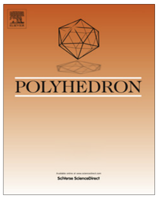
Polyhedron 59 (2013) 101–106

Contents lists available at SciVerse ScienceDirect

Polyhedron

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



Synthesis, characterization and magnetic properties of an oxido-bridged tetranuclear copper(II) complex

Mahendra Sekhar Jana [a], Sudipto Dey [a], José L. Priego [b], Reyes Jiménez-Aparicio [b,*], Tapan Kumar Mondal [a,*], Partha Roy [a,*]

[a] Department of Chemistry, Inorganic Chemistry Section, Jadavpur University, Kolkata 700032, India
[b] Departamento de Química Inorgánica, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Ciudad Universitaria, E28040 Madrid, Spain

ARTICLE INFO

Article history:
Received 1 March 2013
Accepted 20 April 2013
Available online 3 May 2013

Keywords:
Copper
Schiff-base ligand
Tetranuclear complex
Antiferromagnetic

ABSTRACT

A copper(II)–Schiff-base complex, $[Cu_4(O)(\mathbf{L})_2(CH_3COO)_4]$ (**1**) where **HL** = 4-methyl-2,6-bis(((2-trifluoromethyl)phenyl)methyliminomethyl)phenol, has been prepared. It has been characterized by elemental analysis, different spectroscopic methods and single crystal X-ray diffraction study. Single crystal analysis of **1** reveals that four copper atoms coordinate with one oxygen atom forming a distorted tetrahedron in which the oxygen atom occupies the center and copper atoms reside in the corners. The temperature dependent magnetic property of complex **1** shows strong antiferromagnetic interactions between the copper atoms.

1. Introduction

Multinuclear complexes of copper(II) are of great interest to researchers because of their diverse structural aspects as well as for their application in the fields of magnetism, biology, catalysis, etc. [1–14]. Multinuclear complexes can be prepared by choosing appropriate ligand systems with suitable donor atoms. A mononuclear complex can be transformed into a multinuclear complex by the judicial choice of the bridging ligand, metal ion and reaction conditions. Schiff-base ligands are well known in the syntheses of multinuclear complexes. Schiff-bases are able to stabilize various metal ions in different oxidation states. A Schiff-base ligand of a dialdehyde, 4-methyl-2,6-diformylphenol, was reported by Robson for the first time in 1970 [15,16]. Since then a huge number of multinuclear complexes of Schiff-base ligands of 4-methyl-2,6-diformylphenol have been reported in a number of research articles. A very recent review article has well documented acyclic and cyclic compartmental ligands of this aldehyde, along with other ligands [17]. Schiff-base ligands of such aldehydes are suitable to produce multinuclear complexes where the phenolic oxygen atom bridges two metal ions and ancillary ligands, e.g. halide, carboxylate etc., coordinate to the metal ions to further stabilize the system.

Cu(II)–Schiff-base complexes have found numerous applications in catalysis, biological sciences, magnetism etc. Copper(II) compounds have shown catalytic activity in the epoxidation of olefins [7,8,12,18], oxidation of alkanes [19], sulfoxidation [20,21], catechol oxidation [22,23] etc. On the other hand, copper(I) complexes have been used as catalysts in the "click reaction" or Huisgen 1,3-dipolar cycloaddition reaction of organic azides and alkynes. This reaction has been widely applied to generate triazole for different purposes.

Cu(II) complexes produce variable and distorted geometries and have a simple electronic configuration. These properties encourage researchers to explore the magnetic properties of multinuclear metal–organic complexes of Cu(II). Schiff-base complexes with a μ_4-oxido–Cu_4 moiety have been reported in the literature and the magnetic properties of these complexes have been extensively studied. The four copper atoms arrange themselves in the corners and the oxygen atom occupies the center of a distorted tetrahedron. Previously, Ray and co-workers reported the temperature dependent magnetic properties of μ_4-O-bridged Cu(II) complexes in detail [2,3,24,25]. There are recent reports on the synthesis of μ_4-O–Cu(II) complexes and their applications in catalysis [10,11]. Study of the magnetic properties of these complexes has shown them to be antiferromagnetic in nature.

Here we report the synthesis, characterization and magnetic properties of $[Cu_4(O)(\mathbf{L})_2(CH_3COO)_4]$ (**1**) where **HL** = 4-methyl-2,6-bis(((2-tri-fluoromethyl)phenyl)methyliminomethyl)phenol. Single crystal analysis of **1** has revealed the existence of four copper atoms coordinating with one oxygen atom, forming a distorted tetrahedron. Temperature dependent magnetic properties of complex **1** show strong antiferromagnetic interactions amongst the copper atoms.

---

* Corresponding authors. Tel.: +91 33 2457 2267; fax: +91 33 2414 6414 (T. Kumar Mondal, P. Roy), fax: +34 91 394 4352 (R. Jiménez-Aparicio).

E-mail addresses: reyesja@quim.ucm.es (R. Jiménez-Aparicio), tkmondal@chemistry.jdvu.ac.in (T. Kumar Mondal), proy@chemistry.jdvu.ac.in (P. Roy).

0277-5387/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.poly.2013.04.042

2. Experimental

2.1. Materials and physical methods

Copper(II) acetate monohydrate and 2-trifluoromethyl-1-phenylmethanamine were purchased from Sigma Aldrich and used as received. All other reagents were of analytical reagent grade. The solvents used for the spectroscopic studies were purified and dried by standard procedures before use [26]. The ESI-MS was recorded on a Qtof Micro YA263 mass spectrometer. FT-IR spectra were obtained on an RX-1 Perkin Elmer spectrophotometer with the samples prepared as KBr pellets. Elemental analysis was carried out in a 2400 Series-II CHN analyzer, Perkin Elmer, Norwalk, CT. Absorption spectra were recorded on a Lambda 25 Perkin Elmer spectrophotometer. The luminescence property was measured using an LS-55 Perkin Elmer fluorescence spectrophotometer at room temperature (298 K) in acetonitrile solution with a 1 cm path length quartz cell. Fluorescence lifetimes were measured using a time-resolved spectrofluorometer from IBH, UK. The instrument uses a picoseconds diode laser (NanoLed-03, 370 nm) as the excitation source and works on the principle of time-correlated single photon counting [27]. The goodness of fit was evaluated by χ^2 criterion and a visual inspection of the residuals of the fitted function to the data. The variable-temperature magnetic susceptibilities were measured on a polycrystalline sample with a Quantum Design MPMS*XL* SQUID (Superconducting Quantum Interference Device) susceptometer.

All the experiments were carried out in air and room temperature unless reported otherwise. 4-Methyl-2,6-diformylphenol was synthesized following a published method [28].

2.2. Synthesis of 4-methyl-2,6-bis(((2-trifluoromethyl)phenyl)methyliminomethyl)phenol(**HL**)

The ligand **HL** was synthesized following a literature method with a slight modification [29,30]. 2-Trifluoromethyl-1-phenylmethanamine (0.857 g, 8 mmol) in 10 mL of acetonitrile was added to a solution of 4-methyl-2,6-diformylphenol (0.656 g, 4 mmol) in 15 mL of acetonitrile. The reaction mixture was refluxed for 4 h. The solution was filtered, concentrated on a rotary evaporator to dryness and kept at 4 °C overnight. The yellow colored solid Schiff base ligand was recrystallized from acetonitrile. (Yield = 1.7 g, 89%) *Anal.* Calc. For $C_{25}H_{20}N_2OF_6$: C, 62.76; H, 4.21; N, 5.86. Found: C, 62.73; H, 4.10; N, 5.92%. ^{1}H NMR δ_H (300 MHz, $CDCl_3$, Me_4Si): 2.31 (3H, s, Ar–CH_3), 5.01 (4H, s, CH), 7.26–7.72 (10H, m, Ar–CH), 8.70 (2H, s, HC=N). HRMS: *m*/*z* (ESI) 479.09 ($[HL+H]^+$ requires 479.1513).

2.3. Synthesis of $[Cu_4(O)(\mathbf{L})_2(CH_3COO)_4]$ (**1**)

Copper(II) acetate monohydrate (0.6 mmol, 0.120 g) was added to an acetonitrile solution (10 mL) of 4-methyl-2,6-bis(((2-trifluoromethyl)phenyl)methyliminomethyl)phenol (0.3 mmol, 0.144 g) under stirring conditions. The mixture was allowed to stir for 1 h while the solution became green in color. After that it was refluxed for 1 h. The mixture was then cooled to room temperature and filtered to remove any precipitate or undissolved material, if any. The filtrate was kept at room temperature. Single crystals suitable for X-ray diffraction were obtained within a few days. (Yield = 0.26 g, 60%) *Anal.* Calc. For $C_{58}H_{50}Cu_4F_{12}N_4O_{11}$: C, 47.68; H, 3.45; N, 3.83. Found: C, 47.63; H, 3.40; N, 3.88%.

2.4. X-ray data collection and structure determination

The crystal data of complex **1** are summarized in Table 1. The structure of the complex was determined by single crystal X-ray diffraction analysis. Single crystal data collection was performed with an automated Bruker SMART APEX CCD diffractometer using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Reflection data were recorded using the ω scan technique. Unit cell parameters were determined from least-squares refinement of setting angles with θ in the range $1.62 \leqslant \theta \leqslant 26.50°$. Out of 34748 data collected, 2575 with $I > 2\sigma(I)$ were used for the structure solution within the *hkl* parameters $-17 \leqslant h \leqslant 17$, $-14 \leqslant k \leqslant 17$ and $-41 \leqslant l \leqslant 37$. The structure was solved and refined by full-matrix least-squares technique on F^2 using the SHELXS-97 program [31]. The absorption corrections were done by the multi-scan technique. All data were corrected for Lorentz and polarization effects, and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated using SHELXL-97 [31] and their positions calculated based on the riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and they participated in the calculation of the final *R*-indices.

2.5. Magnetic measurements

The variable-temperature magnetic susceptibilities were measured on a polycrystalline sample with a Quantum Design MPMS*XL* SQUID (Superconducting Quantum Interference Device) susceptometer over a temperature range of 2–300 K at constant field of 1 T. Each raw data set was corrected for the diamagnetic contribution of both the sample holder and the complex to the susceptibility. Molar diamagnetic corrections were calculated on the basis of Pascal constants. The fitting of the experimental data was carried out using the MATLAB V.5.1.0.421 program.

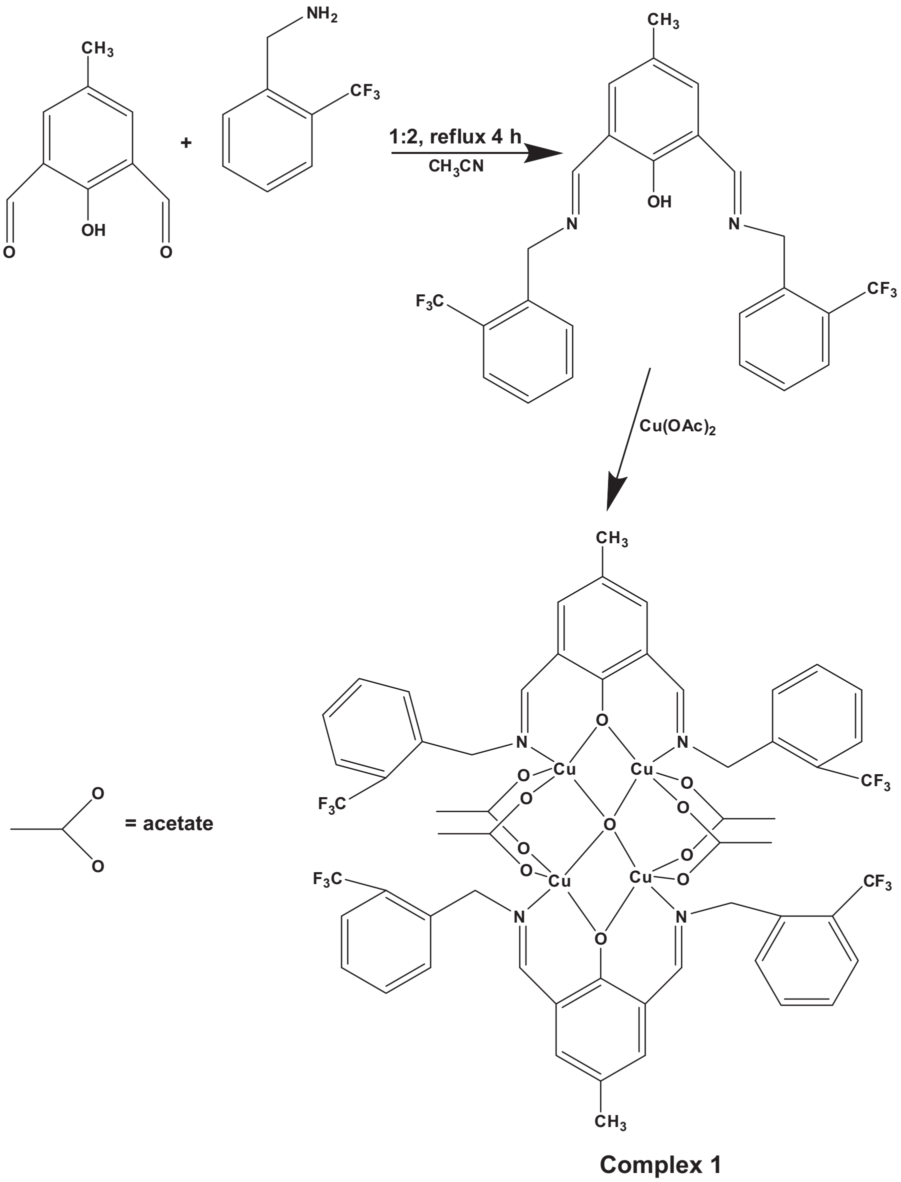
3. Results and discussion

3.1. Synthesis and FT-IR spectra

The synthetic procedure for complex **1** is shown in Scheme 1. The ligand **HL** was synthesized by the Schiff-base condensation between 4-methyl-2,6-diformylphenol and 2-trifluoromethyl-1-phenylmethanamine in a 1:2 ratio in acetonitrile. Complex **1** was prepared by the reaction between one equivalent of **HL** and two equivalents of the copper(II) salt in acetonitrile. No external base was used to deprotonate the phenolic proton of the ligand.

Table 1
Crystal data for complex **1**.

	Complex **1**
Formula	$C_{58}H_{50}Cu_4F_{12}N_4O_{11}$
Formula weight	1461.22
T (K)	293(2)
Color	green
Crystal system	tetragonal
Space group	I41/a
a (Å)	13.6052(3)
b (Å)	13.6052(3)
c (Å)	32.8012(13)
V (Å^3)	6071.6(3)
Z	4
Crystal dimensions (mm)	0.24 × 0.24 × 0.23
Minimum and maximum transmission factors	0.708–0.711
F(000)	2952
D_{calc} (g cm^{-3})	1.599
λ(Mo Kα) (Å)	0.71073
θ (°)	25.00–1.62
Reflection collected/unique	34748, 2575
Absorption correction	multi-scan
R_{int}	0.0375
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0826$, $wR_2 = 0.1978$
Goodness-of-fit (GOF) on F^2	1.050



Scheme 1. Synthesis of complex **1**.

The FT-IR spectra of the ligand and complex **1** were recorded with the samples prepared as KBr pellets. The FT-IR spectrum of the ligand shows strong ν_{C-H} bands in the region 2800–3000 cm^{-1}. The FT-IR spectrum of **1** shows the retention of these bands in the said region [32,33]. The ligand and complex exhibit very strong bands at 1637 and 1623 cm^{-1} respectively, confirming the presence of the C=N bond in the ligand and the retention of this bond in the complex. Complex **1** shows a band at around 600 cm^{-1}, indicating that the ligand is coordinated to the metal atoms [34]. This band is absent in the spectrum of the ligand, as anticipated.

3.2. Description of the crystal structure of complex 1

An N_2O donor Schiff-base ligand (**HL**), 4-methyl-2,6-bis(((2-trifluoromethyl)phenyl)methyliminomethyl)phenol, was used to obtain complex **1**. **HL** has not been used to synthesize any other transition metal complexes, but similar types of Schiff-base ligands with an N_2O donor system have been used to get multinuclear complexes with different transition metal ions using different bridging ligands under various reaction conditions. Different transition metal ions produce complexes with this type of ligand with varied nuclearity. Hexanuclear zinc [30], dinuclear copper [13], tetranuclear copper [11–13,24,25], tetranuclear cobalt [35,36], polymeric copper [18] etc. have been reported. Among these, tetranuclear copper(II) complexes have a similar structural metal–donor connectivity to complex **1**.

Complex **1** crystallizes in the tetragonal space group with acetonitrile. A perspective view of **1** with a partial atom numbering scheme is shown in Fig. 1. Selected bond lengths and bond angles are given in Table 2. It is found to be a discrete tetranuclear complex of Cu(II). It has the crystallographic site symmetry 4-. Only one copper atom is present in the asymmetric unit. Four copper atoms arrange themselves around the μ_4-oxido oxygen atom (O1) in a distorted tetrahedral geometry. The metal–oxygen–metal bond angles range from 103.23(5)° to 112.68(2)°. The copper atom is in a pentacoordinated environment. It is bonded to the μ_4-oxido oxygen atom O1, one oxygen atom O2 and one nitrogen atom N1

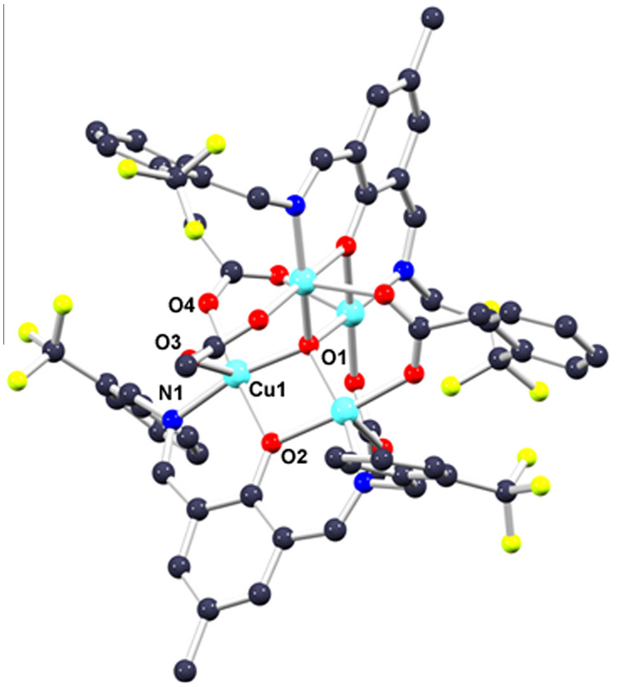


Fig. 1. A perspective view of complex **1**. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond lengths (Å) and bond angles (°) of complex **1**.

Cu1–O1	1.9243(7)	Cu1–O4	1.944(5)
Cu1–O2	1.970(4)	Cu1–N1	1.988(6)
Cu1–O3	2.259(6)	Cu1–Cu1	3.0164(14)
O1–Cu1–O4	97.50(18)	O1–Cu1–O2	78.44(14)
O4–Cu1–O2	175.4(2)	O1–Cu1–N1	166.65(19)
O4–Cu1–N1	92.6(3)	O2–Cu1–N1	91.1(2)
O1–Cu1–O3	98.92(15)	O4–Cu1–O3	93.5(3)
O2–Cu1–O3	89.2(2)	N1–Cu1–O3	89.1(2)

from the Schiff-base ligand (**HL**), and two oxygen atoms O3 and O4 from two different μ_2-bridging acetato ligands. The copper atom Cu1 is in a distorted square pyramidal atmosphere, as revealed by the trigonal index, τ. The value of τ has been found to be 0.146. The value of the trigonal index is defined as the difference between the two largest donor–metal–donor angles divided by 60, a value which is 0 for an ideal square pyramid and 1 for an ideal trigonal bipyramid geometry [37]. The O1, O2, N1 and O4 atoms form the basal plane of the distorted square pyramid, whereas O3 from the bridging acetate moiety occupies the apical position. The Cu1–O3 bond distance (2.259(6) Å) is quite long compared to other metal–donor bond distances. The metal–metal bond distances vary from 3.016 to 3.203 Å. All the bond distances are in good agreement with the relevant published values [10,11].

3.3. UV–Vis and fluorescence spectra

The UV–Vis spectra of the ligand **HL** and complex **1** were recorded in methanol at room temperature. The ligand shows a peak at 263 nm, indicating a $\pi \rightarrow \pi^*$ transition. In the spectrum of the ligand, the band at 347 nm may be assigned to an $n \rightarrow \pi^*$ transition. The UV–Vis spectrum of complex **1** is shown in Fig. 2. Complex **1** shows spectral bands at 265 and 411 nm. The band at 265 nm may be assigned to a $\pi \rightarrow \pi^*$ transition, indicating the presence of the ligand in the metal complex. During the formation of the complex, the band at 347 nm is shifted to a lower energy, *viz.* 410 nm, suggesting that the nitrogen atom of the C=N group is coordinated to the metal ion. This band may be attributed to a ligand to metal charge transfer transition. In addition to these two bands, another broad band appears in the region 657–755 nm. This band may be attributed to the d–d transition usually observed in copper(II) complexes.

The emission spectra of the ligand and complex **1** were recorded in methanol at room temperature. The emission spectrum of complex **1** is shown in Fig. 3. The free ligand shows an emission band at 548 nm when excited at 347 nm, whereas complex **1** exhibits an emission band at 474 nm when excited at 410 nm. We have also studied the fluorescence decay behavior of **HL** and complex **1**. The observed fluorescence decay fits well with a bi-exponential nature for both the ligand and the complex (see Supplementary information). We have used the mean fluorescence lifetime ($\tau_f = a_1\tau_1 + a_2\tau_2$, where a_1 and a_2 are the relative amplitudes of the decay process) to study the excited state stability of the complex. The fluorescence lifetime (τ) of the free ligand is 2.99 ns and that of the metal bound ligand has been found to be 3.62 ns. The lifetime data of the compounds were recorded at 298 K in acetonitrile solution when excited at 370 nm.

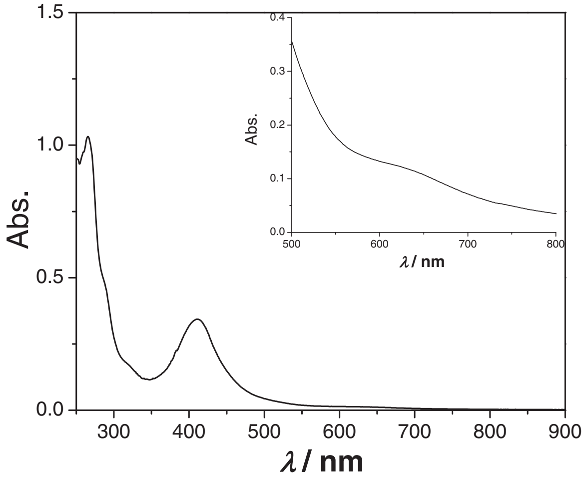


Fig. 2. UV–Vis spectrum of complex **1** in methanol at room temperature.

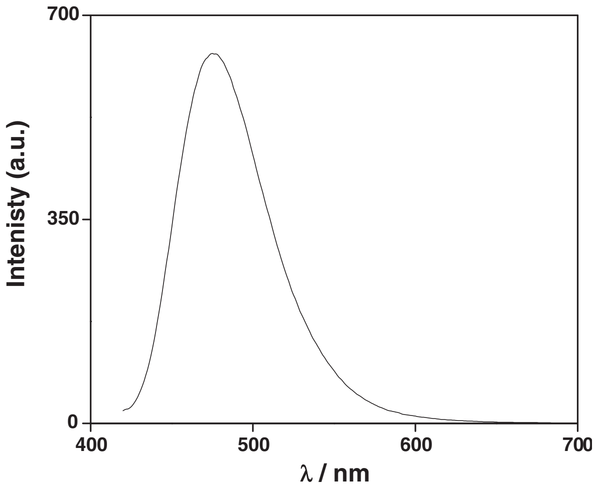


Fig. 3. Emission spectrum of complex **1** recorded in methanol at room temperature (λ_{ex} = 410 nm).

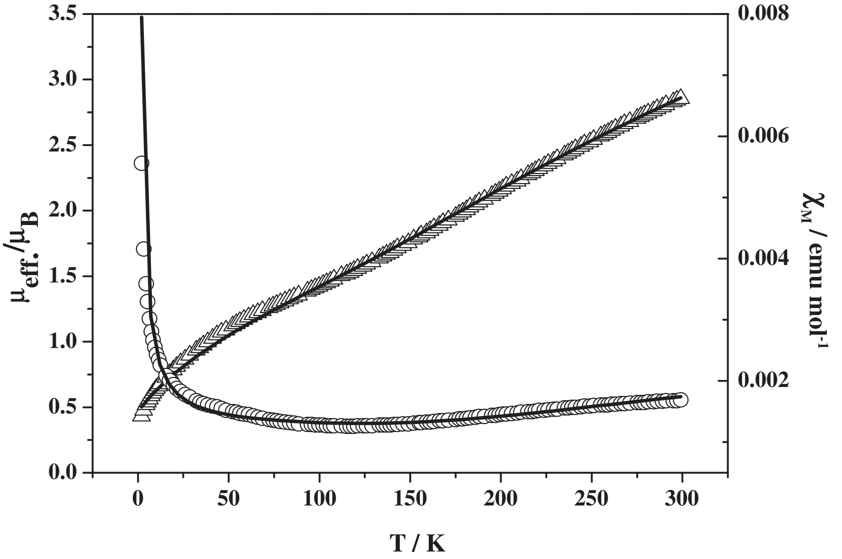


Fig. 4. The variations of molar magnetic susceptibility (χ_M) and magnetic moment (μ_{eff}) with temperature for complex **1**.

3.4. Magnetic properties of complex 1

Variable-temperature magnetic susceptibility measurements were performed on a powdered crystalline sample of complex **1** at 1 T in the range 2.0–300 K. The variations of the molar magnetic susceptibility (χ_M) and magnetic moment (μ_{eff}) with temperature for **1** are illustrated in Fig. 4. The magnetic moment at room temperature is 2.86 μ_B smaller than the spin only value for four $S = ½$ spins by a tetramer unit (3.46 μ_B). The magnetic susceptibility slowly decreases from room temperature until about 100 K and then increase mainly from 25 K. This shape suggests the existence of a maximum above room temperature. However, the magnetic moment shows an intense decrease with decreasing temperature.

The magnetic exchange interactions between the metallic atoms in a cluster can be treated with the isotropic spin Hamiltonian.

$$H = -2\sum_{i<j} J_{ij} S_i \cdot S_j$$

In a tetranuclear cluster of the type [M_4(μ_4-oxido)] six magnetic interaction pathways are possible (Scheme 2a), but with all these parameters magnetic analysis of this system is not simple. In order to avoid over-parametrization, a simplification of this system is desirable. So, the study of the magnetic properties of [$Cu_4(\mu_4\text{-}O)$] complexes is usually carried out using several approximations [24,25,38–42]. The most used simplifications are the following: (a) To consider only four types of magnetic interaction pathways, as has been used in the fit of the magnetic data of the complex [$Cu_4(L)(\mu_4\text{-}O)$]·H_2O (L = tetranucleating macrocyclic ligand, L^{6-}) [38]. (b) To consider two exchange parameters, J_1 and J_2 as used [39,40] in the fit of the magnetic data of the complexes [$L_2Cu_4(\mu_4\text{-}O)(\mu_2\text{-carboxylato})_4$] (carboxylato = acetato, benzoato) and [$Cu_4(\mu_4\text{-}O)\{(py)C(CN)NO\}_4(O_2CMe_2)$]. (c) To consider the tetranuclear unit as being formed by two dimers with $S = ½$ spins and only one exchange parameter, J. This approach has been used in the fit of the magnetic data of the complexes [$Cu_4(\mu_4\text{-}O)(\mu\text{-cip})_2(\mu_{1,3}\text{-}O_2CPh)_4$]·2MeOH (Hcip = 2,6-bis(cyclohexyliminomethylene)-4-methylphenol) and [$Cu_4(\mu_4\text{-}O)(\mu\text{-bip})_2(\mu\text{-}O_2CPh)_4$]·0.5$CH_2Cl_2$ (Hbip = 2,6-bis(benzyliminomethyl)-4-methylphenol) [24,25].

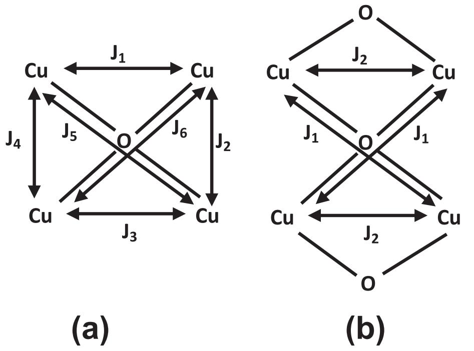
In complex **1** each bridging acetate ligand displays a short [1.933(6) Å] and a large [2.249(6) Å] Cu–O distance and therefore the exchange interactions thought these ligands could be neglected. In addition, the Cu–Cu distances between the copper atoms joined by the asymmetric carboxylate ligands is larger (3.203 Å) than the copper atoms bonded by the oxo ligands (3.016 Å), which also advises the ruling out the interaction between these copper atoms in order to avoid over-parametrization effects. Thus, the six possible interactions can be reduced to only two, similar to some of the above-mentioned models [39,40]: One exchange interaction (J_1) mediated by the μ_4-O^{2-} oxygen atom bridging the Cu(II) atoms of the tetramer unit and the other one (J_2) through the μ_2-O oxygen belonging to the ligand L (Scheme 2b). Thus, the used spin Hamiltonian is:

$$H = -2[J_1(S_1 \cdot S_3 + S_1 \cdot S_4 + S_2 \cdot S_3 + S_2 \cdot S_4) + J_2(S_1 \cdot S_2 + S_3 \cdot S_4)]$$

The magnetic susceptibility expression derived from this Hamiltonian is shown in the following equation

$$\chi_{Cu_4} = (1 - \chi_p)\frac{g^2N\beta^2}{kT}\left[\frac{10e^{2x} + 2e^{-2x} + 4e^{-2y}}{5e^{2x} + 3e^{-2x} + e^{-4x} + 6e^{-2y} + e^{-4y}}\right] + \chi_p \times \frac{g^2N\beta^2}{3kT}S(S+1) + \text{TIP}$$

with $x = J_2/kT$; $y = J_1/kT$



Scheme 2. (a) Possible magnetic interactions pathways in [$Cu_4(\mu_4\text{-}O)$]. (b) Magnetic interactions considered in complex **1**.

In this equation two terms corresponding to the presence of a paramagnetic impurity (χ_p) and the existence of temperature independent paramagnetism (TIP) have been added.

With this model, the following parameters have been obtained: $g = 2.2$, $J_1 = -7\ \text{cm}^{-1}$, $J_2 = -230\ \text{cm}^{-1}$, $\text{TIP} = 2.2 \times 10^{-3}$ mL/mol and $\chi_p = 3.0\%$, the quality of the fit being $\sigma^2 = 6.4 \times 10^{-4}$. The experimental and calculated curves are displayed in Fig. 4. The g value is very typical for Cu(II) complexes. Both coupling constants are negative and therefore both magnetic interactions are antiferromagnetic, which fit well with the magnetic data. As has been observed previously [39], the magnetic interchange through the phenoxido group is higher than through the oxido bridge, which is in accordance with the parameters calculated for complex **1**. The large antiferromagnetic coupling ($-230\ \text{cm}^{-1}$) mediated by the phenoxido group is also in accord with the Cu–$\text{O}_{\text{phenoxido}}$–Cu angle (99.96°) because it is known [24] that angles larger than 97.6° lead to antiferromagnetic coupling, which increases with increasing angles. The calculated coupling constant values (J_1 and J_2) are also in accordance with those calculated for an analogous compound [39,40]. The amount of paramagnetic impurity (2.9%) is very similar to that calculated (3%) in the similar complex $[\text{Cu}_4(\mu_4\text{-O})(\mu\text{-cip})_2(\mu_{1,3}\text{-O}_2\text{CPh})_4]\cdot 2\text{MeOH}$ [24].

4. Conclusions

We have been able to synthesize a μ_4-oxido-bridged tetranuclear copper(II) complex with an N_2O donor Schiff-base ligand. This complex has been characterized using elemental analysis, different spectroscopic techniques and a single crystal X-ray diffraction study. The magnetic properties have been studied extensively. The complex shows strong antiferromagnetic interactions between the copper atoms.

Acknowledgements

MSJ wishes to thank CSIR, New Delhi and SD wishes to thank UGC, New Delhi for their fellowships. Financial support received from the Spanish Ministerio de Ciencia e Innovación, MICINN, (CTQ2011-23066) and Comunidad de Madrid (S2009/MAT-1467) is gratefully acknowledged.

Appendix A. Supplementary data

CCDC 793601 contains the supplementary crystallographic data for article. 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.2013.04.042.

References

[1] Q. Zhu, C. Tian, C. Shen, T. Sheng, S. Hu, X. Wu, CrsystEngComm 15 (2013) 2120.
[2] A.R. Paital, P.K. Nanda, S. Das, G. Aromi, D. Ray, Inorg. Chem. 45 (2006) 505.
[3] M. Bera, W.T. Wong, G. Aromi, J. Ribas, D. Ray, Inorg. Chem. 43 (2004) 4787.
[4] E.E. Chufán, S.C. Puiu, K.D. Karlin, Acc. Chem. Res. 40 (2007) 563.
[5] S. Sarkar, S. Sen, S. Dey, E. Zangrando, P. Chattopadhyay, Polyhedron 29 (2010) 3157.
[6] X. Yu, L. Wang, X. Feng, M. Bao, Y. Yamamoto, Chem. Commun. 49 (2013) 2885.
[7] K.C. Gupta, A.K. Sutar, Coord. Chem. Rev. 252 (2008) 1420.
[8] K.C. Gupta, A.K. Sutar, C.-C. Lin, Coord. Chem. Rev. 253 (2009) 1926.
[9] D. Saha, T. Maity, T. Dey, S. Koner, Polyhedron 35 (2012) 55.
[10] M. Nandi, P. Roy, H. Uyama, A. Bhaumik, Dalton Trans. 40 (2011) 12510.
[11] P. Roy, M. Manassero, Dalton Trans. 39 (2010) 1539.
[12] P. Roy, M. Nandi, M. Manassero, M. Riccó, M. Mazzani, A. Bhaumik, P. Banerjee, Dalton Trans. (2009) 9543.
[13] P. Roy, K. Dhara, M. Manassero, P. Banerjee, Eur. J. Inorg. Chem. (2008) 4404.
[14] A.M. Kirillov, M.N. Kopylovich, M.V. Kirillova, M. Haukka, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Angew. Chem., Int. Ed. 44 (2005) 4345.
[15] R. Robson, Aust. J. Chem. 23 (1970) 2217.
[16] R. Robson, Inorg. Nucl. Chem. Lett. 6 (1970) 125.
[17] P.A. Vigato, V. Peruzzo, S. Tamburini, Coord. Chem. Rev. 256 (2012) 953.
[18] P. Roy, K. Dhara, M. Manassero, P. Banerjee, Inorg. Chem. Commun. 11 (2008) 265.
[19] A.M. Kirillov, M.V. Kirillova, A.J.L. Pombeiro, Coord. Chem. Rev. 256 (2012) 2741.
[20] H.M. Mohammed, K.-J. Zahed, G. Dadkhoda, J. Chem. Res. 5 (2004) 364.
[21] S. Velusamy, A.V. Kumar, R. Saini, T. Punniyamurthy, Tetrahedron Lett. 46 (2005) 3819.
[22] E. Mijangos, J. Reedijk, L. Gasque, Dalton Trans. (2008) 1857.
[23] A. Panja, S. Goswami, N. Shaikh, P. Roy, M. Manassero, R.J. Butcher, P. Banerjee, Polyhedron 24 (2005) 2921.
[24] M. Sarkar, R. Clérac, C. Mathonière, N.G.R. Hearns, V. Bertolasi, D. Ray, Inorg. Chem. 50 (2011) 3922.
[25] M. Sarkar, R. Clérac, C. Mathonière, N.G.R. Hearns, V. Bertolasi, D. Ray, Inorg. Chem. 49 (2010) 6575.
[26] D.D. Perrin, W.L.F. Armarego, D.R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford, UK, 1980.
[27] B. Valuer, Molecular Fluorescence: Principles and Applications, Wiley-VCH, Weinheim, 2001.
[28] R.R. Gagne, C.L. Spiro, T.J. Smith, C.A. Hamann, W.R. Thies, A.K. Schiemke, J. Am. Chem. Soc. 103 (1981) 4073.
[29] J.J. Grzybowski, F.L. Urbach, Inorg. Chem. 19 (1980) 2604.
[30] P. Roy, K. Dhara, M. Manassero, J. Ratha, P. Banerjee, Inorg. Chem. 46 (2007) 6405.
[31] G.M. Sheldrick, SHELXL97: Programs for Crystal Structure Analysis, University of Göttingen, Göttingen, Germany, 1997.
[32] R. Karmakar, C. Roy Choudhury, D.L. Hughes, S. Mitra, Inorg. Chim. Acta 360 (2007) 2631.
[33] P. Roy, J. Coord. Chem. 62 (2009) 2003.
[34] J.T. Guy Jr., J.C. Cooper, R.D. Gilardi, J.L. Flippen-Anderson, Inorg. Chem. 27 (1988) 635.
[35] D. Mandal, D. Ray, Inorg. Chem. Commun. 10 (2007) 1202.
[36] S.S. Tandon, S.D. Bunge, R. Rakosi, Z. Xu, L.K. Thompson, Dalton Trans. 33 (2009) 6536.
[37] A.W. Addison, T.N. Rao, J. Reedijk, J. Vanrijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
[38] Y. Miyazato, E. Asato, M. Ohba, T. Wada, Bull. Chem. Soc. Jpn. 85 (2012) 895.
[39] R. Shakya, S.S. Hindo, L. Wu, S. Ni, M. Allard, M.J. Heeg, S.R.P. da Rocha, G.T. Yee, H.P. Hratchian, C.N. Verani, Chem. Eur. J. 13 (2007) 9948.
[40] A. Escuer, G. Vlahopoulou, S.P. Perlepes, F.A. Mautner, Inorg. Chem. 50 (2011) 2468.
[41] G.M. Chiarella, D.Y. Melgarejo, A.V. Prosvirin, K.R. Dunbar, J.P. Fackler Jr, J. Cluster Sci. 21 (2010) 551.
[42] P. Weinberger, R. Schamschule, K. Mereiter, L. Dlhán, R. Boca, W. Linert, J. Mol. Struct. 446 (1998) 115.