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# Synthesis, structure and magnetic property of an asymmetric chlorido bridged dinuclear copper(II) complex containing a didentate Schiff base

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ABSTRACT

A dinuclear complex, $[Cu_2(\mu\text{-}Cl)_2Cl_2(pbba)_2]$ (**1**) [pbba = N-((pyridin-2-yl)benzylidene)benzylamine], has been isolated from the reaction of a 1:1 M ratio of $CuCl_2{\cdot}2H_2O$ and pbba in MeOH solution at room temperature. Compound **1** has been characterized using microanalytical, spectroscopic, thermal and other physico-chemical results. Single crystal X-ray diffraction measurements show that each metal center in **1** adopts a distorted square pyramidal geometry with a $CuN_2Cl_3$ chromophore ligated through two N atoms of pbba and two bridging and one terminal chloride atom. The centrosymmetric dinuclear unit contains an asymmetric di-μ-chlorido bridge. Variable-temperature magnetic susceptibility measurements indicate weak intramolecular ferromagnetic coupling ($J = +5.02 \pm 0.13\ cm^{-1}$) through chlorido bridges and weak intermolecular antiferromagnetic ($J' = -0.32 \pm 0.01\ cm^{-1}$) interactions among the dinuclear entities, coupled with weak zero-field splitting arising from the $S = 1$ ground state.

## 1. Introduction

Dinuclear copper(II) complexes with monoatomic bridges, such as halides, have been the center of attraction due to their interesting structures, catalytic and magnetic properties [1–9], and also as models for the active sites of biomolecules [10]. Depending on the nature of the co-ligands, chlorido bridged compounds [11] with planar $Cu(\mu\text{-}Cl)_2Cu$ bridging loops show different molecular structures [9,12–20] with varied bond distances and angles. The crystalline architectures of these compounds are found to be interesting due to the variations of the nature of forces such as weak intramolecular and/or intermolecular interactions. The magnetic super-exchange pathways [9,12–19] in these compounds depend on structural parameters, such as Cu–Cl and Cu···Cu distances, Cu–Cl–Cu angles and of course on the nature of the magnetic orbitals. This reflects that the structural parameters have great influence on the magnetic properties, so a detailed knowledge of these parameters is essential for magneto-structural/-chemical correlations. Several theoretical analyses [21–26] have been carried out to untangle this behavior and a range of magnetic interactions, like ferromagnetic (F) and antiferromagnetic (AF) exchanges, have been found [9,12–19]. In some of our earlier work, we reported the syntheses, characterization and magnetic properties of some copper(II) compounds in combination with pseudohalido/carboxylato/hydroxido bridging units and Schiff base/amine spacers of varied denticities [27]. In view of the importance of the copper(II) compounds and our interest in magneto-structural correlations of transition metal complexes, we wished to extend such work to copper(II) chloride in combination with a didentate Schiff base, N-((pyridin-2-yl)benzylidene)benzylamine (pbba; Scheme 1). We have successfully isolated and characterized one neutral dinuclear copper(II) chlorido complex of the type $[Cu_2(\mu\text{-}Cl)_2Cl_2(pbba)_2]$ (**1**). Details of the synthesis, crystal structure, thermal and magnetic behaviors of this compound are described below.

## 2. Experimental

### 2.1. General remarks and physical measurements

#### 2.1.1. Materials

High purity 2-benzoylpyridine (Lancaster, UK), benzylamine (Spectrochem, India) and copper(II) chloride dihydrate (E. Merck, India) were purchased from their respective concerns and used as received. The Schiff base N-((pyridin-2-yl)benzylidene)benzylamine (pbba) was prepared following a reported method [28]. All

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other chemicals and solvents used were AR grade. The synthetic reactions and work-up were done in the open air.

### *2.1.2. Physical measurements*

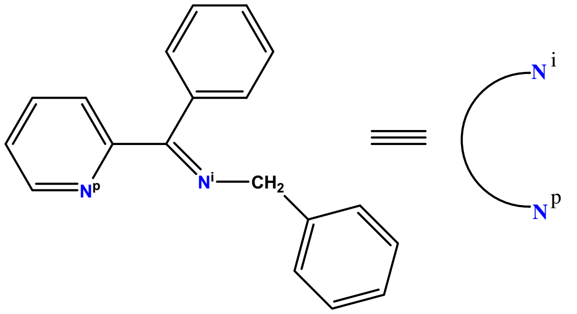
Elemental analyses (carbon, hydrogen and nitrogen) were performed on a Perkin–Elmer 2400 CHNS/O elemental analyzer. The IR spectrum (KBr disc, 4000–400 $cm^{-1}$) was recorded using a Perkin–Elmer FTIR model RX1 spectrometer. Thermal behavior was examined with a Perkin–Elmer Diamond TG/DT analyzer, with heating from 30 to 700 °C under nitrogen. Ground state absorption (in DMF) was measured with a Shimadzu model UV-2450 UV–VIS spectrophotometer. Variable-temperature magnetic measurements were carried out with a Quantum Design SQUID MPMS-XL susceptometer working in the 2–300 K temperature range. The magnetic field was 0.1 T. The diamagnetic corrections were evaluated from Pascal's constants.

### *2.2. Synthesis of $[Cu_2(\mu\text{-}Cl)_2Cl_2(pbba)_2]$ (**1**)*

Pbba (124.5 mg, 0.4571 mmol) in MeOH (5 ml) was added slowly to a $CuCl_2{\cdot}2H_2O$ (77.9 mg, 0.4569 mmol) solution (10 ml) in the same solvent. After filtration through a fine glass-frit, the supernatant green solution was kept in air for slow evaporation. Green rectangular crystals of **1** were deposited within two days, which were separated by filtration and dried *in vacuo* over silica gel indicator. Yield: 650.9 mg (80%). *Anal.* Calc. for $C_{38}H_{32}N_4Cl_4Cu_2$ (**1**): C, 56.10; H, 3.96; N, 6.89%. Found: C, 56.00; H, 3.85; N, 6.78%. IR (KBr, $cm^{-1}$): $\nu$(C=C) + $\nu$(C=N) 1613, 1593, 1571. UV–Vis ($\lambda_{max}$/nm): 280, 707, 917.

### *2.3. X-ray data collection and structure refinement*

A single crystal of **1** suitable for X-ray analysis was selected from those obtained by slow evaporation of a methanol solution at room temperature. Diffraction data were collected on a Bruker SMART CCD area-detector diffractometer using graphite monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). Intensity data were reduced using SAINT [29] and the empirical absorption corrections were performed with the SADABS [30] program. The structure was solved by SHELXS-97 [31] and refined by full-matrix least-squares methods based on $|F|^2$ using the program SHELXL-97 [31]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were located geometrically and refined using a standard riding model. Materials for publication were prepared using PLATON [32], DIAMOND [33] and MERCURY 3.1 [34] programs. A summary of the crystallographic data and structure determination parameters for **1** is given in Table 1.



**Scheme 1.** ($N^i$,$N^p$) donor set in pbba.

**Table 1**
Crystallographic data and structure refinement for **1**.

| Complex | 1 |
|---|---|
| Formula | $C_{38}H_{32}N_4Cl_4Cu_2$ |
| Formula weight | 813.58 |
| Crystal system | monoclinic |
| Space group | *C*2/*c* |
| *a* (Å) | 21.319(5) |
| *b* (Å) | 12.495(5) |
| *c* (Å) | 15.790(6) |
| $\alpha$ (°) | 90 |
| $\beta$ (°) | 122.12(4) |
| $\gamma$ (°) | 90 |
| *V* ($Å^3$) | 3562(3) |
| $\lambda$ (Å) | 0.71073 Å |
| $\rho_{calcd}$ (g $cm^{-3}$) | 1.517 |
| *Z* | 4 |
| *T* (K) | 293(2) |
| $\mu$ ($mm^{-1}$) | 1.528 |
| *F*(000) | 1656 |
| Crystal size ($mm^3$) | 0.20 × 0.16 × 0.06 |
| $\theta$ ranges (°) | 1.982–28.364 |
| *h*/*k*/*l* | −28,28/−16,16/−21,21 |
| Reflections collected | 28029 |
| Independent reflections | 4428 |
| $T_{max}$ and $T_{min}$ | 0.9135 and 0.7488 |
| Data/restraints/parameters | 4428/0/217 |
| Goodness-of-fit (GOF) on $F^2$ | 1.107 |
| Final *R* indices [$I > 2\sigma(I)$] | *R* = 0.0462 and *wR* = 0.1308 |
| *R* indices (all data) | *R* = 0.0771 and *wR* = 0.1648 |
| Largest peak and hole (e$Å^{-3}$) | 1.560 and −0.604 |

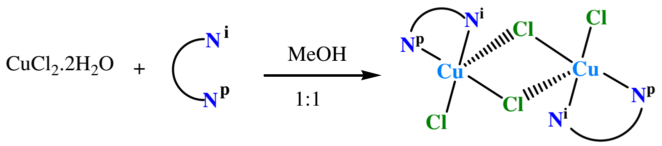
Weighting scheme: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, calcd $w = 1/[\sigma^2(F_o^2) + (0.0894P)^2]$; where $P = (F_o^2 + 2F_c^2)/3$.

## 3. Results and discussion

### *3.1. Synthesis and spectroscopic studies*

The Schiff base pbba was prepared by refluxing benzylamine and 2-benzoyl pyridine in a 1:1 M ratio in dehydrated ethanol. The neutral didentate chelator is of the ($N^i$, $N^p$) type where $N^i$ and $N^p$ are N(imine) and N(pyridine) donor centers, respectively. The penta-coordinated dinuclear compound $[Cu_2(\mu\text{-}Cl)_2Cl_2(pbba)_2]$ (**1**) was obtained in the one-pot reaction of a 1:1 M ratio of $CuCl_2{\cdot}2H_2O$ and the Schiff base (pbba) in MeOH solution at room temperature (Scheme 2).

Complex **1** was characterized by microanalytical (C, H and N), spectroscopic and other physicochemical results. The microanalytical data are in good conformity with the formulation. The moisture-insensitive compound is stable over long periods of time in powdery and crystalline states, and is soluble in MeOH, EtOH, MeCN, DMF and DMSO, but is insoluble in water. In IR spectrum, $\nu$(C=N) plus $\nu$(C=C) stretching frequencies [20] of the metal bound Schiff base are observed in the range 1620–1570 $cm^{-1}$ [35]. The complex displays multiple absorption bands and a shoulder in the 200–1100 nm range. A green solution of **1** shows a broad band at 707 nm assignable to the d–d transition ($d_{xz}$, $d_{yz} \rightarrow d_{x^2-y^2}$) with a low-energy shoulder at 917 nm, consistent with the square pyramidal (sp) geometry [36a] of the copper(II) centers. Additionally, a sharp band at 280 nm may be assigned to a ligand-based transition [36b].



**Scheme 2.** Schematic representation of the reaction.

### *3.2. Description of the crystal structure of* $[Cu_2(\mu\text{-}Cl)_2Cl_2(pbba)_2]$ (**1**)

In order to define the coordination sphere conclusively, a single-crystal X-ray diffraction study of **1** was made. An ORTEP representation of **1** and perspective views of the packing diagrams are shown in Figs. 1–3. Selected bond distances and angles relevant to the coordination spheres can be found in Table 2 and non-covalent interaction parameters are given in Table 3.

The structure of **1** consists of a centrosymmetric dinuclear unit, $[(Cl)Cu(pbba)(\mu\text{-}Cl)_2\text{-}Cu(pbba)(Cl)]$, with di-μ-chlorido bridges (Fig. 1). Each copper(II) center, bound by the unsymmetrical bidentate N-donor Schiff base pbba, is linked to each other through two bridging chloride units, Cl2 and its symmetry equivalent Cl2*a* (where $a = 1/2 - x,\ 1/2 - y,\ 1 - z$), affording a square planar arrangement for the $Cu(\mu\text{-}Cl)_2Cu$ core with a crystallographic inversion center. The bridging is to an appreciable extent unsymmetrical in nature with different Cu–Cl bond distances [Cu–Cl2 2.2660(14) Å and Cu–Cl2*a* 2.6330(12) Å; Table 2]. The fifth coordination site around each copper(II) is occupied by a terminal Cl1 atom with a Cu1–Cl1 distance of 2.2733(13) Å. The Cu···Cu non-bonding distance within the complex is 3.5195(15) Å. Two different bridging angles in the four-membered loop are: Cl2–Cu1–Cl2*a* 88.46(5)° and Cu1–Cl1–Cu1*a* 91.54(5)°. Each copper(II) center adopts a distorted square pyramidal ($\tau = 0.37$) geometry [37] with one imine N atom (N2), one pyridine N atom (N1) of pbba, one terminal Cl atom (Cl1) and one bridging Cl atom (Cl2) forming the *base* of the pyramid and the other bridging Cl atom (Cl2*a*) occupy the *apical* position (Fig. 2). It is worth noting that for the Cu1 center, Cl2*a* occupies the *basal* position of the square pyramid and Cl2 is in the *apical* position, whereas in the case of the other copper (Cu1*a*) center, Cl2 is in the *basal* plane and Cl2*a* is in the *apical* position. The *terminal* Cl atoms Cl1/Cl1*a* reside in *basal* arrangements around both Cu centers.

To be succinct, the geometry of the complex consists of two square pyramids sharing one *base-to-apex* edge (SP-I in Scheme 3), but with nearly parallel *basal* planes [9]. The *axial–equatorial* configuration of the two Cl bridges is depicted clearly in Fig. 2. The copper(II) centers deviate by 0.250 Å from the mean plane. Among the four equatorial atoms, N1 and Cl2 deviate (N1: 0.311 Å and N3: 0.233 Å) towards the *apical* Cl2*a* atom, whereas N2 and Cl1 show a considerable deviation (N2: 0.305 Å and Cl1: 0.239 Å) in the opposite direction to Cl2*a* from the mean plane.

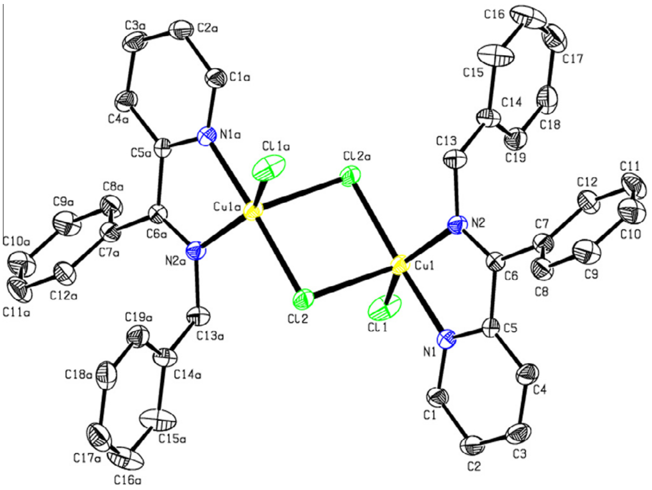


**Fig. 1.** PLATON view of $[Cu_2(\mu\text{-}Cl)_2Cl_{2(pbba)2}]$ (**1**). Displacement ellipsoids are drawn at the 50% probability level.

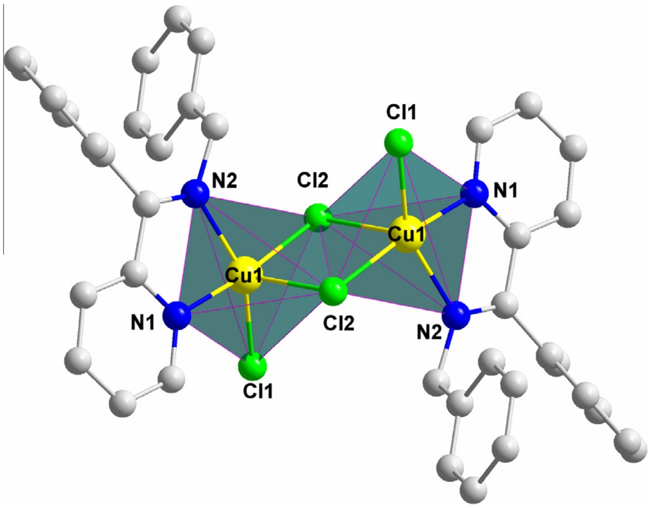


**Fig. 2.** Square pyramidal coordination environment of the two copper(II) centers showing the SP-I configuration in complex **1**.

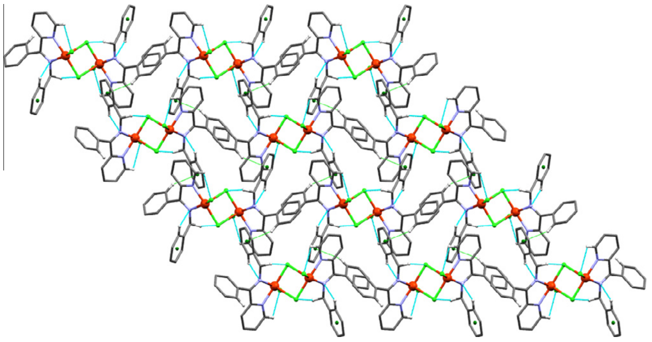


**Fig. 3.** Perspective view of the 2D sheet structure of **1** formed through weak intramolecular C–H···Cl and C–H···N hydrogen bonds (sky blue dotted lines) and intermolecular C–H···π interactions (green dotted lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Similar dinuclear copper(II) complexes having a $Cu(\mu\text{-}Cl)_2Cu$ core with square pyramidal copper(II) centers and with nearly parallel *basal* planes [9,12–16] are tabulated in Table 4. The two unequal Cu–Cl distances in **1** are shorter compared to those reported in the literature [9,12–16]. It is important to mention that the bridging Cu–Cl–Cu angle in **1** is remarkably larger [91.54(5)°] than the average value [89.40(5) Å] for those complexes; consequently, the Cu···Cu separation is longer (3.5195 Å) than those found in the reported [9,12–16] dichlorido bridged copper(II) complexes (Table 4).

Structure of **1** is stabilized by different kinds of intramolecular C–H···Cl and C–H···N hydrogen bonds (Table 3). The weak C–H···Cl hydrogen bonds between the terminal and bridging chloride units (Cl1 and Cl2) and H atoms (H1 and H13B) of the pyridine and

**Table 2**
Selected bond distances (Å) and bond angles (°) in **1**.

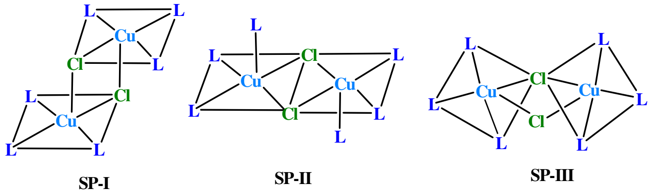
| Bond distances | | Bond angles | |
|---|---|---|---|
| Cu1–N1 | 2.005(3) | N2–Cu1–N1 | 79.33(12) |
| Cu1–N2 | 2.063(3) | N2–Cu1–Cl2*a* | 94.27(9) |
| Cu1–Cl1 | 2.2733(13) | N1–Cu1–Cl2*a* | 172.85(9) |
| Cu1–Cl2*a* | 2.6330(12) | N1–Cu1–Cl1 | 92.58(10) |
| Cu1–Cl2 | 2.2660(14) | N2–Cu1–Cl1 | 150.47(9) |
| | | Cl2–Cu1–Cl2*a* | 88.46(5) |
| | | Cu1–Cl2*a*–Cu1 | 91.54(5) |

Symmetry code: $a = 1/2 - x,\ 1/2 - y,\ 1 - z$

**Table 3**
Hydrogen bond and C–H···π interaction parameters (Å, °) for **1**.

| *Hydrogen bond parameters (Å, °)* | | | | | |
|---|---|---|---|---|---|
| D–H···A | D–H | H···A | D···A | D–H···A | Symmetry code |
| C1–H1···Cl1 | 0.93 | 2.76 | 3.234(5) | 113 | |
| C13–13B···Cl2*a* | 0.97 | 2.75 | 3.224(5) | 111 | 1/2 – *x*, 1/2 – *y*, 1 – *z* |
| C19–H19···N2 | 0.93 | 2.53 | 2.875(5) | 102 | |
| *C–H···π interactions (Å, °)* | | | | | |
| D–H···A | D–H | H···A | D···A | D–H···A | Symmetry code |
| C8–H8···Cg5 | 0.93 | 2.64 | 3.476(5) | 150 | *x*, 1 – *y*, – 1/2 + *z* |

Cg(5): C(14)–C(15)–C(16)–C(17)–C(18)–C(19)



**Scheme 3.** Different conformations of dichlorido bridged square pyramidal dinuclear copper(II) complexes.

–$CH_2$ groups of the Schiff base (Table 3) are in operation to strengthen the molecular architecture of the dinuclear unit in **1**. The intramolecular C–H···N hydrogen bonds between the imine N atom (N2) and the H atom (H19) of the benzene ring of pbba further stabilize the dinuclear moiety. These dinuclear units are associated with each other through weak intermolecular C–H···π interactions (C8–H8···Cg5, symmetry code = *x*, 1 – *y*, –1/2 + *z*), leading to the formation of a 2D sheet structure stabilizing the entire crystal lattice (Fig. 3); the phenyl H atom (H8) and the phenyl ring of pbba (Cg5: C14–C15–C16–C17–C18–C19) are involved in such interactions.

### 3.3. Thermal study

To examine the thermal stability of compound **1**, thermogravimetric analysis (TGA) was made between 40 and 800 °C in a static atmosphere of nitrogen. The TG curve (Fig. S1) shows that compound **1** is stable up to 203 °C and then gradual decomposition (obs.: 78.18%, calcd.: 83.98%) occurs in the 203–572 °C temperature range, corresponding to the removal of the four halido and two Schiff base ligands. The residue after heating above 600 °C corresponds to the formation of metallic copper (obs.: 18.79%, calcd.: 15.65%).

### 3.4. Magnetic properties

The magnetic behavior (Fig. 4) of **1** was investigated in the 2–300 K temperature range. The room temperature (300 K) $\chi_M T$ value (0.875 $cm^3\,mol^{-1}$ K) increases (0.93 $cm^3\,mol^{-1}$ K) continuously down to 10 K and then decreases (0.76 $cm^3\,mol^{-1}$ K at 2 K) (Fig. 4a). This is indicative of an $S = 1$ ground state for the dinuclear complex. The overall feature is characteristic of a weak intramolecular ferromagnetic (F) exchange and a very weak intermolecular antiferromagnetic (AF) interaction coupled presumably with a very weak zero-field splitting (D) of the $S = 1$ ground state. The fitting of the susceptibility data is carried out following the Bleaney–Bowers formula [Eq. (1)] [1, p. 104] considering the mean field approach as arising from the intermolecular interactions and with use of ORIGIN v.7.0 software [38]; the temperature independent paramagnetism (TIP) parameter is the standard for two copper(II) ions [for each copper(II), $\chi = 60 \times 10^{-6}$ $cm^3\,mol^{-1}$] [1, p. 8].

$$\chi_M = \frac{Ng^2\beta^2}{k_B T} \cdot \frac{2\exp(J/k_B T)}{1 + 3\exp(J/k_B T)} \tag{1}$$

The Hamiltonian used is $H = -JS_1S_2$. The best-fit parameters obtained are: $J = +5.02 \pm 0.13$ $cm^{-1}$, $J'$ (intermolecular + *D*) = –0.32 ± 0.01 $cm^{-1}$, $g = 2.12 \pm 0.01$ and $R = 1.0 \times 10^{-4}$; the *R* factor is defined as $\Sigma_i[(\chi_m T)_{obs} - (\chi_m T)_{calc}]^2 / \Sigma_i[(\chi_m T)_{obs}]^2$.

**Table 4**
Comparative structural and magnetic properties of binuclear copper(II) chloride complexes with a planar Cu(μ-Cl)$_2$Cu core and SP-I configuration similar to complex **1**.

| Compound | Axial Cu–Cl distance, *R* (Å) | Cu–Cl–Cu angle, α (°) | α/R (°/Å) | Cu···Cu separation (Å) | *J*-value[#] ($cm^{-1}$) | Refs. |
|---|---|---|---|---|---|---|
| $[Cu_2(\mu\text{-}Cl)_2(L^H)_2](ClO_4)_2$ | 2.896 | 86.21 | 29.769 | 3.542 | +0.257 | [12a] |
| $[Cu_2(\mu\text{-}Cl)_2(L^{OMe})_2](ClO_4)_2$ | 2.831 | 85.08 | 30.053 | 3.449 | +0.306 | [12a] |
| $[Cu_2(\mu\text{-}Cl)_2(L^{Me})_2](ClO_4)_2$ | 2.844 | 87.11 | 30.629 | 3.526 | +0.327 | [12a] |
| $[Cu_2(\mu\text{-}Cl)_2(L^{Cl})_2](ClO_4)_2$ | 2.830 | 87.30 | 30.848 | 3.522 | +0.188 | [12a] |
| $[CuCl(HL1)]_2{\cdot}H_2O$ | 2.732 | 84.83 | 31.050 | 3.382 | –0.274 | [9] |
| $[Cu_2Cl_2(qsalBr)_2]{\cdot}DMF$ | 2.818 | 84.863 | 30.115 | 3.498 | –6.91 | [12b] |
| $[CuCl(HL2)]_2{\cdot}H_2O$ | 2.677 | 84.46 | 31.550 | 3.337 | +43.2(5) | [12c] |
| $[\{Cu(\mu\text{-}Cl)_2(Opo)(pz^{Ph})\}_2]$ | 2.83 | 93.63 | 33.0 | 3.753 | +8.72 | [13a] |
| $[CuCl_2(ppmma)]_2$ | 2.696 | 89.73 | 33.283 | 3.510 | ∼ 0 | [13b] |
| $[CuCl_2(PyTn)]_2$ | 2.906 | 88.6 | 30.489 | 3.612 | +13.73 | [13c] |
| $[Cu_2Cl_4(Mebta)_4]$ | 2.629 | 88.1 | 33.511 | 3.437 | +3.35 | [13d] |
| $[Cu_2(amp)_2Cl_4]$ | 2.806 | 85.82 | 30.584 | 3.479 | –9.4 | [14a] |
| $[CuCl_2(HL3)]_2(ClO_4)_2$ | 2.922 | 94.7 | 32.409 | 3.86 | +10.70 | [14b] |
| $[Cu_2Cl_2(L4)_2](ClO_4)_2$ | 2.640 | 86.435 | 32.740 | 3.376 | –1.95 | [14b] |
| $[CuCl(L5)]_2(ClO_4)_2$ | 2.657 | 88.81 | 33.425 | 3.494 | +0.58 | [14c] |
| $[CuCl(L6)]_2(ClO_4)_2$ | 2.581 | 88.2 | 34.17 | 3.396 | +1.14 | [15a] |
| $[CuCl(Hfsaaep)]_2$ | 2.846 | 95.27 | 33.475 | 3.825 | +0.15 | [15b] |
| $[CuCl(Pypep)]_2{\cdot}2H_2O$ | 2.831 | 91.1 | 32.170 | 3.693 | –2.32 | [15c] |
| $[\{Cu(\mu\text{-}Cl)_2(terpy)\}_2](PF_6)_2$ | 2.72 | 89.9 | 33.1 | 3.510 | –2.95 | [16a] |
| $[CuCl_2(tmso)]_2$ | 3.020 | 88.5 | 29.30 | 3.736 | –8.34 | [16b] |
| $[CuCl_2(dmen)]_2$ | 2.734 | 86.13 | 31.50 | 3.458 | +3.15 | [16c] |
| $[Cu_2Cl_4(tmen)_2]$ | 3.147 | 96.8 | 30.759 | 4.089 | –2.8 | [16d] |
| $[Cu_2(\mu\text{-}Cl)_2Cl_2(pbba)_2]$ | 2.633 | 91.54 | 34.766 | 3.5195 | +5.02 | Our work |

[#] Hamiltonian $H = -JS_1S_2$ where $L^X$ = N,N-bis[(3,5-dimethylpyrazole-1-yl)methyl]benzylamine (X = H, OMe, Me, Cl); HL1 = N-(2-hydroxyethyl)-5-nitrosalicylaldimine); HqsalBr = 8-(5-bromo-salicylideneamino)quinoline; $H_2L2$ = [2-((E)-(2-hydroxy-ethylimino)methyl)-4-bromophenol]; $pz^{Ph}$ = 3-phenyl-pyrazolyl; OpoH = 2-hydroxypyridine-*N*-oxide; ppmma = phenyl-N-[(pyridine-2-yl)methylene]methaneamide; PyTn = 2-(pyrazol-1-yl)-2-thiazoline; Mebta = 1-methylbenzotriazole; amp = 5-amino-methyl-3-methyl-pyrazole; L3 = 1,5-bis(pyridin-4-ylmethyl)-1,5-diazacyclooctane; L4 = 1-(pyridin-2-ylmethyl)-1,4-diazacycloheptane; L5 = 1-(Imidazol-4-ylmethyl)-1,5-diazacyclooctane; L6 = 1-(2-pyridylmethyl)-1,5-diazacyclooctane; $H_2$fsaaep = 3-[*N*-2-(pyridylethyl)formimidoyl]salicylic acid; PypepH = N-(2-(4-imidazolyl)ethyl)-pyridine-2-carboxamide; terpy = 2,2′;6′,2″-*terpyridine*; tmso = tetramethylene sulfoxide; dmen = N,N′-dimethylethylenediamine and tmen = N,N,N′,N′-tetramethylethylenediamine.

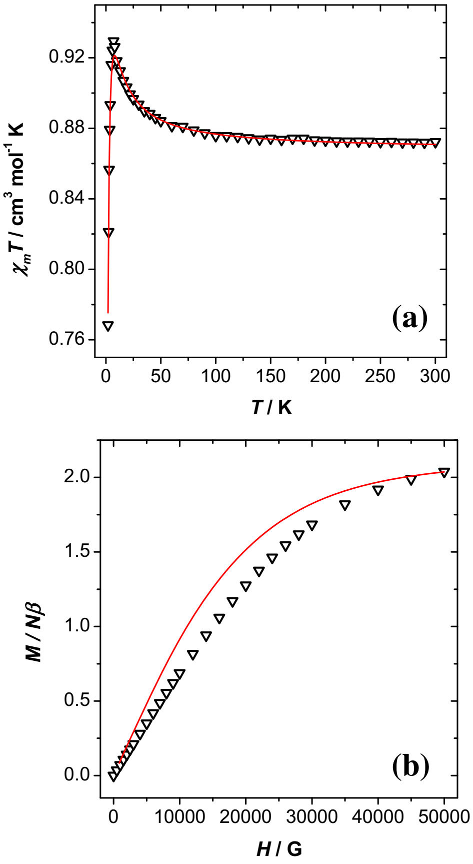


**Fig. 4.** (a) Plot of the $\chi_M T$ vs. $T$ for **1**. Solid line indicates the best fit (see text) and (b) plot of the reduced magnetization ($M/N\beta$) vs. H at 2 K for **1**.

The reduced molar magnetization at 2 K is given in Fig. 4b. The tendency for saturation magnetization at 5 T is close to 2.0 $N\beta$, as expected for an $S = 1$ ground state. The curve does not follow the Brillouin formula for $S = 1$ (ground state) and $g = 2.1$ due to the magnetic exchange and zero-field splitting parameters.

Dichlorido bridged dinuclear copper(II) complexes have been studied by different research groups to establish magneto-structural correlations [21–26]. These show that the exchange coupling constant $J$ depends on the value of the Cu–Cl–Cu bridging angle ($\alpha$), as well as on the distance of the longer axial Cu–Cl bond (R). However, these parameters are not the only ones that play an important role in determining the magnetic coupling; the different arrangements of the magnetic orbital of copper(II) have a great influence on the magnetic behavior of dinuclear copper(II) complexes [9,12–19].

The geometry around the metal(II) center in these compounds is generally a square pyramid with a different degree of distortion towards a trigonal bipyramid. The literature shows that the two square pyramids give rise to three types of geometries (Scheme 3): (i) square pyramids sharing one *base-to-apex* edge but with parallel *basal* planes (SP-I) [9,12–16], (ii) square pyramids sharing a *basal* edge with coplanar *basal* planes (SP-II) [17,18] and (iii) square pyramids sharing one *base-to-apex* edge with the two bases nearly perpendicular to one another (SP-III) [19a]. Generally, dichlorido bridged dinuclear copper(II) complexes with SP-I and SP-II configurations lead to ferromagnetic or antiferromagnetic coupling, depending on the nature of co-ligands, but the comparatively rare SP-III geometry shows ferromagnetic coupling.

The configuration of the metal centers in **1** is SP-I, as evident from its structural features (Fig. 1). Willett and coworkers [21] and Hatfield and coworkers [22] have shown that the singlet–triplet gap ($J$) in such complexes (SP-I) varies in a regular way with the quotient $\alpha/R$, where $\alpha$ is the Cu–Cl–Cu bridging angle, and $R$ is the longer out-of plane Cu–Cl bond distance. It was found that for values of this quotient $\alpha/R$ (°/Å) lower than 32.6 and higher than 34.8, the exchange interaction is antiferromagnetic. For values falling between these limits it is ferromagnetic. In the case of complex **1**, the value of the quotient $\alpha/R$ is 34.766 °/Å suggesting a ferromagnetic interaction between the two copper(II) ions.

A theoretical study by Mrozinski and co-workers [13d] has established a correlation of the magnetic coupling and the parameters $\alpha$ and $R$; for small $\alpha$ values and short Cu–Cl distances ($R$), the magnetic coupling is ferromagnetic. With the $\alpha$ and $R$ values [$\alpha = 91.54(5)°$ and $R = 2.2660(14)$ Å] of complex **1**, a small ferromagnetic coupling is predicted, which is in agreement with the experimental result ($J = +5.02 \pm 0.13$ cm$^{-1}$). An examination (Table 4) of the $\alpha$ and $R$ values of the reported dichlorido bridged SP-I type of copper(II) complexes [9,13–16] and complex **1** reflects that the major reason for ferromagnetic coupling in **1** is the much shorter $R$ value [2.2660(14) Å], although the much higher $\alpha$ value [91.54(5)°] is likely to decrease the magnitude of the ferromagnetic coupling.

## 4. Conclusion

One neutral dichlorido bridged dinuclear copper(II) compound containing an unsymmetrical didentate (N,N) Schiff base as an end-capping ligand has been isolated. Structural analysis reveals that each copper(II) center, with a distorted square pyramidal geometry in the compound **1**, is linked to each other by asymmetric di-μ-chlorido bridges in the SP-I conformation. The structure of **1** is stabilized by intramolecular C–H···Cl and C–H···N hydrogen bonds and intermolecular C–H···π interactions forming a 2D sheet structure. Variable-temperature magnetic susceptibility measurement shows weak intramolecular ferromagnetic coupling through the chlorido bridges and weak intermolecular antiferromagnetic interactions among the dinuclear entities coupled with weak zero-field splitting arising from the $S = 1$ ground state. A comparison of the magnetic behavior of **1** with related dichlorido bridged dinuclear copper(II) complexes containing mono-, di- and tridentate N-/O-donor ligands with similar Cu(μ-Cl)$_2$Cu cores reveals a good magneto-structural correlation and untangles the nature of the interactions.

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## Appendix A. Supplementary data

CCDC 1004055 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2014.12.031.

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