



## Structural and characterization of novel copper(II) azodye complexes

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## ABSTRACT

The synthetic methods of novel Cu(II) and adduct complexes, with selective azodyes containing nitrogen and oxygen donor ligands have been developed, characterized and presented. The prepared complexes fall into the stoichiometric formulae of  $[\text{Cu}(\text{L}_n)_2](\text{A})$  and  $[\text{Cu}(\text{L}_n)_2(\text{Py})_2](\text{B})$ , where two types of complexes were expected and described. In type [(A) (1:2)] the chelate rings are six-membered/four coordinate, whereas in type [(B) (1:2:2)] they are six-membered/six coordinate. The important bands in the IR spectra and main <sup>1</sup>H NMR signals are tentatively assigned and discussed in relation to the predicted assembly of the molecular structure. The IR data of the azodye ligands suggested the existing of a bidentate binding involving azodye nitrogen and C–O oxygen atom of enolic group. They also showed the presence of Py coordinating with the metal ion. The coordination geometries and electronic structures are determined from the framework of the proposed modeling of the formed novel complexes. The complexes (1–5) exist in *trans*-isomeric [N,O] solid form, while adduct complexes (6–10) exist in *trans* isomeric (Py) form. The square planar/octahedral coordination geometry of Cu(II)/adduct is made up of an N-atom of azodye, the deprotonated enolic O-atom and two Py. The azo group was involved in chelation for all the prepared complexes. ESR spectra show the simultaneous presence of a planar *trans* and a nearly planar *cis* isomers in the 1:2 ratio for all N,O complexes  $[\text{Cu}(\text{L}_n)_2]$ . The ligands in the dimmer are stacked over one another. In the solid state of azo-rhodanine, the dimmers have inter- and intramolecular hydrogen bonds. Interactions between the ligands and Cu(II) are also discussed.

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## 1. Introduction

Interest in the study of azodye has been growing because of their antimicrobial, anti-tuberculosis, and anti-tumor activities [1–4]. Azodyes play also an important role in inorganic chemistry, as they easily form stable complexes with most transition metal ions. The behaviour of azodye complexes has attracted the attention of the bioinorganic chemists since a number of these complexes are recognized to serve as models for biologically important species [5–7]. Azo sulphadrag is a subject of current and growing interest and that may have numerous applications, e.g., anticancer [8], antibacterial [9], antiviral [10], antifungal [11] and other biological properties [12,13]. Azo sulphadrag containing moieties are of great interest because of their great versatility as ligands [14], due to presence of several potential donor atoms, their flexibility and ability to coordinate in either neutral or deprotonated form. They also contain C=N–NH structure unit, which form a strong chelate ring giving possible electron delocalization associated with extended conjugation that may affect the nature of the complex formed. They can yield complexes some of which are biologically relevant [15]. Metal binding substances, many of which function by chelation, form a

class of substances which have furnished many useful drugs and other substances of value in selectively used in medicine for their antibacterial properties. The combined antibacterial activity of sulphanamides and antimicrobial activity of heavy metal with a view to established the relationship and importance of metal–drug interactions have investigated [16]. The metal chelates of sulphadrag have been found to be more bacteriostatic than the drugs themselves [17].

In continuation of our studies on the ligating properties of azo sulphadrag, we report herein the preparation and characterization of copper(II) complexes with 5-(4'-derivatives phenylazo)-3-(4-methoxyphenyl)-2-thioxothiazolidinone (HL<sub>n</sub>) and pyridine adduct of copper(II) complexes of HL<sub>n</sub>.

## 2. Experimental

The standard chemical rhodanine, aniline and 4-alkyl-anilines (alkyl: OCH<sub>3</sub>, CH<sub>3</sub>, Cl and NO<sub>2</sub>; Aldrich Chemical Co.) were used without any further purification.

## 2.1. Preparation of 3-(4-methoxyphenyl)-2-thioxo-4-thiazolidinone

3-(4-Methoxyphenyl)-2-thioxo-4-thiazolidinone was prepared by adding equimolar amounts of 4-methoxyaniline to a solution of

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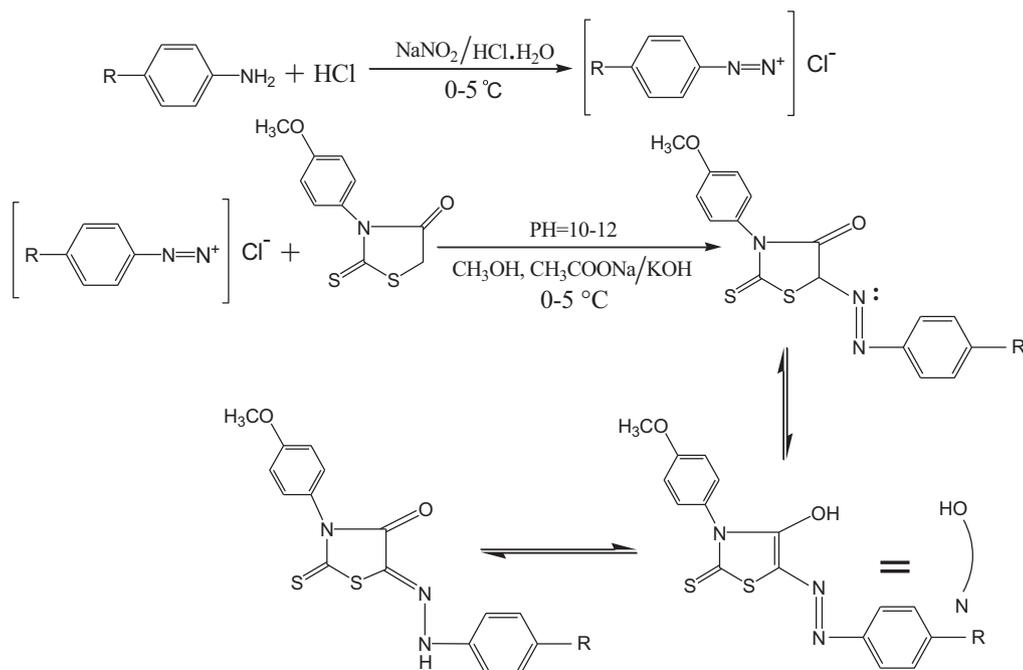
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trithiocarbodiglycolic acid [18] in bidistilled water with constant stirring on a steam bath. The white precipitate was filtered off, washed with hot bidistilled water, and recrystallized from absolute ethanol, empirical formula  $C_{10}H_9NO_2S_2$  (molecular weight: 239.30). Its purity was checked by elemental analysis (found: C 50.05, H 3.78, N 5.80%; calcd.: C 50.19, H 3.79, N 5.85%).

## 2.2. Synthesis of 5-(4'-derivatives phenylazo)-3-(4-methoxyphenyl)-2-thioxothiazolidinone ( $HL_n$ )

5-(4'-Alkylphenylazo)-3-(4-methoxyphenyl)-2-thioxothiazolidinone ( $HL_n$ ) were typically prepared by adding a 25 mL of distilled water containing hydrochloric acid (12 M, 2.68 mL, 32.19 mmol) were added to aniline (10.73 mmol) or 4-alkyl anilines. To the resulting mixture, stirred and cooled to 0 °C, a solution of sodium nitrite (10.73 mmol, in 20 mL of water) was added drop wise. The so-formed diazonium chloride was consecutively coupled with an alkaline solution of 3-(4-methoxyphenyl)-2-thioxo-4-thiazolidinone (10.73 mmol) in 20 mL of ethanol containing 602 mg (10.73 mmol) of potassium hydroxide. The red precipitates, which formed immediately were filtered and washed several times with water. The crude product obtained was purified by crystallization from hot ethanol (yield ~55–75%), then dried in vacuum desiccator over  $P_2O_5$ .

The resulting formed ligands are: 5-(4'-methoxyphenylazo)-3-(4-methoxyphenyl)-2-thioxothiazolidinone ( $HL_1$ ), 5-(4'-methylphenylazo)-3-(4-methoxyphenyl)-2-thioxothiazolidinone ( $HL_2$ ), 5-(4'-phenylazo)-3-(4-methoxyphenyl)-2-thioxothiazolidinone ( $HL_3$ ), 5-(4'-chlorophenylazo)-3-(4-methoxyphenyl)-2-thioxothiazolidinone ( $HL_4$ ), and 5-(4'-nitrophenylazo)-3-(4-methoxyphenyl)-2-thioxothiazolidinone ( $HL_5$ ) were characterized by microanalyses, IR and  $^1H$  NMR spectroscopy.



$n=1$ , R = OCH<sub>3</sub> ( $HL_1$ );  $n=2$ , CH<sub>3</sub> ( $HL_2$ );  $n=3$ , H ( $HL_3$ );  $n=4$ , Cl ( $HL_4$ ); and  $n=5$ , NO<sub>2</sub> ( $HL_5$ )

The formation mechanism of azodye ligands ( $HL_n$ )

## 2.3. Synthesis of copper(II) complexes (1–5)

A hot solution of  $CuCl_2 \cdot 2H_2O$  (0.01 mol) in  $CH_3OH$  (30 cm<sup>3</sup>) was added to the appropriate ligands (0.022 mol) in  $CH_3OH$  (30 cm<sup>3</sup>).

The reaction mixtures were maintained under reflux temperature for 1.5 h to ensure complete reaction. Polycrystalline solid complexes were immediately formed. The solid complexes were filtered off while hot, washed several times with water and a small quantity of methanol, followed by  $Et_2O$ , and finally dried in a vacuum over at  $P_2O_5$ .

## 2.4. Preparation of adduct copper(II) complexes (6–10)

The metal complexes (1–5) were placed in a conical flask of 50 mL capacity and dissolved in a minimum quantity of pyridine. After stirring the solution for 45 min, and followed by the addition of n-hexane (30 mL) slowly, dark colored compounds were formed on standing for ~24 h. Adducts thus obtained were collected by filtration, washed with hot water and hexane and dried under vacuum over  $CaCl_2$ .

## 2.5. Measurements

C, H, and N microanalyses were carried out at the Cairo University Analytical Center, Egypt. The complexes were determined after decomposition by aqua-regia, by complexometric titration using EDTA using meroxide as indicator at pH ~ 10 [19].  $^1H$  NMR spectrum was obtained with a Jeol FX90 Fourier transform spectrometer with  $DMSO-d_6$  as the solvent and TMS as an internal reference. Infrared spectra were recorded using Perkin-Elmer 1340 spectrophotometer. Ultraviolet–visible (UV–vis) spectra of the complexes were recorded in Nuzol solution using a Unicam SP 8800 spectrophotometer. The magnetic moment of the prepared solid complexes was determined at room temperature using the Gouy method. Mercury(II) (tetrathiocyanato)cobalt(II) [ $Hg\{Co(SCN)_4\}$ ],

was used for the calibration of the Gouy tubes. Diamagnetic corrections were calculated from the values given by Selwood [20] and Pascal's constants. Magnetic moments were calculated using the equation,  $(\mu_{eff}) = 2.84 [T\chi_M^{coor.}]^{1/2}$ . EPR measurements of powdered

**Table 1**  
Analytical data of azorhodanine derivatives (HL<sub>n</sub>).

Ligands <sup>a</sup>	Formula/color	Exp. (Calcd.)%		
		C	H	N
HL <sub>1</sub>	C <sub>17</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> S <sub>2</sub> Orange	54.67 (54.69)	4.05 (4.02)	11.25 (11.26)
HL <sub>2</sub>	C <sub>17</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> S <sub>2</sub> Brown	57.12 (57.14)	4.23 (4.20)	11.76 (11.77)
HL <sub>3</sub>	C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> S <sub>2</sub> Dark yellow	55.96 (55.98)	3.81 (3.79)	12.24 (12.24)
HL <sub>4</sub>	C <sub>16</sub> H <sub>12</sub> N <sub>3</sub> O <sub>2</sub> S <sub>2</sub> Cl Brown	50.86 (50.86)	3.20 (3.18)	11.12 (11.13)
HL <sub>5</sub>	C <sub>16</sub> H <sub>12</sub> N <sub>4</sub> O <sub>4</sub> S <sub>2</sub> Brown	49.77 (49.49)	3.12 (3.09)	14.43 (14.43)

<sup>a</sup> HL<sub>1</sub>–HL<sub>5</sub>, air stable, colored, insoluble in water, but soluble in hot ethanol and soluble in coordinating solvent.

samples were recorded at room temperature (Tanta University, Egypt) using an X-band spectrometer utilizing a 100 kHz magnetic field modulation with diphenylpicrylhydrazyl (DPPH) as a reference material. The conductance measurement was achieved using Sargent Welch scientific Co., Skokie, IL, USA.

### 3. Results and discussion

The structure of the ligand was elucidated by elemental analyses, IR, electronic and <sup>1</sup>H NMR spectra. The results of the elemental analysis (Table 1) are in good agreement with the proposed formula. The HL<sub>n</sub> ligand was allowed to react with Cu(II) ion in the molar ratio 1:2 (M:L). Also, the ligand was allowed to react with these metal ion in the presence of secondary ligand (Py) in the molar ratio 1:2:2 (M:L:Py). The obtained complexes were characterized by elemental analyses, IR, electronic, ESR spectra as well as conductivity and magnetic measurements.

#### 3.1. Stoichiometries of the novel copper(II) complexes

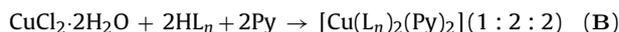
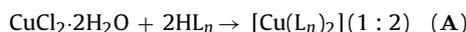
The stoichiometries of the complexes have been deduced from their elemental analysis (Table 2), which indicates that the metal complexes fall into two distinct categories, namely 1:2 (monomeric) (metal:ligand) (A) and 1:2:2 (adduct) (metal:ligand:ligand) (B). HL<sub>n</sub> is mononucleating and hence requires one metal ion for coordination. All the products were partially soluble in common organic solvents. Microanalytical data are in good agreement with stoichiometry proposed for complexes (Table 2).

The elemental analysis correspond to the general formula [Cu(L<sub>n</sub>)<sub>2</sub>](A), and [Cu(L<sub>n</sub>)<sub>2</sub>(Py)<sub>2</sub>](B) for all complexes. The principal ligand HL<sub>n</sub> undergoes mono deprotonation to form L<sub>n</sub> in Cu(II) complexes and acts as a bidentate ligand thus occupying two

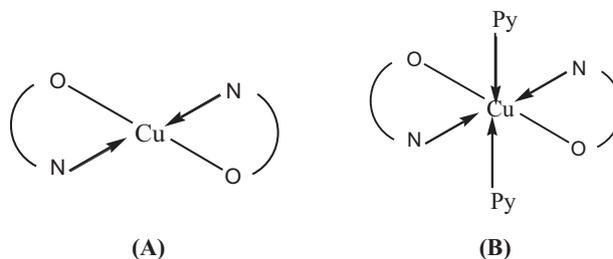
positions of an geometrical structure. In all complexes, ligand/mixture ligand acts as a bidentate/monobasic chelating agent.

The formation of the complexes may be represented by the following reactions.

CuCl<sub>2</sub>·2H<sub>2</sub>O reacts with the HL<sub>n</sub> (n = 1–5) in 1:2 in methanol and 1:2:2 in n-hexane (mole ratios), giving partially soluble products.



where L<sub>n</sub> represents the anion of the corresponding monofunctional bidentate HL<sub>n</sub>, Py = pyridine.



Structures of [Cu(L<sub>n</sub>)<sub>2</sub>](A) and [Cu(L<sub>n</sub>)<sub>2</sub>(Py)<sub>2</sub>](B) products obtained from the reaction of 1:2 and 1:2:2 molar ratios, respectively.

Structures of [Cu(L<sub>n</sub>)<sub>2</sub>](A) and [Cu(L<sub>n</sub>)<sub>2</sub>(Py)<sub>2</sub>](B) products obtained from the reaction of 1:2 and 1:2:2 molar ratios, respectively.

#### 3.2. Molar conductance of the complexes

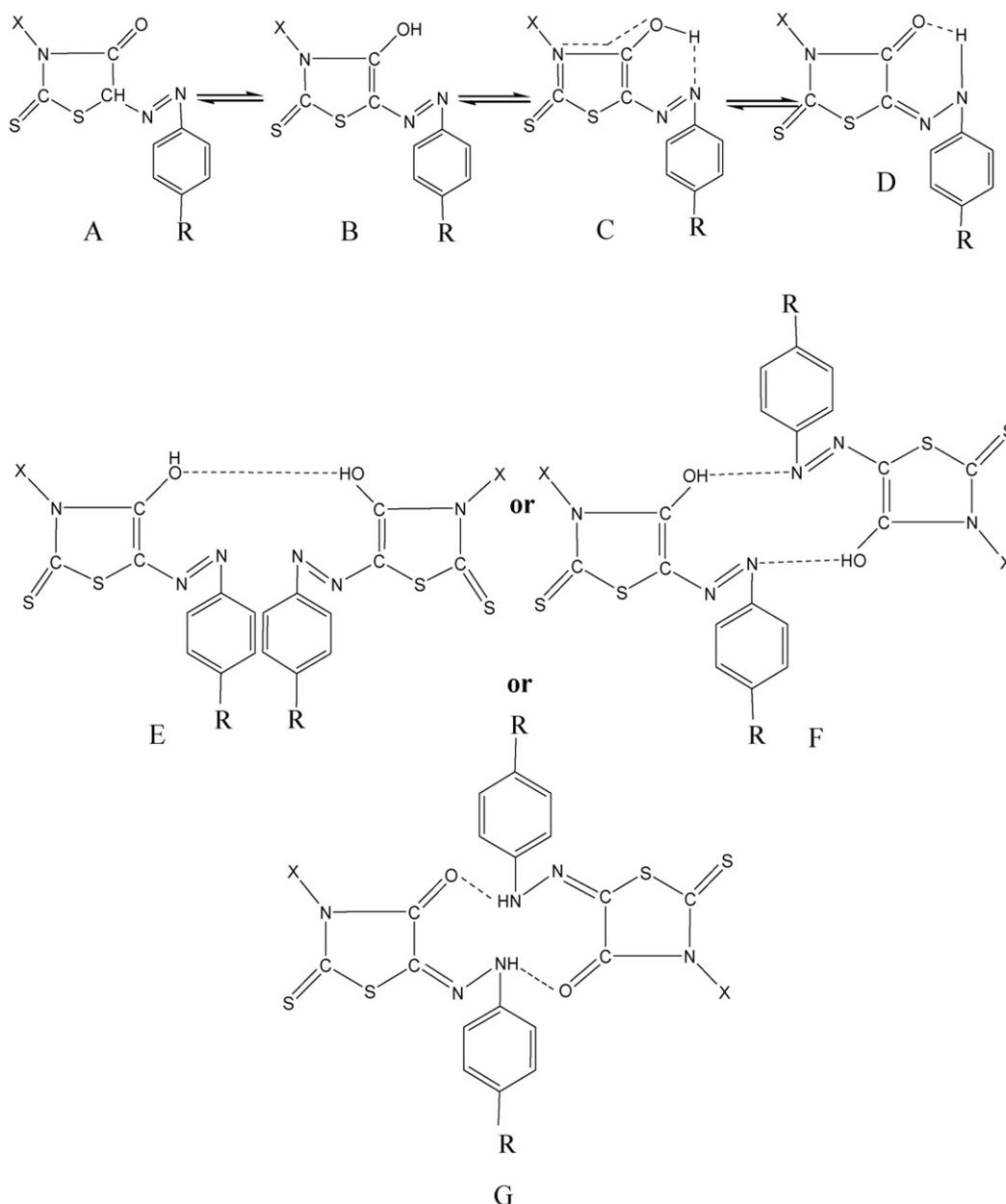
The molar conductance of 10<sup>-3</sup> M of solutions of the complexes in DMSO is measured at 25 ± 2 °C. It is concluded from the results

**Table 2**  
Analytical data of Cu(II) complexes.<sup>a</sup>

Complexes <sup>b</sup>	Mol. ratio	Exp. (Calcd.)%			
		C	H	N	Metal
[Cu(L <sub>1</sub> ) <sub>2</sub> ](1)	1:2	50.50 (50.40)	3.66 (3.71)	10.65 (10.38)	8.05 (7.85)
[Cu(L <sub>2</sub> ) <sub>2</sub> ](2)	1:2	51.35 (51.29)	3.88 (3.77)	10.48 (10.56)	8.30 (7.99)
[Cu(L <sub>3</sub> ) <sub>2</sub> ](3)	1:2	51.34 (51.23)	3.54 (3.47)	11.53 (11.21)	8.84 (8.48)
[Cu(L <sub>4</sub> ) <sub>2</sub> ](4)	1:2	46.88 (46.91)	3.05 (2.93)	10.48 (10.26)	7.99 (7.76)
[Cu(L <sub>5</sub> ) <sub>2</sub> ](5)	1:2	45.87 (45.74)	2.95 (2.86)	13.67 (13.34)	7.89 (7.57)
[Cu(L <sub>1</sub> ) <sub>2</sub> (Py) <sub>2</sub> ](6)	1:2:2	54.74 (54.57)	4.23 (4.13)	11.88 (11.58)	6.97 (6.57)
[Cu(L <sub>2</sub> ) <sub>2</sub> (Py) <sub>2</sub> ](7)	1:2:2	56.54 (56.44)	4.32 (4.28)	11.67 (11.97)	6.98 (6.79)
[Cu(L <sub>3</sub> ) <sub>2</sub> (Py) <sub>2</sub> ](8)	1:2:2	55.65 (55.53)	4.10 (3.97)	12.66 (12.34)	7.43 (7.00)
[Cu(L <sub>4</sub> ) <sub>2</sub> (Py) <sub>2</sub> ](9)	1:2:2	51.54 (51.61)	3.53 (3.48)	11.75 (11.47)	6.79 (6.51)
[Cu(L <sub>5</sub> ) <sub>2</sub> (Py) <sub>2</sub> ](10)	1:2:2	53.79 (53.99)	3.71 (3.64)	14.78 (15.00)	6.54 (6.81)

<sup>a</sup> Microanalytical data as well as metal estimations are in good agreement with the stoichiometries of the proposed complexes, air stable, non-hydroscopic, high melting temperature and colored.

<sup>b</sup> L<sub>1</sub>–L<sub>5</sub> are the anions of the ligands HL<sub>1</sub>–HL<sub>5</sub>.



n=1	R = OCH <sub>3</sub>	
n=2	R = CH <sub>3</sub>	
n=3	R = H	
n=4	R = Cl	
n=5	R = NO <sub>2</sub>	X = <i>p</i> -OCH <sub>3</sub> Ph

**Fig. 1.** General formula and proton numbering of the 5-(4'-derivatives phenylazo)-3-(4-methoxy phenyl)-2-thioxothiazolidinone (HL<sub>n</sub>).

that Cu(II) chelates with HL<sub>n</sub> ligands under investigation were found to have molar conductance values in the range from 1.25 to 8.56 Ω<sup>-1</sup> mol<sup>-1</sup> cm<sup>2</sup> indicating their non-electrolytic nature [21].

### 3.3. Infrared spectra and nature of coordination

The infrared spectra of HL<sub>n</sub> (Table 3) give interesting results and conclusions. The ligands exhibit two bands at ~3400–3200 cm<sup>-1</sup> due to asymmetric and symmetric stretching vibrations of N–H group and intramolecular hydrogen bonding NH⋯O systems (Fig. 1D), respectively. When the OH group is involved in intramolecular hydrogen bond (Fig. 1C), the OH⋯N and N⋯O bond

distances are the same. However, if such a mechanism is taking place in case of intermolecular hydrogen bond, the OH⋯O and OH⋯N bond distances differ (Fig. 1E and F, respectively).

The broad absorption of a band located at ~3400 cm<sup>-1</sup> is assigned to νOH. The low frequency bands indicate that the hydroxyl hydrogen atom is involved in keto ↔ enol (1A ↔ 1B, in Fig. 1) tautomerism through hydrogen bonding.

On the other hand, the OH group (Fig. 1B) exhibits more than one absorption band. The two bands located at 1330 and 1370 cm<sup>-1</sup> are assigned to in-plane deformation and that at 1130 cm<sup>-1</sup> is due to νC–OH. This observation has been seen previously [22–24], where the different modes of vibrations of C–H and C–C band are identified

**Table 3**  
Important IR bands and their assignments for 5-(4'-derivatives phenylazo)-3-(4-methoxyphenyl)-2-thioxothiazolidinone (HL<sub>n</sub>) and their Cu(II) complexes.

Compound <sup>a</sup>	$\nu(\text{N}=\text{N})$	$\delta\text{OH}, \nu\text{C}-\text{OH}, \gamma\text{OH}$	$\nu\text{C}-\text{O}$	M-O	M-N	M-Npy	$\nu\text{Py}$
HL <sub>1</sub>	1545	1290, 1205, 818	1240	–	–	–	
HL <sub>2</sub>	1549	1292, 1202, 819	1244	–	–	–	
HL <sub>3</sub>	1552	1294, 1205, 820	1246	–	–	–	
HL <sub>4</sub>	1557	1296, 1207, 823	1249	–	–	–	
HL <sub>5</sub>	1562	1297, 1209, 825	1255	–	–	–	
1	1525	–	1248	440	450	–	
2	1529	–	1254	442	455	–	
3	1532	–	1257	443	460	–	
4	1536	–	1260	445	470	–	
5	1541	–	1266	446	479	–	
6	1526	–	1250	441	480	275	1572, 625, 500
7	1530	–	1256	440	485	281	1580, 633, 509
8	1534	–	1261	444	495	276	1585, 640, 515
9	1536	–	1262	446	505	280	1593, 646, 618
10	1543	–	1270	445	518	285	1604, 652, 622

<sup>a</sup> Numbers as given in Table 2.

by the presence of characteristic bands in the low frequency side of the spectrum in 600–200 cm<sup>-1</sup>.

The ligands show also a medium broad band located at ~3460 cm<sup>-1</sup> due the stretching vibration of some sort of hydrogen bonding. El-Sonbati et al. [25,26] have reported detailed studies for the different types of hydrogen bonding which are favorable to exist in the investigated molecules. These hydrogen bonding types are:

1. Intramolecular hydrogen bond between the nitrogen atom of the –N=N– system and hydrogen atom of the hydroxyl hydrogen atom (Fig. 1C). This is evident by the presence of a broad band centered at 3460 cm<sup>-1</sup>.
2. Hydrogen bonding of the OH...N type between the hydroxyl hydrogen atom and the N-Ph group (Fig. 1C).
3. Intermolecular hydrogen bonding is possible to form a cyclic dimer through OH...OH (E) or OH...N=N (F) or NH...O=C (G) (Fig. 1).

In general, hydrogen bonding involving both NH and OH groups are proton donors and both –N and –O atoms are proton acceptors. It is of interest since such multiplicity of proton donor and acceptor sites are prevalent in biological systems. Both intra and intermolecular OH–N and NH–O may form a number of structures in simultaneous equilibrium.

Again; the three bands of  $\delta\text{OH}$  at 1380, 1340 and 1310 cm<sup>-1</sup> and the two bands of  $\nu\text{C}-\text{O}$  at ~1240 cm<sup>-1</sup> are together strong indications to keto  $\leftrightarrow$  enol equilibria.

By comparing the infrared spectra of the free ligands to that of the prepared complexes the following points are observed.

1. In the IR spectra of all ligands the band at ~1545 cm<sup>-1</sup> due to the  $\nu(\text{N}=\text{N})$  mode is observed. In the metal chelates, this frequency is lowered by 10–25 cm<sup>-1</sup> indicating the bonding of the azo nitrogen to the copper atom. The  $\nu(\text{C}-\text{N})$  vibration appearing at ~1480 cm<sup>-1</sup> in the ligands suffers a downward shift of ~10 cm<sup>-1</sup>, thereby supporting the assumption that the copper ion is coordinated to one of the azo nitrogen atoms.
2. The absence of any peak attributed to the C–OH moiety, in the 3440 and 3180 cm<sup>-1</sup> region, implies that the ligands exist predominantly in solution as the form shown in Fig. 1A. However, in solution and in the presence of copper ion these compounds exist in a tautomeric equilibrium 1B  $\leftrightarrow$  1C. The main change is observed in the carbonyl stretching vibration, thus suggesting that the form shown in Fig. 1C is prevailed. This tautomeric form losses enolic proton when complexed with copper ion as mononegative chelating agents produces the CO/OH mode of the

free ligands. New bands assigned to  $\nu(\text{OH})$  in the free ligands is absent, suggesting the cleavage of intramolecular hydrogen bonding of  $\nu\text{OH}$  group and coordination of oxygen to the metal ion. The positive shift of  $\nu(\text{C}-\text{O})$  by 5–15 cm<sup>-1</sup> in all the complexes further confirms the complexation through the oxygen [27–29]. IR spectra of the Cu(II) complexes indicate the coordination *via* deprotonation.

3. The bands of  $\delta\text{OH}$  at 1295 cm<sup>-1</sup>,  $\nu\text{C}-\text{OH}$  at 1210 and  $\gamma\text{OH}$  at 823 cm<sup>-1</sup> display sharp decreases in their intensities to such an extent that they nearly vanish. This can be taken as an indication for the complete removal of OH group by the Cu(II) ion reacting with the ligands. Since the ligand reacts with Cu(II) ion, as gathered from the results of elemental analysis, the Cu(II) ion therefore, would displace only one proton from the OH group contained in the ligands molecule. The possible structure of the Cu(II) complexes could be suggested based on: (i) the absence of one anion, (ii) the disappearance of C=O, (iii) the coordination of azo group. Under such conditions, the ligand is of bidentate nature with respect to the evidence above.
4. The bands observed in the region 450–520 cm<sup>-1</sup> has been assigned to the  $\nu(\text{Cu}-\text{N})$  vibrations on the foot note of the earlier observations [30]. Two bands due to  $\nu(\text{Cu}-\text{N})$  in these complexes suggest that the ligands occupy *trans* position. The medium intensity bands around 440  $\pm$  5 cm<sup>-1</sup> in the complexes are attributed to the  $\nu(\text{Cu}-\text{O})$  vibration.
5. All complexes exhibit  $\nu(\text{C}=\text{C})$  in the 1595–1610 cm<sup>-1</sup> region; while the phenyl ring vibration appears at 1480–1510 cm<sup>-1</sup>. The presence of a *p*-substituted benzene ring in the ligands as well as in the complexes is indicated by strong and sharp bands around 630–650 cm<sup>-1</sup>. The defined band at ~2960 cm<sup>-1</sup> in the complexes is assigned to  $\nu(\text{C}-\text{H})$  vibration of the aromatic system.
6. The observation of new bands which do not appear in the parent complexes (1–5) in the 1575–1608 and 275–285 cm<sup>-1</sup> regions are assigned to  $\nu(\text{C}=\text{N})$  (Py ring) and  $\nu(\text{M}-\text{N})$  (Py ring) vibration modes, indicating the presence of pyridine in complexes (6–10).

The HL<sub>n</sub> ligand takes its usual anionic (L<sub>n</sub>) to chelate Cu(II) through N– of azo group and oxygen atom of enol group as potential binding sites. The observed shifts in the vibrational modes of C–C, C=C, C–N and C–H after complexation indicate that the aromaticity of the complex differ from one complex to another.

### 3.4. <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectroscopy was used to differentiate stereoisomers. El-Sonbati and coworkers [22–26] investigated the <sup>1</sup>H NMR spectra of azo rhodanine and its derivatives with various transition

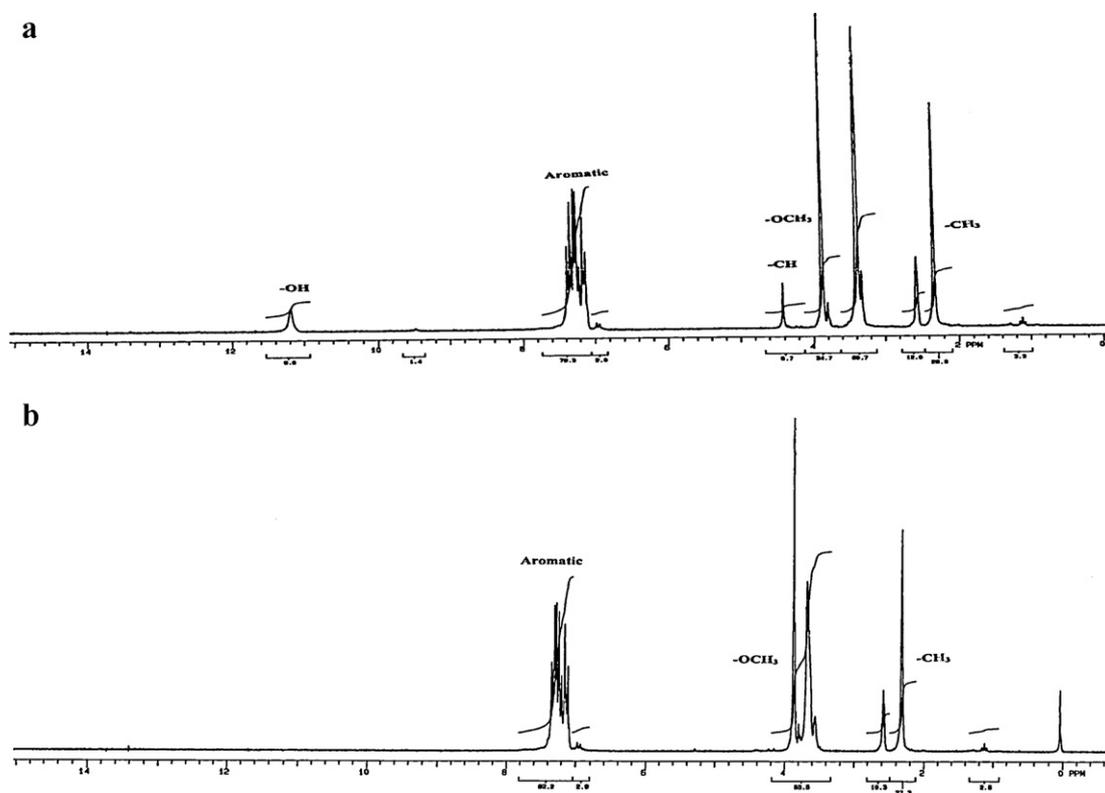


Fig. 2.  $^1\text{H}$  NMR chemical shift (DMSO- $d_6$ ) (ppm vs. TMS); (a)  $\text{HL}_2$ ; (b)  $\text{HL}_2$  with  $\text{D}_2\text{O}$ .

metal salts. The  $^1\text{H}$  NMR spectra of  $\text{HL}_2$  shown in Fig. 2 are in agreement with the proposed structures. Fig. 2a exhibits signal for CH ( $\sim 4.42$  ppm), favoring formation of an intramolecular hydrogen bond with the N=N (azodye) group. Electron-withdrawing substituents reduce the intramolecular hydrogen bond as indicated by the marked shift of the hydroxyl signal to higher field in the *p*- $\text{NO}_2$  and *p*-Cl compounds. Electron-donating substituents give the opposite effect, arising from the increasing basicity of the azo-nitrogen. The broad signals assigned to the OH protons at  $\sim 11.2$ – $11.68$  ppm are not affected by dilution. The previous two protons disappear in the presence of  $\text{D}_2\text{O}$  as seen in Fig. 2b. According to El-Sonbati and coworkers [22–26], hydrogen bonding leads to a large deshielding of the protons. The shifts are in the sequence: *p*- $\text{NO}_2 > p\text{-Cl} > \text{H} > p\text{-OCH}_3 > p\text{-CH}_3$ . In the meantime, the  $^1\text{H}$  NMR of the  $\text{HL}_2$  exhibits signals at  $\delta$  (ppm) 3.9 (s, 3H,  $\text{OCH}_3$ ) and 2.3 (s, 3H,  $\text{CH}_3$ ). The aromatic protons have resonance at 7.10–7.45 ppm for the ligands

### 3.5. Spectral studies of copper(II) complexes

$\text{HL}_n$  exhibits bands at  $26,360$ – $26,180\text{ cm}^{-1}$  (CS) ( $n \rightarrow \pi^*$ ),  $30,560$ – $30,260\text{ cm}^{-1}$  (CO) ( $n \rightarrow \pi^*$ ),  $32,980$ – $33,150\text{ cm}^{-1}$  (H-bonding and association),  $40,250$ – $39,900\text{ cm}^{-1}$  (phenyl) (Ph-Ph\*), ( $\pi\text{-}\pi^*$ ) [31] and  $29,620$ – $29,355\text{ cm}^{-1}$  transition of phenyl rings overlapped by composite broad  $\pi\text{-}\pi^*$  of azo structure. In the complexes, the ( $n \rightarrow \pi^*$ ) transition shifts to lower energy at  $28,670\text{ cm}^{-1}$  and the band due to the H-bonding and association is absent as expected. The (CO) ( $n \rightarrow \pi^*$ ) transition disappears with the simultaneous appearance of new bands, being attributed to  $\pi \rightarrow \pi^*$  (C=C) as a sequences of enolization. The band due to  $\pi \rightarrow \pi^*$  transition moves to lower energy. These shifts or disappearance of the bands are indicative of coordinating of the ligands to metal.

The spectra of complexes (1–5) show two absorption bands in the region  $14,150$ – $15,700\text{ cm}^{-1}$  and  $20,150$ – $22,500\text{ cm}^{-1}$

assignable to the transition  ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$  and  ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ , respectively, indicating the possibility of a square planar complexes [32,33]. The observed trend in the low energy d–d band maximum shifts to a larger wavelength with increasing of donating group. Thus, the observed red shifts in d–d band is affected both by the steric effect group in *p*-positions in aniline moieties.

In general, most of the azo compounds give spectral localized bands in the wavelength range  $46,620$ – $34,480$  and  $31,250$ – $270,370\text{ cm}^{-1}$ . The first region is due to the absorption of the aromatic ring compared to  ${}^1\text{B}_b$  and  ${}^1\text{L}_b$  of mono substituted benzene, while the second is due to the conjugation between the azo group and the aromatic nuclei, with intermolecular charge transfer resulting from  $\pi$ -electron migration to the diazo group from electron donating substituents. The *p*-substituents increase the conjugation with a shift to a longer wavelength as a result of the Hamett's constant effect [1,24]. The position of the  $\pi\text{-}\pi^*$  transition of the azo groups remains as one of the most interesting, yet unresolved questions of molecular spectroscopy. For azobenzenes, as the possibilities of the mesomerism became greater, the stabilization of the excited state is increased relative to that of the ground state and a bathochromic shift of the absorption bands follows [24]. Based on MO theory [34] the energy terms of the molecular orbital became more closely spaced as the size of the conjugated system increases. Therefore, with every additional conjugated double bond the energy difference between the highest occupied and the lowest vacant  $\pi$ -electron level became smaller and the wavelength of the first absorption band corresponds to this transition is increased. The azo group can act as a proton acceptor in hydrogen bonds [24] and the role of hydrogen bonding in azo aggregation has been reported and acknowledge for some time [35].

### 3.6. Magnetic moment of copper(II) complexes

The room temperature magnetic moments of  $[\text{Cu}(\text{L}_n)_2]$  fail in the range  $1.81$ – $1.92$  B.M. which are typical for square planar ( $\text{D}_{4h}$ ) and

**Table 4**  
ESR spectral assignments of copper(II) complexes.

Compound <sup>a</sup>	$g_{\parallel}$	$g_{\perp}$	$ g $	$G$	$\alpha^2$	$A_{\parallel} \times 10^{-4}$	$\beta^2$	$f^b$
1	2.224	2.035	2.096	>4	0.80	170	0.65	131
2	2.235	2.042	2.106	>4	0.81	158	0.67	141
3	2.244	2.044	2.187	>4	0.86	201	0.66	111
4	2.250	2.060	2.123	>4	0.55	87	0.73	115
5	2.270	2.060	2.130	>4	0.60	95	0.78	105

<sup>a</sup> Numbers as given in Table 2.

<sup>b</sup> For square planar structure,  $f$  ratio has typical values 100–135  $\text{cm}^{-1}$  and greater ones for dominant pseudotetrahedral symmetry.

tetrahedrally distorted ( $D_{2h}$ ) mononuclear copper(II) complexes and did not indicate any antiferromagnetic at this temperature. The relatively higher 1.91 B.M. value observed for  $[\text{Cu}(\text{L}_2)_2]$ , seem to suggest the relatively high tetrahedral distortion from square planar geometry for these complexes than others in polycrystalline state. On the other hand,  $\mu_{\text{eff}}$  data for  $[\text{Cu}(\text{L}_1)_2]$  and  $[\text{Cu}(\text{L}_{3-5})_2]$  fall in the 1.81–1.89 B.M. range and are well consistent with a square planar geometry ( $D_{4h}$ ) around the copper centers. The  $\mu_{\text{eff}}$  values of the mononuclear Cu(II) complexes are normal within the range reported for one unpaired electron in a square planar or tetrahedral geometry. However, it is impossible to differentiate between these two geometries on the basis of electronic spectra. Hence, may be distinguished on the basis of ESR spectra.

### 3.7. ESR spectra of copper(II) complexes

To obtain further information about the stereochemistry and the site of the metal ligand bonding and to determine the magnetic interaction in the metal complexes. ESR spectra of the complexes were recorded in the solid state. The spin Hamiltonian parameters of the complexes were calculated and summarized in Table 4. The analysis of spectra of all copper(II) complexes gives agree well with the values reported for distorted square planar geometry around Cu(II) ion [36,37]. The spectra shows the relation  $g_{\parallel} > g_{\perp} > g_e$  which is typical of axially symmetric  $d^9$  Cu(II) having one unpaired electron in  $d_{x^2-y^2}$  orbital [38]. The absence of signal corresponding to ( $\Delta M_s = \pm 2$ ) in the half field indicates the absence of any Cu–Cu interaction thus ruling out possibility of dimeric structure. In axial symmetry, the  $G$ -parameter defined as  $G = g_{\parallel} - 2/g_{\perp} - 2$ , reflects the spin interaction between Cu(II) center in complexes. In the present work,  $G$  value comes out to be 4.0 which again indicates absence of Cu–Cu interaction, thus supporting proposed monomeric structure. Kivelson and Neiman have reported that  $g_{\parallel}$  values less than 2.3 indicates considerable covalent character of M–L bond and greater than 2.3 indicates ionic character. The present value comes out to less than 2.3 which indicate considerable covalent character of Cu–L bond [39].

As a measure of the covalency of the in-plane  $\sigma$ -bonding,  $\alpha^2$  indicates complete ionic character, whereas  $\alpha^2 = 0.5$  denotes 100% covalent bonding, with the assumption of negligible small values of the overlap integral [39]. The  $\beta^2$ , the larger the covalency of the bonding. From this analysis, the in-plane bonds of the complexes correspondent to signals 1, 2, 3, 4 and 5 are largely covalent, with the covalent character increasing from 2 to 3 to 1 to 4 to 5. The values of  $\alpha^2$  indicate that approximately 80% of the spin population is in the copper  $d_{x^2-y^2}$  orbital of most of the Cu(II) species concerned. The  $g$  values obtained from ESR spectra indicate, as has been pointed out by Kivelson and Neiman [39] and by Faber and Rogers [40], that covalent bonding reduces the magnitude of the  $g$  factor.

The data given in Table 4 indicate that  $A_{\parallel} \times 10^{-4} \text{ cm}^{-1}$  shifts to higher with  $g_{\parallel}$  (Fig. 3);  $|g|$  (Fig. 4) and  $\alpha^2$  with  $|g|$  (Fig. 5) give straight line relationship for each chromophore from electron-withdrawing to electron-donating substituents

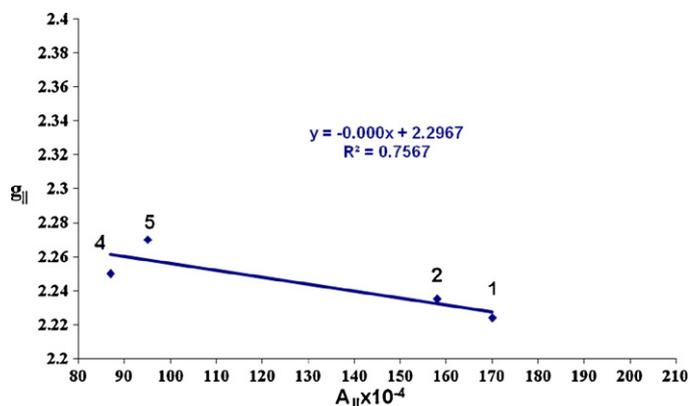


Fig. 3. The relation between  $g_{\parallel}$  and  $A_{\parallel} \times 10^{-4} \text{ cm}^{-1}$ .

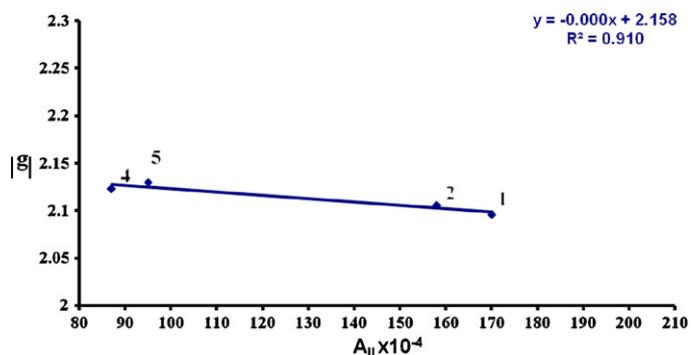


Fig. 4. The relation between  $|g|$  and  $A_{\parallel} \times 10^{-4} \text{ cm}^{-1}$ .

The ESR parameters obtained from a complex are very close to our values for one system. By analogy with  $[\text{Cu}(\text{L}_n)_2]$  complexes, which present *trans* molecules. All the ESR parameters are given in Table 4.  $g_{\parallel}$  and  $|A_{\parallel}|$  values indicate a square planar coordination geometry for the  $\text{CuN}_2\text{O}_2$  moiety. All the spectra are almost super-imposable. Whatever the electron-withdrawing or donor power and the ortho, meta or para-position of the substituent on the aromatic ring, the consonant variation observed in  $g_{\parallel}$  value is only of the same magnitude as the experimental error. In fact, the ESR parameters which relate to electron density in  $\text{CuN}_2\text{O}_2$  plan are relatively insensitive to the substitution in these ligand aryl groups. Moreover the empirical factor  $f$  is an indication of the stereochemistry of the copper(II) complexes. Addition has suggested that this ratio may be an empirical indication of the tetrahedral distortion of a square planar geometry [41]. The lowest values of the empirical factor for the *trans* species are indicative of a planar *trans* arrangement whereas the slightly higher values of the empirical factor for the *cis* compounds indicate only a nearly planar *cis* arrangement.

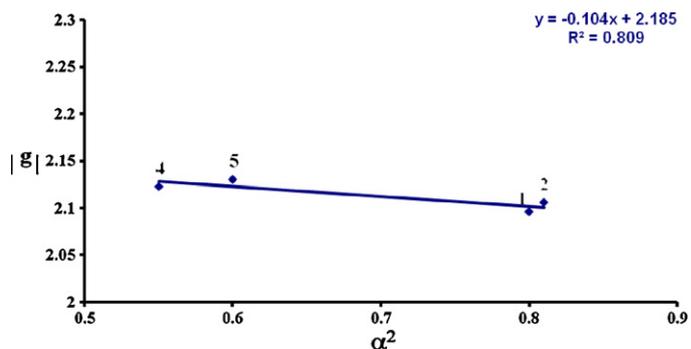


Fig. 5. The relation between  $|g|$  and  $\alpha^2$ .

**Table 5**  
Electronic spectral data (cm<sup>-1</sup>) of adducts copper(II) complexes.

Compound <sup>a</sup>	d–d	π–π*	L→M
<b>6</b>	11,470	31,750	23,200
<b>7</b>	11,525	31,950	22,737
<b>8</b>	11,935	31,650	22,830
<b>9</b>	12,815	33,220	28,830
<b>10</b>	12,280	31,950	22,730

<sup>a</sup> Numbers as given in Table 2.

Also, for square planar structure, empirical factor has typical values 105–135 cm<sup>-1</sup> and greater ones for dominant pseudotetrahedral symmetry. It is noteworthy that the substitution of the aryl group by a generates a small distortion around the metallic ion.

### 3.8. Electronic spectra and magnetic moment of adduct copper(II) complexes

The electronic spectra of the complexes are presented in Table 5. The electronic spectra of Cu(II) adduct complexes (**6–10**) differ considerably from that of Cu(II) complexes (**1–5**). In the case of hexa-coordinated copper(II) complexes with moderate Jahn–Teller distortion the lowest energy transition  $d_{z^2} \rightarrow d_{x^2-y^2}$  ( ${}^2B_{1g} \rightarrow {}^2B_{2g}$ ) occur in the 13,425–11,150 cm<sup>-1</sup> region [42,43]. The bands present in the higher wavelength region commensurate that these complexes have distorted octahedral structure (while the present complexes have square planar structure). A shoulder which appears near 22,830 cm<sup>-1</sup> (Table 5) is attributed to the π–Cu(II) LMCT transition [44]. The high intensity bands observed in the lower wavelength region (32,050–28,980 cm<sup>-1</sup>) are due to π–π\* transitions of ligand-to-metal charge-transfer transitions. The charge transfer may be from p orbital of coordinated oxygen/or nitrogen to the vacant d orbitals of copper(II) [45]. The room temperature magnetic moments are in the range 1.93–2.20 B.M. These magnetic moment values indicate the presence of one unpaired electron, as expected for copper(II) complexes.

### 3.9. ESR spectral of adduct Cu(II) complexes

The ESR spectra of compounds (**6–10**). The spin Hamiltonian, orbital reduction and bonding parameters of these complexes are given in Table 6. The observed  $g_{\parallel}$  values for all complexes are less than 2.3 commensurate a significant covalent character of the metal–ligand bond in agreement with the observation of Kivelson and Neiman [39]. The trend  $g_{\parallel} > g_{\perp} > g_e$  (2.0023) for these complexes suggests that the unpaired electron is localized in the  $d_{x^2-y^2}$  orbital [6] of the copper(II) ion. The  $g$  values reflect that the Cu(II) center has a tetragonal distorted octahedral geometry with  $d_{x^2-y^2}$  orbital as a ground state [46]. The  $g_{\parallel}$  values is an important function for indicating covalent character of M–L; for ionic character,  $g_{\parallel} > 2.3$  and for covalent character  $g_{\parallel} < 2.3$ . In the present complex, the  $g_{\parallel}$  is less than 2.3 indicating appreciable covalent character for the Cu–L bond. In addition, the  $g$  values are related to the  $G$ -factor by the expression,  $G = (g_{\parallel} - 2)/(g_{\perp} - 2) = 4$ , which measures

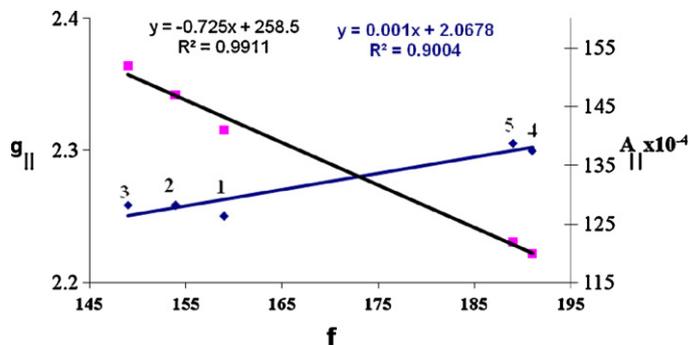
**Table 6**  
Spin Hamiltonian and orbital reduction parameters of adduct copper(II) complexes.

Complex <sup>a</sup>	$g_{\parallel}$	$g_{\perp}$	$g_{av}$	$G^b$	$\alpha^2$	$A_{\parallel}^c$	$A_{\perp}^c$	$A_{av}^c$	$K_{\parallel}$	$K_{\perp}$	$K$	$f$
<b>6</b>	2.2503	2.0344	2.1063	7.73	0.97	141	93	53	0.656	0.472	0.354	159
<b>7</b>	2.2586	2.0225	2.1011	12.70	0.96	147	93	55	0.668	0.377	0.343	154
<b>8</b>	2.2587	2.0344	2.1090	7.99		152			0.739	0.473		149
<b>9</b>	2.2997	2.0464	2.1320	6.75	0.98	120	93	46	0.542	0.318	0.368	191
<b>10</b>	2.3056	2.0494	2.1347	6.44		122			0.74	0.58		189

<sup>a</sup> Numbers as given in Table 2.

<sup>b</sup> The higher  $G$  values for pyridine adducts as compared to parent complexes indicate that there is a large separation between the copper center in adducts.

<sup>c</sup> Units in cm<sup>-1</sup>.



**Fig. 6.** The relation between  $g_{\parallel}$ ,  $A_{\parallel} \times 10^{-4}$  and  $f$ .

the exchange interaction between copper centers in the solid. According to Hathaway [47], if the value of  $G$  is greater than 4, the exchange interaction between copper(II) centers in the solid state is negligible, whereas when it is less than 4, a considerable exchange interaction exists in the solid complex. The calculated  $G$  value for these complexes indicates that there are no interactions between the copper centers (see Table 6). The value of in-plane sigma bonding parameter  $\alpha^2$  which is usually taken as a measure of covalency was estimated for each species, from the expression,

$$\alpha^2 = A_{\parallel}/0.035 + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$$

The parameters  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}$  and  $A_{\perp}$  of complexes and the energies of the d–d transitions are used to calculate the orbital reduction parameters ( $K_{\parallel}$ ,  $K_{\perp}$ ), the bonding parameter ( $\alpha^2$ ), the dipolar interaction term ( $p$ ) and the Fermi contact interaction term ( $K$ ).

The  $\alpha^2$  values for the complexes 1, 2 and 4 support the covalent nature [48] of their bonding. Hathaway [49] pointed out that of pure  $\sigma$ -bonding,  $K_{\parallel} \approx K_{\perp} \approx 0.77$  and for in-plane  $\pi$ -bonding  $K_{\parallel} < K_{\perp}$ , while for out-of-plane  $\pi$ -bonding  $K_{\perp} < K_{\parallel}$  the following simplified expressions were used to calculate  $K_{\parallel}$  and  $K_{\perp}$ :

$$K_{\parallel}^2 = \left[ \frac{(g_{\parallel} - 2.0023)}{8\lambda_0} \right] \times \text{d-d transition}$$

$$K_{\perp}^2 = \left[ \frac{(g_{\perp} - 2.0023)}{2\lambda_0} \right] \times \text{d-d transition}$$

The observed  $K_{\parallel} > K_{\perp}$  relation indicates the absence of significant in-plane  $\pi$ -bonding. Giordano and Bereman [50] suggest the identification of bonding groups from the values of dipolar term  $p$ . The reduction of  $p$  values (0.0194–0.0227) from the free ion value (0.036 cm<sup>-1</sup>) might be attributed to the presence of covalent bonding.

The plot of  $g_{\parallel}$  and  $A_{\parallel} \times 10^{-4}$  cm<sup>-1</sup> versus of  $f$  gives straight line with increase the value of  $f$  decrease  $g_{\parallel}$  and increase the  $A_{\parallel} \times 10^{-4}$  cm<sup>-1</sup>, Fig. 6. This can be explained. The electron withdrawing  $p$ -substituent increase the positive charge on the metal ion leading to an increase in  $f$  and  $A_{\parallel} \times 10^{-4}$  cm<sup>-1</sup> and subsequently a decrease in  $g_{\parallel}$ .

The above results show clearly that the effect electron density on the ESR parameter on the stereochemistry of Cu(II) polymer complexes. It is important to not that the existence of electron density enhances on the coordination sites and simultaneously increases the value of ESR parameters (Tables 4 and 6).

#### 4. Conclusion

This study has suggested that HL<sub>n</sub> behaves as a chelating bidentate monobasic ligand, bonding through C–O group and nitrogen atom of the azo group. The CS breathing mode of the ligand is observed. It remains unaltered in the complexes with absence of coordinations through the sulphur atom of the CS group. The IR data reveal that the anions are not binded to the metal ions and the metal ions do not occupy all the available sites in the metal chelate due to steric constraints.

The stoichiometric data of Cu(II)/adduct complexes and their physico-chemical investigations indicate that the probable coordination number of copper(II) in these complexes is four-coordinate.

Substituents effect on reactivities depend mainly on the rate controlling step and the nature of the transient specie, while Hamett's relationship studies the reactivity trends in ligands and complexes with the stability, i.e., the lower the stability the higher the reactivities. Based on Hamett's relationship, electron withdrawing substituents enhance the stabilities of these complexes owing to the decrease of electron density at the metal atoms and thus the increase of the positive charge on the metal. Therefore, this effect results in decreasing reactivity. In contrast, the electron donating substituents increase the electron density at the metal, hence leading to decrease the stability of the metal chelates.

The study indicates the possibilities of significant variations of the structure and, therefore, properties of metal chelate complexes caused by diverse structural modifications of the azo-containing ligands. Studied in this respect is dominated by problems arising from the influence of strong electron-withdrawing and electron-releasing substituents in the aryl rings of the aromatic and heterocyclic azo compounds, which is essential for defining basicity and ligating abilities of the nitrogen centers in the azo groups. It is expected that the investigation into these problems may be promoted by further extended studies of the series containing relevant azo ligands. This will lead to gain a deeper insight into the mechanism and preparative application of the azo coupling reactions under the phase transfer catalysis conditions.

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