Inorganic Chemistry Communications 24 (2012) 216–220

Contents lists available at SciVerse ScienceDirect

Inorganic Chemistry Communications

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

# Hydroxo-bridged 1-D coordination polymer of Cu(II) incorporating with salicyladimine precursor: Spectral and temperature dependent magneto structural correlation

Amitabha Datta [a,*], Jack K. Clegg [b], Jui-Hsien Huang [a,*], Andrej Pevec [c], Eugenio Garribba [d], Matilde Fondo [e]

[a] *Department of Chemistry, National Changhua University of Education, Changhua 50058, Taiwan*
[b] *School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane St Lucia, QLD 4072, Australia*
[c] *Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, SI-1000 Ljubljana, Slovenia*
[d] *Dipartimento di Chimica e Farmacia, Centro Interdisciplinare per lo Sviluppo della Ricerca Biotecnologica e per lo Studio della Biodiversita della Sardegna, Universitá di Sassari, Via Vienna 2, I-07100 Sassari, Italy*
[e] *Departamento de Quimica Inorganica, Facultad de Química, Universidad de Santiago de Compostela, Campus Vida s/n, E-15782 Santiago de Compostela, Spain*

## ARTICLE INFO

*Article history:*
Received 26 May 2012
Accepted 3 July 2012
Available online 13 July 2012

*Keywords:*
Copper(II)
Salicyladimine
Hydroxo bridge
Spectroscopic study

## ABSTRACT

A hydroxo-bridged 1-D coordination polymer, $[Cu(L)(H_2O)]n$ (**1**), has been synthesized in good yield by employing a tetradentate Schiff base ligand, (6,6′-(1*E*,1′*E*)-(2-hydroxypropane-1,3-diyl)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(2-methoxyphenol)), generated by condensation of *o*-vanillin with 1,3-diaminopropane-2-ol. Compound **1** has been fully characterized by elemental analyses, fourier transform IR, UV/vis and EPR measurements. Single crystal X-ray structure reveals that the central $Cu^{II}$ atom adopts a distorted octahedral geometry, to form 1-D network manifesting by the bridging participation of hydroxo group from neighboring Schiff base unit. The magnetic behavior of **1** shows that the $^{\chi}{}_{M}T$ product at 300 K is 0.47 $cm^3$ $kmol^{-1}$.

The design of high or low nuclearity transition metal clusters with novel magnetic properties is a major goal of current research in the field of condensed matter physics and material chemistry [1]. 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. Especially, $Cu^{II}$ complexes are of particular interest from both structural and functional points of view. From the standpoint of magneto-chemistry dinuclear complexes of $Cu^{II}$ have been synthesized to establish magneto-structural correlations [2,3], and trinuclear complexes have got attention in order to study spin frustration and antisymmetric exchange phenomena [4], as well as for the rational synthesis of ferromagnetic entities [5,6]. Infinite lattices constitute a further well-studied class of $Cu^{II}$ complexes leading to the formation of 1-D, 2-D and 3-D architectures [7,8], while $Cu^{II}$ polynuclear complexes with aesthetically pleasing structures and interesting magnetic properties are a hot topic in current research [9,10]. The $d^9$ configuration of the $Cu^{II}$ ion has one unpaired electron ($S=1/2$), and the nearly quenched orbital angular momentum of the $Cu^{II}$ ion provides a *g* factor close to 2, suggesting the absence of any large internal magnetic fields. The coordination sphere around the $Cu^{II}$ ion can be modulated relatively easily, and the stereochemical diversity has led to the isolation of a number of mono- and multinuclear $Cu^{II}$ complexes. Schiff bases have extensively been used as building blocks together with various metals for producing a great variety of topologies [11,12]. Tetradentate Schiff bases with $N_2O_2$ donor sets have been preferred by authors as such ligands effectively act as a chelate and can block the coordination sites of metal ions leaving the metal ion coordinatively unsaturated [13–15]. Among these Schiff base mediated complexes, electron paramagnetic resonance spectroscopy can notably indicate large coupling through intensity variation and can also extract small coupling with the use of multifrequency experimentation [16].

We now describe the synthesis [17] and X-ray structural characterization of a new hydroxo-bridged polynuclear copper complex, $[Cu(L)(H_2O)]n$ $[L=[(C_6H_3)(OMe)(O)CH=NCH_2CHOHCH_2N=CH(C_6H_3(O)(OMe)]$ (**1**) where $Cu^{II}$ ions are incorporated within a tetradentate Schiff-base ligand [18]. The complex has been characterized by elemental analysis, IR and UV–vis spectra, EPR and variable temperature magnetic measurements. The structure of the complex was determined by X-ray diffraction using single crystal.

The reaction of copper(II) acetate with 6,6′-(1*E*,1′*E*)-(2-hydroxypropane-1,3-diyl)bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(2-methoxyphenol) in methanol affords the polynuclear coordination compound $[Cu(L)(H_2O)]n$ (**1**) [18]. Single-crystal X-ray

---

* Corresponding authors. Tel.: +886 7 5919465; fax: +886 7 5919348.
*E-mail addresses:* amitd_ju@yahoo.co.in (A. Datta), juihuang@cc.ncue.edu.tw (J.-H. Huang).

1387-7003/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2012.07.017

studies revealed that **1** crystallizes in the monoclinic space group *Pnma* [19]. A view of the molecular structure of **1** is depicted in Fig. 1. The structure possesses a crystallographic mirror plane that passes through the atoms O3, C10, Cu1 and O4. The ligand is not planar and twisted into a boat-like conformation with the aromatic rings inclined to each other with the angle of 33.81(7)°. The copper(II) ion has a distorted octahedral coordination geometry. The equatorial plane is occupied by the $N_2O_2$ donor set of the deprotonated tetradentate Schiff base ligand, with the axial positions occupied by a water molecule (O4) and a hydroxyl group from an adjacent complex (O3). This results in the formation of a one-dimensional (1-D) coordination polymer that propagates parallel to the crystallographic *a*-axis (Fig. 2). The presence of Jahn–Teller distortion is evident in the axial bond lengths with the copper – water and copper – alcohol bond lengths (2.720(3) Å and 2.593(4) Å, respectively) significantly elongated compared to bond lengths in the equatorial plane ($Cu_1-O_2=1.954(2)$ Å and $Cu_1-N_1=2.009(3)$ Å). Each of the one dimensional coordination polymer chains interact with adjacent chains through hydrogen bonding (Table S1, Fig. 3) forming infinite 2-D layers (Fig. 4) perpendicular to the *b*-axis. The coordinated water molecules act as a hydrogen bond donor, producing two pairs of bifurcated hydrogen bonds to the methoxy oxygen and coordinated oxygen atoms (Table S1, Fig. 3). The coordinated water molecule also acts as a hydrogen bond acceptor, with the coordinated alcohol group acting as a donor (Table S1, Fig. 3).

A strong sharp absorption band around 1627 $cm^{-1}$ in the spectrum of the Schiff base ligand may be assigned for the imine stretching frequency. This band is shifted to the lower wave numbers upon complexation with the metal as 1567 $cm^{-1}$, which can be attributed to the coordination of the nitrogen atom of the imine group to the metal ions [20]. The phenolic $\nu_{Ar-O}$ in the free ligand exhibits a strong band at 1207 $cm^{-1}$. However, in the complex, this band also shifts to the lower frequency region at 1183 $cm^{-1}$, providing evidence for coordination to the metal ions through the deprotonated phenolic oxygen atoms [21]. Sharp bands appearing at nearly 422 and 378 $cm^{-1}$ correspond to the Cu–N and Cu–O stretching frequencies, respectively, in the complex.

In the complex, the bands in the 460–345 nm range may be assigned for the $n\rightarrow\pi^*$ transition of the imine group [22] and the bands at higher energies (310–220 nm) are associated with the aromatic $\pi\rightarrow\pi^*$ intraligand charge-transfer transitions. A broad band in the range 620–650 nm can be correlated to the *d–d* transition, which is typical for a copper(II) Schiff base complex.

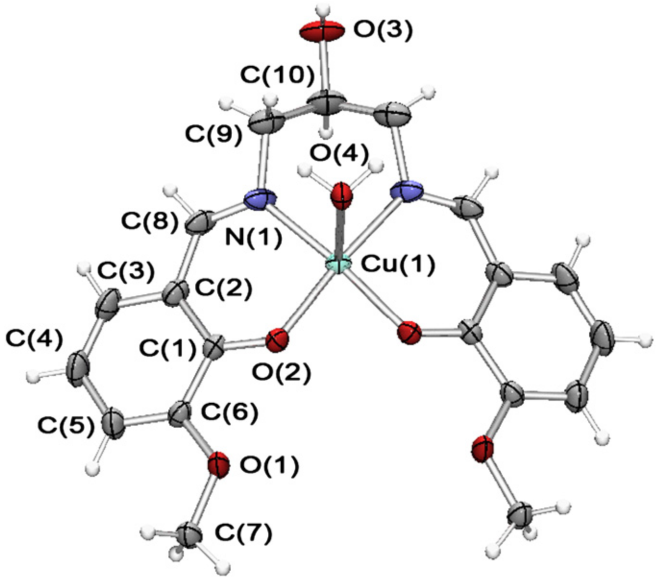

**Fig. 1.** ORTEP representation of **1** shown with 50% probability ellipsoids. Symmetry codes: (i) x, −y+1.5, z; (ii) x+0.5, −y+1.5, −z+1.5; (iii) x−0.5, −y+1.5, −z+1.5. Selected bond lengths [Å] and angles [°]: $Cu_1–N_1$ 2.011(3), $Cu_1–O_2$ 1.9514(19), $Cu_1–O_4$ 2.720(3), $Cu_1–O_3^{ii}$ 2.593(4); $N_1–Cu_1–O_2$ 90.84(10), $N_1–Cu_1–O_4$ 85.54(9), $N_1–Cu_1–N_1^{i}$ 94.05(16), $N_1–Cu_1–O_2^{i}$ 175.07(9), $N_1–Cu_1–O_3^{ii}$ 90.63(8).

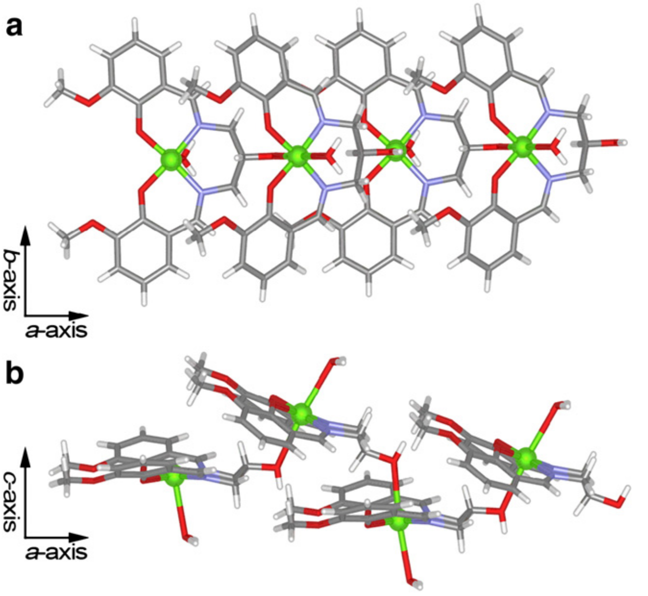

**Fig. 2.** Two views of the one-dimensional polymeric chain in **1**. a) Viewed down the crystallographic *c*-axis. b) Viewed down the *b*-axis.

Variable-temperature (2–300 K) magnetic susceptibility data were collected on polycrystalline samples for **1**. The magnetic behavior is represented in Fig. 5 in the form of $\chi_M T$ *vs. T* and the $\chi_M T$ product at 300 K is 0.47 $cm^3$ $kmol^{-1}$. This product slightly decreases until *ca.* 14 K. Below this temperature, a more pronounced decrease of the $\chi_M T$ value is observed. The corresponding $\chi_M$ *vs. T* plots show that $\chi_M$ increases on cooling and it does not exhibit any maximum in the temperature range studied. These features are typical of very weak antiferromagnetic coupling. The $M/N\mu_\beta$ *versus H* graphs (Fig. 6) also agrees with a very week or null magnetic coupling, as the $M/N\mu_\beta$ value at 50,000 G tends to 1, and is in agreement with an $S=1/2$ ground state. These results are consistent with the crystal structure where Cu1···Cu1 distances of 6.4829(7) Å were observed.

Consequently, the magnetic data have been analyzed through the theoretical expression (1) proposed for a uniform chain of local spins $S=1/2$ ions [23].

$$\chi_M=\left(Ng^2\mu_B{}^2/kT\right)\frac{0.25+0.14995x+0.30094x^2}{1.0+1.9862x+0.68854x^2+6.0626x^3} \quad (1)$$

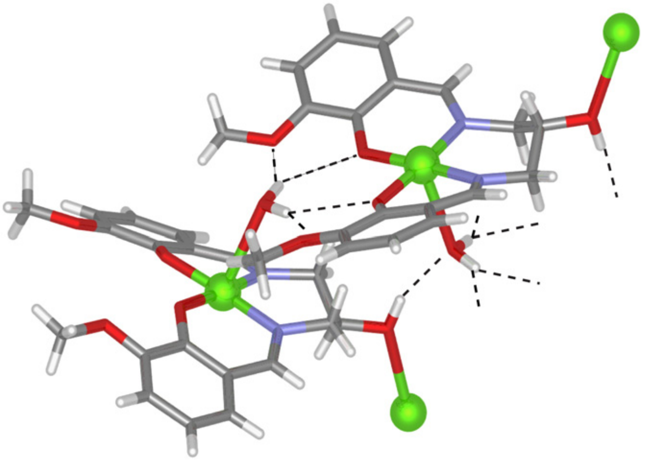

**Fig. 3.** View of two fragments of adjacent polymeric chains highlighting the hydrogen bonding interactions. Dashed lines indicate hydrogen bonds.