Journal of Molecular Structure 1054-1055 (2013) 76-82

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Molecular structure, vibrational and EPR spectra of Cu(II) chloride complex of 4-amino-1-methylbenzene combined with quantum chemical calculations

T. Bardakçı *, M. Kumru, S. Güner

Department of Physics, Faculty of Arts and Sciences, Fatih University, 34500 Büyükçekmece, İstanbul, Turkey

HIGHLIGHTS

- Frequencies and the geometry parameters of L and [CuCl₂L₂] were
- calculated. • The DFT results were compared with FT-FIR, FT-IR, and dispersive Raman data.
- The normal modes have been assigned on the basis of the PED.
- EPR was performed to investigate the molecular arrangement around the copper atom.

A R T I C L E I N F O

Article history: Received 19 July 2013 Received in revised form 11 September 2013 Accepted 18 September 2013 Available online 25 September 2013

Keywords: IR and Raman spectra EPR DFT 4-Amino-1-methylbenzene Aniline derivatives Cu(II) complex

ABSTRACT

Transition metal complex of $CuCl_2$ with L = 4-amino-1-methylbenzene, i.e., $[CuCl_2L_2]$, has been synthesized and characterized by elemental analyses, FT-IR, dispersive Raman and EPR methods. The geometrical structure and vibrational spectra of L and $[CuCl_2L_2]$ have been investigated in terms of density functional calculations employing the 6-311G+(d,p) basis set. The normal modes have been assigned on the basis of the percent potential energy distribution (PED) of the internal motions in each vibrational modes. The effects of the coordination on vibrational modes have been investigated. The experimental vibrational and EPR spectral studies and theoretical calculations find the title complex as a doublet with one unpaired electron.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Aniline and its derivatives are widely used in electro-optical and microelectronic devices such as diodes and transistors, and as pharmaceuticals [1–5]. The aniline derivative 4-amino-1-meth-ylbenzene ($4-C_7H_9N$), which is abbreviated as L in this study, con-

sists of a methyl group attached to aniline at the para position. It is also known as *p*-toluidine, *p*-methylaniline, 4-methylaniline, *p*aminotoluene and 4-aminotouluene. L and related compounds have wide applications as an intermediate in the production of dyes [6] and as ligands in coordination chemistry [7–16].

Despite extensive studies on vibrational spectra of transition metal complexes of aniline and its derivatives [7-16], to the best of our knowledge, neither complete vibrational or theoretical study has been performed on CuCl₂ complex of L, i.e., on [CuCl₂L₂]. In this

G R A P H I C A L A B S T R A C T





CrossMark

^{*} Corresponding author. Tel.: +90 212 8663300/2059; fax: +90 212 8890832. *E-mail address*: tayyibe.b@gmail.com (T. Bardakçı).

^{0022-2860/\$ -} see front matter @ 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.molstruc.2013.09.025

study, we investigate IR and Raman spectra of L and its $[CuCl_2L_2]$ complex experimentally. To assign the experimental vibrational bands in terms of internal vibrations in the modes, we performed density functional theory (DFT) calculations. We have already shown that the hybrid DFT functional B3LYP is superior to the HF and MP2 methods in investigating vibrational spectra of L [3]. The effects of coordination on the vibrational modes have also been discussed. Moreover, we have investigated the structure of the [CuCl_2L_2] complex based on the experimental vibrational and EPR spectra as well as theoretical DFT studies.

2. Experimental

2.1. Material and synthesis

The ligand, L and CuCl₂ at the reagent grade were purchased from Aldrich Chemical Company Inc., and used without further purification.

 $[CuCl_2L_2]$ was synthesized by adding two moles of L to one mole of CuCl_2 in ethyl alcohol with constant stirring. The precipitated complex was filtered, washed with diethylether and dried in vacuum. All these processes were carried out at room temperature. The experimental C, H, N and Cu contents of the synthesis complex agree very well with the theoretically expected contents of the $[CuCl_2L_2]$ (see Table 1).

2.2. FT-IR measurements

The 3500–500 cm⁻¹ region FT-IR spectra of L and [CuCl₂L₂] were recorded on a Nicolet 6700 Fourier Transform IR (FT-IR) spectrometer with attenuated total reflectance (ATR) sampling technique at room temperature. The far region (650–50 cm⁻¹) FT-IR (FT-FIR) spectra of L and [CuCl₂L₂] were recorded on the same spectrometer but by preparing polyethylene (PE) pellets. PE pellets were prepared as described previously taking the sample/PE ratio as 1/10 [17], i.e., ~8 mg of PE and 0.8 mg of sample were mixed and ground in a mortar. The metalic die was heated to 230 °C, and the temperature of the die surface was expected to be 120-140 °C (since the melting point of PE is 120–130 °C). The mixture of PE and samples were added to the die, and put under 6-ton pressure for 2 min. Then the die was disassembled and the PE pellet was put in the pellet holder of FT-IR spectrometer to record the far IR region of the spectrum. Since the expansion is big for far region, the spectra of the title molecules appear discontinuous.

2.3. Dispersive Raman measurements

The room temperature $3500-50 \text{ cm}^{-1}$ region Raman spectra of L and [CuCl₂L₂] were recorded with Dispersive Raman Microscope (DXR) by using a laser of 532 nm wavelength. At the laser powers that do not burn the present dark-colored complex, a good-resolved dispersive Raman spectrum could not be recorded.

2.4. EPR measurement

A conventional X-Band Bruker EMX model EPR spectrometer employing an AC magneticfield (5 kHz) modulation technique

Table 1

Elemental analysis of the $[CuCl_2L_2]$ as percentage.

| Comp. | Found (cal.)% | | | | | | | |
|--|------------------|------------------|----------------|----------------|--|--|--|--|
| | Cu | С | Ν | Н | | | | |
| [CuCl ₂ L ₂] (Theoretical) | 18.49 (18.22) | 48.16 (48.21) | 7.84 (8.03) | 5.17 (5.21) | | | | |

was used to record the first-derivative absorption signals at the room temperature. A cylindrical quartz tube was used to place the powder sample in the cavity. Operating conditions were chosen as 0.2 mW microwave power, 1 Oe modulation amplitude, 3300 Oe centerfield, 600 Oe sweep width, 81.92 ms time constant and 83.89 s sweep time with multiple accumulations to enhance the signal-to-noise ratio.

3. Quantum chemical calculations

Quantum chemical calculations were performed with Gaussian 03 software package [18] on a linux server cluster. The structures and normal modes were visualized by Gausview 03 program [19]. The geometry optimizations, vibrational spectra calculations, and percent potential energy distribution (PED) of free L and [CuCl₂L₂] complex in the gas phase were performed by the DFT exchange-correlation functionals BVP86 and B3LYP employing the 6-311G+(d,p) basis set. BVP86 is a combination of Becke's 1988 exchange functional [20], Vosko's correlation functional V for local spin density part [21] and Perdew's 1986 gradient correlation functional [22] while B3LYP consists of Becke's three-parameter exchange and Lee–Yang–Parr's correlation functional [23–25].

4. Results and discussion

4.1. Molecular structure

The optimized molecular structures of free L and $[CuCl_2L_2]$ complex in the gas phase at the room temperature (see Fig. 1 and Table 2) have been obtained in terms of BVP86 and B3LYP density functionals with the 6-311G+(d,p) basis set. The standard error S and the mean absolute error MAE in the bond lengths relative to the previous X-ray data of L [26] are respectively 0.183 and 0.014 with B3LYP, and 0.184 and 0.018 with BVP86. S and MAE for the bond angles are respectively 0.464 and 1.213 with B3LYP, and 0.470 and 1.125 with BVP86. Therefore, B3LYP performs slightly better than BVP86 both for the bond lengths and the bond angles.

DFT calculations predict some changes in the geometry parameters of L with coordination. For instance, C–N bond has been increased from 1.404 Å to 1.439 Å with BVP86, and from 1.401 Å to 1.442 Å with B3LYP. N–H bond has also been increased 0.007 Å with two of the methods. C–C bonds generally remain unchanged; however bonds close to Nitrogen atom i.e. C2–C3 and C3–C4 have been decreased because of coordination.

 $[CuCl_2L_2]$ complex can in principle be found in doublet, quartet and sextet spin states with one, three and five unpaired electrons, respectively. The present DFT calculations exclusively predict doublet ground state with one unpaired electron for the complex at the room temperature (Table 3). The quartet and sextet spin states lie ~80 and ~160 kcal/mol above the ground-state doublet, respectively. Thus these two higher energy spin states are not accessible at the room temperature. DFT calculations predict the Cu–N bonds by 0.17 Å shorter than the Cu–Cl bonds (Table 4).

4.2. Vibrational assignments

All observed IR and Raman normal modes of L and $[CuCl_2L_2]$ (Figs. 2–4) have been assigned with the aid of DFT calculations (Table 5). The DFT calculations overestimate generally the vibrational frequencies due to the neglect of crystal packing effects and anharmonicity as well as the basis set and electronic correlation incompleteness. Therefore, we derived scaling factors on L and applied them to $[CuCl_2L_2]$ to approximately account for the computational errors. For the frequencies above and below 1623 cm⁻¹, the BVP86 scaling factors are 0.974 ($R^2 = 0.79$) and 1.005 ($R^2 = 0.996$) and, the



Fig. 1. The optimized geometries of (a) the ligand L (b) the complex [CuCl₂L₂].

| Table 2 | |
|--|--|
| Geometry parameters of free L and [CuCl ₂ L ₂]. | |

| | Experimental ^a | BVP86 – 6-311G | G+(d,p) | B3LYP – 6-311G+(d,p) | | |
|--------------------------|---------------------------|----------------|-------------------------------------|----------------------|-------------------------------------|--|
| | | L | [CuCl ₂ L ₂] | L | [CuCl ₂ L ₂] | |
| Interatomic distance (Å) | | | | | | |
| C1–C2 | 1.40 | 1.398 | 1.397 | 1.392 | 1.392 | |
| C2–C3 | 1.39 | 1.409 | 1.403 | 1.401 | 1.395 | |
| C3–C4 | 1.36 | 1.409 | 1.403 | 1.401 | 1.395 | |
| C4–C5 | 1.39 | 1.397 | 1.397 | 1.391 | 1.392 | |
| C5–C6 | 1.40 | 1.406 | 1.407 | 1.399 | 1.399 | |
| C6–C1 | 1.39 | 1.406 | 1.407 | 1.398 | 1.399 | |
| C—N | 1.43 | 1.404 | 1.439 | 1.401 | 1.442 | |
| C-CH ₃ | 1.55 | 1.512 | 1.511 | 1.510 | 1.509 | |
| N—H | 1.02 | 1.018 | 1.025 | 1.010 | 1.017 | |
| C—H (ring) | 1.08 | 1.094 | 1.092 | 1.086 | 1.084 | |
| C—H (methyl) | 1.09 | 1.102 | 1.101 | 1.094 | 1.093 | |
| H···H (amino) | | 1.683 | 1.687 | 1.671 | 1.665 | |
| H· · ·H (methyl) | | 1.776 | 1.776 | 1.764 | 1.765 | |
| Angle (Degree) | | | | | | |
| C6-C1-C2 | 121.5 | 121.8 | 121.5 | 121.7 | 120.6 | |
| C1C2C3 | 119.2 | 120.6 | 119.6 | 120.6 | 118.1 | |
| C2-C3-C4 | 120.3 | 118.0 | 119.9 | 118.1 | 120.6 | |
| C3–C4–C5 | 120.5 | 120.6 | 119.6 | 120.6 | 121.7 | |
| C4–C5–C6 | 120.5 | 121.8 | 121.5 | 121.7 | 121.7 | |
| C5-C6-C1 | 117.8 | 117.2 | 117.8 | 117.2 | 117.2 | |
| N15-C3-C2 (C4) | | 120.9 | 120.0 | 120.9 | 120.9 | |
| C11–C6–C1 (C5) | | 121.4 | 121.1 | 121.4 | 121.4 | |
| H—N—H | 113.0 | 111.6 | 110.8 | 111.7 | 111.7 | |
| C—C—H (methyl) | | 111.5 | 111.4 | 111.4 | 111.4 | |
| H—C—H (methyl) | 109.5 | 107.2 | 108.1 | 107.5 | 107.5 | |
| H—N—C | | 115.0 | 112.0 | 115.3 | 115.3 | |

^a Taken from Ref. [26].

4.2.1. N—H vibrations

B3LYP scaling factors are 0.952 ($R^2 = 0.79$) and 0.976 ($R^2 = 0.996$), respectively. These scaling factors are similar to the previously derived factors for L [3].

Table 3

Computed relative energies (kcal/mol) of different spin states of [CuCl₂L₂].

| | Relative energy (kcal/mol) | |
|---------|----------------------------|--------------------|
| | BVP86/6-311G+(d,p) | B3LYP/6-311G+(d,p) |
| Doublet | 0.0 | 0.0 |
| Quartet | 81.7 | 83.2 |
| Sextet | 153.3 | 167.1 |

For primary amines, N—H streetching vibrations generally occur at 3500–3300 cm⁻¹ region [27,28]. In this study, the asymmetric and the symmetric N–H vibrations of L are observed at 3418 and 3337 cm⁻¹ in accordance with the literature. They downshift to 3301 and 3234 cm⁻¹, i.e., by 117 and 103 cm⁻¹, upon coordination. The modes at ~1600 and ~1500 cm⁻¹ contain coupled C–C stretching and NH₂ scissoring vibrations. They downshift by ~15 cm⁻¹ upon coordination. The NH₂ rocking vibration appears in the previous studies at 1074 cm⁻¹ for the free L and ~1100 cm⁻¹ for its transition metal complexes [3,7,8,16,29]. Analogously, in this study, DFT calculations show that NH₂ rocking vibration (41%) occurs at

${\sim}1100~\text{cm}^{-1}$ (scaled) for the complex, and at ${\sim}1075~\text{cm}^{-1}$ (scaled) for the free L.

4.2.2. C–N vibrations

Mixing of the several bands makes the identification of C–N vibrations difficult. Silverstein [30] assigned C–N stretching

2.130-2.094

2.082-2.081

| Table 4Key geometry parameters of $[CuCl_2L_2]$ complex in the gas phase around the coordination site at different spin states. | | | | | | | | | |
|---|-------------------|-------------|--------------------|--|--|--|--|--|--|
| Interatomic distance (Å) | BVP86 6-311G+(d,p |) | B3LYP 6-311G+(d,p) | | | | | | |
| | Cu–Cl | Cu-N | Cu-Cl | | | | | | |
| Doublet | 2.261-2.261 | 2.090-2.090 | 2.272-2.272 | | | | | | |

2.257-2.250

2 265-2 257



Quartet

Sextet

Fig. 2. The experimental mid region FT-IR spectra of L (top) and [CuCl₂L₂] (bottom).



Fig. 3. The experimental far region FT-IR spectra of L (top) and [CuCl₂L₂] (bottom).

vibration in the region 1382–1266 cm⁻¹ for aromatic amines. Correspondingly to this information, in this study C–N stretching vibration (11%) occurs at 1265 cm⁻¹ for the [CuCl₂L₂], and at \sim 1270 for the free L.

4.2.3. C-H vibrations

The aromatic C–H stretching vibrations appear in the region 3100–3000 cm⁻¹ [31–37]. They appear at \sim 3200 cm⁻¹ for L, and \sim 3100 cm⁻¹ for the complex. The asymmetric and symmetric methyl C–H stretchings appear usually in the regions of 2980–2920 cm⁻¹ and 2870–2840 cm⁻¹, respectively [3,7–16,38,39]. Consistent with these literature values, the asymmetric C–H stretchings are at 2913 and 2860 cm⁻¹ for L and at 2915 and 2860 cm⁻¹



2.265-2.262

2.271-2.250

Cu-N 2.089-2.089

2.133-2.084

2.117-2.116

Fig. 4. The experimental dispersive Raman spectra of L (top) and $\left[CuCl_2L_2 \right]$ (bottom).

for the complex. The symmetric C–H stretching appears at 2739 cm^{-1} for L and at 2732 cm^{-1} for the complex.

4.2.4. C-C vibrations

CC stretching modes are observed between the 1600 and 1200 cm^{-1} region both for free L, and complex [CuCl₂L₂], as in line with the previous study [3]. The CH in plane and out of plane bending vibrations usually couple with the C–C stretchings.

4.2.5. Metal-halogen and metal-ligand vibrations

The [ML₂X₂] complexes (M = metal; L = ligand; X = halogen) with one M–L and two M–X stretching IR bands that are mostly found below 600 cm⁻¹ [7,12,40] have molecular point group of C_i and polymeric octahedral geometry around the metal center due to packing in the solid state [41]. In the IR spectrum of the complex, there is only one Cu–N stretching at 155 cm⁻¹ and two Cu–Cl stretchings at 204 and 305 cm⁻¹. The present calculations find the Cu–N and the Cu–Cl bond lengths of the complex different to each other. These suggest distorted polymeric octahedral environment around the Cu(II) ion. It should be mentioned at this point that the calculations are performed in the gas phase, i.e., for single isolated molecules whereas the experiments refer to the solid-state bridged polymerical samples. Therefore, the vibrational calculations are especially useful to examine how the coordination affects the frequencies of the modes qualitatively.

4.3. EPR study

The experimental and simulated EPR spectra of the $[CuCl_2L_2]$ complex recorded for its powder and ethyle alcohol solution forms at the room temperature are shown in Fig. 5. Both spectra have similar line shapes that are characteristic for a polycrystalline sample containing a paramagnetic ion with rhombic field symmetry.

Table 5

Experimental and calculated wavenumbers of free L and [CuCl₂L₂].

| Free L – 6- | 311G+(d,p) | | | | $[CuCl_2L_2] - 6-311G+(d,p)$ | | | | | PED (%) assignments | | |
|------------------|----------------|------------|------------|-----------|------------------------------|---------------|----------------|------------|------------|---------------------|------------|--|
| Experimen | tal | BVP86 | | B3LYP | | Experiment | tal | BVP86 | | B3LYP | | |
| FT-IR | Disp. Raman | Unscaled | Scaled | Unscaled | Scaled | FT-IR | Disp. Raman | Unscaled | Scaled | Unscaled | Scaled | |
| 3418 s | 3419 m, sh | 3572 | 3479 | 3660 | 3484 | 3301 s | | 3478 | 3388 | 3568 | 3397 | 100 υNH ₂ (asym.) |
| 3337 s | 3336 s | 3474 | 3384 | 3564 | 3393 | 3234 s | | 3385 | 3297 | 3481 | 3314 | 100 υNH ₂ (sym.) |
| 3223 m | 3225 w | 3095 | 3015 | 3166 | 3014 | 3158 w, | | 3114 | 3033 | 3188 | 3035 | 91 υCH ring |
| 3096 w | | 3092 | 3012 | 3163 | 3011 | 3118 m | | 3113 | 3032 | 3187 | 3034 | 92 υCH ring |
| 3056 w, | 3052 s | 3076 | 2996 | 3148 | 2997 | 3061 vw | | 3092 | 3012 | 3165 | 3013 | 90 υCH ring |
| sh | | | | | | | | | | | | |
| 3010 m | 3014 m, sh | 3076 | 2996 | 3147 | 2996 | 3036 m | | 3092 | 3012 | 3164 | 3012 | 90 υCH ring |
| 2913 m | 2915 s | 3033 | 2954 | 3093 | 2945 | 2915 m | | 3042 | 2963 | 3102 | 2953 | 97 υCH ₃ (asym.) |
| 2860 m | 2860 m | 3004 | 2926 | 3066 | 2919 | 2860 m, sh | | 3013 | 2935 | 3075 | 2927 | 99 υCH ₃ (asym.) |
| 2739 w | 2738 w | 2948 | 2871 | 3014 | 2869 | 2732 w | | 2954 | 2877 | 3021 | 2876 | 99 υCH ₃ (sym.) |
| 1623 vs | 1615 s | 1618 | 1626 | 1666 | 1626 | 1613 w | 1607 sh | 1602 | 1610 | 1653 | 1613 | 81 υCC; 14 βNH ₂ (sciss.) |
| 1581 w, sh | | 1603 | 1611 | 1653 | 1613 | 1594 w | | 1581 | 1589 | 1638 | 1599 | 87 βNH ₂ (sciss.); 13 υCC |
| | | 1572 | 1580 | 1619 | 1580 | 1568 s | | 1580 | 1588 | 1630 | 1591 | 68 υCC; 17 βNH ₂ (rock.) |
| 1516 vs | 1516 w | 1503 | 1511 | 1549 | 1512 | 1514 vs | | 1578 | 1586 | 1545 | 1508 | 61 βCCH; 30 υCC |
| | | 1453 | 1460 | 1500 | 1464 | | | 1495 | 1502 | 1500 | 1464 | 62 βCH ₃ (asym.); 30 βCCH |
| 1455 w, | | 1440 | 1447 | 1489 | 1453 | 1455 vw | 1456 vs | 1453 | 1460 | 1490 | 1454 | 96 βCH ₃ (asym.) |
| 511 | | 1414 | 1421 | 1457 | 1422 | | | 1440 | 1447 | 1459 | 1424 | 55 βCCH; 32 βCH ₃ (asym.); 13 βNH ₂ |
| | 1381 m | 1363 | 1370 | 1415 | 1381 | 1379 w | | 1414 | 1421 | 1415 | 1381 | 93 βCH ₃ (sym.) |
| 1345 w, sh | | 1341 | 1348 | 1354 | 1322 | | 1354 s | 1363 | 1370 | 1363 | 1330 | 63 βCCH; 21 βNH ₂ ; 12 υCC |
| 1324 m | 1321 w | 1298 | 1304 | 1331 | 1299 | 1327 w | | 1349 | 1356 | 1335 | 1303 | 39 βCCH; 23 υCC; 20 βCH₃ |
| 1270 s | 1275 m | 1268 | 1274 | 1294 | 1263 | | 1265 m | 1301 | 1308 | 1239 | 1209 | 48 βCCH; 21 βNH ₂ ; 11 υCC; 11 υCN |
| | 1214 s | 1202 | 1208 | 1232 | 1202 | 1221 m | | 1214 | 1220 | 1231 | 1201 | 39 βCCH; 28 βCH ₃ ; 26 υCC |
| 1177 m | 1178 w, sh | 1167 | 1173 | 1204 | 1175 | 1181 w | | 1201 | 1207 | 1207 | 1178 | 80 βCCH |
| 1124 m | 1127 vw | 1119 | 1125 | 1151 | 1123 | 1148 vw | | 1168 | 1174 | 1168 | 1140 | 41 βNH ₂ (rock.); 52 βCCH |
| 1074 m | 1077 vw | 1058 | 1063 | 1090 | 1064 | 1091 s | | 1132 | 1138 | 1130 | 1103 | 50 βCCH; 27 βNH ₂ ; 14 βCH ₃ |
| 1044 vw | 1031 vw | 1020 | 1025 | 1061 | 1036 | 1044 m, sh | | 1093 | 1098 | 1061 | 1036 | 80 τCCC-CH ₃ |
| | 1013 vw | 998 | 1003 | 1030 | 1005 | 1022 m, sh | 1022 w | 1019 | 1024 | 1038 | 1013 | 50 βCCH; 27 βNH ₂ (rock.); 13 βCCH ₃ |
| 954 w | | 966 | 971 | 1000 | 976 | | | 1005 | 1010 | 1022 | 997 | 64 γNH ₂ (wag.); 33 γCCC |
| 931 vw | | 914 | 919 | 961 | 938 | | | 971 | 976 | 1005 | 981 | 65 βCH ₃ ; 25 βCH |
| | | 895 | 899 | 939 | 916 | 963 vw | | 941 | 946 | 979 | 956 | 83 γCH; 15 γCCC |
| 833 w, sh | 840 vs | 830 | 834 | 850 | 830 | 937 w | 0.40 | 933 | 938 | 955 | 932 | 66 γCH; 13 γCH ₃ ; 10 γNH ₂ |
| 815 s | | /8/ | 791 | 824 | 804 | 832 w, sh | 843 W | 910 | 915 | 842 | 822 | 63 ring breath.; 18 ν CH ₃ ; 17 ν CN |
| 750 ch | 741 | 784 | 788 | 820 | 800 | 8135 | 817 W | 822 801 | 820 | 840 | 820 | 82 γ CH; 12 γ CCC |
| 730 SII 601 m | 741 W 712 w | 734 602 | 738 605 | 750 | 752 | 742 m | 753 ₩ | 801 702 | 805 796 | 829 740 | 809 722 | 48 wCC: 31 wCCH ₂ : 21 wCN |
| 031 111 | 644 m | 638 | 641 | 659 | 643 | 706 m | 755 W | 723 | 730 | 716 | 699 | 41 vCH: 30 vCCC: 20 vCH ₂ |
| | 535 vw | 576 | 579 | 592 | 578 | 684 m | 672 w | 689 | 692 | 671 | 655 | 50 yNH_2 (wag.): 42 yCCC |
| 501 m | | 488 | 490 | 508 | 496 | | | 648 | 651 | 663 | 647 | 32 γNH ₂ (wag.); 59 γCCC |
| | 465 m | 455 | 457 | 469 | 458 | 638 m | | 642 | 645 | 645 | 630 | 48 γNH ₂ (wag.); 42 γCCC |
| | 410 w | 402 | 404 | 418 | 408 | | | 621 | 624 | 627 | 612 | 63 γNH ₂ (wag.); 33 γCCC |
| | 334 s | 394 | 396 | 410 | 400 | 536 m | | 600 | 603 | 532 | 519 | 55 γ CCC; 17 γ NH ₂ (wag.); 14 γ CH ₃ |
| | | 310 | 312 | 321 | 313 | 513 w, sh | | 508 | 511 | 528 | 515 | 56 γCCC; 16 γNH2 (wag.); 14 γCH ₃ |
| 174 | | 290 | 291 | 299 | 292 | 486 w | 460 | 463 | 465 | 478 | 467 | 42 vCCH ₃ ; 34 vCN; 23 vCC |
| 174 vw | | 270 | 271 | 264 | 258 | 473 vw | 460 w | 457 | 459 | 473 | 462 | 42 ν CCH ₃ ; 33 ν CN; 23 ν CC |
| 131 W | | 134 30 | 132 | 139 28 | 130 27 | 443 M | 412 w | 399 305 | 401 307 | 417 | 407 300 | 93 YUU 34 WCH: 33 WNH-: 22 WCH |
| | | 20 | 20 | 20 | 21 | 390 m | 712 W | 380 | 382 | 395 | 386 | эн үсп, ээ үмп ₂ , 2э үсп ₃ 38 вссн• 33 всм• 27 вссч |
| | | | | | | 330 III | | 374 | 376 | 390 | 381 | 39 BCCH: 32 BCN: 29 BCCH |
| | | | | | | 374 vw | | 373 | 375 | 389 | 380 | 34 γCN: 31 γCCH ₂ : 31 γCCC |
| | | | | | | 305 m | | 330 | 332 | 333 | 325 | 41 βCCH ₃ ; 27 βCCC; 16 βCN; 15 |
| | | | | | | 281 m | | 286 | 287 | 297 | 290 | 41 βCCH ₃ ; 37 βCN; 21 βCCC |
| | | | | | | 270 vw | | 285 | 286 | 295 | 288 | 38 βCCH ₃ ; 38 βCN; 21 βCCC |
| | | | | | | 258 w | | 278 | 279 | 288 | 281 | 41 τCCCH; 38 τCCC-CH ₃ ; 19 τCCCN |
| | | | | | | 229 w | | 272 | 273 | 280 | 273 | 35 τCCC-CH ₃ ; 36 τCCCH; 23 τCCCN |
| | | | | | | 204 W | | 209 | 210 | 218 | 213 | 35 TLLL-LH ₃ ; 30 TLLLN; 11 ULLL |
| | | | | | | 155 M | | 1/1 | 1/2 | 180 | 176 | 40 TULU-UH3; 25 TULUN; 11 UUUN |
| | | | | | | 137 w | | 130 | 137 | 145 147 | 140 | 44 ICCCN, 20 TCCC-CH3; 22 TCCCH 32 TCCC-CH2: 32 TCCCN: 18 VCUCI |
| | | | | | | 123 w | | 129 | 130 | 135 | 135 | 46 τCCCN· 25 τCCC_CH_· 22 τCCCU |
| | | | | | | 107 w | | 114 | 115 | 119 | 116 | 50 τCCC-CH ₂ : 23 τCCCN· 19 τCCCH |
| | | | | | | 92 w | | 105 | 106 | 111 | 108 | 52 τCCC-CH ₃ ; 25 τCCCN: 22 τCCCH |
| | | | | | | 76 w | | 62 | 62 | 63 | 61 | 30 τCCC-CH ₃ ; 31 τCCCN; 34 τCCCH |

Table 5 (continued)

| Free L – (| Free L – 6-311G+(d,p) | | $[CuCl_2L_2] - 6-311G+(d,p)$ | | | | | | PED (%) assignments | | | |
|-----------------|-----------------------|----------|------------------------------|----------|--------|-------|----------------|----------|---------------------|----------|--------|---|
| Experimental BV | | BVP86 | BVP86 | | B3LYP | | Experimental | | BVP86 | | | |
| FT-IR | Disp. Raman | Unscaled | Scaled | Unscaled | Scaled | FT-IR | Disp. Raman | Unscaled | Scaled | Unscaled | Scaled | |
| | | | | | | | | 54 | 54 | 56 | 55 | 48 τCCC-CH3; 27 τCCCN; 10 γCuCl2 |
| | | | | | | | | 48 | 48 | 47 | 46 | 50 τCCC-CH ₃ ; 29 τCCCN; 21 τCCCH |
| | | | | | | | | 46 | 46 | 46 | 45 | 43 τCCC-CH ₃ ; 41 τCCCH; 14 τCCCN |
| | | | | | | | | 45 | 45 | 38 | 37 | 84 γCH ₃ |
| | | | | | | | | 42 | 42 | 37 | 36 | 78 γCH ₃ ; 19 τCCCH |
| | | | | | | | | 30 | 30 | 30 | 29 | 40 τCCC-CH ₃ ; 28 τCCCH; 15 τCCCN |
| | | | | | | | | 20 | 20 | 19 | 19 | 47 τCCC-CH ₃ ; 21 τCCCN; 27 τCCCH |
| | | | | | | | | 12 | 12 | 12 | 12 | 59 τCCC-CH ₃ ; 18 τCCCN; 18 γCuCl ₂ |

υ, stretching; τ, torsion; β in plane deformation; γ out of plane deformation.



Fig. 5. The experimental and simulated room temperature X-band EPR spectra of $[CuCl_2L_2]$ as powder and in EtOH solution.

Many Cu(II)-coordinated complexes exhibit hyperfine peaks or quasi-isotropic behavior (almost a single peak) due to solvent effects [42,43]. Although any part of the recorded EPR spectra does not include any hyperfine peak, the solution spectrum has a shoulder at its parallel part and the amplitude of perpendicular part is smaller compared with the powder EPR spectrum. Each part would have 4 peaks due to nuclear spin (I = 3/2) of copper atom. g_x and g_y can be defined as the Lande splitting factors when the externally applied DC field is in perpendicular while g_7 is in parallel alignment, respectively. They follow the trend $g_z > g_y > g_x$ and $g_{ll} > g_{\perp} > g_e$ (g_e is free electron g-value) suggesting Cu complexes have approximate axial symmetry D_{4h} (square planar, or octahedral with tetragonal distortion) with B_{1g} as the ground state of Cu(II) ion [16,44]. The unpaired electron is located mainly on the b_{1g} antibonding molecular orbital, which is the linear combination of $d_x^2 - y^2$ orbital of the copper and \emptyset_L ligand orbital of the adequate symmetry [45–47]. The character of the Cu complexes can be estimated from the g_{ll} (or g_z) values which are sensitive to the bond covalency [45]. The centers giving $g_z \ge 2.3$ are ionic in their nature and $g_z < 2.3$ have the dominant covalent character. Our sample has $g_z \approx 2.18$ values for both powder and solution forms.

The anisotropic spin-Hamiltonian \hat{H}_{aiso} of rhombic symmetry is given by the expression

$$\widehat{H}_{aiso} = \beta_e(g_x B_x \widehat{S}_x + g_y B_y \widehat{S}_y + g_z B_z \widehat{S}_z)$$
(1)

where β_e and *S* denote Bohr magneton and the electronic spin angular momentum of the magnetic ion, respectively.

In a randomly oriented powder system, each paramagnetic center has similar properties as it would have in a large crystal. However, the crystallite symmetry axes of each powder molecule are subjected to every possible direction of any externally applied DC magnetic field. Hence, the overall paramagnetic system exhibits resonances at all fields, B_R varying between perpendicular and parallel aligments. For a general orientation of a single crystallite containing a paramagnetic ion, the resonance field is obtained from Eq. (1) [42,48–51] as

$$B_{R} = hf/g_{eff}\beta_{e}$$

$$= \left[g_{x}^{2} \sin^{2}\theta\cos^{2}\theta + g_{y}^{2} \sin^{2}\theta \sin^{2}\theta + g_{z}^{2} \cos^{2}\theta\right]^{-1/2} hf/\beta_{e}$$
(2)

where the angles θ and \emptyset describe the orientation of the magnetic field H in the *g*-tensor principal axis, *h* and *f* are the Plank's constant and the microwave frequency, respectively. Exact theoretical fit of experimental spectra requires summation from 0 to 90 degrees both for θ and \emptyset .

The probability of each spin center experiencing a resonant field is proportional to $\sin \theta$. The intensities of the absorption resonance peaks can be thus obtained by inserting a weighting factor in Eq. (2) [11,52,53]. As the resonance curves of each individual magnetic center have their own intrinsic line shapes and widths for the powder systems, the line width and line shape characteristics of spectra are analyzed in detail by EPR spectroscopy. These curves reach to their maximum at the resonance field B_R . That is, regardless of how far it is from the exact resonance field, B_R , any center can give absorption at any field even if it becomes undetectable experimentally. The contribution from any center to the whole absorption line at any field depends on the intrinsic line width. Therefore, an angle-dependent equation is used to describe the line width characteristics [42,54].

$$W_{eff}^2 = W_x^2 \sin^2 \theta \cos^2 \emptyset + W_y^2 \sin^2 \theta \sin^2 \emptyset + W_z^2 \cos^2 \theta \qquad (3)$$

To simulate the experimental spectra, we wrote a software in Matlab scientific language. The best fit is obtained by using the Lorentzian line shape function for intrinsic line properties (see Fig. 5). The simulations reveal that the solution and powder spectra have almost the same magnitude of EPR and line width fit parameters (see Table 6) and exhibit all characteristics features of the EPR peaks except the additional weak shoulder due to solvent. Since the environment of paramagnetic ion is not affected much from the solution due to its polymeric nature, the powder and solution EPR spectra are quite similar.

5. Conclusions

The FT-IR (including mid and far regions) and dispersive Raman spectral studies of free L and the synthesized $[CuCl_2L_2]$ complex, where L = 4-amino-1-methylbenzene, have been performed. The

Table 6

Anisotropic EPR and line width simulation parameters of [CuCl₂L₂].

| Samples | g _x | g _y | g _z | g ave | <i>W_x</i> (Oe) | W _y (Oe) | W _z (Oe) | |
|---------------------------------|----------------|----------------|----------------|----------------|------------------------------|------------------------|------------------------|--|
| Powder form Solution form | 2.008 2.009 | 2.037 2.038 | 2.184 2.185 | 2.076 2.077 | 10 10 | 10 10 | 10 10 | |

The average *g*-factor is calculated from expression, $g_{ave} = (g_x + g_y + g_z)/3$.

geometry and vibrational spectra of the isolated complex in the gas phase have been calculated with BVP86 and B3LYP density functionals using the 6-311G+(d,p) basis set. The calculated vibrational frequencies of the free and complexed L after a scaling procedure agree reasonably well with the corresponding experimental frequencies. The experimental vibrational and EPR spectra suggest that the [CuCl₂L₂] complex has distorted polymeric octahedral geometry around the Cu(II) center and coordination takes place through nitrogen atom of the free ligand, and the calculations find the title complex as a doublet with one unpaired electron.

Acknowledgement

Authors would like to thank Dr. Ahmet Altun for critically reading the manuscript.

References

- [1] M.E. Vaschetto, B.A. Retamal, A.P. Monkman, J. Mol. Struct. (Theochem) 468 (1999) 209–221.
- [2] J. Whysner, L. Verna, G.M. Williams, Pharmacol. Ther. 71 (1996) 107–126.
- [3] A. Altun, K. Golcuk, M. Kumru, J. Mol. Struct. (Theochem) 637 (2003) 155-169.
- [4] G. Inzelt, V. Kertesz, Electrochim. Acta 42 (1997) 229–235.
- [5] V. Arjunan, S. Mohan, Spectrochim. Acta Part A 72 (2009) 436-444.
- [6] P. Patnaik, A Comprehensive Guide to the Hazardous Properties of Chemical Substances, A John Willey & Sons, 2007.
- [7] A. Altun, K. Golcuk, M. Kumru, Vib. Spectrosc. 33 (2003) 63-74.
- [8] K. Golcuk, A. Altun, M. Somer, M. Kumru, Vib. Spectrosc. 39 (2005) 68-73.
- [9] A. Altun, K. Golcuk, M. Kumru, Vib. Spectrosc. 31 (2003) 215–225.
- [10] A. Altun, K. Gölcük, M. Kumru, J. Mol. Struct. (Theochem) 625 (2003) 17–24.
- [11] K. Golcuk, A. Altun, M. Kumru, Spectrochim. Acta 59A (2003) 1841–1847.
- [12] K. Golcuk, A. Altun, M. Kumru, J. Mol. Struct. 657 (2003) 385–393.
- [13] S. Akyuz, T. Bulat, A.E. Ozel, G. Basar, Vib. Spectrosc. 14 (1997) 151–154.
- [14] E. Akalin, S. Akyuz, J. Mol. Struct. 482-483 (1999) 175-181.
- [15] S. Yurdakul, A.I. Sen, Vib. Spectrosc. 20 (1999) 27-33.
- [16] K. Golcuk, A. Altun, S. Guner, M. Kumru, B. Aktas, Spectrochim. Acta Part A 60 (1-2) (2004) 303–309.
- [17] E. Kendix, G. Moscardi, R. Mazzeo, P. Baraldi, S. Prati, E. Joseph, S. Capelli, J. Raman Spectrosc. 39 (2008) 1104–1112.
- [18] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox,

H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.

- [19] GaussView, Version 4.1, Roy Dennington II, Todd Keith and John Millam, Semichem, Inc., Shawnee Mission, KS, 2007.
- [20] A.D. Becke, Phys. Rev. A 38 (1988) 3098-3100.
- [21] S.H. Vosko, L. Wilk, M. Nusair, Can. J. Phys. 58 (1980) 1200-1211.
- [22] J.P. Perdew, Phys. Rev. B 33 (1986) 8822–8882.
- [23] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [24] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [25] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11623.
- [26] W. Tzeng, K. Narayanan, J. Mol. Struct. (Theochem) 446 (1998) 93–102.
- [27] G. Varsanyi, Assignments of Vibrational Spectra of 700 Benzene Derivatives, Wiley, New York, 1974.
- [28] A. Ismael, J.A. Paixã, R. Fausto, M.L.S. Cristiano, J. Mol. Struct. 1023 (2012) 128– 142.
- [29] C. Engelter, D.A. Thornton, M.E. Ziman, J. Mol. Struct. 49 (1978) 7–15.
- [30] M. Silverstein, G.C. Basseler, C. Morill, Spectrometric Identification of Organic Compound, Wiley, New York, 1981.
- [31] M. Kumru, V. Küçük, T. Bardakçı, Spectrochim. Acta Part A 90 (2012) 28–34.
- [32] V. Küçük, A. Altun, M. Kumru, Spectrochim. Acta Part A 85 (2012) 92–98.
- [33] M. Kumru, V. Küçük, M. Kocademir, Spectrochim Acta Part A 96 (2012) 242– 251
- [34] V. Balachandran, S. Lalitha, S. Rajeswari, Spectrochim Acta Part A 97 (2012) 1023-1032.
- [35] M. Karabacak, D. Karagoz, M. Kurt, J. Mol. Struct. 892 (2008) 25-31.
- [36] V. Arjunan, T. Rani, S. Mohan, J. Mol. Struct. 994 (2011) 179–193.
- [37] G.O. Ildiz, S. Akyuz, Vib. Spectrosc. 58 (2012) 12–18.
- [38] S. Ramalingam, S. Periandy, B. Narayanan, S. Mohan, Spectrochim. Acta Part A 76 (2010) 84–92.
- [39] M. Kurt, M. Yurdakul, Ş. Yurdakul, J. Mol. Struct. (Theochem) 711 (2004) 25– 32.
- [40] E. Akalin, S. Akyuz, Vib. Spectrosc. 53 (2010) 140–145.
- [41] R.J.H. Clark, C.S. Williams, Inorg. Chem. 4 (1965) 350-357.
- [42] S. Güner, M.K. Sener, H. Dinçer, Y. Köseoğlu, S. Kazan, M.B. Koçak, J. Magn. Magn. Mater. 300 (2006) e530.
- [43] E. Forizs, L. David, O. Cozar, C. Craciun, M. Venter, M. Kilyen, J. Mol. Struct. 408 (409) (1997) 195.
- [44] R. Kripal, S. Misra, J. Magn. Magn. Mater. 294 (2005) 72.
- [45] M. Labanowska, E. Bidzinska, A. Parab, M. Kurdziela, Carbohydr. Polym. 87 (2012) 2605.
- [46] N.V. Loginova, T.V. Kovalcuk, R.A. Zheldakov, A.A. Chernyavskaya, N.P. Osipovic, G.K. Glushonok, G.I. Polozov, V.N. Povalishev, V.L. Sorokin, O.I. Shadyro, Polyhedron 25 (2006) 3603.
- [47] H.J. Hathaway, D.E. Billing, Coord. Chem. Rev. 5 (1970) 143.
- [48] A. Kalkan, S. Güner, Z.A. Bayır, Dyes Pigments 74 (2007) 636.
- [49] J.A. DeGray, P.H. Rieger, Bull. Magn. Reson. 8 (1986) 95.
- [50] M. She, X. Chen, X. Yu, Can. J. Chem. 67 (1989) 88.
- [51] J.A. Weil, J.R. Bolton, J.E. Wertz, Electron Paramagnetic Resonance, John Wiley and Sons Inc., 1994.
- [52] Y.D. Kurt, B. Ülküseven, S. Güner, Y. Köseoğlu, Transit. Metal Chem. 32 (2007) 494–500.
- [53] A. Abragam, B. Bleaney, EPR of Transition Ions, Oxford University Press, Oxford, 1970.
- [54] R. Öztürk, S. Güner, B. Aktaş, A. Gül, Supramol. Chem. 17 (2005) 233.