complexes: (a) M = Cu(II); (b) M = Ni(II), Co(II), or Zn(II). AA = bidentate amine. R = PO_4^{2-}.

For the metal ions Zn(II), Ni(II), and Co(II), $\Delta \log K$ should be at least −0.4 assuming octahedral coordination and statistical factors only.[16] The values reported in Table II are close to this figure and so it may reasonably be assumed that *O*-phosphoserine is a tridentate ligand in these mixed-ligand complexes as shown in Figure 3.

Ternary Systems Involving Histamine. In ternary systems containing histamine–M^{2+}–phosphoserine in a 1:1:1 molar ratio, both protonated and normal ternary complexes are formed with all the metal ions studied. Since the basicities of the amine groups of histamine (9.87) and that of phosphoserine (9.75) are quite similar, it is difficult to say whether the proton in the MHAL complex is on the amine group of phosphoserine or histamine. Therefore the overall formation constants for the formation of protonated ternary complexes according to equilibrium 9 are listed in Table III. These constants follow the normal Irving–Williams order.[17]

For Cu(II), Ni(II), and Co(II), the $\Delta \log K$ values for the ternary normal complexes with histamine are somewhat more negative than the corresponding values with bipyridyl and phenanthroline. This could be due either to the steric requirements of histamine or to its reduced ability to accept π electrons in comparison to phenanthroline or bipyridyl. The latter effect has been shown to stabilize mixed-ligand complexes.[16]

Values of $\Delta \log K$ for Cu(II), Ni(II), and Co(II) with histamine are sufficiently similar to those observed in the mixed-ligand complexes of phenanthroline and bipyridine that it may be asserted that the phosphate group is not bound in the case of Cu(II) while it is bound in the case of Ni(II) and Co(II). Further support for these structures comes from comparing the $\Delta \log K$ value for phosphoserine (−1.19) with that of serine (−0.63)[18] in the case of Cu(II). The more negative value for phosphoserine is consistent with the loss of phosphate binding. Phosphate binding is indicated by the similarity of $\Delta \log K$ values for phosphoserine and serine with Ni(II) and Co(II).

The Zn(II) results for histamine are unusual in that a positive $\Delta \log K$ value is observed. Zn(II) can adopt many different coordination geometries which are readily interconvertible.[19] In the case of the bis(histidine) complex, the geometry is essentially tetrahedral[20] while in the case of the aquo–bis(glycine) complex it is octahedral.[21] It is not unreasonable to assume that the binary histamine complex is tetrahedral like the histidine complex while the mixed-ligand complex is octahedral like the bis(glycine) complex. If so, then

the positive $\Delta \log K$ value may be attributed to the shift from tetrahedral to octahedral coordination and concomitant water binding. The $\Delta \log K$ values for Zn(II) with phenanthroline and bipyridine are of the order expected statistically. This would indicate that both the binary and ternary complexes are essentially octahedral in these cases.

The present study shows that the coordination number, the geometry of the metal ion, and the nature of the ligands play an important role in determining the stabilities and structures of the mixed-ligand complexes. These factors may be a few of the many reasons that cause certain metal ions to catalyze and others to inhibit enzymatic reactions.

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Registry No. Histamine, 51-45-6; 1,10-phenanthroline, 66-71-7; 2,2′-bipyridyl, 366-18-7; *O*-phospho-DL-serine, 17885-08-4; Cu, 7440-50-8; Ni, 7440-02-0; Co, 7440-48-4; Zn, 7440-66-6.

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Anisotropic Mixed-Valence Systems. Dimers of the Delocalized Clusters $[Ru_3O(CH_3CO_2)_6(L)_3]^{n+}$

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A series of ligand-bridged cluster dimers of the type $[(py)_2Ru_3O(CH_3CO_2)_6(L)Ru_3O(CH_3CO_2)_6(py)_2]^{2+}$ (L = pyrazine (pyr), 4,4′-bipyridine (4,4′-bpy), *trans*-1,2-bis(4-pyridyl)ethylene (BPE), 1,2-bis(4-pyridyl)ethane (BPA); pyridine (py)) has been prepared. As shown by cyclic voltammetry, the extensive reversible redox chemistry of the individual clusters, e.g., $[Ru_3O(CH_3CO_2)_6(py)_2(pyr)]^{3+/2+/+/0/-/2-}$, appears in the dimers but is even more complex. In the individual clusters, electrons are gained or lost from a series of delocalized, intracluster levels and it is concluded that in the dimers the cluster units can be treated as single "super" redox sites with regard to electronic interactions through the bridging ligands. The extent of intercluster interaction depends both on the bridging ligand and on the electron content of the clusters. In the "mixed-valence" dimers $[(py)_2Ru_3O(CH_3CO_2)_6(pyr)Ru_3O(CH_3CO_2)_6(py)_2]^{m+}$ (m = 1, 3), there appear to be discrete (Ru_3O^+–$Ru^0{}_3O$ or $Ru^{2+}{}_3O$–Ru^+) cluster sites and difference spectra in the near-infrared region provide evidence for low-energy cluster–cluster charge transfer (CCCT) or intervalence transfer (CCIT) absorption bands. Intercluster electronic coupling appears to increase with electron content and in the 1– mixed-valence dimer may be sufficient that the dimer is delocalized.

Introduction

In the study of mixed-valence compounds, the systems chosen for study have largely been symmetrical dimers with a ligand bridging two metal sites, e.g., $(C_5H_5)Fe(C_5H_4$–$C_5H_4)Fe(C_5H_5)$, $[(NH_3)_5Ru(pyr)Ru(NH_3)_5]^{4+}$, and $[(bpy)_2ClRuORuCl(bpy)_2]^{2+}$.[1] Oxidation of the dimers leads to mixed-valence ions for which an adequate description of oxidation state can be difficult to obtain. In one limiting case the excess electron is trapped on one of the metal sites because of differences which exist in the equilibrium inner- and outer-coordination spheres of the metal in the two different oxidation states. In a second, electronic coupling between the sites is sufficiently strong to overcome the vibrational trapping energy and create a new chemical system in which the inner- and outer-coordination spheres at the two metal sites are equivalent. Electronic coupling occurs by orbital overlap which can be promoted by mixing with appropriate orbitals of the bridging ligand. Closely related chemical examples are known where the two different limiting cases have been found.[1-7]

The description of oxidation state in mixed-valence systems and the transition between different limiting forms pose problems of description similar to those which occur in other areas of chemistry including valence tautomerisms in organic chemistry and Jahn–Teller distortions. Mixed-valence systems are important candidates for the study of such problems because systematic variations can be made in the redox sites, in nonbridging ligands, and in the connecting chemical link between the redox sites.

We have extended[8,9] the earlier work of Spencer and Wilkinson[10,11] on the oxo-bridged, triangular clusters $Ru_3O(CH_3CO_2)_6L_3$ (Figure 1). Electrochemical and chemical isolation studies have shown that the clusters undergo a series of reversible one-electron transfers to give the electron-transfer related clusters $Ru_3O(CH_3CO_2)_6L_3{}^{3+/2+/+/0/-}$. The results of spectral studies on the 2+, 1+, and 0 clusters suggest that the multiple electron transfers involve the gain (or loss) of electrons from a series of levels which are largely delocalized Ru–Ru or Ru–O–Ru in character.

We have developed a synthetic procedure for linking cluster units using bridging ligands like pyrazine as in the dimer $[(py)_2Ru_3O(CH_3CO_2)_6(pyr)Ru_3O(CH_3CO_2)_6(py)_2]$ (py is pyridine; pyr is pyrazine). The resulting dimers (of trimers!) are of interest to us because: (1) a redox and metal–metal interaction anisotropy exists in them since there are separate

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