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Subhra Basak, Soma Sen, Georgina M. Rosair, Cédric Desplanches, Eugenio Garribba, et al.. A novel  $\mu$ 1,1-azido-,  $\mu$ 2-alkoxo-, and  $\mu$ 2-phenoxo-bridged tetranuclear copper(II) complex with a quinquedentate schiff-base ligand: magneto-structural and DFT studies. Australian Journal of Chemistry, 2009, 62 (4), pp.366-375. 10.1071/CH08511 . hal-00381986

**HAL Id: hal-00381986**

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Submitted on 20 Sep 2023

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# A Novel $\mu_{1,1}$ -Azido-, $\mu_2$ -Alkoxo-, and $\mu_2$ -Phenoxo-Bridged Tetranuclear Copper(II) Complex with a Quinquedentate Schiff-Base Ligand: Magneto-Structural and DFT Studies

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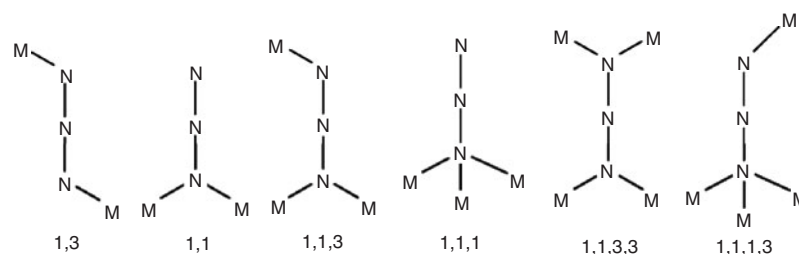
A novel tetranuclear copper(II) complex  $[\text{Cu}_4\text{L}_2(\mu_{1,1}\text{-N}_3)_2]\cdot\text{CH}_3\text{CN}$  (**1**) has been synthesized using a symmetrical quinquedentate  $\text{N}_2\text{O}_3$ -donor Schiff-base ligand **H<sub>3</sub>L** (*N,N'*-(2-hydroxypropane-1,3-diyl)bis(2-hydroxyacetophenimine)) and characterized by elemental analysis, Fourier-transform (FT)-IR, UV-visible, electron paramagnetic resonance spectroscopy, and cyclic voltammetry. The X-ray single-crystal structure of **1** reveals three kinds of bridges among the four metal centres: one from the exogenous azido ligand and two from the phenoxo and alkoxo moieties of the Schiff base. The same structure highlights the remarkable versatility of copper(II) to adopt an array of stereochemistries. Four unusual eight-membered metallacycles exist in **1**. The  $\mu_{1,1}$ -azido,  $\mu_2$ -alkoxo, and  $\mu_2$ -phenoxo bridges among the four copper centres have facilitated interesting magnetic interactions that have been elucidated by variable-temperature magnetic susceptibility measurements and backed up by density functional theory calculations. Detailed analyses have shown that the antiferromagnetic effect through the alkoxo-bridged  $\text{Cu}^{\text{II}}$  centres combined with the ferromagnetic interaction through the azido-bridged metal centres results in an  $S = 0$  ground state.

## Introduction

Exchange-coupled multinuclear complexes bridged by pseudo-halides have received growing interest because of their diverse magnetic interactions.<sup>[1]</sup> The main rationale for synthesizing such complexes stems from the understanding of the fundamental science of magnetic interactions and magneto-structural correlations in molecular systems.<sup>[2]</sup> The use of different bridging ligands and well-designed polydentate Schiff-base ligands has afforded an impressive array of multinuclear transition metal coordination complexes with their intriguing architectures and

topologies.<sup>[3]</sup> As a bridging ligand, the azide ion can act as an efficient and versatile magnetic coupler<sup>[4]</sup> owing to its di- (either end-on (EO) or end-to-end (EE)), tri- or tetradentate bridging modes (Scheme 1).

From the magnetic point of view, the EO bridging mode of the azide can mediate either ferromagnetic or antiferromagnetic interactions depending on the metal–N(azido)–metal (M–N–M) bond angles, whereas the complexes with EE bridges produce antiferromagnetic coupling with a few exceptions of even ferromagnetic interactions.<sup>[5]</sup> The choice of the metal atoms along



**Scheme 1.** Different bridging modes of azide ions.

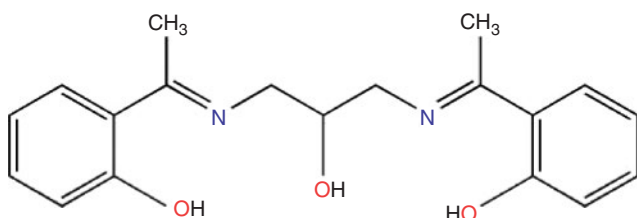


Fig. 1. Structure of  $\mathbf{H}_3\mathbf{L}$ .

with the bridging ligands, the steric and electronic requirements of the co-ligands, and counterions present in the system also influence the intra- and interlayer structure, and hence the magnetic properties.<sup>[6]</sup>

Among transition metals, there is a major interest in copper due to its important role in biological systems.<sup>[7]</sup> One of the simplest and commonest cases of multinuclear  $\text{Cu}^{\text{II}}$  complexes is that of the tetranuclear species showing a variety of arrangements such as linear, cubane, rectangular, and cyclic  $\text{Cu}_4$  centres.<sup>[8]</sup> Magneto-structural correlations for such phenoxo- and alkoxo-bridged systems show that the crucial geometrical parameter is the Cu–O–Cu angle in determining the magnetic behaviours of the complexes.<sup>[9]</sup>

Our research group has already reported various pseudohalide-bridged metal complexes using different tri- and tetradentate Schiff-base ligands.<sup>[5d,10]</sup> Herein, we describe the synthesis, physicochemical characterization, magnetic properties, and density functional theory (DFT) studies of a novel tetranuclear  $\text{Cu}^{\text{II}}$  complex  $[\text{Cu}_4\text{L}_2(\mu_{1,1}\text{-N}_3)_2]\cdot\text{CH}_3\text{CN}$  (**1**) with a symmetrical  $\text{N}_2\text{O}_3$ -donor quinque-dentate Schiff-base ligand  $\mathbf{H}_3\mathbf{L}$  (*N,N'*-(2-hydroxypropane-1,3-diyl)bis(2-hydroxyacetophenimine)) (Fig. 1), derived from the condensation of 2-hydroxyacetophenone and 1,3-diaminopropan-2-ol in stoichiometric amounts. To the best of our knowledge, **1** is the first structurally characterized copper(II) complex to elucidate the coordination behaviour of this Schiff-base ligand ( $\mathbf{H}_3\mathbf{L}$ ). However, Arici et al.<sup>[11]</sup> have determined the structure of the trinuclear nickel(II) complex with the reduced form of  $\mathbf{H}_3\mathbf{L}$  (acting as a quadridentate  $\text{N}_2\text{O}_2$ -donor ligand) by single-crystal X-ray analysis. Song et al.<sup>[12]</sup> have reported an open cubane structure in a  $\mu_{1,1}$ -azido- and  $\mu_3$ -alkoxo-bridged tetranuclear copper(II) complex using the Schiff-base ligand formed by the reaction between salicylaldehyde and 1,3-diaminopropan-2-ol. The present complex **1** is a unique and rare example of a tetranuclear copper(II) Schiff-base complex showing three different kinds of bridging units, i.e. two  $\mu_{1,1}$ -azido, two  $\mu_2$ -alkoxo, and two  $\mu_2$ -phenoxo groups at the same time. Both the antiferromagnetic interaction associated with the alkoxides and the ferromagnetic interaction arising from the azides exist in **1**, resulting in a diamagnetic  $S = 0$  ground state.

## Results and Discussion

### Infrared Spectroscopy

The infrared spectrum of **1** is in a good agreement with the structural data given in the present paper. The sharp bifurcated bands at 2101 and 2071  $\text{cm}^{-1}$  indicate the presence of the asymmetric stretch of the azido bridge, which is attributable to an EO bridging mode.<sup>[12,13]</sup> The medium band at 1303  $\text{cm}^{-1}$  is assigned to the azido symmetric stretching mode,  $\nu_s(\text{N}_3)$ . The strong sharp absorption band of the imine group in the free ligand appears at 1612  $\text{cm}^{-1}$ , whereas this band shifts to a lower frequency at  $\sim 1601$   $\text{cm}^{-1}$  on coordination of the imino nitrogen

atom with the metal ion.<sup>[14,15a,15b]</sup> The phenolic  $\nu_{\text{Ar-O}}$  in the free ligand exhibits a strong band at 1280  $\text{cm}^{-1}$  that also shifts to the lower-frequency region at  $\sim 1234$   $\text{cm}^{-1}$ , providing evidence for coordination to the metal ion through the deprotonated phenolic oxygen atom.<sup>[15c]</sup> Bands appearing at 447 and 375  $\text{cm}^{-1}$  correspond to  $\nu_{\text{Cu-N}}$  and  $\nu_{\text{Cu-O}}$ , respectively.

### UV-Visible Spectroscopy

The electronic spectral data for the complex in  $\text{CH}_3\text{CN}$  also support its environment. The UV-visible spectrum of **1** displays four bands. The broad absorption bands at 352 and 441 nm can be assigned to the charge-transfer transitions of the azido nitrogens and phenoxo or alkoxo oxygens to the copper ions.<sup>[12]</sup> An intense band at 267 nm is very likely to be due to an intraligand  $\pi \rightarrow \pi^*$  charge-transfer transition.<sup>[16]</sup> A broad band at 610 nm is assigned to the d-d transitions that are typical for a  $\text{Cu}^{\text{II}}$  Schiff-base complex.<sup>[17]</sup>

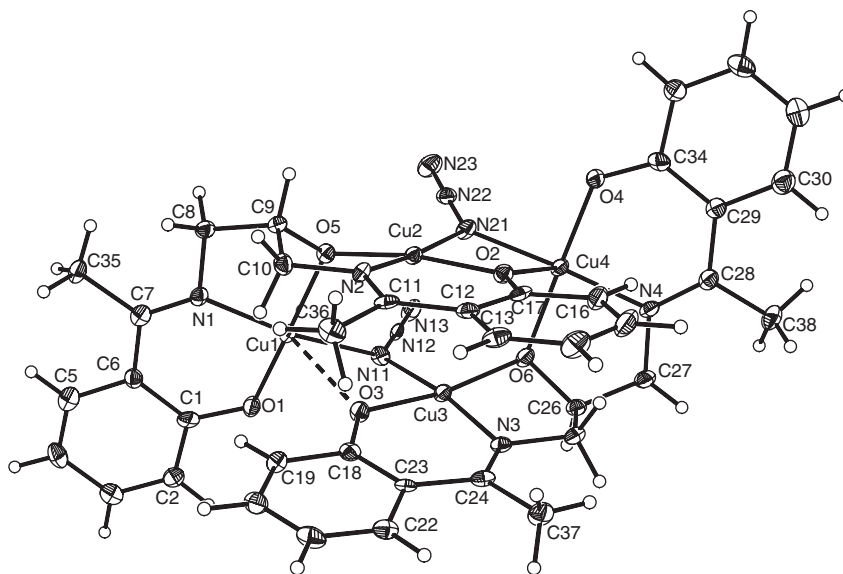
### Description of Crystal Structure of **1**

Crystals of the title complex could not be obtained straightforwardly by the reaction of  $\text{Cu}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ ,  $\mathbf{H}_3\mathbf{L}$ , and  $\text{NaN}_3$  in 1:1:1 molar ratio in  $\text{CH}_3\text{OH}$ , but modification of the molar ratio to 10:10:9 in a  $\text{CH}_3\text{OH}/\text{CH}_3\text{CN}$  medium under reflux conditions gave good-quality, larger-sized single crystals of **1**. The elemental analysis is consistent with the formula  $[\text{Cu}_4\text{L}_2(\mu_{1,1}\text{-N}_3)_2]\cdot\text{CH}_3\text{CN}$ . The presence of the  $\text{CH}_3\text{CN}$  in the lattice probably helps to stabilize the crystal structure, which may not be possible only in the  $\text{CH}_3\text{OH}$  medium.

The ORTEP drawing of **1** with the atom labelling scheme is shown in Fig. 2, with selected bond dimensions listed in Table 1. In fact, each of the two deprotonated Schiff-base ligands ( $\text{L}^{3-}$ ) present in **1** behaves as a quinque-dentate  $\text{N}_2\text{O}_3$ -donor ligand and remains in contact with the three copper(II) centres through the two imino N atoms, two phenoxo O atoms (a  $\mu_2$ -bridging and a terminal non-bridging), and one  $\mu_2$ -bridging alkoxo O atom. The two  $\mu_2$ -phenoxo groups of the two  $\text{L}^{3-}$  moieties show asymmetric bridging modes as 2.546(3) and 1.871(3) Å for Cu1–O3 and Cu3–O3 respectively, 2.428(3) and 1.876(3) Å for Cu4–O2 and Cu2–O2 respectively. The long contacts are pseudo-axial with respect to the Cu coordination geometry in that the Cu–O bonds lie distinctly away from the perpendicular to the square plane (28.4° (Cu1–O3) and 22.5° (Cu4–O2)). However, the two single  $\mu_2$ -alkoxo groups bridge symmetrically with the metal centres, forming almost equal bond distances of 1.901(3) and 1.871(3) Å for Cu1–O5 and Cu3–O3 respectively, as well as 1.938(3) and 1.973(3) Å for Cu3–O6 and Cu4–O6 respectively.

There are many tetranuclear  $\text{Cu}^{\text{II}}$  complexes in the Cambridge Structural Database<sup>[18]</sup> but few with azido bridges.<sup>[12,19]</sup> None of them shows  $\mu_{1,1}$ -azido,  $\mu_2$ -alkoxo, and  $\mu_2$ -phenoxo bridging units at the same time among the four metal centres as exist in the case of **1**. This complex consists of the four eight-membered metallacycles (Cu4–O6–Cu3–O3–Cu1–O5–Cu2–N21, Cu4–O6–Cu3–N11–Cu1–O5–Cu2–O2, Cu4–O6–Cu3–N11–Cu1–O5–Cu2–N21, and Cu4–O6–Cu3–O3–Cu1–O5–Cu2–O2) either in the boat or chair conformation due to the special array of metal centres and ligating atoms. The complex almost contains a pseudo two-fold symmetry axis perpendicular to the view axis as represented in Fig. 3.

Among the four copper(II) centres, the pairs Cu1 and Cu2 as well as Cu3 and Cu4 are singly bridged by the  $\mu_2$ -alkoxo oxygen atoms O5 and O6, respectively. Other pairs of the linked copper(II) centres (Cu1/Cu3 and Cu2/Cu4) are doubly bridged

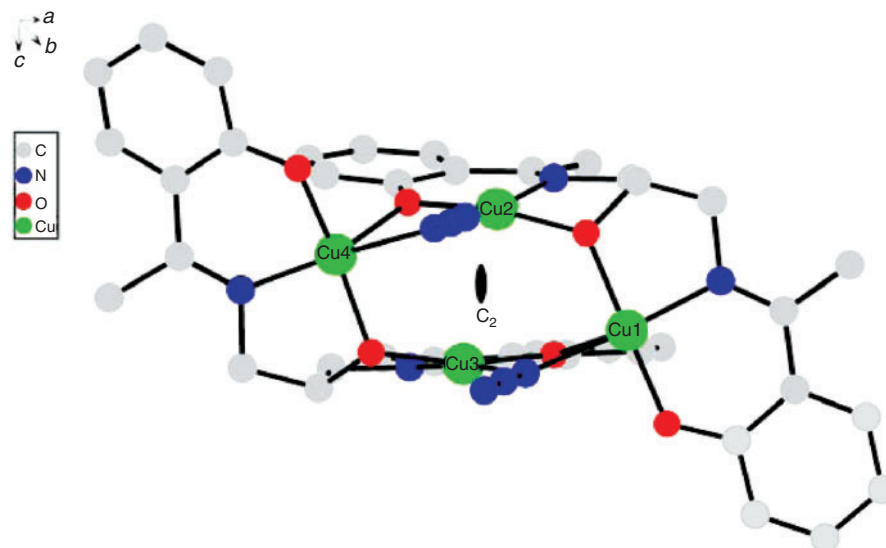


**Fig. 2.** ORTEP view of **1** with atom labelling scheme. Ellipsoids are shown at the 40% probability level. The  $\text{CH}_3\text{CN}$  molecule present in the lattice is omitted for clarity.

**Table 1.** Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **1**

Bond lengths			
Cu1–O1	1.877(3)	Cu4–O4	1.888(3)
Cu1–O5	1.947(3)	Cu4–O6	1.973(3)
Cu1–N1	1.953(4)	Cu4–N21	2.003(4)
Cu1–N11	2.054(4)	Cu4–N4	1.949(4)
Cu1–O3	2.546(3)	Cu4–O2	2.428(3)
Cu2–O5	1.901(3)	Cu3–O3	1.871(3)
Cu2–O2	1.876(3)	Cu3–O6	1.938(3)
Cu2–N2	1.949(4)	Cu3–N3	1.945(4)
Cu2–N21	1.974(4)	Cu3–N11	1.981(4)
Cu1...Cu2	3.3615(9)	Cu1...Cu3	3.3250(8)
Cu1...Cu4	5.540(1)	Cu2...Cu3	2.9583(8)
Cu2...Cu4	3.1994(8)	Cu3...Cu4	3.3958(9)
Bond angles			
O1–Cu1–O5	178.60(13)	O4–Cu4–O6	170.95(13)
O1–Cu1–N1	94.41(14)	O4–Cu4–N4	93.44(14)
O5–Cu1–N1	85.01(14)	N4–Cu4–O6	85.39(14)
O1–Cu1–N11	90.67(14)	O4–Cu4–N21	89.78(14)
N11–Cu1–O5	89.72(13)	N4–Cu4–N21	174.22(16)
N1–Cu1–N11	170.05(15)	O6–Cu4–N21	90.67(14)
O3–Cu1–O5	89.80(11)	O4–Cu4–O2	99.06(12)
O3–Cu1–O1	91.57(11)	N4–Cu4–O2	113.83(13)
O3–Cu1–N1	122.63(14)	O6–Cu4–O2	89.60(11)
O3–Cu1–N11	65.65(14)	O2–Cu4–N21	70.30(13)
O2–Cu2–O5	170.30(13)	O3–Cu3–O6	168.47(13)
O2–Cu2–N2	93.97(14)	O3–Cu3–N3	94.10(14)
O5–Cu2–N2	86.83(14)	O6–Cu3–N3	87.26(14)
O2–Cu2–N21	83.89(14)	O3–Cu3–N11	81.99(14)
O5–Cu2–N21	96.41(14)	O6–Cu3–N11	98.03(14)
N2–Cu2–N21	172.99(15)	N3–Cu3–N11	171.75(15)
Cu2–O5–Cu1	121.71(15)	Cu3–O3–Cu1	96.49(13)
Cu3–O6–Cu4	120.51(15)	Cu2–O2–Cu4	95.18(12)
Cu3–N11–Cu1	110.93(18)	Cu2–N21–Cu4	107.14(18)
N13–N12–N11	178.80(5)	N23–N22–N21	178.90(5)
N22–N21–Cu2	127.20(3)	N22–N21–Cu4	125.60(3)
N12–N11–Cu3	125.50(3)	N12–N11–Cu1	120.10(3)

by the  $\mu_2$ -phenoxo oxygen atoms (O3 and O2 respectively) from the two trianionic Schiff-base moieties  $\text{L}^{3-}$  and by the EO azido nitrogen atoms (N11 and N21 respectively). Cu1 and Cu4 are five-coordinate, whereas Cu2 and Cu3 are both four-coordinate. The five-coordinated  $\text{Cu}^{\text{II}}$  centre may possess either square-pyramidal (SP) or trigonal bipyramidal (TBP) geometry, and can be evaluated by the structural index parameter,  $\tau$  ( $\tau = |\theta - \Phi|/60$ , where  $\theta$  and  $\Phi$  are the two largest coordination angles;  $\tau = 0$  and 1 for perfect SP and ideal TBP geometries, respectively).<sup>[20]</sup> In **1**, the calculated  $\tau$  values for Cu1 and Cu4 are 0.143 and 0.055, respectively. Therefore, the geometry about Cu1 and Cu4 can be best described as distorted square-pyramid. The basal plane of each square pyramid involves a nitrogen atom from a bridging azido group, an imine nitrogen atom, a phenoxo oxygen atom, and a bridging alkoxy oxygen atom from the  $\text{N}_2\text{O}_2$ -donor set (N11, N1, O1, and O5 atoms for Cu1; and N21, N4, O4, and O6 atoms for Cu4) of one Schiff base. The apical site is occupied by the oxygen atom (O3 for Cu1, and O2 for Cu4) from the bridging phenoxo group of another Schiff-base ligand. In the  $\text{CuN}_2\text{O}_3$  coordination sphere, both the Cu1 and Cu4 atoms are displaced from their mean equatorial planes by 0.085(2) and 0.115(2)  $\text{\AA}$ , respectively, towards the axial phenolic oxygen atoms. The Cu–N (imino and azido) bond distances span the range 1.94–2.05  $\text{\AA}$ , confirming the equatorial binding. The Cu–O (alkoxy and phenoxo) equatorial bond distances range from 1.87 to 1.97  $\text{\AA}$ . The axial bonds Cu4–O2<sub>phenoxo</sub> (2.428(3)  $\text{\AA}$ ) and Cu1–O3<sub>phenoxo</sub> (2.546(3)  $\text{\AA}$ ) are considerably elongated, characteristic of the SP structure of copper(II). The Cu1–O3 bond length is a long Cu–O distance, so it is depicted as a dotted line in Fig. 2. The O3–Cu1–N11 and O2–Cu4–N21 bond angles are shorter (65.65(14) $^\circ$  and 70.30(13) $^\circ$  respectively) than the other bond angles incorporating the axial oxygen atom, resulting in a Cu1–O3 or Cu4–O2 bond inclined to the equatorial azido group. The probable reason for this may be the bridging nature of both the phenoxo oxygen (O3 or O2) and azido nitrogen atoms (N11 or N21) attached to the metal centres. One six-membered  $\text{CuOC}_3\text{N}$ , and the other five-membered

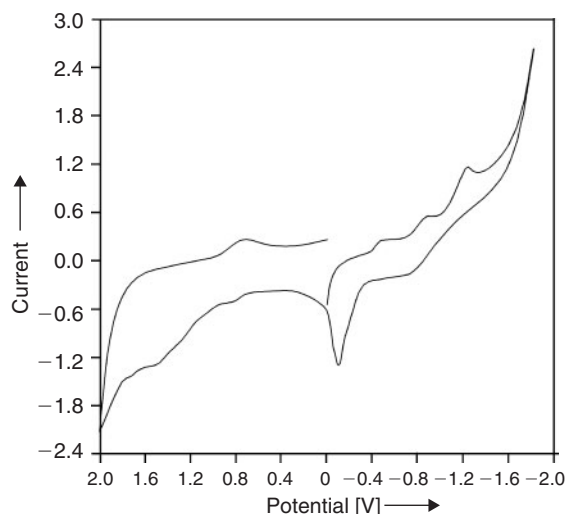


**Fig. 3.** View of **1** showing the presence of a pseudo- $C_2$  axis perpendicular to the view axis. The trace of the  $C_2$  axis is represented as an ellipsoid. Hydrogen atoms have been omitted for clarity.

$\text{CuOC}_2\text{N}$  chelate rings are formed around each of the two distorted square-pyramidal copper centres.

Each of the four-coordinate Cu2 and Cu3 centres possesses distorted square-planar coordination geometry bound by an imino nitrogen, a bridging phenoxo oxygen, a bridging alkoxo oxygen from the NOO donor set of the same Schiff-base moiety, and one nitrogen atom coming from the  $\mu_{1,1}$ -bridging azido group. Cu2 and Cu3 atoms are displaced from their least-squares plane by 0.025(2) and 0.037(2) Å, respectively (N2, O2, O5, and N21 atoms for Cu2; and N3, O3, O6, and N11 atoms for Cu3). The angles around the Cu2 atom are either less or greater than the ideal value of  $90^\circ$  (O5–Cu2–N2 ( $86.83(14)^\circ$ ), O2–Cu2–N21 ( $83.89(16)^\circ$ ), O2–Cu2–N2 ( $93.97(17)^\circ$ ), and O5–Cu2–N21 ( $96.41(17)^\circ$ ). The *trans* angles N2–Cu2–N21 ( $172.99(19)^\circ$ ) and O2–Cu2–O5 ( $170.30(12)^\circ$ ) also deviate from the ideal value of  $180^\circ$  (Table 1), evidence for the tetrahedral distortion of the square plane around the Cu2 centre. The situation is similar for the Cu3 atom. The six-membered chelate rings ( $\text{CuOC}_3\text{N}$ ) in **1** are all planar, whereas the five-membered ( $\text{CuOC}_2\text{N}$ ) chelate rings have envelope conformations where the Cu centres are distorted SP (Cu1 and Cu4) but twisted (at the O–C bond) in case of distorted square-planar Cu centres (Cu2 and Cu3).

The two coordinated  $\mu_{1,1}$ -azide ions are nearly linear (N13–N12–N11  $178.8(5)^\circ$ , and N23–N22–N21  $178.9(5)^\circ$ ), but these are coordinated to the metal centres in the bent fashion (N22–N21–Cu2  $127.2(3)^\circ$ , N22–N21–Cu4  $125.6(3)^\circ$ , N12–N11–Cu3  $125.5(3)^\circ$ , and N12–N11–Cu1  $120.1(3)^\circ$ ). For the N,O-bridged copper atoms (Cu2...Cu4 and Cu1...Cu3), the Cu...Cu separation ranges from 3.1994(8) to 3.3250(8) Å, whereas the distance is longer, 3.3615(9) to 3.3958(9) Å for the singly alkoxo O-bridged metal centres (Cu1...Cu2 and Cu3...Cu4). However, the separations between the non-bridging copper centres are 2.9583(8) and 5.540(1) Å for Cu2...Cu3 and Cu1...Cu4, respectively. In fact, the Cu2...Cu3 distance is the shortest one compared with the other Cu...Cu separations in the system. The centroids of the two six-membered chelate rings involving Cu2 and Cu3 are only 3.264(2) Å apart, and there is negligible slippage ( $<0.02$  Å) with respect to the perpendicular distance between the planes.

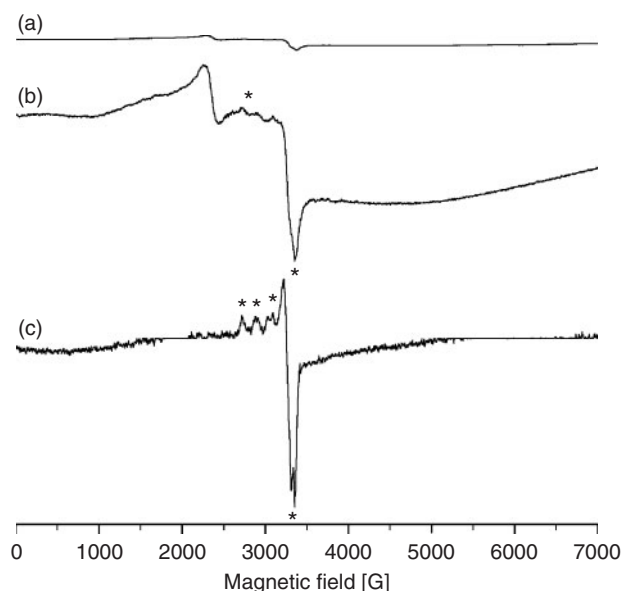


**Fig. 4.** Cyclic voltammogram of **1** in  $\text{CH}_3\text{CN}$  solution using a platinum electrode at a scan rate of  $50 \text{ mV s}^{-1}$  with  $n\text{-Bu}_4\text{NClO}_4$  as the supporting electrolyte.

#### Electrochemical Study

The cyclic voltammogram (Fig. 4) of **1** exhibits three cathodic waves at  $-0.50$ ,  $-0.80$ , and  $-1.20$  V. Each of the first and second responses is assigned to one-electron reduction ( $\text{Cu}^{\text{II}}$  to  $\text{Cu}^{\text{I}}$ ) for the two copper centres, respectively. The third one, which is much steeper than the other two, is assigned to the overlap of two one-electron reductions for the remaining two copper centres. In addition, there is a characteristic feature of a redissolution process, and it is believed that the four electron reduction processes cause a partial decomplexation and release of  $\text{Cu}^+$  ions, which in turn undergo further reduction from  $\text{Cu}^{\text{I}}$  to  $\text{Cu}^0$ , leading to a deposition of metallic copper at the electrode surface.<sup>[21]</sup> The electrodeposited copper is redissolved and characterized by a sharp anodic stripping at  $-0.10$  V. An oxidative response is also observed at  $+0.78$  V, which was tentatively assigned to oxidation of the coordinated ligand. The results





**Fig. 5.** X-band EPR spectra recorded at 120 K on **1**: (a) a polycrystalline sample with usual instrumental gain; (b) a polycrystalline sample with 100-fold amplification with respect to the usual instrumental gain; and (c) a polycrystalline sample dissolved in DMF with 100-fold amplification with respect to the usual instrumental gain. Asterisks indicate the signals attributable to a monomeric  $\text{Cu}^{2+}$  impurity.

suggest that the  $\text{Cu}^{\text{I}}$  species is unstable and undergoes rapid decomposition.

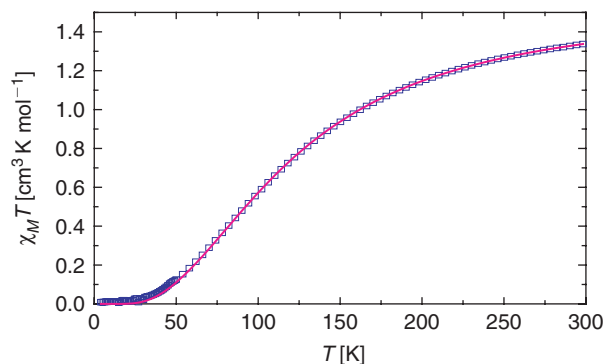
#### X-Band EPR Spectra

The electron paramagnetic resonance (EPR) spectrum of **1**, measured on the polycrystalline powder, is characterized by a very weak signal between 120 and 298 K, which, working with normal instrumental parameters, can hardly be distinguished from the baseline (Fig. 5a). This supports an  $S = 0$  ground spin state.<sup>[22]</sup> On amplifying the instrumental gain 100-fold, the resonances of a monomeric  $\text{Cu}^{\text{II}}$  impurity are observable; the signal at 2360 G appears to be associated with the ground state of the complex (Fig. 5b). When the powder is dissolved in an organic solvent ( $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CN}$ , or DMF), the absence of EPR signals persists, indicating that the structure is maintained in these solvents; moreover, the absorption at 2360 G disappears in solution. Only in DMF is a weak signal observed (Fig. 5c), attributable to a paramagnetic impurity whose parameters are consistent with those of salicylaldehydeimine or derivatives of salen ( $N,N'$ -bis(salicylidene)ethylenediimine).<sup>[23]</sup>

#### Magnetic Susceptibility Measurement and DFT Calculations

$\text{Cu}^{\text{II}}$  complexes with  $\mu_{1,1}$ -azido bridges are usually strongly ferromagnetic, but Thompson and coworkers, systematically studying the magneto-structural correlations of such a class of compounds, proposed that for values of the  $\text{Cu-N-Cu}$  angle larger than  $\sim 108.5^\circ$ , the coupling should be antiferromagnetic.<sup>[24]</sup> Recently, Triki et al., through DFT calculations and a comparison of several structures in the literature, found that an antiferromagnetic coupling is also produced by an asymmetric EO azido bridge.<sup>[25]</sup>

For the  $\mu_2$ -hydroxo/alkoxo and  $\mu_2$ -phenoxo ligands, a linear relationship has been shown between the  $\text{Cu-O-Cu}$  angle



**Fig. 6.** Plot of observed  $\chi_M T$  versus  $T$  (□) for **1** (molar value refers to four copper atoms). Solid line corresponds to the best fit.

( $\theta$ ) and exchange coupling constant ( $J$ )<sup>[26,27]</sup>

$$2J (\text{hydroxo/alkoxo}) = -74.5\theta + 7270 \quad (1)$$

$$2J (\text{phenoxo}) = -32.0\theta + 2462 \quad (2)$$

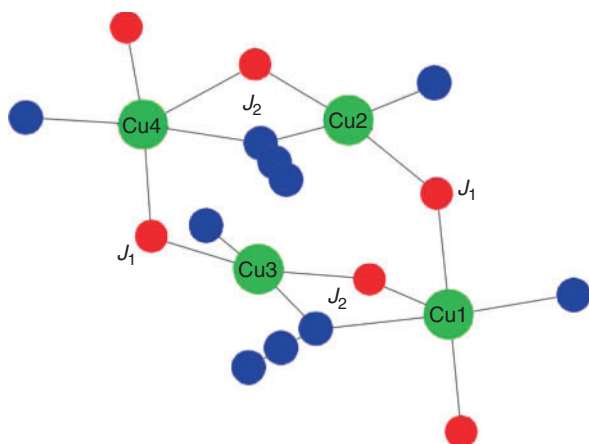
with  $J$  measured in  $\text{cm}^{-1}$ . Therefore, the angles at which change from ferromagnetic and antiferromagnetic coupling occurs are  $\sim 97.5^\circ$  and  $\sim 77.1^\circ$ , respectively.

A search of the Cambridge Structural Database<sup>[18]</sup> for polynuclear structures containing azido and phenoxo/alkoxo bridges yields 21 structures; magnetic data are reported for 14 of them. If, for simplicity, we focus our attention on the dinuclear  $\text{Cu}^{\text{II}}$  complexes containing one phenoxo bridge and one EO azido bridge, nine structures are found, all with antiferromagnetic behaviour and with  $J$  from  $-66$  to  $-408 \text{ cm}^{-1}$ . The  $\text{Cu-O-Cu}$  angles are in the range  $98.3$ – $106.1^\circ$ , where antiferromagnetic coupling should occur, whereas for  $\text{Cu-N-Cu}$  angles of  $91.0$ – $106.2^\circ$ , the behaviour should be ferromagnetic.<sup>[28]</sup>

In order to shed light on the magnetic behaviour of **1**, a magnetic susceptibility measurement was performed. A plot of molar magnetic susceptibility times the temperature ( $\chi_M T$ ) as a function of absolute temperature is shown in Fig. 6. At room temperature, the  $\chi_M T$  product has a value of  $1.32 \text{ cm}^3 \text{ K mol}^{-1}$ , slightly below the one expected for four uncoupled  $\text{Cu}^{\text{II}}$  atoms ( $1.5 \text{ cm}^3 \text{ K mol}^{-1}$  with Landé factor  $g = 2.0$ ). At low temperature, the  $\chi_M T$  product tends to 0, indicating that the ground state of **1** is diamagnetic. Theoretically, as all copper atoms are non-equivalent from a crystallographic point of view, four different exchange pathways are expected. Fitting the data with four different  $J$  values would obviously lead to an overparameterization of the problem. However, the interactions between  $\text{Cu1}$  and  $\text{Cu3}$  and between  $\text{Cu2}$  and  $\text{Cu4}$  are expected to be similar. Likewise, the interactions between  $\text{Cu1}$  and  $\text{Cu2}$  and between  $\text{Cu3}$  and  $\text{Cu4}$  are expected to be virtually the same. Indeed,  $\text{Cu1}$  and  $\text{Cu3}$ , as well as  $\text{Cu2}$  and  $\text{Cu4}$ , are doubly-bridged by an azido group in an EO fashion and the oxygen of a phenoxo group.  $\text{Cu1}$  and  $\text{Cu2}$ , as well as  $\text{Cu3}$  and  $\text{Cu4}$  are linked through the oxygen of an alkoxo group. Thus the more general zero-field Hamiltonian used to fit the data is represented by Eqn 3 and Fig. 7:

$$\hat{H} = -J_1[\vec{S}(\text{Cu1}) \cdot \vec{S}(\text{Cu2}) + \vec{S}(\text{Cu3}) \cdot \vec{S}(\text{Cu4})] - J_2[\vec{S}(\text{Cu1}) \cdot \vec{S}(\text{Cu3}) + \vec{S}(\text{Cu2}) \cdot \vec{S}(\text{Cu4})] \quad (3)$$

$S_{\text{Cui}}$  is the spin of  $\text{Cu}$ , where  $i = 1, 2$  etc. With such a Hamiltonian, the product of magnetic susceptibility and temperature can be derived as a function of temperature. This expression

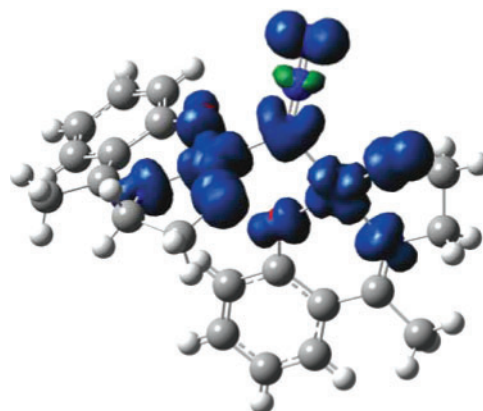


**Fig. 7.** Structural representation of Cu<sub>4</sub> core and exchange coupling constants.

is, however, quite complicated and can be found in the supplementary material of ref. [12]. If only one  $J$  constant is assumed ( $J_1 = J_2$ ), best fit gives  $g = 2.24$  and  $J = -117 \text{ cm}^{-1}$ . Experimental and calculated curves fit reasonably well. However, this is an unrealistic situation. As a matter of fact, this value is reasonable for two copper atoms bridged by an oxo ligand, but not for a copper dinuclear unit linked by an azido ligand. Indeed, in this last case, a ferromagnetic interaction is expected (see below).

In a more refined approach, two  $J$  constants,  $J_1$  and  $J_2$ , can be used to fit the magnetic data. In that case, the best fit is  $g = 2.00$ ,  $J_1 = -153 \text{ cm}^{-1}$  and  $J_2 = +191 \text{ cm}^{-1}$  and a perfect fit of the curve is obtained. It can be argued that  $J_1$  and  $J_2$  might be correlated, and then a large uncertainty may be associated with these values. In order to check this point, we turned to DFT calculations.  $J$  was calculated between Cu1 and Cu2 and between Cu2 and Cu4. The calculation was carried out using the experimental geometry, without any optimization. For each magnetic pathway, the calculation was done on a dinuclear fragment of the whole molecule. This dinuclear fragment was composed of the two copper atoms and their surrounding ligands. For each dinuclear fragment, the energy of the broken symmetry and of the high-spin state was calculated by DFT (for more details, see DFT methodology and computational details). Let us also recall that, not taking into account any relativistic term, the DFT calculation is not able to cope with the through-space coupling, which can be not completely negligible for the shortest Cu–Cu distances. The values of  $J$  obtained are  $J_1 = -153 \text{ cm}^{-1}$  between Cu1 and Cu2, and  $J_2 = +134 \text{ cm}^{-1}$  between Cu2 and Cu4. If these values are used to simulate the magnetic data, a very good simulation is obtained using a  $g$  value of 2.03, with a quality similar to the one obtained with the fitted values  $g = 2.00$ ,  $J_1 = -153 \text{ cm}^{-1}$  and  $J_2 = +191 \text{ cm}^{-1}$ . The  $J_1$  and  $J_2$  values obtained by DFT calculations are, within the errors of DFT calculations, similar to the  $J_1$  and  $J_2$  values obtained from the fitting of two  $J$  values. These last values, namely  $J_1 = -153 \text{ cm}^{-1}$  and  $J_2 = +191 \text{ cm}^{-1}$ , can thus be reasonably trusted.

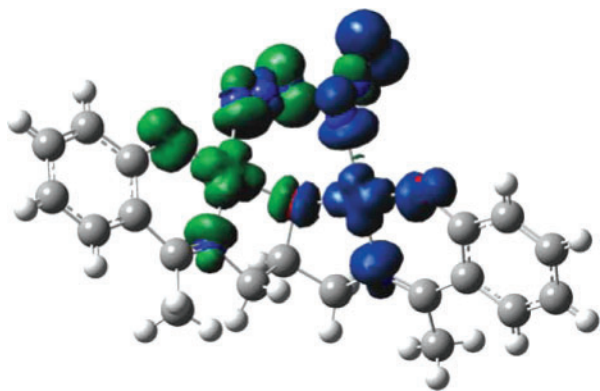
We will now discuss the sign of the two  $J$  coupling constants. We first discuss the ferromagnetic interaction between Cu2 and Cu4, which are linked by an azido ligand in an EO fashion through the N21 atom remaining in an equatorial position of the two copper centres. Cu2 and Cu4 are also linked by a phenoxo oxygen atom O2 that is in an apical position of the distorted square-pyramidal Cu4 atom with the Cu4–O2 distance 2.428(3) Å. It is well known from simple ligand field



**Fig. 8.** Spin density for the ferromagnetic ground state of the dinuclear fragment Cu<sub>2</sub>Cu<sub>4</sub> (positive spin density in dark blue, negative spin density in green). For interpretation of the references to colour in this figure legend, the reader is referred to the online version of this article.

theory that in the square-planar or SP environment, the unpaired electron of the copper atom is located towards the four short equatorial distances (O2, O5, N2, and N21 for Cu2; O4, O6, N4, and N21 for Cu4), in a so-called  $d_{x^2-y^2}$  orbital. Thus, the pathway through the O2 bridge will only contribute a negligible amount to the coupling between Cu2 and Cu4, and the  $J$  value will be governed by the azido bridge. It is now well documented that EO azido bridges favour ferromagnetic interactions between copper centres, from theoretical<sup>[4b]</sup> and experimental<sup>[29]</sup> points of view. Ruiz et al. explain the ferromagnetic interaction by a small difference between the two singly occupied molecular orbitals of the ferromagnetic state.<sup>[4b]</sup> When this energy difference is small, the model developed by Hay et al.<sup>[30]</sup> predicts a ferromagnetic interaction. This discussion is confirmed by the observation of the spin density of the ferromagnetic ground state for the dinuclear moiety. Positive spin density is observed on the two copper atoms, having the expected  $d_{x^2-y^2}$  shape and directed towards the short equatorial distances. Some positive delocalized spin density also appears in the ligands bonded to the copper atoms. This spin density appears in the  $\sigma$  system, as expected from simple ligand field considerations. It can be observed also that the spin density is positive on the N21 bridging atom belonging to the azido ligand (Fig. 8). This rules out for the ferromagnetic interaction the so-called spin polarization mechanism that was initially proposed.<sup>[31]</sup> All these discussions apply *mutatis mutandis* to the similar interaction between Cu1 and Cu3.

Between Cu1 and Cu2, the magnetic interaction is through an O bridging ligand of an alkoxo group, namely O5. The Cu–O–Cu angle of 121.71(15)° would be expected to give a highly negative  $J$  value ( $-1797 \text{ cm}^{-1}$ ) on the basis of Eqn 1.<sup>[26]</sup> However, the observed value is much lower ( $-153 \text{ cm}^{-1}$ ). Eqn 1 is normally valid only for doubly bridged dinuclear copper(II) complexes and it is thus normal that, having only a single oxygen (alkoxo) bridge in **1**, the observed interaction is smaller. However, the fact that the interaction is approximately 10 times smaller than expected can hardly be attributed only to the absence of one of the two bridges. The decrease of the observed interaction compared with the calculated one can also possibly be understood by looking at the position of the two magnetic orbitals. Cu1 is in a distorted SP environment and Cu2 has a distorted square-planar geometry. The base of the square pyramid (for Cu1) is constituted by O1, O5, N1, and N11. The distorted square-planar environment



**Fig. 9.** Spin density for the broken symmetry state of the dinuclear fragment Cu1Cu2 (positive spin density in dark blue, negative spin density in green). For interpretation of the references to colour in this figure legend, the reader is referred to the online version of this article.

of Cu2 is formed by O2, O5, N2, and N21. In each case, the metal and its four neighbours are almost planar, defining two mean planes for the environment of the copper atoms. The spin density for the broken symmetry state has been drawn in Fig. 9. One copper bears positive spin density, whereas the second bears negative spin density, as expected for a broken symmetry state. Again, the spin density is located in a  $d_{x^2-y^2}$  type of orbital directed towards the four short distances around the copper centres. Some delocalization into the  $\sigma$  system of the surrounding ligand is observed as in the previous case. It can be easily seen from the picture that these two planes in which is located the spin density are not coplanar, indicating the magnetic orbitals are themselves not coplanar. If the orbitals bearing the unpaired electrons are located in non-coplanar planes, their overlap tends to diminish. Following the Kahn model,  $J \approx 2K_{ab} + 4\beta S_{ab}$  (where  $K_{ab}$ ,  $\beta$ , and  $S_{ab}$  are respectively the two-electron exchange integral, the one-electron transfer integral and the overlap integral of the two orbitals a and b bearing the unpaired electrons), a decrease of the overlap between the magnetic orbitals ( $S_{ab}$ ) leads to a decrease of the  $4\beta S_{ab}$  term, which contributes to the antiferromagnetic interaction.<sup>[2]</sup> The experimental interaction is thus less antiferromagnetic than the value expected for a planar compound. All the discussion is also valid for the interaction between Cu3 and Cu4 where the Cu–O–Cu angle is 120.51°.

## Conclusions

The present paper reports the synthesis, structural characterization, and magnetic and DFT studies of a novel tetranuclear copper(II) complex  $[\text{Cu}_4\text{L}_2(\mu_{1,1}\text{-N}_3)_2] \cdot \text{CH}_3\text{CN}$  **1** exploiting the quinquedentate  $\text{N}_2\text{O}_3$ -donor set of a Schiff-base ligand **H<sub>3</sub>L**. Actually, here the coordination behaviour of **H<sub>3</sub>L** has been first explored with the copper(II) ion. The uniqueness and originality of the structure lies in the presence of three different kinds of bridging units ( $\mu_{1,1}$ -azido,  $\mu_2$ -alkoxo, and  $\mu_2$ -phenoxo) and the formation of four unusual eight-membered metallacycles in the complex **1**. For copper(II) Schiff-base complexes, existence of three such bridging groups at the same time is quite uncommon in the literature. Complex **1** shows an  $S = 0$  ground state as a result of the antiferromagnetic interaction through the alkoxo bridges combined with the ferromagnetic interaction through the EO azido bridges. Further scope of research should be aimed at the synthesis of copper complexes with higher nuclearities using

this Schiff-base ligand and the theoretical investigation of their physical properties.

## Experimental

### Materials

All the starting chemicals and solvents used for the synthesis were of high-purity analytical grade. 2-Hydroxyacetophenone, 1,3-diaminopropan-2-ol, and sodium azide were purchased from Aldrich Chemical Co. Inc., and used as received.  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  was prepared by the treatment of  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  (AR grade, E. Merck, India) with 60%  $\text{HClO}_4$  (AR grade, E. Merck, India) followed by slow evaporation on a steam bath. It was then filtered through a fine glass frit, and stored over  $\text{CaCl}_2$  in a desiccator.

Caution! Azido complexes and perchlorate salts of metal ions in the presence of organic ligands are potentially explosive. Only a small amount of material should be prepared, and must be handled with care.

### Physical Measurements

The infrared spectrum of **1** was recorded on a Perkin–Elmer RX I Fourier-transform (FT)-IR spectrophotometer with a KBr disc ( $4000\text{--}300\text{ cm}^{-1}$ ). The electronic spectrum was measured on a Perkin–Elmer Lambda 40 UV-visible spectrophotometer using HPLC-grade  $\text{CH}_3\text{CN}$  in the range 200–800 nm. Elemental analyses (C, H, N) were carried out using a Perkin–Elmer 2400 II elemental analyser.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained for the structural confirmation of the quinquedentate Schiff-base ligand using a Bruker 300 MHz FT-NMR and Bruker WM250 spectrometers, respectively with tetramethylsilane as an internal standard in  $[\text{D}_6]\text{DMSO}$  solvent. The electrospray ionization (ESI) mass spectrum of the ligand was performed on a JEOL JMS-AX500 mass spectrometer. X-band EPR spectra of **1** were recorded on a polycrystalline sample or in  $\text{CH}_3\text{CN}$  and DMF solution with a Bruker EMX spectrometer at 120 and 298 K, respectively. The spectra were simulated with the computer program Bruker *WINEPR SimFonia*.<sup>[32]</sup> Electrochemical study was performed ( $\text{CH}_3\text{CN}$  solution) on a CH 600A electrochemical analyser using a platinum electrode, a platinum wire counter-electrode, and tetrabutylammonium perchlorate (0.1 M) as the supporting electrolyte with a scan rate of  $50\text{ mV s}^{-1}$ . The potentials are referenced to the saturated calomel electrode without junction correction ( $-0.2415\text{ V}$  versus normal hydrogen electrode), with a value of 0.52 V for the ferrocene–ferrocenium couple ( $\text{Cp}_2\text{Fe}^{+/0}$ ). Magnetic susceptibility measurement for **1** was carried out on a polycrystalline sample with a Quantum Design MPMS-5S SQUID magnetometer working in the range 2–300 K under an applied magnetic field of 5000 Oe. Diamagnetic corrections were estimated from Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder.

### DFT Methodology and Computational Details

The calculated coupling constant  $J$  is deduced from two separate DFT computations carried out for the highest spin state and for the broken symmetry state. The hybrid  $B3LYP$ <sup>[33]</sup> functional has been used as implemented in the *Gaussian 98* program.<sup>[34]</sup> The basis used in all calculations is the triple- $\zeta$  basis-set proposed by Ahlrichs et al.<sup>[35]</sup> for transition metals, and the double- $\zeta$  basis set proposed by the same authors for the other atoms.<sup>[36]</sup> The  $J$  values obtained are deduced from the energy difference  $E_{\text{HS}} - E_{\text{BS}} = -J$ , where  $E_{\text{HS}}$  and  $E_{\text{BS}}$  are the energies



of the high spin and the broken symmetry states, respectively. We assume that the energy of the broken symmetry state is a good approximation of low spin state energy, following Ruiz et al.<sup>[37]</sup>

#### Synthesis of the Schiff-Base Ligand (**H<sub>3</sub>L**)

The ligand was prepared by the reflux condensation of 2-hydroxyacetophenone (0.272 g, 2 mmol) and 1,3-diaminopropan-2-ol (0.090 g, 1 mmol) in methanol for 7 h. The resulting solution yielded shiny lemon-yellow crystals of the ligand on slow evaporation. The solid ligand was dried, and stored under vacuum over CaCl<sub>2</sub> for subsequent use. Yield: 0.235 g (72%). (Calc. for C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>O<sub>3</sub> (326.39): C 69.9, H 6.8, N 8.6. Found: C 69.8, H 6.7, N 8.5%.)  $\nu_{\max}$ (KBr)/cm<sup>-1</sup> 3380br ( $\nu_{\text{O-H}}$ ), 1612s ( $\nu_{\text{C=N}}$ ), 1254s ( $\nu_{\text{CO}}$ , phenoxo), 1055s ( $\nu_{\text{CO}}$ , alkoxo).  $\delta_{\text{H}}$  (20°C) 2.26 (s, 6H, CH<sub>3</sub>), 3.46–3.49 (m, 4H, CH<sub>2</sub>), 3.99 (m, 1H, CH), 5.89 (s, 1H, CHOH), 6.98 (d, *J* 8.2, 2H, ArC(3)H), 7.03 (t, *J* 8.0, 2H, ArC(5)H), 7.50 (t, *J* 7.8, 2H, ArC(4)H), 8.01 (d, *J* 8.0, 2H, ArC(6)H), 15.86 (bs, 2H, ArC(2)OH).  $\delta_{\text{C}}$  (20°C) 14.30 (CH<sub>3</sub>), 43.38 (CH<sub>2</sub>), 67.98 (CHOH), 115.97 (ArC(3)H), 117.48 (ArC(1)), 118.58 (ArC(5)H), 128.40 (ArC(6)H), 133.66 (ArC(4)H), 159.95 (ArC(2)OH), 171.60 (>C=N). *m/z* (ESI) 326 (M<sup>+</sup>, 100%).

#### Synthesis of [Cu<sub>4</sub>L<sub>2</sub>( $\mu_{1,1}$ -N<sub>3</sub>)<sub>2</sub>].CH<sub>3</sub>CN **1**

To a 30-mL CH<sub>3</sub>OH/CH<sub>3</sub>CN (1:1 v/v) solution of Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.370 g, 1 mmol) was added 0.326 g (1 mmol) of solid **H<sub>3</sub>L**, and the mixture was stirred vigorously until the ligand was completely dissolved in the solution. Then, NaN<sub>3</sub> (0.058 g, 0.90 mmol) dissolved in 10 mL of CH<sub>3</sub>OH was added slowly to the above mixture, and the resulting dark green solution was stirred for 20 min. The mixture was refluxed for 40 min at 45°C, filtered off, and kept undisturbed at room temperature. After 3 days, dark green rhombic-shaped X-ray diffraction-quality single crystals were separated out from the filtrate. Yield: 0.934 g (91%). (Calc. for C<sub>38</sub>H<sub>38</sub>Cu<sub>4</sub>N<sub>10</sub>O<sub>6</sub>·CH<sub>3</sub>CN (1026.01): C 46.8, H 4.0, N 15.0. Found: C 46.7, H 4.1, N 15.0%.)

#### Crystallographic Data Collection and Refinement of the Structure

The molecular structure of **1** was determined by the single crystal X-ray diffraction method. Intensity data and cell parameters were collected at 100 K on a Bruker X8 Apex 2 CCD diffractometer equipped with a graphite monochromator (Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å) using the Bruker Apex 2 software.<sup>[38a]</sup> Multi-scan absorption correction was applied using SADABS.<sup>[38b]</sup> The structures were refined by full matrix least-squares procedures on  $F^2$ . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the aromatic rings, methyl, methylene, and imine (>C=N) groups were constrained to ideal geometry, and treated as riding on the bound atom. All of the crystallographic computations were carried out using SHELXTL,<sup>[38c]</sup> PLATON 99,<sup>[38d]</sup> and ORTEP<sup>[38e]</sup> programs. Further crystallographic data are summarized in Table 2.

#### Supplementary Information

CCDC 643537 contains the supplementary crystallographic data for **1**. Copies of this information can be obtained free of charge from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

**Table 2.** Crystallographic data and refinement parameters for **1**

Complex	<b>1</b>
Empirical formula	C <sub>40</sub> H <sub>41</sub> Cu <sub>4</sub> N <sub>11</sub> O <sub>6</sub>
$M_w$	1026.01
Crystal size [mm <sup>3</sup> ]	0.26 × 0.20 × 0.08
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> [Å]	10.9257(8)
<i>b</i> [Å]	14.6464(13)
<i>c</i> [Å]	14.6485(13)
$\alpha$ [°]	62.790(3)
$\beta$ [°]	71.052(3)
$\gamma$ [°]	87.730(4)
Volume [Å <sup>3</sup> ]	1955.1(3)
<i>Z</i>	2
$D_c$ [Mg m <sup>-3</sup> ]	1.743
$\lambda$ (Mo K $\alpha$ ) [Å]	0.71073
<i>T</i> [K]	100(2)
$\mu$ [mm <sup>-1</sup> ]	2.211
$\theta_{\min}$ , $\theta_{\max}$ [°]	2.37, 24.10
Total data, unique data	28866, 6093 [ $R_{\text{int}}$ 0.0643]
Final <i>R</i> indices [ $I > 2\sigma(I)$ ] <sup>A</sup>	$R_1$ 0.0365, $wR_2$ 0.0740
<i>R</i> indices (all data) <sup>A</sup>	$R_1$ 0.0717, $wR_2$ 0.0877
Goodness-of-fit on $F^2$	0.993
Largest diff. peak and hole [e Å <sup>-3</sup> ]	0.547 and -0.431

$$^A R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}}{1/[\sigma^2(F_o^2) + [(ap)^2 + bp]]}, \quad \text{where } p = [\max(F_o^2, 0) + 2F_c^2]/3.$$

#### Acknowledgements

Subhra Basak gratefully acknowledges the DRDO, New Delhi, India, for financial assistance. Our thanks are also extended to the All India Council for Technical Education (AICTE), New Delhi, India. We are thankful to Professor S. Bhattacharya and Dr S. Halder, Department of Chemistry, Jadavpur University, Kolkata, India, for the electrochemical study.

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