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Ternary Complexes of Some Metal Ions with 2,2'-Bipyridyl or 1,10-Phenanthroline as Primary Ligand and Naptalam as a Secondary Ligand

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In order to explore complexation as a possible mode of action of some pesticides, the binary and ternary complexes of the type MAL+, where M=Co(II), Ni(II), Cu(II), or Zn(II), A=2,2'-bipyridyl (bpy) or 1,10-phenanthroline (phen) and L=naptalam, have been studied potentiometrically in solution. Protonation constant of naptalam and the stability constants of its binary as well as ternary complexes have been reported at constant ionic strength (0.1 M KNO₃) and temperature (25°). The values of characterising constant (Δ log K) have been found to be positive, zero or small negative. These values have been used to interpret the extent of M→N-base π-interactions in these systems. On the basis of formation of considerably stable binary and ternary metal complexes of these pesticides, a new mechanism for their mode of action has been proposed.

IT has been observed in our recent investigation[1] that salicylanilide and dithionon form considerably stable complexes with some metal ions of biological importance, such as Co(II), Ni(II), Cu(II), Zn(II), Zr(IV), La(III) and Th(IV), thereby suggesting complexation as a possible mode of action of these pesticides. It has been noticed that some specific structural requirements[2] are essential for complexation to occur and for a compound to show biological activity[3]. Binary complexes of naptalam with Co(II), Ni(II), Cu(II) and Zn(II) as well as ternary complexes with 2,2'-bipyridyl (bpy) or 1,10-phenanthroline (phen) as a primary ligand and naptalam as the secondary ligand have, therefore, been studied in solution to provide further evidence on complexation as a possible mode of action of this pesticide.

Experimental

Metal nitrates used were of AR grade. 2,2'-Bipyridyl and 1,10-phenanthroline were obtained from Fluka AG, Switzerland. Naptalam was synthesized from phthalic anhydride and 1-naphthylamine, using the usual method of dissolving their equimolar amounts in benzene and mixing both the solutions with constant stirring. The precipitate thus obtained was filtered, washed with benzene and recrystallized from acetone. Other chemicals used were of B.D.H. AnalaR grade. Standard solutions of these compounds were prepared by direct weighing and the metal nitrate solutions were standardized by appropriate standard methods. A 70% aqueous dioxane (v/v) was employed to keep the ligands and other complexes in solution, because of solubility reason.

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Method and calculations :

The binary systems were investigated with 1 : 1 and 1 : 2 molar ratio of a metal ion and naptalam, while the ternary systems with 1 : 1 : 1 molar ratio of a metal ion, a primary ligand (bpy or phen) and the secondary ligand. The change in pH of the solution at each addition of 0.1 M NaOH was recorded with a Beckman pH meter equipped with a glass calomel assembly and each system was repeated several times to get reproducible values. In each measurements, the pH value was corrected for 70% dioxane-water medium using the method of Van Uitert and Haas[4]. Curves were plotted between m vs pH of the solution (m=moles of base added/mole of ligand or metal).

The dissociation constants of bpy and phen and the corresponding stability constants of their metal complexes have been taken from literature[5]. The protonation constant (Table 1) of naptalam has

TABLE 1—STABILITY CONSTANTS OF BINARY METAL COMPLEXES OF NAPTALAM, T=25°, μ=0.1(KNO₃)

Ligand	pKa	Metal ions	log K_{ML}^{M}	log $K_{ML_2}^{ML}$	log $\beta_{ML_2}^{M}$
Naptalam	6.19	Co(II)	2.65	2.00	4.65
		Ni(II)	2.27	1.94	4.21
		Cu(II)	3.45	2.50	5.95
		Zn(II)	2.36	1.78	4.14

been calculated by the method of Chaberek and Martell[6]. The stability constants (Table 1) of binary metal complexes with this ligand have been calculated employing the methods developed by L'Heureux and Martell[7], as well as by Rossotti and Rossotti[8].
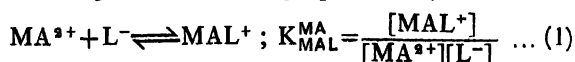
The stability constants of ternary complexes (Table 2) have been evaluated assuming that the

Primary ligand	Secondary ligand	Metal ion	$\log K^{MA}_{MAL}$	$\log \beta^{M}_{MAL}$	Δ log K
bpy	naptalam	Co(II)	2.72	8.78	+0.07
		Ni(II)	2.22	9.35	−0.05
		Cu(II)	3.75	11.75	+0.30
		Zn(II)	2.48	7.78	+0.12
phen	naptalam	Co(II)	2.70	9.95	+0.05
		Ni(II)	2.27	11.07	0.00
		Cu(II)	3.81	13.06	+0.36
		Zn(II)	2.52	9.07	+0.16

species MA²⁺ is practically completely formed before the formation of ternary MAL⁺ complex, according to the following equilibrium,

$$MA^{2+}+L^- \rightleftharpoons MAL^+ \; ; \; K^{MA}_{MAL} = \frac{[MAL^+]}{[MA^{2+}][L^-]} \; \dots (1)$$

where A=bpy or phen and L=naptalam. This assumption also holds good for Co(II) and Zn(II) because in the vicinity of inflexion point in titration curves of ternary systems, only MA²⁺ species is involved in complexation of secondary ligand L and the pH and m of this region have been considered for calculation where the constant value of K^{MA}_{MAL} have been found. Similar assumptions have also been considered by Sigel et al[9-11] and Tandon et al[12] for these metal ions. Thus the relationship employed to calculate the stability constants of ternary complexes is the same as used for binary complexes[6,7] under the present experimental conditions as discussed earlier[13]. The overall stability constants and Δ log K values (Table 2) for mixed ligand complexes have been calculated by the well known relations[2],

$$\log \beta^{M}_{MAL} = \log K^{M}_{MA} + \log K^{MA}_{MAL} \; .. (2)$$

$$\text{and} \quad \Delta \log K = \log K^{MA}_{MAL} - \log K^{M}_{ML}$$

$$= \log K^{ML}_{MLA} - \log K^{M}_{MA} \; \dots (3)$$

where $\log K^{ML}_{MLA} = \log \beta^{M}_{MAL} - \log K^{M}_{ML}$

These values have been used to interpret the influence of various factors involved in the formation of ternary complexes.

Results and Discussion

Binary complexes of naptalam :

Potentiometric titration curves of naptalam has shown an inflexion at m=1, indicating the dissociation equilibrium HL⇌H⁺+L⁻. The dissociation of single proton from carboxyl group of naptalam has been assumed. The overall stability constants of binary complexes of naptalam follow the trend Cu(II)>Co(II)>Ni(II)>Zn(II) which is not in accordance with the Irving-William sequence[14],

Relative concentrations of different complexed species of naptalam have been computed as the percentage of total M(II) bound to them and representative species distribution plot of Cu(II) complexes of naptalam is shown in Fig. 1 (dotted lines). From this figure, it is obvious that the concentration of CuL increases continuously and attains a limiting value (60%) above pH 7.0. The concentration of CuL₂ is negligible in pH range 2-5, but above this range, its concentration increases
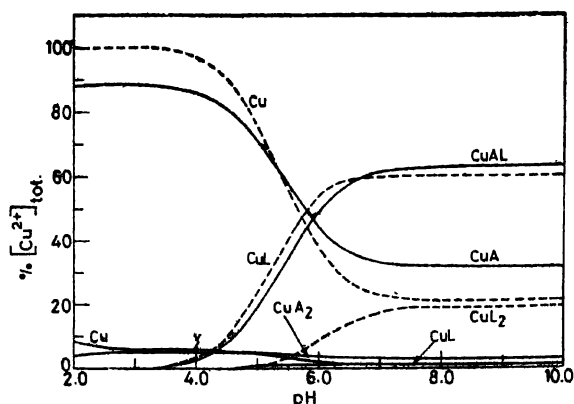

Fig. 1. Species distribution curves [as the percentage of total Cu(II) present] of several species present in an aqueous solution of binary system (dotted lines) of Cu(II) and naptalam ($C_M = 1 \times 10^{-3}M$ and $C_L = 2 \times 10^{-3}M$) and ternary system (solid lines) of Cu(II), 2,2'-bipyridyl and naptalam (each $1 \times 10^{-3}M$).

rapidly acquiring a constant value (≃20%) at higher pH range. As a result of formation of CuL and consequently CuL₂, the concentration of free Cu(II) decreases continuously, but in the higher pH range (7.5-14) its concentration becomes constant indicating no further coordination of Cu(II) in its complexes. Similar results have been obtained for other systems studied, where the concentrations of different species have been found to be according to their respective stability constants.

Ternary complexes :

The log K^{MA}_{MAL} values (Table 2) obtained as a result of association of secondary ligand with 1 : 1 MA²⁺ complex of bpy or phen have been found to be greater than the corresponding log K^{M}_{ML} values, with a few exceptions. The formation tendency of ternary complexes has been expressed by Δ log K values (Table 2), most of which are positive. There are four possible binding sites in naptalam, two

due to —C⟨O/O, one in —C=O and the other due to —NH group. A single inflexion has indicated that —NH group is not involved in bonding. Hence, this ligand is an O ligand and the species MA²⁺ shows discriminating behaviour towards this ligand resulting in high stability of ternary

complexes. The positive values of $\Delta \log K$ in ternary complexes of Cu(II) have been found to be due to the good π-accepting properties of hetero-aromatic N-bases[6], which finds further support from the work of Bhattacharya and his coworkers[15-17] on the ternary complexes of Cu(II) and Ni(II) with some π-bonding ligands. The positive values of $\Delta \log K$ for Co(II) and Zn(II) may also be explained as being due to the discriminating pro-perties of MA^{2+} towards secondary ligand, but this effect is less pronounced here. Due to d^{10} electron configuration, Zn(II) is a poor π-electron donor but it is still one[18,19]. The positive $\Delta \log K$ values for Co(II) may partly be due to the greater coordi-nation tendency of $3d_z^2$ orbital in the low spin complex towards the electron pair of the ligand than that of the orbitals in high spin aquo complex[20]. Thus the positive $\Delta \log K$ values for the systems of Co(II) and Zn(II) may be due to neutralization of charge and partly due to π-accept-ing properties of N-bases which finds further support from the work of Sigel et al[21-23] in the case of ternary complexes of these metal ions with bpy or phen and an amino acid.

Analysis of representative species distribution curve (Fig. 1, solid lines) of bpy-Cu(II)-naptalam reveals that about 88% of Cu(II) coordinates as CuA^{2+} which, with increasing pH, changes in the form of ternary $CuAL^+$ complex. The concentra-tion of $CuAL^+$ increases rapidly beyond pH 4 and attains a limiting value ($\simeq 63\%$) in higher pH range. The concentrations of other species, such as CuA_2^{2+}, CuL^+ and CuL_2 have been found to be negligible. Similar results have also been obtained for phen-Cu(II)-naptalam with a difference in concentrations of various species by 2-3%. Similarly, the concen-trations of the species in the systems containing Co(II), Ni(II) and Zn(II) have been computed and found to be lower than those obtained in the case of Cu(II). It has thus been concluded that the concentrations of ternary MAL^+ complexes are always more than the concentrations of binary ML^+ complexes resulting in positive $\Delta \log K$, except in the case of Ni(II).

On the basis of the nature of titration curves, stability constants of ternary complexes and $\Delta \log K$ values, a tentative structure of the ternary com-plexes of naptalam (Fig. 2) has been proposed. The positive values of $\Delta \log K$ supports the view that metal binding is through carboxyl and carbo-nyl oxygen atoms of naptalam and with both the nitrogen atoms of bpy or phen molecule. The stability constants of ternary complexes of napta-lam are low because it forms a seven membered ring.

On the basis of the above, it is evident that naptalam forms stable binary and ternary metal complexes involving some biomolecules possessing π-electron accepting properties. There is thus a possibility that this pesticide is coordinated with metal ions of enzymes forming binary metal com-plexes, which are converted into mixed ligand
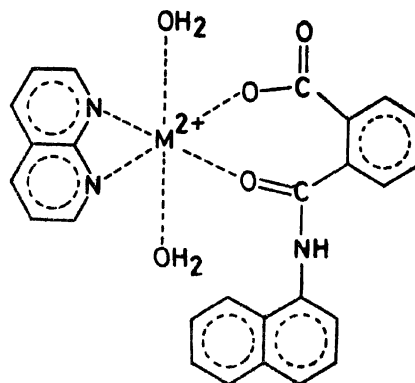

Fig. 2. Tentative structure of ternary complex of Cu(II) with bipyridyl and naptalam.

complexes as a result of 'reproportionation' between the parent binary metal complexes of this pesticide and some biomolecules. Thus, all the enzymatic equilibria are disturbed because of the formation of such species causing different biological acti-vities.

Acknowledgement

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