

## THE CHELATION BETWEEN DIVALENT TRANSITION METAL IONS AND CARBOXYPHENYLHYDRAZO- $\beta$ -DIKETONE ORGANIC LIGANDS IN 75 % DIOXAN-WATER SOLVENT

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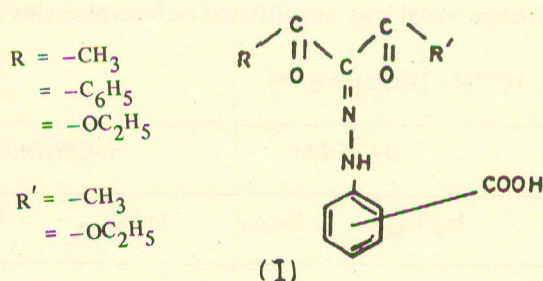
The dissociation constants for different carboxyphenyl-hydrazo- $\beta$ -diketones ligands as well as the stability constants for divalent metal complexes of Cu(II), Ni(II), Co(II), Zn(II), Mn(II) and Cd(II) ions, have been calculated pH-metrically in 75 % dioxan-water solvents. The relations between  $\log K_{MA}$  and both second ionization potential & dissociation constants are discussed.

### INTRODUCTION

Various  $\beta$ -diketones have been studied for the complex formation with divalent metal ions[1]. Also the azo compounds were used as complexing agents[2]. Recently, the combination compounds between these two classes (carboxyphenylHydrazo- $\beta$ -diketones) were used as good complexing agents[3,4].

In this article, the dissociation and the stability constants of chelate compounds between carboxyphenyl-hydrazo- $\beta$ -diketone organic ligands and divalent transition metals are calculated. Also the influence of the structure of the ligands on its ability for chelation is discussed.

The interested tridentate ligands selected for this study are expressed by general formula(I) defining the substituent group R and R' in each case



The hydrazo structure for this class of compounds was confirmed by spectroscopic[4] and polarographic[5] means.

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### EXPERIMENTAL

1. *Preparation of the Organic Ligands.* The organic ligands were prepared from the corresponding diazotized amine coupled with the selected  $\beta$ -diketones in aqueous alcoholic sodium acetate solution[6]. The crude products were recrystallized from suitable organic solvents.

a) *o*-carboxyphenylhydrazo-acetylacetone (*o*-CPHAA) was prepared recently as yellow needles (m.p. 228°)[3a].

b). *o*- and *m*-carboxyphenylhydrazo-diethylmalonate was also prepared and recrystallized from ethanol as yellow and reddish-yellow needles m.p. 135°[7], 138°[8], for *o*- and *m*-carboxy derivatives respectively.

c). *o*-carboxyphenylhydrazo-benzoylacetone. The crude product was recrystallized from acetic acid, giving yellow fine needles m.p. 148-150°[8].

2. *Preparation of Solutions.* Stock solution of copper, nickel and cobalt were prepared from their nitrates while the other metal ions zinc, manganese and cadmium were prepared as sulphates. All the materials used are of the BDH grade. Standardization of metal ions were performed by titration with disodium salt of EDTA using suitable indicators. Standard potassium hydroxide solution was prepared in the usual way as well as the organic solvent was purified follow the recommended method.

3. *Measurements and Calculations* pH-metric titrations used in this investigation are similar to that described previously[9]. The organic ligands ( $5 \times 10^{-3}$  M) were titrated in absence and presence of  $2.5 \times 10^{-3}$  M. metal ions with 0.1 M potassium hydroxide in 75 % dioxan-water solvent.

In the pH regions below 4.0 and above 10.0, the corrected values of  $[H^+]$  and  $[OH^-]$  were calculated in

order to refine the results [10a]. The pH readings are corrected in dioxan-water solvents [11] and also the hydrogen ion activity was calculated from hydrogen ion concentration.

The dissociation constants of organic ligands as well as the stability constants  $K_{MA}$ ,  $K_{MA_2}$  and  $\beta_2$  (overall stability) of the formed complexes are calculated as mentioned previously [10] considering organic ligands a diprotonated ligand, after subjecting the data to the least square analysis.

## RESULTS AND DISCUSSION

The titration of the organic ligands in absence and in presence of divalent metal ions in 75 % dioxan-water solvent was repeated twice in which reproducibility of about 0.05 pH unit has been found.

The dissociation constants  $pK_1$  and  $pK_2$  for organic ligands are given in Table 1. The summation of dissociation constants ( $pK_1 + pK_2$ ) of the different ligands are decreased

in the following order (the acidity increased): *o*-CPHAA > *o*-CPHDEM > *o*-CPHBA > *m*-CPHDEM.

The stability constants  $K_{MA}$ ,  $K_{MA_2}$  and  $\beta_2$  (overall stability) of complexes formed between the organic ligands ( $H_2A$ ) and divalent metal ions Cu, Ni, Co, Zn, Mn and Cd are shown in Table 2.

The values of the stability constants are believed to be fairly accurate since no evidence of hydrolysis of the organic ligands was detected in the titration of this compound. Fig. 1. shows the pH-metric titration curves of divalent metal chelates of ligand (*o*-CPHBA) as an example, and KOH at 30°. Cupric ion curve shows a large depression in pH than that for other metal ions, confirming the formation of more stable chelate compound. The steep inflection at  $m = 4$  (where  $m$  = number of moles of base per mole of metal) indicates that the complexes  $MA_2^{2-}$  (1:2) were formed, where M is referred to the divalent metal ion. In Cu-ligand complex curve, there is a weak inflection at  $m = 2$ , except in case of Cu-*m*-CPHDEM complex, a clear evidence for the formation of MA (1:1) complex.

Table 1. Dissociation constants of the different organic ligands ( $H_2A$ ) in 75 % dioxan-water solvent at 30° and ionic strength 0.1 ( $H_2A$ ) =  $5 \times 10^{-3}$  M.  $V_0 = 30$  ml (KOH = 0.1 M).

Organic ligands	Dissociation constants		
	$pK_1$	$pK_2$	$pK_T = (pK_1 + pK_2)$
<i>o</i> -CPHAA	$6.08 \pm 0.02$	$13.90 \pm 0.04$	19.98
<i>o</i> -CPHBA	$5.59 \pm 0.02$	$13.68 \pm 0.02$	19.27
<i>o</i> -CPHDEM	$5.98 \pm 0.01$	$13.72 \pm 0.04$	19.70
<i>m</i> -CPHDEM	$6.40 \pm 0.02$	$11.89 \pm 0.04$	18.29

Table 2. Stability constants of the chelate compounds between divalent metal ions and different carboxyphenylhydrazo- $\beta$ -diketone in 75 % dioxan-water at 30° and  $\mu = 0.1$ .

$$[M] = 2.5 \times 10^{-3} \text{ M.}, [H_2A] = 5 \times 10^{-3} \text{ M.}, [KOH] = 0.1 \text{ M.}$$

Metal ion	<i>o</i> -CPHAA		<i>o</i> -CPHBA		<i>o</i> -CPDEM		<i>m</i> -CPHDEM	
	$\log K_{MA}$	$\log \beta_2$	$\log K_{MA}$	$\log \beta_2$	$\log K_{MA}$	$\log \beta_2$	$\log K_{MA}$	$\log \beta_2$
Cu	18.88	30.37	16.42	28.28	16.04	27.72	12.07	22.93
Ni	14.31	24.99	13.56	24.52	13.57	24.47	11.41	21.40
Co	13.57	23.85	12.71	22.39	12.91	22.91	11.06	20.54
Zn	13.06	22.85	12.16	21.14	12.57	22.08	10.76	19.76
Mn	12.83	22.23	11.91	20.75	12.22	21.20	10.50	18.25
Cd	13.18		13.01	22.32	12.82	22.22	11.01	19.68

The decreasing in the stability constants for the divalent metal complexes with respect to the organic ligands is in the following order:

OCPhAA > *o*-CPHDEM > *o*-CPHBA > *m*-CPHDEM which is similar to that of the summation of the dissociation constants Table 1, for the different ligands. The general trend, for the chelate stability of divalent metal ions for the different studied organic ligands is the same and the order of stability were found to follow: Mn < Co < Ni < Cu > Cd > Zn, which agrees with Irving and Williams[1] conclusion and which found to be the same order with  $\beta$ -diketones itself[11].

It is clear from Table 2 that the *o*-carboxyl-ligands has a greater tendency to form chelate compounds with metal ion than that the  $\beta$ -diketones itself[1,11] and this may be due to the presence of multidentate sites in the ligand. Also, a higher stability values for the complexes of *o*-CPHDEM with respect to *m*-CPHDEM ligands which can be attributed to the presence of carboxylic group in ortho position and consequently sharing in chelation process.

Fig.2. represents the relation between second ionization potentials (2nd  $I_p$ ) of divalent metals and  $\log K_{MA}$  for different ligands. The stability constants increase by increasing a second ionization potentials, indicating an increase in tendency of the formation chelate compounds. The same conclusion is also obtained from the relation between electronegativity of the divalent metal ions and the stability of the chelate compounds.

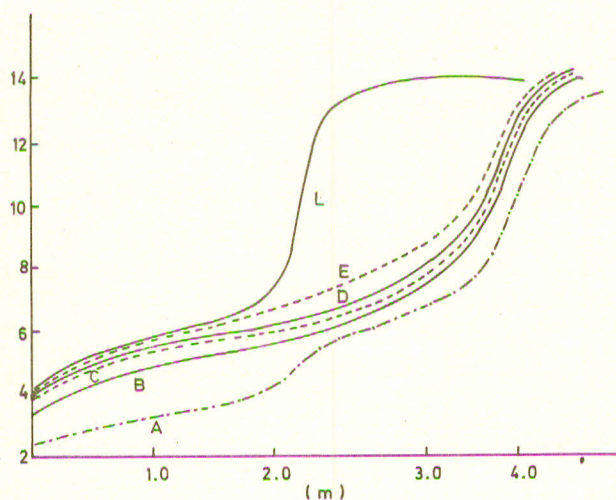


Fig.1. pH-metric titration of divalent metal chelates of *o*-carboxyphenylhydrazo-benzoylacetone (*o*-CPHBA) in 75% dioxan-water and 0.1 KOH at 30°C with 2:1 molar ratio of ligand to metal ion. A = Cu(II), B = Ni(II), C = Co(II), D = Zn(II), E = Mn(II), and L = Ligand alone ( $m$  = number of moles of base added per mole of metal ion).

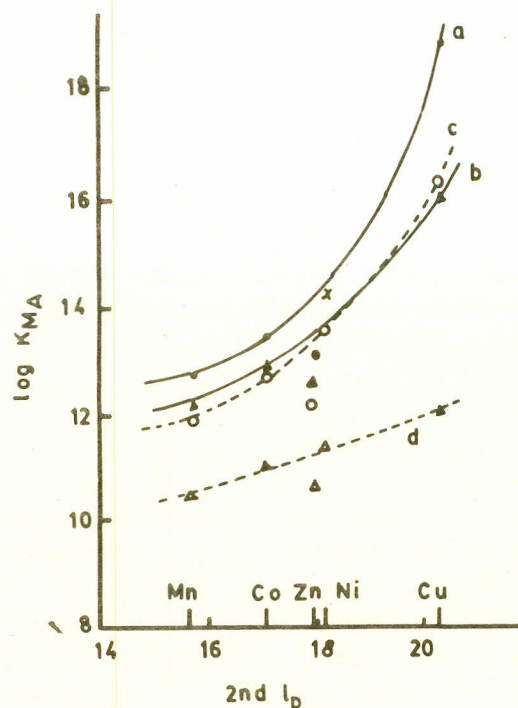


Fig. 2.  $\log K_{MA}$  for metal-ligand complexes vs. second ionization potential a = *o*-CPHAA, b = *o*-CPHDEM, c = *o*-CPHBA and d = *m*-CPHDEM.

The higher value in the stability of the copper complexes, (Fig.2) is due to the greater tendency of copper ion to form a chelate compounds. This increase in stability of copper complexes agrees with the general behavior of copper in chelation with other  $\beta$ -diketones[11]. Also, the chelating ability of metal ion with the organic ligands is increased with the increase of dissociation constants of the ligand.

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