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COMPLEXES OF 4-BENZOYL-3-METHYL-1-PHENYL-2-PYRAZOLIN-5-ONE
N(4)PHENYL THIOSEMICARBAZONE (HBATB4ph)

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RESEARCH ARTICLE

SYNTHESIS, SPECTROSCOPIC AND BIOLOGICAL STUDIES OF COPPER(II) COMPLEXES OF 4-BENZOYL-3-METHYL-1-PHENYL-2-PYRAZOLIN-5-ONE N(4)PHENYL THIOSEMICARBAZONE (HBATB4ph)Ayman K. El-Sawaf^{1,2*}¹College of Science and Humanity Studies, Prince Sattam bin Abdulaziz University, KSA²Chemistry Department, Faculty of Science, El-Minufiya University, El-Minufiya, Egypt

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ABSTRACT

A new thiosemicarbazone, 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N (4)-phenyl thiosemicarbazone (HBATB4ph), has been synthesized and characterized experimentally and theoretically. The complexing ability of this thiosemicarbazone towards copper (II) salts have been explored. The reactions of the hot ethanolic solutions of copper(II) salts with HBATB4ph led to the formation of the novel complexes compositions [Cu(HL)X₂] (X= Cl⁻ or Br⁻), [Cu(HL)(H₂O)₂](ClO₄)₂ and [Cu(L)(H₂O)X] (X=NO₃⁻, CH₃COO⁻ or SO₄⁻). The newly synthesized complexes have been characterized by elemental analyses, molar conductance, magnetic susceptibility, I.R., electronic and ESR spectral studies. Visible and ESR spectra indicate that the complexes are monomeric having square planar geometry. These complexes were screened for their antibacterial activities on different species of bacteria and their biopotency has been discussed.

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INTRODUCTION

Thiosemicarbazones are important nitrogen-sulfur donor ligands for transition metal ions because of their mixed soft – hard character and versatile coordination behavior [1, 2]. The donor atoms N and S of the chelated thiosemicarbazones exert two opposite electronic effects: the thiolate sulfur is a hard donor which stabilize the higher oxidation state of the metal atom whereas imine nitrogen is a soft donor and will stabilize the lower oxidation state of the metal [3].

Thiosemicarbazones and their metal complexes have aroused considerable interest in coordination chemistry not only because of their versatile ligating properties but also due to their broad range of biological activities [4-6] and the activity is enhanced by the functional groups of the parent aldehyde or ketone [7]. Thiosemicarbazones are of considerable interest because of their chemistry and potentially beneficial biological activities, such as antitumor, antibacterial, antiviral and antimalarial activities [8 – 11]. The biological activities of thiosemicarbazones are considered to be due to their ability to form chelates with metals. Biological activities of metal

complexes differ from those of either ligands or the metal ions, and increased and/or decreased biological activities are reported for several transition metal complexes, such as copper(II) and nickel(II) complexes [12,14].

We have previously reported the structural and spectral studies of several transition metal complexes of N(4)-substituted thiosemicarbazones with the aim to correlate the structural features and chelating ability to the antimicrobial properties [10 - 14]. This study discusses synthesis and characterization of Cu(II) complexes of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)phenyl thiosemicarbazone (HBATB4ph). Analytical, spectral, magnetic, electron spin resonance and molar conductivities were used to investigate the chemical structure of the ligand and its copper(II) complexes.

Experimental**Material**

All materials and solvents were obtained from commercial suppliers and used without further purification.

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2.2. Synthesis of the Schiff base ligand (HBATP4ph)

The 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)phenyl thiosemicarbazone, was prepared by refluxing equimolar amounts of a hot ethanolic solution of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one and phenylthiosemicarbazide for 4 hours. The formed precipitate was filtered off, washed with ethanol and dried over anhydrous CaCl_2 , m.p. = 164°C . The reaction step is illustrated in Scheme 1. ^1H NMR (300 MHz, DMSO) δ = 11.85 (s, 1H, H6), 10.12 (s, 1H, H7), 2.65 (s, 3H, H17), 2.95 (s, 1H, H15), 7.68 (m, 2H, H8, H12), 7.43 (m 2H, H9, H11), 7.72 (m, 2H, H26, H30). (mp = $218\text{--}220^\circ\text{C}$, yield = 84%). The structure of the ligand is given in Chart 1 and the formation is given in Scheme 1.

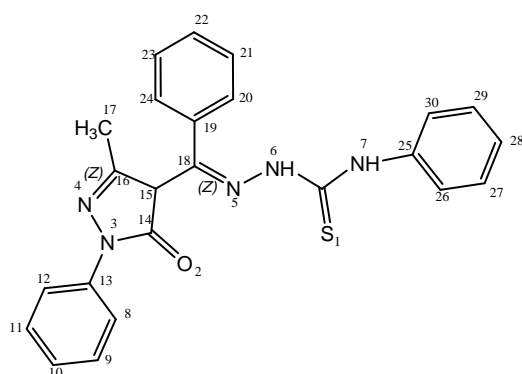
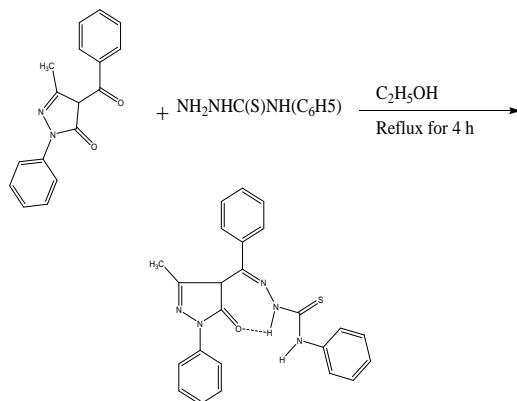


Chart 1 Numbering scheme for ligand HBATP4ph



Scheme 1 Schematic representation for the formation of the ligand HBATP4ph

Theoretical calculations

The optimization and frequency calculations of the stable conformers for HBATP4ph were performed using B3LYP, B3P86 and PBE0 hybrid functionals as implemented in Gaussian09 [15]. Three basis sets were used 6-31G (d), 6-31+G(d,p) and a larger basis 6-311+g(d,p) where polarized and diffusion functions were taken into consideration. The minima of ground states (GSs) were confirmed by the absence of imaginary frequencies. Excited energies were calculated at the same level of theory, *i.e.*, using the same hybrid functionals and basis sets. ^1H -NMR chemical shifts predictions were calculated within GIAO approach at the same level of theory [16]. The solvent effects were taken into account implicitly by using the polarizable continuum model formalism PCM [17].

Synthesis of the copper complexes

All the copper complexes were prepared by adding of the appropriate copper salts (0.01 mole in 25 mL in ethanol) to a hot solution of the ligand (HBATB4ph) (0.01 mole in 30 mL ethanol). The reaction mixture was magnetically stirring and refluxed for about 2 hours. The separated complex was filtered off, washed several times with ethanol, and finally dried under vacuum over anhydrous calcium chloride.

Antimicrobial studies

The antimicrobial activities of the copper(II) complexes and free ligand were tested against two gram positive bacteria [Staphylococcus aureus (ATTC 25923 and Bacillus subtilis (ATTC 6633)] and two gram negative bacteria [Escherichia coli (SPA 27) and Pseudomonas aeruginosa (ATTC 27583)] using the disc-agar diffusion method [18]. Stock cultures of the tested organisms are maintained on nutrient agar media by sub culturing in Petri dishes. The media are prepared by adding the components as per manufacturer's instructions and sterilized in the autoclave at 120°C and atmospheric pressure for 20 min. Each medium is cooled to 40°C and 25 ml of it, is poured into a petri dish and allowed to solidify. After solidification, petri plates with media are spread with 1.0 ml of bacterial suspension prepared in sterile distilled water. The wells are bored with cork borer and the agar plugs are removed. To each agar well, concentration of $100\ \mu\text{g}$ for each compound in DMSO ($70\ \mu\text{l}$) were applied to the corresponding well (5 mm). All the plates are incubated at 37°C for 24 h and they are observed for the growth inhibition zones. The presence of clear zones around the wells indicate that the ligand and its complexes are active. The diameter of zone of inhibition is calculated in millimeters. The well diameter is deducted from the zone diameter and the values are tabulated. A control test was performed with test medium supplemented with DMSO with the same procedures used in the experiments, to ensure the solvent had no effect on the growth of microorganisms (negative control). Standard discs of Ampicillin and Tetracycline were also screened under similar conditions as positive controls for antibacterial activity. Minimum inhibitory concentrations (MICs) were determined by the micro-dilution broth method following the procedures recommended by the National Committee for Clinical Laboratory Standards [19].

Physical measurements

Elemental Microanalyses (C, H and N) were performed in the Microanalytical Unit, Cairo University. The electronic spectra were measured in Nujol mulls using a Perkin – Elmer Lambda 4B spectro-photometer. ^1H NMR spectra was obtained on 300 MHz VARIAN NMR spectrometers. Chemical shifts (ppm) are reported relative to TMS. The electronic spectra of the ligands and their complexes were obtained in Nujol mulls using a Shimadzu UV–240 UV–Vis recording spectrophotometer. Molar conductivities of the metal complexes in DMF ($10^{-3}\ \text{M}$) were measured using a dip cell and a Bibby conductimeter MCI at room temperature. The resistance measured in ohms and the molar conductivities were calculated according to the equation:

$\Lambda = V \times K \times Mw/g \times \Omega$, where Λ , molar conductivity ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$); V , volume of the complex solution (mL); K , cell constant 0.92 cm^{-1} ; Mw , molecular weight of the complex; g , weight of the complex; and Ω , resistance measured in ohms. The magnetic susceptibilities were measured at room temperature by a modified Gouy method using a Johnson Matthey magnetic susceptibility balance. Diamagnetic correction were made using Pascal's constant [20]. The magnetic moments were calculated from the equation $\mu_{\text{eff}} = 2.811 (\text{Mcorr T})^{1/2}$. The electron spin resonance (ESR) spectra were obtained in the X-band at room temperature on Bruker Elexsys 500 E spectrometer with a microwave frequency 9.82 GHz and a modulation frequency 10 KHz. The thermogravimetric analysis (TGA) were carried out under nitrogen atmosphere using a Shimadzu DT-50 thermal analyzer from room temperature to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$. Cyclic voltammetry (CV) was carried out using an EG and GPAR computer measuring system for the electrochemical analysis model 250. Current-voltage curves were recorded on a Hewlett-Packard model 7440 A X, Y-recorder. Analytical cell model C-1H and a platinum working electrode (Bioanalytical systems) were used together with a platinum counter electrode and an Ag/AgCl reference electrode. Acetonitrile was used as a solvent and lithium perchlorate as a supporting electrolyte for all electrochemical measurements.

RESULTS AND DISCUSSION

Conformational analysis of HBATP4ph

The conformational analysis of HBAT4ph at MM level of theory shows that the later possesses two conformers 1 and 2 [Figure 1] with Boltzmann contribution of 72% and 28%, respectively. The conformer 2 is more stable than 1 by a relative energy of 2.3 kcal/mol. The stability of the conformer 2 is due to the formation of an hydrogen bond between the keto group CO at C14 and the hydrogen atom of NH at 7 position (see chart 1 and Figure 1).

formation of an hydrogen bonding as the one obtained for conformer 2. HOMO and LUMO orbitals delocalizations for conformers 1 and 2 show similar behaviours [Figure 2]. The higher stability of conformer 2 compared with 1 may refer to the higher delocalization of LUMO orbital in pyrazolone of conformer 2 compared with conformer 1. This is confirmed by the low LUMO energy of conformer 2 compared with the one of conformer 1 (LUMO 2 kcal/mol).

¹H-NMR Spectrum of the ligand

The ¹H-NMR spectrum of HBATB4Ph in DMSO-d₆ [Figure 3] confirms its purity and displays two resonances at δ (p.p.m.) = 11.85 (1H) and δ = 10.12 (1H), which disappeared upon adding D₂O and are assignable to N(H)CS and N(H)Ph, respectively. The downfield shift of the N(6)H resonance can be attributed to intramolecular hydrogen bonding to the carbonyl oxygen of the pyrazolone ring, indicating that HBATB4ph exists as the (Z-isomer [21] as shown in Scheme 1. The higher frequency signal for N(7)H is probably due to the inductive electron withdrawing effect of the phenyl group at N(7) more acidic and probably able to hydrogen bond to N(5). The spectrum also shows resonances at δ = 7.22-7.78 (m) corresponding to phenyl rings attached to the nitrogen of the pyrazolone, and protons of the phenyl attached to C=N group and protons of the phenyl attached to NH group. The spectrum also shows singlet at δ = 2.65 (s) corresponding to C-CH₃.

¹H-NMR chemical shift of conformers 1 and 2 were predicted at the B3LYP/6-31+G(d,p) level of theory. The solvent effects were taken in consideration by using Polarizable continuum model. DMSO solvent is described by its dielectric constant. The correlation coefficients of linear correlations between the predicted and experimental chemical shifts of protons attached to the carbon atoms for both conformers are 84 and 84%, respectively. Surprisingly, the predicted chemical shifts of protons H6 and H7 attached to nitrogen atoms are not reproduced for both conformers.

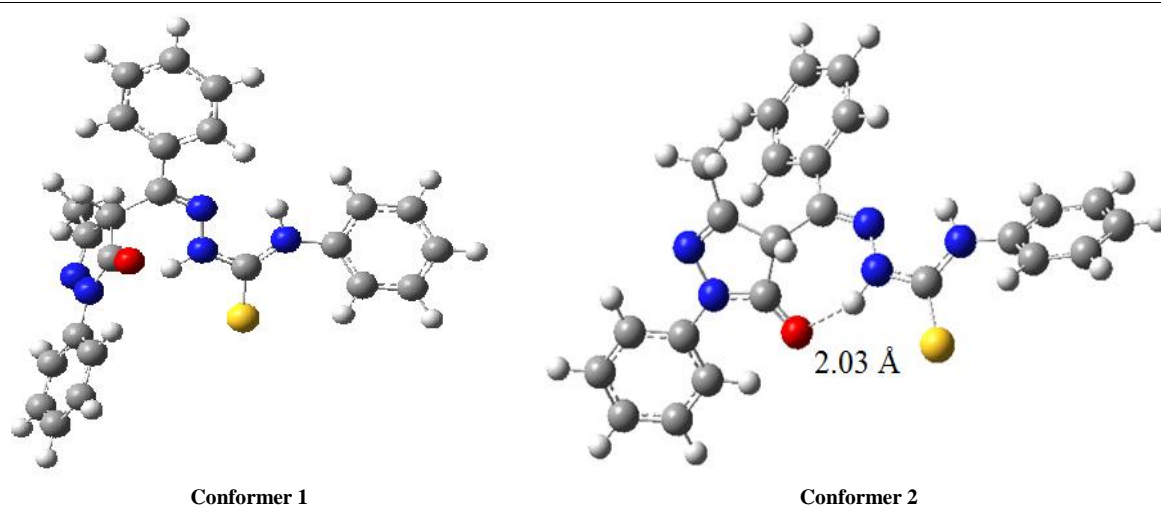


Figure 1 Stable conformers of HBAT4ph

However, for the conformer 1, the torsional angle C14-C15-C18-N5 is 64° , and the plane of the two parts joined by C15-C18 are almost perpendicular to each other, which avoid the

For instance, the predicted chemical shifts for H6 for conformers 1 and 2 are 7.45 and 9.69, respectively (exp (H6) = 11.85 ppm). However, when the weighted chemical shifts

were calculated by considering Boltzmann distributions for both conformers the variation between the experimental and predicted chemical shift become negligible (less than 0.2 ppm). This effect highlights that the chemical shifts of protons attached to nitrogen are strongly influenced by the geometrical structure of the compound (For example, hydrogen bonding occurs in conformer 2, which is not appears in case of conformer 1). The downfield shift of the N(6)H resonance can be attributed to (i) the presence of intermolecular hydrogen bonding between N(6)H and d-DMSO solvent, and (ii) to the intramolecular hydrogen bonding between N(6)H and keto group of pyrazolone moiety [Figure 1, conformer 2].

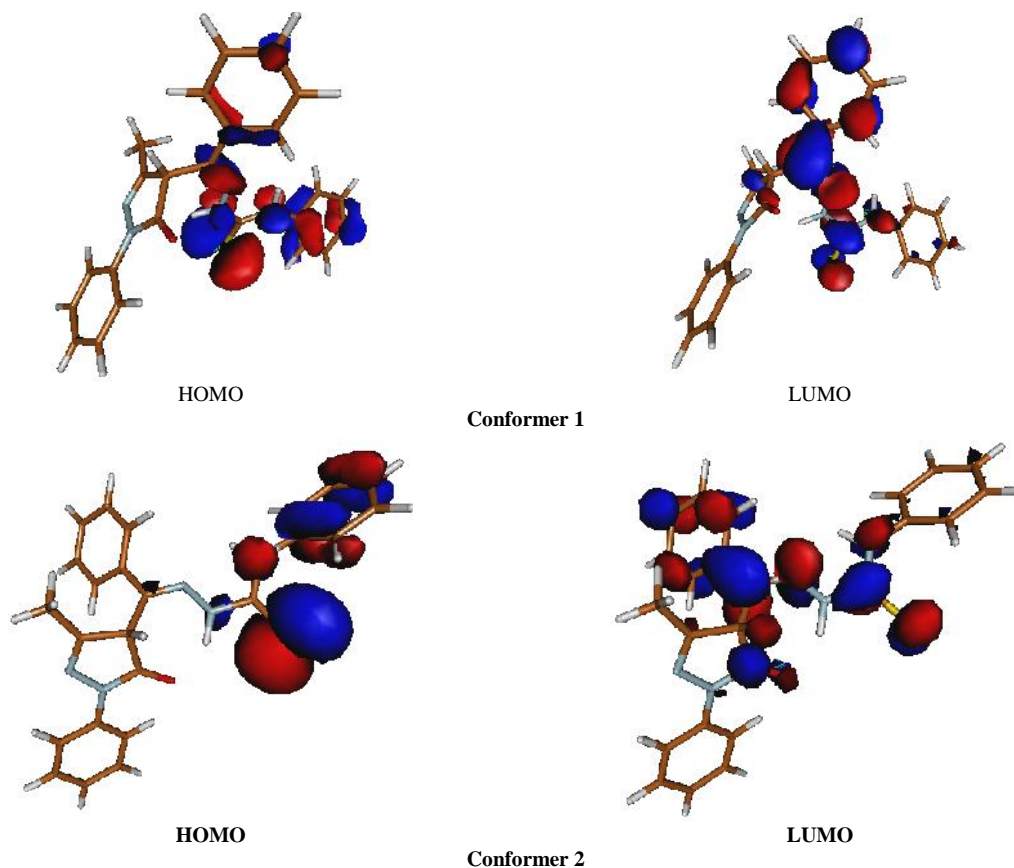


Figure 2 HOMO and LUMO orbitals of conformers 1 and 2

Mass spectrum of the ligand

The mass spectrum of the Schiff base ligand supported the suggested structure of the ligand and reveals molecular ion peak m/e at 427, consistent with the molecular weight of the ligand. Moreover, the molecular ion of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)phenyl thiosemicarbazone undergoes fragmentation via many pathways (see Scheme 2) with the elimination of NH_2ph , H_2S , CO , CHphN_2 , CphN_3 , CHphN_2S , CHphNS and CphNS particles; this is due to primary localization of the charge on the heteroatoms of the thiosemicarbazone residue. The region of the high mass number contains low-intensity ion peak that indicates the loss of an NH_2ph molecule by the molecular ion ($\text{M}^+ \text{a}$). The detachment of an H_2S molecule ($\text{M}^+ \text{b}$) confirms the existence of the thiol form of the molecular ion. The mass spectrum also contains peak that corresponds to ejection of a CO molecule from the molecular ion ($\text{M}^+ \text{c}$); Low-intensity

ion peak formed as a result of the loss of a CHphN_2 group by the molecular ion ($\text{M}^+ \text{d}$) is also observed in the mass spectrum. The mass spectrum of the ligand contains metastable peaks that indicates the existence of $\text{M}^+ [\text{M} - 28]^+$ and $\text{M}^+ [\text{M} - 55]^+$ transitions. The elementary compositions of the starting and resulting ions indicate ejection of a CO molecule in the first case and detachment of a CphN_3 fragment in the second case. The molecular ion also undergoes fragmentation with the elimination of 59 and 60 amu to give ions f and g [Scheme 2].

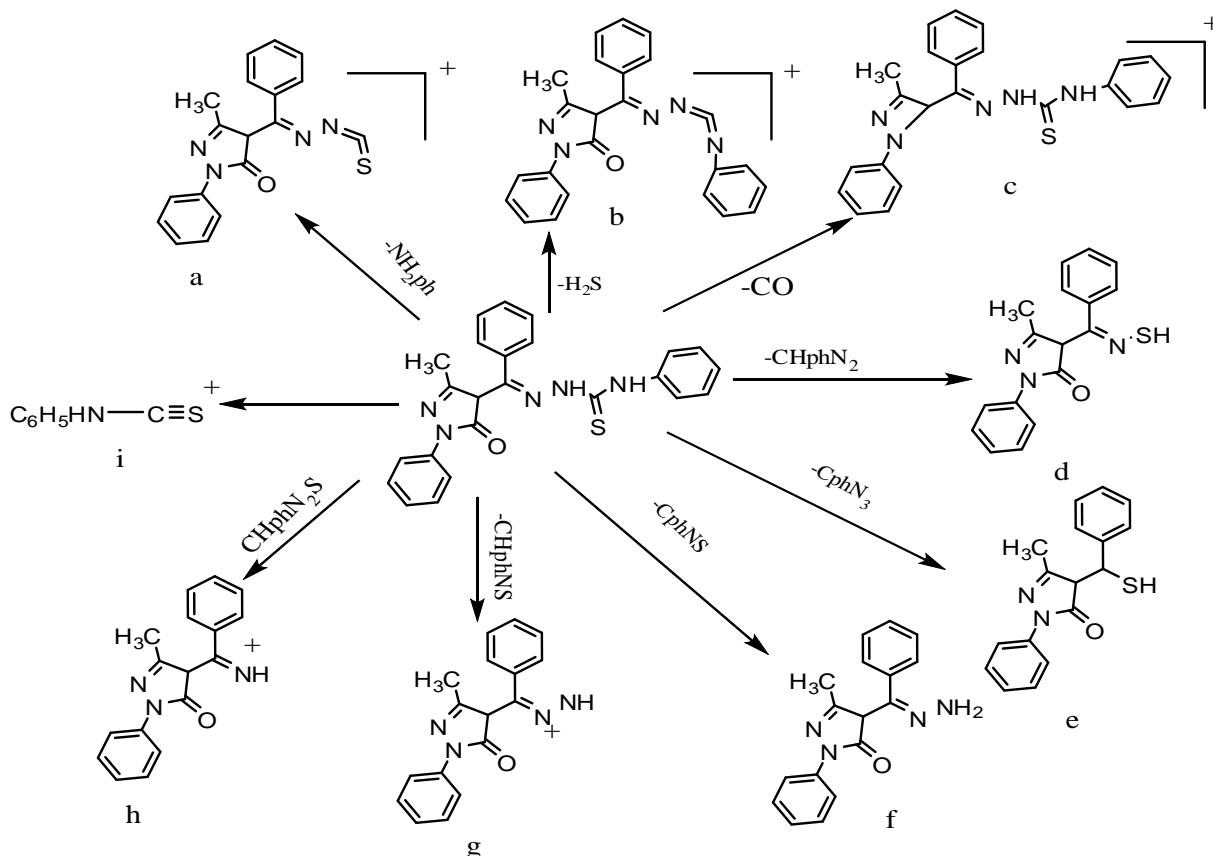
Fragments with m/e 60 ($\text{M}^+ \text{i}$), the intensity of the peak of which is 20-30%, are formed in the case of localization of the charge on the sulfur atom. Finally, intense ion h peak is formed as a result of cleavage of the N-N bond with migration of a hydrogen atom through a five-membered transition state ($\text{M}^+ \text{h}$).

Infrared spectra

The infrared spectral bands which provide structural evidence for the mode of attachment of HBATP4ph and its anion to the metal ions are shown in Table 2. The hydrate water molecules have been omitted from Table 2 (and subsequent tables) for convenience. In the higher frequency region of the ligand [Figure 4], two medium bands are observed at 3350 and 3125 cm^{-1} which may be due to $[\text{N}(4)\text{H}]$ and $[\text{N}(2)\text{H}]$ vibrations, respectively [22]. These two bands are more or less unaltered in the spectra of the complexes indicating that these groups do

not take part in coordination. The medium intensity band at 1605 cm^{-1} in free HBATP4ph has been assigned to $(\text{C}=\text{N})$, and this band shifts to lower wave numbers by $15\text{-}35\text{ cm}^{-1}$ in the spectra of the complexes, indicating coordination via the azomethine nitrogen. The $(\text{C}=\text{N})$ mode may be coupled with $(\text{C}=\text{S})$ to give the intense band observed at 1360 cm^{-1} , and the lower frequency shift of this band in the spectra of the complexes supports coordination of the azomethine nitrogen.

Based on the above spectral evidences, it is confirmed that the ligand is coordinated to the $\text{Cu}(\text{II})$ ion as a bidentate anion, coordinating via the azomethine nitrogen and thione/thiolate sulfur.



Scheme 2 Proposed thermal decomposition pattern of HBATP4ph

This is confirmed by the bands in the range $440\text{-}460\text{ cm}^{-1}$, which have been assigned to the $(\text{Cu}-\text{N})$ bond [23]. The band at 970 cm^{-1} in the spectrum of the ligand assignable to $(\text{N}-\text{N})$ [24] undergoes a small positive shift in all complexes and has also been attributed to coordination of the azomethine nitrogen to the copper ions [25]. The band at 1240 cm^{-1} in the HBATP4ph spectrum, which has $(\text{C}=\text{S})$ character, disappears in the some complexes owing to the change in the nature of $\text{NH}-\text{C}(=\text{S})-\text{N}$ to $\text{N}=\text{C}(\text{S})-\text{N}$ on complexation [26,27]. A medium intensity band at 830 cm^{-1} in the spectrum of the free ligand, assigned to the thioamide IV band, which has a significant contribution from (CS) , shifts to *ca.* 780 cm^{-1} for complexes with the neutral ligand and to *ca.* 750 cm^{-1} for the anionic ligand, indicating coordination of the thione/thiolate sulfur atom [28]. As is expected, greater decreases in the thioamide IV band occur for the anionic form of the ligand owing to $\text{C}-\text{S}$ formally becoming a single bond [29]. In addition, a band at *ca.* 345 cm^{-1} is assignable to (CuS) [30] and confirms coordination of the thione/thiolate sulfur. The thioamido-pyrazolone ring's $(\text{C}=\text{O})$ is found at *ca.* 1635 cm^{-1} and is essentially unchanged in the spectra of the copper(II) complexes, indicating the carbonyl oxygen is not involved in coordination [31].

The spectrum of the chloro complex shows two medium intensity $(\text{Cu}-\text{Cl})$ bands at 320 and 310 cm^{-1} indicative of terminal chloro ligands [32]. We are unable to assign $(\text{Cu}-\text{Br})$ bands with our spectrometer.

The inclusion of the water molecules in the coordination sphere of $[\text{Cu}(\text{HBATP4ph})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ and $[\text{Cu}(\text{BATP4ph})(\text{NO}_3)(\text{H}_2\text{O})]$ is supported by the presence of bands at 3460 , 1600 , 960 and 650 cm^{-1} owing to (OH) , (H_2O) , $\text{rock}(\text{H}_2\text{O})$ and $\text{wagg}(\text{H}_2\text{O})$, respectively [33]. The latter two modes are missing from the spectra of the remainder of the complexes isolated with water molecules, indicating hydrate rather than coordinated water [34].

The IR spectrum of the acetato complex $[\text{Cu}(\text{BATP4ph})(\text{OAc})]$ shows two strong bands at 1530 and 1440 cm^{-1} , corresponding to $\text{as}(\text{CO}_2)$ and $\text{s}(\text{CO}_2)$, respectively with $\Delta(\text{as}-\text{s})=90\text{ cm}^{-1}$. This is consistent with the bidentate nature of the coordinated acetate ion [35]. The nitrate complex, $[\text{Cu}(\text{BATP4ph})(\text{NO}_3)(\text{H}_2\text{O})]$, has two strong bands at 1420 and 1270 cm^{-1} with the separation of 150 cm^{-1} corresponding to ν_1 and ν_4 and a medium band at 1010 cm^{-1} corresponding to ν_2 of the nitrate group [Figure 5], indicating the presence of a

terminal monodentate nitrate group [36-38]. In complex [Cu(BATP4ph)(SO₄)]H₂O, the chelating bidentate SO₄²⁻ group was indicated by the appearance of ν(S-O) bands at 1157 and 1020 cm⁻¹ [Figure 6], which are characteristic for the high symmetry T_d (tetrahedral) point group [39]

The spectrum of the perchlorate complex, [Cu(HBATP4ph)(H₂O)₂](ClO₄)₂, shows a strong, stretching frequencies ν₃ and ν₄ at 1140 cm⁻¹ and 625 cm⁻¹ and a weak band at 930 (ν₁) cm⁻¹, indicating the presence of ionic perchlorate in the complex [40], in agreement with the molar conductivity results (Table 1).

Table 1 Colors, partial elemental analyses, molar conductivities and magnetic susceptibilities of the copper(II) complexes of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)phenyl thiosemicarbazone

No.	Compound	Color	Found (Calcd.) %] M ^a	μ _{eff} (B.M.)
			C	H	N		
1	HBATP4ph	white	67.1 (67.4)	5.2 (5.0)	16.7 (16.4)	--	--
2	[Cu(HBATP4ph)Cl ₂]	green	51.8 (51.3)	4.2 (3.8)	12.7 (12.5)	17.4	1.9
3	[Cu(HBATP4ph)Br ₂]. H ₂ O	green	46.1 (46.4)	3.2 (3.6)	9.2 (9.0)	18.3	1.6
4	[Cu(BATP4ph)(NO ₃)(H ₂ O)]	green	50.8 (50.6)	3.2 (3.9)	14.4 (14.7)	14.2	1.7
5	[Cu(BATP4ph)(OAc)]H ₂ O	Dark green	55.6 (55.1)	4.4 (4.4)	12.7 (12.4)	16.5	1.8
6	[Cu(BATP4ph)(SO ₄)]H ₂ O	Light green	47.1 (47.6)	4.2 (3.8)	11.8 (11.6)	13.2	1.7
7	[Cu(HBATP4ph)(H ₂ O) ₂](ClO ₄) ₂	Dark green	41.4 (41.2)	3.4 (3.5)	10.1 (10.0)	122.3	1.8

^a 10⁻³ M in DMF and expressed as cm² mol⁻¹

Table 2 Infrared spectra (cm⁻¹) of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)phenyl thiosemi-carbazone and its copper(II) complexes.

No.	Compound	[N(4)H]	(C=N)	(C=S)	(CuN)	(CuS)	(CuCl)
1	HBATP4ph	3315m3	1605m	830m	--	--	--
2	[Cu(HBATP4ph)Cl ₂]	3290s	1590s	795m	455s	340w	310m 315sh
3	[Cu(HBATP4ph)Br ₂]. H ₂ O	3310m	1584m	788s	460m	344m	a
4	[Cu(BATP4ph)(NO ₃)(H ₂ O)]	3285m	1596m	765m	456m	345m	--
5	[Cu(BATP4ph)(OAc)]H ₂ O	3305m	1588s	755s	460m	338m	--
6	[Cu(BATP4ph)(SO ₄)]H ₂ O	3310s	1590s	768s	442w	330w	--
7	[Cu(HBATP4ph)(H ₂ O) ₂](ClO ₄) ₂	3290m	1585m	790m	445s	337m	--

^a Not assignable with our spectrometer.

Molar conductivity measurements

The molar conductance values of the complexes in 10⁻³ M DMF solutions are listed in Table 1, and reveal that the halo, nitrate, sulfato and acetate complexes are essentially non-electrolytes, while the perchlorate complex dissociates in DMF and behaves as 1:2 electrolyte [41]. The relatively high molar conductivity values for the chloro and bromo complexes are due to partial decomposition of these complexes in solution with the DMF solvent molecules displacing the halo ligands.

Electronic spectra and magnetic moments

In order to obtain some structural information of the complexes, the magnetic moments, as well as the electronic absorption have been studied. The magnetic moments of the complexes are calculated from magnetic susceptibility measurements and the values of all the Cu (II) complexes at room temperature are found to be in the range 1.6-1.9 B.M. The values of the magnetic moments, which are close to the spin only value of 1.7 B.M. (Table 1) indicate the presence of one unpaired electron [42]. This indicates that these complexes are monomeric in nature and the absence of metal-metal interaction.

Listed in Table 3 are the energies of the solid state electronic transitions for the thiosemicarbazone ligand, as well as their copper(II) complexes. Omitted from Table 3 are the higher energy π→π* transitions at ca. 35000 cm⁻¹ which is not significantly altered on complex formation [12]. The higher energy band at 28500 cm⁻¹ for HBATP4ph is likely to be owing to the thiosemicarbazone moiety's azomethine n→π* transition and is not altered significantly in the spectra of most complexes. A second n→π* band originating from the thioamide portion of the thiosemicarbazone moiety is found at 24300 cm⁻¹ in the spectrum of HBATP4ph.

In the copper (II) complexes this latter band generally shifts to higher energies and sometimes merges with n→π* transition associated with the azo-methine portion. Also present at energies below 30000 cm⁻¹ in the spectra of the copper(II) complexes are S→Cu^{II} charge transfer bands [43], as well as Br→Cu^{II} charge transfer bands [44]. The Cl→Cu^{II} [45] and O→Cu^{II} [46] bands are generally found in the 30000 cm⁻¹ region of the spectrum. This series of complexes has very broad bands due to the n→π* transitions, and it is difficult to assign energies to the transition between 20000 and 30000 cm⁻¹. Similarly, it is difficult to assign energies of more than one d→d band although shoulders [47] are assigned in Table 3. Most complexes show one band in the region 14300-14600 cm⁻¹ and shoulder in the region 18000-19000 cm⁻¹, assignable respectively to transitions ²B_{1g} → ²A_{2g} and ²B_{1g} → ²B_{2g} of a square planar structure [48].

The solution spectra (DMSO) of the 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)phenyl thiosemicarbazone and its copper(II) complexes are presented in Table 4. A peak associated with an n→π* transition of the heterocyclic ring portion of the pyrazolone moiety is observed at 34500 cm⁻¹ in the spectrum of the thiosemicarbazone and is unshifted in the spectra of their copper(II) complexes. A second band at 30300 cm⁻¹, due to the n→π* transition of the azomethine portion of

the thiosemicarbazone moiety, has a molar absorptivity, ϵ , of approximately 3×10^4 (or $\log \epsilon$ is ca. 4.4) for the coordinated and uncoordinated ligand [49].

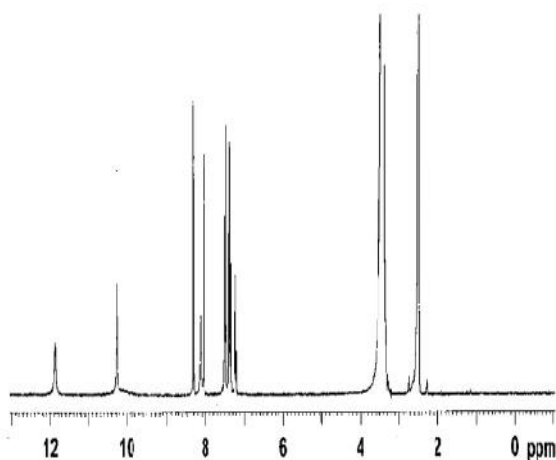


Figure 3 ^1H NMR spectrum of the ligand HBATB4Ph in DMSO- d_6

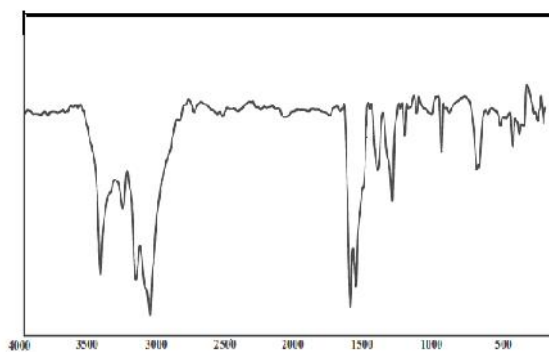


Figure 4 IR spectrum of the ligand HBATB4Ph

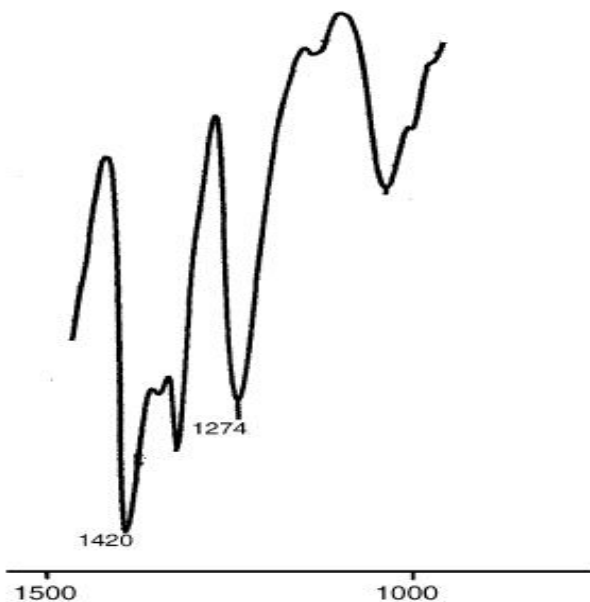


Figure 5 Partial view of the IR spectrum of the complex $[\text{Cu}(\text{BATP4ph})(\text{NO}_3)(\text{H}_2\text{O})]$

Although a $\text{Cl} \rightarrow \text{Cu}^{\text{II}}$ charge-transfer band might also be expected in this region of the spectrum [50], it does not add significantly to the magnitude of ϵ based on the similarity of values for $[\text{Cu}(\text{HBATP4ph})\text{Cl}_2]$ to the other complexes of this

study. A second $n \rightarrow \pi^*$ transition associated with the thione portion of the thiosemicarbazone moiety appears as a low energy shoulder at 26500 cm^{-1} .



Figure 6 IR spectrum of the complex $[\text{Cu}(\text{BATP4ph})(\text{SO}_4)]\text{H}_2\text{O}$

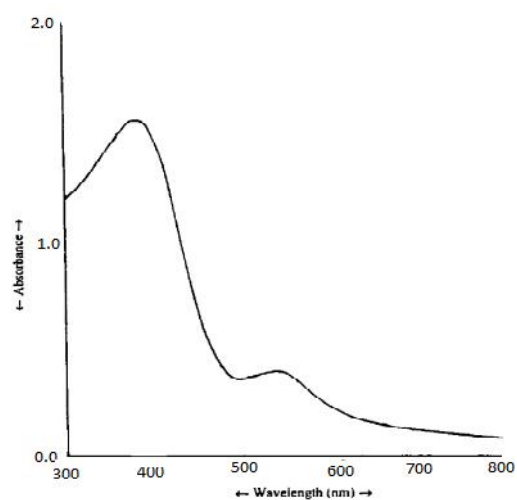


Figure 7 Absorption spectrum of $[\text{Cu}(\text{HBATP4ph})\text{Cl}_2]$ complex in DMSO.

In the complexes this band generally merges with the $n \rightarrow \pi^*$ transition of the azomethine portion of the thiosemicarbazone moiety and, therefore, bands in this region of the complexes are assignable to $\text{S} \rightarrow \text{Cu}^{\text{II}}$ and other ligand-to-copper(II) charge-transfer bands [50]. The solution $d \rightarrow d$ bands are altered from their energies in the solid state, suggesting that significant interaction with DMSO solvent molecules occurs [Figure 7].

The predicted maximum absorption bands λ_{MAX} of HBAT4ph were obtained using B3LYP, B3P86 and PBE0 hybrid functionals combined with a larger basis set 6-311+G(d,p). Previous studies reported that the reproduction of the experimental λ_{MAX} of polyphenolic compounds is slightly influenced by conformational analysis effect, i.e., λ_{MAX} of conformers are very closed [51, 52]. λ_{MAX} is less 2 nm between conformers 1 and 2. Thus, one can consider only the stable conformer. Here, the maximum absorption bands λ_{MAX} for the stable conformer 2 obtained using B3LYP, B3P86 and PBE0 are 329, 330 and 318 nm, respectively. By using B3P86 and B3LYP hybrid functionals, the experimental λ_{MAX} is well reproduced (λ_{MAX} between the predicted and experimental values is less than 1 nm). It is worth to mention that λ_{MAX} corresponds to HOMO-1 \rightarrow LUMO electronic transition. PBE0 underestimated the experimental λ_{MAX} by 12 nm. The reliability

of B3P86 and B3LYP to reproduce ϵ_{MAX} is in agreement with reported literature for some polyphenolic compounds [51].

Table 3. Solid state electronic spectra (cm⁻¹) 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)phenyl-thiosemicarbazone and its copper(II) complexes.

No.	Compound	Intraligand and charge transfer bands	d-d bands
1	HBATP4ph	28500, 24300	18460, 14400sh
2	[Cu(HBATP4ph)Cl ₂]	29470, 24380	14600
3	[Cu(HBATP4ph)Br ₂]. H ₂ O	28640, 23980	18610, 14480sh
4	[Cu(BAP4ph)(NO ₃)(H ₂ O)]	29230, 24210	18600, 14530sh
5	[Cu(BATP4ph)(OAc)(H ₂ O)]	30130, 23990	18450, 14490sh
6	[Cu(BATP4ph)(SO ₄)]H ₂ O	29750, 23840	18400, 14430sh
7	[Cu(HBATP4ph)(H ₂ O) ₂](ClO ₄) ₂	30100, 24600	18500, 14700sh

Table 4 Solution (DMSO) electronic spectra (cm⁻¹) 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)phenyl-thiosemicarbazone and its copper(II) complexes.

No.	Compound	Intraligand and charge transfer bands	d-d bands
1	HBATP4ph	30300(4.40) 26550	
2	[Cu(HBATP4ph)Cl ₂]	29470(4.43), 26680	15760(2.23)
3	[Cu(HBATP4ph)Br ₂]. H ₂ O	29690(4.70), 26960	16240(2.55)
4	[Cu(BAP4ph)(NO ₃)(H ₂ O)]	29270(4.79), 27110	16140(2.52)
5	[Cu(BATP4ph)(OAc)(H ₂ O)]	29980(4.47), 26790	15410(2.43)
6	[Cu(BATP4ph)(SO ₄)]H ₂ O	29950(4.67), 27740	14890(2.29)
7	[Cu(HBATP4ph)(H ₂ O) ₂](ClO ₄) ₂	30150(4.52), 27540	15170(2.23)

Electron spin resonance spectra

In order to obtain further information concerning the geometry of the copper complexes, ESR spectra were recorded in the polycrystalline state and bonding parameters were calculated using Knebnul's approximation [53]. The spectra of all Cu(II) complexes show two peaks at room temperature, an intense absorption at high field and less intense one at low field [Figure 8], from which $g_{//}$, g_{\perp} , $\langle g \rangle$ and A have been calculated. The trend $g_{//} > g_{\perp} > 2.003$ observed for all complexes indicates that the unpaired electron most likely resides in the $d_x^2 - y^2$ orbital, thus implying a ${}^2B_{1g}$ as a ground state [54].

Kivelson and Nieman [55] have shown that $g_{//}$ is a moderately sensitive function for indicating covalency. Relatively speaking, $g_{//} > 2.3$ is characteristic of an ionic environment and $g_{//} < 2.3$ of a covalent environment in metal-ligand bonding. Using this criterion the data show considerable covalent character of the metal-ligand bond in the present complexes. Based on the values of $g_{//}$, the covalency order may be $OAc^- > SO_4^{2-} > NO_3^- > BF_4^- > Br^- > Cl^-$. The $\langle g \rangle$ values in the range of 2.09- 2.30 are in agreement with an orbitally non-degenerate ground state [56]. In complexes having D_{4h} symmetry, g values for the cu(II) ion with a ${}^2B_{1g}$ ground state are given by the expressions [57].



Figure 8 ESR spectrum of [Cu(HBATP4ph)Cl₂] complex in the polycrystalline state at 298K

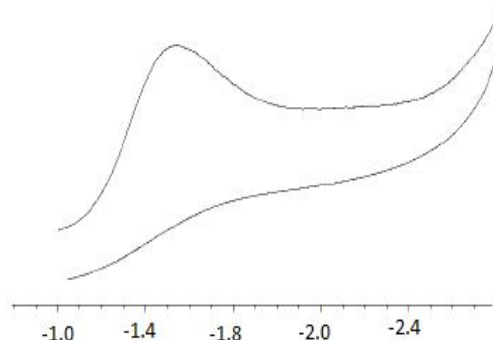


Figure 9 Cyclic Voltammogram of the free ligand in acetonitrile on Pt electrode VS. Ag/Ag⁺ electrode

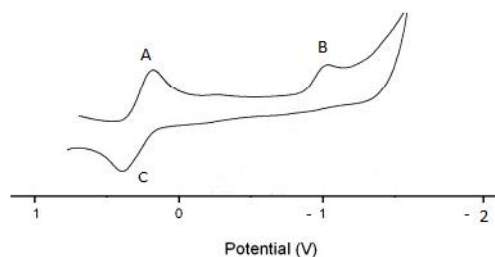


Figure 10 Cyclic voltammogram of [Cu(HBATP4ph)Cl₂] complex in 0.1 M LiClO₄ in acetonitrile on Pt electrode, V=100 mV S⁻¹, (VS. Ag/Ag⁺ electrode)

$$g_{//} = 2 - [k_{//}^2 \lambda / ({}^2B_{1g} \rightarrow {}^2B_{2g})] \quad (1)$$

$$g_{\perp} = 2 - [k_{\perp}^2 \lambda / ({}^2E_g \rightarrow {}^2B_{2g})] \quad (2)$$

Where K is the orbital reduction factor and λ the spin orbit coupling constant.

Equation (3) follows.

$$(g_{//} - 2) / (g_{\perp} - 2) = G = k_{//}^2 ({}^2E_g \rightarrow {}^2B_{2g}) / k_{\perp}^2 ({}^2B_{1g} \rightarrow {}^2B_{2g}) \quad (3)$$

In the view of the close similarity of the spectra, it is worth checking the g values obtained from the ESR spectra used to evaluate $k_{//}$ and k_{\perp} by the above expressions. For all complexes, $k_{\perp} > k_{//}$. If the assignment of the electronic energy levels, ${}^2B_{1g} < {}^2B_{2g} < {}^2A_{1g} < {}^2E_g$ was used, lower numerical values of ${}^2B_{2g} < {}^2E_g$ were used. Lower numerical values of the ${}^2B_{2g} \leftarrow {}^2B_{1g}$ transition would significantly reduce the values of $k_{//}$ such that $k_{\perp} > k_{//}$. This is another reason why the assignment ${}^2B_{1g} < {}^2A_{1g} < {}^2B_{2g} < {}^2E_g$ is preferred.

The spin-orbit coupling constant, λ , is reduced in all the complexes from the free ion value of -828 cm^{-1} , signifying the extent of mixing of metal and ligand orbitals. It is pertinent to state that the g values obtained by Knebhul's approximation are subject to inaccuracies in as much as they ignore the effect of hyperfine coupling constants, However, in the present systems, the effect is likely to be the same in all the complexes. Thus the relative g values may be same although absolute values may be substantially in error.

In axial symmetry, the g -values are related by expression, $G = (g_{\parallel} - 2)/(g_{\perp} - 2) = 4$, where G is a measure of the exchange interaction between Cu(II) centers in a polycrystalline solid [58]. According to Hathaway [59], if the value of $G > 4$, the exchange interaction is negligible, while $G < 4$ indicates considerable exchange interaction in solid complexes. Following this criterion, G values is less than four for the various copper(II) complexes indicating that exchange interaction between copper(II) centers is considerable in the polycrystalline solid. This is consistent with weak bridging by the coordinated sulfur atoms to neighboring copper(II) centers, which is common for 4-coordinate copper(II) complexes containing sulfur [60]. We have calculated the molecular orbital coefficients, (α^2), by using simple relationship [61]

$$g = 2.0023 - [8\lambda\alpha^2/\Delta_{xy}]$$

The quantity α^2 is a function which depends on the nature of the copper-ligand bond, decreasing with increasing covalency from 1.0 to a minimum theoretical value of 0.50. All complexes are seen to be fairly covalent, α^2 varying from 0.53 to 0.78.

In order to quantify the degree of distortion of the Cu(II) complexes, we selected $f(\alpha) = g_{\parallel}/A_{\parallel}$, obtained from the ESR spectrum, which is regarded as an index of tetrahedral distortion. Values of 110–120 are typical for planar complexes, while the range 130–150 is characteristic of slight to moderate distortion and 180–250 cm^{-1} indicates considerable distortion [62,63]. The ratio $g_{\parallel}/A_{\parallel}$ (116 - 120) for the Cu complexes are evidence in support of the square planar geometry with no appreciable tetrahedral distortion.

Table 5 E.s.r spectral parameters of the copper(II) complexes of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)phenylthiosemicarbazone.

No.	Compound	Temp.	g_{\parallel}	g_{\perp}	MgO	G
1	[Cu(HB ATP4ph)Cl ₂]	RT	2.213	2.095	2.134	2.242
2	[Cu(HB ATP4ph)Br ₂]. H ₂ O	RT	2.196	2.090	2.125	2.178
3	[Cu(B ATP4ph)(NO ₃)(H ₂ O)]	RT	2.192	2.088	2.123	2.182
4	[Cu(B ATP4ph)(OAc)]H ₂ O	RT	2.187	2.056	2.100	3.340
5	[Cu(B ATP4ph)(SO ₄)]H ₂ O	RT	2.189	2.068	2.108	2.779
6	[Cu(HB ATP4ph)(H ₂ O) ₂](ClO ₄) ₂	RT	2.195	2.091	2.126	2.143

Electrochemical properties

Generally the electrochemical properties of the complexes depend on a number of factors such as chelate ring size, axial ligation degree and distribution of unsaturation and substitution pattern of unsaturation and substitution pattern in the chelate ring, charge type and coordination number [64]. The redox

behaviors of the thiosemicarbazone ligand and its copper (II) complexes have been investigated by cyclic voltammetry in acetonitrile solution at a platinum electrode in the range from +1.0 to -2.0 V. Voltammetric data are given in Table 6. The cyclic voltammogram of the ligand shows an irreversible cathodic wave in the negative margin at -1.44 V [Figure 9] which can be attributed to the reduction of the imine and thioamide groups present in the thiosemicarbazone moiety, and its value is comparable to that observed for other thiosemicarbazones [65, 66].

The Cu(II) complexes addition to the peak of ligand exhibits a reduction process occurring at A and is directly associated with reoxidation peak at C in the reverse scan, suggesting one electron redox change [Table 6] originating from the chemically reversible [Cu(HB ATP4ph)Cl₂] → [Cu(HB ATP4ph)Cl₂]⁻ but electrochemically quasi-reversible Cu(II)/Cu(I) redox couple [67]. Analysis of the cyclic voltammetric response of peak A/C [Figure 10] for these complexes indicates that the ratio of i_{pa}/i_{pc} is approximately equal to unity and the peak-to-peak separation (ΔE_p) is in the range of 0.43-0.34 V. In the absence of either uncompensated solution resistance or anomalous electrode surface effects, the marked departure of ΔE_p from 0.059 V can be qualitatively assumed as an index of occurrence of significant geometrical reorganizations accompanying the redox changes [68]. It is expected that the Cu(II)/Cu(I) redox couple experiences some structural reorganization barrier in view of the likely rearrangement from square planar Cu(II) to tetrahedral Cu(I).

Table 6 Cyclic voltammetric data for copper(II) complexes of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)phenylthiosemicarbazone.

No.	Compound	E _{pa}	E _{pc}	ΔE_p	E1/2
1	[Cu(HB ATP4ph)Cl ₂]	0.71	0.37	0.34	0.54
2	[Cu(HB ATP4ph)Br ₂]. H ₂ O	0.76	0.41	0.35	0.59
3	[Cu(B ATP4ph)(NO ₃)(H ₂ O)]	0.74	0.38	0.36	0.56
4	[Cu(B ATP4ph)(OAc)]H ₂ O	0.80	0.43	0.37	0.37
5	[Cu(B ATP4ph)(SO ₄)]H ₂ O	0.77	0.38	0.39	0.58
6	[Cu(HB ATP4ph)(H ₂ O) ₂](ClO ₄) ₂	0.79	0.36	0.43	0.58

Thermal studies

Because the infrared spectra and elemental analyses show the presence of water molecules in the chemical structures of metal complexes. The thermal analyses (TGA) was carried out on some of the copper(II) complexes in the temperature range 20-800°C and the results are collected in Table 7, showing good agreement in weight loss between calculated and found formulae.

The TGA data show that the investigated complexes display a weight loss within the temperature range 37 - 140°C assignable to the loss of water of hydration. The TGA curves also show that the coordinated water molecules in complexes (3 and 6) loss within the temperature range 78 - 248°C. The third step (132–355°C) for all complexes is the elimination of the anion. The fourth step (292–680°C) is the complete decomposition of the complexes which ended with copper sulfide formation.

Table 7 TGA data for some of copper(II) complexes of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one N(4)phenylthiosemicarbazone.

No.	Compound	Temperature range °C	Weight loss Found/(calcd.)	Assignment
1	[Cu(HBATP4ph)Cl ₂]	270-310 310-580	12.82(12.36) 83.87(83.10)	Loss of two chloride ions Decomposition of the complex forming CuS
2	[Cu(HBATP4ph)Br ₂]. H ₂ O	65-130 130-290 290-780	2.98(2.69) 24.12(23.65) 85.23(85.78)	Loss of one molecule of hydrated water Loss of two coordinated bromide ions Decomposition of the complex forming CuS
3	[Cu(BAP4ph)(NO ₃)(H ₂ O)]	80-170 170-280 280-590	3.65(3.16) 11.42(10.88) 84.21(83.33)	Loss of one molecule of coordinated water Loss of one coordinated nitrate Decomposition of the complex forming CuS
4	[Cu(BATP4ph)(OAc)]H ₂ O	35-90 90-280 280-440	2.98(3.17) 10.65(10.41) 82.97(83.25)	Loss of one molecule of hydrated water Loss of one coordinated acetate ion Decomposition of the complex forming CuS
5	[Cu(BATP4ph)(SO ₄)]H ₂ O	30-95 95-3000 300-520	3.14(2.98) 15.75(16.93) 84.88(84.27)	Loss of one molecule of hydrated water Loss of one coordinated sulfate ion Decomposition of the complex forming CuS

Antimicrobial activity

The question about the involvement of the metal complexes in medical treatment is of special interest, as it is known that the bacteria can achieve resistance to antibiotics through biochemical and morphological modifications [69]. Therefore, researching new compounds of antimicrobial activity is of paramount importance [70-72]. It seems therefore to be of considerable interest to assess the biological potential of the novel thiosemicarbazone ligand and its copper(II) complexes against two Gram positive bacteria (*Staphylococcus aureus* and *Bacillus subtilis*), two Gram negative bacteria (*Escherichia coli* and *Pseudomonas aeruginosa*) and standard drugs (ampicillin and tetracycline) in DMSO solvent at a concentration of 100 µg/ml.

The moderate activity of the Schiff base ligand may be arises from the presence of imine and thione groups which imports in elucidating the mechanism of transformation reaction in biological system [73]. All the copper(II)-thiosemicarbazone complexes have moderate antibacterial activities against these bacteria. The increased activity of the metal chelate can be explained on the basis of Tweedy's chelation theory [74]. It is known that chelation tends to make the ligand act as more powerful and potent bactericidal agent, killing more of the bacteria than the ligand. It is observed that in a complex, the positive charge of the metal is partially shared with the donor atoms present in the ligands and there may be π-electron delocalization over the whole chelation.

Table 8 Antibacterial activity data of the ligand and its copper(II) complexes.

No.	Compound	<i>Staphylococcus aureus</i>		<i>Bacillus subtilis</i>		<i>Escherichia coli</i>		<i>Pseudomonas aeruginosa</i>	
		WD ^a	MIC ^b	WD ^a	MIC ^b	WD ^a	MIC ^b	WD ^a	MIC ^b
1	HBATP4ph	11	225	10	198	10	148	9	146
2	[Cu(HBATP4ph)Cl ₂]	13	114	14	114	12	143	13	134
3	[Cu(HBATP4ph)Br ₂]. H ₂ O	12	180	10	137	11	146	10	138
4	[Cu(BAP4ph)(NO ₃)(H ₂ O)]	11	202	10	139	10	141	12	142
5	[Cu(BATP4ph)(OAc)]H ₂ O	12	198	10	141	11	134	10	140
6	[Cu(BATP4ph)(SO ₄)]H ₂ O	14	102	13	138	15	132	15	136
7	[Cu(HBATP4ph)(H ₂ O) ₂](ClO ₄) ₂	111	135	110	138	12	134	11	135
	Ampicillin	22	19	21	11	19	13	17	11
	Tetracycline	23	15	21	12	22	14	20	10

^a WD, disc diffusion method. Diameter of zone of inhibition (mm)

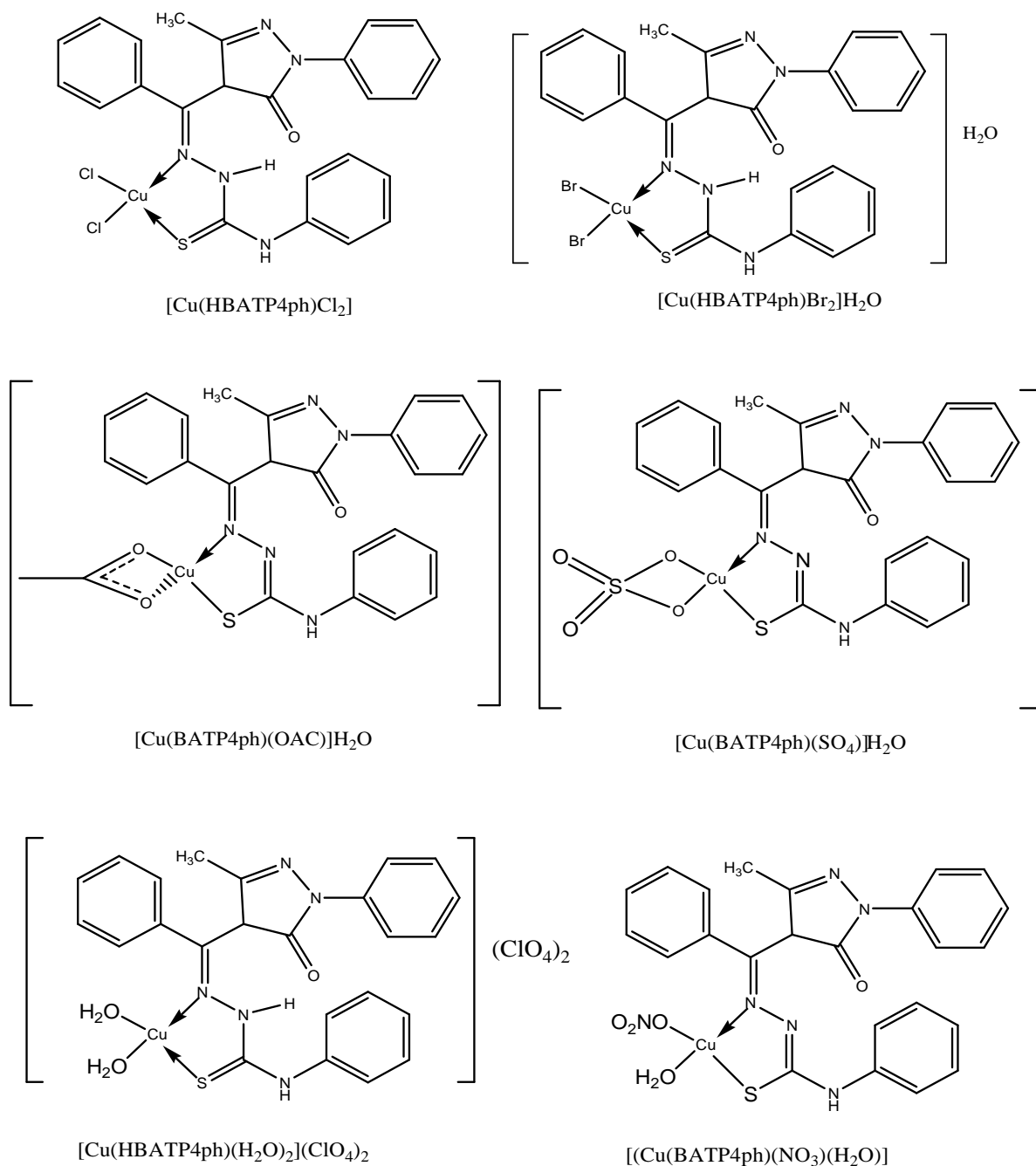
^b MIC, minimum inhibitory concentration. Values given as µg/ml for both compounds and antibiotics

Test substances which produce a zone of inhibition of diameters 9 mm or more are regarded as positive, i.e. having constructive antimicrobial activity; while in those cases where the diameter is below 9 mm, the bacteria are resistant to the sample tested and the sample is said to have no antimicrobial activity. Ampicillin and Tetracycline were used as standards. The data of inhibition zone of growth (in mm) and minimum inhibitory concentration (in µg/L) are given in Table 8.

The results show that the complexes exhibited better activity than the ligand, although they could not reach the effectiveness of the standards used in the study.

This increases the lipophilic character of the metal chelate and favors its permeation through the lipid layers of cell membrane [75] and blocking the metal binding sites on enzymes of microorganism.

The variation in the effectiveness of different compound against different organisms depends either on the impermeability of the cells of the microbes or differences in ribosomes of microbial cells. Though there is a marked increase in the bacterial activity of copper(II) complexes as compared to the free ligand, it could not reach the effectiveness of Ampicillin and tetracycline



Scheme 3

The elemental analysis, IR, ¹H NMR, mass, and electronic spectra, magnetic moment measurement, as well as the electron spin resonance and thermal analyses are compatible with the proposed structures [Scheme 3].

In the absence of detailed structural studies, mode of coordination in all the complexes remain somewhat speculative; We are trying to obtain crystals suitable for X-ray analysis but have not so far been successful.

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