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A new tetranuclear copper(II) complex using a Schiff base ligand: Synthesis, structural, and magnetic studies

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ABSTRACT

This paper reports on the synthesis, X-ray, and magnetic properties of tetranuclear Cu^{II} complex $[CuL_4]$ with square-like structure. A Schiff base ligand used for synthesis in this work derives from condensation of acetylacetone with DL-valine amino acid. The structure of the synthesized ligand was investigated by FTIR and NMR. Investigation of the crystal packing diagrams demonstrates extensive C–H···O interactions of hydrogen bonding, causing to the production of network structures. The complex exhibits exchange interaction among the Cu^{II} ions by a bridging carboxylate pathway. Analysis of the magnetic data through spin Hamiltonians of the form $\hat{H} = -2J(\hat{S}_1\hat{S}_4 + \hat{S}_4\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_1) - 2J'(\hat{S}_1\hat{S}_2 + \hat{S}_3\hat{S}_4)$ (J has a positive value for a ferromagnetic interaction and negative value for an antiferromagnetic interaction) lead to the following parameters set of best-fit: $J = 3.04\ cm^{-1}$, $J' = 0\ cm^{-1}$, $g = 2.09$, and $ZJ = -0.109\ cm^{-1}$.

1. Introduction

Chemical research has been focused recently on the development and progress of molecular assemblies, ensembles, and all means of structured aggregates [1,2]. The chemistry and the design of polynuclear transition complexes were investigated intensively in the last two decades to build an understanding of the relationship between their magnetic properties and structures [3]. Herein, several tetranuclear complexes were studied and significant insight has been obtained [4–9]. For the tetranuclear cupper (II) complex, there are numerous illustrations of Cu4 arrays, that exhibit various types of structures: pin-wheel, cyclic, roof-shaped, dimeric, square planar, face-to-face, and cubane type [10–17]. Therefore, the structure of the cupper ions can be displayed in numerous geometries such as: square, linear, rectangular, tetrahedral, heterocubane, butterfly, and heterocubane [18–25].

The most common method to attain tetranuclear cupper (II) complexes is metal self-association made by bridging ligands such as imidazolate, hydroxo, diazine, oximate, and carboxylate [26–31]. However, using the novel flexible polydentate ligands, that can coordinate to several metal ions simultaneously, is one of the efficient methods for preparation of polynuclear complexes [32]. In this, multinuclear metal complexes that contain tridentate ligands that have a planar pincer-like N, O, O-chelating architecture are considered of excessive interest because to their possible application in different fields, for example: electronics, molecular photonic, and analysis [33–36]. In addition, a carboxylate group may bridge two metallic ions to produce several polynuclear complexes that include discrete entities and three dimensional systems. Furthermore, Schiff base cupper(II) complexes have found several applications in the fields of catalysis, biological sciences, and magnetism [37–46].

Recently, our group has published a new coordination polymer by the use of a chiral tridentate Schiff base ligand and Cu(II) [47]. The use of copper(II) with a similar non-chiral ligand provided tetranuclear system which has interesting magnetic properties such as the generation of molecular architectures with various nuclearity [48]. In this paper, we report on the synthesis as well as structural properties and magnetic characterization of a newly introduced copper(II) tetranuclear complex that exhibits a square shape. The study includes simulation instigation of the complex.

2. Experimental

2.1. Materials and instruments

All reactions were carried out in aerobic conditions. Copper(II) chloride dihydrate, potassium hydroxide, DL-valine, and acetylacetone were purchased from Sigma-Aldrich and used as received.

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Solvents of the finest available commercially grade were used without any extra purification procedures.

2.2. Synthesis of ligand (LHK)

A cold KOH aqueous solution of (10 mL) (0.88 g, 20 mmol) was added gradually to a cold solution in aqueous form (10 mL) of DL-valine (2.34 g. 20 mmol), under continuous stirring. After 30 min of extra stirring, acetylacetone (2.0 g, 20 mmol) in methanol (10 mL) was introduced dropwise. The solution was then stirred continuously overnight, concentrated, washed using petroleum ether, dissolved in methanol, and finally filtered. The removal of the solvent introduced a crude product of DL-LHK with a yield of 85%.

Melting point (M.p.) 169–170 °C. Analytical calculation (Anal. Calc.) for each atom of $C_{10}H_{15}O_3N^-$, K^+ (MW = 236.27) are: C = 49.94, H = 6.85, O = 20.46, N = 5.39, K = 17.33%. The results found in the present study are: C = 50.84, H = 6.35, O = 20.34, N = 5.93, K = 16.52%.

2.3. Synthesis of complex-1 [$Cu_4(L_4)$]

DL-LHK was dissolved in 10 mL of methanol (237 mg, 1 mmol), and $CuCl_2{\cdot}2H_2O$ (170 mg, 1 mmol) was introduced slowly dropwise under continuous stirring. Addition of triethylamine (0.3 mL) presented a deep-green solution. Low-rate evaporation of the solvent for few days to introduced crystals of (1) [Cu_4L_4] that exhibited a form of block blue-green crystals. The reaction yield was 65.9%.

2.4. Characterization

The X-ray measurements were performed at a temperature of 300 K using a Nonius-Kappa-CCD using Mo Ka radiation (λ = 0.71073 Å) with 2θ scans. Direct methods to solve the structures and refined with the full-matrix using the least-squares method by utilizing 3570 reflections with $I > 2\sigma$, where I was measured for θ in the range of 2.80–29.18°. No further correction for absorption was applied to the measured results. The structures were realized by a direct method of using the Sir2004 software [49], then further refined by SHELXL-1997 software [50]. Both software were integrated in the WingX crystallographic software package [51]. All atomic displacements have been refined for non-hydrogen atoms using anisotropic terms. Either hydrogen atoms were placed theoretically, or using the difference maps of electron density and constrained during refinement. The final goodness-of-fit is $S = 0.731$, which is slightly lower than 1 that can be explained by weak diffraction of small crystal of complex

Fourier transform infrared (FT-IR) spectra were measured using a Nexus-Nicolet spectrometer at a resolution of 8 cm^{-1}. FT-IR technique was used in the absorption mode in the range of 400–4000 cm^{-1}. Here, 120 scans were used with ~100 μg of the compound that was scraped. The compound was then compressed together with 23 ± 2 mg of KBr in a cold isostatic press (CIP) at 150 MPa in order to obtain a 200–250 μm thick pellet. The FT-IR spectra introduced an absorbance ($A = -\log(I/I_0)$) as a function of the incident wave numbers, where I_0 and I are the intensities of incident light and absorbed by the sample, respectively.

Hydrogen-1 nuclear magnetic resonance spectroscopy (^{1}H NMR) spectra were measured by a Bruker spectrometer (300 MHz) in CDCl3 chloroform. Chemical shifts were referred to tetramethylsilane (TMS) by the residual signals from the solvent. The elemental analyses of the compound (hydrogen, carbon, nitrogen, oxygen, and potassium) were determined by a Carlo-ERBA analyser Model EA 1108.

Magnetic measurements were conducted for a polycrystalline sample of the complex by a SQUID magnetometer (Quantum Design model MPMS-XL). The magnetometer was operated in the temperature range of 2–300 K using a dc magnetic fields between −5 and 5 T. The magnetic results were corrected for the sample holder as well as for atomic diamagnetism using the known Pascal's constants.

The intensities of FT-IR (KBr, cm^{-1}) were: 1629 ν_{as} (OCO), 1595 (C–N), and 1396 ν_{sym} (OCO). The ^{1}H NMR (at 300 MHz, CDCl3, 25 °C, TMS) were: 11.2 (D, 1H, NH), 4.9 (s, 1H, CHb), 3.8 (dd, 1H, CHa), 2.1 (m, 1H, CHc), 1.9 (s, 3H, CH_3d), 1.8 (s, 3H, CH_3e), and 0.9 (m, 6H, CH_3).

3. Results and discussions

3.1. Syntheses and spectroscopy

Schiff base ligands are synthesized by condensation of aldehydes or ketones and primary amines [52]. Recently, several examples reported that polynuclear complexes exhibit interesting magnetic properties due to the (N, N, O) or (O, N, O) ligands [48,53–55]. The objective of the current study is to use an amino acid as the principal amine for the condensation like a carboxylic group that may generate numerous coordination modes with metal ions. Nevertheless, the amino acids are not soluble in the typical organic solvents used for this reaction. They are soluble in water, however, the imine function in the Schiff base ligand produced is very sensitive to water. In contrary, when a minimal amount of water is used in methanol, the no reaction can occur due to the precipitation of the amine in the mixture of solvents [47,52]. Therefore, the present work on the generation of Schiff base from DL-valine amino acid using KOH as a base to generate the anionic product of the amine that is able to react with acetylacetone. This enables obtaining the ligand, in a salt form, with good yield and high purity. This ligand is then characterized by elemental and spectroscopic methods, and used as the chelating ligand in the synthesis of tetranuclear copper(II) complex shown in Scheme 1.

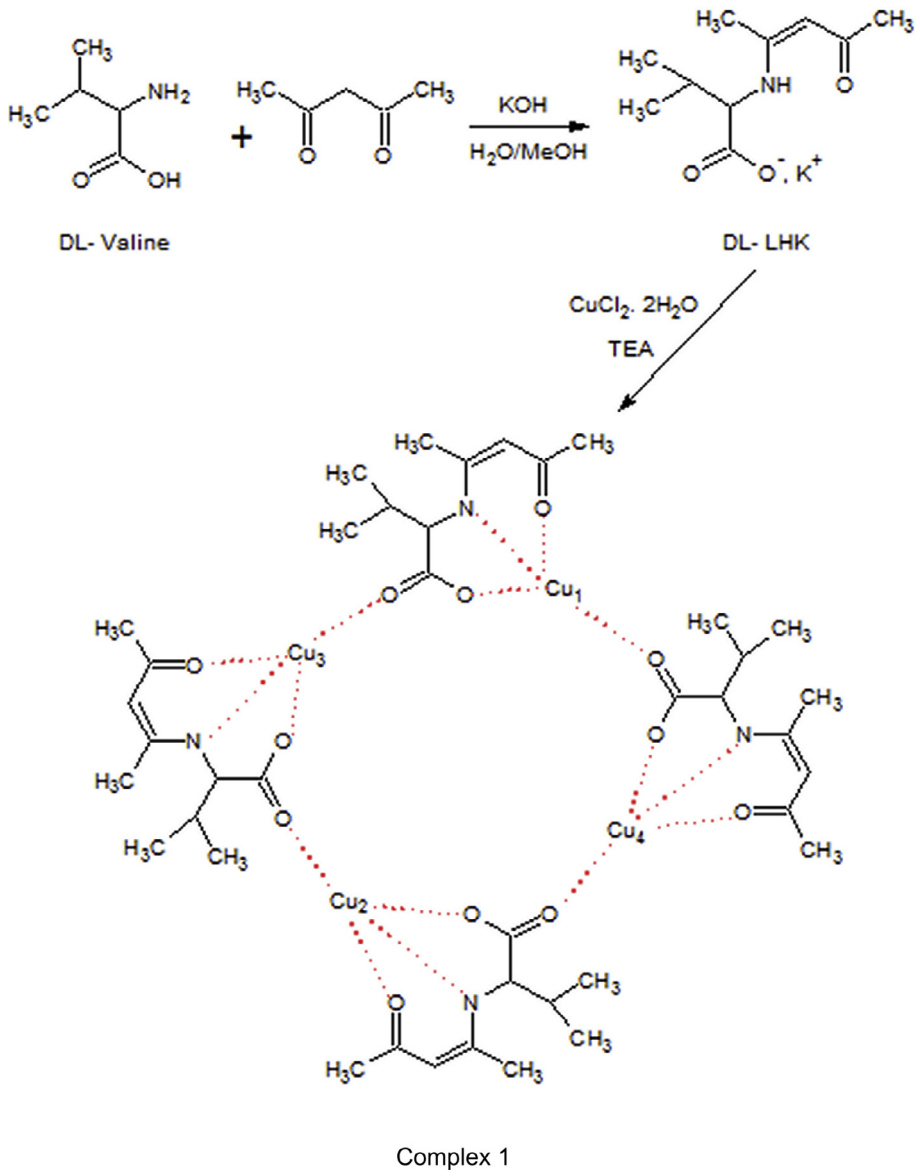
FT-IR measurements were performed for the DL-LHK ligand (see Fig. SI1, Supplementary information). The results reveal strong band at 1595 cm^{-1} which can assigned to C–N stretching. Two bands at 1396 and 1629 cm^{-1} were observed and assigned to the symmetric and asymmetric O=C–O stretching frequencies, respectively.

The formation of Schiff base ligand is confirmed by ^{1}H NMR measurements of HLK. The measurements are presented in Fig. SI2 (Supplementary information), and they confirm the presence of: (i) a doublet signal at 11.2 ppm which is assigned to the amine NH group; (ii) the singlet signal at d 4.9 ppm that is assigned to the hydrogen atom of (C=CHb) group; (iii) the dd signal at 3.8 ppm that is assigned to the hydrogen atom N-CHa; (iv) the multiple signal at 2.1 ppm that is assigned to the hydrogen atom of (C–CHc); (v) the singlets appears at 1.9 and 1.8 ppm that are assigned to the hydrogens He and Hd of the two acetylacetone methyl groups; and (vi) and the multiple at 0.9 ppm is attributed to the six hydrogen of the two methyl which belongs to the valine part.

Tetranuclear copper(II) complex is attained in this work by reacting copper(II) chloride dihydrate with the ligands at equimolar ratios (1:1) in methanol as solvent. Triethylamine is included in the reaction to deprotonate the ligands. The yield of the reaction is blue-green crystals, and they appear after few days of relaxed evaporation of the solvent as described by the reaction scheme in Scheme 1.

3.2. X-ray structure of complex-1

The dark blue-green block crystals of complex-1 are obtained from methanol solvent by the relaxed evaporation method.



Scheme 1. Synthesis pathway of DL-LHK and complex **1**.

Crystals of complex-1 are crystallized in monoclinic space group $P2_1/n$ (No. 14) with the unit cell parameters $a = 15.4683(9)$ Å, $b = 21.6096(7)$ Å, $c = 15.8957(10)$ Å, and $\beta = 118.586(8)°$. The molecular structure of the complex with atom numbers is shown in Fig. 1(a). The equivalent thermal parameters and atomic coordinates are given in Table SI1 (Supplementary information). The data collection and refinement processes are shown in Table 1. Particular bond lengths and angels are presented in Table 2. View of the crystal packing of the compound is presented in Fig. SI1 (Supplementary information). All other refinement factors are available in the crystallographic information file (CIF): CCDC-1511785.

The asymmetric units that correspond to the four copper(II) ions are: two ligands with D configuration and two other ligands with L configuration. The formula of the refined complex is $[Cu_4(L\text{-}L)_2\ (D\text{-}L)_2]$. The metallic cluster can be given as a square Cu4 where every cupper ion (II) is coordinated to a ligand with L conformation and another ligand with D conformation, and each ligand coordinate two metals at the same time. Here, two ligands with the same configuration (D or L) are facing each other (see Fig. 1(b)). Each Cu(II) ion is coordinated with two deprotonated tridentate (O, N, O) L^{1-} ligands with dissimilar conformations to have an approximately square-planar CuO_3N type that is delivered by two oxygen atoms and a nitrogen atom of the first ligand, and an oxygen atom of the acid function for the second ligand. The subunits are joined together by one bridging system that consists of three bridging carbonyl oxygen atoms where each atom belongs to a different ligand.

For a square-like architecture, all copper(II) ions are normally surrounded by four donor atoms (one nitrogen and three oxygen atoms). The bond angles are: 170.42(15)°, 170.21(18)°, 173.70 (15)°, 166.38(15)°, 169.48(14)°, 172.77(14)°, 164.94(14)°, and 175.11(18)° for: O1–Cu1–O2, O9–Cu1–N1, O4–Cu2–O5, O12–Cu2–N2, O6–Cu3–N3, O7–Cu3–O8, O3–Cu4–N4 and O10–Cu4–O11, respectively. Those values are slightly less than the ideal square-planar angle (i.e. 180°) which indicates a slightly distorted square-planar geometry. Herein, Cu1 ion is placed somewhat above the mean basal of N1–O2–O9–O1 plane by 0.002(4) Å; Cu2 ion is also above the mean basal of N2–O4–O12–O5 plane by 0.061(4) Å; Cu3 ion is displaced by 0.019(4) Å from the mean basal of N3–07–O6–O8; and Cu4 is displaced by 0.059(4) Å from the

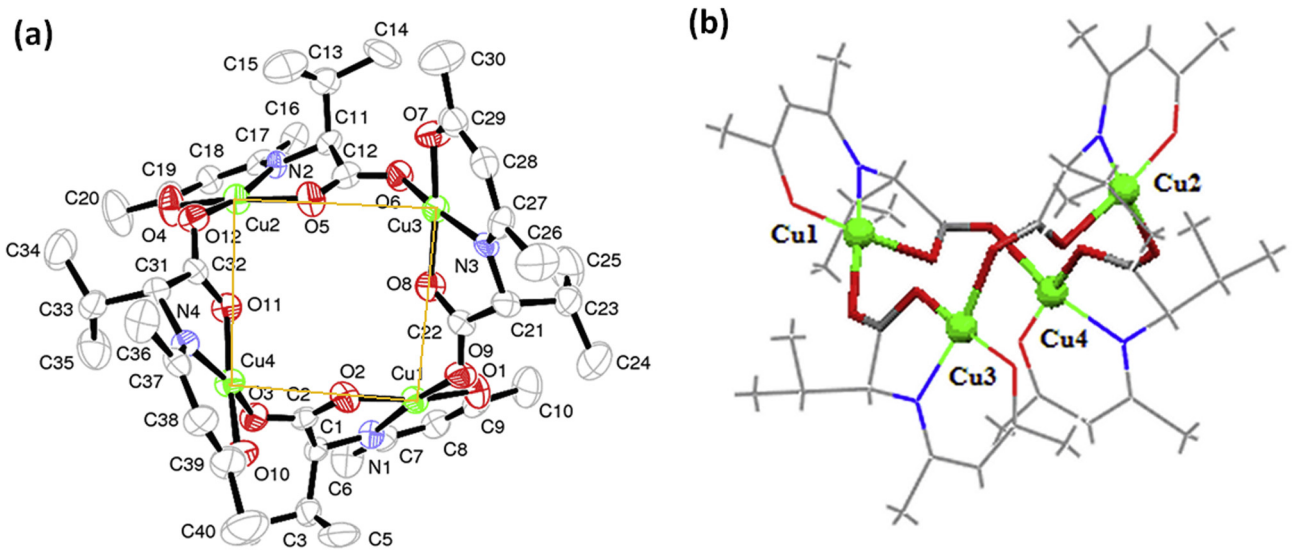


Fig. 1. (a) Ortep diagram of the complex showing 50% probability the asymmetric unit and all H atoms were omitted for clarity (apical view). The orange line shows the shape of square. (b) Lateral view of the complex. (Colour online.)

Table 1
Crystal and structure refinement data for the complex.

Formula	$Cu_4\ C_{40}\ H_{60}\ N_4\ O_{12}$
M (g mol^{-1})	1043.08
Crystal shape – color	plate – green–blue
Size (mm)	0.03 × 0.05 × 0.08
Crystal system	monoclinic
Space group (n°)	$P2_1/n$ (No.14)
T (K)	293
λ (Kα Mo) (Å)	0.71073
a (Å)	15.4683(9)
b (Å)	21.6096(7)
c (Å)	15.8957(10)
B (°)	118.586(8)
V (Å^3)	4665.7(4)
Z	4
D (g cm^{-3})	1.485
μ (mm^{-1})	1.859
F(000)	2159
Θ range (°)	2.8–29.2
Reflections (hkl)	$-21 \le 13$ $-27 \le 27$ $-21 \le 16$
Num. reflection	8734
Ind. reflection	3570
Num. parameters	542
R_{int}	0.0395
$R_1^{(a)}$	0.0434
$\omega R_2^{(b)}$	0.0803
Goodness-of-fit (GOF) on F^2	0.731
Δρmaximum/Δρminimum (e Å^{-3})	0.328/−0.304

mean basal of N4–011–O3–O10. The four Cu(+II) units and the carboxylate-bridging groups form a 16-membered ring (–Cu–O–C–O) 4 where the four copper ions are placed at the corners of a flattened tetrahedron. The separations of Cu···Cu are between 4.891 Å and 5.072 Å along the edges and between 6.199 Å and 6.438 Å along both flattened edges. The previous values are good agreement with the values found in similar structures in the literature [56–61]. It should be noted here that the tetranuclear units are connected within the network to each other by C–H···O intramolecular hydrogen bonds, leading to a dense 3D packing as shown in Table 3 and Fig. 2.

3.3. Magnetic studies

Magnetic susceptibility (χ_M) measurements as a function of temperature (T) were conducted for a powdered crystalline sample of complex-1 within the range T = 2.0–300 K and shown in Fig. 3. The main feature of the magnetic measurements of the complex in the figure is the weak ferromagnetic exchange interaction due to the intramolecular interactions among the four Cu(II) ions. The $\chi_M T$ value of 1.68 cm^3 K mol^{-1} at 300 K is as predictable for the quasi-isolated spin doublets of the four cupper magnetically independent (4 × 0.375 cm^3 K mol^{-1}). Decreasing the temperature causes $\chi_M T$ to increase with a maximum of 2.72 cm^3 K mol^{-1} at 4.0 K, that is approximately similar to the expected value for the four ferromagnetically coupled copper with (spin number (S) = 2 and $\chi_M T$ = 3 cm^3 K mol^{-1}). This behavior can be assigned to the governing ferromagnetic interactions in the compound that is revealed by the high value of saturation magnetization (M) as a function of the magnetic field strength (H) that is measured at 2 K as presented in Fig. 4. This value of magnetization is approximately equal to the expected value for four copper, i.e. 4 μB.

The magnetic behavior of the system has been modeled considering two coupling constants as shown in Fig. 5. The results of model are in agreement with the presence of two types of long and short metal–metal distances revealed in the structure. In the model, spin Hamiltonian is given by:

$$\hat{H} = -2J(\hat{S}_1\hat{S}_4 + \hat{S}_4\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_3\hat{S}_1) - 2J'(\hat{S}_1\hat{S}_2 + \hat{S}_3\hat{S}_4) \quad (1)$$

where J and J' are the exchange coupling constants, and $\hat{S}$ the operator of the spin moment.

Therefore, the expression for magnetic susceptibility can be driven from this Hamiltonian as:

$$\chi_M T = \frac{Ng^2\beta^2}{K} \cdot \frac{4\exp(2y) + 10\exp(4y+2x) + 2\exp(4y-2x)}{1 + 6\exp(2y) + 5\exp(4y+2x) + 3\exp(4y-2x) + \exp(4y-4x)} \quad (2)$$

with $x = J/(KT)$, $y = J'/(KT)$, g is the gyromagnetic factor, N is the Avogadro's number, β is Bohr's magneton, and K is the Boltzmann constant.

Table 2
Selected bond lengths (Å) and angles (°) for the complex.

Bond lengths (Å)			
Cu1–O1	1.884(4)	Cu3–O6	1.920(3)
Cu1–O2	1.935(3)	Cu3–O7	1.891(4)
Cu1–O9	1.942(4)	Cu3–O8	1.960(3)
Cu1–N1	1.915(5)	Cu3–N3	1.910(4)
Cu2–O4	1.883(3)	Cu4–O3	1.925(3)
Cu2–O5	1.971(3)	Cu4–O10	1.888(4)
Cu2–O12	1.954(3)	Cu4–O11	1.970(3)
Cu2–N2	1.909(4)	Cu4–N4	1.894(4)
Angles (°)			
O1–Cu1–O2	170.42(15)	O6–Cu3–O7	89.31(15)
O1–Cu1–O9	88.58(18)	O6–Cu3–O8	92.91(14)
O1–Cu1–N1	95.60(19)	O6–Cu3–N3	169.48(14)
O2–Cu1–O9	92.43(14)	O7–Cu3–O8	172.77(14)
O2–Cu1–N1	84.92(15)	O7–Cu3–N3	94.64(16)
O9–Cu1–N1	170.21(18)	O8–Cu3–N3	84.37(15)
O4–Cu2–O5	173.70(15)	O3–Cu4–O10	92.42(17)
O4–Cu2–O12	88.86(15)	O3–Cu4–O11	89.61(13)
O4–Cu2–N2	94.88(16)	O3–Cu4–N4	164.94(14)
O5–Cu2–O12	93.61(12)	O10–Cu4–O11	175.11(18)
O5–Cu2–N2	84.05(13)	O10–Cu4–N4	94.62(18)
O12–Cu2–N2	166.38(15)	O11–Cu4–N4	84.46(16)

Table 3
Hydrogen bonding interactions in the crystal packing of the complex: length of D-H, H...A, and D...A (Å), and angle D-H...A (°).

D–H...A	D–H	H...A	D...A	*D–H...A*
C4–H4C...O3	0.9600	2.3500	2.984(7)	*123.00*
C14–H14C...O6	0.9600	2.5100	3.097(6)	*119.00*
C24–H24C...O9	0.9600	2.5600	3.129(6)	*118.00*
C34–H34B...O12	*0.9600*	*2.5800*	*3.175(6)*	*121.00*

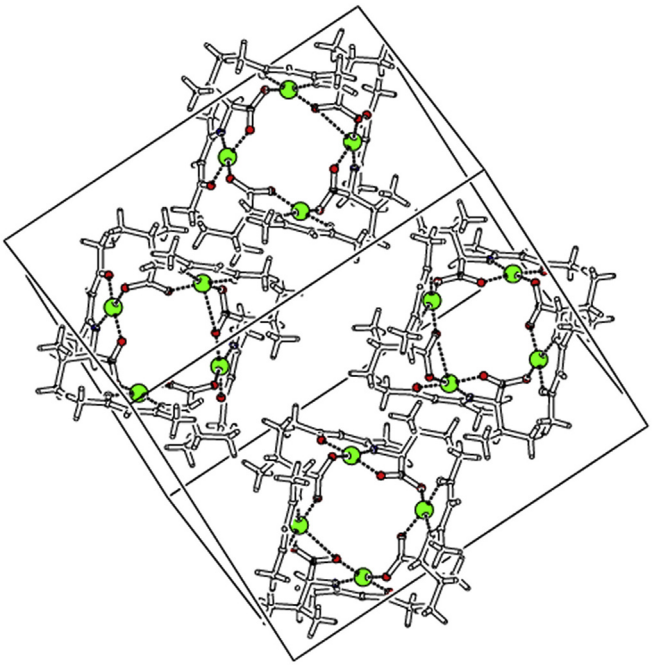


Fig. 2. Molecular packing of the crystal structure of the complex **1**.

In this model, we have joined an intermolecular parameter in the approximation of the molecular field *ZJ*, leading to the following Van-Vleck equation:

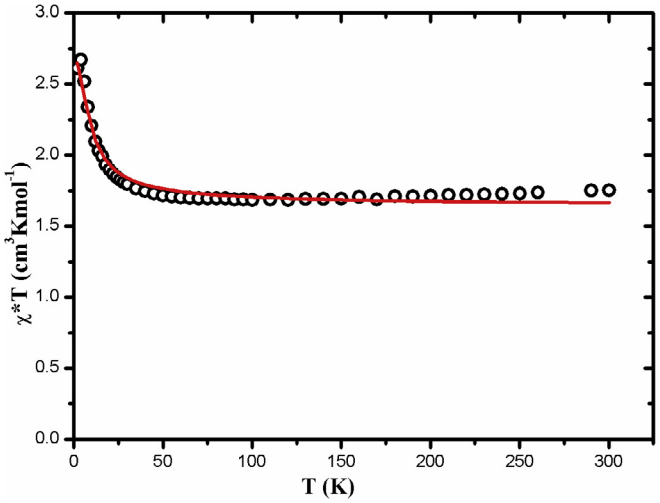


Fig. 3. Plot of $\chi_M T$ vs. *T* for a powdered sample of complex **1**. The solid line represents the best theoretical fit.

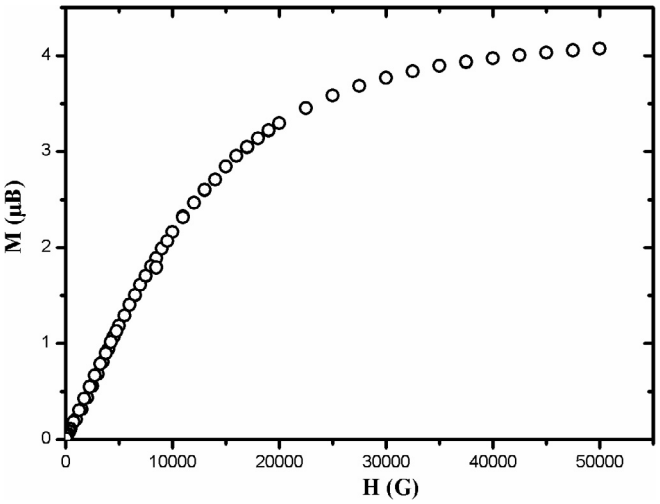


Fig. 4. Field dependence of magnetization at 2.0 K of complex **1**.

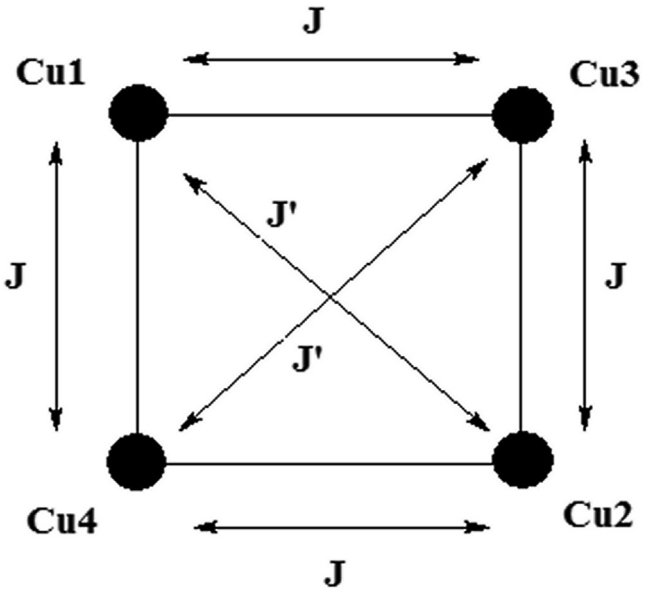


Fig. 5. Possible magnetic interactions between Cu atoms within the complex.

$$\chi' \frac{\chi}{1-(2ZJ/Ng^2\mu^2B)\chi} \quad (3)$$

The model produces the following parameters: $J = 3.04\ cm^{-1}$, $J' = 0\ cm^{-1}$, $g = 2.09$, and $ZJ = -0.109\ cm^{-1}$. The experimental and calculated results are shown in Fig. 3. The value of g a typical value for Cu(II) complexes [37]. The exchange coupling parameter between Cu···Cu located at the two aplatic edges at $J' = 0\ cm^{-1}$ are due to the long exchange path [37,56]. Taking into account that the geometry of copper is a square-plane stabilized by the effect of dipole–dipole interaction between spins ($ZJ = -0.109\ cm^{-1}$), the spin is thus in the orbital (dx^2-dy^2) and the angle between the two planes containing the two adjacent copper are between (80.59° and 86.69°). The interactions tend towards orthogonality, therefore they are ferromagnetic with $J = 3.04\ cm^{-1}$ and weak because of the long exchange path between the metallic centers.

4. Conclusion

In this work the synthesize of a new tetranuclear copper(II) complex with new NO_2 donor Schiff base ligand was performed. The ligand has been studied using elemental analysis as well as various spectroscopic techniques, while the complex has been investigated using a X-ray diffraction of single crystal. The magnetic characteristics including magnetic susceptibility and magnetization were studied systematically. The complex reveals ferromagnetic interactions among the copper atoms.

Appendix A. Supplementary data

CCDC 1511785 contains the supplementary crystallographic data for complex-1. These data can be obtained free of charge via http://dx.doi.org/10.1016/j.poly.2017.05.043, 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.2017.05.043.

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