

## CHELATING BEHAVIOUR OF 3-ARYLPHENYL HYDRAZO PENTANE-2,4 DIONE

Part IX. Spectroscopic and electrometric studies on cobalt (II) complexes of *o,m,p*- and *o*-sulphonic (4-methyl)phenyl hydrazopentane-2,4-dione

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Spectroscopic studies in solution and in solid state of the ligands and their complexes with cobalt were carried out. The composition of these complexes is 1:1 and 1:2 metal:ligand as revealed by spectrophotometric and conductometric measurements. The stability constants of these complexes were determined by spectrophotometric and pH-metric methods and compared with those of copper and nickel ions with the same ligands. The solid complexes of cobalt ion with the p-derivatives was isolate and the coordination sites were revealed by ir. studies.

## INTRODUCTION

The chemistry of cobalt (II) has been extensively studied experimentally and theoretically [1]. Several articles have been reported on the complexes of cobalt (II) with acetylacetone [2-5]. Cobalt forms complexes with 3-arylhydrazopentane-2,4-dione and its *o*-carboxy derivative revealed by spectroscopic and pH-metric methods [6,7]. Recently the complexes of 3-*m*-tolylazo-acetylacetone have been reported [8]. The complexes of Cu(II) [9] and Ni(II) [10]. Sulphonic hydrazo derivatives of pentane-2,4-dione have been studied in our laboratory and their stability constants were computed. The aim of the present work is to study the different types of complexes of cobalt (II) with *o*, *m*, *p*- and *o*-sulphonic (4-methyl) phenyl hydrazopentane-2,4-dione (*o*-5(4-Me) PHP) in solution and in solid state to investigate their structure and stability. Micro analysis of the solid complex was performed to confirm its suggested structure.

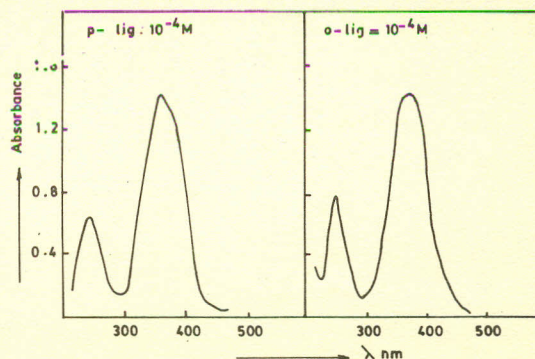
## EXPERIMENTAL

The chemicals used are of the purest types by Merck and BDH. Cobalt nitrate solution was prepared and standardized chelatometrically [11]. The ligands were prepared as previously described [9]. The instruments used for spectroscopic, pH-metric and conductometric are the same as those previously reported [9].

## RESULTS AND DISCUSSION

*A. Spectroscopic studies.* These comprise spectrophotometric studies in solutions and IR studies of solid ligands and their cobalt (II) complexes.

(i) *Spectrophotometric studies.* All the ligands studies in the present work show absorption spectra in-solution in the ultra violet and visible regions Fig. 1. The two band maxima obtained depend slightly on the substituent position in the phenyl ring. In pHP, they exist at 242 and 358 nm., which may be due to the  $\pi - \pi^*$  electronic transition in the phenyl ring and a composite electronic  $\pi - \pi^*$  transition in azo group and carbonyl group of acetylacetone respectively. Substitution in the phenyl ring by a  $-\text{SO}_3\text{H}$  does not affect greatly the electronic transition of the composite band, while it affects that of the aromatic transition of phenyl system. The position of these two bands shows that the ligands are in hydrazo forms [8,12,13] as many of

Fig. 1. Ultra-violet spectra for *o*-SPHP and *p*-SPHP organic ligand.

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the hydrazones absorb in these regions. The increase of pH from 2 to 10 does not change significantly the absorbance of the ligands as well as the position of the maxima. This is in agreement with the potentiometric results [9], as there is only one species in the solution in this pH range which is the mononegative ion of the ligand.

Cobalt (II) gives orange complexes with *o*-derivatives, and deep brown complexes with *m*, *p*- derivatives. The suitable pH for formation of the different Co-SPHP complexes was revealed by studying the effect of pH on the absorbance of the system containing Co-L ratio about 1:20 to prevent any precipitation of cobalt hydroxide. A gradual increase of absorbance by increase of pH as shown by Fig (2a) as an example of their behaviour. From a relation between the pH and absorbance at certain wave length it can be concluded that different types of complexes can be formed. At constant pH 8–8.5 in 1.0 M buffer ammonia increasing the concentration of the ligand the maximum Co(II) band at 510 nm. disappeared completely and absorbance increases by increase of ligand concentration Fig (2b), with the appearance of a new maximum or a shoulder for the complex. Using the ligand of the same concentration as a blank the complex has a band maximum at 450, 460, 450 and 460 nm. for *o*, *m*-, *p*- and *o*- S(4-Me) pHP ligands respectively.

The composition of the complexes formed was studied by the different recommended spectrophotometric methods, Job's, [14] Molar ratio [15], slope ratio [16], straight line and limiting logarithmic [17] method. The results show that these ligands give with cobalt (II) complexes of the 1:1 and 1:2 metal:ligand ratios. Example of these methods is the molar ratio method shown Fig (3). Beer's law was tested in 1.0 M. ammonia buffer using solutions of 1:2 ratio's, where straight lines were obtained

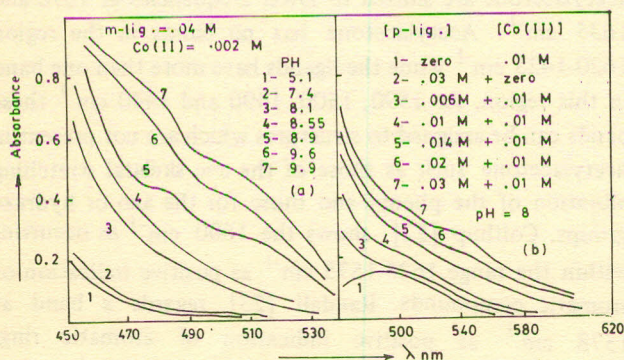


Fig. 2(a). Effect of pH on the absorption spectra of *nm*-SPHP-Co(II) complexes.

Fig. 2(b). Effect of conc. of *p*-SPHP ligand on the absorption spectra of cobalt nitrate.

passing through the origin as represented in Fig (4). This shows that these solutions can be used for the practical determination of cobalt (II).

The stability constants of the complexes formed in solution were obtained by using the data of the molar ratio method. The graphical representation of this method is given in Fig. (5). The values obtained for "B" overall stability constants of cobalt complexes cited together with the B values for Cu(II) [9] and Ni(II) [10] complex, with the same ligands, are summarized in Table 1.

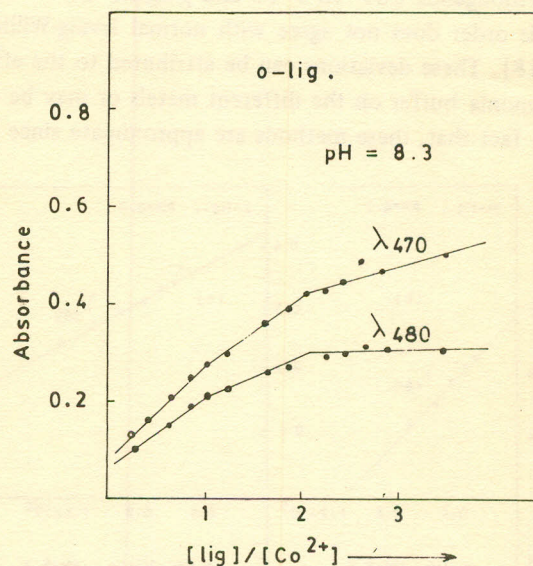


Fig. 3. Molar ratio method for *o*-SPHP - co(II) complexes.

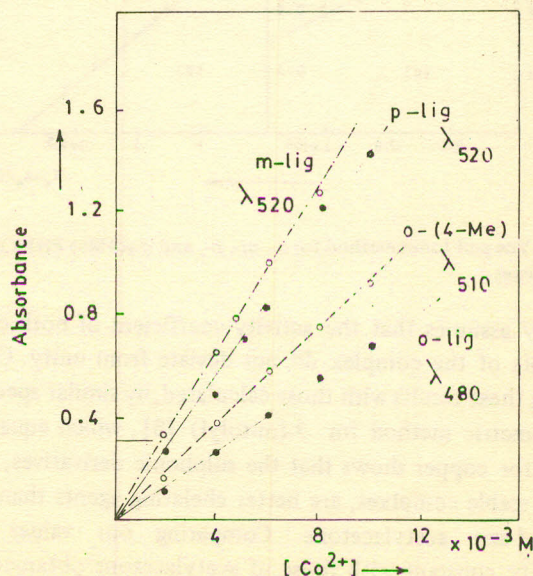


Fig. 4. Obedience of Beer-Lambert's law for Co-ligand complexes.

Table 1. The overall stability "B" of Co (II), Cu(II) and Ni(II) complexes with different sulphonic ligands

Metal ion	Overall stability constant with different ligands			
	<i>o</i> -ligand	<i>m</i> -	<i>p</i> -	<i>o</i> -S (4. Me) - ligand
Cu(II)	$2.74 \times 10^{17}$	$4.47 \times 10^{16}$	$7.83 \times 10^{16}$	$66.2 \times 10^{17}$
Ni(II)	$1.59 \times 10^{17}$	—	$8.78 \times 10^{17}$	$45.5 \times 10^{17}$
Co(II)	$2.46 \times 10^{17}$	$6.7 \times 10^{17}$	$11.6 \times 10^{18}$	$15.7 \times 10^{17}$

Ortholigands  $\text{Cu} > \text{Ni} > \text{Co}$  and *p*-ligand  $\text{Co} > \text{Ni} > \text{Cu}$  this order does not agree with normal Irving-Williams rule [18]. These deviations can be attributed to the effect of ammonia buffer on the different metals or may be due to the fact that, these methods are approximate since one

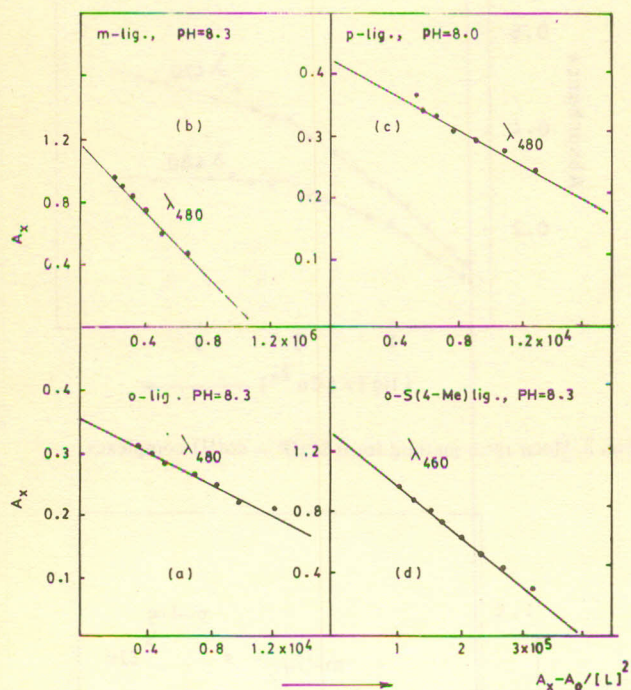


Fig. 5. Yoe and Jones method for *o*-, *m*-, *p*-, and *o*-s(4Me) PHP-Co (II) complexes.

usually assumes that the activity coefficient of both components of the complex do not deviate from unity. Comparing these results with those calculated, by similar spectrophotometric method for 3-(*m*-tolyl) [8], which equal 10 [11] for copper shows that the sulphonic derivatives, give more stable complexes, are better chelating agents than the *m*-tolyl-azo acetylacetone. Comparing our values for stability constant with those of acetylacetone obtained by Calvin and Wilson [19], using pH-metric data, were formed to be much higher.

(ii) *Infra-red studies.* The preparation of ligands was given in a previous article [9]. The isolation of the solid complex of cobalt with *p*-SPHP ligand was carried out by mixing 40 ml of 0.2 M. solution of the ligand with 20 ml cobalt ion of the same molarity with continuous stirring and heating. The solid obtained was washed with bidistilled water, dried in air, the elemental analysis gave the following results:

Formula:  $\text{CoL}_2 \cdot 2\text{H}_2\text{O}$ ; Found: C, 37.5; H, 3.6; N, 8.2; Calculated:  $\text{CoL}_2$ , C, 37.35; H, 3.40; N, 7.92; S, 9.05.

The IR spectra of the ligands show a broad band at 3460-3520  $\text{cm}^{-1}$  which corresponds to stretching frequencies of the ..OH of  $\text{SO}_3\text{H}$  group at 3460, 3495, 3460 and 3520  $\text{cm}^{-1}$  for *o*-, *m*-, *p*- and *o*-S (4-Mc) derivatives respectively Table (2). This band is absent in both acetylacetone (20) and PHP [21], as they are deprived of this group. Another band appears in case of *o*-, *m*- and *o*-S(4-Me) PHP at 3100, 3080 and 3100  $\text{cm}^{-1}$  respectively may be for the -NH of hydrazo structure of these ligands bonded to one of the carbonyls of acetylacetone moiety. In the region of 1700-1400  $\text{cm}^{-1}$ , acetylacetone gives two bands at 1725 and 1708  $\text{cm}^{-1}$  for the keto and Chelated carbonyl groups and one at 1620 for c-c stretching [20]. According to presence of azo group in the present ligands, two bands, in acetylacetone are shifted to lower frequencies at 1670 and 1635  $\text{cm}^{-1}$ . Acetylacetone has no bands in the region 1620-1425  $\text{cm}^{-1}$  while the ligands have more than one band in this region. At 1590, 1500, 1490 and 1440  $\text{cm}^{-1}$  these bands can be assigned to structures which are not present in acetylacetone such as those of the c=c skeletal stretching vibration of the phenyl and those for the azo or hydrazo groups. Colthup [22], shows the 1600  $\text{cm}^{-1}$  as occurring within the range 1625-1575  $\text{cm}^{-1}$  as positive indication of aromatic compounds. Randall [23] regards a band at 1578  $\text{cm}^{-1}$  as positive indication of aromatic ring. Herzberg [24] identify absorption at 1575  $\text{cm}^{-1}$  to the N=N stretching vibration. Le Fevere [25] identify 1577-1578  $\text{cm}^{-1}$  to N=N-and ring vibration. In the present ligands the 1590-1580  $\text{cm}^{-1}$  band can be assigned to the -N=N and

Table 2. Infra-red absorption band frequencies  $\text{cm}^{-1}$ 

<i>o</i> -5(4-Me) PHP	<i>m</i> - SPHP	<i>p</i> - SPHP	<i>p</i> - Cu-complex	Ac.Ac Cu-complex	<i>p</i> - nickel	<i>p</i> - Cobalt	<i>p</i> - manganese	<i>p</i> - Cadmium	<i>p</i> - Lead	AC.AC, Assignment
3495(6)	3460(6)	3520 3410	3110	—	3300	3360 3260	3240	3460	3300	3550(W)st.OH
3080	3080	3080	"	"	"	"	"	"	"	— CH.Ar
2920	2920	2920	"	"	"	"	"	"	"	2920CH al
—	—	—	—	—	—	—	—	—	—	2620
—	—	—	—	—	—	—	—	—	—	2350
1670(5)	1660vs.	1670	1670	—	1630	1640	1625	1630	1620	1725 C=O
1635(w)	1635(5)	1635	—	—	—	—	—	—	—	1708 C-C
—	—	—	—	—	—	—	—	—	—	1620
1580(w)	1590 m	1530	—	1582	—	—	—	—	—	—
—	1525	1520	1520	1560	1510	1520	—	—	—	—
1500 a	—	1515	1500	1530	1500	1510	1510	1510	1510,1500	—
1490	1490	1505	—	—	—	—	1495	1490	1490	—
—	1440	—	1430	1425	1430	1430	—	—	—	1425 CH <sub>3</sub> dg.
—	—	1415 w	1415	—	1420	—	1415	1410sh	1400	—
1400	—	1405	—	—	—	1385	1405	—	—	—
1370	1360	1375	1370	1362	1375	1370	1360	1360	1355	1365 S <sub>CH<sub>3</sub></sub> C-C str.
1320	1325	1325	1320	—	1325	1330	1320	1320	1315	—
—	—	1300	1310	—	1305	1315	1300	1295	1295	— $\gamma$ C-CH <sub>3</sub> + $\gamma$ C-C
—	1290	1270	1280	1278	1285	1290	1280	—	1280	1252 $\gamma$ C-CH-
1240	1220	—	—	—	—	1250	—	—	—	—
1190	1200	1200	1200	1193	1200	1200	1200	1190	1200	1175
—	—	1190, 75	1180	—	1180	1160	1160	—	1170	1162
1135	1120	1125	1130	—	1120	1130	1115	1120	1125	—
1090	1080	—	1070	—	1060	1070	1050	1050	—	—
1040	1050	1035	1040	1020	1030	1040	1025	—	1030	1025
990	1000	1005	1015	—	1005	1015	1000	1010	1000	1003 s(CH <sub>3</sub> )
—	—	975	—	—	—	—	—	975	975	975 $\gamma$ C-C, $\gamma$ C-O
930	940	940	945	940	950	955	940	935	935	918
820	800	—	780	795	810	810	800	—	775	780 $\pi$ (CH)-
775	780	—	—	—	—	—	—	—	—	—
730	750	755	765	—	750	765	750	765	755	—
700	720	700	715	720	700	710	700	700	695	— $\gamma$ C-CH-rigid + $\gamma$ -M.O3
—	630	625	630	635	625	640	620	630	630	— $\pi$ CH <sub>3</sub> -C-C
—	—	—	600	612	—	600	—	—	—	— ring def. $\gamma$ M-O
—	—	590	570	—	580	570	583	580	—	—
530	—	—	520	—	—	510	555	—	—	—
—	—	—	495	—	—	475	495	—	—	—
—	—	—	425	—	—	—	—	—	—	—
—	—	400	395	—	385	405	400	395	395	—

it could arise from ring vibration. Also Snavelly [26] assigned the  $1525\text{ cm}^{-1}$  band to azo while the  $1425\text{ cm}^{-1}$  to  $\text{CH}_3$  deformation and  $1365\text{ cm}^{-1}$  in the present ligand. The bands at  $1110\text{ cm}^{-1}$  and at  $1290\text{ cm}^{-1}$  can be related to the C-N stretching vibration as they are not present in acetylacetone and C-O stretching and OH deformation vibration. All ligands give strong intensive band at  $1200$  which can be assigned to the presence of sulphonic group [27].

In the presence of Co(II) all the bands of the p-ligands suffer changes in position and intensity. The bands at  $3520\text{ cm}^{-1}$  for OH stretching shifts in the cobalt complex to  $3220\text{ cm}^{-1}$ . The carbonyl bands at  $1670$  and  $1635\text{ cm}^{-1}$  becomes one strong and sharp band at  $1640\text{ cm}^{-1}$ . The azo band at  $1530\text{ cm}^{-1}$  is splitted in cobalt (II) complex into a doublet at  $1520$  and  $1510\text{ cm}^{-1}$ . The expectation for the sharing of one nitrogen atom of azo in chelation can explain this doublet. The change of frequency of bands at  $1405$  and  $1375\text{ cm}^{-1}$  for C-N and C-O vibrations supports the above conclusion. Strong band at  $1330\text{ cm}^{-1}$  instead of the C-N band at  $1325\text{ cm}^{-1}$  and the C-O band at  $1220$  and C-N band at  $1125\text{ cm}^{-1}$  disappeared, these changes in bands can be attributed to the role of groups as carbonyls and N=N in complexation where as the band at  $1200\text{ cm}^{-1}$  for the  $\text{SO}_3^-$  is not affected by metal, and its OH band is seen in the spectrum.

p-sulphonic acid has bands at  $590\text{ cm}^{-1}$  and  $400\text{ cm}^{-1}$  which are sensitive to the presence of metal ions. In the cobalt complex it gives bands at  $570$ ,  $510$ ,  $495$ ,  $420$  and  $405\text{ cm}^{-1}$ , the band at  $590\text{ cm}^{-1}$  in the free ligand is shifted to  $570\text{ cm}^{-1}$  which can be assigned to the M-N stretching modes [28], those at  $420$  and  $405\text{ cm}^{-1}$  can be assigned to the M-O stretching mode [24].

**b. Electrometric Studies:** The pH-metric titration of 30 ml. of *o*-, *m*-, *p*- and *o*-S(4-Me) PHP ligands, at  $30^\circ\text{C}$  and 0.1 ionic strength, in presence and in absence of Co(II) was carried out. Every ligand was taken in a ratio 1:1, 1:2 or 1:10 cobalt to ligand beside its titration curve. The curves of 1:1 and 1:2 give an inflection at  $m=1$  and  $m=2$  respectively (where  $m$ =mole of base per mole of metal). The inflections are due to 1:1 and 1:2 complexes respectively. The titration curve of 1:1 gives a buffer zone at pH 8-5 at  $m = 1-2$  also the curve of 1:2 gives this zone at  $m = 2-4$  at the same pH. This buffer zone may be due to one of the following:

a. Formation of cobalt hydroxide, which can be excluded as no precipitation is formed:

b. Disproportionation due to the expression:

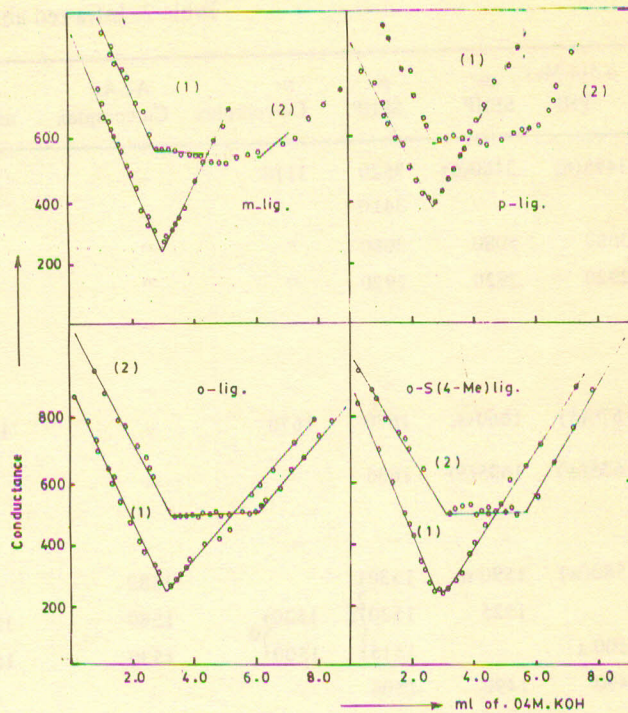
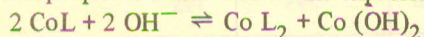
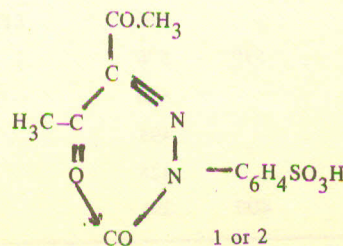


Fig. 6. Conductometric titration of 40 ml *o*-, *m*-, *p*-, and *o*-S(4 Me) PHP-ligand in presence and absence of .001 M cobalt nitrate.  
 1.00 3 M Lig + Zero Co(II)  
 2.00 3 M Lig + 0.00 (M) Co(II)

c. Or due to formation of hydroxocomplex of the type  $(\text{CoL}(\text{OH})_2)^{2-}$

The values of the stability constants were computed [25] and given else where [10]. The values obtained compared with those of the spectrophotometric method, are higher may be due to the effect of ammonia buffer which compactes the ligands for the metal ion.

The conductometric titrations 40 ml of ligands in presence and absence of cobalt, using 0.04 M KOH as a titrant are shown in Fig. (6). The breaks in the curves denote the formation of 1:1 and 1:2 complexes in agreement with the spectrophotometric results. The titration curve of the 1:3 Co(II):ligand ratio shows the break at 1:2 denoting that the 1:2 type is the highest complex which can be formed. On the basis of the above results the structure of the complexes formed can be represented by the formula



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