

Experimental and theoretical investigations on magneto-structural correlation in trinuclear copper(II) hydroxido propellers

Luca Rigamonti^{a,c,*}, Alessandra Forni^{b,c}, Maurizio Sironi^c, Alessandro Ponti^d, Anna M. Ferretti^d, Carlo Baschieri^a, Alessandro Pasini^c

^aUniversità degli Studi di Modena e Reggio Emilia, Dipartimento di Scienze Chimiche e Geologiche, via G. Campi 103, 41125 Modena, Italy

^bIstituto di Scienze e Tecnologie Molecolari – Consiglio Nazionale delle Ricerche (ISTM-CNR), via C. Golgi 19, 20133 Milano, Italy

^cUniversità degli Studi di Milano, Dipartimento di Chimica, via C. Golgi 19, 20133 Milano, Italy

^dLaboratorio di Nanotecnologie, Istituto di Scienze e Tecnologie Molecolari – Consiglio Nazionale delle Ricerche (ISTM-CNR), via G. Fantoli 16/15, 20138 Milano, Italy

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ABSTRACT

The trinuclear copper(II) compounds $[\text{Cu}_3(\mu_3\text{-OH})(^G\text{L}1)_3](\text{ClO}_4)_2$ (**1–4**) and $[\text{Cu}_3(\mu_3\text{-OH})(^G\text{L}2)_3](\text{ClO}_4)_2$ (**5–8**) with tridentate NNO Schiff base ligands $^G\text{L}1^-$ and $^G\text{L}2^-$ derived from 5-G-substituted salicylaldehydes (G = NO₂, Br, H, Me) and the diamines 1,2-ethanediamine and 1,3-propanediamine, respectively, were investigated aiming at shedding light on possible magneto-structural correlation in this class of complexes. All derivatives contain $[\text{Cu}_3(\mu_3\text{-OH})(\text{L})_3]^{2+}$ cations with partial cubane Cu_3O_4 cores, and the metal ions are linked together in a pyramidal fashion by a triple-bridging hydroxido group, giving rise to propellers with three $[\text{Cu}(\text{L})]^+$ blades. In these spin-frustrated magnetic systems, the three copper(II) ions within a cluster communicate anti-ferromagnetically ($-2J \hat{S}_i \hat{S}_j$ convention) through the bridging OH group with coupling constants J ranging from $-4.5(1)$ for **4** (G = Me) to $-10.1(1) \text{ cm}^{-1}$ for **1** (G = NO₂), and stabilization of the doublet $S = 1/2$ ground state. The structural features of the complexes reveal very minimal deviations upon variation of G or the diamine flexibility along the whole series of compounds, preserving almost constant magnetic cores. Similar conclusions are also drawn by DFT *gas-phase* geometry optimizations of the $[\text{Cu}_3(\mu_3\text{-OH})(\text{L})_3]^{2+}$ cations. Therefore, confident of excluding structural influences on the magnetic super-exchange path, the modulating factor of J in our derivatives can be sought after the different electronic demand of G. Atomic NBO charges support this point, revealing small but systematic variations in the electron density flow along the blades and the positive charge on copper (II) ions with the electronic nature of G, with the most remarkable effect given by the nitro group. Topological analysis of electron density according to the Quantum Theory of Atoms In Molecules further support the distinguishing role of this group with respect to the other substituents taken into consideration, besides providing indirect information about the super-exchange path.

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1. Introduction

The study of structural, electronic and magnetic features in oligonuclear complexes and small clusters is currently a topic of much significance in the development of magnetochemistry [1,2]. In fact, the possibility of predicting the magnetic behavior through magneto-structural correlation studies would allow the proper modulation of the reaction conditions to get new compounds with desired properties [2–5]. With this aim, chemists and physicists

* Corresponding author at: Università degli Studi di Modena e Reggio Emilia, Dipartimento di Scienze Chimiche e Geologiche, via G. Campi 103, 41125 Modena, Italy.

E-mail addresses: luca.rigamonti@unimore.it, luca.rigamonti@yahoo.com (L. Rigamonti).

have extensively worked in recent years on the development of effective experimental approaches [3,4] and theoretical descriptions [5].

Trinuclear copper(II) complexes comprise three interacting half-integer spin ions. These systems have been topic of active research in coordination chemistry due to the changing of the magnetic interactions between the three metal centers modulated by different bridges, such as oxido [6], azido [7], halogenido [8,9] ions or other molecules [10–15], and by different structures ranging from perfectly linear to triangular [6–15], leading to varied and fascinating magnetic features. The exchange coupling constants can span strong to weak, and ferro- to antiferro-magnetic values, depending on the bridge and symmetry, and hence overlap of magnetic orbitals [1,2,8,10,15–17]. Furthermore, theoretical studies

have revealed potential applications in quantum computing devices of molecular antiferromagnetic triangles with $S = 1/2$ spins [18].

Another common bridging group is the hydroxido ion, and trinuclear $\text{Cu}_3(\mu_3\text{-OH})$ compounds with a partial cubane core have been studied [19–23] not only for their magnetic properties [24,25], but also as catalysts [26] and mimic systems of the active site of some copper enzymes [27,28]. In these derivatives, the three copper ions are bridged by a tetrahedral hydroxido group and arranged in a triangular fashion, with the magnetic interactions mainly occurring through super-exchange pathway involving the OH, giving rise to systems showing the 'spin frustration' phenomenon [1,2]. The Cu–Cu coupling constant can be either ferro- or antiferro-magnetic, with stabilization of $S = 3/2$ or $1/2$ spin ground state, respectively [1,3,4,16,17,29]. Among all the possible peripheral ligands that complete the coordination sphere of each copper ion, a class is given by tridentate Schiff bases, derived from the condensation of different carbonyl derivatives with aminoalcohols [30], aminoacids [31], and especially diamines [22,23,29,32–46], whose molecular structures resemble propellers.

A few years ago, we reported the template synthesis and characterization of trinuclear copper(II) complexes $[\text{Cu}_3(\text{L})_3(\mu_3\text{-OH})](\text{ClO}_4)_2$ where L^- are tridentate NNO Schiff base ligands derived from the monocondensation of 5-substituted salicylaldehydes (5-G-salH, G = H, NO_2) with the aliphatic diamines 1,2-ethanediamine (en) and 1,3-propanediamine (tn) [29]. Fascinated by their structural and magnetic features, in this paper our focus is devoted to enrich the series of trinuclear copper(II) propellers $[\text{Cu}_3(\text{}^{\text{C}}\text{L})_3(\mu_3\text{-OH})](\text{ClO}_4)_2$ (**1–4**) and $[\text{Cu}_3(\text{}^{\text{C}}\text{L}_2)_3(\mu_3\text{-OH})](\text{ClO}_4)_2$ (**5–8**), G = NO_2 , Br, H, Me, where $\text{}^{\text{C}}\text{L}^-$ is with en and $\text{}^{\text{C}}\text{L}_2^-$ is with tn (Scheme 1), by synthesizing the compounds bearing the mild electron acceptor Br and the weak electron donor Me, in addition to the ones already published with NO_2 and H [29].

In particular, here we are interested in seeking a correlation, if any, between the electronic and structural features of these systems, as modulated by the substituents G on the sal moieties and the length of the diamine, and their magnetic properties. In fact, the subtle but systematic modulating effect exerted by different electron-acceptor and -donor groups on the nonlinear optical properties of push–pull copper complexes with 5-substituted salH were investigated by us some years ago [47], and studies of the elec-

tronic tuning power of substituents on the magnetic and catalytic abilities of other metal complexes have been also recently documented [48]. Furthermore, only very few examples of trinuclear $\text{Cu}_3(\mu_3\text{-OH})$ compounds derived from salH with complete structural and magnetic characterizations have been reported thus far [29,39,41,42], while more is known on trinuclear complexes with acetylacetonone and other ketones [22,23,29], for which magneto-structural models have been already proposed [22,36].

The crystal structures of the derivatives **2**, **4**, **5**, **6** and **7** were determined, together with the characterization of their magnetic behavior, and those properties will be presented together with the ones of **1** and **3**, previously published by us [29], in order to have a complete overview of the series. Furthermore, theoretical calculations were performed on $[\text{Cu}_3(\mu_3\text{-OH})(\text{L})_3]^{2+}$ isolated cations of **1–7** in order to fully characterize these systems and better clarify, in the absence of crystal packing effects, their inherent electronic and structural features which can affect the magnetic properties.

2. Experimental

2.1. General procedures

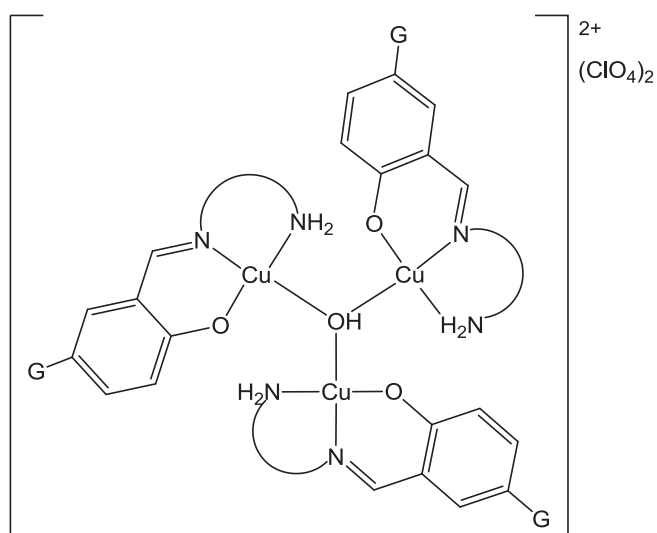
All used chemicals were reagent grade. Solvents were used as received. Elemental analyses were performed at the Microanalytical Laboratory at the Università degli Studi di Milano. ESI-MS spectra were recorded on methanol (MeOH) or acetonitrile (CH_3CN) solution with a LCQ Advantage Thermofluxional Instrument. Infrared spectra were recorded as KBr disks using a JASCO FT-IR 410 spectrophotometer with a 2 cm^{-1} resolution. Synthesis of **1**, **3**, **5** and **7**, and crystal structures of **1**· $3\text{H}_2\text{O}$ and **3**· $3.5\text{H}_2\text{O}$ were previously reported [29]. *Caution: perchlorate salts of metal complexes with organic ligands are potentially explosive, only small amounts of the material should be handled with care.*

2.2. Synthesis of $[\text{Cu}_3(\text{}^{\text{Br}}\text{L})_3(\mu_3\text{-OH})](\text{ClO}_4)_2$ (**2**)

NaOH (1.80 mL of a 0.850 mol L^{-1} aqueous solution, 1.53 mmol) was added to a solution of 5-Br-salH (0.223 g, 1.11 mmol) in MeOH (120 mL). The yellow solution was heated to reflux, then a solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.408 g, 1.10 mmol) and en (74.0 μL , 1.11 mmol) in MeOH (4 mL) and H_2O (4 mL) was added under vigorous stirring and the mixture left under reflux for 3 h. The green solution was concentrated to 20 mL, yielding the title compound as green solid, washed with MeOH, diisopropyl ether ($i\text{Pr}_2\text{O}$) and dried in vacuo; from the filtrate, after one night, further deep green crystalline solid suitable for X-ray diffraction formed, that was collected and dried in vacuo (overall yield: 0.280 g, 67.4%). Elemental analysis calcd (%) for $\text{C}_{27}\text{H}_{31}\text{Br}_3\text{Cl}_2\text{Cu}_3\text{N}_6\text{O}_{12}$ (1132.83): C, 28.63; H, 2.76; N, 7.42. Found: C, 28.65; H, 2.79; N, 7.30%. IR (KBr), ν (cm^{-1}): 3338, 3281 (NH_2), 1639 (C=N), 1090 (ClO_4). ESI-MS (CH_3CN): m/z 304 ($[\text{Cu}(\text{}^{\text{Br}}\text{L})]^+$, 85%), 345 ($[\text{Cu}(\text{}^{\text{Br}}\text{L})_2(\text{CH}_3\text{CN})]^+$, 100).

2.3. Synthesis of $[\text{Cu}_3(\text{}^{\text{Me}}\text{L})_3(\mu_3\text{-OH})](\text{ClO}_4)_2$ (**4**)

NaOH (0.0972 g, 2.43 mmol) was added to a solution of 5-Me-salH (0.246 g, 1.80 mmol) in MeOH (200 mL). The yellow solution was heated to reflux and a solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.665 g, 1.80 mmol) and en (120 μL , 1.80 mmol) in MeOH (4 mL) and H_2O (4 mL) was added under vigorous stirring and the mixture left under reflux for 3 h. The green solution was concentrated to 10 mL, yielding the title compound as dark green solid, washed with MeOH, $i\text{Pr}_2\text{O}$ and dried in vacuo (0.381 g, 64.2%). Elemental analysis calcd (%) for $\text{C}_{30}\text{H}_{40}\text{Cu}_3\text{Cl}_2\text{N}_6\text{O}_{12}$ (938.22): C, 38.40; H, 4.30; N, 8.96. Found: C, 38.69; H, 4.17; N, 8.56%. IR (KBr), ν (cm^{-1}): 3336,



Scheme 1. Molecular scheme of the trinuclear copper(II) complexes $[\text{Cu}_3(\text{L})_3(\mu_3\text{-OH})](\text{ClO}_4)_2$ object of the present work, in which the arch stands for $(\text{CH}_2)_2$ (en, compounds **1–4**) or $(\text{CH}_2)_3$ (tn, compounds **5–8**) bridge, and G = NO_2 , Br, H and Me, respectively, in the two series.

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