CHELATING BEHAVIOUR OF SUBSTITUTED 3—ARYLHYDRAZO PENTANE—2,4—DIONE.

Part V*. Physico Chemical Studies of Copper Complexes with o—,m—,p—and 4—Me—o—Sulphonic Benzene—Hydrazo Pentane—2,4—Dione

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The dissociation constants of four sulphonic derivatives of 3—benzenehydrazopentane—2,4—dione were determined, as well as the stability constants and composition of their complexes with copper were studied spectrophotometrically. Conductometric titrations confirmed the spectrophotometric results. pH—metric and IR studies of the copper complexes are also carried out.

INTRODUCTION

The products of coupling derivatives of benzene diazonium compounds and pentane—2,4—dione proved to be efficient complexing agents[1]. The o—, m—, p— carboxy derivatives have been studied with copper [2—4] and cobalt and nickel[5]. The stability and IR spectra of the solid complexes of these derivatives with a series of transition metals were also reported[6]. The products of coupling sulphonic derivatives of benzene diazonium chloride with pentane—2,4—dione are used in the present work as complexing agents for Cu^{++} in aqueous solutions.

EXPERIMENTAL

Preparation of Ligands. The ligands were synthesized by coupling diazonium salts of aniline sulphonic derivatives with acetylacetone in sodium acetate and recrystallized from methanol. The acid form of the ligands were obtained by using Dowex—50 cation exchanger.

The elemental analyses of the solids obtained are:

	Found			
	C	H	N	S
o—SBHP	43.43	3.6	9.21	10.6
m—SBHP	43.30	3.6	9.30	10.5
p—SBHP	43.40	3.6	9.20	10.6
4—Me—o—SBHP	45.40	4.3	8.90	10.1

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	Calculated			
	C	H	N	S
o—SBHP	43.13	3.60	9.15	10.45
m—SBHP	43.13	3.60	9.15	10.45
p—SBHP	43.13	3.60	9.15	10.45
4—Me—o—SBHP	45.00	4.06	8.75	10.00

Solution of copper acetate was used and standardized by EDTA[7]. The solid complex of copper and P—SBHP was prepared by adding ligand dropwise to the copper acetate solution with continuous stirring. Green crystals gradually separated, washed by distilled water and dried in air. The results of ligands of solid are:

	Found			
	C	H	N	S
$CuL_2.2H_2O$	37.22	3.1	7.82	9.35

	Calculated			
	C	H	N	S
$CuL_2.2H_2O$	37.1	3.37	7.87	8.55

Apparatus. The UV and visible spectra and pH—measurements used instruments previously reported[2,3]. The IR spectra were taken for the solids as KBr discs in the range 300—4000 cm^{-1} using Beckman IR—12 spectrometer. The conductivity measurements were carried out by Beckman conductane bridge model RC—16B_2 and RC 216B_2 using conductivity water.

RESULTS AND DISCUSSION

a) *Spectrophotometric Studies.*

    All studies were done in aqueous solutions in 1 cm quartz cells using bidistilled water as reference solution, and comprises the following:

    (1) *Determination of pK_2 of o–, m–, p– and 4–Me–O–sulphonic benzene hydrazopentane–2,4–dione (–SBHP).* The spectra of ligands contain two characteristic bands given in Table 1.

    The first band, in the UV. part, can be assigned to II − II* transition of the carbonyl group of acetylacetone, while the second band, in the visible part, can be attributed to II − II* transition in the azo part of the ligand. Comparing these bands with those of BHP shows that the presence of the sulphonic groups shifts the bands to longer wave–length, i.e. facilitating the transitions, also the shift depends on its position in the ring. The increase of pH of solution in the range 2 to 7 gives no appreciable increase of absorbance as –SO·H ionization is not accompanied by change in color[8]. From pH 7 to 13 the absorbance increases and the modified limiting absorbance method[9] was used for calculating pK_2 and the values obtained are given in Table 1.

    2. *Effect of pH.* The pH of solutions of Cu^{++} and excess ligand was varied from 2 to 12 and the results are shown in Fig. 1. It is seen that the absorbance is not changed till pH 4 then increases by increase of pH. The position of the maximum is shifted to shorter wavelength by increase of pH. The change of absorbance may be due to liberation of H^+ during complexation[10] and the shift in position may be due to formation of different types of complexes. The relation between pH and absorbance at one wavelength has the shape of titration curves.

    (3) *Effect of Ligand Concentration.* By increasing the concentration of ligand in solution containing constant
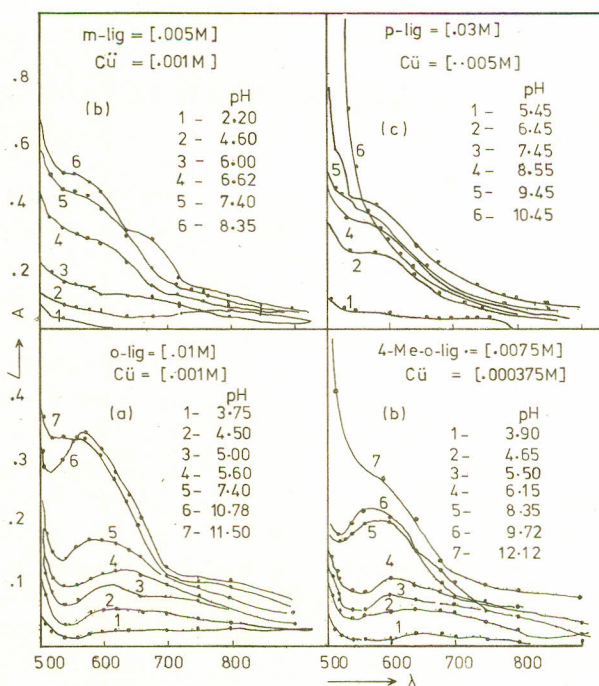

Fig. 1. Effect of pH on the absorption spectra of o–, m–, p–, and –4– Me– O–SBHP ligands–Cu^{++} complexes.

amount of Cu^{++} and having constant pH 5.5 or 6, the absorbance increased and the position at 800 nm for Cu^{++} was shifted to 610 nm in case of o–ligands and 580 nm for p–ligand and 620 nm for m–derivative. The excess ligand interfered with the maximum and when using the ligand as reference, the band maxima for the complexes are obtained at 450, 430, 446 and 470 nm for o–, m–, p– and 4–Me–o–SBHP respectively.

    (4) *Composition of the Complexes in Buffered Solution.* the continuous variation method[11] as well as the molar ratio method[12] (Fig. 2) reveal the formation of 1:1 and

Table 1. Spectrophotometric results of the legand and their copper complexes

Legand	Max. nm		pK_2	Copper complexes	
				β	ε 500 nm mol.$^{-1}$ cm^{-1}
o–SBHP	250	370	11.0	7.24 z 10^{17}	50
m–SBHP	245	360	10.5	4.27 x 10^{16}	200
P–SBHP	247	357	10.8	7.83 x 10^{16}	160
p–Me–o–SBHP	250	370	11.0	6.63 x 10^{18}	33
BHP	242	358	–	–	–
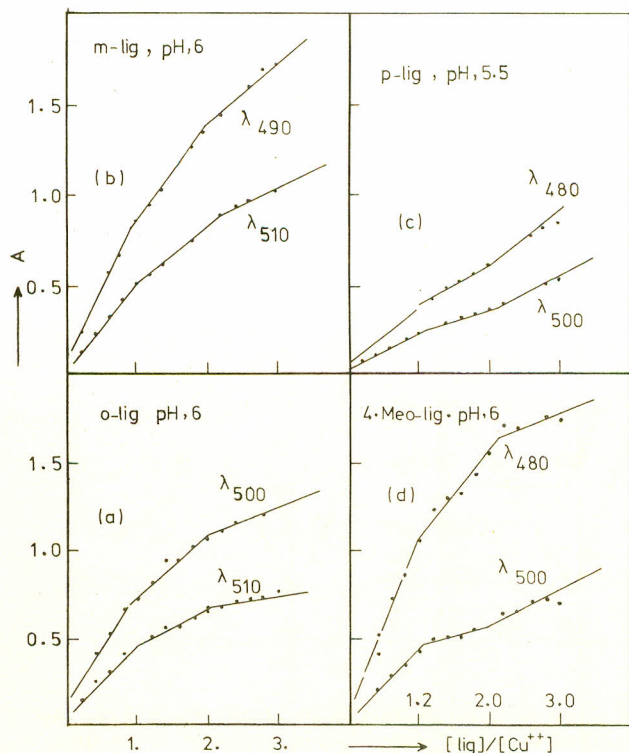
Fig. 2. Molar ratio method $o-$, $m-$, $p-$, and $-4-$Me$-$O$-$SBHP$-$copper complexes.

Fig. 3. Straight line method $o-m-$ $p-$, and $--$4$-$Me$-$OO$-$SBHP$-$copper complexes.

1:2 Cu^{++}/L complexes. The slope ratio[13] and straight line[14] methods give 1:1 complex.

(5) *Effect of Cu^{++} Concentration.* Straight lines were obtained when plotting a relation between absorbance of solution and concentration of Cu^{++} in presence of excess ligands. The molar absorptivity of the complexes are taken from the slopes of the straight lines and given in Table 1.

(6) *Stability Constants.* The data obtained for the molar ratio method are used for determining the stability constant by using the straight line form:

$$A_x = A_m - \left(-\frac{\varepsilon_2}{\varepsilon_2\ \varepsilon_0} \cdot \frac{1}{\beta}\right)\frac{(A_x - A_0)[H^+]^2}{[L]^2}$$

Fig. 4 shows the relation between A_x (absorbance at concentration of ligand [L]) and $A_x - A_0 / [L]^2$ which is straight line for each ligand used. Slope of the straight line gives β, the overall stability constant of the complex of molar absorptivity ε_2. E_0 is for free Cu^{++} and A_0 its absorbance. The values obtained are given in Table 1. From these values the $o-$ligands give more stable complexes than $m-$ and $p-$derivatives, perhaps due to $-SO_3^-$ which can have a role in complexation.

b) *Conductometric Results*
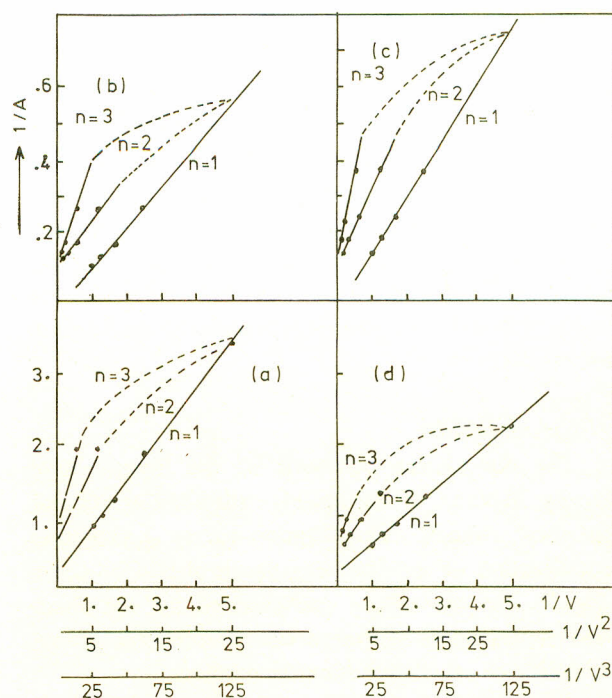
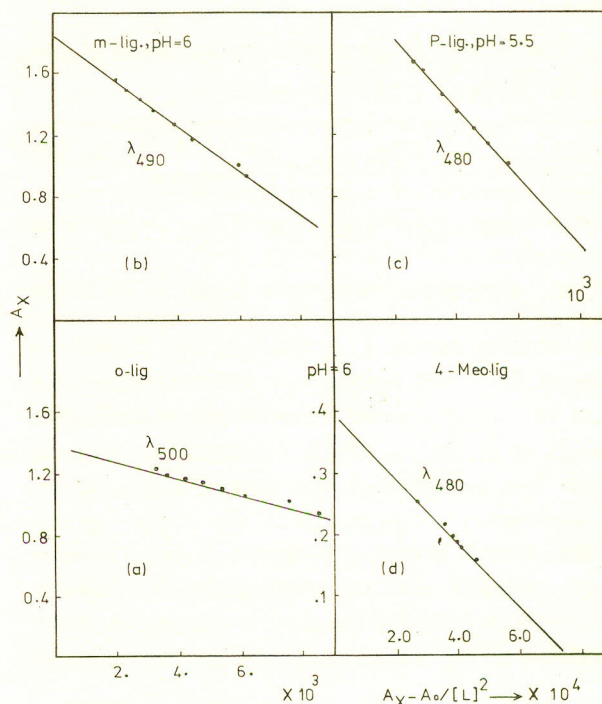Conductivity measurements were carried out in

Fig. 4. Joe and Jones method for $o-$, $m-$, $p-$ and $-4-$Me$-$Oo$-$SBHP$-$Cu^{++} complexes.

two ways:

(1) Titration of free ligand or mixtures of free ligand and copper by standard KOH solution Fig. 5.

(2) Titration of Cu^{++} solution with the ligand Fig. 6.

In the first the titration curves of the free ligand correspond to those of strong acids, as the titration involves $-SO_3H$ group, the hydrazo hydrogen is not detected. In presence of Cu^{++} (Fig. 5 curve 2) two breaks appeared one for the $-SO_3H$ at the place of free ligand and the second due to hydrazohydrogen liberated by complexation. By varying the ratio of the metal to ligand it was found that the highest complex formed is the 1:2. Fig. 6 shows the titration of Cu^{++} with the ligands, where two breaks are observed at 1:1 and 1:2, which agrees with the spectrophotometric results.

c) pH—metric Results

The dissociation constants of the ligands were obtained by titration of the ligands with KOH at 30° and constant ionic strength. The titration curves representing the neutralization of the four ligands are shown by curve 4 in Fig. 7. The curves are characterized by one sharp inflection representing neutralization of sulphonic group. The pK values are calculated using the relation,

$$pH = pK + \log \frac{[salt]}{[acid]}$$

The intersections of the straight lines obtained at zero pH give the values:

	$-o-$	$m.p$	$p-$	4—Me $-o-$SBHP
pK_1	2.14 $\pm$ 0.01	2.22 $\pm$ 0.01	2.50 $\pm$ 0.02	2.40 $\pm$ 0.02
pK_2	10.96 $\pm$ 0.02	10.60 $\pm$ 0.02	10.70 $\pm$ 0.01	11.00 $\pm$ 0.02

The titration curves, 1, 2 and 3 in Fig. 7 represent mixtures of Cu^{++} and ligands with different ratios. The curves of $m-$ and $p-$ ligands show separate neutralization of $-SO_3H$ as it has no role in complexation, while in $o-$ligands it is accompanied with that of hydrazohydrogen. Complexation occurs in case of $m-$ and $p-$ at pHs higher than 5 while in case of $0-$ligands it occurs at lower values in agreement with the spectrophotometric results. The Bjerrum's method [15] was used to calculate the stabilith constants of the formed complexes and the values are

	$o-$	$m-$	$p-$	4—Me $-o-$SBHA
log	22.83 $\pm$ 0.03	22.1 $\pm$ 0.08	21.97 $\pm$ 0.02	22.8 $\pm$ 0.06

These values are higher than those obtained by spectrophotometric methods. This can be attributed to the use of acetate buffer which may interact with the metal ions leading to less stability of complexes. Also pH—metric measurements are done at 30° whereas spectrophotometric
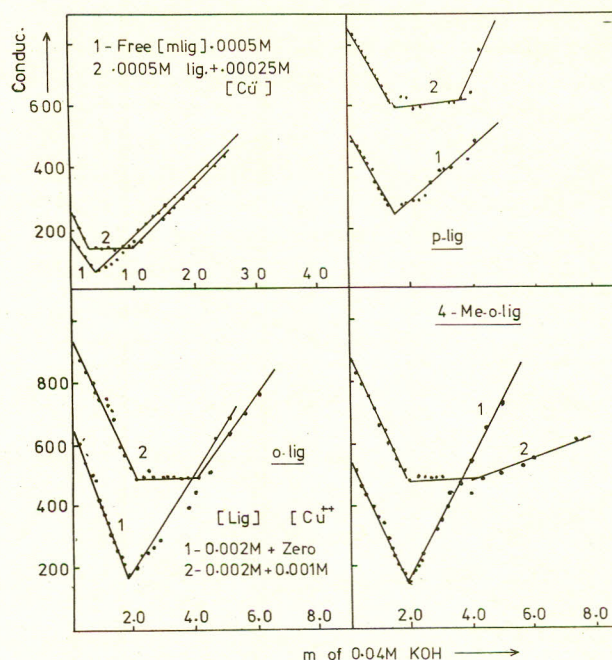

Fig. 5. Conductometric titration of 40 ml $o-$, $m-$, $p-$ and $-4-$ Me$-o-$SBHP legands in presence and in absence of copper nitrate.
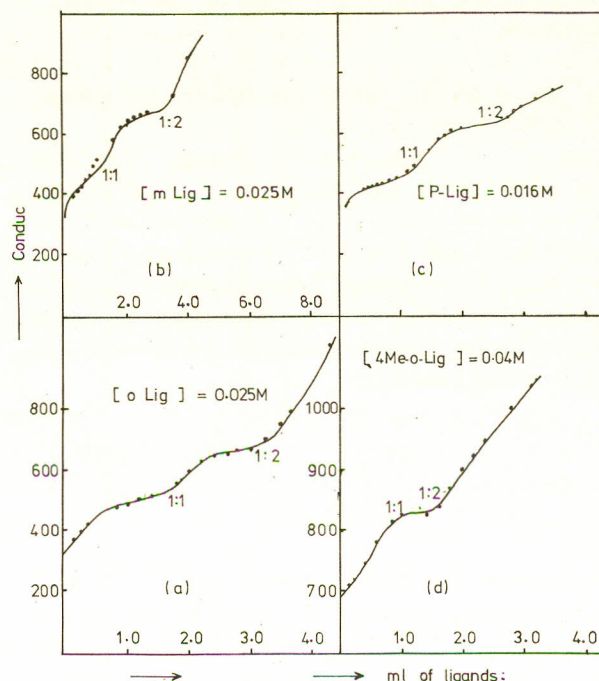

Fig. 6. Conductometric titration of 40 ml copper nitrate using legands as titrant at 30°

results are at room temperature (20°) which also affects the values of stability constant.

d) Infrared Spectra

Fig. 8. shows the IR spectra of free ligand $p-$ SBHP and its copper complex. A broad intensive band which is due to $-NH$ and OH of the free ligand at 3520 cm^{-1} is
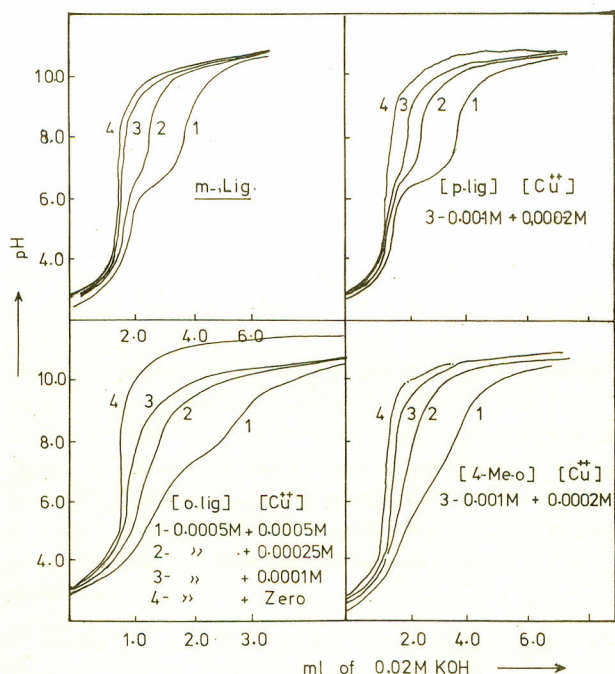
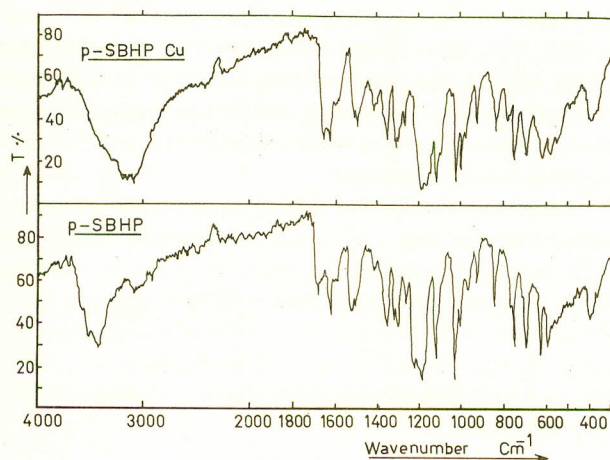Fig. 7. pH-metric titration of 30 ml mixture of *o*–, *p*–, and 4–Me–o–SBHP and its metal·ion complex.

Fig. 8. 1R spectra of p–SBHP and its metal ion complex.

shifted to 3110 cm^{-1} in the Cu^{++} complex. The band at 1690 cm^{-1} which can be assigned to the C=O group of ligand is shifted splitted to two weaker bands at 1670 and 1635 cm^{-1} which denotes its effective role in com-

plexation. The bands at 1325 cm^{-1} for C–N and at 1220 cm^{-1} for C–O disappeared or shifted due to complex formation and appearance of bands at 570 cm^{-1} for M–N stretching mode and at 395 cm^{-1} for M–O stretching frequency[16]. These results mean that the hydrazo and carbonyl groups are the essential centers of chelation in *p*–SBHP. pH–metric results denotes that the *o*– igands also shares with the sulphonic group in chelation and so it is tridentate ligands while the *m*– and *p*– derivatives are bidentate.

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