

## Chelating Behaviour of Substituted 3-Arylhydrazopentan-2,4-Dione (Part X)

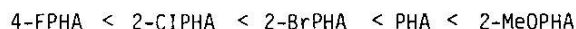
### Structure of Copper (II) Complexes of 2-Methoxy,2-Chloro, 2-Bromo and 4-Fluorophenylhydrazopentan-2,4-Dione.

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**Summary:** Infra-red and U.V. visible spectra studies were carried out on Copper (II) complexes of 2-methoxy phenylhydrazoacetylacetone (2-MeOPHA), 2-chlorophenylhydrazoacetylacetone (2-Cl-PHA), 2-Bromophenylhydrazoacetylacetone (2-Br PHA), and 4-Fluorophenylhydrazoacetylacetone (4-FPHA) organic ligands. The composition of complexes was found to be 1:2 (metal to ligand) stoichiometry and the structure of complexes was proposed to be square planar. The proton-ligand dissociation constant (pK) and the stability constants ( $\log K_1$  and  $\log K_2$ ) of their copper complexes have been determined pH-metrically at 30°C and at ionic strength 0.1 in 75% dioxane-water medium. The stability constants was found to be in the following order.



## Introduction

Investigations on the complexes formed between transition metals and the coupling products of different  $\beta$ -diketones and the diazonium salts aniline, aminocarboxylic acids and aminosulphonic acids have been carried out by several authors [1-4]. However, nothing is known about the complexing ability of 2-methoxy, 2-chloro, 2-bromo and 4-fluoro phenylhydrazopentane-2,4-dione ligands (abbreviated by 2-MeOPHA, 2-CIPHA, 2-BePHA and 4-FPHA respectively) towards Cu(II) ion.

In this work we studies the effect of electron withdrawing ( $F^-$ ,  $Cl^-$ ,  $Br^-$ ) and electron repelling ( $MeO^-$ ) groups substituted in the phenyl ring of phenyl-hydrizo-pentan-2,4-dione on the dissociation constants of the free

ligands and the stability constants of their Cu(II) complexes. This was accomplished by pH-metric titrations with KOH in dioxane-water mixture (75% dioxane). The geometric structure and coordination sites of the solid Cu(II) complexes were suggested on the bases of their IR and UV- visible spectra.

## Experimental

### Materials:

Copper (II), nitrate,  $Cu(NO_3)_2 \cdot H_2O$ , acetylacetone, dioxane, sodium acetate, 2-methoxy, 2-chloro, 2-bromo, 4-fluoro aniline and dimethyl formamide were BDH chemicals. Potassium hydroxide was AR grade.

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Absolute ethyl alcohol was Merck grade.

Dioxane was purified by refluxing it with sodium metal and  $\text{LiAlH}_4$  for 10 hrs. followed by distillation. This procedure was repeated twice to insure complete removal of the acetals.

*Preparation of organic ligands:*

2-Methoxy, 2-chloro, 2-bromo and 4-fluoro phenylhydrazopentane-2,4-dione were prepared by coupling the corresponding diazonium salts of aniline and acetylacetone in sodium acetate solution (5a). The crude products were recrystallized from absolute ethanol, where yellow needles of 2-MeOPHA and 2-BrPHA; orange-yellow crystals of 2-CIPHA and golden yellow crystals of 4-FPHA were obtained. Their melting points were  $135^\circ$ ,  $122^\circ$  (5b),  $135^\circ$  and  $110^\circ\text{C}$ , respectively. They are insoluble in water, but soluble in organic solvents.

*Preparation of copper (II) complexes:*

The complexes were prepared by the slow addition of a  $1 \times 10^{-1}$  M of an aqueous solution of copper (II) nitrate to an ethanolic solution of  $5 \times 10^{-2}$  M of the ligand (molar ratio 1:4, metal to ligand) at  $60^\circ\text{C}$  and pH 6-7 with continuous stirring. Deep brown crystals of 2-MeOPHA, 2-BrPHA and 4-FPHA-Cu(II) complexes were precipitated from the solution when left overnight. Brown crystals were obtained in the case of 2-CIPHA-Cu(II) complex after refluxing its solution for three hours. The complexes were collected and washed thoroughly with warm water and ethanol, and then dried. The solid complexes are insoluble in water, partially soluble in organic solvents, but completely soluble in DMF.

Analytical data of the complexes indicate 1:2 metal : Ligand stoichiometry as shown in Table 1.

*Spectra and pH-metric measurements:*

Copper ion in solid complexes was determined using vari atomic absorption spectrometer. Infrared spectra of the compounds were recorded on a Perkin-Elmer Spectrometer model 437 using KBr discs. UV-visible spectra were recorded on a Unicam SP800 and Perkin-Elmer 550 S using quartz cells 1 cm pathlength. pH-measurements are similar to those described previously [6]. The correction of pH-readings in 75 % dioxane-water medium, was taken as 0.28 [7]. The dissociation constants of the organic ligands as well as the stability constants  $K_{ML}$ ,  $K_{ML_2}$  and  $\beta$  (overall stability) of the formed Cu(II) complexes were calculated as mentioned before [6]. The organic ligands were considered as a monoprotated ligands, the calculated data were subjected to the least square analysis. 2-MeOPHA complex was taken as an example to study the effect of pH on the complex formation, effect of ligand concentration at constant concentration of metal ion and the composition of complex in 50 % dioxan-water solution in acetate buffer.

**Results and Discussion**

*1-Spectroscopic studies:*

The infra-red and electronic spectra determination of the free ligands and their solid complexes, were helpful in identification of the structure of solid complexes. As many authors have stated [8,9] the hydrazo structure in such type of ligands is the more stable form than both keto and enol forms. In the i.r. spectrum of 4-FPHA ligand, the  $>\text{N-H}$  vib-

Table-1: Results of Analysis of Solid Organic Ligands and Their Copper Complexes

		% Calculated				% Found				Melting Point
		C	H	N	M	C	H	N	M	
4-FPHA	$C_{11}H_{11}O_2N_2F$	59.4	4.95	12.60	-	59.5	4.85	12.90	-	110°
2-CIPHA <sup>5b</sup>	$C_{11}H_{11}O_2N_2Cl$	55.35	4.61	11.74	-	55.40	4.50	11.70	-	122° <sup>5b</sup>
2-BrPHA	$C_{11}H_{11}O_2N_2Br$	46.6 <sup>f</sup>	3.88	9.90	-	46.1	3.81	9.95	-	135°
2-MeOPHA	$C_{12}H_{14}O_3N_2$	61.54	6.00	11.90	-	61.3	5.91	11.81	-	135°
(4-FPHA) <sub>2</sub> -Cu(II)	$CuC_{22}H_{20}O_4N_4F_2$	52.20	3.95	11.07	12.5	52.14	4.00	11.04	12.47	178°
(2-CIPHA) <sub>2</sub> -Cu(II)	$CuC_{22}H_{20}O_4N_4Cl_2$	49.02	3.70	10.40	11.5	51.10	4.09	11.00	11.00	185°
(2-BrPHA) <sub>2</sub> -Cu(II)	$CuC_{22}H_{20}O_4N_4Br_2$	42.07	3.20	9.92	10.10	42.06	3.18	8.96	10.25	198°
(2-MeOPHA) <sub>2</sub> -Cu(II)	$CuC_{24}H_{26}O_6N_4$	56.5	5.10	11.00	12.45	56.90	5.11	11.01	12.65	217°

rational band was very weak and disappeared in the spectrum of its Cu(II) complex, indicating that the hydrogen atom of hydrazo-group in the ligand is replaced by the metal upon complexation. In the same time two new medium and weak bands appeared in the complex spectrum at  $445\text{ cm}^{-1}$  and  $325\text{ cm}^{-1}$  respectively, which were assigned to  $\nu_{M-N}$  stretching vibrations [10,11] supporting the sharing of nitrogen atom in chelation process. The position of conjugated  $\nu_{C=N}$  band [12] was variable in region  $1500\text{--}1600\text{ cm}^{-1}$  and was dependent on the substituted group in the molecule. This band is shifted to lower frequency in 1:2 complex (Table 2). A new medium band appeared at  $545\text{ cm}^{-1}$  confirming the presence of  $\nu_{M-O}$  bond [13], which supports the sharing of carbonyl group in chelation process. Two strong doublet are observed in the i.r. spectrum of the copper complex of (4-FPHA) at  $520, 528\text{ cm}^{-1}$  and at  $635, 638\text{ cm}^{-1}$ , while two strong bands at  $520\text{ cm}^{-1}$  and at  $635\text{ cm}^{-1}$  appeared in the spectrum of the free

ligand. These doublet band in the case of the metal complex may be attributed to the geometrical symmetry of the molecule.

The i.r. spectra of 2-CIPHA organic ligand and its copper complex shows a very slight small changes. The very weak band for  $>NH$  vibration in the free ligand is affected, and at the same time a medium band at  $550\text{ cm}^{-1}$  appeared in the solid complex and is assigned to the  $\nu_{M-N}$  asymmetric stretching vibration. This indicates that the nitrogen atom of hydrazo-group takes part in complex formation. Besides, the observed frequency at  $1635\text{ cm}^{-1}$  in the i.r. spectrum of the free ligand which is assigned to  $\nu_{C=O}$  vibration is shifted to  $1640\text{ cm}^{-1}$  in the complex, and a new medium band for  $\nu_{M-O}$  was observed at  $643\text{ cm}^{-1}$ . This indicates the sharing of carbonyl group in the chelation process (Table 2).

The i.r. spectra of both 2-BrPHA and 2-MeOPHA ligands and their copper complexes also indicate that the

Table-2: Important infra-red bands for organic ligands and Cu (II) complexes.

Compounds	Frequency in $\text{cm}^{-1}$					
	$\nu\text{N-H}$	$\nu\text{C=O}$	$\nu\text{C=N}$	$\nu\text{M-O}$	$\nu\text{M-N}$	$\nu\text{M-N}$
4-FPHA	3100-2920 w.b.b.	1625 s.b.	1608 s.b.	-	-	-
$\text{Cu(II)-(4-FPHA)}_2$	3080-2920 v.w.b.b.	1645 w.sh.	1595 s.b.	545 s.b.	445 s.b.	325 w.b.
2-CIPHA	3020-2888 v.w.b.b.	1635 s.b.	-	-	-	-
$\text{Cu(II)-(2-CIPHA)}_2$	3000-2880 v.w.b.b.	1640 s.b.	-	643 m.b.	550 m.b.	-
2-BrPHA	3000 w.b.	1630 s.b.	1587 m.b.	-	-	-
$\text{Cu(II)-(2-BrPHA)}_2$	3080-2900 v.w.b.b.	1640 w.sh.	1565 s.	645 m.b.	415 m.b.	345 w.b.
2-MeOPHA	3100-2900 v.w.b.b.	1625 s.b.	1600 m.b.	-	-	-
$\text{Cu(II)-(2-MeOPHA)}_2$	3080-2900 v.w.b.b.	1640 w.sh.	1558 m.b.	645 m.b.	415 w.b.	364 w.b.

w = weak, m = medium, s = strong, v = very, b = band, b.b. = broad band, sh = shoulder.

nitrogen atom of the hydrazo group shares in complexation process together with the oxygen atom of the carbonyl group. New bands, for  $\nu\text{M-N}$  frequencies appeared at 415, 345  $\text{cm}^{-1}$  and 415, 364  $\text{cm}^{-1}$  for 2-bromo and 2-methoxy derivatives, respectively [10,11] (Table 2). The observed carbonyl bands at 1630  $\text{cm}^{-1}$  for the 2-bromo and at 1625  $\text{cm}^{-1}$  for the 2-methoxy derivatives are shifted in the spectra of their complexes, while a new band appeared at 645  $\text{cm}^{-1}$  in their spectra corresponding to  $\nu\text{M-O}$  which supports the sharing of the carbonyl group in complexation.

The observed band  $\nu\text{C=O}$  in the spectra of the free ligands 4-FPHA, 2-CIPHA, 2-BrPHA and 2-MeOPHA suffered shifts to higher frequency and became weaker and overlapped with the adjacent bands in the spectra of its  $\text{Cu(II)}$ -complexes.

The electronic absorption spectra of arylhydrazopentane-2,4-dione and their substituted derivatives are characterised by two intense absorption bands. The first band ( $\log \epsilon_{\text{max}} \approx 4.2$ ) at  $\approx 360$  nm. is due to  $\pi-\pi^*$  transition in hydrazo group. The second absorption band ( $\log \epsilon \approx 3.7$ ) at 267 nm. is attributed to  $\pi-\pi^*$  transition through  $\nu >\text{C=O}$  group in pentane-2,4-dione branch. The comparison of the electronic spectra of the free ligands and their solid copper complexes in DMF solvent produce additional strong evidence for the sharing of both hydrazo and carbonyl groups in complexation process, Table 3. This evidence is based on the red shift of the free ligands bands to lower frequencies in the spectra of their copper complexes, (Table 3). Two main bands were observed in the electronic spectra of each complex. A band between 500-600 nm. involves the transition  ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$  and the band

Table-3: U.V. and Visible Absorption Maxima for Complexes and their Organic Ligands in DMF solvent at Room Temperature.

Complexes			Organic Ligands		
Formula	wave length nm	log $\epsilon$	Formula	wave length	log $\epsilon$
(4-FPHA) <sub>2</sub> -Cu(II)	281	4.3802	4-FPHA	267	3.7482
	368	4.4886		362	4.1818
	600	2.6021			
	750	2.1702			
(2-CIPHA) <sub>2</sub> -Cu(II)	268	4.0492	2-CIPHA	267	3.6990
	364	4.6021		362	4.1931
	580	2.7482			
(2-BrPHA) <sub>2</sub> -Cu(II)	269	4.3802	2-BrPHA	266	3.720
	365	4.6513		348	4.3617
	580	2.6990			
	750	2.3010			
(2-MeOPHA) <sub>2</sub> -Cu(II)	278	4.2304	2-MeOPHA	267	3.9031
	400	4.4472		390	4.3063
	500	2.4871			
	700	1.6990			

between 700-780 nm involves  ${}^2B_{1g} \rightarrow {}^2E_g$  transition. These observations suggest square planar symmetry for these complexes [14,15].

#### 2-Potentiometric measurements:

The pH-titration curves for the free 2-MeOPHA ligand and in presence of copper (II) ion at 1:1 and 1:2 metal ligand ratio, are shown in Fig.(1) (They were taken as an example of these titrations). Only one proton is dissociated, since the ligand behaves as a monoprotic species. The dissociated proton ion constant  $K_1$  was

calculated as mentioned previously [6]. Since the ionic product,  $pK_w$ , of water in 75% dioxan-water medium is approximately 18.7 [16], both the hydrogen-ion and hydroxyl-ion concentration terms are negligible in the region of proton dissociation.

The electron releasing polar effect of methoxy group enhances the electron density on hydrazo group. On the other hand, the electron withdrawing effect of 4-Fluoro, 2-Chloro and 2-Bromo derivatives decrease the electron density on hydrazo group. Therefore, the order of acidity increases in the following manner (Table 4).

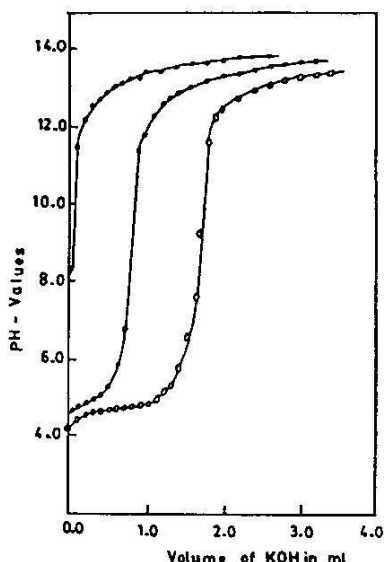


Fig. 1:

Titration curves in 75% Dioxan-water of:

- 1- 2-MeOPHA ligand  $2 \times 10^{-3}$  M.
- 2- 2-MeOPHA ligand  $2 \times 10^{-3}$  M + Cu(II)  $1 \times 10^{-3}$  M.
- 3- 2-MeOPHA ligand  $2 \times 10^{-3}$  + Cu(II)  $2 \times 10^{-3}$  M.

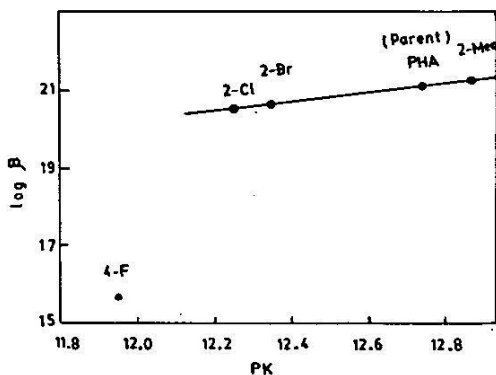


Fig. 2: Relation between pK of organic ligands and  $\log \beta$  of Cu (II) complexes.

2-MeOPHA < PHA < 2-BrPHA < 2-ClPHA  
< 4-FPHA

The titration curves obtained in the presence of Cu(II) ion showed an

inflection at  $m=2$  (where  $m$  = moles of base added per mole of metal); corresponding to the formation of bis-chelates, represented by the equation.



From the titration curves of metal-ligand mixtures,  $\log K_1$ ,  $\log K_2$  and  $\log \beta$  (overall stability) values were evaluated from the linear plots of  $\log n/1-n$  and  $\log 2-n/n-1$  vs. pL. The difference between  $\log K_1$  and  $\log K_2$  values was found to be less than 1.78 log unit, therefore, the stabilities were calculated by the least square method.

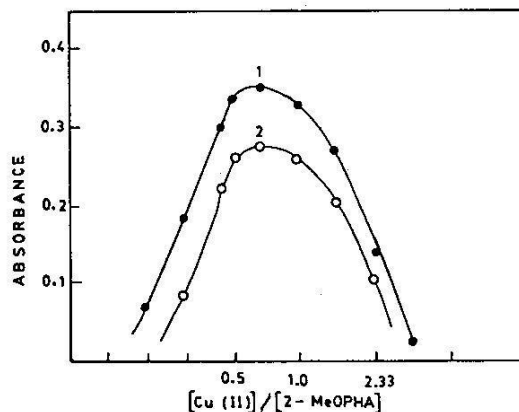


Fig. 3: Job method at pH = 6.0 in acetate buffer at: 1-  $\lambda = 475$  nm., 2-  $\lambda = 488.5$  nm.

The most representative values are noted in (Table 4). The stability constants of organic ligands - copper complexes was found to be increased in the following order:

4-FPHA < 2-ClPHA < 2-BrPHA < PHA  
< 2-MeOPHA

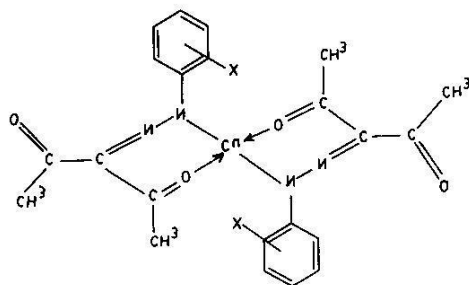
Also, spectrophotometric study was carried out on a mixture of copper (II) ions and 2-MeOPHA ligand in 50 % dioxane-water medium as an example to confirm the composition of complexes in solution. The effect of pH on this

Table-4: Dissociation constant and stability constants of Cu(II) - Organic ligand complexes at 30°C and 0.1M KCl in 75% dioxane-water mixture.

Compound	Dissociation constant pK	Stability constants of Cu(II) Complexes	
		$\log K_{ML}$	Log " $\beta$ "
4-FPHA	11.95 ± 0.10	7.92 ± 0.08	16.61 ± 0.10
2-CIPHA	12.25 ± 0.15	10.33 ± 0.04	20.52 ± 0.08
2-BrPHA	12.35 ± 0.14	10.41 ± 0.08	20.72 ± 0.08
PHA	12.74 ± 0.04	10.83 ± 0.10	21.07 ± 0.10
2-MeO PHA	12.86 ± 0.14	10.94 ± 0.09	21.14 ± 0.09

complex in acetate buffer indicate that the optimum pH value is 6.0. Job [17] and molar ratio [18] methods were applied to insure the 1:2 metal-ligand composition of the complexes (Fig.3).

It can be concluded from the results obtained by different analytical techniques that the composition of the formed complexes is 1:2 copper to ligand ratio. The chelation process performed through one carbonyl group of pentan-2,4-dione and the other chelation cite through nitrogen of hydrazo group from both ligand molecules (Fig.4). As mentioned previously [4], the coordination involves the nitrogen atom adjacent to the phenyl group since the hydrazotautomer is the most stable form.

Fig.4: Schematic structure of complexes for Cu(II)L<sub>2</sub>.

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