# Copper(II) complexes derived from di-2-pyridyl ketone-$N^4$-phenyl-3-semicarbazone: Synthesis and spectral studies

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## ARTICLE INFO

## ABSTRACT

Five copper(II) complexes $[CuLCl]_2 \cdot CuCl_2 \cdot 4H_2O$ (**1**), $[CuLOAc]$ (**2**), $[CuLNO_3]_2$ (**3**), $[CuLN_3]$ (**4**) and $[CuLNCS] \cdot 3/2H_2O$ (**5**) of di-2-pyridyl ketone-$N^4$-phenyl-3-semicarbazone (HL) were synthesized and characterized by elemental analyses and electronic, infrared and EPR spectral techniques. In all these complexes the semicarbazone undergoes deprotonation and coordinates through enolate oxygen, azomethine and pyridyl nitrogen atoms. All the complexes are EPR active due to the presence of an unpaired electron. EPR spectra of all the complexes in DMF at 77 K suggest axial symmetry and the presence of half field signals for the complexes **1** and **3** indicates dimeric structures.

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## 1. Introduction

Semicarbazones are the condenzation products of semicarbazides with aldehyde or ketone and these compounds are having the formula $R_2C=N–NH–(CO)–NH_2$. These are compounds with versatile structural features and can exist in two tautomeric forms, keto (A) and enol (B) (Scheme 1). These classes of compounds usually react with metallic cations giving complexes in which semicarbazones behave as chelating ligands. The coordination possibilities of the semicarbazones are increased if the substituents of the aldehyde or ketone include additional donor atoms. These compounds are associated with diverse pharmacological activities, such as antibacterial and antifungal, antihypertensive, hypolipidemic, antineoplastic, hypnotic and anticonvulsant [1,2]. Recently 4-arylsubstituted semicarbazones have acquired an important role as anticonvulsants with oral activity [3]. The biological activity is due to the ability to form chelates with transition metal ions bonding through oxygen and azomethine nitrogen atoms. Compared with thiosemicarbazone analogues, there are considerably less reports on the synthesis, structures and spectroscopic characterization of semicarbazones and their metal complexes [4]. Semicarbazones derived from di-2-pyridyl ketone have a small negative charge resides on the nitrogen atom of the pyridine ring which enhances its biological activity [5]. Copper(II) complexes based on a semicarbazone as superoxide dismutase
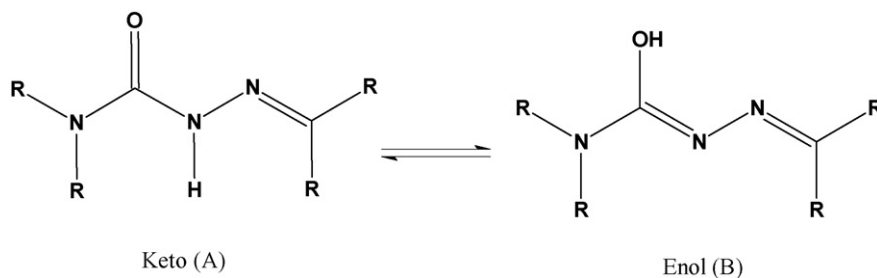
mimics have been reported recently [6]. There are some reports on ruthenium(II) complexes of thiosemicarbazone and semicarbazone [7]. Antimicrobial activities of some chloro complexes of imidazole-2-carbaldehyde semicarbazone have also been evaluated [8]. Transition metal complexes of citral semicarbazone have been studied recently [9]. Also there is a report on the synthesis, crystal structures and spectral properties of nickel(II) complex of 2-formylpyridine semicarbazone [10]. The choice of di-2-pyridyl ketone is mainly due to the fact that this heteroaromatic moiety can provide a further binding site for metal cations [11–13]. It is rigid, and provides two aromatic nitrogens whose unshared electron pairs are beautifully placed to act co-operatively in binding cations. We have recently reported the synthesis, spectral characterization and structural studies of cadmium(II) and zinc(II) complexes of the present semicarbazone with the aim to correlate the structural features and chelating ability [10,11]. This paper deals with the synthesis and characterization of copper(II) complexes of di-2-pyridyl ketone-$N^4$-phenyl-3-semicarbazone, HL (Fig. 1).

## 2. Experimental

### 2.1. Materials

Di-2-pyridyl ketone (Aldrich) and $N^4$-phenylsemicarbazide (Aldrich) were used as received. Solvents used were methanol and water. Copper(II) salts, sodium azide and potassium thiocyanate were used as received.

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*E-mail address:* mrp@cusat.ac.in (M.R.P. Kurup).

**Scheme 1.**

## 2.2. Physical measurements

Elemental analyses were carried out using a Vario EL III CHNS analyzer at SAIF, Kochi, India. Infrared spectra were recorded on a JASCO FT-IR-5300 spectrometer in the range 4000–400 cm$^{-1}$ using KBr pellets. Electronic spectra were recorded on a Cary 5000, version 1.09 UV–VIS–NIR spectrophotometer in the 200–900 nm range using solutions in DMSO. Magnetic susceptibility measurements were carried out on a Vibrating Sample Magnetometer using Hg[Co(SCN)$_4$] as a calibrant. The EPR spectra of polycrystalline samples at 298 K and solution at 77 K were recorded on a Varian E-112 X-band EPR spectrometer with 100-kHz field modulation and g factors were quoted relative to the standard marker TCNE (g = 2.00277). Molar conductivity measurements were made in DMSO solutions.

## 2.3. Synthesis of di-2-pyridyl ketone-$N^4$-phenylsemicarbazone

Di-2-pyridyl ketone-$N^4$-phenyl-3-semicarbazone (HL) was prepared (Fig. 2) by the earlier reported method [11].

## 2.4. Synthesis of complexes

### 2.4.1. Synthesis of [CuLCl]$_2$·CuCl$_2$·4H$_2$O (**1**) and [CuLOAc] (**2**)

A solution of the semicarbazone HL (0.317 g, 1 mmol) in 20 ml of methanol was treated with a methanolic solution of the appropriate copper(II) salt (1 mmol). The solution was heated under reflux for 4 h. The complexes formed were filtered, washed with ether and dried over P$_4$O$_{10}$ *in vacuo*.

### 2.4.2. Synthesis of [CuLNO$_3$]$_2$ (**3**)

The complex **3** was synthesized by refluxing a mixture of methanolic solutions of the HL (0.317 g, 1 mmol) and Cu(NO$_3$)$_2$ (0.120 g, 0.5 mmol) for 3 h. The complex formed was collected, washed with ether and dried over P$_4$O$_{10}$ *in vacuo*.



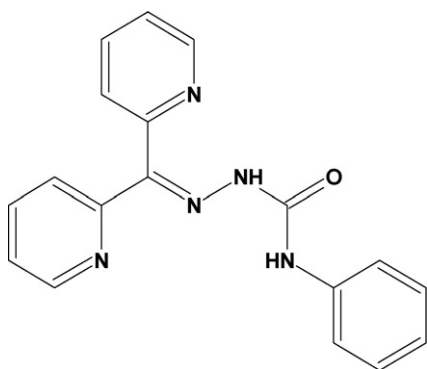**Fig. 1.** Molecular structure of HL.

### 2.4.3. Synthesis of [CuLN$_3$] (**4**)

A solution of HL (0.158 g, 0.5 mmol) in 20 ml of methanol was treated with a methanolic solution of Cu(OAc)$_2$·H$_2$O (0.099 g, 0.5 mmol). The solution was heated under reflux for 1 h and sodium azide (0.032 g, 0.5 mmol) was added in portions to the solution and further refluxed for 2 h. The resulting solution was allowed to stand at room temperature and after slow evaporation the complex was separated out, which was collected, washed with ether and dried over P$_4$O$_{10}$ *in vacuo*.

### 2.4.4. Synthesis of [CuLNCS]·3/2H$_2$O (**5**)

For the synthesis of this complex, methanolic solutions of HL (0.158 g, 0.5 mmol) and Cu(OAc)$_2$·H$_2$O (0.099 g, 0.5 mmol) were mixed and refluxed for 1 h and methanolic solution of KCNS (0.048 g, 0.5 mmol) was added and further refluxed for 3 h. The resulting solution was allowed to stand at room temperature and after slow evaporation the complex was separated out, which was collected, washed with ether and dried over P$_4$O$_{10}$ *in vacuo*.

## 3. Results and discussion

### 3.1. Synthesis of complexes

The semicarbazone, HL was synthesized by the direct condensation of di-2-pyridyl ketone with $N^4$-phenylsemicarbazide. The elemental analysis data obtained was in good agreement with the stochiometry of di-2-pyridyl ketone-$N^4$-phenylsemicarbazone, HL. The ligand can exist in two tautomeric forms, keto and enol forms due to the presence of –NH–C=(O) functional group. However the spectral studies reveal the existence of keto form in the solid state.

The complexes [CuLCl]$_2$·CuCl$_2$·4H$_2$O (**1**), [CuLOAc] (**2**) and [CuLNO$_3$]$_2$ (**3**) were formed by the reaction of the semicarbazone HL with copper chloride, copper acetate and copper nitrate in 1:1, 1:1 and 2:1 molar ratios respectively. In complexes [CuLN$_3$] (**4**) and [CuLSCN]·3/2H$_2$O (**5**) acetate anion was metathetically displaced by azide or thiocyanate anion. In all complexes ligand is coordinated in deprotonated enolate form. The conductivity measurements were carried out in DMSO solutions and all the complexes except **1**, were found to be non-electrolytes [14]. Attempts to isolate single crystals suitable for X-ray diffraction studies were unsuccessful. The colors, elemental analyses, stoichiometries of HL and its complexes are presented in Table 1.

### 3.2. Magnetic susceptibilities

Magnetic moments of the complexes were calculated from magnetic susceptibility measurements. Mononuclear Cu(II) complexes **2**, **4** and **5** exhibit magnetic moments in the range 1.76–2.04 B.M., which are close to the spin-only value [15]. Magnetic moments of binuclear Cu(II) complexes **1** and **3** lie in the range 1.36–1.47 B.M. Low values of magnetic moments for the binuclear complexes may be attributed to the presence of strong antiferromagnetic spin–spin interactions.
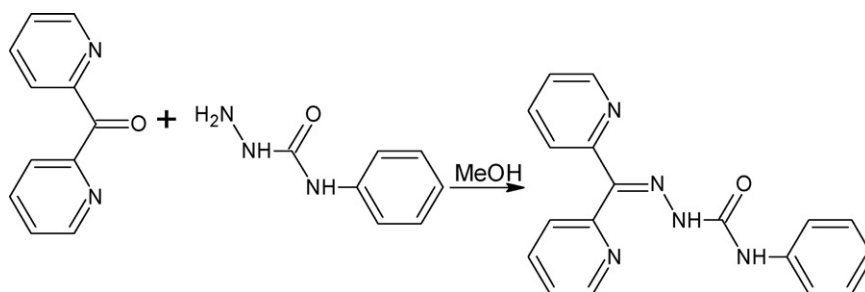
**Fig. 2.** Method of preparation of HL.

**Table 1**
Colors, elemental analyses, magnetic susceptibilities and molar conductivities of Cu(II) complexes of HL.

| Compound | Color | Found (calculated) % | | | $\mu$ (B.M.) | [a] $\Lambda_{M^*}$ |
|---|---|---|---|---|---|---|
| | | C | H | N | | |
| HL | Yellow | 67.44 (68.13) | 4.80 (4.76) | 22.14 (22.07) | – | – |
| [CuLCl]$_2$·CuCl$_2$·4H$_2$O (**1**) | Green | 41.38 (41.69) | 3.51 (3.50) | 13.36 (13.50) | 1.36 | 91 |
| [CuLOAc] (**2**) | Brown | 54.48 (54.73) | 3.61 (3. 90) | 15.82 (15. 96) | 1.76 | 2 |
| [CuLNO$_3$]$_2$ (**3**) | Green | 49.86 (48. 92) | 3.60 (3.19) | 19.71 (19.02) | 1.47 | 24 |
| [CuLN$_3$] (**4**) | Green | 51.4 (51.24) | 3.1 (3.34) | 26.1 (26.56) | 2.04 | 5 |
| [CuLNCS]·3/2H$_2$O (**5**) | Brown | 48.43 (49.08) | 3.11 (3.69) | 18.47 (18.07) | 2.01 | 20 |

[a] $\Omega^{-1}$ cm$^2$ mol$^{-1}$.

## 3.3. Infrared spectral studies

The significant IR bands with the tentative assignments of the semicarbazone, HL and copper(II) complexes are presented in Table 2. The characteristic IR bands of the complexes differ from their uncomplexed semicarbazone, HL and provide significant indications regarding the coordination and bonding sites of the semicarbazone.

The presence of a strong band at 1718 cm$^{-1}$ for the semicarbazone, HL is assigned to C=O stretching vibration, which is absent in all complexes. This indicates that in these complexes HL has undergone deprotonation and coordinated in the enolate form. It is further corroborated with the appearance of a band in the 413–456 cm$^{-1}$ region due to a $\nu$(Cu–O) in the spectra of the complexes [16–18]. The $\nu$(NH) band of the imino group is observed at 3369 cm$^{-1}$ in the IR spectrum of HL and this band disappears in the spectra of the complexes, providing a strong evidence for the ligand coordination around copper(II) ion in the deprotonated form [15]. The intense band at 1591 cm$^{-1}$ in the spectrum of HL has been assigned to $\nu$(C=N) of the semicarbazone moiety. This band is shifted to lower wavenumbers by 23–35 cm$^{-1}$ in the spectra of complexes indicating coordination *via* the azomethine nitrogen [19–21]. Coordination of azomethine nitrogen is consistent with the presence of a band in the 504–511 cm$^{-1}$ region, assignable to $\nu$(Cu–N$_{azomethine}$) for these complexes [15,22]. But with loss of a proton from N, another strong band is found in the region 1599–1597 cm$^{-1}$ which may be due to the newly formed C=N bond due to enolization of the semicarbazone, which again confirms the coordination *via* enolate oxygen. The increase in $\nu$(N–N) in the spectra of complexes in the range 1143–1154 cm$^{-1}$ is due to enhanced double bond character through chelation, thus offsetting the loss of electron density *via* donation to the metal ion, and is supportive of azomethine coordination. Coordination of the pyridyl nitrogen causes the out-of-plane bending vibrational band to shift from 601 cm$^{-1}$ to higher frequencies 625, 615, 623, 634, 621 and 621 cm$^{-1}$ respectively for the complexes **1**–**5** [23,24]. The presence of broad bands at 3435 and 3423 cm$^{-1}$ for the complexes **1** and **5** indicates the presence of lattice water [25].

The asymmetric and symmetric stretching vibrations of the acetate group appear at 1520 and 1384 cm$^{-1}$ respectively for the acetato complex **2** having the separation value $\Delta\nu$ = 136 cm$^{-1}$ suggests the presence of chelating acetate group linked with the metal center for the complex [26,27]. For the nitrato complex **3**, three strong bands at 1542, 1384 and 1298 cm$^{-1}$ are observed corresponding to $\nu_1$, $\nu_2$ and $\nu_4$ of the nitrato group indicating the presence of a terminal monodentate coordination of the nitrato group [28]. A combination of ($\nu_1 + \nu_2$) which is considered as diagnostic for the monocoordinated nitrato group has been observed at 1698 cm$^{-1}$. The bands due to $\nu_3$, $\nu_5$ and $\nu_6$ could not be assigned due to the richness of the spectrum of the complex. The azido complex **4** shows a single strong band at 2054 cm$^{-1}$ due to the asymmetric stretching mode and the band associated with symmetric stretching mode is located at 1387 cm$^{-1}$ [29]. Thiocyanato complex **5** has a very strong band at 2091 cm$^{-1}$, a medium band at 775 cm$^{-1}$ and a weak band at 493 cm$^{-1}$ corresponding to $\nu$(CN), $\nu$(CS) and $\delta$(NCS), respectively [30]. The intensity and band position indicate the unidentate coordination of the thiocyanate through nitrogen atom.

## 3.4. Electronic spectral studies

The tentative assignments of the significant electronic spectral bands of the semicarbazone and its copper(II) complexes recorded

**Table 2**
Infrared spectral assignments of the semicarbazone and Cu(II) complexes.

| Compound | $\nu$(NH) | $\nu$(C=N) | $\nu$(CO) | $\nu$(N=C) | $\nu$(N–N) | $\nu$(Cu–N$_{azo}$) | $\nu$(Cu–O) |
|---|---|---|---|---|---|---|---|
| HL | 3369 | 1591 | 1718 | – | 1129 | – | – |
| [CuLCl]$_2$·CuCl$_2$·4H$_2$O (**1**) | – | 1568 | – | 1599 | 1154 | 504 | 447 |
| [CuLOAc] (**2**) | – | 1562 | – | 1598 | 1146 | 507 | 413 |
| [CuLNO$_3$]$_2$ (**3**) | – | 1568 | – | 1597 | 1147 | 508 | 456 |
| [CuLN$_3$] (**4**) | – | 1562 | – | 1599 | 1144 | 504 | 414 |
| [CuLNCS]·3/2H$_2$O (**5**) | – | 1556 | – | 1598 | 1143 | 511 | 413 |

**Table 3**
Electronic spectral assignments of HL and its Cu(II) complexes.

| Compound | $\pi-\pi^*$ | $n-\pi^*$ | LMCT | $d-d$ |
|---|---|---|---|---|
| HL | 40,000 | 30,770 | – | – |
| [CuLCl]$_2$·CuCl$_2$·4H$_2$O (**1**) | 38,460 | 32,360 | 23,830 | 14,590 |
| [CuLOAc] (**2**) | 38,670 | 32,170 | 23,910 | 15,200 |
| [CuLNO$_3$]$_2$ (**3**) | 38,700 | 32,030 | 23,900 | 16,000 |
| [CuLN$_3$] (**4**) | 38,680 | 32,020 | 23,910 | 14,600 |
| [CuLNCS]·3/2H$_2$O (**5**) | 38,480 | 32,470 | 23,910 | 15,300 |

in DMSO are presented in Table 3. HL has absorption at 40,000 cm$^{-1}$ due to the $\pi-\pi^*$ transitions of the pyridyl rings and imine function of the semicarbazone moiety. Another band at 30,770 cm$^{-1}$ for HL corresponds to $n-\pi^*$ transition of the amide function [31]. These bands were shifted upon complexation which is an indication of the enolization followed by the deprotonation of the semicarbazone during complexation. The $\pi-\pi^*$ bands are shifted to longer wavelengths in complexes due to the weakening of C=O bond and the conjugation system enhanced on complexation. The $n-\pi^*$ bands in the complexes have shown a blue shift due to donation of lone pair of electrons to the metal and hence the coordination of azomethine with a reduction of intensity. Strong bands in the 23,830–23,910 cm$^{-1}$ range observed in the spectra of all Cu(II) complexes are assigned to O → Cu and N → Cu LMCT transitions. In the chloro complex **1**, a shoulder observed at 23,300 cm$^{-1}$ is assigned as Cl → Cu charge-transfer transition [32]. All the complexes gave $d-d$ bands in the 14,950–16,000 cm$^{-1}$ range [33,34]. For the Cu(II) complexes there are three spin allowed transitions, $A_{1g} \leftarrow B_{1g}$, $B_{2g} \leftarrow B_{1g}$ and $E_g \leftarrow B_{1g}$, but it is difficult to resolve them into separate bands due to the very low energy difference between these bands.

### 3.5. Electron paramagnetic resonance spectra

EPR spectra of the complexes recorded in polycrystalline state at room temperature provide information about the coordination environment around Cu(II) in these complexes. The EPR spectral assignments of the Cu(II) complexes are presented in Table 4 and the experimental and simulated best fits [35] of EPR spectra of the complexes are given in Figs. 3 and 4.

The EPR spectra of the compounds **1** and **3** in the polycrystalline state at 298 K show only one broad signal at $g_{iso} = 2.089$ and 2.129, respectively. Such isotropic spectra arise from extensive
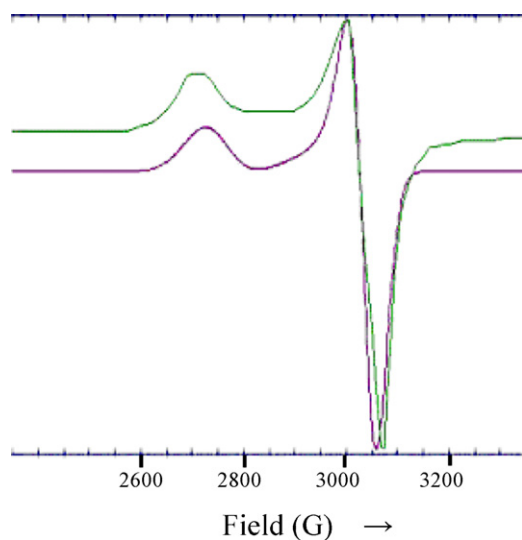


**Fig. 3.** Experimental (green) and simulated best fit (purple) of the EPR spectra of [CuLN$_3$] (**4**) in polycrystalline state at 298 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

exchange coupling through misalignment of the local molecular axes between different molecules in the unit cell (dipolar broadening) and enhanced spin lattice relaxation. This type of spectra unfortunately give no information about the electronic ground state of the Cu(II) ion present in the complex. For the compounds **2** and **4** we got axial spectra with well defined $g_{||}$ and $g_\perp$ features. The variation in $g_{||}$ and $g_\perp$ values in these complexes indicate the geometry of the compounds in the solid state is affected by the nature of the coordinating gegenions. The geometric parameter $G$ is calculated as $G = g_{||} - 2.0023/g_\perp - 2.0023$ for axial spectra and it is a measure of exchange interaction between copper centers in the polycrystalline compound. If $G > 4.4$, exchange interaction is negligible and if it is less than 4.4, considerable exchange interaction is indicated in the solid complex [36–38]. The geometric parameter $G$ for the compounds **2** and **4** are 3.258 and 2.448, respectively, which shows that exchange interaction is strong. For the complexes **2** and **4**, $g_{||} > g_\perp > 2$ and $G$ values falling in the range 2–4 are consistent with a $d_{x^2-y^2}$ ground state. For the compound **5** we got three $g$ values $g_1 = 2.028$, $g_2 = 2.104$ and $g_3 = 2.306$ which indicate rhombic distortion in geometry. In the spectra with $g_3 > g_2 > g_1$ rhombic spectral values, $R = g_2 - g_1/g_3 - g_2$ may be significant. If $R > 1$, a predominant $d_z^2$ ground state is present and if $R < 1$ a predominant $d_{x^2-y^2}$ state is present and if $R = 1$ then the ground state is approximately an equal mixture of $d_z^2$ and $d_{x^2-y^2}$. For the complex **5**, $R < 1$ suggesting a $d_{x^2-y^2}$ ground state, which indicates that exchange interaction is negligible.

The solution spectra of all complexes were recorded in DMF at 77 K. An axial spectrum was obtained for compound **1** with 2.250, 2.061 and $178.33 \times 10^{-4}$ cm$^{-1}$ as $g_{||}$, $g_\perp$ and $A_{||}$ values. In the low field region, seven hyperfine lines are obtained that are moderately resolved suggesting a dimeric structure with two copper centers. This seven line hyperfine splitting is due to interaction of the electrons with two copper nuclei ($^{65,63}$Cu, $I = 3/2$) so that electrons are exchanged between two Cu(II) ions via the bridging chlorine atoms at a rate faster than EPR time scale. The binuclear nature was confirmed by the presence of half field signal ($\Delta M_s = \pm 2$) at 1570 G with $g$ value 4.133. It is observed that $g$ values of this complex in the solid state at 298 K and in DMF at 77 K are not much different from each other hence the geometry around the Cu(II) ion is unaffected on cooling the solution to liquid nitrogen temperature. As $g_{||} > g_\perp$, the possibility of trigonal bipyramidal geometry has been ruled out and square pyramidal structure is suggested. In the compound **2**, an axial spectrum is obtained with $g_{||} = 2.250$ and $g_\perp = 2.045$ values. Spectrum of this complex has four copper hyperfine lines in both parallel and perpendicular regions. $A_{||}$(Cu) and $A_\perp$(Cu) are calculated to be $150 \times 10^{-4}$ and $16 \times 10^{-4}$ cm$^{-1}$, respectively. $A_{av}$ is calculated by using the formula $A_{av} = 1/3 (A_{||} + 2A_\perp)$ and it is $60.666 \times 10^{-4}$ cm$^{-1}$. For the nitrato complex **3**, in the parallel region three of the copper hyperfine lines are moderately resolved while perpendicular features overlap the fourth one. Appearance of seven lines in the perpendicular region is due to nitrogen superhyperfine splitting. Here the $g_{||} = 2.240$, $g_\perp = 2.051$ and $A_{||} = 159 \times 10^{-4}$ cm$^{-1}$. The presence of half field signal indicates a dimeric structure for this complex ($g = 4.332$). For the azido complex **4** also we got an axial spectrum with $g_{||} = 2.233$, $g_\perp = 2.047$ and $A_{||} = 152 \times 10^{-4}$ cm$^{-1}$ values. The spectrum shows well resolved four hyperfine lines in the parallel region corresponding to monomeric Cu(II) complex. In thiocyanato complex **5**, an axial spectrum is obtained with four hyperfine lines having $g_{||} = 2.223$, $g_\perp = 2.066$ and $A_{||} = 195 \times 10^{-4}$ cm$^{-1}$ values. Here for the complexes **2–5**, $g_{||} > g_\perp$ which suggest a square planar geometry. For all the compounds $g_{av}$ is also calculated using the equation, $g_{av} = 1/3(g_{||} + 2g_\perp)$ and it is in the range 2.109–2.124. According to Kivelson and Neiman considerable covalent character is suggested for M–L bond as for all the complexes $g_{||} < 2.3$ [39].

**Table 4**
EPR spectral assignments of Cu(II) complexes in polycrystalline state at 298 K and solution at 77 K.

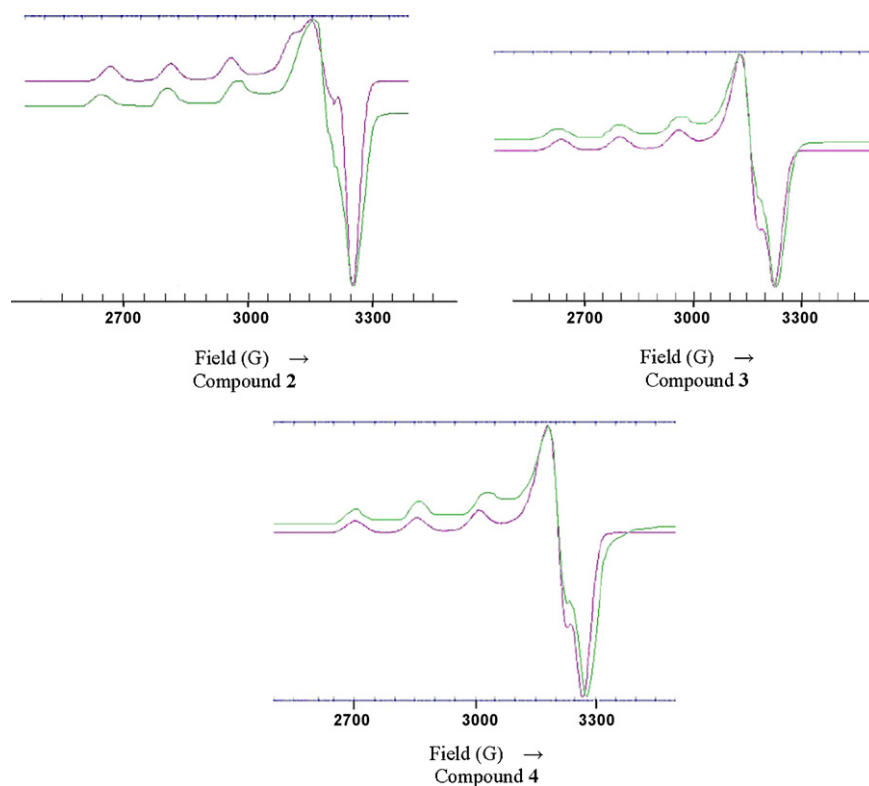| Compound | Polycrystalline state (298 K) | | | | DMF solution (77 K) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $g_{iso}$ | $g_{\parallel}/g_3$ | $g_{\perp}/g_1, g_2$ | $G$ | $g_{\parallel}$ | $g_{\perp}$ | $g_{av}$ | $A_{\parallel}{}^a$ | $A_{\perp}{}^a$ | $A_{av}{}^a$ |
| [CuLCl]$_2$·CuCl$_2$·4H$_2$O (**1**) | 2.089 | – | – | – | 2.250 | 2.061 | 2.124 | 178.33 | – | – |
| [CuLOAc] (**2**) | – | 2.262 | 2.082 | 3.258 | 2.250 | 2.045 | 2.113 | 150 | 16 | 60.666 |
| [CuLNO$_3$]$_2$ (**3**) | 2.129 | – | – | – | 2.240 | 2.051 | 2.114 | 159 | – | – |
| [CuLN$_3$] (**4**) | – | 2.315 | 2.130 | 2.448 | 2.233 | 2.047 | 2.109 | 152 | – | – |
| [CuLNCS]·3/2H$_2$O (**5**) | – | 2.306 | 2.104, 2.028 | – | 2.223 | 2.066 | 2.118 | 195 | – | – |

[a] A values in $10^{-4}$ cm$^{-1}$.



**Fig. 4.** Experimental (green) and simulated best fit (purple) of the EPR spectra of complexes **2–4** in frozen DMF at 77 K. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The EPR bonding parameters are given in Table 5. The EPR parameters $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$(Cu) and the energies of $d$–$d$ transitions were used to evaluate the bonding parameters $\alpha^2$, $\beta^2$ and $\gamma^2$ which may be regarded as measures of covalency of the in-plane $\sigma$ bonds, in-plane $\pi$ bonds and out-of-plane $\pi$ bonds, respectively. The value of in-plane $\sigma$ bonding parameter $\alpha^2$ was estimated from the expression [40]

$$\alpha^2 = -\frac{A_{\parallel}}{0.036} + (g_{\parallel} - 2.00277) + \frac{3}{7}(g_{\perp} - 2.00277) + 0.04$$

The orbital reduction factors, $K_{\parallel}^2 = \alpha^2 \beta^2$ and $K_{\perp}^2 = \alpha^2 \gamma^2$ were calculated using the following expressions [41].

$$K_{\parallel}^2 = \frac{(g_{\parallel} - 2.00277)\, E_{d-d}}{8\lambda_0}$$

$$K_{\perp}^2 = \frac{(g_{\perp} - 2.00277)\, E_{d-d}}{2\lambda_0}$$

where $\lambda_0$ is the spin orbit coupling constant with a value of $-828$ cm$^{-1}$ for Cu(II) $d^9$ system.

**Table 5**
EPR bonding parameters of Cu(II) complexes.

| Compound | $\alpha^2$ | $\beta^2$ | $\gamma^2$ | $K$ | $K_{\parallel}$ | $K_{\perp}$ | $f^a$ |
|---|---|---|---|---|---|---|---|
| [CuLCl]$_2$·CuCl$_2$·4H$_2$O (**1**) | 0.807 | 0.674 | 0.635 | – | 0.738 | 0.716 | 126.17 |
| [CuLOAc] (**2**) | 0.721 | 0.785 | 0.536 | – | 0.753 | 0.622 | 150.00 |
| [CuLNO$_3$]$_2$ (**3**) | 0.739 | 0.774 | 0.630 | – | 0.756 | 0.682 | 140.88 |
| [CuLN$_3$] (**4**) | 0.711 | 0.718 | 0.551 | – | 0.714 | 0.626 | 146.90 |
| [CuLNCS]·3/2H$_2$O (**5**) | 0.829 | 0.614 | 0.704 | – | 0.7137 | 0.764 | 114.01 |

[a] Expressed in units of cm.

According to Hathaway [42], for pure σ bonding $K_\parallel \approx K_\perp \approx 0.77$, and for in-plane π bonding, $K_\parallel < K_\perp$; while for out-of-plane π bonding, $K_\perp < K_\parallel$. In all the complexes, except **5** it is observed that $K_\perp < K_\parallel$ which indicates the presence of significant out-of-plane π bonding. In the complex **5**, $K_\parallel < K_\perp$, indicating in-plane π bonding. Furthermore, $\alpha^2$, $\beta^2$ and $\gamma^2$ have values less than 1 which is expected for 100% ionic character of bonds; suggest the covalency of the bonds. The empirical factor $f = g_\parallel/A_\parallel$ (cm$^{-1}$) is an index of tetragonal distortion and depends on the nature of the coordinated atom. In all the compounds, $f$ falls in the range 114–150 cm$^{-1}$ corresponding to a Cu(II) center with medium to extreme distortion [43].

## Acknowledgements

## References

[1] H. Beraldo, D. Gaminob, Mini Rev. Med. Chem. 4 (2004) 31–39.
[2] D.X. West, P.B. Sonawane, A.S. Kumbhar, R.G. Yerande, Coord. Chem. Rev. 123 (1993) 49–71.
[3] T. Matsukura, H. Tanaka, Biochemistry 65 (2000) 817–823.
[4] T.S. Lobana, R. Sharma, G. Bawa, S. Khanna, Coord. Chem. Rev. 253 (2009) 977–1055.
[5] H. Cerecetto, M. González, Curr. Top. Med. Chem. 2 (2002) 1185–1211.
[6] R.N. Patel, K.K. Shukla, A. Singh, M. Choudhary, U.K. Chauhan, S. Dwivedi, Inorg. Chim. Acta 362 (2009) 4891–4898.
[7] V. Mahalingam, N. Chitrapriya, F.R. Fronczek, K. Natarajan, Polyhedron 27 (2008) 2743–2750.
[8] M.C. Rodríguez-Argüelles, S. Mosquera-Vázquez, J. Sanmartin-Matalobos, A.M. García-Deibe, C. Pelizzi, F. Zani, Polyhedron 29 (2010) 864–870.
[9] R. Sharma, S.K. Agarwal, S. Rawat, M. Nagar, Transit. Met. Chem. 31 (2006) 201–206.
[10] E.R. Garbelini, M. Hörner, V.F. Giglio, A.H. da Silva, A. Barison, F.S. Nunes, Z. Anorg, Allg. Chem. 635 (2009) 1236–1241.
[11] T.A. Reena, E.B. Seena, M.R.P. Kurup, Polyhedron 27 (2008) 1825–1831.
[12] T.A. Reena, E.B. Seena, M.R.P. Kurup, Polyhedron 27 (2008) 3461–3466.
[13] O. Pouralimardan, A.-C. Chamayou, C. Janiak, H.H. Monfared, Inorg. Chim. Acta 360 (2007) 1599–1608.
[14] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81–122.
[15] E.B. Seena, M.R.P. Kurup, Polyhedron 26 (2007) 829–836.
[16] R.C. Chikate, A.R. Belapure, S.B. Padhye, D.X. West, Polyhedron 24 (2005) 889–899.
[17] P. Bindu, M.R.P. Kurup, T.R. Satyakeerty, Polyhedron 18 (1998) 321–331.
[18] J. Jezierska, B. Jezowska-Trzebiatowska, G. Petrova, Inorg. Chim. Acta 50 (1981) 153–157.
[19] A. Sreekanth, H.-K. Fun, M.R.P. Kurup, Inorg. Chem. Commun. 7 (2004) 1250–1253.
[20] B.S. Garg, M.R.P. Kurup, S.K. Jain, Y.K. Bhoon, Transit. Met. Chem. 13 (1988) 92–95.
[21] B.S. Garg, M.R.P. Kurup, S.K. Jain, Y.K. Bhoon, Transit. Met. Chem. 13 (1988) 247–249.
[22] P.B. Sreeja, M.R.P. Kurup, Polyhedron 23 (2004) 575–581.
[23] V. Philip, V. Suni, M.R.P. Kurup, Polyhedron 25 (2006) 1931–1938.
[24] V. Philip, V. Suni, M.R.P. Kurup, M. Nethaji, Spectrochim. Acta A 64 (2006) 171–177.
[25] V. Stefov, V.M. Petruševski, B. Šoptrajanov, J. Mol. Struct. 293 (1993) 97–100.
[26] A. Sreekanth, U.L. Kala, C.R. Nayar, M.R.P. Kurup, Polyhedron 23 (2004) 41–47.
[27] R. Kruszynski, A. Turek, J. Coord. Chem. 57 (2004) 1089–1098.
[28] A.B.P. Lever, E. Mantovani, B.S. Ramaswami, Can. J. Chem. 49 (1971) 1957–1961.
[29] S. Sasi, M.R.P. Kurup, E. Suresh, J. Chem. Cryst. 37 (2007) 31–36.
[30] R.A. Bailey, S.L. Kozak, T.W. Michelsen, W.N. Mills, Coord. Chem. Rev. 6 (1971) 407–445.
[31] V.L. Siji, M.R.S. Kumar, S. Suma, M.R.P. Kurup, Spectrochim. Acta A 76 (2010) 22–28.
[32] M.J.M. Campbell, Coord. Chem. Rev. 15 (1975) 279–319.
[33] R.P. John, A. Sreekanth, V. Rajakannan, T.A. Ajith, M.R.P. Kurup, Polyhedron 23 (2004) 2549–2559.
[34] M. Joseph, M. Kuriakose, M.R.P. Kurup, E. Suresh, A. Kishore, G. Bhat, Polyhedron 25 (2006) 61–70.
[35] G. Swarnabala, M.V. Rajasekharan, Inorg. Chem. 28 (1989) 662–666.
[36] I.M. Proctor, B.J. Hathaway, P. Nicholis, J. Chem. Soc. A (1968) 1678–1684.
[37] S.K. Jain, B.S. Garg, Y.K. Bhoon, Spectrochim. Acta 42A (1986) 959–968.
[38] B.J. Hathaway, D.E. Billing, Coord. Chem. Rev. 5 (1970) 143–207.
[39] D. Kivelson, R. Neiman, J. Chem. Phys. 35 (1961) 149–155.
[40] A.H. Maki, B.R. McGarvey, J. Chem. Phys. 29 (1958) 31–35.
[41] B.N. Figgis, Introduction to Ligand Fields, Interscience, New York, 1996, p. 295.
[42] B.J. Hathaway, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol.5, Pergamon, Oxford, 1987, p. 533.
[43] L. Latheef, M.R.P. Kurup, Spectrochim. Acta A 70 (2008) 86–93.