CHELATING BEHAVIOUR OF SUBSTITUTED 3-ARYLHYDRAZO PENTANE-2, 4-DIONE (SBHP) LIGANDS

Part VI*. Complexes of Nickel II with o-,m-, p-and 4-Me-o-Sulphonic Benzene Hydrazo-Pentane 2, 4-Dione

G.A. El-Inany, K.A.R. Salib** and A.A. Taha

Chemistry Department, Faculty of Education, Ain-Shams University, Heliopolis, Cairo, Egypt

Nickel ion gives with o-, m- p-, and 4-Me-o-sulphonic benzenehydrazopentane-2,4 dione *(SBHP)* ligands complexes of composition 1:1 and 1:2 metal: ligand as revealed from spectrophotometric and conductometric measurements. The stability constants of these complexes are determined by spectrophotometric and pH-metric methods. The solid complex of p-ligand was isolated and its ir spectrum was compared with that of the free ligand.

INTRODUCTION

In a previous paper [1] on copper (II) complexes with o-, m-, p- and 4-Me-o-sulphonic benzene hydrazo-pentane-2, 4-dione ligands, the composition and stability constants of these complexes were determined. The results show that the values of stability constants for these complexes are higher than those obtained for o-, m-, and p-carboxy derivatives reported in our previous work [2-4]. Nickel (II) gives with the hydrazosulphonic derivatives deep green coloured complexes which can be used for the spectrophotometric determination of this ion. The present investigation consists of spectrophotometric and conductometric studies of the composition of the complexes and a quantitative pH-metric study for the interactions of nickel(II)with o-, m-, p- and 4-Me-o-sulphonic benzene hydrazo pentane-2,4-dione ligands. The coordination sites of these ligands were suggested on the basis of the ir spectrum of the p-SBHP-Ni-(II) (2:1) complex.

EXPERIMENTAL

The preparation of pure ligands in acid form and their solutions was previously reported [1]. Solutions of nickel nitrate were used and standardized by EDTA [5]. The apparatus used for conductivity measurements and determining the ir spectra of Cu(II) complex [1] were used for Ni(II) complexes. The UV and visible spectra and pH

measurements were described in earlier publications [2, 3]. During the pH-metric and conductometric titrations, the ionic strength was kept constant at 0.1 M using KNO_3 and the solutions were stirred with nitrogen and kept at $30 \pm 0.05^\circ$

RESULTS AND DISCUSSION

(i) Spectrophotometric results. Spectra of aqueous solutions of nickel nitrate and excess ligand, at different pH values, were measured against redistilled water, as reference solution, in the range 450—600 nm where the ligands and nickel ion have no absorbence (Fig. 1-a). The absorbence increases by the increase of pH in the range 3-9, which can be attributed to the fact that the ion of the ligand is the complexing unit. After pH = 9 the absorbence decreases due to change in the composition of the complex. Fig. 1-b represents the effect of pH on the absorbence of the system at one wavelength which shows that one type of complex is formed before pH = 9 and another type can be noticed after this pH.

The absorbence of solutions of constant concentration of nickel and different concentrations of one of the ligands at constant pH ~ 8.0 (adjusted by 5 ml. ammonia buffer (1 M) per 10 ml. solution) increases steadily as shown by Fig. 2-a. The maximum of nickel ion at 650 nm changes by the addition of ligand to 630, 610, 600 and 580 nm in the case of o-ligand or to a shoulder at 500 — 470 nm in p-ligand or 600, 580, 560 nm in 4-Me-o-ligand by changing the metal: ligand ratio from 2:1 to 1:1 to 1:2 to 1:4 respectively. The changes of the position of the maximum
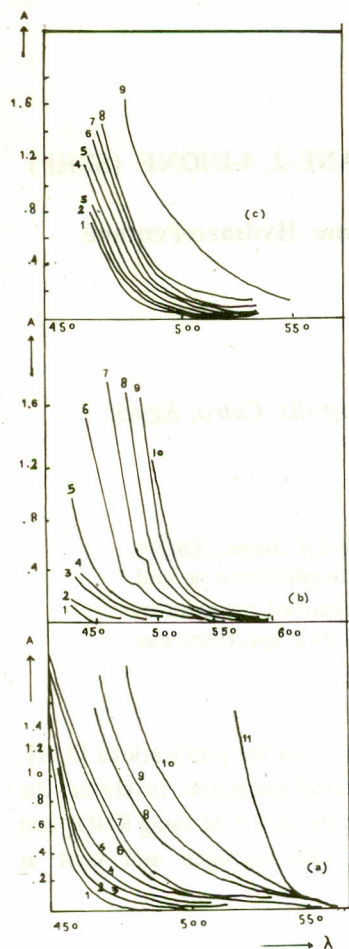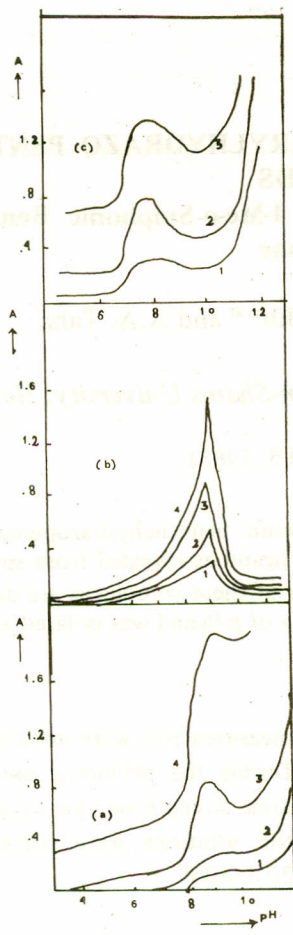

Fig.(1a)

Fig.(1b)
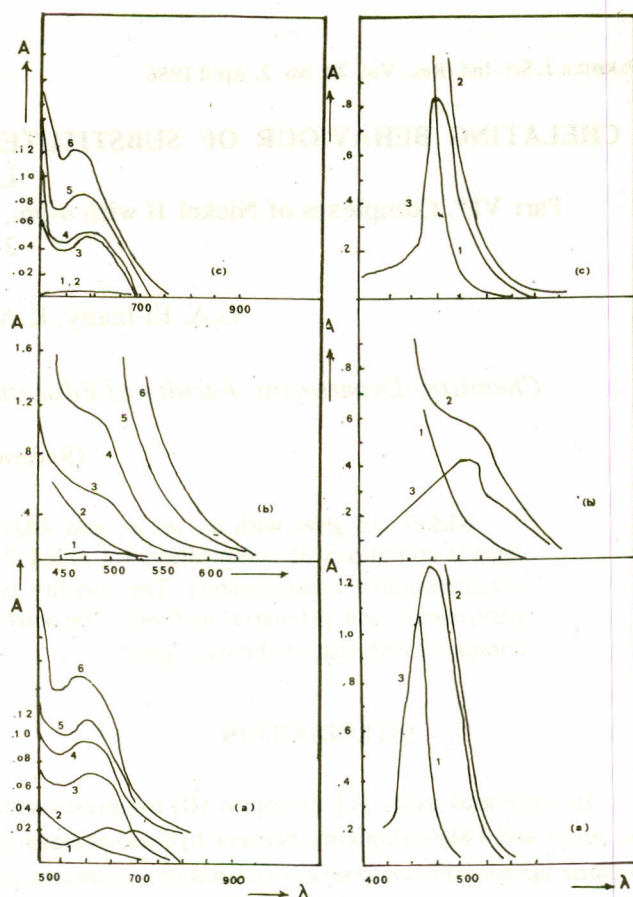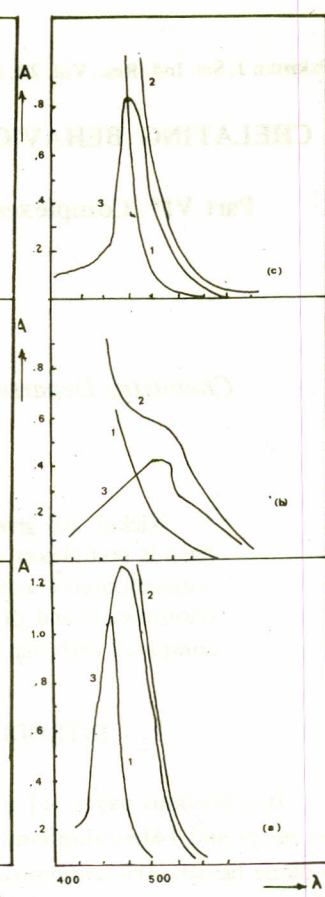

Fig.(2a)

Fig.(2b)

Fig. (1a) Absorption spectra o-, p- and 4 Me-o-SBHP-Ni^{2+} complexes at different pH values.

(a) [o-lig.] = 0.002 M, [Ni^{2+}] = 0.004 M

pH		pH	
(1) 3.90		(2)	4.85
(3) 6.00		(4)	7.40
(5) 8.20		(6)	8.65
(7) 8.90		(8)	11.30
(9) 11.62		(10)	11.95
		(11)	12.66

(b) [p-lig.] = 0.02 M, [Ni^{2+}] = 0.0005 M

pH		pH	
(1) 7.50		(2)	7.75
(3) 8.30		(4)	8.60
(5) 8.20		(6)	9.98
(7) 10.52		(8)	11.00
(9) 11.50		(10)	12.00

(c) [4-Me-o-lig.] = 0.02 M, [Ni^{2+}] = 0.005 M

(1) 5.00		(2)	6.63
(3) 6.82		(4)	7.00
(5) 7.12		(6)	7.50
(7) 8.10		(8)	11.20
(9) 12.00			

Fig. (1b). Effect of pH on the absorbance of o-, -p and 4-Me-o-SBHP-Ni^{2+} complexes. at different wavelengths.

(a) [o-lig.] = 0.02 M, [Ni^{2+}] = 0.004 M

λ (nm)	λ (nm)
(1) 520	(3) 480
(2) 500	(4) 460

(b) [p-lig.] = 0.02 M, [Ni^{2+}] = 0.0005 M

λ (nm)	λ (nm)
(1) 560	(3) 540
(2) 550	(4) 530

(c) [4-Me-o-lig.] = 0.02 M, [Ni^{2+}] = 0.0005M

λ (nm)	λ (nm)
(1) 490	(3) 470
(2) 480	

Fig. (2a): Effect of concentration of o-, p- and 4-Me-o-SBHP ligands on the absorption spectra of Ni^{2+}

(a) [o-lig.]   [Ni^{2+}]

(1)	Zero	+ 0.01M
(2)	0.04 M	+ Zero
(3)	0.005 M	+ 0.01 M
(4)	0.01 M	+ 0.01 M
(5)	0.02 M	+ 0.01 M
(6)	0.04 M	+ 0.01 M

pH = 8.3

(b)   [p-lig.]   [Ni^{2+}]

(1)	Zero	+ 0.0025 M
(2)	0.01 M	+ Zero
(3)	0.00125M	+ 0.0025 M
(4)	0.0025 M	+ 0.0025 M
(5)	0.005 M	+ 0.0025 M
(6)	0.01 M	+ 0.0025 M

pH = 8.0

(c)   [4-Me-o-lig.]   [Ni^{2+}]

(1)	Zero	+ 0.01 M
(2)	0.04 M	+ Zero
(3)	0.005 M	+ 0.01 M
(4)	0.01 M	+ 0.01 M
(5)	0.02 M	+ 0.01 M
(6)	0.04 M	+ 0.01 M

pH = 8.3

Fig. (2b): Absorption spectra of Ni^{2+} -o-, p-, and 4-Me-o-SBHP complexes using H$_2$O or the ligand as a reference.

(a)
(1) 0.01 M free o-lig.
(2) 0.01 M o-lig. + 0.005 M Ni^{2+}, Ref. H$_2$O
(3) 0.01 M o-lig. + 0.005 M Ni^{2+}, Ref. lig.

(b)
(1) 0.008 M Free p-lig.
(2) 0.008 M p-lig. + 0.002 M Ni^{2+}, Ref. H$_2$O
(3) 0.008 M p-lig. + 0.002 M Ni^{2+}, Ref. lig.

(c)
(1) 0.01 M free 4-Me-o-lig.
(2) 0.01 M 4-Me-o-lig. + 0.005 M Ni^{2+} Ref. H$_2$O
(3) 0.01 M 4-Me-o-lig. + 0.005 Ni^{2+} Ref. lig.

by changing the concentration of the ligand indicates the formation of different types of complexes. Using the ligand as a reference with the same concentration as in solution shows that the complex has another maximum at 490 nm in *p*-ligand and 460 nm for *o*-ligands, Fig. 2-b.

The metal: ligand ratios of the complexes were traced by applying the continuous variation [6], molar ratio [7], slope ratio [8] and straight line [9] methods. The results
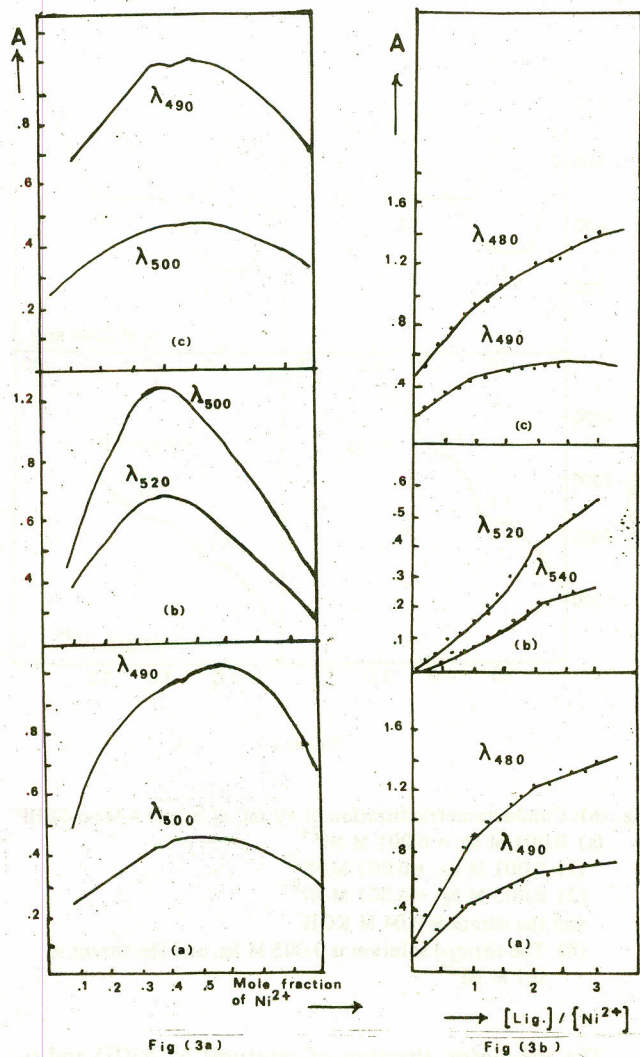
obtained revealed the formation of 1:1 and 1:2 (M:L) complexes as obtained from Fig. 3 a, b, c and d.

On keeping the concentration of ligand constant and changing that of nickel ion, the absorbence increases regularly with the metal concentration. The plot of absorbence as a function of nickel ion concentration gave straight lines shown in Fig. 4 useful for the determination of nickel.

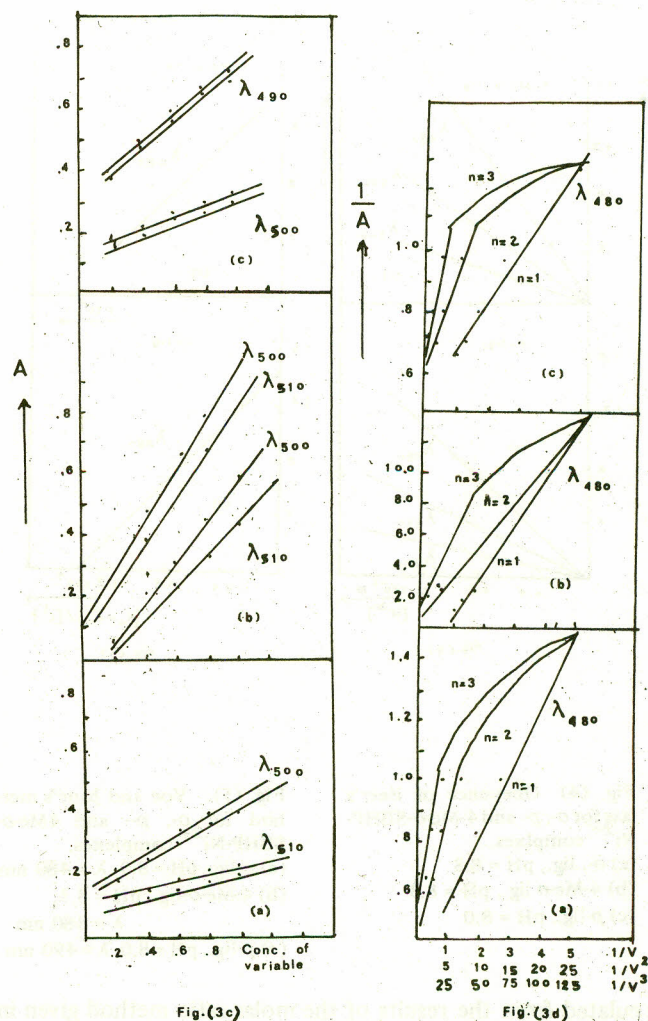The stability constants of the 1:2 complexes are cal-

Fig. (3a): Job's method for *o*-, *p*- and 4-Me-*o*-SBHP-Ni^{2+} complexes.

   (a) *o*-lig., pH = 8.3
   (b) *p*-lig., pH = 8.0
   (c) 4-Me-*o*-lig., pH = 8.3

(Fig. (3b): Molar ratio method for *o*-, *p*- and 4-Me-*o*-SBHP-Ni^{2+} complexes

   (a) *o*-lig., pH = 8.3
   (b) *p*-lig., pH = 8.0
   (c) 4-Me-*o*-lig., pH = 8.3

Fig. (3c): Slope ratio method for *o*-, *p*-, and 4-Me-*o*-SBHP-Ni^{2+} complexes.

   (a) *o*-lig., pH = 8.3
   (b) *p*-lig., pH = 8.0
   (c) 4-Me-*o*-lig., pH = 8.3

Fig. (3d): Straight line method for *o*-, *p*-, and 4-Me-*o*-SBHP-Ni^{2+} complexes.

   (a) *o*-lig., pH = 8.3,   λ = 480 nm
   (b) *p*-lig., pH = 8.0,   λ = 480 nm
   (c) 4-Me-*o*-lig., pH = 8.3, λ = 480 nm

Fig. (4)

Fig. (5)

noticed corresponding to two neutralization points, the first for the $-SO_3H$ and the second for $-NH$ in the complex. Also Fig. 6-b contains two breaks, the first when the 1:2 metal: ligand complex is formed and the second when the metal is in excess and the 1:1 complex is formed.
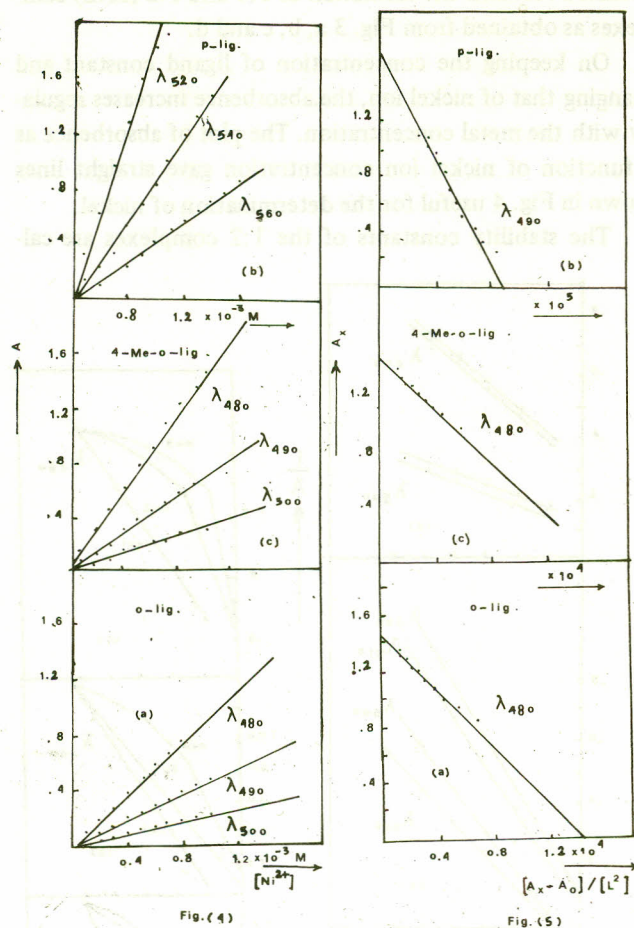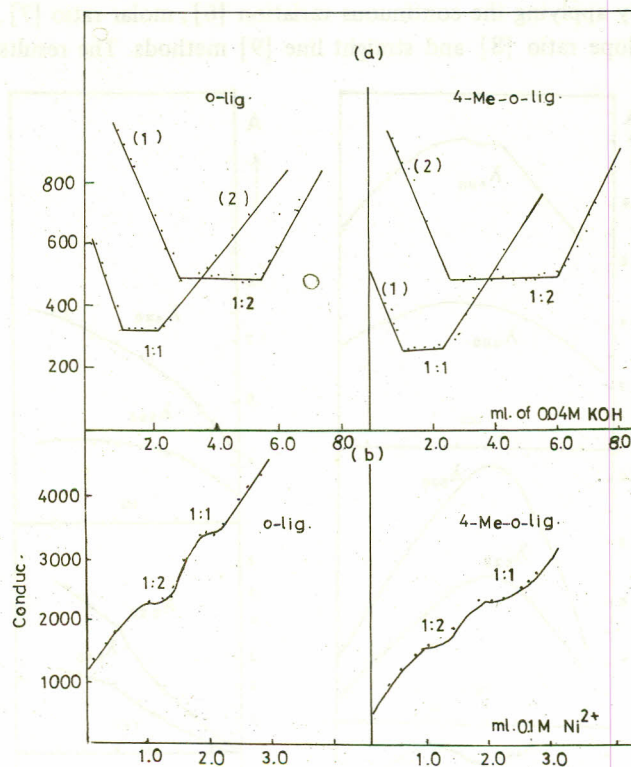

Fig.(6)

Fig. (4) Obeyence of Beer's law for *o*-, *p*- and 4-Me-*o*-SBHP-Ni^{2+} complxes.
(a) *o*-, lig., pH = 8.3
(b) 4-Me-*o* lig., pH = 8.3
(c) *p*-lig., pH = 8.0

Fig. (5): Yoe and Jone's method for *o*-, *p*-- and 4Me-*o*-SBHP-Ni^{2+} complexes.
(a) *o*-lig., pH = 8.3, λ = 480 nm
(b) 4-Me-*o*-lig., pH = 8.3,
λ = 480 nm
(c) *p*-lig., pH = 8.0, λ = 490 nm

Fig. (6): Conductometric titration of 40 ml. of *o*- and 4-Me-*o*-SBHP.
(a) 0.001 M lig. + 0.001 M Ni^{2+}
(1) 0.001 M lig. + 0.001 M Ni^{2+}
(2) 0.003 M lig. + 0.001 M Ni^{2+}
and the titrant is 0.04 M KOH.
(b) The titrated solution is 0.005 M lig. and the titrant is 0.1 M Ni^{2+}

culated from the results of the molar ratio method given in Table 1 and Fig.5 and the values obtained are:

Ligand	*o*-SBHP	*p*-SBHP	4-Me-*o*-SBHP
β	1.6×10^{17}	8.7×10^{-17}	4.5×10^{17}

From this, it is seen that the *p*-derivatives gives the higher value denoting that there is an *ortho* effect in buffered solution in case of *ortho* ligands.

(ii) Conductometric and pH-metric results. The different types of complexes are confirmed by conductometric titrations of ligands with nickel solution (Fig. 6-b), or mixtures of ligand and nickel with KOH solution (Fig. 6-a). In the latter case two breaks are

The pH-metric titration of mixtures of Ni(II) and *o*-, *m*-, *p*-, and 4-Me-*o*-SBHP ligands are presented in Fig. 7. The titration curves of 1:1 mixture showed steep inflection at m = 1 corresponding to the formation of NiL complex. A buffer zone was obtained at m = 1–2. This buffer zone may be due to the formation of hydroxo complex or due to disproportionation to NiL$_2$ complex. A steep inflection at m = 2 was obtaned in the case of 2:1 ligand: metal ratio. This may be due to the formation of 2:1 complex. Another buffer zone at m=2-4 at pH range 8-9 was obtained. The data obtained in these titrations are used to calculate the stability constant of the 2:1 Ni(II)

complexes with the different ligands using Bjerrum's method [10] and the results obtained at 0.1 ionic strength and 30° are:

	o-SBHP	*m*-SBHP	*p*-SBHP	4-Me-*o*-SBHP	AcAc
Log β	23.5±0.05	21.8±0.04	21.0±0.02	22.4-±0.07	10.77

These results are higher than those obtained in the spectrophotometric data which were carried out in ammonia buffer, which suggests that ammonia competes with these ligands leading to the lowering observed in the spectr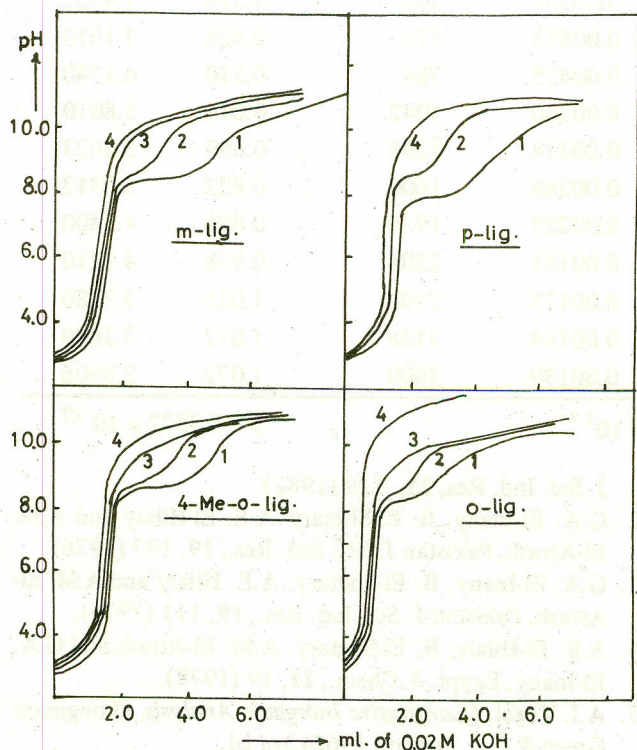ophotometric values. The values obtained are higher than those obtained for the nickel acetylacetone in the literature [11], which shows that these ligands have other coordination sites such as the azomethine nitrogen which can take part in complexation. Also, the basicity of these ligands (pK = 10.6 − 11) is higher than that of AcAc (pK = 8.9) [12] and leads to more stable complexes.
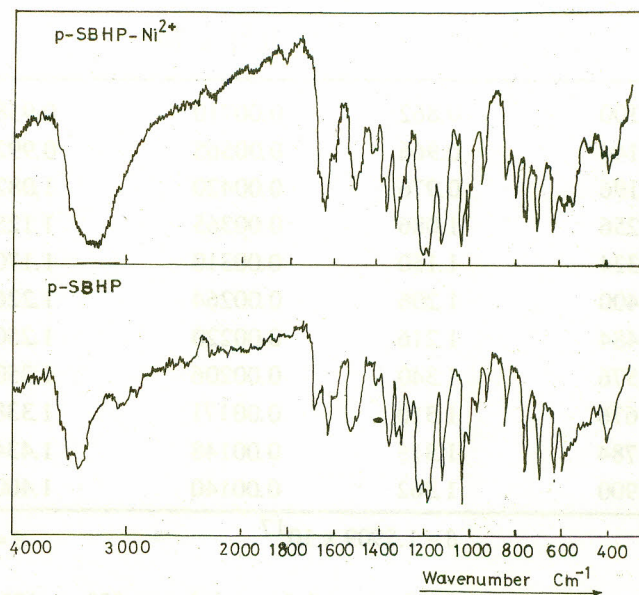

Fig. (7): pH-metric titration of 30 ml mixture of *o*-, *m*-, *p*- and 4-Me-*o*-SBHP ligands and Ni^{2+} at 30°

	[*o*-lig]		$[Ni^{2+}]$
(1)	0.0005 M	+	0.0005 M
(2)	0.0005 M	+	0.0025 M
(3)	0.0005 M	+	0.0001 M
(4)	0.0005 M	+	Zero

	[*m*-lig.] or [*p*-lig.]		$[Ni^{2+}]$
(1)	0.001 M	+	0.001 M
(2)	0.001 M	+	0.0005 M
(3)	0.001 M	+	0.0001 M
(4)	0.001 M	+	Zero

	[4-Me-*o*-lig.]		$[Ni^{2+}]$
(1)	0.001 M	+	0.001 M
(2)	0.001 M	+	0.0005 M
(3)	0.001 M	+	0.0002 M
(4)	0.001 M	+	Zero

Fig. (8): Infrared spectra of *p*-SBHP and its Ni^{2+} complex.

(iii) Infrared spectrum of p-SBHP-Ni (2:1) complex: The solid complex was obtained by mixing *p*-SBHP ligand and 20 ml. (0.2 M) nickel nitrate in the molar ratio 2:1 (L:M) with continuous stirring. A green complex was separated and washed with water and then air-dired. The elemental analysis of this corresponds to the formula NiL$_2$. 2H$_2$O:

	Found				Calculated			
	C	H	N	S	C	H	N	S
NiL$_2$.2H$_2$O	37.5	3.6	7.6	9.14	37.36	3.39	7.92	9.06

The ir spectrum of this complex was compared with that of the free ligand. The stretching vibration of the C=O at 1685 cm^{-1} in the free ligand [12] is shifted to 1630 cm^{-1} in the nickel complex, showing that this group is involved in complex formation. The band at 1530 cm^{-1} which can be assigned to the stretching vibration of the N-N bond [13] is also shifted to 1510 cm^{-1} in the spectrum of the complex, which denotes that this group is involved too in coordination. The azomethine nitroge is a stronger Lewis base compared to the secondary amine nitrogen and would preferetially coordinate to the metal ion. The appearance of two

Table 1: Yoe and Jones method for o-, p- and 4-Me-o-SBHP ligands-Nickel complexes.

	[o-SBHP] = [Ni^{++}] = 0.1 M, pH = 8.3, λ 480, A$_o$ = 0.152		[4-Me-o-SBHP] = [Ni^{++}] = 0.1 M, pH = 8.3, λ 480, A$_o$ = 0.152		[p-SBHP] = [Ni^{++}] = 0.02 M, pH = 8.0, λ 490, A$_o$ = 0.017		
$L^2 \times 10^6$	A_x	$\dfrac{A_x - A_o}{[L^2] \times 10^{-6}}$	A_x	$\dfrac{A_x - A_o}{[L^2] \times 10^{-6}}$	$L^2 \times 10^8$	A_x	$\dfrac{A_x - A_o}{[L^2] \times 10^{-4}}$
100	0.862	0.00710	0.958	0.00806	400	0.315	7.4500
144	0.966	0.00565	0.992	0.00583	576	0.426	7.1010
196	0.976	0.00420	1.082	0.00475	784	0.510	6.1740
256	1.086	0.00365	1.125	0.00380	1042	0.611	5.8010
324	1.150	0.00310	1.170	0.00314	1296	0.699	5.2623
400	1.206	0.00264	1.226	0.00269	1600	0.822	5.0313
484	1.216	0.00220	1.250	0.00227	1936	0.896	4.5400
576	1.340	0.00206	1.250	0.00191	2304	0.978	4.1710
676	1.310	0.00171	1.338	0.00175	2704	1.025	3.7280
784	1.315	0.00148	1.434	0.00164	3136	1.072	3.3640
900	1.362	0.00140	1.400	0.00139	3600	1.072	2.9306

$\beta = 1.5909 \times 10^{17}$ $\qquad\qquad$ $\beta = 4.455 \times 10^{17}$ $\qquad\qquad$ $\beta = 8.7377 \times 10^{17}$

new bands in the spectrum of the complex at 580 an 475 cm^{-1}, which can be assigned to the M-N and M-O stretching frequencies respectively [14, 15], emphasize the previous suggestions. The stretching bands due to the H$_2$O molecules in the complex hinder the stretching vibrations of the N-H bond.

Thus, it can be concluded that coordination occurs through one of the oxygen atoms of the acetylacetone moiety and the azomethine nitrogen of the hydrazo group. The structure of the complex can be represented by:
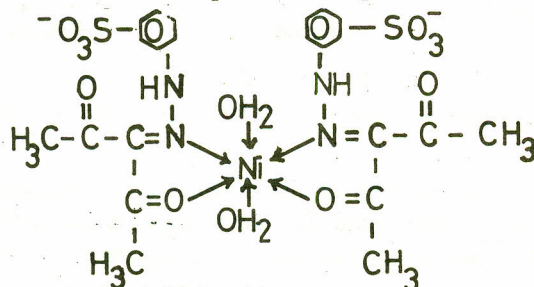
REFERENCES

1. G.A. El-Inany, Atef A. Taha and B. El-Shetary Pakistan J. Sci. Ind. Res, 25, 129 (1982).

2. G.A. El-Inany, B. El-Shetary A.E. El-Hilaly and A.M. El-Atrash, Pakistan J. Sci. Ind. Res., 19, 107 (1976).

3. G.A. El-Inany, B. El-Shetary, A.E. Hilaly and A.M. El-Atrash, Pakistan J. Sci. Ind. Res., 19, 111 (1976).

4. A.E. El-Hilaly, B. El-Shetary, A.M. El-Atrash and G.A. El-Inany, Egypt, J. Chem., 21, 19 (1978).

5. A.I. Vogel, Quantitative Inorganic Analysis, (Longmans Green & Co., London 1962) 3rd ed..

6. P. Job, Ann. Chim., 9, 113 (1928) and 11, 97 (1936).

7. J.H. Yoe and A.L. Jones, Ind. Eng. Chem. Analyt., 16, 111 (1944).

8. H.E. Bent and G.L. French. J. Am. Chem. Soc., 63, 568 (1941).

9. E.I. Asmus, Z. Anal. Chem., 178, 104 (1960).

10. A. Albert and E. Serjeant, Dissociation Constants of Acids and Bases (Methuen and Co. Ltd, London) 1st ed. p. 162.

11. G.R. Choppin and A. Dadgar, J. Coordination Chem., 1, 179 (1971).

12. F.C. Lingafetter, Coord. Chem. Rev., 1, 151 (1966).

13. G.A. El-Inany, K.A.R. Salib, S.B. El-Maraghy and S.L. Stefen, Egypt. J. Chem. (in press).

14. E.B. Powell and N. Sheppard, Spectro Chem Chim. Acta, 17, 68 (1961).

15. C. Duval, R. Freymann and Le Compte, J. Bull. Soc. Chim. France, 19, 106 (1952).