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Mixed Ligand Complexes of Pyrophosphate

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Potentiometric equilibrium measurements have been made at 30°C for the formation of ternary complexes of pyrophosphate and Cu(II), Ni(II) with 2,2′-bipyridyl (bipy), *o*-phenanthroline (phen), oxalic acid (ox), iminodiacetic acid (IMDA), nitrilotriacetic acid (NTA) in 1 : 1 : 1 ratio. The ionic strength was maintained constant by using 0.2M KNO_3 as the supporting electrolyte. The comparison of Δ log K values reveals that the order of stability of ternary complexes is phen $\simeq$ bipy > ox > IMDA > NTA. The order with respect to the metal ions is Ni(II) > Cu(II).

INTRODUCTION

Nucleotides contain a heterocyclic nitrogenase base (either purine or pyrimidine derivative), a pentose sugar and the phosphate (mono, di or tri) moiety. The study of metal interactions with these molecules becomes very important and interesting from the viewpoint of a bioinorganic chemist, as these systems mimic many biological reactions. A large number of papers have appeared on metal-nucleotide, metal-nucleoside or metal-nucleic base complexes to explore the nature of the bonding[1,2]. A series of papers by Sigel *et al.*[3–5] have appeared recently on ternary complexes of nucleotides, nucleosides and nucleic bases[6] on one side and several ligands, viz., *o*-phenanthroline (phen), 2,2′-bipyridyl (bipy), oxalic acid (ox), nitriloacetic acid (NTA), iminodiacetic acid (IMDA)[7], on the other. However, very little is known on the ternary complexes of pyrophosphate. In view of this we have undertaken an investigation of the interaction of pyrophosphate with Cu(II) and Ni(II) metal ions and biologically important ligands (phen, bipy, ox, NTA, IMDA).

EXPERIMENTAL

Pyrophosphate was obtained from Sigma Chemicals while *o*-phenanthroline, 2,2′-bipyridyl, oxalic acid, nitrilotriacetic acid and iminodiacetic acid were obtained from E. Merck. Stock solutions of *o*-phen and bipy in the diprotonated form, ox, IMDA and NTA were prepared from double-distilled water. For every titration, a fresh solid ligand (pyrophosphate) was weighed out into the reaction cell to avoid possible hydrolysis. Metal salts of Cu(II) and Ni(II) were of AnalaR grade, and the metal ions were standardized volumetrically by titration with the sodium salt of EDTA in the presence of suitable indicator as outlined by Schwarzenbach[8]. Carbonate free sodium hydroxide was prepared by the method of Schwarzenbach and Biederman[9] and was standardized by titration with potassium hydrogen phthalate.

The experimental method employed consisted of potentiometric titration of the ligand with a standard sodium hydroxide solution, in the absence and presence of the metal ions being investigated. During the course of titration a stream of nitrogen was passed over the solution to eliminate the adverse effect of atmospheric carbon dioxide. The ionic strength was maintained constant by using 0.2 M KNO_3 as the supporting electrolyte and relatively low concentration of the ligand and metal ion (2×10^{-3} M) ruled out the possibility of having other species like hydroxo, polymeric, etc.

RESULTS AND DISCUSSION

Binary systems

The potentiometric titration curve of the free ligand (diprotonated) $H_2P_2O_7^{2-}$ showed an inflection at a = 1 (where a = moles of base added per mole of the ligand) and followed by a buffer region. The dissociation constants were calculated in the buffer region of a = 0 to 1 and a = 1 to 2.

The titration curves for the binary systems ($M-P_2O_7^{4-}$) showed inflections at m = 1 and 2 (where m = moles of base added per mole of metal ion). The formation constants were calculated in the region at m = 1 to 2.

Ternary systems

(i) Cu(II)-Bipy/phen-$P_2O_7^{4-}$ *systems:* The titration curves of these systems showed a small inflection at m = 3 and followed by a steep inflection at m = 4. The region m = 0 to 2 represents the complete formation of Cu(II)-bipy/phen of 1 : 1 binary complex and the region m = 2 to 3 represents the formation of protonated ternary complex. The protonated ternary formation constants K_{MLHA}^{ML} was calculated in the region m = 2 to 3 taking into consideration the species H_2A, HA, H_2L, HL, M, MA, MHA and ML by using computer programme SCOGS[10]. The normal ternary constant K_{MLA}^{ML} was calculated in the buffer region m = 3 to 4 taking into consideration H_2A, HA, H_2L, HL, M, MA, ML species.

(ii) Cu(II)-ox/IMDA-$P_2O_7^{4-}$ *systems:* The formation curves of these systems showed inflection at m = 2, followed by another inflection at m = 4. The normal ternary constants K_{MLA}^{ML} was calculated in the region m = 2 to 4.

(iii) Cu(II)/Ni(II)-NTA-$P_2O_7^{4-}$ *systems:* The titration curves of these ternary systems showed an inflection m = 3, followed by another inflection at m = 5. The 1 : 1 binary complex [M-NTA] is completely formed in the buffer region of m = 0 to 3. The ligand pyrophosphate adds to the binary complex in the buffer region m = 3 to 5. The normal ternary constants were calculated taking into consideration the species H_3L, H_2L, HL, H_2A, HA, M, ML, MA

(iv) Ni(II)-bipy/phen-$P_2O_7^{4-}$ systems: The formation curves for these systems showed two inflections at m = 2 and 4. In ternary systems of Ni(II)-IMDA/ox-$P_2O_7^{4-}$ precipitation was observed. Hence the mixed ligand formation constants cannot be computed.

The stability constants pertaining to the interaction of pyrophosphate and Cu(II), Ni(II) metal ion with variety of other ligands are compiled in Table 1. Although these stability constants for pyrophosphates and Cu(II), Ni(II) binary systems were reported, we have remeasured them as it is preferable to determine the binary and ternary complexes under the same conditions. Otherwise the experimental difference might show up in Δ log K (defined as the difference in the overall 1 : 1 : 1 stability constants and corresponding 1 : 1 binary complexes).

TABLE 1
FORMATION CONSTANTS OF TERNARY COMPLEXES OF PYROPHOSPHATE AT 30°C and μ = 0.2 M (KNO_3)

Primary ligand (L)	Cu(II)			Ni(II)	
	$\log K^{ML}_{MLHA}$	$\log K^{ML}_{MLA}$	Δ log K	$\log K^{ML}_{MLA}$	Δ log K
Bipy	4.57	7.67	–0.75	4.72	–0.70
Phen	5.87	7.71	–0.71	4.81	–0.61
Ox	–	5.95	–2.47	ppt.	–
IMDA	–	4.94	–3.48	ppt.	–
NTA	–	3.26	–5.16	2.41	–3.01

A = $P_2O_7^{4-}$; pK_a = 5.84; pK_{2a} = 8.0.

$\log K^{Cu}_{Cu}(P_2O_7^{4-})$ = 8.42; $\log K^{Ni}_{Ni}(P_2O_7^{4-})$ = 5.42.

Usually, the role of secondary ligands on the stability of 1 : 1 metal-ligand complex is quantified in terms of Δ log K. Δ log K is the difference between overall 1 : 1 : 1 ternary complexes and the corresponding 1 : 1 binary complexes. Thus if the Δ log K values are positive or less negaive than the statistical values the ternary complexes are more stable than the binary complex. If they are negative, the binary complexes are more stable than the ternary complexes. However, it should be noted here that negative values of Δ log K do not preclude the formation of ternary complexes in solution.

The perusal of the Δ log K values shows that the binary (1 : 1) complexes are more stable than the ternary (1 : 1 : 1) complexes because in all the systems negative Δ log K values have been obtained. However it can be seen that the system M-bipy/phen-$P_2O_7^{4-}$ system has less negative Δ log K values than the other systems studied: M-ox/IMDA/NTA-$P_2O_7^{4-}$. This trend can be explained in terms of electrostatic repulsion between primary ligands such as ox/IMDA/NTA and secondary ligand $P_2O_7^{4-}$, because donor atoms in primary and secondary ligands are oxygens only. One could expect more electrostatic repulsion between negative charges of NTA and $P_2O_7^{4-}$ than ox and $P_2O_7^{4-}$. This is exactly what is observed in Δ log K values: ox < IMDA < NTA.

Bhattacharya *et al.*[11] has shown that the Cu(II)-bipy/phen(1 : 1) complex has discriminating qualities towards secondary ligands to be bonded. It prefers OO > NO > NN. These trends he has explained in terms of Cu(II) → bipy/phen π-interactions which make ternary complexes more stable (less negative Δ log K or positive Δ log K values). Same explanation can be extended here to M-bipy/phen-$P_2O_7^{4-}$ which has less negative Δ log K values than the other systems studied: M-ox/IMDA/NTA-$P_2O_7^{4-}$.

When bipy is bonded to Cu(II), the metal assumes preferably square-planar geometry; the incoming ligand $P_2O_7^{4-}$ has less coordinating sites on [Cu(II)-bipy] than on the [Ni(II)-bipy] (1 : 1) primary complex. The same trend is reflected in the Δ log K values.

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