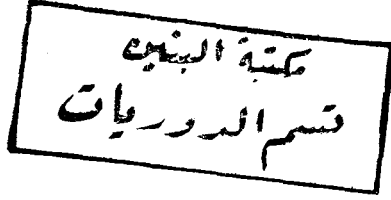




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SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF SOME MIXED-LIGAND COMPLEXES OF NICKEL (II), COPPER (II), ZINC (II) AND PALLADIUM (II) WITH BIOLOGICALLY ACTIVE NITROGEN-SULPHUR CONTAINING MOLECULES

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Key Words: Biologically active ligands, Mixed-ligand complexes, Nitrogen-sulphur containing molecules, Spectroscopic properties

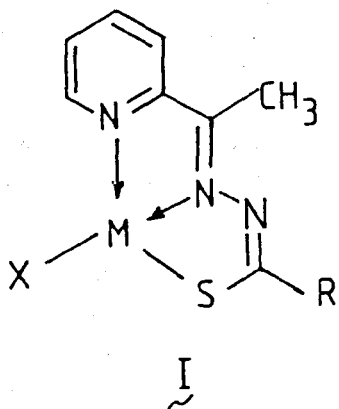
ABSTRACT

The reaction of the biologically active complexes, chloro-2-acetylpyridinehydrazinecarbothiopiperidinamide metal (II) and chloro-2-acetylpyridinecarbothiomorpholinamide metal (II), I , ($M=Ni(II), Cu(II), Zn(II)$ and $Pd(II)$) with S-methylhydrazinecarbodithioate Schiff bases, II ($R_1=R_2=CH_3$; $R_1=H, R_2=Ph$) have been studied. A series of mixed-ligand metal (II) complexes, III , were isolated and characterized using elemental analysis, infrared, ultraviolet-visible, 1Hnmr and esr spectra. The spectral results of the mixed-ligand complexes, III , are compared with those of the reactants I and II and used to provide evidence concerning the coordination geometry of the central metal in these complexes.

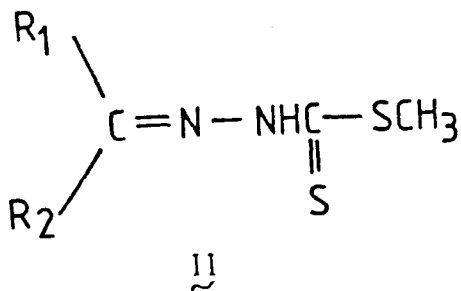
INTRODUCTION

Thiosemicarbazones in general and α -N-heterocyclic carboxaldehyde thiosemicarbazones in particular still attract special attention due to their wide-range of chemotherapeutic activities, among them antitumor (Das and Livingstone, 1976; Mohan *et al.*, 1988, 1986; Scovill *et al.*, 1982) antibacterial (Dobek *et al.*, 1980; Maiti *et al.*, 1988) antimalarial (Klayman *et al.*, 1984, 1983, 1982, 1979) and antiviral (Shipman *et al.*, 1981) activities. In many cases the activity is enhanced when the drugs administered as metal complexes (Das and Livingstone, 1987; Maiti *et al.*, 1988; Mohan *et al.*, 1988, 1986; Scovill *et al.*, 1982; Shipman *et al.*, 1981). A large number of metal chelates of the type I have been synthesized and characterized (El-Toukhy *et al.*, 1989; Scovill *et al.*, 1982; Westet *al.*, 1984):

The cytotoxic activity of this class of chelates was attributed to the presence of a labile uni-negative ligand X (Das and Livingstone, 1978) and the coordinatively unsaturated central metal ion, which renders these chelates good Lewis acids (El-Sayed *et al.*, 1972; Iskander *et al.*, 1984). Their antitumor activity may also be due to their interaction with nucleophilic sites in DNA or other similar targets to form a wide variety of adducts within cells. The carcinostatic activity was also reported for some transition metal complexes derived from S-methylhydrazinecarbodithioate Schiff bases (Das and Livingstone, 1976; Mohan *et al.*, 1988).



Prompted by this knowledge, the present investigation involving the synthesis and spectroscopic characterization of some mixed-ligand complexes of Ni(II), Cu(II), Zn(II) and Pd(II) ions have been explored, from the reaction of I, (M=Ni(II), Cu(II) Zn(II) or Pd(II); X=Cl, R= Piperidyl or morpholy) with the potentially monobasic bidentate ligands, S-methylhydrazinecarbodithioate Schiff bases, II, (R₁=R₂=CH₃; R₁=H, R₂=Ph).



Replacement of X in I by the bidentate ligand II may, expectedly, contribute to the biological activity of this type of chelates.

EXPERIMENTAL

Materials:

The reactants I [M(NNS)Cl], (M=Ni(II), Cu(II), Zn(II) or Pd(II); X=Cl; R=Piperidy1 or morpholy1) (El-Toukhy *et al.*, 1989) and II, HNS, (R₁=R₂=CH₃ and R₁=H, R₂=Ph) were prepared following procedures previously reported. (El-Toukhy *et al.*, 1989 and Iskander *et al.*, 1979).

Preparation of mixed ligand metal (II) chelates of the general formula (M(NNS)), III.

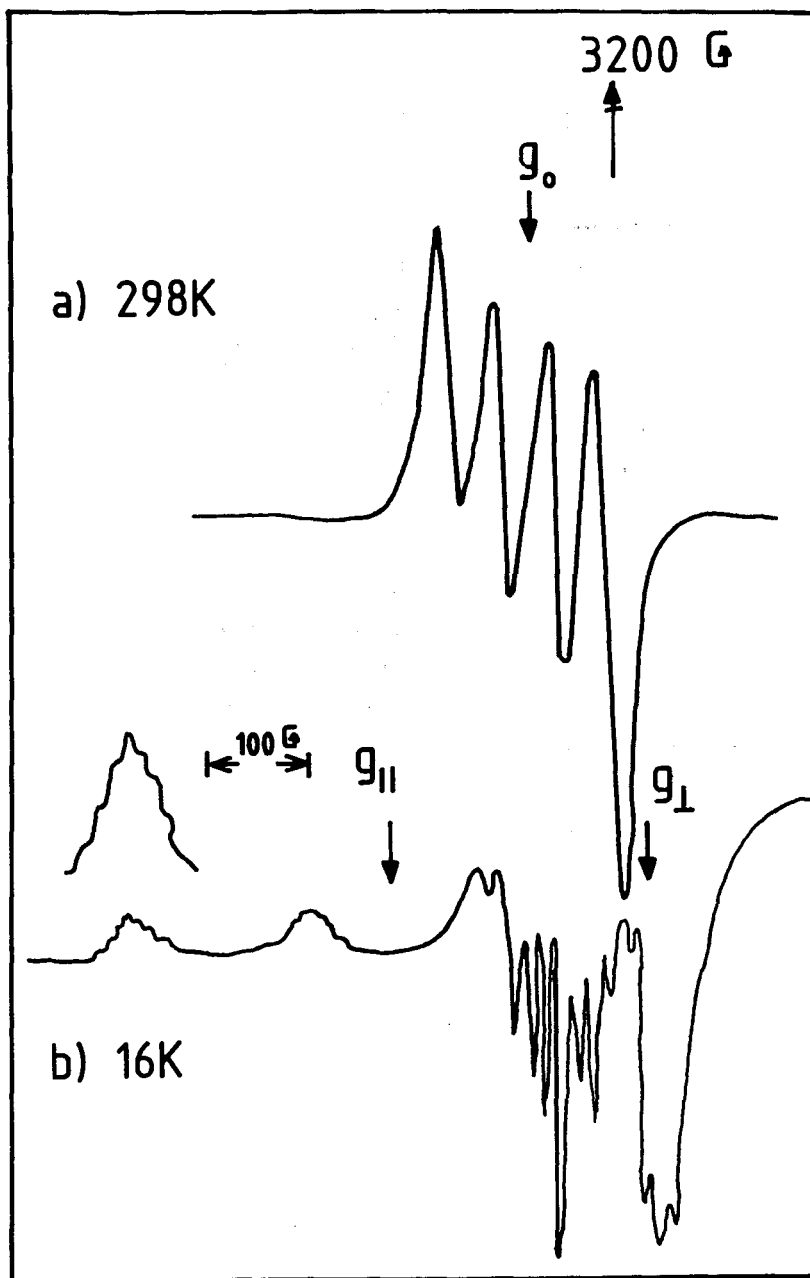
A clear solution of the appropriate [M(NNS)Cl] complex (0.01 mol) in dry methylene chloride (50ml) was treated with a solution of HNS (II, R₁=R₂=CH₃ or R₁=H, R₂=Ph) (0.01 mol) in methylene chloride (30ml). The reaction mixture was refluxed for 2h, evaporated to half its volume and left to cool. The mixed ligand complex, [M(NNS)(NS)], which separated out was filtered off and crystallized from methylene chloride-petroleum ether (40-60°C).

Physical Measurements

The solution electronic spectra of the prepared complexes were recorded on a Perkin-Elmer 552 spectrophotometer in matched quartz cells at room temperature. The solvent methylene chloride was used as reference. Infrared spectra (KBr disks) were obtained with a Pye Unicam SP2000 spectrophotometer calibrated with the 906.5 or 3026.3 cm⁻¹ absorption bands of polystyrene. ¹Hnmr spectra were recorded with a Varian instrument of the type EM-390-90 MHz NMR Spectrometer. The magnet temperature was adjusted at 38°C. Tetramethylsilane (TMS) signal ($\delta = 0$) was employed as an internal standard. Pure d¹-Chloroform (Aldrich) was used as solvent. Esr spectra were recorded at 100 KHz modulation and 10G modulation amplitude on a Varian E-9 Spectrometer. 10mW incident power was used and resonance conditions were at adjusted ca 9.75 GHz(X-band) at room temperature and at ca.9.10GHz at 16K. Spectra at low temperature were obtained with an Air Products LTD-3-110 Heli- Tran liquid helium transfer refrigerator. The field was calibrated with a powder sample of DPPH(g=2.0037) (Wertz and Bolton, 1972).

RESULTS AND DISCUSSION

The potentially monobasic tridentate ligands 2-acetylpyridinehydrazinecarbothiopiperidinamide, HAPP, and 2-acetylpyridinecarbothiomorpholinamide, HAPM, react with excess metal (II) chloride yielding neutral four coordinate complexes, [M(APP)Cl] (L₁R=NC₅H₁₀) and [M(APM)Cl] (L₁R=NC₄H₈O), respectively. Since the monodentate chloro ligand in I is labile, it can easily be substituted by the potentially monobasic bidentate ligand, namely, S-methylisop-

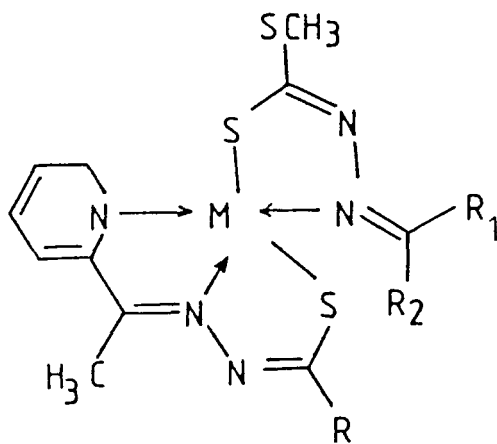


Magnetic Field, G

ropylidenehydrazinecarbodithioate, HAS, ($\text{II}, R_1=R_2=\text{CH}_3$) or S-methylbenzylidenehydrazinecarbodithioate, HBS, ($\text{II}, R_1=\text{H}, R_2=\text{Ph}$), yielding the mixed-ligand metal (II) complexes, III . The elemental analysis of the prepared complexes are given in Table 1. All these mixed-ligand metal (II) complexes are quite stable at room temperature and do not show any sign of decomposition after long standing. All of the complexes do not show sharp melting points but they decompose above 200°C .

In comparison with the sharp ir spectral band of the parent complexes, I , (El-Toukhy *et al.*, 1989) and the free ligands II , (El-Sayed *et al.*, 1974, 1972) the ir spectra, in general, of the mixed-ligand complexes, III , show broad or splitted stretching bands due to the presence of more or less the same bonded atoms or groups in the two different chelating ligands. The ir spectra lack any bands in the NH stretching frequency region indicating the deprotonation of the NH group, i.e. the ligands behave as monobasic chelating agents. (El-Sayed *et al.*, 1974, 1972).

The participation of the azomethine nitrogen atom in coordination to the central metal ion is usually deduced from the displacement of the band chiefly assigned to the N-N stretching (Mohan *et al.*, 1988). The spectra of the complexes under study show a low-wavenumber displacement of $\nu(\text{N-N})$ from ca. 1065 cm^{-1} for the ligand to ca. 1035 cm^{-1} in the complexes, III . On the other hand, the $\nu(\text{C=N})$ wavenumber, ca. 1590 cm^{-1} in the spectra of the free ligands, is raised by an average of 20 cm^{-1} in the



III
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Table 1
Analytical Data for Mixed Ligand Complexes, *III

Compound	Colour	M %	N %	S %
[Ni (APP) (AS)]	Greenish brown	12.60 (12.26)	17.25 (17.46)	19.77 (19.95)
[Ni (APP) (BS)]	Brown	11.24 (11.15)	15.73 (15.88)	17.89 (18.15)
[Ni (APM) (AS)]	Greenish brown	12.34 (12.22)	17.29 (17.39)	19.83 (19.87)
[Ni (APM) (BS)]	Brown	10.96 (11.11)	15.87 (15.82)	17.69 (18.08)
[Cu (APP) (AS)]	Dark green	13.35 (13.08)	17.23 (17.30)	19.46 (19.77)
[Cu (APP) (BS)]	Greenish brown	11.76 (11.90)	15.53 (15.75)	17.81 (17.99)
[Cu (APM) (AS)]	Olive green	12.77 (13.02)	17.42 (17.23)	19.38 (19.69)
[Cu (APM) (BS)]	Brown	11.66 (11.85)	15.62 (15.68)	17.83 (17.92)
[Zn (APP) (AS)]	Yellow	13.27 (13.41)	16.98 (17.23)	19.14 (19.69)
[Zn (APP) (BS)]	Yellow	12.34 (12.21)	15.58 (15.69)	17.60 (17.90)
[Zn (APM) (AS)]	Yellow	13.55 (13.36)	17.02 (17.16)	19.26 (19M61)
[Zn (APM) (BS)]	Yellow	12.27 (12.16)	15.24 (15.62)	17.55 (17.86)
[Pd (APP) (AS)]	Orange	19.74 (20.13)	15.79 (15.90)	18.28 (18.16)
[Pd (APP) (BS)]	Brown	18.14 (18.46)	14.53 (14.57)	16.27 (16.65)
[Pd (APM) (AS)]	Orange	19.68 (20.06)	15.71 (15.84)	17.88 (18.10)
[Pd (APM) (BS)]	Brown	18.14 (18.39)	14.45 (14.52)	16.44 (16.60)

a Calculated values are given in parantheses.

Table 2

Electronic and Selected Infrared Spectral Data for Mixed-Ligand Metal (II) Complexes, III

Compound	Band Maxima, nm (log ϵ , Mol ¹ cm ⁻¹)				Infrared Spectral bands, cm ⁻¹				ν (M-N pyridine)
	ν (C=N)	ν (C-S)	ν (M-N)	ν (M-S)					
[Ni (APP) (AS)]	330, (4.20)	380(sh), (3.49)	460 (Sh), (2.85)	695 (1.92)	1620	1320, 780	420	275	320
[Ni (APP) (BS)]	360, (4.26)	405, (4.37)	470(sh) (2.76)	630(sh), 715 (1.98) (1.63)	1615	1320, 785	415	270	315
[Ni (APM) (AS)]	340 (4.28)	385(sh) (3.66)	455(sh), (3.00)	680 (2.12)	1615	1315, 780	420	275	320
[Ni (APM) (BS)]	365, (4.41)	415, (4.39)	465(sh), (2.89)	640(sh), 720 (2.06) (1.75)	1620	1320, 780	415	275	310
[Cu (APP) (AS)]	325, (4.37)	420(sh), (3.87)	650, (2.65)	730(sh) (1.86)	1610	1315, 775	410	280	315
[Cu (APP) (BS)]	335 (4.34)	410, (3.92)	655(Sh), (2.73)	740(Sh) (1.94)	1605	1310, 775	420	275	310
[Cu (APM) (AS)]	325, (4.40)	425(Sh), (3.79)	650, (2.78)	735(Sh) (1.74)	1610	1310, 770	415	280	310
[Cu (APM) (BS)]	330, (4.28)	425(Sh), (3.87)	650, (2.86)	740(Sh) (1.83)	1605	1305, 775	415	275	310
[Zn (APP) (AS)]	310, (4.42)	345(Sh), (4.18)	410 (4.31)		1600	1310, 780	410	270	310
[Zn (APP) (BS)]	315, (4.37)	350, (4.20)	420, (4.33)	430(Sh) (3.94)	1600	1310, 775	410	270	310
[Zn (APM) (AS)]	310, (4.18)	340(Sh), (4.23)	415 (4.37)		1605	1315, 780	415	275	310
[Zn (APM) (BS)]	320 (4.35)	345, (4.16)	425, (4.37)	440(Sh) (3.91)	1600	1310, 775	420	270	310
[Pd (APP) (AS)]	320, (4.47)	380(Sh), (4.18)	415, (4.34)	510 (3.22)	1605	1305, 775	415	280	315
[Pd (APP) (BS)]	310, (4.38)	360, (4.14)	385(Sh), (4.26)	420, 505 (4.37) (3.35)	1600	1305, 780	415	285	310
[Pd (APM) (AS)]	320, (4.41)	385(Sh), (4.25)	410, (4.36)	515 (3.18)	1600	1310, 775	420	285	310
[Pd (APM) (BS)]	415, (4.27)	355, (4.21)	380(Sh) (4.35)	420, 510 (4.27) (3.28)	1595	1305, 775	410	285	315

Table 3
 'Hnmr Spectra of (APP), APM, AS and BS Ligands and Their Mixed Ligand Diamagnetic Metal (II) Complexes in CDCl_3

Compound	C-CH ₃	-C-CH ₃	-SCH ₃	=CH	α -CH ₂	β -CH ₂	γ -CH ₂	Aromatic Protons	NH
APP	2.30 2.40 2.50	-	-	-	-	3.90	1.80	7.30 - 8.70	15.10
APM	2.36 2.43 2.60	--	--	--	--	3.70	4.07	7.16 - 7.96	15.12
BS	--	--	--	2.67	7.94	--	--	7.20 - 7.86	10.90
AS	--	1.97	2.05	2.58	--	--	--	---	10.50
[Ni (APP) (AS)]	2.30	2.82	3.30	2.55	--	3.90	1.73	7.10 - 8.63	--
[Ni (APP) (BS)]	2.24	--	--	2.64	8.35	3.93	1.75	7.05 - 9.25	--
[Ni (APM) (AS)]	2.18	2.80	3.25	2.52	--	3.90	--	7.32 - 8.86	--
[Ni (APM) (BS)]	2.15	--	--	2.60	8.31	3.92	--	7.24 - 9.14	--
[Zn (APP) (AS)]	1.86	2.15	2.33	2.52	--	3.91	1.78	7.32 - 8.94	--
[Zn (APP) (BS)]	1.84	--	--	2.55	7.86	3.88	1.81	7.28 - 8.97	--
[Zn (APM) (AS)]	1.82	2.20	2.39	2.53	--	3.87	--	7.13 - 8.76	--
[Zn (APM) (BS)]	1.80	--	--	2.58	7.75	3.88	--	7.30 - 8.93	--
[Pd (APP) (AS)]	1.92	2.41	2.49	2.54	--	3.83	1.75	7.21 - 8.79	--
[Pd (APP) (BS)]	1.89	--	--	2.61	7.97	3.86	1.76	7.33 - 9.14	--
[Pd (APM) (AS)]	1.90	2.33	2.48	2.52	--	3.89	--	7.30 - 8.75	--
[Pd (APM) (BS)]	1.88	--	--	2.63	8.00	3.91	--	7.00 - 9.34	--

Table 4

Esr Spectral Data for Mixed Ligand Copper (II) Complexes.

Compound	Temperature -K	Esr Parameters					Ground State
		g_0 (A_0) ^a	g_{11} (A_{11}) ^a	g_{\perp}	$\langle g \rangle^b$	G^c	
[Cu (APP) (AS)]	298	2.12 (88)					
	16		2.16 (150)	2.03	2.07	5.33	$d_x^2y^2$
[Cu (APP) (BS)]	300	2.09 (98)					
	11		2.21 (172)	2.04	2.05	5.52	$d_x^2y^2$
[Cu (APM) (AS)]	300	2.13 (90)					
	11		2.14 (165)	2.03	2.06	4.66	$d_x^2y^2$
[Cu (APM) (BS)]	299	2.07 (97)					
	16		2.09 (170)	2.01	2.03	9.00	$d_x^2y^2$

a Units are 10^{-4} cm^{-1} b $\langle g \rangle = \frac{1}{3} g_{11} + \frac{2}{3} g_{\perp}$ (g_{\perp})c $= (g_{11} - 2) / (g_{\perp} - 2)$

spectra of the complexes. These changes are typical of the coordination of the ligand to the metal ion through an azomethine nitrogen atom (Maiti *et al.*, 1988; Mohan *et al.*, 1988) Both bands at ca. 1330 and 800 cm^{-1} assigned to the $\nu(\text{C}=\text{S})$ vibrations of the free ligands are shifted towards lower wavenumbers in the complexes, III, suggesting coordination through the sulphur atom (Maiti *et al.*, 1988; Mohan *et al.*, 1988). In the far infrared region, the metal complexes show bands at ca. 420 and 280 cm^{-1} which are assigned to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{S})$ vibrations, respectively (Adams, 1967). In all these complexes, III, the $\nu(\text{M}-\text{N})$ pyridine appeared at ca. 315 cm^{-1} which is somewhat higher in energy than the 250-270 cm^{-1} range usually assigned for this band (Ferraro, 1971).

The electronic spectra of the mixed-ligand complexes are summarized in Table 2. The colour as well as the spectra of the complexes remain practically unchanged upon dissolution in methylene chloride solvent (very poorly coordinating solvent), indicating retention of the structure environment around the central metal ion in

solution. The main contribution to these spectra in the near uv region is due to intraligand transitions within the conjugated thiol form of the ligands. This is exemplified here by the spectra of the zinc complexes, where no bands related to charge transfer processes were observed indicating that the energy separation between the filled d-shell and the empty ligand orbitals are still too great to provide accessible spectra (Lever, 1968). Besides, the ligand absorptions, viz., additional contributions due to ligand-to-metal charge-transfer (LMCT) transitions from filled orbitals on the donor groups to the metal d vacancy would as expected occur down to 450 nm. Deductions about the main structural features of the complexes in solution can be made on the basis of their electronic spectra in the visible-near ir spectra (d-d transitions) for Ni(II), Cu(II) and Pd(II) complexes. Further information can be obtained from the esr spectra of Cu(II) complexes. The observed spectral characteristics of $\text{M}(\text{II})$ complexes (M=Ni(II) and Cu(II)), Table 2, are similar to those reported for Ni(II) (El-Sayed *et al.*, 1974; Lever, 1968) and Cu(II) (Lever, 1968; Davies *et al.*, 1985) complexes in five-coordinate geometries, most probably distorted square pyramidal structures. This can be explained as follows: The conjugation in the thiosemicarbazone ligands APP and APM in $\text{M}(\text{II})$ suggests planarity of the bicyclic tridentate molecule, occupying three sites in the equatorial plane. The fourth site and the apical site of the square pyramid are occupied by the N and S atoms of the bidentate ligands, II . It is, however, difficult to distinguish between five coordinate Ni(II) or Cu(II) complexes of square pyramidal and trigonal bipyramidal symmetries particularly if distortion occurs (El-Sayed *et al.*, 1974). The Pd(II) chelates most probably possess a square planar structure in which the AS and BS ligands behave as monobasic monodentate, bonded to the Pd ion via the thiol sulphur atom.

The Ni(II), Pd(II), and Zn(II) complexes are diamagnetic as characterized by ^1H nmr spectroscopy. Table 3, contains ^1H nmr data and their respective assignments. The most notable features in the spectra of these complexes are: 1) the absence of the NH resonance at 10.50 and 10.90 ppm for HAS and HBS ligands, respectively, indicative of metal (II) ion coordination to the thiol ligands. 2) The chemical shift of the SCH_3 signals at ca. 2.55 ppm are essentially constant and independent of the central metal ion and the rest of the molecule. 3) Due to restricted rotation around the C=N bond, in both the ligand, II ($\text{R}_1=\text{R}_2=\text{CH}_3$), and its mixed-ligand complexes, their spectra show two signals, one for each methyl group indicating that they are magnetically non-equivalent. It was suggested that the signal of the methyl group syn to the N-N bond, III , resonated at higher fields as compared with the other (Iskander *et al.*, 1979). 4) the resonance of R_1 and R_2 signals in III , show down field shifts as compared to the parent organic ligands due to a quasiaromatic character of the chelate ring (Iskander *et al.*, 1979). The larger down field shifts observed in

transition metal, Ni(II), chelates as compared with non-transition, Zn(II), chelates, Table 3, suggest an increase in electron delocalization in the chelate ring, consequently an increase in its aromatic character. This is another evidence for LMCT which arises through the formation of $d_{\pi}-d_{\pi}$ bonding between the central metal ion with the sulphur atom giving additional aromatic character to the ring, with subsequent deshielding of the groups attached to the chelate ring (Iskander *et al.*, 1979). Similar deshielding effects were previously observed in many Ni(II) chelates with sulphur containing ligands (Hendrickson and Martin, 1975; Iskander *et al.*, 1979). 5) The tridentate ligand, HAPP, and its Ni(II), Pd(II) and Zn(II) complexes show a broad signal at ca. 3.83-3.93 ppm due to α -CH₂ protons of the piperidyl moiety, while the β - and γ -CH₂ protons appear in a single broad peak at ca. 1.75-1.81 ppm. The spectrum of the morpholyl ligand, HAPM, shows two poorly resolved multiplets at 3.70 and 4.07 ppm, for the α -CH₂ and β -CH₂ protons, respectively. In its metal(II) complexes, III, (M=Ni(II), Zn(II) or Pd(II), R=morpholyl) the α -CH₂ and β -CH protons appear together as only one poorly resolved multiplet centered at ca. 3.88 ppm.

The X-band esr spectra of the mixed-ligand Cu(II) complexes, III, were measured in methylene chloride solution at room and liquid helium temperatures (11-16K). Copper(II) complexes having sulphur coordination generally have the g_{\perp} parameter close to 2.03 and g_{\parallel} lies in the range 2.08 to 2.15 (West *et al.*, 1984). The esr spectral data are collected in, Table 4. Particular spectra are shown in Figure 1. The g -values suggest coordination by sulphur in agreement with the ir results discussed earlier. The room temperature esr spectra are typical of isotropic spectra observed for mononuclear Cu(II) complexes (four hyperfine lines are observed with $g_0 \approx 2.10$ and $A_0 \approx 92 \times 10^4 \text{cm}^{-1}$, indicative of an electron interacting with only one copper nucleus). Also there are no observable $\Delta M_s = 2$ transitions, which means that the products are monomeric. The frozen methylene chloride solution spectra of III, (M=Cu(II)) are apparently of the axial symmetry with $g_{\parallel} > g_{\perp}$, small exchange coupling (G in the range of 4-9) (Bew *et al.*, 1972; Davies *et al.*, 1985) and $d_{x^2-y^2}$ ground state, Table 4. This indicates square pyramidal geometry around the Cu(II) center. Close examination of the spectra reveals that each g_{\parallel} line is split into seven lines due to the coupling of the metal d electron with three nitrogen nuclei. The nitrogen superhyperfine coupling constants are $7.1 \times 10^4 \text{cm}^{-1}$.

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تحضير ودراسة الخواص الطيفية لبعض متراكبات النيكل والنحاس
والزنك والبلاديوم
مختلطة عوامل التراكم (ليجاند) ذات التأثير البيولوجي
والمحتوية على النيتروجين والكبريت

أحمد الطوخي

يهدف هذا البحث إلى تحضير ودراسة الخواص الطيفية لبعض متراكبات النيكل والنحاس ، والزنك والبلاديوم المحتوية على أكثر من عامل تراكم (ليجاند) والمشتقة من مركبات الثيوسيميكاربازون المعروفة بتأثيرها البيولوجي ضد الأورام السرطانية والملاريا وبعض الفيروسات والميكروبات .

وقد استخدمت نتائج القياسات الطيفية ومنها أطيف الأشعة دون الحمراء وفوق البنفسجية والمرئية وطيف الرنين النووي المغناطيسي لنواة الهيدروجين وطيف الرنين الإلكتروني المغزلي بعد مقارنتها بالخواص الطيفية للمتفاعلات في تحديد الأشكال الفراغية لجميع المتراكبات وكذلك طبيعة الروابط بها .