

Formation constants of ternary complexes of Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) with phenylhydrazones and amino acids

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Abstract. The formation constants of mixed ligand complexes of the type $M(II) LA$, where $M(II) = Cu(II), Ni(II), Co(II), Mn(II)$ or $Zn(II)$ and $L = o$ -hydroxyacetophenonephenylhydrazone (HAPPH), resacetophenonephenylhydrazone (RAPPH) or gallacetophenonephenylhydrazone (GAPPH), $A =$ glycine (Gly), DL-alanine (Ala), or DL-methionine (Met), have been determined *pH*-metrically in 70% (v/v) aqueous methanol at $35 \pm 0.5^\circ C$ and $\mu = 0.1 M$ (KNO_3). The evaluated formation constants have been compared and discussed in terms of donor atoms and the size of the chelate rings. The values for the ternary chelates indicate that they are formed under simultaneous equilibria. Causes for the lower stabilities of the ternary systems as compared to those of the binary systems are discussed.

Keywords. Ternary complexes; phenylhydrazones; amino acids; mixed ligand complexes.

1. Introduction

In recent years, ternary complexes have gained considerable importance because they provide good models for various biological reactions (Sarkar and Wigfield 1968; Lan and Sarkar 1971; Sigel 1973–74; Baxter and Williams 1975). In view of this, in the present investigation, the authors have reported the formation constants of the ternary complexes of Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) with *o*-hydroxyacetophenonephenyl hydrazone (HAPPH), resacetophenonephenylhydrazone (RAPPH), gallacetophenonephenylhydrazone (GAPPH) and amino acids such as glycine, DL-alanine and DL-methionine by *pH*-metric studies in 70% aqueous methanol at $35^\circ C$. The structures of the ligands are given in figure 1.

2. Experimental

The proton–ligand and metal–ligand formation constants for binary systems were determined using Irving–Rossotti *pH*-titration technique (Irving and Rossotti 1954) and formation constants of ternary metal chelates $M(II) LA$ were evaluated by the method of Ramamoorthy and Santappa (1971). All the binary and ternary stability constants were calculated by using the computer program, BEST (Motekaites and

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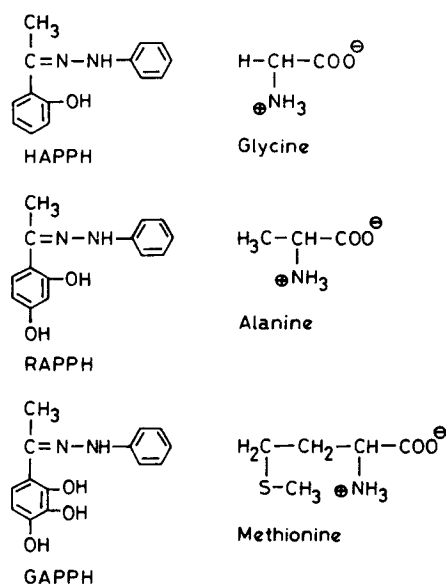


Figure 1. Structures of the phenylhydrazones and amino acids used.

Martell 1982), a FORTRAN program for the refinement of stability constants from *pH*-metric data measured on complex systems containing any number of components. BEST was also used to compute the complete species distribution at various *pH* values. The titrations were performed using a double-walled beaker thermostatted at $35 \pm 0.5^\circ\text{C}$.

HAPPH (m.p. 109°C), RAPPH (m.p. 159°C) and GAPPH (m.p. 144°C) were prepared according to the literature methods (Adams 1919; Vogel 1968). Solutions of the reagents (0.05 M) were prepared in methanol. The metal nitrate solutions (0.1 M) were prepared in double-distilled water and standardised by appropriate standard methods. Lower concentrations (0.05 M) were prepared by proportionate dilution. Standard nitric acid (0.05 M) and potassium nitrate (1 M) solutions were also prepared in double-distilled water.

An Elico digital (LI-120-A) *pH*-meter was used for the *pH* measurements. The experimental procedure involved the titrations of the following solutions (total volume 50 ml) against carbonate-free standard sodium hydroxide solution (0.5 M). The ionic strength of the solution was kept at 0.1 M KNO_3 .

1. 35 ml (solvent) + 2 ml (nitric acid) + 5 ml (KNO_3) + 8 ml (water).
2. 35 ml (solvent) + 2 ml (nitric acid) + 5 ml (KNO_3) + 1 ml (ligand L) + 8 ml (water).
3. 34 ml (solvent) + 2 ml (nitric acid) + 5 ml (KNO_3) + 1 ml (ligand L) + 1 ml (metal salt solution) + 7 ml (water).
4. 35 ml (solvent) + 3 ml (nitric acid) + 5 ml (KNO_3) + 1 ml (ligand A) + 6 ml (water).
5. 35 ml (solvent) + 3 ml (nitric acid) + 5 ml (KNO_3) + 1 ml (ligand A) + 1 ml (metal salt solution) + 5 ml (water).
6. 34 ml (solvent) + 3 ml (nitric acid) + 5 ml (KNO_3) + 1 ml (ligand L) + 1 ml (ligand A) + 1 ml (metal salt solution) + 5 ml (water).

The *pH*-meter readings (*B*) in the aqueous methanol medium were corrected by the method of Van Uitert and Hass (1953).

From the proton–ligand formation curve ($0.2 < \bar{n}_H < 1.8$) of HAPPH, RAPPH and GAPPH, the proton–ligand stability constants were evaluated and were 11.20, 10.26 and 10.12, respectively. From the metal–ligand formation curves, the \bar{n} values ($0.1 < \bar{n} < 1.8$) obtained for the $[M(II)-L]$ system indicated the formation of both 1:1 and 1:2 complexes.

In the ternary systems studied, titration curves for the ternary complex $[M(II)-L-A]$ coincided with either the (1:1) $[M(II)-L]$ or the (1:1) $[M(II)-A]$ binary complexes. This indicates that the formation takes place by simultaneous and not by stepwise equilibrium,



The systems were analysed by calculating K_{MLA} values at different pH values in the buffer region $a = 1.5-2.5$, as

$$K_{MLA} = [T_M - \{(1/2)[A]x\}]/(1/2)^3(A)^3x, \quad (2)$$

$$A = \{2T_M + P - T_{OH} - [H^+]\}/\{2[H^+]/(K_1 + K_1^1)\}, \quad (3)$$

$$x = 1 + 2[H^+]/(K_1 + K_1^1), \quad (4)$$

where K_1 , K_1^1 = dissociation constants of the phenylhydrazones and amino acids, respectively;

T_M = total metal ion concentration;

P = initial concentration of the acid;

T_{OH} = amount of alkali added.

3. Results and discussion

The nature of interaction of ligands L and A with the metal ions in the formation of mixed-ligand complexes was established according to the method suggested by Garey and Martell (1967). The combination of L and A with the metal ion would be stepwise if the 1:1:1 mixed ligand titration curve could be superimposed over the 1:1 ML or 1:1 MA titration curves. It was observed that in each system the MLA curve does not coincide with either the ML or the MA curve. The deviation of the mixed-ligand titration curve from ML or MA starts from the 3.0 pH region. The mixed complex formation, therefore, takes place by simultaneous and not stepwise equilibrium and both the ligands are attached simultaneously to the $M(II)$ ion. The relevant data are presented in table 1.

Table 1. Stability constants.

Ligand	pK_1	$\log K_1$				
		Cu	Zn	Ni	Co	Mn
HAPPH	11.20	7.74	7.16	6.08	5.68	5.11
RAPPH	10.26	6.87	5.96	4.92	4.64	3.93
GAPPH	10.12	9.28	6.27	5.66	5.46	5.04
Gly	9.79	9.10	6.10	6.76	5.64	3.75
Ala	9.91	9.54	5.72	6.42	5.35	3.81
Met	9.41	8.35	5.45	6.34	5.05	3.45

The constants are accurate to $\pm 0.05 \log K$ units.

Table 2. Stability constants of mixed ligand complexes. The $\log K_{MLA}$ values are accurate to $\pm 0.05 \log K$ units.

System	Cu			Zn			Ni		
	$\log K_{MLA}$	$\log K_{ML} + \log K_{MA}$	$\Delta \log K_{MLA}$	$\log K_{MLA}$	$\log K_{ML} + \log K_{MA}$	$\Delta \log K_{MLA}$	$\log K_{MLA}$	$\log K_{ML} + \log K_{MA}$	$\Delta \log K_{MLA}$
M:Gly:HAPPH	12.87	16.84	3.97	9.45	13.26	3.81	9.25	12.84	3.59
M:Gly:RAPPH	10.33	15.97	5.64	9.24	12.06	2.82	8.58	11.68	3.10
M:Gly:GAPPH	12.80	18.38	6.58	8.62	12.37	3.75	8.67	12.42	3.75
M:Ala:HAPPH	14.85	17.28	2.43	12.02	12.88	0.86	12.20	12.50	0.30
M:Ala:RAPPH	16.01	16.41	0.40	11.65	11.68	0.03	10.62	11.34	0.72
M:Ala:GAPPH	17.38	18.82	1.44	11.92	11.99	0.07	11.65	12.08	0.43
M:Met:HAPPH	10.69	16.09	5.40	8.70	12.61	3.91	8.50	12.42	3.92
M:Met:RAPPH	10.54	15.22	4.68	8.54	11.46	2.92	8.76	11.26	2.50
M:Met:GAPPH	11.88	17.63	5.75	8.76	11.72	2.96	8.34	12.00	3.66

System	Co			Mn		
	$\log K_{MLA}$	$\log K_{ML} + \log K_{MA}$	$\Delta \log K_{MLA}$	$\log K_{MLA}$	$\log K_{ML} + \log K_{MA}$	$\Delta \log K_{MLA}$
M:Gly:HAPPH	7.47	11.32	3.85	6.59	8.86	2.27
M:Gly:RAPPH	7.08	10.28	3.20	6.56	7.68	1.12
M:Gly:GAPPH	8.17	11.10	2.93	7.73	8.79	1.06
M:Ala:HAPPH	9.07	11.03	1.96	7.91	8.92	1.01
M:Ala:RAPPH	9.76	9.99	0.23	7.42	7.74	0.32
M:Ala:GAPPH	10.34	10.81	0.47	8.52	8.85	0.33
M:Met:HAPPH	7.17	10.73	3.56	7.85	8.56	0.71
M:Met:RAPPH	7.52	9.69	2.17	6.85	7.38	0.53
M:Met:GAPPH	7.74	10.51	2.77	5.97	8.49	2.52

In general, the logarithms of the stability constants of the mixed-ligand complexes were found to be lower than the sum of individual values for complexes with first and second ligands. Factors like repulsion due to negative charges around the metal ion, simultaneous formation of coordinate bonds and steric factors may contribute to the observed lowering of the stability constant values in the mixed ligand chelates. The values of $\log K_{MLA}$ along with $(\log K_{ML} + \log K_{MA})$ are presented in table 2. The ternary formation curves indicate that the formation of M-phenylhydrazone-Gly/Ala/Met system is simultaneous. The ternary 1:1:1 curve deviates from both the binary curves right from the beginning, the affinities of both the ligands for M(II) being comparable, and therefore the ternary complex is formed in a simultaneous way. This reflects the slight differences in the coordination tendencies of these ligands. The titration curves of the Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) ions studied showed an inflection at $m=2$ indicating the formation of a simultaneous (1:1:1) mixed ligand complex in the buffer region between $m=0$ and $m=2$. This shows that ternary complex formation takes place only in the basic pH region. This was further confirmed by plotting the percentages of the various species present in the solutions against the pH (figures 2 and 3). The order of the stabilities of the ternary complexes with respect to phenylhydrazones is HAPPH > GAPPH > RAPPH while with respect to the amino acids it is Ala > Gly \approx Met. From the perusal of the data (tables 1 and 2) it can be seen that the ternary chelates of phenylhydrazones show similar stability sequences as in the case of binary chelates. Such an observation suggests that the forces that influence the formation of binary and ternary chelates are the same.

From a comparison of $\Delta \log K$ values, it can be observed that among ternary complexes (M(II)-phenylhydrazone-aminoacid) the stability order is Gly > Ala; Met > Ala. In both types of ligands, phenylhydrazones as well as amino acids, the linking atoms are N and O. In all the chelates, phenylhydrazones form six-membered rings whereas with the amino acids the systems form five-membered rings (figure 4). Amino acids are more saturated ligands as compared to phenylhydrazones. Five-membered chelate rings become stable with saturated ligands. Hence, both the types

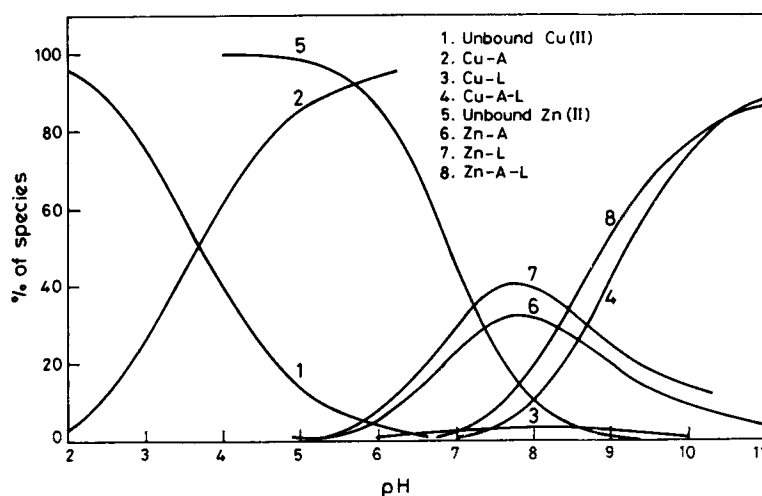


Figure 2. Species distribution curves for the Cu-Ala-HAPPH (1:1:1) and Zn-Ala-HAPPH (1:1:1) systems.

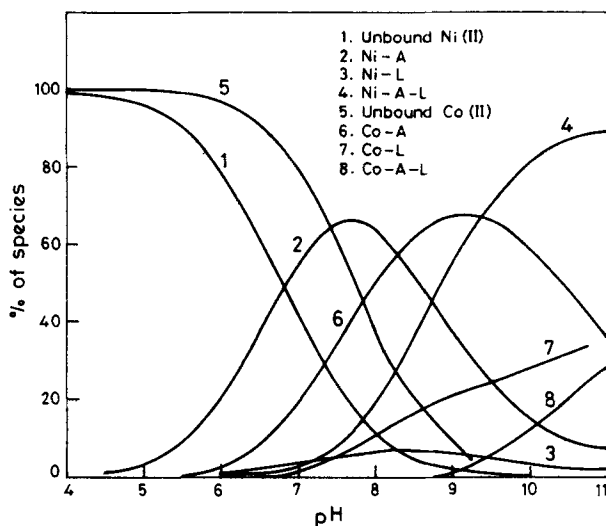


Figure 3. Species distribution curves for Ni-Ala-HAPPH (1:1:1) and Co-Ala-HAPPH (1:1:1) systems.

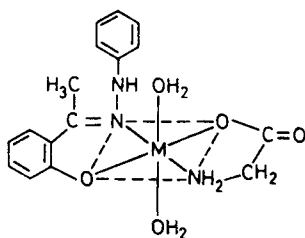


Figure 4. Structure of the ternary complex with *o*-hydroxyacetophenonephenylhydrazone and glycine.

of ligands employed in the present investigations form metal ion complexes of almost the same stability.

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