Spectroscopic and equilibrium characterization of metal complexes of phenoxy acid herbicides

S. S. S. Kushwaha* and Sandhya Gupta

Chemical Laboratories, P. P. N. College Campus (C. S. J. M. University), Kanpur-208 001, Uttar Pradesh, India

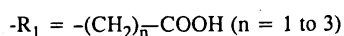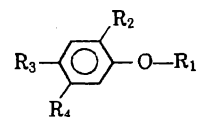E-mail : ssskushwaha41@rediffmail.com   Fax : 91-512-2239080

Abstract : The metal complexes of Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} of phenoxyacetic acid (PAA, inactive) and chloro-substituted phenoxyacids (active) of the type ML_2 or $ML_2.2H_2O$ have been isolated and characterized on the basis of elemental analysis, spectral, magnetic and thermal data. The IR data show that the bonding of the carboxylato group to the metal ion is bidentate. Also, potentiometric solution equilibrium study together with calorimetric measurements for evaluation of stability constants and thermodynamic quantities (ΔG^0, ΔH^0 and ΔS^0) at 25 °C ($I = 0.10$ M, KNO_3) have been made. It is found that in metals, except Cu^{II} in which phenoxy oxygen and one from carboxylato group is involved, both the oxygen atoms of carboxylato group participate in bonding. The complexation processes are found to be enthalpically and entropically favoured. The mode of complexation, stabilities and thermodynamic parameters of active (chloro-substituted derivatives) and inactive (PAA) are observed to be of comparable magnitudes indicating some other second order factors, other than binary metal complexation, are involved during growth regulation by these herbicides.

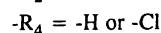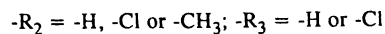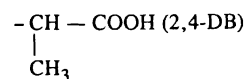Keywords : Phenoxy herbicides, growth regulators, complexation, stability constants, free energy.

Naturally occurring indole-3-acetic acid (IAA) and a large number of synthetic organic compounds, such as, naphthalene-1-acetic acid (NAA), substituted phenoxy acids, etc., have been investigated to be potential plant growth regulators[1-3]. Among these, phenoxy herbicides are most widely used as weed killers and several theories[4-9] on their mode of action have been suggested. On molecular level these theories conclude the importance of specific structural features and their interaction with biomolecules[3,10-13]. It is well established that more and more enzymes are metal ion dependent or metal containing species[14-16]. In general, biological systems involve many chemical and biochemical equilibria involving metal ions, metalloenzymes, metalloproteins, etc. and almost all the models on the biologically active molecules suggested so far consider the phenomenon of complexation which may modify these enzymatic equilibria[12,17-19]. It may be postulated that the application of a herbicide to plants may disturb these enzymatic equilibria by forming metal complexes in biological fluid and thus, causing growth regulation.

Phenoxy acid herbicides have been reported to be good chelators[12,20], and hence to explore this behaviour of a large series of analogs, a detailed synthetic and equilib-rium analysis of the complexation of phenoxyacetic acid (PAA); 2-chlorophenoxyacetic acid (2-CPA); 2,4-dichlorophenoxyacetic acid (2,4-D); 2,4,5-trichlorophenoxyacetic acid (2,4,5- T) and other classes of phenoxy herbicides (Structure 1) with Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}, has been carried out through elemental analysis, electronic and IR spectroscopy, magnetic susceptibility determination and potentiometric measurement using computation methods[21-23]. The species distribution as a function of pH were computed by using the computer program HYSS[24]. The mode of bonding and mechanism of com-

$-R_1 = -(CH_2)_n-COOH$ (n = 1 to 3)

or

$-CH-COOH$ (2,4-DB)
  |
  CH_3

$-R_2 = $ -H, -Cl or $-CH_3$; $-R_3 = $ -H or -Cl

$-R_4 = $ -H or -Cl

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plexation have been investigated from spectral data and the protonation constants of ligands as well as from the stability constants of their binary complexes.

Materials and methods :

The compounds, PAA; 2-CPA; 2,4-D; 2,5-D and 2,4,5-T were obtained from Fluka AG, Buchs, Switzerland and were used after purification. Other phenoxy herbicides were from Riedel-de-Haëm (Seelze, Germany). In potentiometric measurements 60% aq. dioxan (v/v) medium was analysed to keep the ligands and their complexes in solution. Stock solutions of Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} were prepared from analytical grade metal nitrates and standardized by titrating them with disodium salt of EDTA. Carbonate free sodium hydroxide was prepared and standardized by titrating it with potassium hydrogen phthalate (B.D.H., AnalaR dried at 120 °C for two hours). Carbondioxide free doubly distilled water was used for preparation of all the solutions in potentiometric measurements.

Isolation and physical characterization of complexes :

The complexes of Co^{II} were obtained by the reaction of nitrate salt with the sodium salt of phenoxy acids in 70% ethanol. The products were purified by repeated washing with the same solvent followed by sodium-dried ether and then dried *in vacuo*.

The metal complexes of Ni^{II}, Cu^{II} and Zn^{II} were isolated by the reactions of metal nitrates and a slight excess of either free phenoxy acid or its sodium salt in aqueous solution. Also, in most of the cases 1 : 6 aq. ammonia was added to cause precipitation.

The metal ions were estimated by EDTA titration technique. Magnetic susceptibility was measured at room temperature on a Gouy-balance using $Hg[Co(NCS)_2]$ as a calibrant. IR spectra (4000–400 cm^{-1}) in KBr were recorded on a Perkin-Elmer spectrophotometer and the electronic absorption spectra in nujol on a Carl-Zeiss UV-VIS-IR spectrophotometer. TG was performed on a standard Redcraft thermobalance.

Potentiometric measurements :

The following three mixtures : (a) 10 ml (0.01 *M*) HNO_3 + 5 ml (1.0 *M*) KNO_3; (b) mixtures (a) + 10 ml (0.01 *M*) ligand solution and (c) mixture (b) + 2 ml (0.01 *M*) metal solution, were prepared for each system (total volume 50 ml) and titrated against standard carbonate free 0.1 *M* NaOH solution at constant ionic strength of 0.1 *M* (KNO_3) and temperature (25 °C) in 60% aq. (v/v) dioxan medium. The ratio of metal to the ligand was

maintained 1 : 5, so as to explore the possibility of higher or polymeric complexes in solution irrespective of the coordination number of metal[20]. Each of the systems was repeated several times to get reproducible results.

The protonation constants, the concentration stability constants of binary complexes and species distribution have been computed by standard methods[21-24]. The thermodynamic parameters have been estimated using calorimetric and the equilibrium constant data.

Results and discussion

Elemental and spectral analysis :

Elemental analysis, IR and magnetic moment data are represented in Table 1. The complexes of Co^{II}, Ni^{II} and Zn^{II} are soluble in water while those of Cu^{II} are not. These complexes are found to be non-conducting in dimethylformamide (DMF). The presence of water of crystallization in the complexes was established by TG analysis which indicated the loss of water around 120 °C. However, Cu^{II}, Ni^{II} and Co^{II} complexes lose their water molecules around 105 °C.

The magnetic moment values of Co^{II} and Ni^{II} complexes (Table 1) are normal and in good agreement with the values reported for octahedral spin free complexes of these metal ions[25]. All the Cu^{II} complexes have magnetic moments in the range 2.00–2.22 B.M. which corresponds to the presence of one unpaired electron and the square planar structure, uncomplicated by dimerisation. Evidently, the square planar structure is attained through chelation involving phenoxy-oxygen. This evidence is supported from X-ray crystal structure determinations[26], on anhydrous and diaquobis (phenoxyacetato) copper(II) complexes.

From the analysis of electronic spectra (υ_{max} in cm^{-1}) of the synthesized metal complexes of Co^{II}, Ni^{II} and Zn^{II} it is found that they are characteristics of octahedral stereochemistry. Co^{II} complexes show well defined bands around 8290 and 21360 cm^{-1} which may be attributed to υ_1 and υ_3 transitions, respectively. The less intense shoulder band round 17450 cm^{-1} may arise from υ_2 transition. All the Ni^{II} complexes show υ_1, υ_2 and υ_3 bands, respectively, at 10220, 17550 and 27780 cm^{-1}. The electronic spectra of all Cu^{II} complexes display a broad band around 15300 cm^{-1} which may be due to a combination of $^2A_{1g} \leftarrow {}^2B_{1g}$ and $^2E_g \leftarrow {}^2B_{1g}$ transitions in D_{4h} symmerty[26].

The IR spectra (υ_{max} in cm^{-1}) of the complexes exhibit characteristic band in the region 1650–1580 cm^{-1}

Table 1. Analytical, magnetic moment and infrared data of the complexes of phenoxy acids with transition metal ions

Complex	Found (%) (Calcd.)			μ_{eff} (B.M.)	υ_{max} (cm^{-1})		
	Metal	C	H		υ_{as} COO	υ_s COO	$\Delta\upsilon$ (υ_{as}-υ_s COO)
[Co(PAA)$_2$(H$_2$O)$_2$]	14.62 (14.84)	47.89 (48.37)	4.53 (4.57)	4.96	1600	1435	165
[Co(2-CPA)$_2$(H$_2$O)$_2$]	12.68 (12.65)	41.58 (41.21)	3.21 (3.46)	5.06	1595	1435	160
[Co(2,4-D)$_2$(H$_2$O)$_2$]·2H$_2$O	10.40 (10.32)	33.21 (33.63)	3.91 (3.18)	5.20	1590	1435	155
[Co(2,4,5-T)$_2$(H$_2$O)$_2$]·2H$_2$O	9.18 (9.21)	29.88 (30.00)	2.35 (2.52)	4.94	1595	1410	185
[Co(MCPA)$_2$(H$_2$O)$_2$]·2H$_2$O	11.24 (11.12)	40.32 (40.76)	4.21 (4.57)	4.85	1590	1425	165
[Co(2,4-DP)$_2$(H$_2$O)$_2$]	10.47 (10.50)	38.10 (38.37)	3.58 (3.22)	4.92	1595	1410	185
[Co(MCPB)$_2$(H$_2$O)$_2$]·2H$_2$O	10.14 (10.06)	45.28 (45.06)	5.03 (5.51)	4.90	1585	1420	165
[Co(2,4-DB)$_2$(H$_2$O)$_2$]	9.80 (9.97)	40.87 (40.61)	3.98 (3.75)	4.82	1580	1415	165
[Ni(PAA)$_2$(H$_2$O)$_2$]·2H$_2$O	13.61 (13.57)	44.92 (44.37)	5.59 (5.12)	3.26	1610	1450 1440	165
[Ni(2-CPA)$_2$(H$_2$O)$_2$]·2H$_2$O	11.29 (11.70)	38.92 (38.27)	4.64 (4.01)	3.40	1605	1450 1440	160
[Ni(2,4-D)$_2$(H$_2$O)$_2$]·2H$_2$O	10.32 (10.62)	34.28 (34.74)	3.01 (2.92)	3.42	1590	1440	150
[Ni(2,4,5-T)$_2$(H$_2$O)$_2$]	9.14 (9.72)	31.13 (31.80)	2.69 (2.00)	3.44	1595	1435	160
[Ni(MCPA)$_2$(H$_2$O)$_2$]	11.67 (11.90)	43.38 (43.75)	4.55 (4.08)	3.32	1595	1435	160
[Ni(2,4-DP)$_2$(H$_2$O)$_2$]·2H$_2$O	9.43 (9.80)	36.77 (36.08)	3.52 (3.70)	3.28	1585	1415	170
[Ni(MCPB)$_2$(H$_2$O)$_2$]	10.97 (10.68)	48.67 (48.03)	5.96 (5.13)	3.30	1590	1430	160
[Ni(2,4-DB)$_2$(H$_2$O)$_2$]·2H$_2$O	9.88 (9.37)	38.72 (38.30)	4.73 (4.18)	3.36	1590	1425	165
[Cu(PAA)$_2$]	17.92 (17.38)	52.04 (52.53)	3.32 (3.86)	2.12	1645	1425	220
[Cu(2-CPA)$_2$]	14.17 (14.62)	44.59 (44.18)	2.42 (2.78)	2.18	1650	1420	230
[Cu(2,4-D)$_2$]·2H$_2$O	11.29 (11.78)	35.21 (35.59)	2.38 (2.99)	2.16	1650	1415	235
[Cu(2,4,5-T)$_2$]·2H$_2$O	10.07 (10.44)	31.32 (31.56)	1.57 (1.99)	2.10	1640	1435	205
[Cu(MCPA)$_2$]	13.99 (13.74)	46.19 (46.70)	3.73 (3.49)	2.14	1635	1430 1420	210
[Cu(2,4-DP)$_2$]·2H$_2$O	11.73 (11.20)	38.82 (38.06)	3.08 (3.20)	2.12	1635	1435	200
[Cu(MCPB)$_2$]	12.13 (12.25)	50.98 (50.91)	4.20 (4.67)	2.22	1630	1420	210
[Cu(2,4-DB)$_2$]·2H$_2$O	10.58 (10.67)	40.18 (40.30)	3.11 (3.72)	2.16	1630	1425	205
[Zn(PAA)$_2$(H$_2$O)$_2$]	16.83 (16.21)	47.32 (46.60)	4.26 (4.50)	Diamagnetic	1595	1420	175
[Zn(2-CPA)$_2$(H$_2$O)$_2$]	13.30 (13.84)	40.10 (40.65)	3.93 (3.41)	-do-	1585	1425	160
[Zn(2,4-D)$_2$(H$_2$O)$_2$]	12.67 (12.08)	35.63 (35.46)	2.43 (2.51)	-do-	1580	1435 1430	145
[Zn(2,4,5-T)$_2$(H$_2$O)$_2$]	10.38 (10.71)	31.13 (31.46)	1.38 (1.98)	-do-	1590	1430	160
[Zn(MCPA)$_2$(H$_2$O)$_2$]	13.81 (13.07)	43.63 (43.17)	4.57 (4.03)	-do-	1580	1435 1430	145
[Zn(2,4-DP)$_2$(H$_2$O)$_2$]	11.21 (11.48)	37.48 (37.94)	3.73 (3.19)	-do-	1575	1420	155
[Zn(MCPB)$_2$(H$_2$O)$_2$]	11.37 (11.75)	47.83 (47.45)	5.93 (5.07)	-do-	1575	1430	145
[Zn(2,4-DB)$_2$(H$_2$O)$_2$]	10.42 (10.94)	40.56 (40.18)	3.42 (3.71)	-do-	1570	1425	145

(υ_{as} COO) and 1450–1410 cm^{-1} (υ_s COO). The separation ($\Delta\upsilon$) 200–235 cm^{-1} between these two bands for Cu^{II} phenoxycarboxylates indicates unidentate carboxylate coordination involving phenoxy-oxygen in chelation[20] (Structure 2a). The frequency separation ($\Delta\upsilon$) 145–1410

cm^{-1} for Co^{II}, Ni^{II} and Zn^{II} complexes are diagnostic of bridged carboxylate as in Structure 2b[27,28] where both the oxygens are involved in bonding, as υ_{as} COO is expected to decrease and metal $-O=C-$ interaction becomes stronger.

(x = 1, 2 or 3)

(a)   (b)
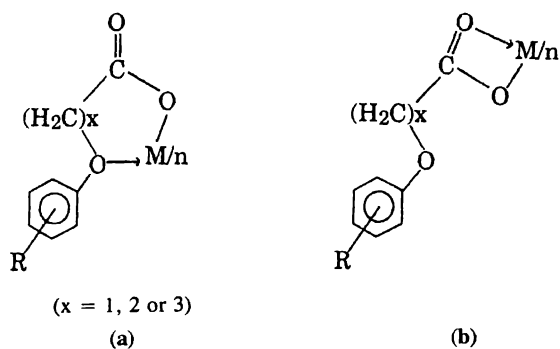
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Tentative structures of binary metal complexes of phenoxy acids
(R = -H or any other substituent group)

From the υ_{as} COO values (Table 1), it is observed that for a metal(II) phenoxyacetates and substituted phenoxycarboxylate, the sequence of υ_{as}COO is :

$$Co^{2+} > Ni^{2+} < Cu^{2+} > Zn^{2+}$$
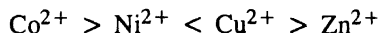
which is in accordance with Irving-Williams order of stability[29] except for Cu^{II}. The exceptional behaviour of Cu^{II} may be due to the difference in the mode of bonding. In these complexes $-C=O$ is not involved in coordination and hence υ_{as} COO is shifted to higher frequency region. Further, the value of $\Delta\upsilon$ significantly depends upon the substituent present in the benzene ring and length of the side chain. As a matter of fact, since phenoxy-oxygen is involved in chelation, the presence of electron attracting groups (Cl) and their number weaken the metal-phenoxy oxygen bonding and strengthen the M-O-CO-interaction, hence υ_{as}COO decreases leading to an increased $\Delta\upsilon$. The broad band in the region 3330–3490 cm^{-1} indicates the presence of water molecules in these complexes. Further, the splitted intense band around 935

cm^{-1} and the weak one around 850 cm^{-1} were observed.

Deprotonation of phenoxy acids :

In all the cases ligand titration curves and proton-ligand formation curves under investigation clearly indicated only one buffer region corresponding to the liberation of single proton. Hence, the dissociation of these acids may be represented by the equilibrium : HL $\rightleftharpoons$ H^+ + L^-. From the proton-ligand formation curves, the values of protonation constants (pK_a) were obtained directly by interpolating at half $\bar{n}_A$ values. These values were refined by computation methods using standard computer program[22-24] and recorded in Table 2.

An examination of these values shows that the protonation constants of phenoxy acids are almost similar (indistinguishable). A slight difference may be expected due to increase in chain length of side chain in this group of compounds or number and position of substituent groups in the ring. A decrease in the pK_a values has been observed with the increase in chloro-substitution in the ring which has been interpreted due to the electron withdrawing nature of the chloro-groups. Also, an increase in the pK_a values on increasing side chain length is observed, showing the weak dissociation ability of long side chain phenoxy herbicides.

The thermodynamic parameters reported in Table 2 show that the dissociation processes of phenoxy herbicides are enthalpically favoured. In the case of carboxylic group deprotonation, the process is endothermic and almost entirely entropic : in fact it consists of charge separation and of a resulting large-scale reorganization of the solvent molecules around the reacting parterns[30]. There is a little variation in the pK_a values of these acids depending upon the structural difference in them. The pK_a values of PAA and those of phenoxy acids having long side chain are comparatively higher than those of

Table 2. Dissociation constants and thermodynamic parameters (ΔH^0, ΔG^0 and ΔS^0) of phenoxy acids (t = 25 °C, μ = 0.10 M KNO_3)

Phenoxy acid	pK_a	ΔH^0 (kJ mol^{-1})	ΔG^0 (kJ mol^{-1})	$-\Delta S^0$ (JK^{-1} mol^{-1})
PAA	4.46	2.6	25.4	76.5
2-CPA	4.43	2.4	24.3	76.8
2,4-D	4.27	2.4	24.4	73.8
2,4,5-T	4.15	2.3	23.7	71.8
MCPA	4.30	2.7	24.5	73.2
2,4-DP	4.36	2.9	24.9	74.8
MCPB	4.38	2.7	25.0	73.8
2,4-DB	4.34	3.0	24.8	73.2

*Uncertainty in ΔH^0 ± 0.1 kJ mol^{-1} and in ΔS^0 ± 0.3 JK^{-1} mol^{-1}.

chloro substituted derivatives. In addition, ΔH^0 and ΔG^0 values are high positive in later and accordingly ΔS^0 values are high negative for these acids. This indicates that phenoxy acids when added into crop may accumulate in aqueous medium followed by dissociation which are thermodynamically controlled processes. It is, therefore, concluded that any chemical or biochemical process involved in the functioning of these herbicides not only depend on the structural features of molecules but also on the pH, thermodynamic conditions and soil as well as plant composition.

The results obtained on deprotonation of phenoxy acids reconfirm the diagnostic role of ΔH^0 and ΔS^0 values during their interaction in biological systems. Thermodynamic approach, therefore, makes it possible to distinguish between the different kinds of forces of interactions which may cause molecular recognition. The differences in ΔH^0 and ΔS^0 values for different phenoxy acids are very small which show similarity in their mode of dissociation in solution.

Interaction of phenoxy acids with metal ions :

Examination of the titration curves indicated clear separation of metal titration curves from the respective ligand titration curves with two inflexion points, the first occurred at ~ 2 ml followed by another reflexion at ~ 3 ml of alkali added. It was observed that in the system of higher metal ligand ratios only two complexes ML and ML_2 are formed with divalent transition metal ions. The single steep inflexion indicated the overlapping formation of protonated and normal metal complexes. At higher pH values precipitation occurs which may be ascribed due to hydrolytic effects. The general order of the stability of these complexes with respect to metal ions is found to be $Cu^{II} > Co^{II} > Ni^{II} > Zn^{II}$, irrespective of the nature of the ligand involved.

Analysis of the representative species distribution curves of Cu^{II}-PAA and Cu^{II}-2,4-D systems, respectively, have been shown in Figs. 1 and 2. The concentrations of CuL^+ and CuL_2 species are approximately 40% and 55%, respectively in the former case whereas 32% and 50%, respectively, in the later case in the higher pH range. In the lower pH range, the concentration of the species CuL_2 has always been found to be lower than the concentration of CuL^+. Similar observations were derived for other systems in which the concentrations have been found to be according to the protonation and stability constants of their complexes (Tables 2 and 3). The total concentration
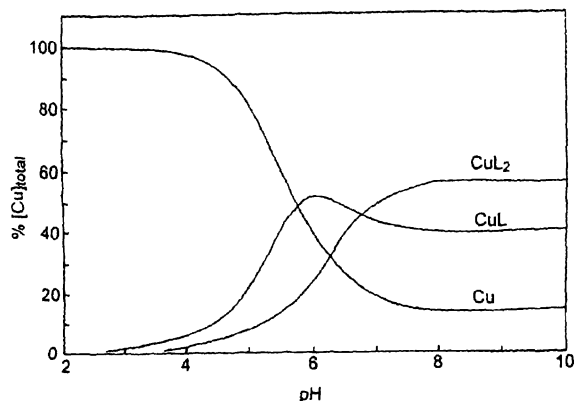

Fig. 1. Species distribution curves of Cu^{II}-PAA system ($C_M = 1 \times 10^{-3} M$ and $C_L = 2 \times 10^{-3} M$).
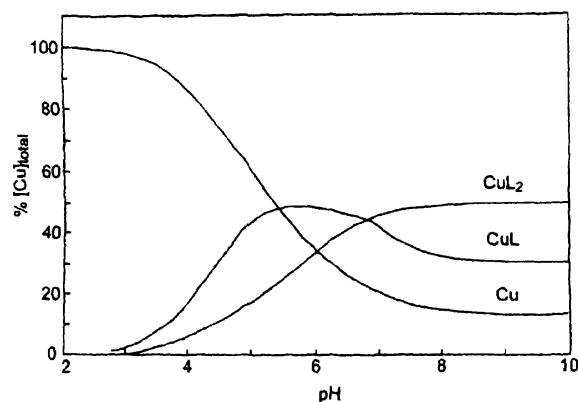

Fig. 2. Species distribution curve of Cu^{II}-2,4-D system ($C_M = 1 \times 10^{-3} M$ and $C_L = 2 \times 10^{-3} M$).

of free metal and bound in various species has always been found to be $\sim 100\%$.

The complexation processes are followed by considerable decrease in the free energy (ΔG^0) and are highly enthalpically as well as entropically favoured (Table 3). For a given metal ion these values are not well distinguishable. This indicates the similarity in the mode of interaction of phenoxy acids under consideration. This suggests that any chemical or biochemical process occurring in a biological system is not only controlled by pH of the medium but also by thermodynamic conditions.

From this part of investigation, it is evident that there is no significant difference between the chelating ability of the biologically active (2-CPA; 2,5-D, 2,4-D, 2,4,5-T etc.) and inactive (PAA) compounds suggesting somewhat similar electronic environment at the oxygen atoms involved in the complexation. On the other hand, halogen substitutions and their positions in the phenyl ring of

Table 3. Stability constants and thermodynamic parameters of binary metal complexes of phenoxy acids (t = 25 °C, μ = 0.10 M KNO$_3$)

Phenoxy acid	Metal ion	log K_{ML}^{M}	log $K_{ML_2}^{ML}$	log β	$-\Delta G^0$ (kJ mol^{-1})	$-\Delta H^0$ (kJ mol^{-1})	$-\Delta S^0$ (JK^{-1} mol^{-1})
PAA	Co^{II}	2.97	2.45	5.42	30.93	13.4	58.82
	Ni^{II}	2.50	1.87	4.37	24.93	11.2	46.07
	Cu^{II}	3.24	2.93	6.17	35.21	14.5	69.50
	Zn^{II}	2.32	1.68	3.99	22.77	9.3	45.20
2-CPA	Co^{II}	2.85	2.40	5.25	29.96	13.2	56.24
	Ni^{II}	2.55	2.00	4.55	25.96	11.0	50.20
	Cu^{II}	3.28	2.97	6.25	35.66	14.2	72.01
	Zn^{II}	2.30	1.65	3.95	22.54	9.2	44.77
2,4-D	Co^{II}	2.75	2.30	5.05	28.81	12.8	53.72
	Ni^{II}	2.44	2.06	4.50	25.68	10.8	49.93
	Cu^{II}	3.22	2.87	6.09	34.75	13.7	70.64
	Zn^{II}	2.27	1.63	3.90	22.25	9.0	44.46
2,4-5-T	Co^{II}	2.65	2.25	4.90	27.96	12.4	52.21
	Ni^{II}	2.50	1.95	4.30	25.54	10.6	46.78
	Cu^{II}	3.20	2.72	5.95	33.78	13.5	68.65
	Zn^{II}	2.25	1.61	3.86	22.02	8.8	44.36
MCPA	Co^{II}	2.90	2.27	5.17	29.50	13.8	53.36
	Ni^{II}	2.46	1.90	4.36	24.89	11.5	44.93
	Cu^{II}	3.16	2.82	5.98	33.95	15.2	62.92
	Zn^{II}	2.23	1.72	3.95	22.54	9.8	42.75
2,4-DP	Co^{II}	2.82	2.20	5.02	28.64	13.2	51.81
	Ni^{II}	2.40	1.96	4.36	24.88	11.2	45.91
	Cu^{II}	3.08	2.80	5.88	33.55	15.0	62.25
	Zn^{II}	2.16	1.60	3.76	21.45	9.6	39.77
MCPB	Co^{II}	2.62	2.06	4.68	26.70	13.2	45.30
	Ni^{II}	2.20	1.90	4.10	23.39	11.0	41.58
	Cu^{II}	2.92	2.60	5.52	31.50	14.9	55.70
	Zn^{II}	2.06	1.56	3.62	20.66	9.5	37.45
2,4-DB	Co^{II}	2.65	2.08	4.73	26.99	13.0	46.95
	Ni^{II}	2.24	1.92	4.16	23.74	10.8	43.42
	Cu^{II}	2.94	2.63	5.57	31.78	14.8	56.98
	Zn^{II}	2.10	1.58	3.68	21.00	9.3	39.26

*Uncertainty in ΔH^0 $\pm$ 0.1 kJ mol^{-1} and in ΔS^0 $\pm$ 0.3 JK^{-1} mol^{-1}.

phenoxy acids have little but an important role in lowering the protonation as well as the overall stability constants of metal complexes. However, conjugation between the phenyl ring and the carboxyl group in the series of substituted phenoxy acids is not possible, thus only the inductive effects of the chloro substituents on the phenyl ring will influence these values. The addition of third chloro substituent in the *meta* position (2,4,5-T) resulted in a further increase in acidic strength. The contribution of some other smaller or second order effects, such as,

simple dissymmetry caused by any one sided substitution, the resonance interaction of chloro groups, etc., which may influence the stability of these complexes, may not be completely ruled out. The order of the stability constant values of the complexes in terms of ligands has been found to be :

2,4-DP > MCPB > 2-CPA > PAA > 2,4-DB > MCPA > 2,4-D > 2,4,5-T
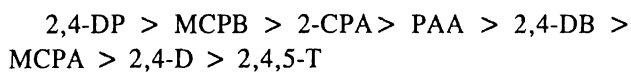
which is in accordance with the basicity of these ligands

(Fig. 3). Phenoxyacetic acid and its chloroderivatives possess such structural characteristics that they may form chelates with the structure of the type (a) or (b) (Structure 2) where metal may participate with either one oxygen from carboxyl group and a phenoxy oxygen atom or both the oxygen atoms of carboxyl group of the ligand.
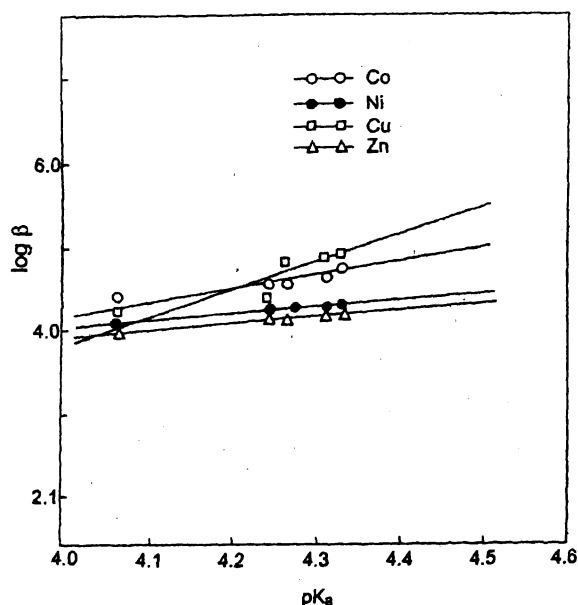

Fig. 3. Dependence of log β on pK_a values of phenoxy acids.

It is, therefore, concluded from above discussion that biologically inactive phenoxyacetic acid and its active substituted derivatives form stable metal complexes both in solid state and in solution. Such a tendency of these agents may be utilized in complexometric analysis of herbicides and in facilitating metabolic processes in biological systems. In part, the similarity in the characterizing parameters of substituted phenoxy herbicides (active) suggests that they share a common mode of action. Also, it may be anticipated purely on chemical ground that ring substitutions in phenoxy acid herbicides and their interaction with bound metals in the form of metal complex species, such as, metalloenzymes, metalloproteins, etc., pre-existing in biological systems must be considered while deciding the mode of action of these herbicides.

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