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An antiferromagnetically coupled hexanuclear copper(II) Schiff base complex containing phenoxo and dicyanamido bridges: Structural aspects and magnetic properties

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1. Introduction

ABSTRACT

A novel hexanuclear complex $[(CuL)_2Cu]_2(\mu-dca)_2](ClO_4)_2\cdot 2L'(1)$ (where $H_2L = (OH)C_6H_4C(CH_3)=N(CH_2)_3-N(CH_2)-N(CH_2)-N(CH_2)-N(CH_2)$ $N=C(CH_3)C_6H_4(OH)$ or N,N'-bis(2-hydroxyacetophenone) propylenediimine and dca = $N(CN)_2^-$ and L' = 2hydroxyacetophenone) has been synthesized and characterized by elemental analysis, UV-Vis, FT-IR spectroscopic and electrochemical methods. Single crystal X-ray structural characterization reveals a centrosymmetric nature of the complex unit, where the metal centers adopt distorted square-planar and distorted octahedral geometries. Structural analysis also reveals μ_2 -phenoxo bridges between terminal and the central copper(II) centers of the asymmetric [(CuL)₂Cu(dca)] unit, the latter being interconnected to its symmetry related counterpart by double $\mu_{1,5}$ -dca bridges, leading to the hexanuclear complex ion $[\{(CuL)_2Cu\}_2(\mu-dca)_2]^{2^+}$. Low temperature susceptibility measurements of 1 revealed the presence of strong antiferromagnetic coupling $(2I = -407 \text{ cm}^{-1})$ between the copper(II) centers.

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Polynuclear complexes are of considerable interest for the development of new magnetic molecular materials [1-3]. Considerable effort has been devoted to the design, synthesis and modification of such complexes, obtained by the appropriate choice of metal ions, ligands and auxiliary ligands, and a detailed examination of their structure-function correlation helps to develop new synthetic routes to novel magnetic materials. Studies of such complexes also find wide applications as model compounds for the investigations of the role of polymetallic active sites in biological systems [4].

On the other hand, the coordination chemistry of copper(II) has developed very rapidly over the last four decades due to a number of reasons. From the standpoint of bioinorganic chemistry, copper(II) coordination complexes have been used for the modelling of active sites in copper(II) biomolecules [5], while from the perspective of magneto-chemistry dinuclear complexes of this ion have been synthesized to establish magneto-structural correlations [6-11], and trinuclear complexes have got attention in order to study spin frustration and antisymmetric exchange phenomena [12], as well as for the rational synthesis of ferromagnetic entities [13,14]. Infinite lattices constitute a further well-studied class of copper(II) complexes leading to the formation of 1D, 2D and 3D architectures [15–21], while copper(II) polynuclear complexes with aesthetically pleasing structures and interesting magnetic properties are a hot topic in current research [22-27]. Plenty of polynuclear metal complexes up to four copper centers, with diverse structures and detailed magnetic behavior, are known in the literature, however complexes with more copper centers, in particular six, are still scarce.

Designing, synthesizing and establishing magneto-structural correlations of polynuclear copper(II) complexes have been a long standing interest of our group. With this purpose, our strategies were to employ different Schiff base coligands for their synthetic ease, structural flexibility and topological richness in conjunction with the counter anions of the copper(II) salts and various pseudohalides, e.g. azide, thiocyanate, cyanate and dicyanamide etc., for their versatile coordination modes, altogether resulting in a wide variety of topologies and functional materials. Tetradentate ligands of salen-type Schiff bases with N₂O₂ donor sets are a long standing choice of our group as they provided suitable coordination environments to form trinuclear complexes with fascinating structures, depending upon the counter ions of the copper(II) salts used



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[28,29]. In our recent paper, we have reported two new tetranuclear copper(II) complexes with one of the N_2O_2 donor Schiff base ligands used earlier, and we have explored the role of the azide ion to increase the nuclearity of the complexes [30].

Considering the versatile coordination modes of dicyanamide (Scheme 1), a larger pseudohalide molecular ion-rod which results in diverse magnetic materials such as ferro-, antiferro- and canted-spin antiferromagnetic materials [31–34], our aim was to explore the possibility of dicyanamide forming a polynuclear complex with more than four copper(II) centers using same Schiff base ligand [30], and to investigate its role in the overall magnetic behavior.

In this paper we report a novel hexanuclear copper(II) complex [{(CuL)₂Cu}₂(μ -dca)₂](ClO₄)₂·2L' (1) obtained by the reactions of copper(II) perchlorate hexahydrate, the Schiff base ligand (H₂L) (Scheme 2) and sodium dicyanamide, and characterized by different physicochemical methods. X-ray crystallographic characterization of **1** reveals its centrosymmetric nature where two asymmetric [(CuL)₂Cu(dca)] units are interconnected by doubly $\mu_{1,5}$ -dca bridges. Within the [(CuL)₂Cu(dca)] unit, terminal copper(II) centres are in slightly distorted square-planar geometries, leaving the central copper(II) to adopt a distorted octahedral geometry. Low temperature magnetic susceptibility studies reveal an overall strong antiferromagnetic behavior of the complex with 2J = -407 cm⁻¹, well fitted with the "pair of independent triangles" model [35].

2. Experimental

2.1. General and physical measurements

All manipulations were performed under aerobic conditions using the materials as received (Aldrich Chemical Co.). The solvents used were of analytical grade. Elemental analyses (carbon, hydrogen and nitrogen) were carried out with a Perkin–Elmer 2400 II elemental analyser. The copper content in the complex has been estimated quantitatively by a standard iodometric procedure. The FT-IR spectrum (4000–200 cm⁻¹) was recorded on a Perkin–Elmer Spectrometer RX I FT-IR system with solid KBr pellets. The electronic spectrum (800-200 nm) was recorded on a Perkin-Elmer Lambda 40 UV-Vis spectrometer using a 1×10^{-5} M solution of the complex in HPLC grade acetonitrile. Electrochemical studies were performed on a VersaStat II cyclic voltammeter instrument using HPLC grade acetonitrile (CH₃CN) as the solvent and tetrabutylammonium perchlorate as the supporting electrolyte at a scan rate of 50 mV s^{-1} , with a platinum wire as the working electrode and a standard calomel electrode as the reference. Variable-temperature magnetic susceptibility measurements were made at Monash University using a Quantum Design MPMS 5 SQUID magnetometer operating in an applied field of 1 T. The powdered samples were contained in calibrated gelatine capsules, which were held at the centre of a drinking straw, the latter being attached to the end of the sample rod. The temperature and field were checked against a standard palladium sample (Quantum Design) of accurately known magnetization and by use of magnetochemical calibrants such as CuSO₄·5H₂O and [Ni(en)₃]S₂O₃. Pascal's constants were used for diamagnetic corrections.

Safety note. Perchlorate salts of transition metal ions in the presence of organic ligands are potentially explosive, and although we have not encountered any problems during the synthesis of the complex, it should be prepared in small quantities and must be handled with caution.

2.2. Preparation of the ligand and complex

2.2.1. Preparation of the Schiff base ligand (H_2L)

2.2.1.1. propylenediimine (H_2L). The Schiff base ligand (H_2L) was prepared according to the published procedure [29] by refluxing 2-hydroxyacetophenone (1.361 g, 10 mmol) and 1,3-diaminopropane



Scheme 1. Different bridging modes of the dca ligand.



Scheme 2. Synthetic scheme of the Schiff base ligand (H₂L) and its coordination modes.

(0.370 g, 5 mmol) in 25 mL methanol solution for an hour. The resulting solution yielded shiny yellow crystals of the ligand upon slow evaporation. They were dried and stored *in vacuo* over CaCl₂ for subsequent use. Yield: 1.319 g (85%): *Anal.* Calc. for C₁₉H₂₂N₂O₂ (310.39): C, 73.52; H, 7.14; N, 9.03. Found: C, 73.41; H, 7.11; N, 9.01%. IR (KBr pellet, cm⁻¹): 1623 s, 3449 mb, 1204 s. UV–Vis (λ , nm): 241, 371.

2.2.2. Preparation of the complex

2.2.2.1. [{(CuL)₂Cu]₂(μ -dca)₂](ClO_4)₂·2L' (**1**). To a methanolic solution (20 mL) of copper(II) perchlorate hexahydrate (1.11 g, 3 mmol), a 10 mL methanolic solution (1.438 g, 2 mmol) of the Schiff base ligand (H₂L) was added, followed by the addition of a 10 mL (0.178 g, 1 mmol) aqueous solution of sodium dicyanamide with slow stirring. The resulting deep reddish brown solution was filtered and kept undisturbed at room temperature. After several days, good quality red brown plate shaped single crystals of **1** separated out from the mother liquor. These were filtered, washed with methanol–water mixture (1:1) and air dried. Yield: 68%. *Anal.* Calc for C₉₆H₉₆Cl₂Cu₆N₁₄O₂₀ (2218.07): C, 51.98; H, 4.36; N, 8.84; Cu, 17.19. Found: C, 51.95; H, 4.32; N, 8.82; Cu, 17.16%. IR (KBr pellet, cm⁻¹): 2260 s, 2218 s, 2150 s, 1592 s, 1164 s, 420 w, 365 w.

2.3. Single-crystal X-ray crystallography

A red brown plate shaped single crystal of **1** with dimensions $0.075 \times 0.15 \times 0.30 \text{ mm}^3$ was mounted on a Bruker P4 diffractometer. Graphite-monochromatized Mo K α radiation (λ = 0.71073 Å)

and the ω scan technique were used at 123(2) K to collect the intensity data. Data collection and unit cell refinement were carried out using the Bruker XSCANS [36] program. No significant loss of intensity was observed. A multi-scan absorption correction was applied to the intensity values ($T_{min} = 0.5192$, $T_{max} = 0.9284$) empirically using sadabs [37]. Data reductions were performed using the Bruker SHELXTL [38] program. The crystal structure was solved by direct methods using the program SHELXS-97 [39], combined with Fourier difference synthesis, and refined with the full matrix least square technique based on F^2 using the program SHELXL-97 [39]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located from the difference Fourier map and treated with suitable riding models with isotropic displacement parameters derived from their carrier atoms, except the hydrogen atoms of the methyl and hydroxyl groups which were refined with isotropic thermal parameters. Molecular graphics and crystallographic illustrations were prepared using ORTEP [40] and Bruker SHELXTL [38] software. Relevant crystallographic and refinement data are listed in Table 1.

3. Results and discussion

3.1. FT-IR spectrum

The infrared spectrum of **1** was recorded within the 4000– 400 cm^{-1} region. The spectral data indicate ligand coordination to the metal. A strong sharp band observed at 1592 cm⁻¹

Table 1

Crystallographic	data	collection	and	structure	refinement	for	1.

Parameters for	1
Empirical formula	C ₉₆ H ₉₆ Cl ₂ Cu ₆ N ₁₄ O ₂₀
Formula weight	2218.07
Crystal system	triclinic
Space group	<i>P</i> 1̄ (No. 2)
a (Å)	11.2318(1)
b (Å)	14.8201(2)
c (Å)	15.1195(2)
α (°)	86.858(1)
β(°)	68.242(1)
γ (°)	78.298(1)
V (Å ³)	2288.28(5)
Ζ	1
<i>T</i> (K)	123(2)
$D_{\text{calc}} (\text{g cm}^{-3})$	1.610
$\mu (\mathrm{mm^{-1}})$	1.509
F (0 0 0)	1138
θ Range for data collection (°)	3.00-27.86
Total data	36830
R _{int}	0.0663
Unique data	10794
Observed data $[I > 2\sigma(I)]$	8389
Data/restraints/parameters	10794/0/631
Final R indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0405$
	$wR_2 = 0.0865$
R indices (all data) ^a	$R_1 = 0.0632$
2	$wR_2 = 0.0936$
Goodness-of-fit on F^2	1.015
Residuals (e A ⁻³)	0.426; -0.716

^a $R = \Sigma(|F_o - F_c|)/\Sigma|F_o|$, $wR = \{\Sigma[w(|F_o - F_c|)^2]/\Sigma[w|F_o|^2]\}^{1/2}$.

corresponds to the $v_{C=N}$ group of the coordinated ligand. The stretching band of phenolic-OH group of the Schiff base ligand, observed at 3449 cm⁻¹, was absent in the complex, indicating its deprotonation followed by coordination to the metal ion. Ligand coordination was also substantiated by the lowering of the phenolic C–O stretching band, which appeared at 1164 cm^{-1} in **1**, otherwise observed at 1204 cm^{-1} in the free Schiff base ligand [41,42]. Coordination of the Schiff base ligand was further confirmed by the appearance of two bands at 420 and 365 cm⁻¹ corresponding to v_{Cu-N} and v_{Cu-O} respectively [43]. Coordination of the dca anion of NaN(CN)₂ was suggested by the appearance of three sharp and strong characteristic stretching frequencies in the 2300-2160 cm⁻¹ region. These bands are attributed to $v_{as} + v_s(C-N)$ combination modes, $v_{as}(C \equiv N)$ and $v_s(C \equiv N)$ vibrations, and are observed at 2292, 2240 and 2180 cm⁻¹ in **1** compared to the bands at 2286, 2232 and 2179 cm⁻¹ usually observed for free dca. The shifts toward higher frequencies of these peaks as compared to free dca are due to the bridging modes of dca in **1**. Furthermore, the absorption bands for $v_{as}(C-N)$ and $v_s(C-N)$ stretching frequencies, usually observed in the range 1400–1300 and 950–900 cm^{-1} for $\mu_{1,5}$ -dca bridged copper(II) complexes [44–46], appeared at 1350 and 940 cm⁻¹ respectively in **1**. The presence of the perchlorate anion was indicated by a broad trifurcated band appearing in the range $1140-1100 \text{ cm}^{-1}$ of the spectrum of **1**.

3.2. Electronic spectrum

The electronic spectrum of **1** shows two bands in the regions 455–330 and 295–205 nm. The lower energy band corresponds to the $n \rightarrow \pi^*$ transition of the imine group, while the higher energy band corresponds to the benzene $\pi \rightarrow \pi^*$ transition of the Schiff base ligand (intra-ligand charge transfer) [29]. The electronic spectrum of **1** also shows an intense band in the high energy region at 300–372 nm, which can be assigned to charge transfer L \rightarrow M (LMCT) bands. Although the specific nature of this transition involving the phenolate group is not clearly understood [either

an O(phenolate) \rightarrow metal(II) LMCT or a metal(II) $\rightarrow \pi^*$ (phenolate) MLCT transition], it is accepted that a higher energy component should exist in the vicinity of 330 nm [47]. Besides these bands associated to ligand/ligand-metal, the electronic spectrum of **1** also shows two weak and less well defined broad bands at 615 and 675 nm, correlated to the d-d transitions in the copper(II) centers with square-planar (in agreement with the coordination environment of Cu1 and Cu2 in **1**) and octahedral geometries (in agreement with the coordination of Cu3 in **1**), respectively [48].

3.3. Description of the structure

The molecular structure of **1** consists of the centrosymmetric hexanuclear complex ion $[{(CuL)_2Cu}_2(\mu-dca)_2]^{2+}$, perchlorate counter ions and two 2-hydroxyacetophenone molecules. An ORTEP view of the asymmetric unit for the complex ion is shown in Fig. 1. The formation of the complex ion (Fig. 2) may be viewed as a dimer of [(CuL)₂Cu(dca)] unit, each being interconnected with its symmetry related counterpart through double $\mu_{1.5}$ -dca bridges. The asymmetric unit consists of three metal ions; two terminal copper(II) centers [Cu1 and Cu2] with similar coordination environments and geometries, which differ for the central copper(II) center [Cu3]. The coordination environment for Cu1 and Cu2 is satisfied by a Schiff base ligand in a *cis* fashion with respect to the phenolate moieties, while for Cu3 both Schiff base and dca ligands are involved. Thus the terminal Cu1(L) and Cu2(L) sub-units are connected to each other through Cu3 *via* double μ_2 -phenoxo bridges. The coordination environment of Cu1 and Cu2 is satisfied by the phenoxo oxygen and imine nitrogen atoms of the Schiff base ligands [Cu1; O101, O123, N110, N114 and Cu2; O201, O223, N210, N214], while that for Cu3 is satisfied by four μ_2 -phenoxo oxygen atoms [0101, 0123, 0201, 0223] and two dca nitrogen atoms N1 and N5* (symmetry related counter part of N5). The four coordinated geometry around Cu1 and Cu2 is considered to be



Fig. 1. An ORTEP view of the asymmetric unit of **1** with atom labelling (thermal ellipsoids are drawn at the 30% probability level, hydrogen atoms and the perchlorate ion are omitted for clarity).



Fig. 2. Hexanuclear view of the complex ion present in 1.

slightly distorted square-planar, as evident from the relative variations in bond lengths and angles (Table 2). The Cu–O and Cu–N bond lengths for Cu1 and Cu2 vary in the range 1.8891(18)–1.9318(18) and 1.9530(2)–1.9850(2) Å, respectively, are in good agreement with related reported complexes [29,30]. *Cisoid* and *transoid* angles for both Cu1 and Cu2 also deviate from their ideal values of 90° and 180° and found to be in the range 78.42(7)–98.42(9)° and 162.51(8)–168.39(9)°, respectively. The copper(II) ions are deviated out of the square plane by 0.026 and 0.037 Å, while the Schiff base donor atoms remain almost coplanar within ±0.09 and ±0.24 Å with respect to the mean square planes around Cu1 and Cu2, respectively.

On the other hand, the central copper(II) [Cu3] of the asymmetric unit is six coordinated and displays a distorted octahedral geometry. Though Cu3 atom is interconnected with the terminal Cu1 and Cu2 atoms *via* double μ -phenoxo bridges, the mode of

Table 2			
Selected bond le	engths (Å) a	nd bond ang	gles (°) for 1

Bond lengths (Å)			
Cu1-0101	1.9318(18)	Cu3-0123	2.0473(16)
Cu1-0123	1.9116(18)	Cu3-0201	1.9691(17)
Cu1-N110	1.962(2)	Cu3-0223	2.5590(19)
Cu1-N114	1.953(2)	Cu3-N1	2.218(2)
Cu2-0201	1.9571(18)	Cu3-N5 ^a	1.978(2)
Cu2-0223	1.8891(18)	N1-C2	1.154(3)
Cu2-N210	1.985(2)	C2-N3	1.308(4)
Cu2-N214	1.962(2)	N3-C4	1.301(4)
Cu3-0101	1.9689(18)	C4-N5	1.154(3)
Bond angles (°)			
0101-Cu1-0123	78.42(7)	0101-Cu3-N5 ^a	91.04(8)
0101-Cu1-N110	89.10(8)	0123-Cu3-0201	86.60(7)
0101-Cu1-N114	168.39(9)	0123-Cu3-0223	74.03(6)
0123-Cu1-N114	92.13(8)	0123-Cu3-N1	102.25(8)
0123-Cu1-N110	166.85(8)	0123-Cu3-N5 ^a	163.38(9)
N110-Cu1-N114	100.74(9)	0201-Cu3-0223	68.70(7)
0201-Cu2-0223	85.09(8)	0201-Cu3-N1	100.63(8)
0201-Cu2-N210	88.87(9)	0201-Cu3-N5 ^a	101.82(8)
0201-Cu2-N214	167.44(8)	0223-Cu3-N1	168.66(7)
0223-Cu2-N210	162.51(8)	0223-Cu3-N5 ^a	95.51(8)
0223-Cu2-N214	90.67(9)	N1-Cu3-N5 ^a	90.37(9)
N210-Cu2-N214	98.42(9)	Cu2-0223-Cu3	89.48(7)
0101-Cu3-0123	74.42(7)	Cu2-0201-Cu3	107.54(9)
0101-Cu3-0201	145.60(8)	Cu1-0123-Cu3	96.57(7)
0101-Cu3-0223	78.49(7)	Cu1-0101-Cu3	98.56(8)
0101-Cu3-N1	111.17(8)	C2-N3-C4	121.7(2)

^a Symmetry codes = -x, -y, -z.

connections are not similar. It is bridged via the axial phenoxo oxygen [O223] and equatorial phenoxo oxygen [O201] to Cu2, but by two equatorial oxygen atoms [0101 and 0123] to Cu1. The mean equatorial plane of the octahedron is formed by the 0101, 0123, O201 and N5* atoms, with N1 and O223 atoms at the two apexes. The equatorial and axial bond lengths vary in the range 1.9691(17)-2.0473(16) and 2.218(2)-2.5590(19) Å, respectively, the latter being sensibly longer compared to the former, indicating the tetragonally elongated octahedral geometry of Cu3, evident of Jahn–Teller distortion with the Cu(II) d⁹ ion. The cisoid and transoid angles in the mean equatorial plane are in the range 74.03(6)-111.17(8) and 145.60(8)-163.38(9)°, while the *trans*-axial angle (N1-Cu3-O223) is 168.66(7)°. The high value of the trans-axial angle compared to equatorial *transoid* angles may be due to the strain imposed by the bulky Schiff base ligands. Cu3 is displaced by 0.357 Å towards the apical N1 atom from the mean equatorial plane. The Cu–O(phenoxo)–Cu angles within the asymmetric unit vary in the range 89.48(7)-107.54(9)°, where the Cu2-O201(phenoxo)-Cu3 angle is sensibly larger (107.54(9)°) compared to the other Cu-O(phenoxo)-Cu angles in the unit. The metal-metal separations within the asymmetric unit are found to be 2.957 (Cu1···Cu3) and 3.167 Å (Cu2···Cu3). The Cu1–Cu2–Cu3 angle of 74.58° indicates the non-linear arrangement of copper(II) ions within the asymmetric unit.

As the molecule lies on an inversion centre, the coordination environment as well as the geometry of the copper(II) centers in the symmetry related counterpart are exactly the same. Moreover, these symmetry related units are connected to each other through Cu3 and Cu3* atoms via double $\mu_{1,5}$ -bridges, forming a very stable close and puckered twelve member ring in a chair form incorporating the Cu3-N1-C2-N3-C4-N5-Cu3*-N1*-C2*-N3*-C4*-N5* atoms. The bond angles related to the bridging dca ligands are 134.0(2) (Cu3–N1–C2) and 158.8(2)° (Cu3–N5*–C4*) with a Cu3···Cu3* separation of 7.043 Å. The Cu-NCNCN-Cu bridging array adopts a "V" type conformation because of the sp² hybridization of the middle nitrogen [N3] atom of dca, where the C-N-C angle (C2–N3–C4) is 121.7(2)° [49]. An approximate C_{2V} symmetry is observed for the dca ligands, with the N1-C2 and C4-N5 bond distances both being 1.154(3) Å, as commonly observed for the $[N(CN)_2]_2^-$ anion. A small degree of π conjugation within $[N(CN)_2]^-$ results in longer C2–N3 (1.309(3)Å) and C4–N3 (1.301(3) Å) bond distances.

The hydrogen bonding parameters for **1** are summarized in Table 3. The complex possesses a classical hydrogen bond of the $O-H\cdots O$ type within the 2-hydroxyacetophenone molecules

Table 3

Hydrogen	bonding	parameters	(Å,	°)	for	1.

$D{-}H{\cdots}A$	d(D-H) (Å)	$d(H{\cdot}{\cdot}{\cdot}A)({\mathring{A}})$	$d(D{\cdots}A)({\mathring{A}})$	\angle (D–H···A) (°)
0301-H1···0310	0.85(4)	1.79(4)	2.574(3)	153(4)
C109–H10A···N3 ¹	0.98	2.62	3.505(4)	150
C109–H10B···O310 ⁱⁱ	0.98	2.56	3.503(3)	161
C109–H10C···O2 ⁱⁱⁱ	0.98	2.46	3.431(3)	171
C116-H11I02	0.98	2.53	3.299(4)	135
C209–H20C···O3 ^{iv}	0.98	2.49	3.293(3)	139
$C211-H21B\cdots O3^{\nu}$	0.99	2.58	3.375(3)	137
C213-H21F03	0.99	2.48	3.285(4)	138
C120-H120···01	0.95	2.46	3.397(4)	169

Symmetry transformations used to generate equivalent atoms: (i) -1 + x, y, z (ii) -x, 1 - y, 1 - z; (iii) -x, -y, 1 - z (iv) 1 - x, -y, -z (v) 1 + x, y, z.

present in the lattice. However, several non-classical C-H···O interactions are also present. The closest C···O distance is 2.46 Å. The presence of two 2-hydroxyacetophenone molecules in the lattice may be inferred from the hydrolysis of the Schiff base ligand (H₂L) under the reaction conditions.

3.4. Electrochemical study

The cyclic voltammogram of **1** is recorded in the potential range -1.2 to +1.2 V. On cathodic scanning, it shows two peaks at -0.70and $-1.02 \text{ V} (E_{\text{pc}})$ (versus SCE). These reduction potentials correspond to the Cu^{II}/Cu^I process of each of the two different types of copper(II) centers and the observed peak-to-peak separation of 320 mV indicates the irreversible nature of the reductions, which is believed to be due to the combined effect of the difference in coordination environment around the two types of copper(II) centers (square planar for Cu1 and Cu2; octahedral for Cu3) and the effective communication between them through the double μ_2 phenoxo bridges. These observations are consistent with the behavior found in some related macrocyclic doubly phenoxobridged dicopper complexes, which show two well-separated one electron reductions [50-52]. On anodic scanning, only one oxidative response is observed at +0.81 V (versus SCE). The process is tentatively assigned to the oxidation of the coordinated ligand $[L]^{2-}$, as the cyclic voltammogram of the free ligand [30] shows only one oxidative response at +0.76 V. The results suggest that the Cu^I complex is unstable and undergoes rapid decomposition upon reduction.

3.5. Magnetic properties

The plot of χT versus temperature for **1**, obtained in a field of 1 T, is shown in Fig. 3. It indicates that strong antiferromagnetic



Fig. 3. Thermal variation of χT (per trinuclear unit) in **1**. Solid lines represent the best fit to the model.



Fig. 4. Schematic diagram of the trinuclear asymmetric unit with donor atoms, showing Cu...Cu separations and designated exchange couplings (2J).

coupling is occurring, such that χT (per Cu₃) decreases from $0.683 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 300 K to reach a plateau value of $0.465 \text{ cm}^3 \text{ mol}^{-1}$ K between *ca*. 100 and 4.2 K. This plateau is indicative of an unpaired spin (per trinuclear moiety) in the ground state. Because there is a centre of inversion in the Cu₆ cluster, a "pair of independent triangles" model was employed to fit the data [35] and the best fit is shown as a solid line in Fig. 3. Such a model is reasonable in view of the very weak $\mu_{1.5}$ -dca coupling expected [53] between each Cu₃ half of the hexanuclear cluster, separated by Cu3···Cu3* = 7.043 Å. μ -Phenoxo bridging is known to yield strong antiferromagnetic coupling, particularly when copper coplanar equatorial $[CuN_2O_2]$ planes are bridged by two μ -PhO groups [54]. This coplanarity does not exist in each half of the present cluster, the central copper(II) [Cu3] being bridged via an axial (2.5590(17)Å) and an equatorial (1.9691(17)Å) phenoxo oxygen to one of the terminal copper(II) atom [Cu2] (Cu2 \cdots Cu3 = 3.167 Å) but by two equatorial oxygens (Cu-O = 1.9689(16)) and other 2.0473(17)Å) to the copper(II) atom [Cu1] $(Cu1 \cdots Cu3 = 2.957 \text{ Å})$. The terminal copper(II) atoms are not bridged directly, but are connected via the central Cu3, and are separated by 3.714 Å.

The "pair of independent triangles" model yielded a good fit for the parameter values g = 2.21, temperature independent paramagnetic susceptibility (TIP) = 200×10^{-6} cm³ mol⁻¹ for Cu₃, $2J_{AB=AC} = -407$ cm⁻¹ and $2J_{BC} = 0$ (Fig. 4). A difference in 2J for the Cu1–Cu3 versus Cu2–Cu3 pathways could not be obtained with certainty. 2J values of this size and magnitude are quite common for Cu(μ -OPh)₂Cu pathways [54].

4. Conclusion

In the present paper we have reported the synthesis and physicochemical characterization of a novel hexanuclear copper(II) Schiff base complex, derived from a symmetrical N₂O₂ donor Schiff base and dicyanamide ion. $\mu_{1,5}$.Bridging mode of dicyanamide is explored to form a complex of six copper(II) centers through doubly bridging between two trimetallic asymmetric units. Structural characterization also reveals both distorted square planar and distorted octahedral copper(II) centers within the asymmetric unit where each terminal copper(II) is connected to the middle copper(II) by double μ_2 -phenoxo bridges. Cryomagnetic investigation reveals strong antiferromagnetic behavior well fitted with the "pair of independent triangles" model [35] as the long chain dca generally exhibits no or a very weak antiferromagnetic interaction.

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Appendix A. Supplementary data

CCDC 799223 contains the supplementary crystallographic data for **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.

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