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Physico-chemical Studies of Ternary Chelates in Solution: Part II* — Stability Constants of Ternary Chelates of Cu(II), Ni(II), Zn(II), Cd(II), Co(II) & Mn(II) with 2,2′-Bipyridyl as Primary Ligand & 2-Phenylacetohydroxamic Acid as Secondary Ligand

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Stability constants of ternary chelates M^{II} (Bipyridyl) (2-phenylacetohydroxamic acid) where M^{II} is Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+} or Mn^{2+} are determined adopting a modified Irving-Rossotti pH-titration technique at different temperatures and ionic strengths. The log $K^{M\ Bip.}_{M\ Bip.PAHA}$ were found to be approximately equal to log $K^{M}_{M\ PAHA}$ values, the former being slightly lower than the latter. This trend in log K values is explained by considering that in M^{II} Bip. complex in addition to L → M σ-bonding there is a strong M → L π-bonding which arises due to dπ-pπ interaction. The effect of ionic strength and temperature on log K values reveals that there is a slight accumulation of negative charge on the metal ion in M^{II} Bip complex resulting in a decrease in the positive charge on the metal ion, suggesting that L → M σ-bonding is slightly stronger than M → L π-bonding in M^{II} Bip.

SOLUTION studies on ternary systems in which two ligands successively combine in steps at different pH regions have been reported by various workers[1-4]. Stability constants of the ternary chelates of the type M^{II} Bip.L where L is an amino acid, polyhydroxy acid, mercapto acid and Bip is 2,2′-bipyridyl, have been determined earlier[5,6]. The methods of determining stability constants of such chelates require the condition that secondary ligand should combine with M^{II} Bip at a pH where is stable and does not undergo hydrolysis. Hydroxamic acids fulfil this condition. In the present investigation we have determined the stability constants of M^{II} Bip.PAHA, where PAHA is 2-phenylacetohydroxamic acid and M^{II} is Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+} or Co^{2+}, adopting a modified Irving-Rossotti pH titration technique.

It was observed that log $K^{M.Bip.}_{M.Bip.\ PAHA}$ values are very close to log $K^{M}_{M.\ PAHA}$ the former being slightly lower. Such a trend was already observed by earlier workers[5-8] and was explained in the light of M→L π-bonding in M^{II} Bip complex. We have undertaken the study of the effect of ionic strength and temperature on $K^{M}_{M.\ PAHA}$ and $K^{M.Bip.}_{M.Bip.\ PAHA}$ to find out the factors responsible for the observed trends in the stability constant values of these complexes.

Materials and Methods

PAHA was prepared by the action of hydroxylamine on ethyl phenylacetate. Metal perchlorates were prepared and estimated by standard methods. Experiments were carried out using a Leeds and Northrup pH meter fitted with glass and calomel electrodes.

The experimental part consisted of the titration of PAHA ($10^{-3}M$), bipyridyl ($10^{-3}M$) and 1:1 mixture of PAHA or bipyridyl and metal ion ($10^{-3}M$) and 1:1:1 mixture of PAHA, bipyridyl and metal ion ($10^{-3}M$) against CO$_2$-free sodium hydroxide ($10^{-1}M$). All the above solutions were acidified with $2\times10^{-3}M$ perchloric acid before titration with sodium hydroxide. These titrations were performed using the above set of solutions with initial ionic strengths 0·02, 0·05, 0·08 and 0·10 at 30°. The titration when $\mu = 0\cdot1$ was also repeated at 40°, 45° and 50°. Sodium perchlorate was used for adjusting the ionic strength.

Results

pH titration curves of Ni^{2+}Bip.PAHA system at $\mu = 0\cdot1$ and 30° are given in Fig. 1. A study of curves II and IV reveals that bipyridyl combines with the metal ion at low pH region (3·0-4·5) and the complex is stable $<p$H 8 beyond which hydrolysis of M^{II}Bip. occurs. Curve VI shows that PAHA coordinates with M Bip. at pH 6-8 where M^{II}Bip. is stable and does not undergo hydrolysis. A study of curves I, IV and VI shows that in the pH region where PAHA combines with M^{II}Bip. the curve IV is coincident with curve I. $\bar{n}_A$, $\bar{n}$ and pL were calculated in this pH region by adopting a modified Irving-Rossotti method. By measuring horizontal distances between curves I and III, III and VI, $\bar{n}_A$ and $\bar{n}$ were calculated using the expressions given by Irving and Rossotti[9]. Such a procedure for calculation was used by earlier workers[6]. From these $\bar{n}$ and pL values at different points on the pH titration curves, log $K^{M.Bip.}_{M.Bip.PAHA}$ values were computed by plotting pL vs log $\left(\frac{1-\bar{n}}{\bar{n}}\right)$

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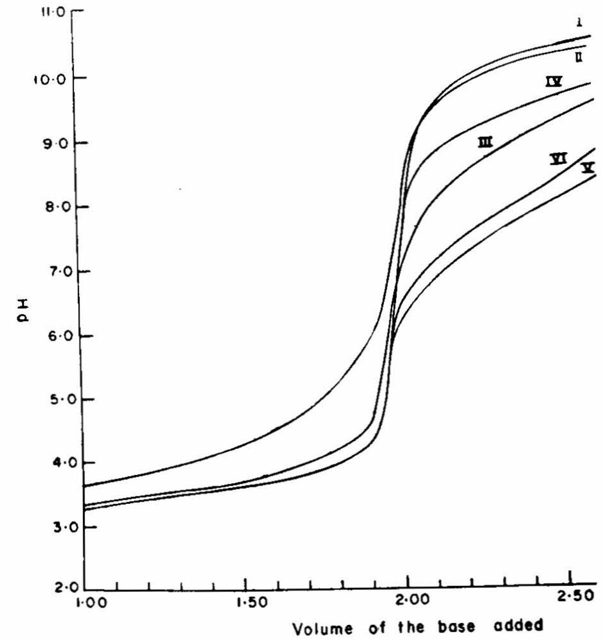

Fig. 1 — pH titration curves of Ni^{2+}Bip.PAHA ternary system at 30° and 0·1 ionic strength [(I) $HClO_4$ ($2 \times 10^{-3}M$); (II) $HClO_4$ ($2 \times 10^{-3}M$) + bipyridyl ($10^{-3}M$); (III) $HClO_4$ ($2 \times 10^{-3}M$) + PAHA ($10^{-3}M$); (IV) $HClO_4$ ($2 \times 10^{-3}M$) + bipyridyl ($10^{-3}M$) + Ni^{2+}($10^{-3}M$); (V) $HClO_4$ ($2 \times 10^{-3}M$) + PAHA ($10^{-3}M$) + Ni^{2+} ($10^{-3}M$); and (VI) $HClO_4$ ($2 \times 10^{-3}M$) + bipyridyl ($10^{-3}M$) + PAHA($10^{-3}M$) + Ni^{2+} ($10^{-3}M$)]

according to the equation $pL = \log K + \log\left(\frac{1-\bar{n}}{\bar{n}}\right)$.

For the sake of comparison log $K^{M}_{M.PAHA}$ values were also computed. All the log K values were found to vary within ±0·03 log units.

Discussion

Curve VI (Fig. 1) is significantly different from curves IV and III indicating the formation of ternary chelates M^{II}Bip.PAHA in solution. A composite curve was calculated by assuming that the only species present were M^{II}Bip. and PAHA without any interaction between them. That curve VI was significantly lower than the composite curve further supports the formation of ternary chelates. Further evidence for the ternary chelate formation was obtained from the experimental observations that (i) hydrolysis occurs in the ternary system at a pH higher than that of M^{II}Bip. system and (ii) in Cu^{2+}PAHA binary system precipitate was invariably obtained before the titration was complete, whereas in the ternary system such precipitates were not obtained.

The log $K^{M\,Bip.}_{M\,Bip.\,PAHA}$ values were found to be much higher than log $K^{M\,(PAHA)}_{M\,(PAHA)_2}$ but close to log $K^{M}_{M\,(PAHA)}$ values. Such a trend was also observed by earlier workers[4-8] using other types of ligands such as amino acids, polyhydroxy acids, etc. This trend in log K values could be explained by considering that in M^{II}Bip. complex in addition to $L \rightarrow M$ σ-bonding there is a strong $M \rightarrow L$ back bonding due to π-interaction of metal d-orbitals and empty p-orbitals of the ligand. Though $L \rightarrow M$ σ-bonding considerably increases the electron density at the metal ion, the $M \rightarrow L$ π-bonding shifts the electron cloud over to ligand orbitals. Bhattacharya *et al.*[5,6] have explained similar trends in log K values in their studies on ternary systems of the type M^{II}Bip.L using polyhydroxy acids, mercapto acids, ethylenediamine, etc., as secondary ligands by assuming that $M \rightarrow L$ π-bonding reduces the electronegativity of M^{II}Bip. as compared with that of M^{II}(aquo).

In the present work as well as in the work reported[4-6] earlier with a variety of ligands such as polypeptides, amino acids, polyhydroxy acids, ethylene- and propylene-diamines it was observed that though log $K^{M\,Bip.}_{M\,Bip.\,L}$ is sufficiently higher than log $K^{ML}_{ML_2}$ it was never exactly equal to log K^{M}_{ML} but always slightly lower, except when the metal ion was Cu^{2} and ligand contained oxygen as donor atoms. In such cases log $K^{M\,Bip.}_{M\,Bip\,L}$ was found to be even higher than log K^{M}_{ML}. In order to find a suitable explanation for this trend the effect of temperature and ionic strength on log $K^{M}_{M.\,PAHA}$ and log $K^{M\,Bip.}_{M\,Bip.\,PAHA}$ were studied.

Effect of ionic strength—The log K^{M}_{ML} and log $K^{M\,Bip.}_{M\,Bip.\,L}$ values were determined at ionic strengths 0·02, 0·05, 0·08 and 0·10. (Table 1).-Linear plots were obtained when log K values were plotted against $\sqrt{\mu}$, $\sqrt{\mu}/1+\sqrt{\mu}$ or $(\sqrt{\mu}/1+\sqrt{\mu})^{-0\cdot3\mu}$ in accordance with the Debye-Hückel, modified Debye-Hückel or Devies equations. But the slopes of these plots did not correspond to the theoretically expected values. At least in the case of Cu^{2} the $\bar{n}_A$ values obtained in the pH region of complex formation unambiguously indicate that PAHA combines predominantly in its undissociated form and hence the expected ΔZ^2 and slope values would be −2·00 and −1·03 respectively. Hence an empirical equation that fits into the data of Cu^{2} chelates was found by plotting

$\log K - \frac{A\Delta Z^2\sqrt{\mu}}{1+\sqrt{\mu}}$ vs μ according to the extended Debye-Hückel equation[10].

$$\log K = \log K^\circ + \frac{A\Delta Z^2\sqrt{\mu}}{1+\sqrt{\mu}} + e\mu$$

where K° = stability constant at infinite dilution; A = Debye-Hückel constant; μ = ionic strength; and ΔZ^2 = the difference in the sums of the squares of charges on product and reactant species.

The value of e was found to be 0·6. The ΔZ^2 values for the interaction of PAHA with the other metal ions were calculated from the plots of log $K - 0\cdot6\mu$ versus $\sqrt{\mu}/1+\sqrt{\mu}$. Taking the Debye-Hückel constant A as 0·5161, ΔZ^2 values for Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+} and Mn^{2+} chelates were found to be −2·00, −2·00, −1·98, −2·44, −2·35 and −2·87 respectively. The ΔZ^2 values indicate that PAHA combines with Cu^{2+}, Ni^{2+} and Zn^{2+} predominantly in its undissociated form according to the equilibrium

$$M^{2+} + \underset{(PAHA)}{HL} \rightleftharpoons ML^{+} + H^{+} \qquad \ldots(1)$$

The higher ΔZ^2 values obtained for Co^{2+}, Cd^{2+} and Zn^{2+} chelates indicate that PAHA combines with

TABLE 1 — STABILITY CONSTANTS OF BINARY AND TERNARY CHELATES AT DIFFERENT IONIC STRENGTHS AT 30°

System	log K value at ionic strength				
	0·00	0·02	0·05	0·08	0·10
PAHA	9·55	9·40	9·33	9·28	9·25
Cu^{2+}PAHA	8·25	8·09	8·01	7·95	7·91
Cu^{2+}Bip.PAHA	8·24	8·10	8·03	7·98	7·95
Ni^{2+}PAHA	5·70	5·55	5·47	5·41	5·38
Ni^{2+}Bip.PAHA	5·47	5·35	5·28	5·23	5·20
Zn^{2+}PAHA	5·97	5·83	5·75	5·70	5·67
Zn^{2+}Bip.PAHA	5·79	5·67	5·60	5·55	5·52
Cd^{2+}PAHA	4·59	4·41	4·32	4·25	4·20
Cd^{2+}Bip.PAHA	4·33	4·15	4·06	3·99	3·95
Co^{2+}PAHA	4·63	4·46	4·36	4·30	4·26
Co^{2+}Bip.PAHA	4·47	4·31	4·23	4·16	4·12
Mn^{2+}PAHA	4·01	3·70	3·59	3·51	3·45
Mn^{2+}Bip.PAHA	3·75	3·48	3·38	3·30	3·25

pK_a of $HBip^+$ at 30° and 0·1 ionic strength was found to be 4·50.

TABLE 2 — STABILITY CONSTANTS OF BINARY AND TERNARY CHELATES AT DIFFERENT TEMPERATURES AT 0·1 IONIC STRENGTH

System	log K at temperatures			
	30°	40°	45°	50°
PAHA	9·25	9·10	9·03	8·95
Cu^{2+}PAHA	7·91	7·75	7·67	7·58
Cu^{2+}Bip.PAHA	7·95	7·80	7·73	7·65
Ni^{2+}PAHA	5·38	5·27	5·22	5·16
Ni^{2+}Bip.PAHA	5·20	5·10	5·05	5·00
Zn^{2+}PAHA	5·67	5·55	5·50	5·44
Zn^{2+}Bip.PAHA	5·52	5·42	5·36	5·31
Cd^{2+}PAHA	4·20	4·09	4·04	3·98
Cd^{2+}Bip.PAHA	3·95	3·86	3·81	3·77
Co^{2+}PAHA	4·26	4·17	4·13	4·08
Co^{2+}Bip.PAHA	4·12	4·04	4·00	3·96
Mn^{2+}PAHA	3·45	3·38	3·35	3·31
Mn^{2+}Bip.PAHA	3·24	3·18	3·15	3·12

these metal ions in both its dissociated and undissociated forms according to the following equilibria:

$$M^{2+} + HL \rightleftharpoons ML^{+} + H^{+} \qquad \ldots(2)$$

$$M^{2+} + L^{-} \rightleftharpoons ML^{+} \qquad \ldots(3)$$

These assumptions are further supported by the observations that PAHA combines with Cu^{2+}, Ni^{2+} and Zn^{2+} in the *p*H regions where PAHA is predominantly in the undissociated form, whereas it combines with Cd^{2+}, Co^{2+} and Mn^{2+} in the *p*H regions where it is present in both dissociated as well as undissociated forms as indicated by $\bar{n}_A$ values in these *p*H regions.

The ΔZ^2 values obtained for the interaction of PAHA with M^{II} Bip. were found to be very close to those of the interaction of PAHA with M^{II} (aquo) the former values being slightly lower than the latter. Though these small differences in ΔZ^2 values could be thought to have arisen due to the experimental errors, neverthless this trend being apparent in all the cases cannot be neglected. Hence, it was thought that the slight lowering of the ΔZ^2 values arises because of the slight lowering of the positive charge on M^{II}Bip. complex compared to M^{II} (aquo).

TABLE 3 — THERMODYNAMIC PARAMETERS OF BINARY AND TERNARY CHELATES AT 30° AND $\mu = 0{\cdot}1$

	$-\Delta G$ kcal/mole	$-\Delta H$ kcal/mole	ΔS e.u.	$-\Delta Z^2$
Cu^{2+}PAHA	10·97	7·04	12·96	2·00
Cu^{2+}Bip.PAHA	11·03	6·77	14·05	1·80
Ni^{2+}PAHA	7·46	4·80	8·75	2·00
Ni^{2+}Bip.PAHA	7·21	4·35	9·44	1·78
Zn^{2+}PAHA	7·86	5·13	9·03	1·98
Zn^{2+}Bip.PAHA	7·65	4·69	9·76	1·78
Cd^{2+}PAHA	5·82	4·78	3·42	2·44
Cd^{2+}Bip.PAHA	5·48	4·16	4·34	2·33
Co^{2+}PAHA	5·90	3·89	6·64	2·35
Co^{2+}Bip.PAHA	5·71	3·52	7·23	2·25
Mn^{2+}PAHA	4·78	3·05	5·71	2·87
Mn^{2+}Bip.PAHA	4·50	2·88	5·35	2·65

Though experimental errors do not permit quantitative estimation of the decrease in the positive charge, the decrease in the positive charge on the metal ion in M^{II} Bip. complex is certainly evident. However, a semiquantitative data for the decrease in the positive charge could be obtained for Cu^{2+}, Ni^{2+} and Zn^{2+} chelates by considering the following equilibrium:

$$M^{(2-x)+}Bip + HL \rightleftharpoons M^{(1-x)+}Bip.L + H^{+} \qquad \ldots(4)$$

The ΔZ^2 is, therefore, equal to $2x$—2, where x is the decrease in the positive charge. These x values were found to be ≈0·1. Such calculations, however, could not be performed for Cd^{2+}, Co^{2+} and Mn^{2+} chelates as it was difficult to say to what extent the equilibria (2) and (3) take part in the overall formation equilibrium of these complexes. But even in these cases the values obtained for ternary system qualitatively suggest that there is a decrease in the positive charge on the metal ion in the complex M^{II}Bip. Hence it could be concluded that in M^{II} Bip complex $L \rightarrow M$ σ-bonding is stronger than $M \rightarrow L$ π-bonding. In the light of these arguments it may be said that because of accumulation of negative charge on the metal ion in M^{II}Bip, the log $K^{M\,Bip.}_{M\,Bip.\,L}$ is always slightly smaller than log K^{M}_{ML}.

Effect of temperature on stability constants — That the positive charge on the metal ion in the complex M^{II} Bip is slightly decreased was further evidenced from the temperature effect studies on log $K^{M\,Bip.}_{M\,Bip.\,L}$ and log K^{M}_{ML} values (Table 2). These log K values were determined at 30° to 50° at constant μ (0·10). From the linear plots of log K vs 1/T, ΔH values were calculated. ΔG and ΔS values were calculated from the following equations:

$$\Delta G = -2{\cdot}303\ TR \log K$$

and

$$\Delta G = \Delta H - T\Delta S$$

A comparison of ΔH and ΔS values of the ternary and binary chelates (Table 3) reveals that both ΔH and ΔS values of ternary chelates are significantly more positive than those of binary chelates. Though the differences in ΔH and ΔS values of binary and ternary chelates lie within experimental errors the differences being apparent in all the cases cannot be overlooked. With the exception of Cu^{2+} chelates the destabilization caused by the lower exothermicity of ternary chelates was found to be more prominent than the stabilization due to more positive ΔS values and hence, log $K^{\mathrm{M\ Bip.}}_{\mathrm{M\ Bip.\ PAHA}}$ is slightly smaller than log $K^{\mathrm{M}}_{\mathrm{M.PAHA}}$. The more prominent stabilization induced by ΔS values of Cu^{2+} chelates could be responsible for the observed trend, log $K^{\mathrm{Cu\ Bip}}_{\mathrm{Cu\ Bip.\ PAHA}} >$ log $K^{\mathrm{Cu}}_{\mathrm{Cu.\ PAHA}}$.

The stability constant values of both binary and ternary chelates were found to follow the order $Cu^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+} > Cd^{2+} > Mn^{2+}$, which is in accordance with the Irving-William order. The ΔH values also follow the same trend. As there is a linear relation between ligand field splitting and log K values, the ligand field stabilization energy would decrease from Cu^{2+} to Mn^{2+} in the same order. That both log K and ΔH values of Cu^{2+} chelates are very large when compared to Zn^{2+} chelates could be due to Jahn-Teller distortion. That Zn^{2+} forms more stable complexes than Ni^{2+} and that Irving-William order is strictly followed indicates that the ligand field produced by PAHA is probably weak. The PAHA binds to metal ion through two oxygen atoms, which are poor donors, and hence would be a weak field ligand. This contention provides theoretical justification to the above conclusion.

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