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Ternary Complexes of Some Phenoxyacetic Acid Herbicides and Pyridines with Metal Ions of Biological Interest

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Ternary complexes of Co(II), Ni(II) and Cu(II) with pyridine (*Py*) or 2-methyl pyridine (*2-MePy*) (primary ligand) and some phenoxyacetic acid herbicides, such as phenoxyacetic acid (*PAA*), 2-chlorophenoxyacetic acid (*2-CPA*), 2,4-dichlorophenoxyacetic acid (*2,4-D*) and 2,4,5-trichlorophenoxyacetic acid (*2,4,5-T*) (secondary ligands) have been studied in solution using a potentiometric *pH*-titration technique in order to test a complexation hypothesis of plant growth regulating activities of these herbicides. From stability constant data, the species distribution have been computed and it was found that the percentage of ternary complex (*MAL*) is about 60% of the total M^{2+} present at high *pH* indicating greater stability of these ternary complexes. The MA^+ species (M^{2+}—*Py* and M^{2+}—*2-MePy*) have shown discriminating behaviour towards the next incoming secondary ligand containing O as donor atoms. Since the stabilities of biologically active (*2-CPA*, *2,4-D* and *2,4,5-T*) and inactive (*PAA*) phenoxyacetic acid herbicides in binary (ML_2) and ternary (*MAL*) metal complexes were found approximately of the same magnitude, chelation may not thus be the probable mode of action of these plant growth regulators.

(Keywords: Plant growth regulators; Potentiometric pH titration)

Ternäre Komplexe einiger Phenoxyessigsäure-Herbizide mit Pyridin und Metallionen von biologischer Bedeutung

Ternäre Komplexe von Co(II), Ni(II) und Cu(II) mit Pyridin (*Py*) oder 2-Methylpyridin (*2-MePy*) als Primärliganden und einigen Herbiziden vom Phenoxyessigsäure-Typ [Phenoxyessigsäure (*PAA*), 2-Chlor-*PAA* (*2-CPA*), 2,4-Dichlor-*PAA* (*2,4-D*) und 2,4,5-Trichlor-*PAA* (*2,4,5-T*)] als Sekundärliganden wurden im Hinblick auf eine Komplexierungshypothese der pflanzenwuchssteuernden Wirkung dieser Herbizide mittels potentiometrischer *pH*-Titration untersucht. Aus den Stabilitätskonstanten wurden die Anteile der einzelnen Spezien in Lösung berechnet. Dabei wurden 60% an ternärem Komplex (*MAL*) — bezogen auf die totale M^{2+}-Menge — bei hohen *pH*-Werten festgestellt und damit die größere Stabilität dieser Komplexe gezeigt. Die

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MA$^+$-Spezies (M^{2+}—*Py* und M^{2+}—*MePy*) zeigte ein unterschiedliches Verhalten gegenüber dem nächsten chelierenden Liganden mit O als Donor. Da die Stabilitäten der biologisch aktiven (*2-CPA*, *2,4-D* und *2,4,5-T*) und inaktiven (*PAA*) Liganden in binären (ML_2) und ternären (*MAL*) Metallkomplexen in der gleichen Größenordnung liegen, scheint die Komplexierung bei der Regulierung des Pflanzenwuchses bei diesen Herbiziden kein entscheidender Faktor zu sein.

Introduction

In our previous investigation[1], it has been observed that the biologically active plant auxins, such as indole-3-acetic acid, indole-3-propanoic acid, indole-3-butanoic acid and naphthalene-1-acetic acid form quite stable complexes in solution with Al(III), Fe(III), Co(II), Ni(II), Cu(II), Zr(IV), La(III) and Th(IV), thereby supporting complexation as the possible mode of action of these plant auxins. Since the stabilities of these complexes were almost of the same magnitude, it thus became necessary to study the ternary complexes of some biologically active (e.g., *2-CPA*, *2,4-D* and *2,4,5-T*) and inactive (*PAA*) herbicides (secondary ligands) and pyridine bases (primary ligand) with Co(II), Ni(II) and Cu(II), in order to differentiate among the binding capacity of these herbicides towards a metal ion. The pyridine bases have been chosen because of their biochemical significance in biological fluids[2].

Experimental

The metal nitrates used were of AR grade. Pyridine and 2-methyl pyridine (BDH), *PAA*, *2,4-D* and *2,4,5-T* (Fluka AG) were commercially available. 2-Chlorophenoxyacetic acid was prepared from 2-chlorophenol[3]. All other chemicals were BDH reagents of AR Grade. Dioxan was used after further purification[4]. Metal nitrate solutions were prepared in carbon dioxide free water and were standardised before use[5]. A 50% aq. dioxan (*v*/*v*) was chosen to keep *PAA*, *2-CPA*, *2,4-D* and *2,4,5-T* and their complexes in solution.

Method and Calculations

The binary systems under investigation contained the metal ion and the secondary ligand in 1:1 and 1:2 molar ratios while the ternary systems contained metal ion, primary ligand and secondary ligand in 1:1:1 molar ratios. The change in the *pH* of the solution during each addition of the standard 0.1 *M*-NaOH was recorded with Elico-Digital *pH* meter LI-20 equipped with glass electrode assembly. Curves were plotted between *n* (moles of base added/moles of ligand or metal) and *pH* of the solution.

The dissociation constant of *Py* and *2-MePy* and corresponding stability constant of binary metal complexes were taken from the literature[6]. The protonation constant of *PAA*, *2-CPA*, *2,4-D* and *2,4,5-T* have been calculated by using the method of *Chabereck* and *Martell*[7]. The following equilibria and the resultant stability constant have been studied:

$$M^{2+} + L^{-} \rightleftharpoons ML^{+}, \quad K^{M}_{ML} = \frac{[ML^{+}]}{[M^{+}][L^{-}]} \tag{1}$$

$$ML^{+} + L^{-} \rightleftharpoons ML_2, \quad K^{M}_{ML^2} = \frac{[ML_2]}{[ML^{+}][L^{-}]} \tag{2}$$

$$MA^{2+} + L^{-} \rightleftharpoons MAL^{+}, \quad K^{MA}_{MAL} = \frac{[MAL^{+}]}{[MA^{2+}][L^{-}]} \tag{3}$$

The values of pK_a of secondary ligands, and stabilities of their binary complexes are listed in Table 1. For the calculation of stability of simple 1:1 chelate, *ML*, the following relation was used:

$$K_{ML} = \frac{[T_M] - [L^{-}]X}{[L^{-}]^2 X} \tag{4}$$

where

$$X = \left[\frac{[\mathrm{H}^{+}]}{K_1}\right] + 1$$

while evaluating the stability constant of ternary complexes, it has been assumed that species MA^{2+} are first formed before the formation of ternary complex[8–11]. Therefore, the relationship necessary for the calculation of formation constant of mixed ligand chelates, MAL^{+}, formed from MA^{2+} and secondary ligand L^{-} is the same as in Eq. (4) for binary complexes[12] where the chelate MA^{2+} takes the place of the metal ion, M^{2+}. The overall stability constant of mixed ligand complexes have been calculated using equilibrium (3) by the well-known relation[2,13]

$$\log \beta = \log K^{M}_{MA} + \log K^{MA}_{MAL} \tag{5}$$

and taking into consideration mutual effect[9,12] of both ligands in a complex, the value of characterising factor ($\Delta \log K_M$), was evaluated by using the following relation[14],

$$\Delta \log K_M = \log K^{ML}_{MLA} - \log K^{M}_{ML} \tag{6}$$

where

$$\log K_{MLA}^{ML} = \log \beta_{MAL}^{M} - \log K_{ML}^{M}$$

The values of overall stability constant and $\Delta \log K_M$ thus calculated are listed in Table 2. The concentrations of various species were computed from DEC-10 using the results of Tables 1 and 2.

Table 1. *Stability constants of binary metal complexes with PAA, 2-CPA, 2,4-D and 2,4,5-T* ($T = 25\,°\mathrm{C}$, $\mu = 0.1\,M$-$\mathrm{KNO_3}$)

Ligand	pK_a	Metal Ion	$\log K_1$	$\log K_2$
PAA	4.38	Co(II)	2.88	2.40
		Ni(II)	2.40	1.81
		Cu(II)	3.15	2.83
2-CPA	4.26	Co(II)	2.71	2.19
		Ni(II)	3.16	2.74
		Cu(II)	3.16	2.74
2,4-D	4.15	Co(II)	2.50	2.17
		Ni(II)	2.41	1.89
		Cu(II)	2.96	1.80
2,4,5-T	4.13	Co(II)	2.47	2.10
		Ni(II)	2.30	1.89
		Cu(II)	3.05	1.60

Results and Discussion

Binary System

The potentiometric titration curves of secondary ligands with metal ions showed an inflexion at $n = 1$ indicating equilibrium, $\mathrm{H}L \rightleftharpoons \mathrm{H}^+ + L^-$. The titration curves were found to be similar in nature for all phenoxyacetic acids showing almost indentical nature of interaction towards a metal ions.

Ternary Systems

1 : 1 : 1 : : M—A—L systems were studied and considerable shifting from the corresponding binary titration curves showed the formation of ternary complexes. The high concentration of ternary complex that occur in 1 : 1 : 1 mixture can be seen from a representative plot of species

distribution of Cu^{2+}—*Py*—*PAA* (Fig. 1) where the percentage of the total concentration of H*A*, H*L*, A^-, L^-, MA^+ and *MAL* species was observed to be dependent on *pH*. It is evident from these plots that the substantial decrease in the concentration of H*A*, H*L*, A^- and L^- increases the concentration of MA^{2+} and *MAL*. In the *Py*—Cu^{2+}—*PAA* system, the concentration of ternary complex reaches nearly 60% of the total Cu^{2+} present at high *pH*. In all the systems, the concentrations of total primary and secondary ligand bonded in different species were found to be ≃ 100%. Further, the concentrations of binary and ternary complexes tend to approach limiting values with increasing *pH*.

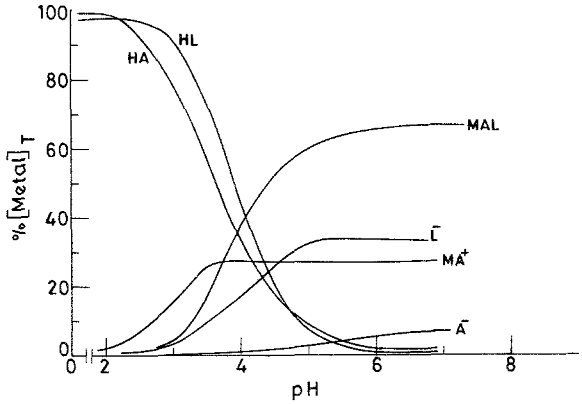


Fig. 1. Influence of *pH* on the concentrations (given as the percentage of total M^{2+} present) of several species present in 50% aq. dioxan solution (*v*/*v*) of the ternary system, Cu^{2+}—*Py*—*PAA* (each $2 \cdot 10^{-3} M$); computed with the constants given in Tables 1, 2

The influence of a hetercaromatic N-base bound to the metal ion, M^{2+}, to the next incoming ligand was observed from the $\Delta \log K_M$ values (Table 2) which were found to be positive for all the ternary complexes, whereas $\Delta \log K_M$ values for *2-MePy*—Ni—*2,4-D* and *2-MePy*—Ni—*2,4,5-T* systems are possitive except for *Py*—Ni—*2,4-D* and *Py*—Ni—*2,4,5-T*, showing that *M*—*A*—*L* type ternary complexes were stabler than *ML* type of complexes. This is in accordance to exception as 2-methyl pyridine is stronger base ($pK_a = 6.21$) than pyridine ($pK_a = 5.44$) where it is likely that the greater availability of σ bonding electrons in former compensates for small π-contribution.

Table 2. *Stability constants of ternary metal complexes of pyridine and 2-methyl pyridine with PAA; 2-CPA; 2,4-D and 2,4,5-T* ($T = 25\,^{\circ}\mathrm{C}$; $\mu = 0.1\,M$-KNO_3)

Primary ligand	Secondary ligand	Metal Ion	$\log K^{MA}_{MAL}$	$\log \beta^{M}_{MAL}$	$\Delta \log K_M$
Pyridine	*PAA*	Co(II)	3.20	5.15	0.32
		Ni(II)	3.07	6.26	0.67
		Cu(II)	3.59	8.09	0.40
Pyridine	*2-CPA*	Co(II)	3.07	5.02	0.36
		Ni(II)	2.65	5.84	0.27
		Cu(II)	3.39	7.39	0.23
Pyridine	*2,4-D*	Co(II)	2.88	4.83	0.38
		Ni(II)	2.30	5.49	—0.11
		Cu(II)	3.15	7.69	0.19
Pyridine	*2,4,5-T*	Co(II)	2.84	4.97	0.37
		Ni(II)	2.21	5.40	—0.09
		Cu(II)	3.13	7.67	0.08
2-Methyl Pyridine	*PAA*	Co(II)	3.42	3.42	0.54
		Ni(II)	3.14	4.83	0.74
		Cu(II)	3.68	4.68	0.53
2-Methyl Pyridine	*2-CPA*	Co(II)	3.19	3.19	0.48
		Ni(II)	2.83	4.52	0.45
		Cu(II)	3.48	4.48	0.32
2-Methyl Pyridine	*2,4-D*	Co(II)	3.15	3.15	0.65
		Ni(II)	2.74	4.43	0.33
		Cu(II)	3.24	4.24	0.27
2-Methyl Pyridine	*2,4,5-T*	Co(II)	3.12	3.12	0.65
		Ni(II)	2.69	4.38	0.39
		Cu(II)	3.22	4.22	0.07

The general order of the stabilities of ternary complexes in terms of secondary ligand was *PAA* > *2-CPA* > *2,4-D* > *2,4,5-T*. Thus, the conjugation between the phenyl ring and the carbonyl group in the series of chloro substituted phenoxyacetic acids is unlikely and only the inductive effect of the chloro substitution on the phenyl ring is effecting the stability constant as well as the pK_a values of these herbicides.

The overall stability ($\log \beta$) of ternary complexes follow the trend Cu(II) > Ni(II) > Co(II) which is in accordance with *Irving-William*'s sequence[15]. The high stability of ternary complexes over binary complexes of phenoxyacetic acids seems to be also due to the absence of *Coulomb*ic repulsion between two dissimilar ligands bound to the same metal ion alongwith the π-accepting properties of a participating heteroaromatic N-base. Thus, the discriminating behaviour of heteroaromatic N-base towards the next incoming ligand, containing O as donor atoms, are well defined for Cu(II), Ni(II) and Co(II). The increased stability of ternary complexes (Table 2) than those of binary, ML^+ type, was found to be due to varying π-electron systems of the primary and secondary ligands. For a given heteroaromatic N-base and a phenoxyacetic acid herbicide, a plot of $\log K^{MA}_{MAL}$ *vs.* $\log K^{M}_{ML}$ was linear (Fig. 2) which shows that the affinity of association of L^- with MA^{2+} in ternary systems follows, in general, the same pattern as it does with aqueous metal ion, $M(H_2O)_n^{2+}$. Thus the coordination of a secondary ligand is favoured by the presence of a heteroaromatic N-base, already attached to the metal ion resulting higher stability of ternary complexes. On this pattern, the structure of ternary complexes of Cu(II) may either be (I) or (II).

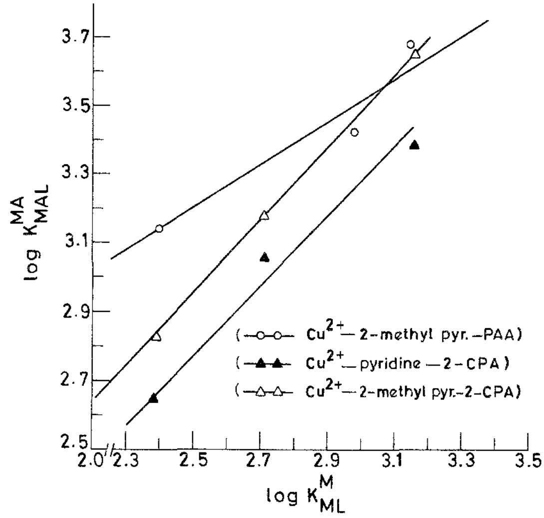
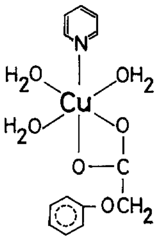


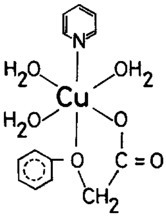
Fig. 2. Plot of $\log K^{Cu}_{CuL}$ *vs.* $\log K^{CuA}_{CuAL}$, Cu^{2+}—*2-MePy—PAA* (—○—○—○—); Cu^{2+}—*Py—2-CPA* (—▲—▲—); Cu^{2+}—*2-MePy—2-CPA* (—△—△—)

The structure (II) will be more stable because it has a five membered chelate ring as compared to structure (I) which has four membered ring[16–18]. This finds further support from the crystal structure of binary complex of Cu(II) phenoxyacetic acid[19]. However, for Co(II) and Ni(II), the higher crystal field stabilisation in an octahedral field, and lower stabilisation in tetrahedral for d^8 ion than d^7

ion renders the occurrence of tetrahedral complex less likely with Ni(II) than those of Co(II). Therefore, we predict that in ternary complexes of the type Ni*AL* there may be a greater driving force for adoptation of octahedral structure. Replacement of pyridine by its 2-methyl derivative in Co(II) complexes causes the six coordination state to be thermodynamically unstable[20]. The same would be expected for Ni(II) complexes. Studies on isolated ternary complexes in solid state are in progress which will provide more information about the bonding sites of the metal ions.



(I)



(II)

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