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Structures and Magnetic Properties of Monomeric Copper(II) Bromide Complexes with a Pyridine-Containing Tridentate Schiff Base

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Two novel copper(II) bromide complexes with pyridine containing Schiff base ligands, Cu(pmed)Br_2 and Cu(dpmed)Br_2 where pmed = *N′*-((pyridin-2-yl)methylene)ethane-1,2-diamine (pmed) and dpmed = *N,N*-diethyl-*N′*-((pyridin-2-yl)methylene)ethane-1,2-diamine (dpmed) were synthesized and characterized using X-ray single crystal structure analysis, optical and magnetic susceptibility measurements. Crystal structural analysis of Cu(pmed)Br_2 showed that the copper(II) ion has a distorted square-pyramidal geometry with the trigonality index of $\tau = 0.35$ and two intermolecular hydrogen bonds, which result in the formation of two dimensional networks in the *ab* plane. On the other hand, Cu(dpmed)Br_2 displayed a near square-pyramidal geometry with the value of $\tau = 0.06$. In both compounds, the NNN Schiff base and one Br atom occupy the basal plane, whereas the fifth apical position is occupied by the other Br atom at a greater Cu-Br apical distance. The reported complexes show $g_{\parallel} > g_{\perp} > 2.0023$ with a $d_{x^2-y^2}$ ground state and a penta-coordinated square pyramidal geometry. Variable temperature magnetic susceptibility measurements showed that the developed copper(II) complexes follow the Curie-Weiss law, that is there are no magnetic interactions between the copper(II) ions since the Cu--Cu distance is too far for magnetic contact.

Key Words : Square pyramidal copper(II) complexes, Tridentate N3 Schiff base, Magnetic property, Structural property

Introduction

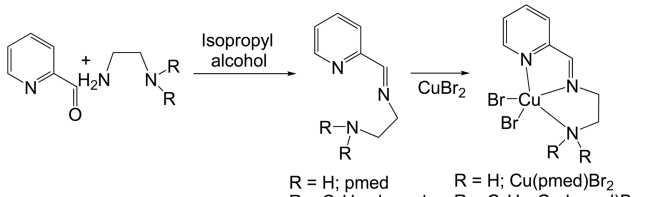
Nitrogen based Schiff base ligands and their metal complexes have been widely studied due to their versatile steric and electronic properties,[1-5] which can be fine-tuned by choosing appropriate amine precursors and ring substituents. In addition, they are potential models for a number of important biological systems and have possible applications as molecule-based magnetic materials.[6-13] The metal halide complexes of less flexible tridentate ligands tend to be monomeric and dimeric in nature, whereas the use of more flexible tridentate ligands tends to give rise to dimeric or polymeric complexes.[14-21] These complexes also exhibit interesting magnetic behaviours. For example, it has been found that the strengths of magnetic interactions between copper(II) metal ions are primarily a function of Cu–X···Cu contact, Cu(II) center geometry, Cu–X···X–Cu distance, Cu–X···X angle, and the electronic nature of the halide ion in copper(II) halide complexes.[22-23] Recently, our focus has been on the transition metal chemistry of N3 tridentate Schiff base ligands, and particularly, on mixed imino–pyridine ligands.[24-28] The design of such ligands incorporating different transition metals and studies of their structural and magnetic properties are in progress. Here, we describe the complexing abilities of two new Schiff-base tridentate ligands containing pyridyl, imine, and amino donor atoms, that is, *N′*-((Pyridin-2-yl)methylene)ethane-1,2-diamine = pmed) and, *N,N*-diethyl-*N′*-(((Pyridin-2-yl)methylene)ethane-1,2-diamine = dpmed) for Cu(II) bromide and the optical and magnetic properties of Cu(pmed)Br_2 and Cu(dpmed)Br_2 from a structural perspective.

Experimental

All reagents and solvents used for syntheses and analyses were purchased from the Aldrich Chemical Company and used as received.

Preparation of Schiff Base. The Schiff base ligands, *N′*-((pyridin-2-yl)methylene)ethane-1,2-diamine (pmed) and *N,N*-diethyl-*N′*-((pyridin-2-yl)methylene)ethane-1,2-diamine (dpmed) were prepared by reacting 2-pyridinecarboxaldehyde with ethylenediamine or *N,N′*-diethylethylenediamine, respectively. The synthetic pathway is shown in Scheme 1.

Synthesis of Copper(II) Complexes. Cu(pmed)Br_2. A solution of $CuBr_2$ (1.12 g, 5 mmol) in 30 mL methanol was added dropwise with constant stirring to a methanolic solution (30 mL) of pmed ligand (0.75 g, 5 mmol), and the



Scheme 1

reaction mixture was stirred for a further 24 h at room temperature. The bluish green precipitates formed were isolated by filtration, washed with methanol and dried under vacuum. Yield: 1.34 g (72%). Anal. Calc. for $Cu(C_8H_{11}N_3)Br_2$: C, 25.79; H, 2.98; N, 11.28. Found: C, 25.61; H, 2.93; N, 11.37%. IR (KBr, cm^{-1}): ν(N-H) 3259, 3230; ν(C=N) 1602; δ (Py) 764. UV–Vis (CH_3CN; λ_{max}): 749, 285 nm.

Cu(dpmed)Br$_2$. This compound was obtained in manner similar to that used to produce Cu(pmed)Br_2, but dpmed was used instead of pmed. Dark green colour. Yield: 1.52 g (71%). Anal. Calc. for $Cu(C_{12}H_{19}N_3)Br_2$: C, 33.62; H, 4.47; N, 9.80. Found: C, 32.25; H, 4.96; N, 9.52%. IR (KBr, cm^{-1}): ν(C=N) 1599; δ (Py) 644. UV–Vis (CH_3CN; λ_{max}): 765, 289 nm.

Physical Measurements. Elemental analyses (C, H and N) were carried out at the Korean Basic Science Institute at Daejeon. IR spectra were obtained using KBr pellets and a Jasco FT-IR spectrophotometer. Electronic absorption spectra were recorded at ambient temperature on a Shimadzu UV-3101PC spectrophotometer. The X-band EPR spectra of powder materials and frozen glass samples (toluene/methanol) at 77 K were recorded on an ESP-300S EPR spectrometer. The field modulation frequency was 100 kHz and diphenylpicrylhydrazyl (DPPH) was used as a reference. Magnetic susceptibilities were measured at different temperatures using a Magnetic Property Measurement System (MPMS7) Quantum Design and the SQUID method. Susceptibility data were corrected for the diamagnetism of constituent atoms using Pascal's constants and for the temperature-independent paramagnetism of copper, which was estimated to be 60×10^{-6} cgsu/Cu atom.

X-ray Single Crystal Structural Analysis. X-ray intensity data were collected on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at a temperature of 296 K. The structures were solved using the direct method and refined by full-matrix least-squares calculation on F^2 using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Amine H atoms were located in a difference map and refined freely using refined distances of N-H = 0.80 (4) and 0.92 (4) Å. Other H atoms were positioned geometrically and refined using a riding model, with C-H = 0.93-0.97 Å with U_{iso} = 1.2 U_{eq} (carrier C) for aromatic- and methylene-H, and U_{iso} = 1.5 U_{eq} (carrier C) for methyl-H atoms.

Results and Discussion

The reaction of equimolar amounts of copper(II) bromide and tridentate Schiff-base ligands (pmed/dpmed) leads to the formation of the monomeric copper(II) complexes, Cu(pmed)Br_2 and Cu(dpmed)Br_2 without any coordinating solvent molecules as revealed by elemental analyses and X-ray single crystal analyses.

Description of Structures. Single crystals of Cu(pmed)Br_2 and Cu(dpmed)Br_2 were grown from slowly evaporating solutions of acetonitrile/hexane. Crystallographic data and structure refinement parameters are summarized in Table 1.

Table 1. Crystal data and details of refinement for Cu(pmed)Br_2 and Cu(dpmed)Br_2

Chemical formula	$C_8H_{11}N_3Br_2Cu$	$C_{12}H_{19}N_3Br_2Cu$
Formula weight	372.56	428.66
T (K)	296(2)	296(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å), α(°)	7.0126(5), 90.00	13.55572(7), 90.00
b (Å), β(°)	6.6349(5), 90.446(8)	7.0292(5), 102.010(8)
c (Å), γ(°)	25.0536(15), 90.00	16.2211(9), 90.00
V (Å^3)	1165.66(14)	1511.97(16)
Z, D_{calc} (g cm^{-3})	4, 2.123	4, 1.883
F(000)	716	844
Crystal description	green, block	green, block
θ Range(°)	2.90-28.31	1.54-28.33
Total reflections	10617	29056
Total unique reflections (R_{int})	2890 (0.0348)	3766 (0.0546)
Data / restraints / parameters	2890 / 0 / 135	3766 / 0 / 163
R_1, wR_2 [$I > 2\sigma$(I)]	0.0289, 0.0623	0.0315, 0.0654
R_1, wR_2 (all data)	0.0474, 0.0676	0.0573, 0.0742
Goodness-of-fit (GOF) on F^2	1.041	1.022
Largest diff. peak and Hole (e Å^{-3})	0.616 and -0.444	0.838 and -0.422

ORTEP views including the atomic numbering scheme are shown in Figures 1(a) and 1(b) for Cu(pmed)Br_2 and Cu(dpmed)Br_2, respectively. Selected bond distances and bond angles are summarized in Table 2.

In both compounds, Cu atoms are coordinated by two Br atoms and the three N atoms of the tridentate Schiff base

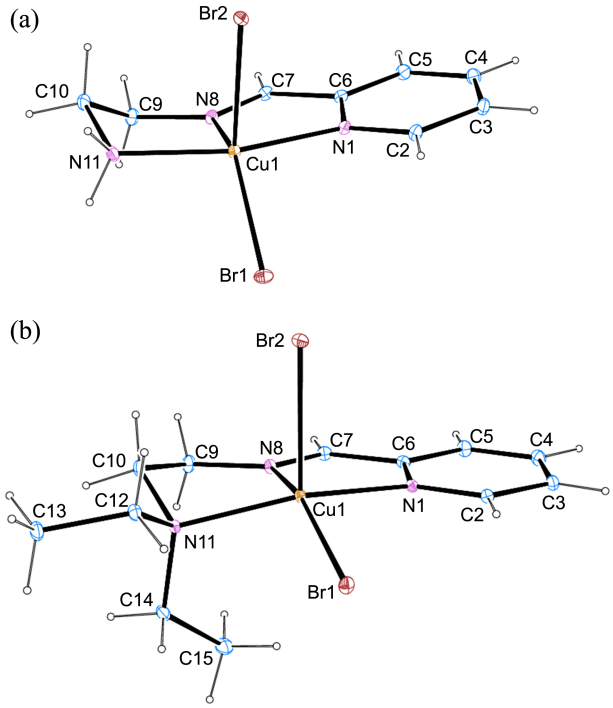


Figure 1. The molecular structures of Cu(pmed)Br_2 (a) and Cu(dpmed)Br_2 (b), showing the atom-numbering schemes.

Table 2. Selected bond lengths (Å) and angles (°) of $Cu(pmed)Br_2$ and $Cu(dpmed)Br_2$

$Cu(pmed)Br_2$			
Bond distances (Å)		Bond angles (°)	
Cu1-N1	2.031(2)	N1-Cu1-N8	79.63(10)
Cu1-N8	1.977(2)	N1-Cu1-N11	161.28(11)
Cu1-N11	2.016(3)	N8-Cu1-N11	82.37(12)
Cu1-Br1	2.3992(5)	N1-Cu1-Br1	98.83(7)
Cu1-Br2	2.6221(5)	N8-Cu1-Br1	140.60(8)
C7-N8	1.261(4)	N11-Cu1-Br1	98.31(9)
N8-C9	1.464(4)	N8-Cu1-Br2	108.75(8)
		N1-Cu1-Br2	90.02(7)
		N11-Cu1-Br2	90.95(10)
		Br1-Cu1-Br2	110.62(2)
$Cu(dpmed)Br_2$			
Bond distances (Å)		Bond angles (°)	
Cu1-N1	2.065(2)	N1-Cu1-N8	79.32(10)
Cu1-N8	1.980(2)	N1-Cu1-N11	155.91(9)
Cu1-N11	2.099(2)	N8-Cu1-N11	81.48(10)
Cu1-Br1	2.4142(5)	N1-Cu1-Br1	96.29(7)
Cu1-Br2	2.6094(5)	N8-Cu1-Br1	159.41(9)
C7-N8	1.267(4)	N11-Cu1-Br1	96.59(7)
N8-C9	1.454(4)	N8-Cu1-Br2	94.46(8)
		N1-Cu1-Br2	93.94(7)
		N11-Cu1-Br2	101.96(7)
		Br1-Cu1-Br2	105.96(2)

ligands. Bond angles around Cu atoms are within the ranges 79.63 (10) to 110.62 (2)° and 79.32 (10) to 105.96 (2)° for $Cu(pmed)Br_2$ and $Cu(dpmed)Br_2$, respectively. The coordination polyhedron around Cu atom is a distorted square pyramidal geometry with a structural index, $\tau = 0.35$ in $Cu(pmed)Br_2$, whereas $Cu(dpmed)Br_2$ exhibits a near square pyramidal environment with $\tau = 0.06$; [$\tau = (\alpha - \beta)/60$, where α is the largest and β is the second largest *trans* angle in the coordination sphere; $\tau = 0$ for a perfect square pyramidal and $\tau = 1$ for a trigonal bipyramidal geometry]. Apical positions in both compounds are occupied by Br2 atoms, as shown in Figure 1.

Table 2 lists the selected bond lengths and bond angles for the reported complexes. The apical Cu1-Br2 bond distances of $Cu(pmed)Br_2$ and $Cu(dpmed)Br_2$ are 2.6221(5) and 2.6094(5) Å, respectively. Longer apical Cu1-Br2 bond distances of $Cu(pmed)Br_2$ and $Cu(dpmed)Br_2$ than those of basal Cu1–Br1 (2.3992(5) for $Cu(pmed)Br_2$ and 2.4142((5) Å for $Cu(dpmed)Br_2$) is a common observation in square pyramidal copper(II) complexes. The dihedral angles between Cu1/N1/N8/N11 of the chelate ring and the Br1/Cu1/Br2 plane are 89.51 (5) and 85.85 (6)° for $Cu(pmed)Br_2$ and $Cu(dpmed)Br_2$, respectively, which are almost perpendicular to each other.

The Cu-N1 bond distances of 2.031 and 2.065 Å for $Cu(pmed)Br_2$ and $Cu(dpmed)Br_2$, respectively, are comparable to those observed in Cu(II) complexes with a five-coordinate system. As shown in Table 2, the Cu1-N8 bond distance of 1.977 Å in $Cu(pmed)Br_2$ (1.980 Å for $Cu(dpmed)Br_2$) is shorter than those of other two Cu-N bonds, 2.016 and 2.031 Å (2.065 and 2.099 Å for $Cu(dpmed)Br_2$), which is consistent with the better π-accepting ability of imine (C=N) than aromatic or amine nitrogen. The observed Cu1-N8 bond lengths are comparable to those observed in other copper(II) complexes containing a nitrogen containing tridentate Schiff base.[36-40] The C7-N8 bond distance of 1.261 Å in $Cu(pmed)Br_2$ (1.267 Å for $Cu(dpmed)Br_2$) is much shorter than N8-C9 bond length of 1.464 Å (1.454 Å for $Cu(dpmed)Br_2$), which demonstrates the double bond character of the imine group.

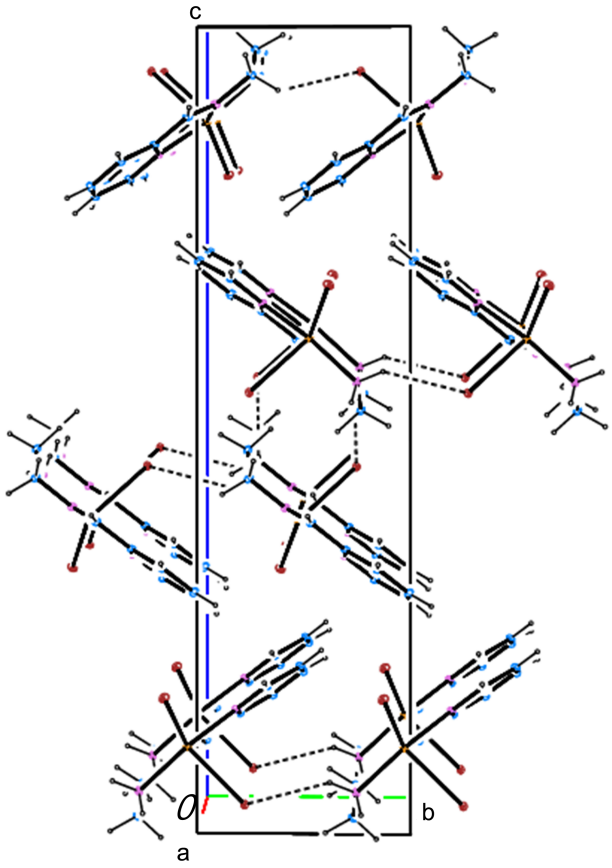


Figure 2. The molecular packing diagram of $Cu(pmed)Br_2$ shows N–H···Br hydrogen bonds (dashed lines).

A structural packing diagram of $Cu(pmed)Br_2$ is presented in Figure 2. In $Cu(pmed)Br_2$, the H(11A) hydrogen interacts with Br(2) of the neighbouring molecule at the x, y+1, z position and the H(11B) atom binds to the Br(2) atom of another adjacent unit at the –x+1, –y, –z+2 position. These two intermolecular hydrogen interactions result in linking the molecules into a two-dimensional network along the *ab* plane. In $Cu(dpmed)Br_2$, two mononuclear molecules are linked by intermolecular π-π interactions at a centroid-centroid distance of 3.560 Å between the C2-C3-C4 planes of pyridine rings, as shown in Figure 3.

Optical and Magnetic Properties. The IR spectrum of $Cu(pmed)Br_2$ complex shows two bands at 3259 and 3230 cm^{-1}, characteristic of asymmetric and symmetric vibrations of a $–NH_2$ group engaged in intermolecular hydrogen bond-

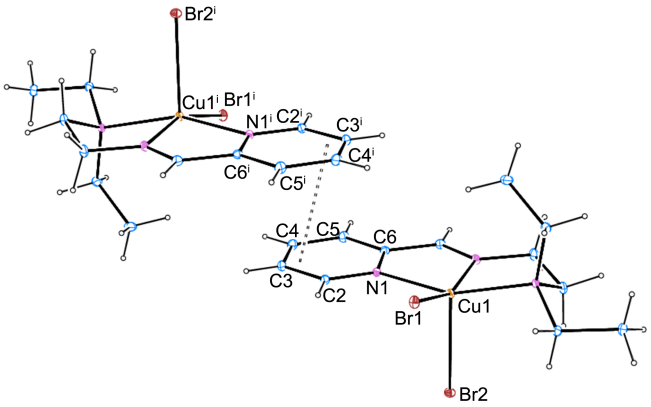


Figure 3. The molecular structures Cu(dpmed)Br_2, showing the intermolecular π-π interactions with dashed lines.

ing. C=N vibration frequencies, ν(C=N), appear at 1602 and 1599 cm^{-1} in Cu(pmed)Br_2 and Cu(pemed)Br_2, respectively, and are in agreement with those observed in azomethine nitrogen coordinated Schiff bases complexes.

UV-Vis spectra in acetonitrile exhibited broad overlapping d–d absorption bands, centered at 749 nm (ε = 175 $M^{-1}cm^{-1}$) for Cu(pmed)Br_2 and at 765 nm (ε = 250 $M^{-1}cm^{-1}$) for Cu(pemed)Br_2. These features are typical for five-coordinate copper(II) complexes with square pyramidal or distorted square pyramidal geometries. Based on these square pyramidal geometries, the broad absorption peaks were resolved into three peaks by Gaussian resolution (Figure 4) and

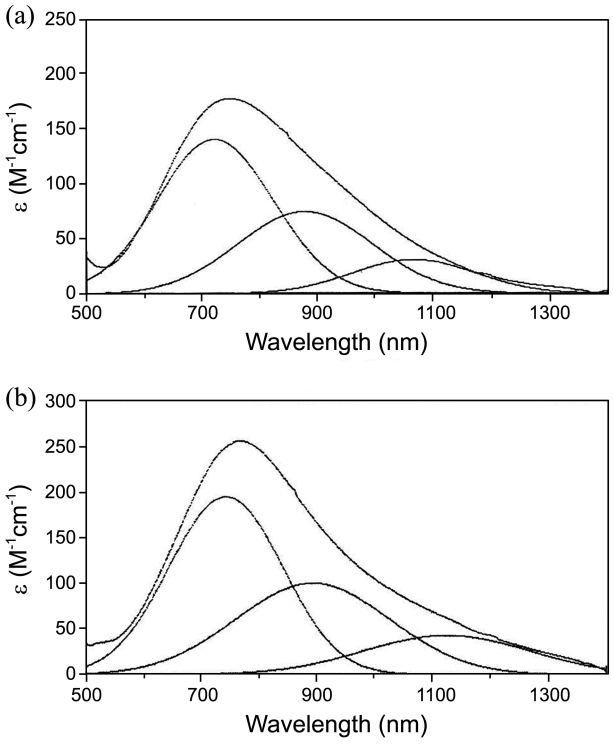


Figure 4. Electronic absorption spectra and transition analysis spectra by Gaussian resolution of Cu(pmed)Br_2 (a) and Cu(dpmed)Br_2 (b).

Table 3. Hydrogen bonds for Cu(pmed)Br_2 [Å and °]

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N(11)-H(11A)···Br(2)^{i}	0.89(3)	2.68(3)	3.440(3)	144(3)
N(11)-H(11B)···Br(2)^{ii}	0.91(4)	2.76(4)	3.588(3)	153(3)

Symmetry code: (*i*) x, y+1, z (*ii*) –x+1, –y, –z+2

tentatively assigned to $d_{z^2} \rightarrow d_{x^2-y^2}$ (ν_1), $d_{xy} \rightarrow d_{x^2-y^2}$ (ν_2) and $d_{xz,yx} \rightarrow d_{x^2-y^2}$ (ν_3). Values of [ν_1 (λ_{max} =1,066 nm, ε = 300 $M^{-1}cm^{-1}$), ν_2 (879, 74) and ν_3 (724, 140)] and [ν_1 (1126, 43), ν_2 (893, 99) and ν_3 (748, 194)] were obtained for Cu(pmed)Br_2 and Cu(pemed)Br_2, respectively. In addition, intense absorption bands were observed in the ~285 nm region for both two complexes, and these were assigned to intraligand transitions (π-π*). The blue shift (16 nm) in the wavelength of Cu(pmed)Br_2 as compared to Cu(pemed)Br_2 indicates that coordination geometry in the *N*-alkylated complex is less distorted than that in the non-*N*-alkylated complex, which may be due to the ligand field strength imparted by the nitrogen donor atoms.

X-band EPR spectra were recorded in the solid-state and in frozen glass samples (toluene/methanol, 50/50% by volume at 77 K). The data are summarized in Table 3. The powdered EPR line shape of Cu(pmed)Br_2 showed an isotropic broad singlet with <g> = 2.808 at 77 K, which resolved into parallel

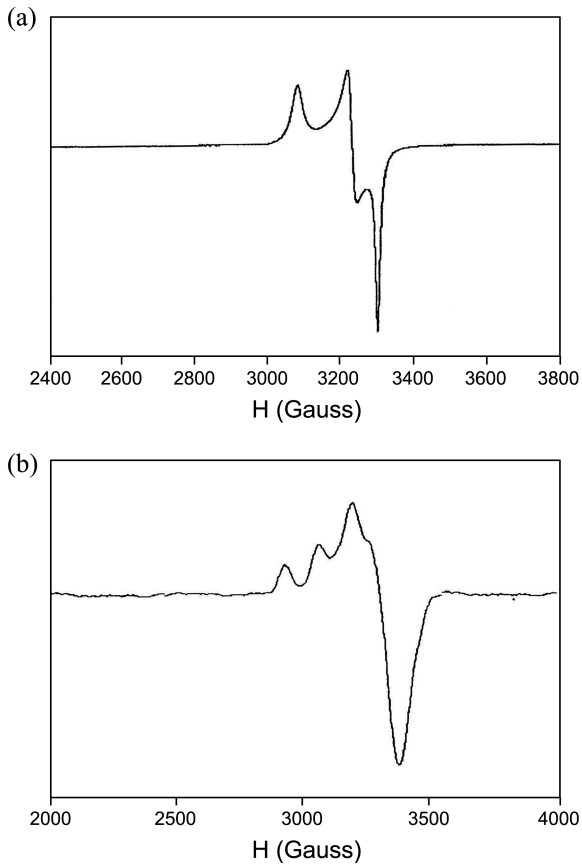


Figure 5. X-band EPR spectra of Cu(dpmed)Br_2 in powder (a) and frozen solution (b) at 77 K.

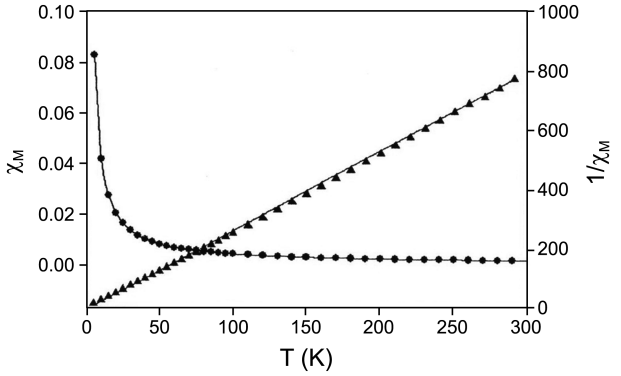


Figure 6. The plots of magnetic susceptibilities χ_m and $1/\chi_m$ *vs.* temperature at 4-300 K for Cu(dpmed)Br_2. Calculated (—) and experimental (●) magnetic data are shown.

($g_{\parallel}$) and perpendicular ($g_{\perp}$) components of $g_{\parallel}$ = 2.260 and $g_{\perp}$ = 2.060 in frozen glass at 77 K. Lack of hyperfine structure in solid state was probably due to intermolecular hydrogen bonding between the H(11) atom and the adjacent terminal bromide Br(2). On the other hand, Cu(pemed)Br_2 exhibited three well resolved g-values of g_{xx} = 2.046, g_{yy} = 2.089 and g_{zz} = 2.191 in the solid state at 77 K and well defined hyperfine splitting with $g_{\parallel}$ = 2.286 and $g_{\perp}$ = 2.072 in solution EPR spectra at 77 K. The EPR spectral feature of $g_{\parallel} > g_{\perp} > 2.0023$ in both complexes is consistent with a penta-coordinated square pyramidal structure with unpaired electrons in a $d_{x^2-y^2}$ orbital. Figure 5 shows EPR spectra of Cu(pemed)Br_2 both in powder and frozen solution at 77 K.

The molar magnetic susceptibilities of powdered samples were measured as a function of temperature in the range 4 K to 300 K and shown in Figure 6. Magnetic susceptibility increased as temperature decreased and no maximum susceptibility was observed, which is in keeping with paramagnetic behavior. In fact, magnetic susceptibility data well fitted Curie-Weiss law, $\chi_m = C/(T - \theta)$, indicating no magnetic interactions between copper(II) ions. A linear regression of χ_m *vs* T results Curie-Weiss temperature of θ = 0.23 K and a Curie constant of C = 0.31 $cm^3\,Kmol^{-1}$ for Cu(pmed)Br_2, and θ = 0.13 K and C = 0.42 $cm^3\,Kmol^{-1}$ for Cu(pemed)Br_2. The calculated intermolecular separations of Cu···Cu and Br1···Br1 were 6.635 Å and 4.594 Å for Cu(pmed)Br_2, and 7.029 Å and 4.625 Å for Cu(pemed)Br_2, which were too great to enable magnetic exchange between copper(II) ions.[46] The calculated effective magnetic moments from the equation, $\mu_{eff} = 2.828(\chi_m \times T)^{1/2}$ were 1.96 B.M. and 1.92 B.M. for Cu(pmed)Br_2 and Cu(dpmed)Br_2, respectively.

Conclusions

Five-coordinated copper(II) bromide complexes, Cu(pmed)Br_2 and Cu(dpmed)Br_2, with tridentate Schiff base containing amine and pyridine moiety, were prepared from the ligands and copper(II) bromide. The copper(II) center of Cu(pmed)Br_2 features a distorted square pyramidal coordination geometry with two Br atoms and the three N atoms of the tridentate ligand. Hydrogen bonds formed between the amine hydrogen atoms and apical Br atoms of neighbouring molecules resulted in the formation of two-dimensional networks in the *ab* plane. On the other hand, Cu(dpmed)Br_2 has an almost square pyramidal geometry and monomeric molecules are stabilized through intermolecular π-π interactions between the pyridine rings. In both compounds, no magnetic interactions occur between the copper(II) metal ions because the Cu-Cu distances are too far for magnetic contact.

Appendix A. Supplementary Data. CCDC 873483 and 873484 contain the supplementary crystallographic data for Cu(pmed)Br_2 and Cu(dpmed)Br_2, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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