

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

Part 1. Spectrophotometric Studies of Copper with 3-Benzenehydrazopentane-2,4-dione and *o*-Carboxybenzenehydrazopentane-2,4-dione

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**Abstract.** The interaction of 3-benzenehydrazopentane-2, 4-dione (BHP) and *o*-carboxybenzenehydrazopentane-2,4-dione (*o*-CBAP) with  $\text{Cu}(\text{H}_2\text{O})_2^{2+}$  was studied spectrophotometrically. The condition of complex formation was determined. It was shown that  $\text{Cu}(\text{H}_2\text{O})_2^{2+}$  forms with BHP 1:2 complex (metal ligand), while it forms with *o*-CBAP 1:1 complex. The structures of these complexes are proposed.

Acetylacetone and its derivatives are well-known strong chelating agents,<sup>1-3</sup> on the other hand azo compounds have been used widely as a complexing ligand with some transition metals.<sup>4-6</sup>

From the structure of acetylacetone it is clear that it contains an active hydrogen atom which can be coupled with any other diazonium compound to give dyes. The product of coupling benzene diazonium compound and acetylacetone is benzenehydrazopentane-2,4-dione (BHP). Ghosh<sup>7</sup> used BHP as complexing agent with Cu(II), Ni(II), Co(II) and Cd(III). The solid complexes were separated and had been studied by physicochemical methods. Other investigations on the complex formation of these ligands and their derivatives are not reported.

The aim of the work was to study the process of complex formation between Cu(II) and 3-arylhydrazopentane-2,4-dione where  $\text{Ar}-\text{C}_6\text{H}_5$  (3-benzenehydrazopentane-2,4-dione, BHP), *o*- $\text{C}_6\text{H}_5-\text{COOH}$ , (*o*-carboxybenzenehydrazopentane-2, 4-dione, *o*-CBAP), in order to know the effect of substituent in the benzene ring and to obtain more information about the chemistry of Cu(II) in aqueous and nonaqueous media.

The investigations were carried out spectrophotometrically.

### Experimental

**Preparation of the Ligands.** The ligands were synthesized by coupling the corresponding diazonium salts of aniline derivatives with acetylacetone in sodium acetate<sup>8</sup> and recrystallised several times from ethanol; (BHP, m.p. 88°; *o*-CBAP, m.p. 228).

**Materials.** Dioxan was used as a nonaqueous solvent and was purified by refluxing over metallic sodium for about 10 hr and then fractions were collected between 100-101 c. The collected dioxan was again refluxed over sodium metal and lithium aluminium hydride for about 4 hr then distilled again and collected at 100.5-101°.

Solution of copper acetate was used and standardized by EDTA using Eirochrome black T as indicator.

**Isolation of the Solid Complexes of Cu (II)-*o*-CBAP and BHP.** In case of *o*-CBAP the complexes were prepared by mixing equimolar solutions of copper acetate ( $1 \times 10^{-1}\text{M}$ ) and the ligand as a K-salt in 25% dioxan-water, and the pH of the mixture was adjusted at 7.5. In case of BHP the complex was isolated by the addition of 50 ml aqueous solution of copper acetate to 100 ml of ethanolic solution of BHP ( $2 \times 10^{-2}\text{M}$ ) in 1:4 molar ratio, dropwise by continuous stirring at pH 7. The complexes were recrystallised from ethanol, dried *in vacuo* then analysed for C, H and N, and the m.p. was noted.

**Apparatus.** The UV and visible spectra were carried out on Beckman DK-recording spectrophotometer and Prolabo Jean and R. constant spectrophotometer, UV Model in the range 220-1000 nm. One centimeter quartz cell was used.

Adjustment of the pH of the solutions was carried out by means of KOH or  $\text{H}_2\text{SO}_4$  on a Chinese pH meter model 25, provided with glass and calomel electrodes and was calibrated by three buffer solutions before every reading. In case of nonaqueous solvent the pH meter was calibrated using Van Uitert<sup>9</sup> equation and Irving<sup>10</sup> method.

The spectra were recorded at room temperature after 5 min of preparing the solutions whereafter the absorbance of solutions becomes constant at room temperature and still fairly stable for 24 hr. No inert electrolyte was added.

The IR spectra were taken for the solids in KBr matrix in the range 300-4000  $\text{cm}^{-1}$  using Beckman IR-12 spectrophotometer previously calibrated.

### Results and Discussion

**Interaction of Copper and 3-Arylhydrazopentane-2,4-dione,  $\text{C}_6\text{H}_5$  (BHP).** The addition of BHP solution to copper acetate changes the colour from blue to brown. It was found that 50% dioxan-water (v/v), is suitable for spectral measurements, since no per-

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precipitate takes place. Measurements before 450 nm were carried out since BHP has no appreciable absorbance in this region.

It was found that the absorbance in the region 450–800 nm increases by changing the concentration of BHP i.e. the molar absorptivity of the formed complex is greatly more than that of  $\text{Cu}(\text{H}_2\text{O})_2^{2+}$ , since the concentration of copper acetate used is very small.

The effect of pH on the absorbance of the solution is shown in Fig. 1. There is an increase in the absorbance with the increase in the pH. There is a shift of the maximum to a shorter wavelength and finally over pH 5.2 a new broad band appears (500–580 nm). This band is not due to the absorbance of the ligand since its absorbance in this region is negligible.

The increase in the absorbance by changing the pH may be taken as an evidence for the formation of more complex species or due to the formation of a hydroxy complex. It is clear that the complex formation is attained over pH 4 and only one type of complex can be formed at 5–7.5 pH. Measurements were impossible above 7.5 due to the precipitation of the complex.

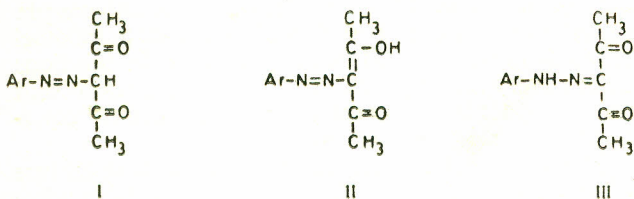
The composition of the formed complex was investigated by different methods.

Figure 2 shows the relation of the absorbance of a series of solutions of copper acetate and BHP having the same molarity but varying in the concentration of the constituents (Job's method).

These solutions were kept at a constant pH 6.2. From this figure it is clear that 1:2 metal ligand is formed.

The formula  $\text{Cu}(\text{BHP})_2$  is confirmed by mole ratio (Fig. 3) straight line<sup>12</sup> and slope ratio<sup>13</sup> methods. The molar absorptivity of the formed complex at  $\lambda$ –500 nm is  $250 \text{ mol}^{-1} \text{ cm}^{-1}$ .

The structure of substituted 3-arylazopentane-2,4-dione was studied by many authors.<sup>14,15</sup> Ketaev *et al.*<sup>15</sup> have reported on the basis of polarographic data that the azo compounds formed by coupling of  $\beta$ -diketones with aromatic diazonium compound have structure III,



Elguero *et al.*<sup>16</sup> on the basis of IR data concluded that if  $\text{Ar}=\text{C}_6\text{H}_5$ , the dye should have the structural formula (I), i.e. there is a hydrogen bond between

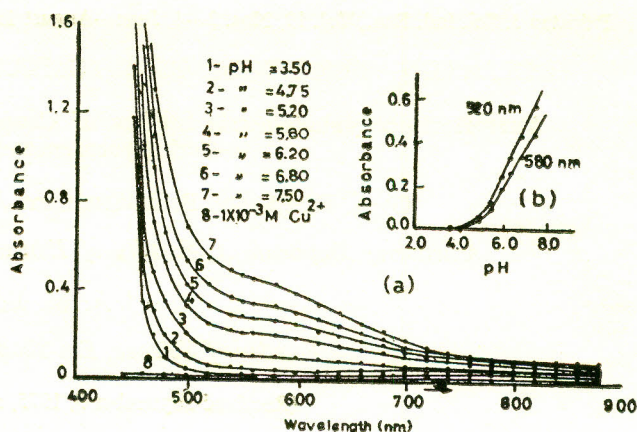
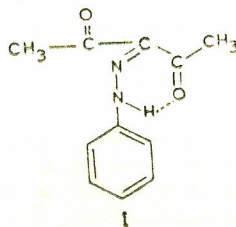


Fig. 1. Absorption spectra of copper benzenehydrazo-pentane-2,4-dione (BHP) system. ( $1 \times 10^{-3} \text{M}$ , copper acetate  $1 \times 10^{-2}$  BHP in 50% dioxan water solvent).

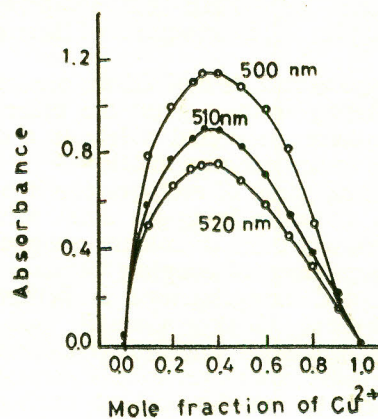


Fig. 2. Continuous variation method for Cu-BHP complexes in acetate buffer at 6.2 pH in 50% dioxan.

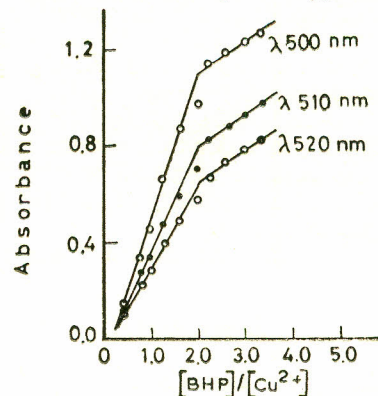


Fig. 3. Molar ratio method for Cu-BHP complexes at pH 6.0 in 50% dioxan.

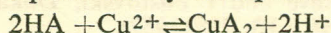
the hydrogen atom of the hydrazo group and one of the carbonyl groups. This was supported by the fact that this hydrogen atom should be more acidic than that of the hydroxyl group of acetylacetone.

The structure of the formed complex in nonaqueous media was confirmed by the isolation of the solid complex. The analysis for C, H and N gives 56.3, 5.1 and 11.45 respectively which is in accordance with the molecular formula  $\text{Cu}(\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}_2)_2$ .

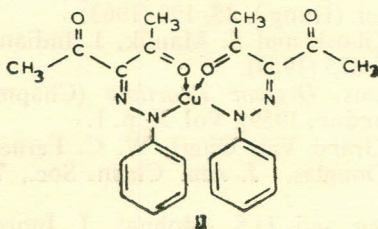
The study of IR spectra of the separated complex may help in determining the structure of the formed complex.

The acetylacetonate complexes of Cu(II) have been studied by many authors.<sup>17,18</sup> In IR spectra of Cu(BHP)<sub>2</sub> complex the NH vibrational band which was very weak in case of the ligand, disappeared in the spectra of the complex, indicating that the hydrogen atom of the hydrazo group in the ligand is replaced by the metal upon complex formation. This shows that the nitrogen atom of the hydrazo group is coordinated to the metal. The observed 1680 cm<sup>-1</sup> band, which is always attributed to the C=O stretching frequency, disappeared in the spectra of the complex proving that the oxygen atom of the carbonyl group is linked to copper. 428-417 cm<sup>-1</sup> bands were assigned to M-O stretching frequency. Usually M-N bond absorbs at higher end of the range 585-413 cm<sup>-1</sup>.<sup>19,20</sup> In case of Cu(BHP)<sub>2</sub> a medium band at 549 cm<sup>-1</sup> was assigned to M-N bond.

The formation of 1:2 complex of BHP (HA) can be represented by the equation:



The structural formula of the complex formed has been schematically shown in structure II. This struc-



ture is preferred as copper with a coordination number 4 favours a square planar. Under this condition benzenehydrazopentene-2,4-dione acts as a bidentate ligand.

*Interaction of Copper and 3-Arylhydrazopentane-2,4-dione, Ar = o-C<sub>6</sub>H<sub>5</sub>COOH, (o-CBAP).*

The effect of substituent in benzene ring on the process of complex formation was studied. In the present study the hydrogen atom in the *ortho* position in benzene ring was substituted by a carboxylic group.

From the study of the spectrum of ligand alone and with Cu<sup>2+</sup> in UV and visible regions at pH 6, it was observed that the spectrum of the ligand which have two maxima at 258 and 370 nm are shifted to longer wavelength, 275 and 396 nm, respectively. Furthermore, the characteristic band of the ligand becomes weak which indicates chelation. It was noted that equilibrium in studied solutions is attained after five minutes of standing.

The effect of pH on the complex formation is illustrated in Fig. 4. It is clear that a new band (640 nm) is created due to the addition of *o*-CBAP to Cu(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> ion. This is usually attributed to a new ligand field environment produced by replacement of water ligand field with molecules of *o*-CBAP. Furthermore, the increase in pH leads to a slight increase in the absorbance of the band at 640 nm. Figure 4 shows that complex formation between the components takes place in a pH range starting from pH 5.

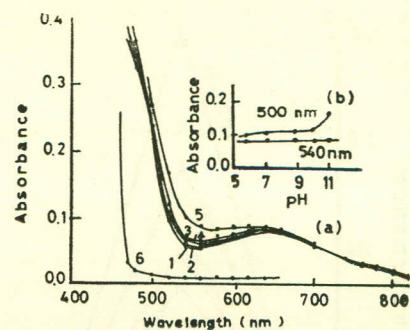
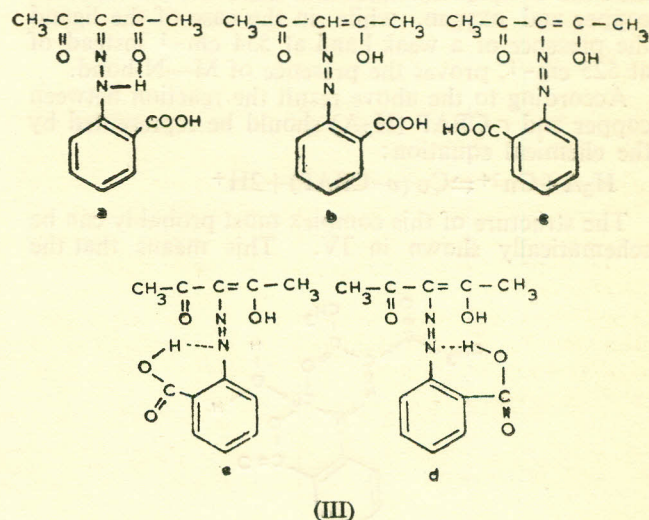


Fig. 4. Absorption spectra of copper (*o*-CBAP) system ( $5.0 \times 10^{-4}$  M copper-acetate,  $2 \times 10^{-3}$  M *o*-CBAP) (1) pH 5.8, (2) pH 7.1, (3) pH 8.9, (4) pH 10.0, (5) pH 11.0 and (6) free *o*-CBAP.

The composition of formed complex was investigated by continuous variation<sup>11</sup> (Fig. 5) and molar ratio<sup>12</sup> methods and the formation of 1:1 complex is confirmed by straight line<sup>13</sup> limiting logarithm<sup>21</sup> and Nach<sup>22</sup> methods.

In case of Cu-BHP system the formed complex is 1:2, but in the last case, it is 1:1. One can propose the structure of *o*-CBAP as a resonating hybrid (III a-e). Structure IIIa has already been proved by Elguero<sup>16</sup> so the other structures can be excluded.



The structural formula of Cu-*o*-CBAP complex was also investigated in the solid state. Analysis for C, H and N of the isolated complex gave 43.5, 3.9 and 8.6% respectively which is in good agreement with the molecular formula Cu(C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>)·H<sub>2</sub>O.

The study of the IR spectra of this solid complex by comparison with that of the ligand can give us a strong evidence about its structure.

In the spectra of *o*-CBAP a strong band at 1680 cm<sup>-1</sup> which is due to the superposition of the vibration of C=O of acetylacetonate, part with that of the carboxyl band. In case of Cu-*o*-CBAP complex a broad band at 3500 cm<sup>-1</sup>, which can be attributed to free OH group in the spectra of *o*-CBAP itself disappeared while another strong band appeared at 1680 cm<sup>-1</sup>.

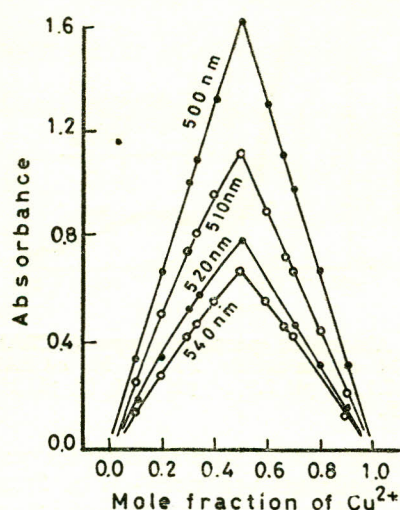
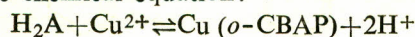


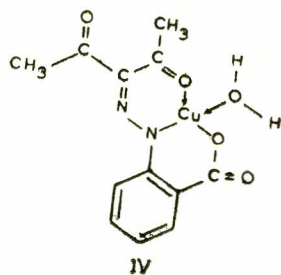
Fig. 5. Continuous variation method for Cu *o*-CBAP complex in 25% dioxan water solvent at 5.8 pH  $[Cu^{2+}] = [o-CBAP] = 8 \times 10^{-3} M$ .

This indicates that the carboxyl group of the ligand shares in the process of complexation. The appearance of weak bands at  $450\text{ cm}^{-1}$  in the IR spectra of the solid complex indicates that there is a link between copper and oxygen, while in the case of the ligand the presence of a weak band at  $534\text{ cm}^{-1}$  instead of at  $525\text{ cm}^{-1}$ , proves the presence of M—N bond.

According to the above result the reaction between copper and *o*-CBAP ( $H_2A$ ) should be represented by the chemical equation:



The structure of this complex most probably can be schematically shown in IV. This means that the



azo, carboxyl and one of the carbonyl groups are shared in the chelation. This proposed structure is confirmed by the fact that in the UV spectra there is a change in the azo band at  $370\text{ nm}$  denoting the role of this group in complexation.

From the proposed structure it can be seen that this ligand is a tridentate. The fourth position around the copper ion can be occupied by one water molecule.

From the above data for the systems Cu-BHP and that of Cu-*o*-CBAP it can be shown that there is a difference in the type of complexes which can be formed. In the first case the ligand forms a 1:2 complex, while in the latter a 1:1 complex is formed with the possibility of having a coordinating water molecule.

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