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Methylene spacer regulated variation in structures and magnetic properties in copper(II) compounds with O, N, O donor Schiff bases

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ABSTRACT

Tetranuclear $[Cu_4(L^1)_2(HL^1)_2(H_2O)](ClO_4)_2 \cdot 2H_2O$ (**1**) and binuclear $[Cu_2(L^2)_2] \cdot CH_3OH$ (**2**) compounds are prepared and the molecular structures elucidated on the basis of X-ray crystallography [H_2L^1 = 2-[(2-hydroxy-ethylimino)-methyl]-6-methoxy-phenol, H_2L^2 = 2-[(3-hydroxy-propylimino)-methyl]-6-methoxy-phenol]. Compound **1** is made up of the cation $[Cu_4(L^1)_2(HL^1)_2(H_2O)_2]^{2+}$ and two ClO_4^- anions which are H-bonded to the cation. The four Cu(II) atoms are not crystallographically equivalent, among then two are in tetragonal $[CuNO_5]$ geometries and the rest two are in square pyramidal geometries. The asymmetric unit of compound **2** consists of one neutral $[Cu_2(L^2)_2]$ moiety and a methanol molecule. Each copper atom in compound **2** has a four-coordinate square-planar environment. Compound **1** can be described as an open cage with a $[Cu_4(\mu_3\text{-}O_{al})_2(\mu_2\text{-}O_{ph})_2]^{4+}$ core (al = alkoxido and ph = phenoxido). Variable temperature solid state magnetic studies between 2–300 K were carried out and the data indicate predominant antiferromagnetic exchange interactions and a spin ground state $S = 0$. The data were fitted with an average J value model, using the spin Hamiltonian $H = -J_{av}(S_1 \cdot S_2 + S_3 \cdot S_4 + S_1 \cdot S_3 + S_2 \cdot S_4)$. The best fit was obtained with $J_{av} = -99.0\ cm^{-1}$. The magnetic properties of compound **2** have also been analyzed and the data show a large antiferromagnetic interaction, in agreement with the $[Cu_2(\mu_2\text{-}O_{al})_2]^{2+}$ core. The best fit of the data was obtained with $J = -891\ cm^{-1}$ ($H = -J\ S_1 \cdot S_2$).

1. Introduction

The chemistry of multinuclear metal compounds is getting higher importance in current years because of their relevance to the multi-metal active sites of various metallo-proteins and metallo-enzymes [1,2]. Among them, the synthesis and characterization of polynuclear Cu(II) compounds have attracted amazing interest over the past decades due to the relevance in exploring their structures and the function of copper centers in several catalytic systems and in understanding the magneto-structural correlations arising from the exchange coupling among Cu(II) centers with the plan of developing new molecular based magnets [3,4]. In this connection, our interest lies in the design, isolation, and characterization of polynuclear Cu(II) compounds using Schiff base ligands. Synthesis and characterization of tetranuclear Cu(II) clusters are very well known in magneto-structural research, bioinorganic modeling, catalysis and multi-electron transfer [5–12]. There are many examples of Cu_4 arrays, which exhibit a large diversity of structural types: cyclic [5], pin-wheel [6], square planar [7], dimeric [8], face-to-face [9], roof-shaped [10], cubane type [11] and so on. Depending upon the flexibility of bridging ligands and the geometries around the copper centers, those compounds can show ferromagnetic as well as antiferromagnetic exchange interactions.

1:1 Condensation of salicylaldehyde and ethanolamine produces a O, N, O donor tridentate ligand (H_2L), which can be made to react with Cu(II) to form tetranuclear copper(II) cluster $[Cu_4L_4]$ where the ligand, H_2L, is in di-negative state [13]. Our attempt with 3-methoxysalicyldehyde and aminoethanol, however, produces tetranuclear analogue of $[Cu_4L_4]$ using the ligand H_2L^1, we have used triethylamine to deprotonate the ligand and isolate a unique tetranuclear Cu(II) compound $[Cu_4(L^1)_2(HL^1)_2(H_2O)_2](ClO_4)_2$. The compound is unprecedented in the sense that the tetranuclear cluster contains simultaneously mono- and di-negative state of the same ligand. The compound is also important because of its structure, which can best be described as an open cage cubane like structure. Interestingly, most of the related tetranuclear Cu(II) clusters assume cubane structures [4,13–19] and, best to our

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knowledge, there are only two reports in the literature regarding the ‘open cage cubane’ geometries of Cu(II) compounds with Schiff base ligands, till date [20,21]. The use of aminopropanol instead of aminoethanol produces a dinuclear compound $[Cu_2(L^2)_2]·CH_3OH$, where H_2L^2 = 2-[(3-hydroxy-propylimino)-methyl]-6-methoxy-phenol]. Thus, with the incorporation of a CH_2 spacer in the ligand moiety, the geometries of the compounds change dramatically as also their magnetic properties. Herein, we report the syntheses, characterizations and magnetic properties of both the compounds.

2. Experimental

All starting materials were commercially available, reagent grade, and used as purchased without further purification.

2.1. Synthesis

Caution! Since the perchlorate compounds of metal ions are potentially explosive, only small amounts of the materials should be handled with care.

2.1.1. Synthesis of ligands

H_2L^1 {2-[(2-hydroxy-ethylimino)-methyl]-6-methoxy-phenol} andH_2L^2{2-[(3-hydroxy-propylimino)-methyl]-6-methoxy-phenol}.

The tridentate ligand, H_2L^1 and H_2L^2 are prepared by the 1:1 condensation of the 3-methoxysalicyldehyde with 2-aminoethanol and 3-aminopropanol in methanol. All the ligands are directly used for the preparation of the compound.

*2.1.2. Synthesis of $[Cu_4(L^1)_2(HL^1)_2(H_2O)](ClO_4)_2·2H_2O$ (**1**)*

Methanol solution (10 ml) of $Cu(ClO_4)_2·6H_2O$ (370.6 mg, 1 mmol) was added to H_2L^1 (1 mmol) in methanol. Then NEt_3 (0.16 ml, 1 mmol) was added to the mixture with continuous stirring and filtered after 30 min. The filtrate was left at room temperature. Deep green diffraction quality single crystals were obtained by slow evaporation of the filtrate in open atmosphere.

Yield: 0.86 g (68 %). *Anal.* Calc. for $C_{40}H_{54}Cl_2Cu_4N_4O_{24}$ (1299.97): C, 36.96; H, 4.19; N, 4.31; Found: C, 36.8; H, 4.3; N, 4.2%. UV–Vis, λ_{max} (nm), (ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)) (acetonitrile), 607 (126), 370 (2910).

*2.1.3. Synthesis of $[Cu_2 (L^2)_2]·CH_3OH$ (**2**)*

Methanol solution (15 ml) of $Cu(ClO_4)_2·6H_2O$ (370.6 mg, 1 mmol) was added to the methanol solution of H_2L^2 (1 mmol). The resulting mixture was stirred for 2 h at room temperature followed by adding excess NEt_3 (0.5 ml, 3 mmol). Deep green crystalline compound was separated by filtration. Then the crystalline compound was dissolved in dichloromethane. X-ray diffraction quality single crystals were obtained from dichloromethane solution in cold condition.

Yield: 0.38 g (66 %). *Anal.* Calc. for $C_{23}H_{30}Cu_2N_2O_7$ (573.59): C, 46.78; H, 4.32; N, 5.46; Found: C, 47.18; H, 4.22; N, 5.52%. UV–Vis, λ_{max} (nm), (ε_{max} ($dm^3\ mol^{-1}\ cm^{-1}$)) (acetonitrile), 558 (145).

2.2. Physical measurements

Elemental analysis (carbon, hydrogen and nitrogen) was performed using a Perkin-Elmer 240C elemental analyzer. IR spectra in KBr (4500–500 cm^{-1}) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra in acetonitrile (1200–350 nm) were recorded in a Hitachi U-3501 spectrophotometer. Magnetic susceptibility measurements between 2–300 K were carried out in a SQUID magnetometer Quantum Design Magnetometer; model MPMP at the “Unitat de Mesures Magnètiques (Universitat de Barcelona)”. Two different magnetic fields were used, 300 G (2–30 K) and 3000 G (2–300 K), with superimposable graphs. Pascal’s constants were used to estimate the diamagnetic corrections for the compounds. The fit was performed by minimizing the function $R = \Sigma[(\chi_M T)_{exp} - (\chi_M T)_{calc}]^2/\Sigma[(\chi_M T)_{exp}]^2$.

Table 1
Crystal data of compounds **1** and **2.**

	1	2
Formula	$C_{40}H_{50}Cl_2Cu_4N_4O_{22}$	$C_{23}H_{30}Cu_2N_2O_7$
Formula weight	1263.94	573.59
Crystal size (mm)	0.15 × 0.16 × 0.18	0.2 × 0.2 × 0.2
T (K)	150	293(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	C_2/c
a (Å)	11.2181(24)	23.6254(13)
b (Å)	20.1729(44)	8.4728(4)
c (Å)	22.9427(49)	25.6412(13)
α (°)	90	90
β (°)	102.301(4)	113.161(4)
γ (°)	90	90
Z	4	8
D_{calc} ($g\ cm^{-3}$)	1.655	1.615
μ (mm^{-1})	1.847	1.850
$F(000)$	2576	2368
Total reflections	36535	39817
Unique reflections	12555	8753
Observed data [$I > 2\sigma(I)$]	6475	4160
Number of parameters	677	312
R_{int}	0.0649	0.0642
R_1, wR_2 (all data)	0.1317, 0.1659	0.1208, 0.1263
R_1, wR_2 [$I > 2\sigma(I)$]	0.0653, 0.1429	0.0464, 0.1066

2.3. X-ray crystallography

Single crystals of **1** and **2** having suitable dimensions were used for data collection by means of a ‘Bruker SMART APEX II’ diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The structure was solved by direct methods and refined by full-matrix least squares on F^2, using the SHELX-97 package [22]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms of the water molecule of crystallization were located by difference Fourier maps and were kept at fixed positions. Other hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on the atoms to which they are attached. Empirical absorption corrections were carried out with the ABSPACK program [23]. The crystallographic and refinement data are summarized in Table 1.

For compound **1**, the unit cell contains some highly disordered solvent molecules, which could not be modeled as discrete atomic sites. We employ PLATON/SQUEEZE to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities. Detail about the SQUEEZE procedure is given in the CIF file.

3. Results and discussions

3.1. Synthesis

Facile condensation of 2-aminoethanol or 3-aminopropanol in 1:1 M ratio with 3-methoxysalicyldehyde separately, afforded two neutral condensates, H_2L^1 and H_2L^2, which have been employed as the tri-dentate chelating ligands in the present work (Scheme 1) [24,25].

Methanol solution of $Cu(ClO_4)_2·6H_2O$ was added separately in a methanol solution of H_2L^1 and H_2L^2 in 1:1 M ratio with constant stirring at ambient temperature. Then few drops of TEA (triethylamine) were added. The solutions were kept for 2 days to separate crystalline compounds. Subsequent re-crystallization of the