

## CHELATING BEHAVIOUR OF SUBSTITUTED 3-ARYLHYDRAZOPENTANE-2,4-DIONE

Part II. Spectrophotometric Studies of Copper (II) with *m*- and *p*-Carboxybenzenehydrazopentane-2,4-dione

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**Abstract.** The complex formation of copper *m*- and *p*-carboxybenzenehydrazopentane-2,4-dione (*m*, *p*-CBAP) system is treated spectrophotometrically. The composition of the formed complexes are given and the structural configuration of these complexes proposed.

Acetylacetone or generally  $\beta$  diketones were used as complexing agents early, as they are strong chelating agents. However, the introduction of different substituents in the main chain of acetylacetone may affect its tendency as a chelating agent towards several cations. These substituted  $\beta$  diketones are very valuable because they form stable complexes with many transition metals,<sup>1-3</sup> on the other hand their complexes with rare earths can mostly be sublimed as an aid in their separation.

In our previous work<sup>4</sup> we studied the complex formation of Cu(II) with *o*-carboxybenzenehydrazopentane-2,4-dione spectrophotometrically.

Recently Ghosh<sup>5</sup> studied the solid complexes of Cu(II), Ni(II), Co(II), and Co(III) with benzenehydrazopentane-2,4-dione.

In this current work we continue our study of complexes of Cu(II) with *m*- and *p*-carboxybenzenehydrazopentane-2,4-dione to correlate the structure and stability with the types of complexes which may be formed.

## Experimental

**Preparation of the Ligands.** The ligands were synthesized by coupling the corresponding diazonium salt of aniline derivatives with acetylacetone in sodium acetate<sup>6</sup> and were recrystallised several times from ethanol (*o*-CBAP, m.p. 176°C; *p*-CBAP 267°).

**Materials.** Copper acetate was used and standardized by EDTA using Eriochrome black T indicator. Dioxane was used as a nonaqueous solvent and purified by refluxing over metallic sodium for about 10 hr, and then fractions were collected between b.p. 100-101°. The collected dioxane was refluxed again over sodium metal and lithium aluminium hydride for about 4 hr and again distilled and collected at 100-101.

**Isolation of the Solid Cu(II)-*m*-CBAP.** The solid complex was isolated by mixing equimolar solution of copper acetate ( $1 \times 10^{-1} M$ ) and the ligands as a K-salt in 25% dioxane-water and the pH of the mixture was adjusted at 6. The complexes were re-

crystallised from ethanol and dried *in vacuo* then analysed for C, H and N.

**Measurements and Apparatus.** The UV and visible spectra were carried out on Beckman DK recording and Prolabo Jean and R constant spectrophotometers UV model in the range of 220-1000 nm. Measurements of the spectra were carried out at room temperature in 1 cm quartz cells using dioxane-water as a reference solution. No inert electrolyte was added. Reading of pH was carried out on Chinese pH meter model 25 provided with a glass calomel electrode. The pH meter was calibrated by three buffers before each experiment. In case of using nonaqueous solvent the pH meter reading was corrected according to Van Uitert<sup>7</sup> equation and Irving<sup>8</sup> method.

The IR spectra for the isolated solid and the ligand were taken in KBr matrix in the range 600-4000  $cm^{-1}$  using Beckman IR-12 spectrophotometer previously calibrated.

## Results and Discussion

**Copper-*m*-carboxybenzenehydrazopentane-2,4-dione (*m*-CBAP).** During the study of the complex formation of the system Cu(II)-*m*-CBAP, a green gelatinous precipitate was formed, but when the reaction was carried out in 25% dioxane (v/v) the green precipitate dissolved.

The ligand has no appreciable absorbance before 440 nm, so the spectrophotometric studies were made in the range of 440-800 nm.

The effect of hydrogen ion concentration on the absorption spectra of Cu-*m*-CBAP are shown in Fig. 1. It can be noticed that the increase of pH leads to an increase of absorbance till pH 8, and thereafter the absorbance became constant (Fig. 1). A new band at 580 nm appears. There is no appreciable contribution from free Cu(II) as its molar absorptivity is very low.

The stoichiometry of the formed complexes were determined by different methods.

A plot of the absorbance of a series of solutions having the same molar concentration but varying in the concentration of the constituents, against the mole fraction of Cu<sup>2+</sup> (Job's method<sup>2</sup>) is shown in

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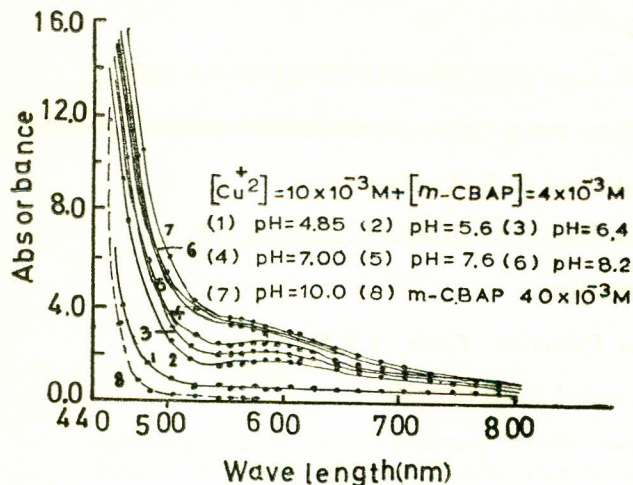


Fig. 1. Absorption spectra of Cu (*m*-CBAP) system at different pH levels.

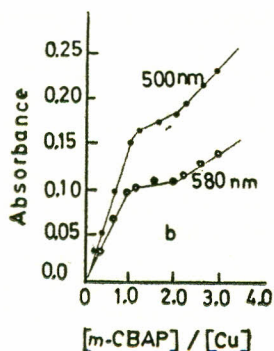
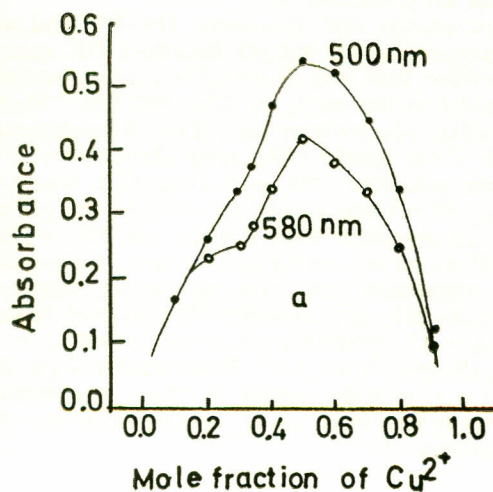
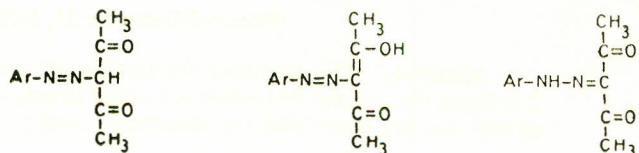


Fig. 2. (a) Continuous variation method for Cu (*m*-CBAP) complexes in 25% dioxane water solvent at pH 5.8. (b) Molar ratio method for Cu (*m*-CBAP) complexes in 25% dioxane water at pH 5.8.

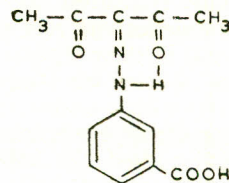
Fig. 2 (a) at different wavelengths. The curves exhibit a maximum at 0.5 mole fraction of  $\text{Cu}^{2+}$  indicating that 1:1 (metal ligand) complex is formed. A shoulder is observed at 0.32 mole fraction proving that 1:2 complex may be formed. The formation of 1:1

and 1:2 complexes is confirmed by molar ratio<sup>10</sup> which is represented graphically in Fig. 2(b). This shows that complex with molar ratio 1:1 is less stable than 1:2.

$\beta$ -Diketones couple with aromatic diazonium compounds in alkaline solutions to give 'mixed azo compounds'<sup>11</sup> which may have one of the following tautomeric structures difficult to establish with certainty. It is generally assumed that the hydrazone is the stable form whenever coupling occurs at a methyl or methylene carbon. Recently, Wiley and Jarboe<sup>12</sup> and Tauner<sup>13</sup> have presented IR absorption data which corroborate this view.



Furthermore Ketaev *et al.*<sup>14</sup>, on the basis of polarographic data and the findings of Elguero *et al.*<sup>15</sup> support the above conclusion. Therefore, our ligand will have more probably structure I.

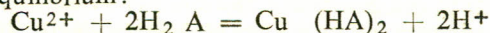


The structure and the composition of the complex was also confirmed by the IR spectra of the isolated solid complex. Analysis for C, H and N gave 50, 4.2 and 9.7% respectively which is in agreement with the molecular formula  $\text{Cu}(\text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_4)_2\text{H}_2\text{O}$  i.e.  $\text{Cu}(\text{m-CBAP})_2\text{H}_2\text{O}$ .

IR spectra of Cu(II) acetylacetonate has been studied previously.<sup>16,17</sup> In the IR spectra of the solid  $\text{Cu}(\text{m-CBAP})_2\text{H}_2\text{O}$  the  $3200\text{ cm}^{-1}$  broad band which is always assigned to NH vibrational band, present in the spectra of the ligand, is absent. This indicates that the nitrogen atom of the hydrazone group of the ligand shares in the process of chelation. The observed  $1680\text{ cm}^{-1}$  medium band which is attributed to the C=O stretching frequency in the ligand becomes less intense in the spectra of the solid complex indicating that the oxygen atom of one of the two carbonyl groups is coordinated to the metal.

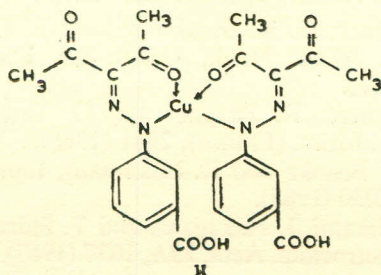
A sharp band at  $1590\text{ cm}^{-1}$ , which was found in the IR spectra of the solid complex, indicates that the carboxyl group of the ligand does not share in the process of complex formation.

Accordingly the reaction between *m*-CBAP ( $\text{H}_2\text{A}$ ) with cupric ion occurs according to the following equilibrium:



This indicates that the copper ion replaces hydrogen atom of the hydrazone group and that the carboxyl

group participation is not involved as would be required in the formation of a 1:1 complex, a structural formula for the 1:2 complex is given in structure II.



*Copper-carboxybenzenehydrazopentane-2,4-dione (p-CBAP)*. When *p*-CBAP was added gradually to  $\text{Cu}^{2+}$  solution in aqueous media a yellowish green precipitate formed. There is no precipitation in dioxane-water mixture as a solvent.

The study of complex formation between copper and *p*-CBAP spectrophotometrically was carried out in the range 440–800 nm using mixed solvent and a solution of *p*-CBAP as a reference.

The absorption spectra of the complex of copper with *p*-CBAP at different pH levels are shown in Fig. 3.

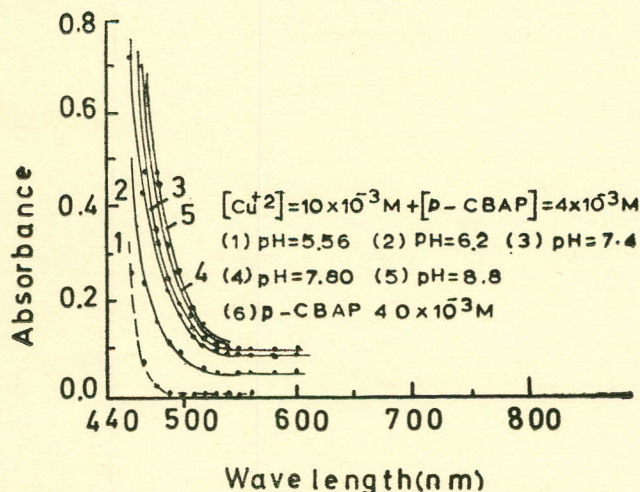


Fig. 3. Absorption spectra of Cu (*p*-CBAP) system at different pH levels.

It is clear that the addition of *p*-CBAP to copper acetate solution leads to an increase of the absorbance in the region between 380–600 nm, in which the absorbance of the ligand is negligible. This can be attributed to a new ligand field environment produced by replacing water ligand in aquo ion of  $\text{Cu}^{2+}$  by *p*-CBAP.

The composition of the complex was established as above. The molar ratio plot<sup>9</sup> (Fig. 4b) shows an intersect at pH 7.5 and a molar ratio 1:2 (metal:ligand). This conclusion is confirmed on the continuous variation plot (Fig. 4a). This indicates that the most probable composition for the complex is 1:2 and the carboxyl group in the *para* position of the benzene ring does not share in the formation of the 1:2 complex. This supports our previous conclusion about the system Cu-*m*-CBAP. This means that

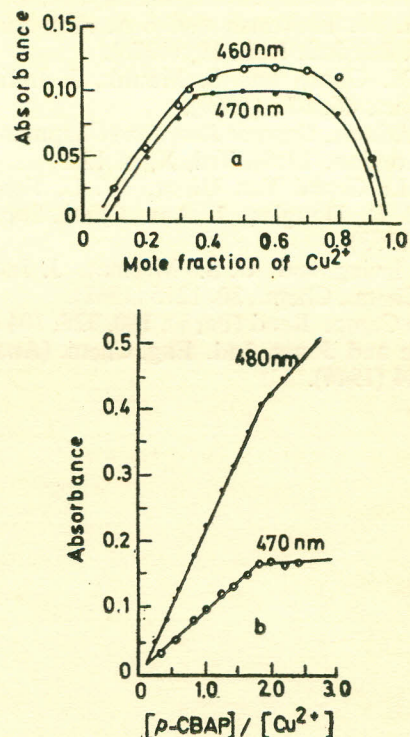


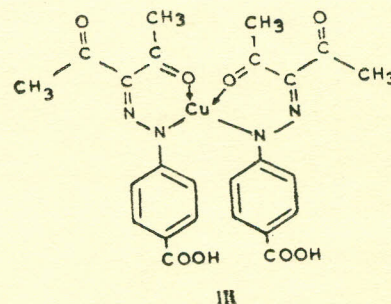
Fig. 4. (a) Continuous variation method for Cu (*p*-CBAP) complexes at pH 7.5 in 25% dioxane water solvent.

(b) Molar ratio method for Cu *p*-CBAP complexes at pH 7.5 in 25% dioxane water solvent.

*m*-CBAP and *p*-CBAP behave as benzenehydrazopentane-2,4-dione towards complex formation.

Similar to that, in case of *m*-CBAP, is the nitrogen atom of the hydrazone group of *p*-CBAP linked to the metal, while the carboxyl group which is in the *para*-position of the benzene ring, does not share in the process of complex formation.

The structural formula of 1:2 complex of Cu-*p*-CBAP can be represented schematically as illustrated in structure III.



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