



1D Copper(II)-Aroylhydrazone Coordination Polymers: Magnetic Properties and Microwave Assisted Oxidation of a Secondary Alcohol

Manas Sutradhar^{1*}, Elisabete C. B. A. Alegria^{1,2}, Tannistha Roy Barman¹,
M. Fátima C. Guedes da Silva¹, Cai-Ming Liu³ and Armando J. L. Pombeiro^{1*}

¹ Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Lisbon, Portugal, ² Área Departamental de Engenharia Química, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, Lisbon, Portugal, ³ National Laboratory for Molecular Sciences, Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China

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*Correspondence:

Manas Sutradhar
manas@tecnico.ulisboa.pt
Armando J. L. Pombeiro
pombeiro@tecnico.ulisboa.pt

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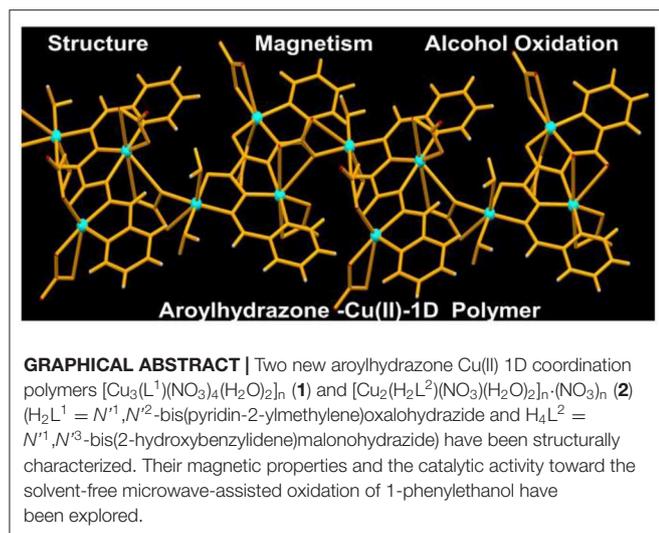
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The 1D Cu(II) coordination polymers $[\text{Cu}_3(\text{L}^1)(\text{NO}_3)_4(\text{H}_2\text{O})_2]_n$ (**1**) and $[\text{Cu}_2(\text{H}_2\text{L}^2)(\text{NO}_3)(\text{H}_2\text{O})_2]_n(\text{NO}_3)_n$ (**2**) have been synthesized using the aroylhydrazone Schiff bases N^1, N^2 -bis(pyridin-2-ylmethylene)oxalohydrazide (H_2L^1) and N^1, N^3 -bis(2-hydroxybenzylidene)malonohydrazide (H_4L^2), respectively. They have been characterized by elemental analysis, infrared (IR) spectroscopy, UV-Vis spectroscopy, electrospray ionization mass spectrometry (ESI-MS), single crystal X-ray diffraction and variable temperature magnetic susceptibility measurements (for **2**). The ligand (L^1)²⁻ coordinates in the *iminol* form in **1**, whereas the *amide* coordination is observed for (H_2L^2)²⁻ in **2**. Either the ligand bridge or the nitrate bridge in **2** mediates weak antiferromagnetic coupling. The catalytic performance of **1** and **2** has been investigated toward the solvent-free microwave-assisted oxidation of a secondary alcohol (1-phenylethanol used as model substrate). At 120°C and in the presence of the nitroxyl radical 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO), the complete conversion of 1-phenylethanol into acetophenone occurs with TOFs up to 1,200 h⁻¹.

Keywords: Cu(II) complexes, coordination polymer, X-ray structure, magnetism, microwave assisted oxidation of alcohols

INTRODUCTION

Transition metal complexes derived from multidentate Schiff base ligands received high significance due to their wide dimension of applications in the areas of molecular magnetism (Benelli and Gatteschi, 2002; Sutradhar et al., 2012, 2013, 2014b, 2015a, 2018; Cho et al., 2016; Andruh, 2018), crystal engineering (Dong et al., 2000; Kitaura et al., 2004; Andruh et al., 2009), supramolecular chemistry (Pradeep and Das, 2013; El-Binary et al., 2016; Dwivedi et al., 2018), catalysis (Sutradhar et al., 2013, 2014b, 2015a,b,c, 2016a,b,c, 2017, 2018, 2019), etc. Molecular magnetism is one of the significant domains determining magneto-structural correlations to design magnetic materials (Benelli and Gatteschi, 2002; Sutradhar et al., 2012, 2013, 2014b, 2015a, 2018; Cho et al., 2016; Andruh, 2018). Single molecule magnets (SMMs) (Karotsis et al., 2010; Glaser et al., 2015; Maniaki et al., 2018) exhibit a large spin ground-state (*S*) value and large negative magnetic anisotropy and are used in potential high-density information storage devices and



quantum computers (Leuenberger and Loss, 2001). Therefore, many efforts have been devoted to rationally establish polynuclear metal complexes and/or clusters elucidating molecular magnetism (Benelli and Gatteschi, 2002; Karotsis et al., 2010; Sutradhar et al., 2012, 2013, 2014b, 2015a, 2018; Glaser et al., 2015; Cho et al., 2016; Andruh, 2018; Maniaki et al., 2018). Coordination polymers and molecular clusters are particular classes of compounds that can display novel magnetic properties including high ground-state spin values and single molecule magnetism behavior (Zheng et al., 2014; Journaux et al., 2018; Yue and Gao, 2019).

The coordination behavior of Cu(II) is versatile, flexible and magnetically attractive. Many Cu(II) complexes are widely explored for magnetic studies focused on the synthesis of polynuclear complexes and/or clusters and their possible application in molecular magnetism (Benelli and Gatteschi, 2002; Sutradhar et al., 2013, 2015a, 2018; Andruh, 2018). Several attempts have been carried out to synthesize polynuclear Cu(II) complexes by designing suitable flexidentate Schiff base ligands to fabricate magnetic properties (Lu et al., 2013; Sutradhar et al., 2013, 2015a, 2018). Moreover, some multinuclear copper complexes show good catalytic performances toward the mild peroxidative oxidation of alkanes and alcohols into more valuable organic products (Pombeiro, 2013, 2019; Sutradhar et al., 2013, 2015a, 2018; Kopylovich et al., 2015) thus contributing to one of the most challenging subjects of modern chemistry. However, such examples are still limited and the study requires further exploration.

Aroylhydrazone Schiff bases are versatile in terms of functionalities, coordination properties and chelating abilities (Sutradhar et al., 2013, 2015a,b,c, 2016a,b,c, 2017, 2018). In continuation of our work in the fields of catalysis and magnetic studies, herein we report the syntheses of two 1D coordination polymers using two different multidentate *N,O* donor aroylhydrazone Schiff bases. The magnetic properties of one of them (complex **2**) are studied using variable temperature magnetic susceptibility measurements. These 1D polymers

are also tested as catalysts toward the microwave assisted peroxidative oxidation of alcohols under mild conditions for the future development of an environment benign catalytic system.

EXPERIMENTAL

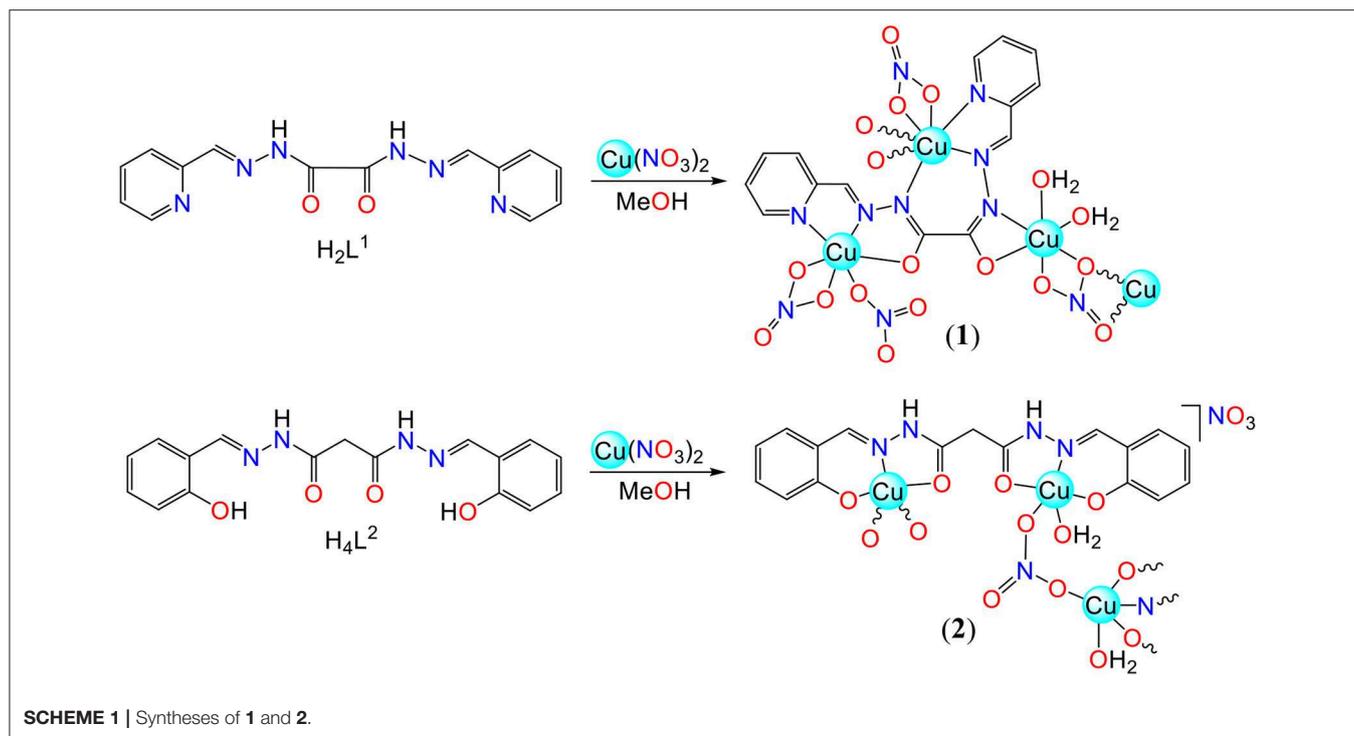
All synthetic work was performed in air. Commercially available reagents and solvents were used as received, without further purification or drying. $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ was used as metal source for the synthesis of the complexes.

C, H, and N elemental analyses were carried out by the Microanalytical Service of Instituto Superior Técnico. Infrared spectra ($4,000\text{--}400\text{ cm}^{-1}$) were recorded on a Bruker Vertex 70 (Bruker Corporation, Ettlingen, Germany) instrument in KBr pellets; wavenumbers are in cm^{-1} . The ^1H NMR spectra were recorded at room temperature on a Bruker Avance II + 400.13 MHz (UltraShieldTM Magnet, Rheinstetten, Germany) spectrometer. The UV-Vis absorption spectra of methanol solutions of **1** and **2** (*ca.* $2 \times 10^{-5}\text{ M}$) in 1.00 cm quartz cells were recorded at room temperature on a Lambda 35 UV-Vis spectrophotometer (Perkin-Elmer) by scanning the $200\text{--}1000\text{ nm}$ region at a rate of 240 nm min^{-1} . Tetramethylsilane was used as the internal reference and the chemical shifts are reported in ppm. Mass spectra were run in a Varian 500-MS LC Ion Trap Mass Spectrometer (Agilent Technologies, Amstelveen, The Netherlands) equipped with an electrospray (ESI) ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 p.s.i. nebulizer pressure. Scanning was performed from m/z 100 to 1,200 in methanol solution. The compounds were observed in the positive mode (capillary voltage = $80\text{--}105\text{ V}$). The catalytic tests were performed under microwave (MW) irradiation using a focused Anton Paar Monowave 300 microwave (Anton Paar GmbH, Graz, Austria) fitted with a rotational system and an IR temperature detector, using a 10 mL capacity reaction tube with a 13 mm internal diameter. Gas chromatographic (GC) measurements were carried in a FISON S Instrument GC 8000 series gas chromatograph with a capillary DB-WAX column (30 m x 0.32 mm), a FID detector, helium as the carrier gas and using the Jasco-Borwin v.1.50 software. The magnetic susceptibility measurements were carried out on a polycrystalline samples with a Quantum Design MPMS-XL5 SQUID magnetometer in the temperature range of $2\text{--}300\text{ K}$ and at an applied field of 2000 Oe. Diamagnetic corrections were estimated from Pascal's constants for all constituent atoms (Kahn, 1993).

Synthesis of the $N^{1,1}, N^{2,2}$ -bis(pyridin-2-ylmethylene)oxalohydrazide (H_2L^1)

The aroylhydrazone Schiff base pro-ligand H_2L^1 (Scheme 1) was prepared by using a similar method reported for the synthesis of $N^{1,1}, N^{3,3}$ -bis(2-hydroxybenzylidene)malonohydrazide (H_4L^2) (Sutradhar et al., 2014a) upon condensation of the oxalyl dihydrazide with pyridine-2-aldehyde.

Yield: 86%. Anal. Calcd for H_2L^1 $\text{C}_{14}\text{H}_{12}\text{N}_6\text{O}_2$: C, 56.75; H, 4.08; N, 28.36. Found: C, 56.68; H, 4.04; N, 28.29. IR (KBr



pellet, cm^{-1}): 3131 $\nu(\text{NH})$, 1681 $\nu(\text{C}=\text{O})$, 1185 $\nu(\text{N}-\text{N})$. ^1H NMR (DMSO- d_6 , δ): 12.67 (s, 2H, NH), 7.47 (s, 2H, $-\text{CH}=\text{N}$), 8.67–7.89 (m, 8H, $\text{C}_5\text{H}_4\text{N}$). UV-Vis λ_{max} (MeOH, nm (ϵ , $\text{LM}^{-1} \text{cm}^{-1}$)): 656 (305), 378 (16,478), 285 (23,434), 237 (32,108). ESI-MS(+): m/z 297 $[\text{M}+\text{H}]^+$ (100%).

Synthesis of $[\text{Cu}_3(\text{L}^1)(\text{NO}_3)_4(\text{H}_2\text{O})_2]_n$ (**1**)

0.930 g $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (4.0 mmol) was added to a 25 mL methanolic suspension of H_2L^1 (0.302 g, 1.02 mmol). The resultant mixture was stirred at room temperature for 20 min and a dark green solution was obtained. The solution was then filtered and the solvent was allowed to evaporate slowly at room temperature. After 2 d, single crystals suitable for X-ray diffraction were isolated, washed 3 times with cold methanol and dried over silica gel.

Yield: 0.523 g (68%, with respect to Cu). Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{Cu}_3\text{N}_{10}\text{O}_{16}$: C, 21.87; H, 1.84; N, 18.22. Found: C, 21.83; H, 1.81; N, 18.17. IR (KBr; cm^{-1}): 3448 $\nu(\text{OH})$, 1610 $\nu(\text{C}=\text{N})$, 1382 $\nu(\text{NO}_3)$, 1252 $\nu(\text{C}-\text{O})_{\text{enolic}}$ and 1154 $\nu(\text{N}-\text{N})$. UV-Vis λ_{max} (MeOH, nm (ϵ , $\text{LM}^{-1} \text{cm}^{-1}$)): 752 (309), 820 (286), 390 (16,248), 282 (22,632), 254 (31,818). ESI-MS(+): m/z 770 $[\text{M}+\text{H}]^+$ (100%).

Synthesis of $[\text{Cu}_2(\text{H}_2\text{L}^2)(\text{NO}_3)(\text{H}_2\text{O})_2]_n(\text{NO}_3)_n$ (**2**)

To a 25 mL methanol solution of H_4L^2 (0.340 g, 1.00 mmol), a 20 mL methanol solution of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (0.670 g, 3.0 mmol) was added and the reaction mixture was stirred for 20 min at room temperature. The resultant dark green solution was filtered and the filtrate was kept in open air. Dark green single

crystals suitable for X-ray diffraction analysis were isolated after 2 days. Crystals were washed 3 times with cold ethanol and dried over silica gel.

Yield: 0.450 g (72%, with respect to Cu). Anal. Calcd for $\text{C}_{17}\text{H}_{18}\text{Cu}_2\text{N}_6\text{O}_{12}$ (**2**): C, 32.65; H, 2.90; N, 13.44. Found: C, 32.60; H, 2.86; N, 13.39. IR (KBr; cm^{-1}): 3432 $\nu(\text{OH})$, 2874 $\nu(\text{NH})$, 1607 $\nu(\text{C}=\text{O})$, 1384 $\nu(\text{NO}_3)$, and 1154 $\nu(\text{N}-\text{N})$. UV-Vis λ_{max} (MeOH, nm (ϵ , $\text{LM}^{-1} \text{cm}^{-1}$)): 756 (296), 359 (14,436), 344 (18,322), 326 (16,862). ESI-MS(+): m/z 581 $[(\text{M}-\text{NO}_3)+\text{H}_2\text{O}]^+$ (100%).

X-Ray Measurements

Crystals of **1** were unstable at room temperature and without solvent. A good quality single crystal of **1** in the mother liquor was mounted in a capillary tube, sealed and measured at the temperature of *ca.* 150 K. A crystal of **2** was immersed in cryo-oil, mounted in a Nylon loop and measured at the temperature of 296 K. Intensity data were collected using a Bruker AXS PHOTON 100 diffractometer with graphite monochromated Mo- $\text{K}\alpha$ (λ 0.71073) radiation. Data were collected using omega scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART (Bruker, 2012) software and refined using Bruker SAINT (Bruker, 2012) on all the observed reflections. Absorption corrections were applied using SADABS (Bruker, 2012). Structures were solved by direct methods by using SHELXS (Sheldrick, 2000) and refined with SHELXL 2018 (Sheldrick, 2015). Calculations were performed using WinGX version 2014.1 (Farrugia, 2012). All non-hydrogen atoms were refined anisotropically. The H-atoms bonded to carbons were included in the model at geometrically calculated positions and refined using a riding model. $U_{\text{iso}}(\text{H})$

were defined as $1.2U_{eq}$ of the parent aromatic and methylene groups and $1.5U_{eq}$ of the parent methyl ones. The hydrogen atoms attached to O were located in the difference Fourier map and refined with their isotropic thermal parameter set at 1.5 times the average thermal parameter of the parent oxygen atom. There was disordered solvent in the structure of **2** that could not be modeled (232 electrons in a void of 471 \AA^3). Platon Squeeze (Spek, 2009) was used to remove that electron density. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms were employed. Crystal structures data are provided in the **Supplementary Material**.

Typical Procedures and Product Analysis for Catalysis

The catalytic microwave-assisted (MW) peroxidative oxidation of 1-phenylethanol was undertaken in a focused Anton Paar Monowave 300 reactor equipped with a rotational system and an IR temperature detector. To a cylindrical pyrex tube (10 mL), 2.5 mmol alcohol, 5 μmol catalyst **1** or **2** (0.2 mol% vs. substrate) and 70% aqueous solution of *tert*-BuOOH (5 mmol) were added. The tube was sealed and placed in the microwave reactor under stirring and irradiation (5 or 20 W) at 80 or 120°C respectively, for 0.5 h. In the end, the reaction mixture was cooled to room temperature, 150 μL of benzaldehyde (internal standard) and 2.5 mL of MeCN (for substrate and organic products extraction) were added. The reaction mixture was stirred for 10 min and in the end a sample (1 μL) was taken from the organic phase and analyzed by GC using a FISONs gas chromatograph (GC 8000) with a FID detector and a capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm) (He as the carrier gas) and the Jasco-Borwin v.1.50 software. The samples were injected at 240°C . Initially the temperature was held at 120°C for 1 min, then elevated $10^\circ\text{C}/\text{min}$ up to 200°C and maintained at this temperature for 1 min. Assignment of product peaks was done by comparison with chromatograms of pure commercial samples.

RESULTS AND DISCUSSION

Syntheses and Characterization

The aroylhydrazone Schiff base N^1, N^2 -bis(pyridin-2-ylmethylene)oxalohydrazide (H_2L^1) and N^1, N^3 -bis(2-hydroxybenzylidene)malonohydrazide (H_4L^2) have been used to synthesize Cu(II) coordination polymers. Reactions of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ with those Schiff bases result in the formation of the 1D coordination polymers $[\text{Cu}_3(\text{L}^1)(\text{NO}_3)_4(\text{H}_2\text{O})_2]_n$ (**1**) and $[\text{Cu}_2(\text{H}_2\text{L}^2)(\text{NO}_3)(\text{H}_2\text{O})_2]_n(\text{NO}_3)_n$ (**2**). In **1** and **2** the coordination forms of the ligands are different (**Scheme 1**). Generally, in the presence of a base, aroylhydrazone coordinates to the metal center via the *iminol (enol)* form. The *amide (keto)* form is typically observed when reacting with a metal salt of the weak conjugated base of strong acid, e.g., nitrate, chloride or sulfate (Sutradhar et al., 2015a, 2016a). The treatment of H_2L^1 with $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ yields the 1D polymer **1** with the *iminol (enol)* coordination form of the ligand without addition of a base. However, this is probably due to the presence of the basic pyridine moiety in H_2L^1 which helps to deprotonate the *enolic* hydrogen of another molecule during complex

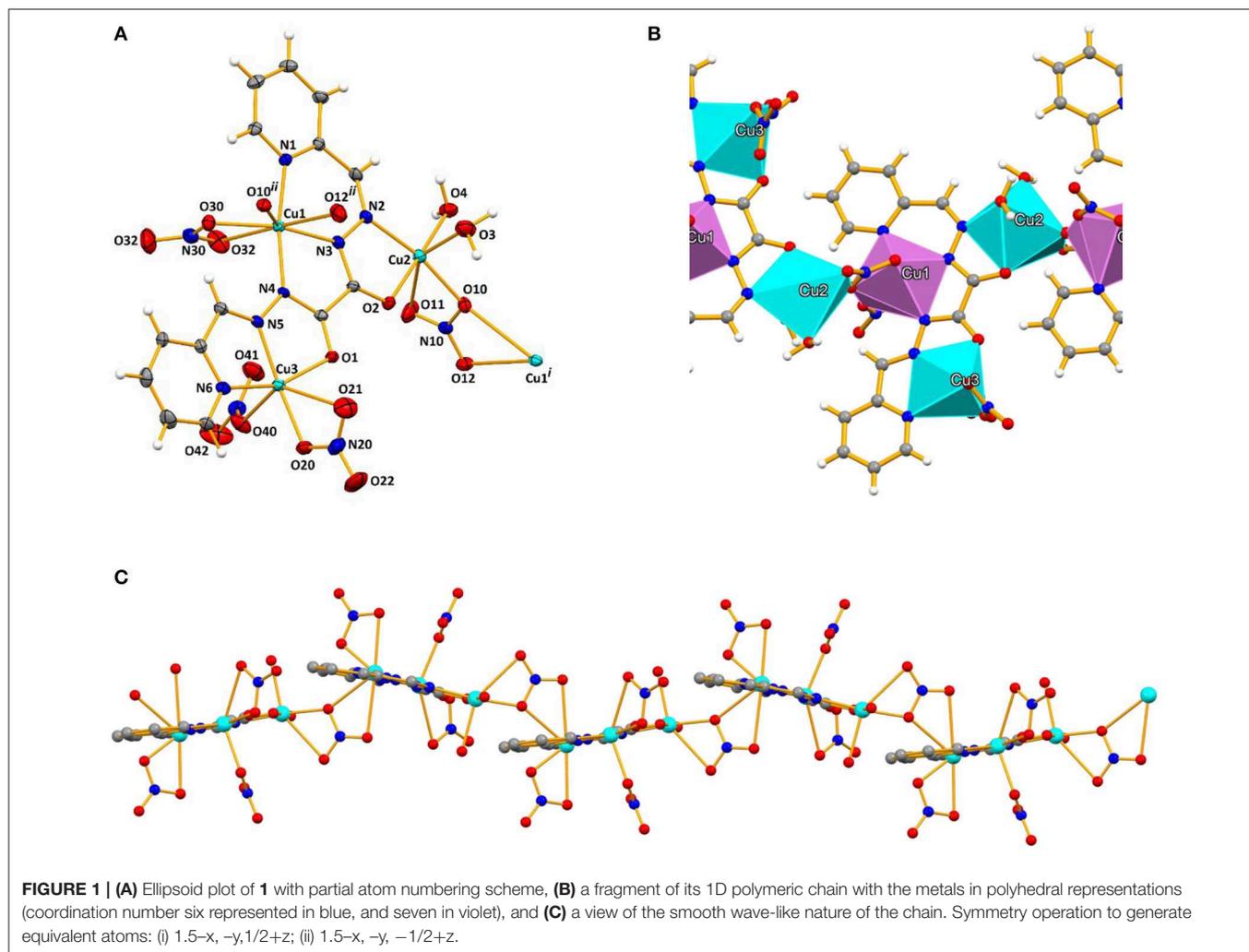
formation. In accord, the ligand exhibits the usual *amide (keto)* coordination in polymer **2**, where no such basic moiety is present in the ligand.

All the characteristic bands of the corresponding coordinated tridentate anionic ligand are found in the IR spectra of **1** and **2**, viz., 3,448, 1,610, 1,252, and 1,154 $\text{v}(\text{N}-\text{N}) \text{ cm}^{-1}$ for **1** and 3,432, 2,874, 1,607, 1,384, and 1,154 cm^{-1} for **2**. In addition, the presence of nitrate was found at ca. 1,382 cm^{-1} . In the UV-Vis spectra, both complexes **1** and **2** exhibit intense ligand to metal charge transfer transitions (LMCT) in the range of 254–390 nm (**Figures S1, S2**). In **1**, less intense absorption bands at 752 and 820 nm are due to d–d transitions attributable to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ and ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_{1g}$ transitions, suggesting a distorted octahedral geometry (**Figure S1**) (Sutradhar et al., 2016b; Sureshbabu et al., 2019). In the case of **2** a less intense absorption band is observed at 756 nm (**Figure S2**) in accord with square pyramidal coordination geometries at the Cu(II) centers (Sutradhar et al., 2016b; Sureshbabu et al., 2019), which is in agreement with the structures obtained by single crystal X-ray analysis. The ESI-MS spectrum of compound **1**, in methanol solution (see experimental section), displays the molecular ion peak at $m/z = 770$ $[\text{I}+\text{H}]^+$ (100%). For **2**, the peak at m/z 581 (100%) suggests the absence of the non-coordinated nitrate ion and the addition of one water molecule. The magnetic properties and catalytic activity toward solvent-free microwave-assisted oxidation of 1-phenylethanol of **1** and **2** are discussed in the following sections.

Description of the Crystal Structures

Single crystals suitable for X-ray analysis were isolated upon slow evaporation of a methanolic solution of **1** or **2** at room temperature. Crystals of **1** are unstable at room temperature and loose crystallinity in the absence of the mother liquor. A special precaution was taken (mentioned in experimental section) to analyze the structure. Crystallographic data for **1** and **2** are summarized in **Table S1** and selected dimensions (bond angle and lengths) are presented in **Table S2**. **Figures 1, 2** represent the structures of the respective complexes.

The multidentate ligand $(\text{L}^1)^{2-}$ in **1** is planar and chelates to three Cu(II) ions through the NNN, the NNO and the NO pockets affording one 6-membered and four 5-membered metallacycles (**Figure 1A**). The copper cations are slightly displaced (maximum of 0.197 \AA) toward the same side of the least-square plane of the organic ligand. Despite the planarity of $(\text{L}^1)^{2-}$, its derived 1D coordination polymer has a smooth wave-like shape imposed by the coordination mode of one of the nitrate anions behaving as bridging $1\kappa\text{OO}':2\kappa\text{OO}''$ donors to Cu1 and Cu2; the least-square planes of adjacent $(\text{L}^1)^{2-}$ ligands make angles of 19.84° . The remaining nitrate ligands work as bidentate (to Cu1 and to Cu3) and as monodentate (to Cu3) ligands. The two water molecules are coordinated to the same copper cation (Cu2). The metal ions assume coordination numbers six (Cu2 and Cu3) and seven (Cu1), with the coordination polyhedron of Cu3 (**Figure 1B**) having no contact atom with the other polyhedra; those of Cu1 and Cu2 share an $\text{O}_{\text{nitrate}}$ atom. The *intrachain* Cu...Cu distances through the azine bridges are of 4.736 and 4.794 \AA , and of 4.451



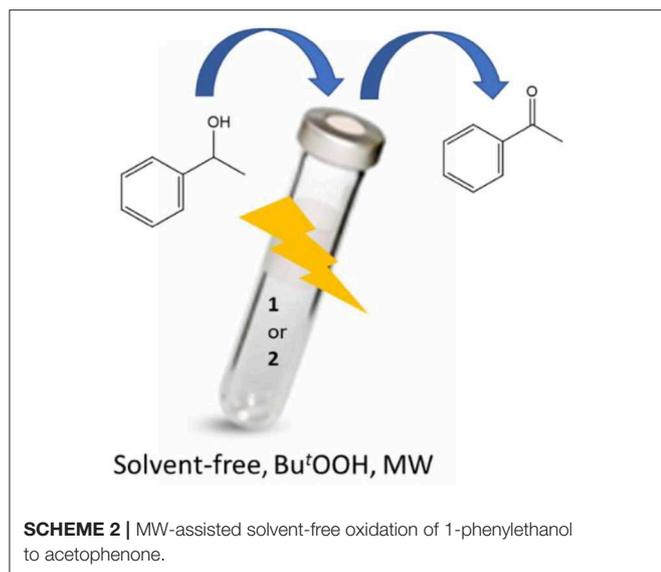
Å through the nitrate bridge. The minimum *interchain* Cu...Cu distance is of 5.692 Å.

The asymmetric unit of **2** contains two Cu(II) ions, one $(\text{H}_2\text{L}^2)^{2-}$, one nitrate and two water ligands, and a nitrate counter-ion. The organic ligand in **2** behaves as a hexadentate chelator acting as an *NOO* donor for each of the Cu(II) ions, therefore giving rise to two six- and two five-membered metallacycles (Figure 1A). Bridging monodentate nitrate anions connect the $\{\text{Cu}_2(\text{H}_2\text{L}^2)\}^{2-}$ moieties and generate a 1D polymeric chain running along the crystallographic *a* axis (Figure 1C). The copper cations adopt square pyramidal geometries ($\tau_5 = 0.04$ for Cu1 and 0.05 for Cu2) and share the $\text{O}_{\text{nitrate}}$ atom that stands in the axial position (Figures 2A,C). In view of the binding mode of the nitrates, the shortest Cu...Cu distance of 4.028 Å is along such ligands, while that along the hydrazone group exclusively (6.469 Å) is much longer than in **1** (see above). Resulting from the presence of a central methylene group in $(\text{H}_2\text{L}^2)^{2-}$ the ligand is highly twisted at this level, with the least-square planes of the two phenyl(methylene)acetohydrazone moieties making angles of 84.85°.

Magnetic Properties

The dc magnetic susceptibility of **2** was measured under 2000 Oe field (Figure 3). The room temperature χT value of 0.775 $\text{cm}^3 \text{K mol}^{-1}$ is a little larger than 0.750 $\text{cm}^3 \text{K mol}^{-1}$ calculated for two isolated Cu^{2+} ions. The χT value for **2** decreases gently with decreasing temperature in the range of 300–25 K, and then decreases sharply. The magnetic data at 50–300 K follow the Curie-Weiss law, with $C = 0.785 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ and $\Theta = -3.20 \text{ K}$ (Figure S3). The small negative Θ value suggests existence of weak antiferromagnetic interaction in **2**.

Based on the crystal structure, complex **2** is an alternative copper(II) chain compound, so two J_1 and J_2 parameters are necessary to describe the magnetic interaction, which are mediated through the ligand bridge and the $\text{O}_{\text{nitrate}}$ bridge, respectively. The magnetic data could be fitted by MagPack software using a Cu_{14} cluster loop approximation (Figure 4). The Hamiltonian of the Cu_{14} cluster loop with alternative J_1 and J_2 magnetic coupling constants is as follows: $H = -2J_1(S_{\text{Cu}1}S_{\text{Cu}2} + S_{\text{Cu}3}S_{\text{Cu}4} + S_{\text{Cu}5}S_{\text{Cu}6} + S_{\text{Cu}7}S_{\text{Cu}8} + S_{\text{Cu}9}S_{\text{Cu}10} + S_{\text{Cu}11}S_{\text{Cu}12} + S_{\text{Cu}13}S_{\text{Cu}14}) - 2J_2(S_{\text{Cu}2}S_{\text{Cu}3} + S_{\text{Cu}4}S_{\text{Cu}5} + S_{\text{Cu}6}S_{\text{Cu}7} + S_{\text{Cu}8}S_{\text{Cu}9} + S_{\text{Cu}10}S_{\text{Cu}11} + S_{\text{Cu}12}S_{\text{Cu}13} + S_{\text{Cu}14}S_{\text{Cu}1})$. The best



through the ligand bridge is weaker than that through the O_{nitrate} bridge.

Catalytic Studies Toward Microwave (MW) Assisted Oxidation of a Secondary Alcohol Under Solvent-Free Conditions

Cu(II) complexes **1** and **2** have been investigated as catalysts for the homogeneous oxidation of a secondary alcohol, 1-phenylethanol, to the corresponding ketone using *tert*-butylhydroperoxide (*tert*-BuOOH, TBHP, aq. 70%, 2 eq.) as oxidizing agent. The oxidation reactions were performed typically at 80 or 120°C, low power (5 or 20 W) microwave irradiation (MW), 0.5 h reaction time without additional solvent (Scheme 2). Results are summarized in Table 1.

Complexes **1** and **2** proved to be essential for the formation of acetophenone, since under similar reaction conditions and in the absence of these metal catalysts only traces of the desired product were detected. For catalytic tests performed only with the free ligand, no product was detected.

Under the studied conditions, the assays with copper catalysts **1** and **2** have shown comparable yields. For instance, for both **1** and **2** and using TBHP as oxidant at 120 °C, in the presence of TEMPO (2,2,6,6-tetramethylpiperidyl-1-oxyl) radical, the almost complete conversion of 1-phenylethanol to the desired product is achieved after the short period of 30 min with a TON of 588 and 522, respectively (Table 1, entries 4 and 11, respectively).

For these encouraging results, the effect of temperature and the presence of TEMPO, a chemically stable nitroxyl radical which has emerged as a promoter for the metal catalyzed transformation of alcohols to the corresponding carbonyl products (Gamez et al., 2004; Sheldon and Arends, 2004; Figiel et al., 2007, 2009; Sheldon, 2008; Ahmad et al., 2009), seem to be determinant. Reactions carried out under the same reaction conditions but at 80°C and in the absence of any additive did not go beyond 15 and 11% in the presence of **1** and **2**, respectively

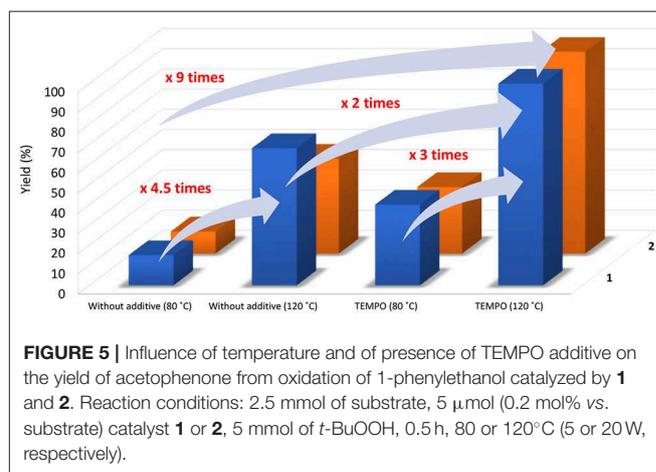
TABLE 1 | Solvent-free MW-assisted oxidation of 1-phenylethanol using **1** and **2** as catalysts precursors (selected data)^a.

Entry	Substrate	Temperature (°C)	Additive (μmol)	Yield ^b (%)	TON [TOF (h ⁻¹)] ^c
1					
1		80	-	15	150 (300)
2		120	-	68	334 (668)
3		80	TEMPO (30)	40	202 (404)
4		120	TEMPO (30)	>99	588 (1.2 × 10 ³)
5		80	TFA (50)	22	111 (222)
6		80	TFA (100)	25	124 (248)
7		80	Hpca (50)	13	102 (204)
2					
8		80	-	11	94 (188)
9		120	-	47	244 (488)
10		80	TEMPO (30)	33	163 (326)
11		120	TEMPO (30)	>99	522 (1.0 × 10 ³)
12		80	TFA (50)	16	81 (162)
13		80	TFA (100)	20	99 (198)
14		80	Hpca (50)	6	32 (64)

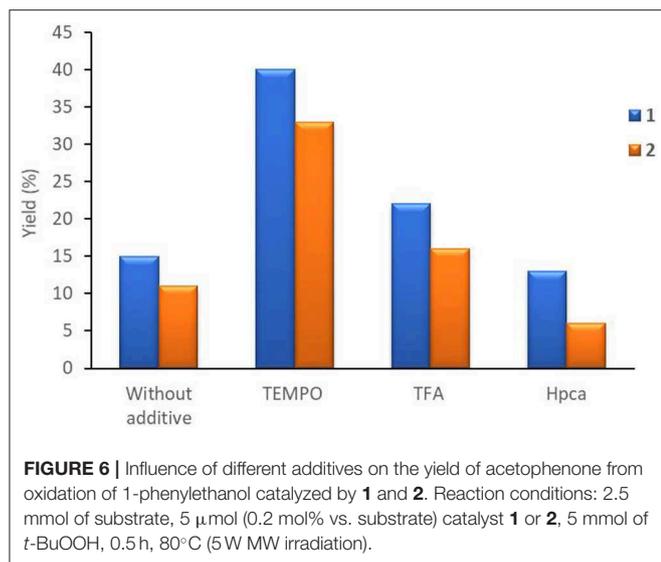
^aReaction conditions: 2.5 mmol of substrate, 5 μmol (0.2 mol% vs. substrate) catalyst **1** or **2**, 5 mmol of *t*-BuOOH (70% aq. solution), 0.5 h, 80 or 120°C, MW irradiation (5 or 20 W, respectively).

^bMolar yield (%) based on substrate, i.e., moles of product per 100 mol of substrate, determined by GC.

^cTurnover number = number of moles of product per mol of metal catalyst; TOF = TON per hour (values in brackets).



(Table 1, entries 1 and 8, respectively) whereas when carried out at 120°C it was possible to observe a significant increase in yield to 68 and 47% for **1** and **2**, respectively (Table 1, entries 2 and 9, respectively). The combination of these two parameters, temperature at 120°C and presence of TEMPO radical (Figure 5), resulted in the complete conversion of 1-phenylethanol into acetophenone and TOFs up to 1200 h⁻¹ (Table 1, entries 4 and 11, for **1** and **2**, respectively).



Considering the promoting effect of acid co-catalysts observed for other Cu-catalyzed oxidation systems (Sutradhar et al., 2016a,c, 2018), which are believed to accelerate the oxidation reactions by improving the oxidation properties of the complexes and by creating unsaturated metal centers (Sutradhar et al., 2015c), the influence of acidic additives on the acetophenone product yield was explored. The addition of trifluoroacetic acid (TFA) has a slight beneficial effect on both catalytic systems, resulting, for example, into a maximum yield of 25% (Table 1, entry 6), in the presence of **1** (at 80°C) (Figure 6). In contrary, the addition of the heteroaromatic 2-pyrazynecarboxylic acid (Hpca) has the opposite effect (Figure 6), i.e., a yield drop is observed when 50 μ mol was used [$n(\text{acid})/n(\text{catalyst } 1 \text{ or } 2) = 10$] (Table 1, entries 7 and 14, for **1** and **2**, respectively).

The promoting effect of TEMPO suggests the involvement of a radical mechanism which possibly involves the formation of *t*-BuOO \cdot and *t*-BuO \cdot radicals by a metal-assisted oxidation or reduction of *t*-BuOOH by a Cu^{II} or a Cu^I center, respectively (Gephart et al., 2012; Dronova et al., 2014), the latter behaving as an H-atom abstractor from the alcohol (Rothenberg et al., 1998; Mahdavi and Mardani, 2012; Frija et al., 2016; Sutradhar et al., 2016a,b, 2018; Ma et al., 2019).

CONCLUSIONS

In this study we have successfully synthesized two 1D Cu(II) coordination polymers using two different multidentate aroylhydrazone Schiff bases. The X-ray crystallographic study indicates that the two ligands show different coordination behaviors. The *N*¹,*N*²-bis(pyridin-2-ylmethylene)oxalohydrazone (H₂L¹), having a basic pyridine moiety, coordinates in the *iminol* form, whereas

the *amide* form is observed in the case of **2**. Both the ligand bridge and the nitrate bridge in **2** mediate weak antiferromagnetic interaction. The effects of temperature and of the additive TEMPO dramatically increase the catalytic efficiency of both Cu(II) compounds in the microwave-assisted oxidation of 1-phenylethanol to acetophenone under solvent-free conditions.

Our study concerns an attempt to design Cu(II) coordination polymers with interesting magnetic properties and also for use as catalyst toward the development of environmentally friendly alcohol oxidation catalytic systems.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/Supplementary Material. The crystallographic datasets generated for this study can also be found in the Cambridge Crystallographic Data Center (<https://www.ccdc.cam.ac.uk/structures/>) under the identifiers 1945551 and 1945552.

AUTHOR CONTRIBUTIONS

MS: overall planning, synthesis and characterization of catalysts, and manuscript writing. EA: catalytic studies and manuscript writing. TB: catalytic studies, GC analysis and manuscript writing. MG: single crystal X-ray diffraction analysis. C-ML: Magnetic studies and manuscript writing. AP: manuscript reading and correcting.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fchem.2020.00157/full#supplementary-material>

Data sheet 1 | Crystal structures data.

REFERENCES

- Ahmad, J. U., Figiel, P. J., Räsänen, M. T., Leskelä, M., and Repo, T. (2009). Aerobic oxidation of benzylic alcohols with bis(3,5-di-tert-butylsalicylaldehyde)copper(II) complexes. *Appl. Catal. A* 371, 17–21. doi: 10.1016/j.apcata.2009.09.011
- Andruh, M. (2018). Heterotrimeric complexes in molecular magnetism. *Chem. Commun.* 54, 3559–3577. doi: 10.1039/C8CC00939B
- Andruh, M., Branzea, G. D., and Gheorghie, R., Madalan, A. M. (2009). Crystal engineering of hybrid inorganic–organic systems based upon complexes with dissymmetric compartmental ligands. *Cryst. Eng. Comm.* 11, 2571–2584. doi: 10.1039/b909476h
- Benelli, C., and Gatteschi, D. (2002). Magnetism of lanthanides in molecular materials with transition-metal ions and organic radicals. *Chem. Rev.* 102, 2369–2388. doi: 10.1021/cr010303r
- Bruker (2012). APEX2. Madison, Wisconsin: Bruker AXS Inc.,
- Cho, Y. I., Ward, M. L., Rose, M. J. (2016). Substituent effects of N4 schiff base ligands on the formation of fluoride-bridged dicobalt(II) complexes via B-F abstraction: structures and magnetism. *Dalton. Trans.* 45, 13466–13476. doi: 10.1039/C6DT02104B
- Dong, Y.-B., Smith, M. D., zur Loye, H.-C. (2000). New inorganic/organic coordination polymers generated from bidentate schiff-base ligands. *Inorg. Chem.* 39, 4927–4935. doi: 10.1021/ic0006504
- Dronova, M. S., Bilyachenko, A. N., Yalymov, A. I., Kozlov, Y. N., Shul'pina, L. S., Korlyukov, A. A., et al. (2014). Solvent-controlled synthesis of tetranuclear cage-like copper(II) silsesquioxanes. Remarkable features of the cage structures and their high catalytic activity in oxidation with peroxides. *Dalton Trans.* 43, 872–882. doi: 10.1039/C3DT52508B
- Dwivedi, N., Sunkari, S. S., Verma, A., Saha, S. (2018). Molecular packing dependent solid state fluorescence response of supramolecular metal-organic frameworks: phenoxo-bridged trinuclear Zn(II) centered schiff base complexes with halides and pseudohalides. *Cryst. Growth Des.* 18, 5628–5637. doi: 10.1021/acs.cgd.8b00948
- El-Bindary, A. A., El-Sonbati, A. Z., Diab, M. A., Ghoneim, M. M., Serag, L. S. (2016). Polymeric complexes - LXII. Coordination chemistry of supramolecular schiff base polymer complexes—a review. *J. Mol. Liq.* 216, 318–329. doi: 10.1016/j.molliq.2015.12.113
- Farrugia, L. J. (2012). WinGX and ORTEP for windows: an update. *J. Appl. Cryst.* 45, 849–854. doi: 10.1107/S0021889812029111
- Figiel, P. J., Leskelä, M., Repo, T. (2007). TEMPO-copper(II) diimine-catalysed oxidation of benzylic alcohols in aqueous media. *Adv. Synth. Catal.* 349, 1173–1179. doi: 10.1002/adsc.200600505
- Figiel, P. J., Sibauhi, A., Ahmad, J. U., Nieger, M., Räsänen, M. T., Leskelä, M., et al. (2009). Aerobic oxidation of benzylic alcohols in water by 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)/copper(II) 2-N-arylpiperidylcarbaldimino complexes. *Adv. Synth. Catal.* 351, 2625–2632. doi: 10.1002/adsc.200900478
- Frija, L. M. T., Alegria, E. C. B. A., Sutradhar, M., Cristiano, M. L. S., Ismael, A., Kopylovich, M. N., et al. (2016). Copper(II) and cobalt(II) tetrazole-saccharinate complexes as effective catalysts for oxidation of secondary alcohols. *J. Mol. Cat. A Chem.* 425, 283–290. doi: 10.1016/j.molcata.2016.10.023
- Gamez, P., Arends, I. W. C. E., Sheldon, R. A., Reedijk J. (2004). Room temperature aerobic copper-catalysed selective oxidation of primary alcohols to aldehydes. *Adv. Synth. Catal.* 346, 805–811. doi: 10.1002/adsc.200404063
- Gephart, R. T., McMullin, C. L., Sapiezynski, N. G., Jang, E. S., Aguila, M. J. B., Cundari, T. R., et al. (2012). Reaction of Cu^I with dialkyl peroxides: Cu^I-alkoxides, alkoxy radicals, and catalytic C–H etherification. *J. Am. Chem. Soc.* 134, 17350–17353. doi: 10.1021/ja3053688
- Glaser, T., Hoeke, V., Gieb, K., Schnack, J., Schroder, C., and Muller, P. (2015). Quantum tunneling of the magnetization in [(Mn6M)-M-III](3+)(M = Cr-III, Mn-III) SMMs: impact of molecular and crystal symmetry. *Coord. Chem. Rev.* 289, 261–278. doi: 10.1016/j.ccr.2014.12.001
- Journaux, Y., Ferrando-Soria, J., Pardo, E., Ruiz-Garcia, R., Julve, M., Lloret, F., et al. (2018). Design of magnetic coordination polymers built from polyoxalamide ligands: a thirty year story. *Eur. J. Inorg. Chem.* 228–247. doi: 10.1002/ejic.201700984
- Kahn, O. (1993). *Molecular Magnetism*. New York: VCH.
- Karotsis, G., Kenedy, S., Teat, S. J., Beavers, C. M., Fowler, D. A., Morales, J. J., et al. (2010). [Mn^{III}Ln^{III}] Calix[4]arene clusters as enhanced magnetic coolers and molecular magnets. *J. Am. Chem. Soc.* 132, 12983–12990. doi: 10.1021/ja104848m
- Kitaura, R., Onoyama, G., Sakamoto, H., Matsuda, R., Noro, S.-i., Kitagawa, S. (2004). Immobilization of a metallo schiff base into a microporous coordination polymer. *Angew. Chem. Int. Ed.* 43, 2684–2687. doi: 10.1002/anie.200352596
- Kopylovich, M. N., Ribeiro, A. P. C., Alegria, E. C. B., Martins, N. M. R., Martins, L. M. D. R. S., Pombeiro, A. J. L. (2015). Catalytic oxidation of alcohols: recent advances. *Adv. Organomet. Chem.* 63, 91–174. doi: 10.1016/bs.adomc.2015.02.004
- Leuenberger, M. N., Loss, D. (2001). Quantum computing in molecular magnets. *Nature* 410, 789–793. doi: 10.1038/35071024
- Lu, Z., Fan, T., Guo, W., Lu, Z., Fan, C. (2013). Synthesis, structure and magnetism of three cubane Cu(II) and Ni(II) complexes based on flexible schiff-base ligands. *Inorg. Chim. Acta.* 400, 191–196. doi: 10.1016/j.ica.2013.02.030
- Ma, Z., Wang, Q., Yang, H., Alegria, E. C. B. A., Guedes da Silva, M. F. C., Martins, L. M. D. R. S., et al. (2019). Synthesis and structure of copper complexes of a N₆O₄ macrocyclic ligand and catalytic application in alcohol oxidation. *Catalysts* 9:424. doi: 10.3390/catal9050424
- Mahdavi, V., Mardani, M. (2012). Selective oxidation of benzyl alcohol with tert-butylhydroperoxide catalysed via Mn (II) 2, 2-bipyridine complexes immobilized over the mesoporous hexagonal molecular sieves (HMS). *J. Chem. Sci.* 124, 1107–1115. doi: 10.1007/s12039-012-0307-4
- Maniaki, D., Pilichos, E., Perlepes, S. P. (2018). Coordination clusters of 3d-metals that behave as single-molecule magnets (SMMs): synthetic routes and strategies. *Front. Chem.* 6:461. doi: 10.3389/fchem.2018.00461
- Pombeiro, A. J. L. (2013). *Advances in Organometallic Chemistry and Catalysis*. Hoboken, NJ: Wiley, 15–25. doi: 10.1002/9781118742952.ch2
- Pombeiro, A. J. L. (2019). “Alkane Functionalization: Introduction and Overview,” in *Alkane Functionalization*, eds A. J. L. Pombeiro and M. F. C. Guedes da Silva (Hoboken, NJ: Wiley), 1–15. doi: 10.1002/9781119379256.ch1
- Pradeep, C. P., Das, S. K. (2013). Coordination and supramolecular aspects of the metal complexes of chiral N-salicyl-beta-amino alcohol schiff base ligands: towards understanding the roles of weak interactions in their catalytic reactions. *Coord. Chem. Rev.* 257, 1699–1715. doi: 10.1016/j.ccr.2013.01.028
- Rothenberg, G., Feldberg, L., Wiener, H., Sasson, Y. J. (1998). Copper-catalyzed homolytic and heterolytic benzylic and allylic oxidation using tert-butyl hydroperoxide. *Chem. Soc. Perkin Trans. 2*, 2429–2434. doi: 10.1039/a805324c
- Sheldon, R. A. (2008). E factors, green chemistry and catalysis: an odyssey. *Chem. Commun.* 29, 3352–3365. doi: 10.1039/b803584a
- Sheldon, R. A., Arends, I. W. C. E. (2004). Organocatalytic oxidations mediated by nitroxyl radicals. *Adv. Synth. Catal.* 346, 1051–1071. doi: 10.1002/adsc.200404110
- Sheldrick, G. M. (2000). *SADABS*. Program for Empirical Absorption Correction. Göttingen: University of Göttingen.
- Sheldrick, G. M. (2015). Crystal structure refinement with SHELXL. *Acta Cryst.* C71, 3–8. doi: 10.1107/S2053229614024218
- Spek, A. L. (2009). Structure validation in chemical crystallography. *Acta Cryst.* D65, 148–155. doi: 10.1107/S090744490804362X
- Sureshbabu, P., Junaid, Q. M., Upadhyay, C., Victoria, W., Pitchavel, V., Natarajan, S., Sabiah, S. (2019). Di and tetranuclear Cu(II) complexes with simple 2-aminoethylpyridine: magnetic properties, phosphodiester hydrolysis, DNA binding/cleavage, cytotoxicity and catecholase activity. *Polyhedron* 164, 202–218. doi: 10.1016/j.poly.2019.02.015
- Sutradhar, M., Alegria, E. C. B. A., Guedes da Silva, M. F. C., Liu, C.-M., Pombeiro, A. J. L. (2018). Peroxidative oxidation of alkanes and alcohols under mild conditions by di- and tetranuclear copper(II) complexes of bis(2-hydroxybenzylidene)isophthalohydrazide. *Molecules* 23:2699. doi: 10.3390/molecules23102699
- Sutradhar, M., Alegria, E. C. B. A., Guedes da Silva, M. F. C., Martins, L. M. D. R. S., Pombeiro, A. J. L. (2016b). Aroylhydrazone Cu(II) complexes in keto form: structural characterization and catalytic activity towards cyclohexane oxidation. *Molecules* 21:425. doi: 10.3390/molecules21040425
- Sutradhar, M., Alegria, E. C. B. A., Mahmudov, K. T., Guedes da Silva, M. F. C., Pombeiro, A. J. L. (2016a). Iron(III) and cobalt(III) complexes with both tautomeric (keto and enol) forms of aroylhydrazone ligands: catalysts

- for the microwave assisted oxidation of alcohols. *RSC Adv.* 6, 8079–8088. doi: 10.1039/C5RA25774C
- Sutradhar, M., Alegria, E. C. B. A., Roy Barman, T., Scorcelletti, F., Guedes da Silva, M. F. C., Pombeiro, A. J. L. (2017). Microwave-assisted peroxidative oxidation of toluene and 1-phenylethanol with monomeric keto and polymeric enol aroylhydrazone Cu(II) complexes. *Mol. Catal.* 439, 224–232. doi: 10.1016/j.mcat.2017.07.006
- Sutradhar, M., Carrella, L. M., Rentschler, E. (2012). A discrete μ_4 -oxido tetranuclear iron(III) cluster. *Eur. J. Inorg. Chem.* 2017, 4273–4278. doi: 10.1002/ejic.201200396
- Sutradhar, M., Guedes da Silva, M. F. C., Pombeiro, A. J. L. (2014a). A new cyclic binuclear Ni(II) complex as a catalyst towards nitroaldol (Henry) reaction. *Catal. Commun.* 57, 103–106. doi: 10.1016/j.catcom.2014.08.013
- Sutradhar, M., Kirillova, M. V., Guedes da Silva, M. F. C., Liu, C.-M., Pombeiro, A. J. L. (2013). Tautomeric effect of hydrazone schiff bases in tetranuclear Cu(II) complexes: magnetism and catalytic activity towards mild hydrocarboxylation of alkanes. *Dalton Trans.* 42, 16578–16587. doi: 10.1039/c3dt52453a
- Sutradhar, M., Martins, L. M. D. R. S., Carabineiro, S. A. C., Guedes da Silva, M. F. C., Buijnsters, J. G., Figueiredo, J. L., et al. (2016c). Oxidovanadium(V) complexes anchored on carbon materials as catalysts for the oxidation of 1-phenylethanol. *ChemCatChem* 8, 2254–2266. doi: 10.1002/cctc.201600316
- Sutradhar, M., Martins, L. M. D. R. S., Guedes da Silva, M. F. C., Alegria, E. C. B. A., Liu, C.-M., and Pombeiro, A. J. L. (2014b). Mn(II,II) complexes: magnetic properties and microwave assisted oxidation of alcohols. *Dalton Trans.* 43, 3966–3977. doi: 10.1039/c3dt52774c
- Sutradhar, M., Martins, L. M. D. R. S., Guedes da Silva, M. F. C., Mahmudov, K. T., Liu, C.-M., and Pombeiro, A. J. L. (2015a). Trinuclear Cu(II) structural isomers: coordination, magnetism, electrochemistry and catalytic activity toward oxidation of alkanes. *Eur. J. Inorg. Chem.* 2015, 3959–3969. doi: 10.1002/ejic.201500440
- Sutradhar, M., Martins, L. M. D. R. S., Guedes da Silva, M. F. C., Pombeiro, A. J. L. (2015b). Vanadium complexes: recent progress in oxidation catalysis. *Coord. Chem. Rev.* 301–302, 200–239. doi: 10.1016/j.ccr.2015.01.020
- Sutradhar, M., Martins, L. M. D. R. S., Guedes da Silva, M. F. C., Pombeiro, A. J. L. (2015c). Oxido vanadium complexes with tridentate aroylhydrazone as catalyst precursors for solvent-free microwave-assisted oxidation of alcohol. *Appl. Catal. A Gen.* 493, 50–57. doi: 10.1016/j.apcata.2015.01.005
- Sutradhar, M., Roy Barman, T., Pombeiro, A. J. L., Martins, L. M. D. R. S. (2019). Catalytic activity of polynuclear vs. dinuclear aroylhydrazone Cu(II) complexes in microwave-assisted oxidation of neat aliphatic and aromatic hydrocarbons. *Molecules* 24:47. doi: 10.3390/molecules24010047
- Yue, Q., Gao, E. Q. (2019). Azide and carboxylate as simultaneous coupler for magnetic coordination polymers. *Coord. Chem. Rev.* 382, 1–31. doi: 10.1016/j.ccr.2018.12.002
- Zheng, Y. Z., Zheng, Z. P., Chen, X. M. (2014). A symbol approach for classification of molecule-based magnetic materials exemplified by coordination polymers of metal carboxylates. *Coord. Chem. Rev.* 258, 1–15. doi: 10.1016/j.ccr.2013.08.031

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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