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**A Cyclic Tetranuclear Cuboid Type Copper(II) Complex Doubly Supported by Cyclohexane-1,4-Dicarboxylate: Molecular and Supramolecular Structure and Cyclohexane Oxidation Activity†**

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**Keywords**

Schiff base/Tetranuclear/Cuboid/Sulfonate/Carboxylate/Cyclohexane Oxidation

**Abstract**

Synthesis, characterization and catalytic study of the new bis( $\mu_4$ -(*ae*)-cyclohexane-1,4-dicarboxylato-O,O',O'',O''')-tetracopper(II) complex  $[(\text{CuL})_2(\mu_4\text{-O,O',O'',O'''}\text{-CDC})]_2 \cdot 2\text{H}_2\text{O}$  (**1**) (HL = 2-(2-pyridylmethyleneamino)benzenesulfonic acid and CDC = cyclohexane-1,4-dicarboxylate) are described. Complex **1** contains four copper(II) centres connected by four Schiff base ligands ( $\text{L}^-$ ) and doubly bridged by two cyclohexane-1,4-dicarboxylate moieties. The *axial-equatorial* conformation of the carboxylate groups of CDC stabilizes a tetracopper di-CDC ring in a *cuboid* type fashion. Compound **1** is applied as an efficient pre-catalyst for the oxidation of cyclohexane by aqueous  $\text{H}_2\text{O}_2$  under mild conditions (50 °C) in  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  medium. Without any promoter, a total yield (based on substrate) of cyclohexanol and cyclohexanone up to 35% was achieved.

## 1. Introduction

Multinuclear copper complexes have been deeply investigated during the last few decades.<sup>1-4</sup> In particular, tetranuclear copper complexes, which provide a wide variety of geometric architectures,<sup>5-10</sup> have been of great interest. The majority of them are of cubane type,<sup>5</sup> and other types, such as open cubane,<sup>6</sup> bicapped cubane,<sup>7</sup> quasi-tetrahedral and rhomboidal<sup>8</sup> or linear,<sup>9</sup> can also be found. They are important not only for their intriguing structures<sup>5-10</sup> but also for their interesting magnetic,<sup>2,7</sup> biological<sup>11</sup> and catalytic<sup>3,4,10,12</sup> properties. Of particular significance is their use as catalysts in oxidation catalysis,<sup>3,4,10,12</sup> but the field remains not fully explored, mainly in the search for systems with higher activity and selectivity under green conditions, namely in the topic of alkane functionalization.

Despite being the most abundant and least expensive potential carbon sources for synthesis, alkanes have been rarely used as starting materials in chemical industry due to their low reactivity.<sup>13</sup> Peroxidative oxidation<sup>14-20</sup> for their functionalization is a promising approach towards the synthesis of the corresponding alcohols and ketones. In fact, cyclohexanol and cyclohexanone can be obtained industrially by oxidation of cyclohexane and they are of a high demand since they can be converted into adipic acid and caprolactam, useful for the preparation of nylons.<sup>13a,e,f,g</sup> However, the industrial oxidation of cyclohexane still requires a considerable temperature (150 °C) and proceeds with a low yield (*ca.* 4%) in order to get a sufficient selectivity (*ca.* 85%), what justifies the need for the search of more active catalysts capable to operate under milder conditions and to lead to higher yields and selectivities.<sup>13a,e,f,g</sup> Copper complexes<sup>10a,13,15a,b</sup> appear particularly promising but their efficiencies and selectivities have still to be improved, what constitutes an aim of the current study.

Moreover, in view of the multi-copper nature of particulate methane monooxygenase (pMMO), an enzyme that catalyzes the oxidation of alkanes to alcohols, particular attention<sup>15,21</sup> should be paid to multinuclear copper catalysts, what is also an objective of this work.

On the other hand, benzenesulfonic acid and its derivatives are well known for coordination polymers and hydrogen bonding interactions via sulfonate oxygens,<sup>22</sup> but Schiff base ligands containing sulfonic acid are rare and have been not investigated extensively.<sup>23</sup> However, we anticipate that the combination of sulfonic and carboxylic acids such as cyclohexane-1,4-dicarboxylic acid (H<sub>2</sub>CDC) may produce a new multinuclear structure. With this aim, the known dichlorobridged dicopper(II) compound [Cu<sub>2</sub>L<sub>2</sub>Cl<sub>2</sub>] (HL = 2-(2-pyridylmethyleneamino)benzenesulfonic acid),<sup>23d</sup> synthesized via a slightly modified reported procedure [see Electronic Supplementary Information], was reacted with cyclohexane-1,4-dicarboxylate (CDC).

Herein, we report the synthesis, molecular and supramolecular structure and catalytic activity of the new bis(μ<sub>4</sub>-(*ae*)-cyclohexane-1,4-dicarboxylato-O,O',O'',O''''-)-tetracopper(II) complex [(CuL)<sub>2</sub>(μ<sub>4</sub>-O,O',O'',O''''-CDC)]<sub>2</sub>·2H<sub>2</sub>O (**1**) containing a interior metal-CDC *cuboid* cage (Scheme 1).

## 2. Experimental Section

### 2.1. Materials and Physical Methods

All the reagents and solvents were purchased from commercial sources and used as received. Synthesis and characterization of the known<sup>23d</sup> dichlorobridged dicopper(II) compound [Cu<sub>2</sub>L<sub>2</sub>Cl<sub>2</sub>] are described in the Electronic Supplementary Information. The water used in all preparations and analyses was double-distilled and de-ionised. Microanalyses were performed by the Microanalytical Service of the Instituto Superior Técnico. IR spectra were recorded in the region 400–4000 cm<sup>-1</sup> on a Bruker Vertex 70 spectrophotometer with samples as KBr disks. Thermal properties were analyzed with a Perkin–Elmer Instruction system (STA6000) at a heating rate of 5°C/min under a dinitrogen atmosphere (see Electronic Supplementary Information).

## 2.2. Synthesis

To an aqueous solution (30 mL) of  $[\text{Cu}_2\text{L}_2\text{Cl}_2]$  (0.360 g, 0.50 mmol) was added dropwise a methanol solution (10 mL) of cyclohexane-1,4-dicarboxylic acid ( $\text{H}_2\text{CDC}$ ) (0.086 g, 0.50 mmol) and triethylamine (0.101 g, 1.00 mmol) affording a dark green solution. After 1 day, dark green crystals of **1**, suitable for X-ray diffraction analysis, formed and were collected by filtration and washed with aqueous methanol (1:1). Yield: 0.318 g (76%).  $\text{C}_{64}\text{H}_{60}\text{N}_8\text{O}_{22}\text{S}_4\text{Cu}_4$  (1676): calcd: C 46.76, H 3.84, N 6.67%; found: C 46.85, H 3.77, N 6.76%. FT-IR (KBr,  $\text{cm}^{-1}$ ) (see Fig. S1):  $\nu(\text{O-H})$ , *ca.* 3450s;  $\nu(\text{C=O})$ , 1724s;  $\nu(\text{C=N})$ , 1618m;  $\nu(\text{OCO})$ , 1552m, 1482m;  $\nu(\text{C-O})$ , 1261s;  $\nu(\text{C-COO})$ , 1157s;  $\nu(\text{SO}_3)$ , 1382m, 775m.

## 2.3. Crystal Structure Determination

The X-ray diffraction data were collected using a Bruker APEX-II PHOTON 100 with graphite monochromated Mo- $\text{K}\alpha$  radiation. Data were collected using omega scans of  $0.5^\circ$  per frame, and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT<sup>24a</sup> on all the observed reflections. Absorption corrections were applied using SADABS.<sup>24a</sup> Structure was solved by direct methods by using the SIR-97 package<sup>24b,c</sup> and refined with SHELXL-97.<sup>24b,c</sup> Calculations were performed using the WinGX System-Version 1.80.03.<sup>24d</sup> The solvated water hydrogen atoms were located from the difference Fourier synthesis and refined isotropically. The other hydrogen atoms were also located in a difference Fourier synthesis but were included in the final refinement at positions calculated from the geometry of the molecules using the riding model, with isotropic vibration parameters. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms were employed. The final refinement converged to  $R_1$  ( $I > 2\sigma(I)$ ) value of 0.0476. The crystallographic data for **1** are summarized in Table 1 and selected bond lengths and angles related to geometries of the metal centres are listed in Table 2.

## 2.4. Peroxidative Oxidation of Cyclohexane

The catalytic cyclohexane oxidation reactions were carried out in MeCN solvent (total volume of 5.0 mL) in round bottom flasks and in open atmosphere, at 50°C. To the stirring suspension of the copper catalyst (**1**) and cyclohexane (0.27 mL, 2.48 mmol) in MeCN, the solid additives or radical scavenger were added whenever required and the reaction started with the addition of H<sub>2</sub>O<sub>2</sub> (50 % in H<sub>2</sub>O, 0.60 mL, 9.70 mmol) in a portion. The concentrations of the reactants in the reaction mixture, at the start of the reaction, were as follows: compound **1** ( $0.6 \times 10^{-3} - 3 \times 10^{-3}$  M), cyclohexane (0.49 M) and H<sub>2</sub>O<sub>2</sub> (2.0 M). The solution samples were analyzed by GC using nitromethane (0.05 mL) as an internal standard. Attribution of peaks was made by comparison with chromatograms of authentic samples. Chromatographic measurements were carried out in a Fisons Instruments GC 8000 series gas chromatograph with a BP20/SGE (30 m x 0.22 mm x 0.25 μm) capillary column (FID detector) and helium as carrier gas, whereas the analyses of the chromatographic peaks were done by the corresponding Jasco-Borwin v.1.50 software.

Analyses in the presence and in the absence of triphenyl phosphine (PPh<sub>3</sub>) were carried out and it was found that the oxygenation of cyclohexane gives rise to the formation of the corresponding cyclohexyl hydroperoxide as the main primary products, according to the method developed by Shul'pin.<sup>19</sup> For precise determination of the product concentrations only data obtained after the reduction of the reaction sample with PPh<sub>3</sub> were typically used, taking into account that the reaction mixture contained the three products: cyclohexyl hydroperoxide (as the primary product), cyclohexanone and cyclohexanol (as the final products) as shown in Scheme 2.

## 3. Results and Discussion

### 3.1. Synthesis and Characterization

The complex [(CuL)<sub>2</sub>(μ<sub>4</sub>-O,O',O'',O''''-CDC)]<sub>2</sub>·2H<sub>2</sub>O (**1**) can be readily obtained in high yield from the reaction of the dichlorobridged dicopper(II) complex

[Cu<sub>2</sub>L<sub>2</sub>Cl<sub>2</sub>] with cyclohexane-1,4-dicarboxylic acid (H<sub>2</sub>CDC) in aqueous methanol (3:1) medium (Scheme 1). Triethylamine was used to deprotonate the carboxylic acid groups, making all the carboxylate oxygen atoms available for coordination. The synthesis proceeds via displacement of chloride ligands in [Cu<sub>2</sub>L<sub>2</sub>Cl<sub>2</sub>] by cyclohexane-1,4-dicarboxylate (CDC) to produce the carboxylate bridged tetracopper(II) complex **1**, which was characterized by micro-analysis, IR spectroscopy (see Experimental Section), thermogravimetry (see Electronic Supplementary Information) and single crystal X-ray diffraction study.

The IR spectrum of the compound **1** (Fig. S1) exhibits the expected bands indicative of the presence of the organic Schiff base and CDC ligands.  $\nu(\text{C}=\text{N})$  is observed at 1618 cm<sup>-1</sup>, whereas the sulfonate group is evidenced by the medium signals at 1382 and 775 cm<sup>-1</sup>. The C=O and C–COO stretching vibrations are seen at 1724 and 1157 cm<sup>-1</sup>, respectively, while the water stretching occurs as a broad band at 3449 cm<sup>-1</sup>.

### 3.2. Crystal Structure Description

The crystal structure of [(CuL)<sub>2</sub>( $\mu_4$ -O,O',O'',O''''-CDC)]<sub>2</sub>·2H<sub>2</sub>O (**1**) bears the {Cu<sub>4</sub>( $\mu_4$ -O,O',O'',O''''-CDC)<sub>2</sub>}<sup>4+</sup> structural core, with an inner inversion centre, where each metal cation is linked to only one of the O atoms of CDC and is further linked to a L<sup>-</sup> Schiff base ligand (Fig. 1). Two crystallization water molecules are also present in the unit cell of **1**. The L<sup>-</sup> ligand acts either as a tridentate chelator to Cu1 or as a tetradentate chelator to both Cu1 (or Cu1<sup>i</sup>) and Cu2 (or Cu2<sup>i</sup>). As a consequence, while Cu1 presents a distorted N<sub>2</sub>O<sub>4</sub> octahedral geometry (quadratic elongation of 1.090 and angle variance of 133.36°),<sup>25</sup> Cu2 has a distorted square pyramidal ( $\tau_5 = 0.28$ ) environment.<sup>26</sup> The basal plane of Cu1 (or Cu1<sup>i</sup>) is occupied by the N<sub>imine</sub>, N<sub>pyridyl</sub> and two O<sub>carboxylate</sub> atoms, the axial sites involving the O<sub>sulfonate</sub> atoms from two L<sup>-</sup> ligands, one of them long [2.821(3) Å] but still within the sum of the Van der Waals radii of Cu and O atoms (1.40 and 1.52 Å, respectively). Concerning Cu2 (and Cu2<sup>i</sup>) the equatorial positions involve the N<sub>imine</sub>, N<sub>pyridyl</sub>, O<sub>sulfonate</sub> and O<sub>carboxylate</sub> atoms, the apical site involving an O atom from a CDC ligand. The O<sub>sulfonate</sub> contacts in **1** assume values of 2.480(3) (Cu1 or Cu1<sup>i</sup>) and 1.978(3) Å (Cu2 and Cu2<sup>i</sup>). The Cu–N<sub>imine</sub> and Cu–N<sub>pyridyl</sub> bond distances involving the Cu1



centres [1.987(3) and 1.986(3) Å, respectively] and those of Cu–O<sub>carboxylate</sub> [1.899(3) and 1.917(3) Å] are shorter than those involving Cu2 [2.032(3) and 2.006(3) Å, and also 1.922(3) Å, in this order]. The apical Cu–O<sub>carboxylate</sub> bond for the Cu2 cations [2.127(3) Å] is the longest distance found in these centres. It should be mentioned that these parameters related to the copper···sulfonate<sup>23,27</sup> and copper···carboxylate<sup>28</sup> bond distances and bond angles are in the usual ranges.

The discrepancy in bond distances for the two types of metal cations may be related with the twisting found in the ligands (L<sup>-</sup>) evidenced by the angles between the least-square planes of their aromatic rings. Indeed, in the N1-containing moiety which chelates to the Cu1 centres that angle is of 80.49° while for the N2-one, connected to both metals, it assumes the value of only 40.07°. Accordingly, the Cu1 cations are only slightly deviated (0.019 Å) from the respective least-square N<sub>2</sub>O<sub>2</sub> equatorial planes while the Cu2-ones are markedly deviated (0.294 Å). The intramolecular Cu···Cu distance is of 3.412 Å.

The ranges of the *cisoid* angles (74.87–101.76° for Cu1 and 80.98(14)–109.28(12)° for Cu2) and the values of the *transoid* angles (169.17(13) and 169.20(13)° for Cu1 and 169.76(12) and 152.79(13)° in Cu2) indicate that the extent of distortion in the basal plane of Cu2 centre is greater than that of Cu1.

The copper atoms are involved in several metallacycles. In particular, and as a result of the double μ<sub>2</sub>-O,O'-carboxylate bridges, one can find eight-membered Cu<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and eighteen-membered Cu<sub>2</sub>C<sub>12</sub>O<sub>4</sub> rings (Fig. 2) which form a *cuboid* type frame.<sup>32</sup> Resulting from the chelation of the L<sup>-</sup> ligand, the metallacycles CuC<sub>2</sub>N<sub>2</sub>, CuCNOS and Cu<sub>2</sub>CO<sub>3</sub> can also be found.

The cyclohexane-1,4-dicarboxylate moiety in **1** is in *axial-equatorial* (*ae*) form also found in the polymeric copper(II) complexes reported by Maji *et al.* and Kurmoo *et al.*<sup>28a,b</sup> The *equatorial-equatorial* (*ee*) conformation<sup>28b-e</sup> was found in a single CDC bridged tetranuclear copper(II) complex reported by Wei *et al.*<sup>28c</sup> and the *axial-axial* (*aa*) was found in a single CDC bridged tetranuclear molybdenum compound reported by Murillo *et al.*<sup>30</sup> Our distorted tetranuclear *cuboid* type frame has been stabilized in the *axial-equatorial* conformation, intramolecularly supported by π···π interactions between the C21-phenyl and N3-pyridyl rings (*centroid···centroid* distance of 4.091 Å) (Fig. S2,

Electronic Supplementary Information), as well as intermolecularly by  $\pi\cdots\pi$  contacts (*centroid* $\cdots$ *centroid* distance of 3.694 Å) between the N3-pyridyl rings (Fig. S3).

As shown in Fig. 3, there are three non-covalent H-bonding interactions involving two pyridyl-C–H, the non-coordinated water molecule and two sulfonate oxygen atoms (O12 and O13) in the crystal lattice of compound **1**. Non-coordinated water molecules act as moderate strong H-donors (D $\cdots$ A distances in the 2.790–3.042 Å and D–H $\cdots$ A angles in 122.10–155.07°, Table 3) to one of the non-coordinated sulfonate oxygen atoms (O13) of vicinal molecules to form an eight-member O13 $\cdots$ H10B–O10–H10A $\cdots$ O13<sup>iii</sup> $\cdots$ H10B<sup>iii</sup>–O10<sup>iii</sup>–H10A<sup>iii</sup> $\cdots$ O13 ring (Fig. S3, Electronic Supplementary Information) ring while the other non-coordinated sulfonate oxygen atom (O12) acts as a bifurcated acceptor (D $\cdots$ A distances in the 3.082–3.222 Å and D–H $\cdots$ A angles in 133.28–163.77°) to two pyridyl-C–H (C15<sup>ii</sup>–H15<sup>ii</sup> and C34<sup>iv</sup>–H34<sup>iv</sup>) of two different vicinal molecules. These three H-bonding interactions assist to form interesting 2-D motif (Fig. 3).

According to the CSD database search on Version 5.34 the number of metal complexes containing cyclohexane dicarboxylate (CDC) ligands is only of 143, the majority being polymeric.<sup>28a,b</sup> Among them, only 13 compounds are of copper. Due to the different possible forms (*aa*, *ae* and *ee*) of CDC, various types of interesting molecular structures are possible.<sup>28–35</sup> Only very few tetranuclear complexes supported either by single<sup>30,31</sup> or by four<sup>32b</sup> CDC moieties can be found in the literature. In order to understand the differences with our complex, a single bridged tetranuclear Cu(II) complex<sup>28c</sup> and a quadruple bridged tetranuclear Sn(IV) complex<sup>32b</sup> are presented in Scheme S1 (Electronic Supplementary Information), whereas a couple of dinuclear complexes supported either by single CDC<sup>32</sup> or by double CDC<sup>33</sup> are shown in Scheme S2. A cyclic hexanuclear molybdenum complex with triple CDC bridges has also been reported by Murillo *et al.*<sup>34</sup> There is only one isolated system with metal-CDC *cuboid* cage, the tetranuclear gallium complex (Fig. S4, Electronic Supplementary Information) reported by Saak *et al.*<sup>29</sup> A few polymeric complexes (e.g., a polymeric Co-compound is shown in Fig. S5) with inter-connected metal-CDC *cuboid* cages are also known.<sup>35</sup> To our knowledge, our compound **1** is the only example of an isolated 3d-metal tetranuclear

complex with a metal-CDC *cuboid* cage inside and the second example of a tetranuclear complex of such a type, after the above gallium compound.<sup>29</sup>

### 3.3. Activity towards Cyclohexane Oxidation

The new tetranuclear Cu(II) complex **1** acts as an efficient pre-catalyst for the peroxidative oxidation of cyclohexane, by aqueous H<sub>2</sub>O<sub>2</sub>, to cyclohexanol and cyclohexanone in acetonitrile, according to the overall reaction of Scheme 2. In fact, after 4 h (optimized reaction time) and in the absence of any additive, it leads to an overall turnover number (TON) of 240 moles of products per mole of catalyst (entry 1, Table 4) and an overall yield of *ca.* 35% (based on cyclohexane, under the conditions of the entry 9 of Table 4), though under different experimental conditions (at higher catalyst concentration) and with the lower TON of 57. These values are considerably higher than those reported for a few Cu-scorpionate complexes, [CuCl<sub>2</sub>{HC(pz)<sub>3</sub>}], [CuCl{SO<sub>3</sub>C(pz)<sub>3</sub>}], [CuCl<sub>2</sub>{HOCH<sub>2</sub>C(pz)<sub>3</sub>}] or [CuCl<sub>2</sub>{CH<sub>3</sub>SO<sub>2</sub>OCH<sub>2</sub>C(pz)<sub>3</sub>}]<sub>2</sub>.<sup>14a,b</sup> The yield is comparable with that (39%) of a tetracopper(II) triethanolamine compound, a highly active Cu-catalyst for cyclohexane oxidation, which however has a higher TON (380).<sup>15a,b</sup> The yield is also much higher than those reported for a dicopper,<sup>3f</sup> a heterometallic copper-magnesium,<sup>4c</sup> one bimetallic copper-lithium<sup>4d</sup> and a couple of tetracopper<sup>4a</sup> complexes which produce traces amount of cyclohexanol and cyclohexanone during hydrocarboxylation of cyclohexane to cyclohexanoic acid.

Although the reasons of the higher catalytic activity of complex **1** are not clearly understood, one can mention that the hydrophilicity of the good number of both sulfonate and carboxylate groups can activate water molecules (*e.g.*, see the H-bonded H<sub>2</sub>O in the molecular structure of **1**, Scheme 1) towards its important role as a promoter/catalyst for proton-shift steps involved in the formation of hydroxyl radicals from hydrogen peroxide,<sup>15d</sup> with a key role in the mechanism of the alkane oxidation (see below). Moreover, the multinuclear character of **1** allows the presence, in close proximity, of copper units in the oxidized (Cu<sup>II</sup>) and reduced (Cu<sup>I</sup>) forms, what is also favourable to that reaction (see below).

A blank test, *i.e.*, a catalyst-free cyclohexane oxidation with H<sub>2</sub>O<sub>2</sub>, shows that no cyclohexanol or cyclohexanone are formed appreciably in the absence of the complex **1** (entry 13, Table 4).

Effects of both basic and acidic additives on the catalytic peroxidative cyclohexane oxidation reaction were tested but no marked differences in yields and TONs were observed (compare entries 3 and 4 with 1, Table 4). The use of an acid additive could create unsaturation at a metal centre upon ligand protonation and/or enhance the oxidative power of the metal catalyst,<sup>13d,16a</sup> whereas the presence of a base could assist proton-transfer steps involved in the formation of the hydroxyl radical from H<sub>2</sub>O<sub>2</sub>.<sup>19</sup> However, such effects were not observed in the present case.

The X-ray structure of the catalyst reveals an available empty space of 16.1 Å<sup>3</sup> (0.9 % of the unit cell volume) as determined by PLATON.<sup>24e</sup> This void is too small to accommodate a cyclohexane molecule whose volume (108 Å<sup>3</sup>) has been estimated.<sup>24f</sup> Although the removal of crystallization water molecules from the structure would increase the void to 71.9 Å<sup>3</sup> (4.2 % of the unit cell volume), cyclohexane could still not have access to its interior. This is consistent with a free radical mechanism (see below) without requiring a direct interaction between the metal and alkane

Other factors for the present catalytic reaction system, such as the amounts of the oxidant (H<sub>2</sub>O<sub>2</sub>) and the catalyst, were also tested. An increase in the H<sub>2</sub>O<sub>2</sub> results in the enhancement (Fig. S6, Electronic Supplementary Information and Table 4) of the yield and the corresponding TON (*e.g.* from 7.9% to 29.4% and from 65 to 240 upon changing the H<sub>2</sub>O<sub>2</sub> concentration from 0.3 M to 2.0 M). Increasing the catalyst amount in the 0.6 x 10<sup>-3</sup> – 3.0 x 10<sup>-3</sup> M range results in a modest yield promotion (from 29.4 to 34.6%, entries 1, 8 and 9, Table 4) and a marked drop in the overall TON (from *ca.* 240 to 57, entries 1, 8 and 9, Table 4).

In order to get an insight into the mechanism of the reaction, this was also carried out in the presence of different types of radical traps, *i.e.*, CBrCl<sub>3</sub> (carbon radical trap), Ph<sub>2</sub>NH (oxygen radical trap) and BHT (2,6-di-*tert*-butyl-4-methylphenol, carbon and oxygen radical trap), and a drastic decrease of catalytic activity (84–91%) was observed (entries 5–7, Table 4), confirming that the cyclohexane (CyH) oxidation reaction proceeds mainly *via* a radical mechanism involving both carbon-centred and oxygen-centred radicals (Scheme 3). Hence, it can be suggested<sup>3a,b,13b,c,14a,f,18a,b</sup> that it involves the metal-assisted decomposition of H<sub>2</sub>O<sub>2</sub> into the hydroxyl radical (HO•) (equations i and ii, Scheme 3)<sup>16b</sup>, followed by the generation of cyclohexyl radical (Cy•) from cyclohexane

(CyH) upon H-abstraction by the HO• radical (equation iii, Scheme 3). The formation of this radical from H<sub>2</sub>O<sub>2</sub> involves proton-transfer steps among H<sub>2</sub>O<sub>2</sub>, hydroperoxo and peroxy metal-species, as suggested for vanadium,<sup>13b,c,14f,18a,b</sup> copper<sup>6a,b,14a,15a-c</sup> and rhenium<sup>15d</sup> catalysts.

The cyclohexyl radical, upon reaction with a possible metal-hydroperoxo intermediate species [Cu]-OOH (formed according to equation iv, Scheme 3), can lead to the formation of cyclohexane hydroperoxide (CyOOH)<sup>18c-f</sup> (equation v, Scheme 3) which can undergo metal-promoted decomposition to form O-centred organo radicals [cyclohexyloxy] (CyO•, upon O–O bond cleavage) [equation viii(a), Scheme 3] and cyclohexylperoxy (CyOO•, upon O–H bond rupture) [equation ix(a), Scheme 3]. CyOO• can also be formed upon reaction of Cy• with O<sub>2</sub> (equation vi, Scheme 3).<sup>17,18</sup> Cyclohexanol (CyOH) could then be formed by H-abstraction from cyclohexane (CyH) by CyO• [equation viii(b), Scheme 3] or upon decomposition of CyOO• to both cyclohexanol and cyclohexanone [equation ix(b), Scheme 3].<sup>3a,b,13b,c,15a-c,19,20</sup>

The involvement of CyOOH is recognized by the increase in the amount of cyclohexanol with the decrease of that of cyclohexanone upon treatment of the final reaction solution with an excess of PPh<sub>3</sub> prior to the GC analysis, following the method reported by Shul'pin.<sup>19d,e</sup> PPh<sub>3</sub> reduces the CyOOH, still present at the end of the essay, to CyOH (with formation of O=PPh<sub>3</sub>), thus leading to a quantitative conversion of that peroxide to the alcohol, instead of its decomposition to both alcohol and ketone (reactions viii and ix, Scheme 3).

It is worthwhile to mention that only a scant number of reports of metal complexes with sulfonate-carboxylate ligands<sup>22c</sup> is known, and moreover they have never been applied as catalysts in alkane oxidation reaction. Our studies provide the first example of a copper complex containing both carboxylate and sulfonate bridging ligands which is being applied as a catalyst for alkane oxidation.

## 4. Conclusions

Upon replacement of the chloride ligands of the known dichlorobridged dicopper(II) compound  $[\text{Cu}_2\text{L}_2\text{Cl}_2]$  by cyclohexane dicarboxylate (CDC) anions, the novel bis( $\mu_4$ -(*ae*)-cyclohexane-1,4-dicarboxylato-O,O',O'',O''')-tetracopper(II) complex  $[(\text{CuL})_2(\mu_4\text{-O,O',O'',O''''}-\text{CDC})]_2 \cdot 2\text{H}_2\text{O}$  (**1**) was obtained which is of a rare type, having a metal-CDC *cuboid* cage. In fact, it is the only discrete tetranuclear copper(II) system with such a cage and a second example of a tetranuclear complex of this type, after a gallium compound.

This synthetic methodology based on chloride ligand replacement by an organocarboxylate to produce a multinuclear system in aqueous methanol medium is an easy synthetic procedure in comparison to other approaches.<sup>14a,b,15a,b,15g,16a,16b</sup> The obtained metal complex **1** containing a mixed ligand (carboxylate and sulfonate) system is an efficient pre-catalyst for the oxidation of cyclohexane by aqueous  $\text{H}_2\text{O}_2$  under mild conditions and without any promoter, leading to a total (cyclohexanol and cyclohexanone) yield up to 35%. To our knowledge, this constitutes an unprecedented application in alkane oxidation of a catalyst with bridging sulfonate and carboxylate ligands.

In summary, a simple and efficient protocol for the synthesis of an effective catalyst is presented and the extension of this study to the preparation of further copper complexes with these types of bridging ligands and to their applications in oxidation catalysis deserves to be explored.

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**Table 1.** Crystallographic data for [(CuL)<sub>2</sub>(μ<sub>4</sub>-O,O',O'',O''''-CDC)]<sub>2</sub>·2H<sub>2</sub>O (**1**).

	<b>1</b>
Formula	C <sub>64</sub> H <sub>60</sub> N <sub>8</sub> O <sub>22</sub> S <sub>4</sub> Cu <sub>4</sub>
FW	1675.60
Crystal colour	Green
Crystal system	Triclinic
Space group	P-1
<i>a</i> /Å	8.6702(6)
<i>b</i> /Å	14.5121(10)
<i>c</i> /Å	15.1558(11)
<i>α</i> /°	113.704(3)
<i>β</i> /°	95.764(2)
<i>γ</i> /°	95.945(3)
<i>V</i> /Å <sup>3</sup>	1715.4(2)
<i>Z</i>	1
<i>T</i> /K	299(2)
2 <i>θ</i> /°	5.12 – 52.76
<i>μ</i> (Mo Kα)/mm <sup>-1</sup>	1.428
<i>ρ</i> <sub>calcd</sub> /g cm <sup>-3</sup>	1.622
<i>F</i> (000)	856
Absorption-correction	Multi-scan
Index ranges	-10 < <i>h</i> < 10 -18 < <i>k</i> < 18 -18 < <i>l</i> < 18
Reflections collected	22514
Independent reflections	6991
<i>R</i> <sub>int</sub>	0.0865
<i>R</i> <sub>1</sub> <sup>a</sup> / <i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.0476 / 0.0968
<i>R</i> <sub>1</sub> <sup>a</sup> / <i>wR</i> <sub>2</sub> <sup>b</sup> [for all <i>F</i> <sub>o</sub> <sup>2</sup> ]	0.1102 / 0.1133
GOF on <i>F</i> <sup>2</sup>	0.860

**Table 2.** Selected bond lengths (Å) and angles (°) for [(CuL)<sub>2</sub>(μ<sub>4</sub>-O,O',O'',O''''-CDC)]<sub>2</sub>·2H<sub>2</sub>O (1).

For Cu1			
Cu1–N1	1.987(3)	N1–Cu1–O41	169.17(13)
Cu1–N3	1.986(3)	N3–Cu1–O43	169.20(13)
Cu1–O41	1.899(3)	O11–Cu1–N1	74.87
Cu1–O43	1.917(3)	O11–Cu1–N3	101.76
Cu1–O11	2.480	O11–Cu1–O41	96.12
Cu1····O21	2.821	O11–Cu1–O43	84.25
		N1–Cu1–N3	81.25(13)
		N1–Cu1–O43	91.85(12)
		N3–Cu1–O41	95.01(13)
		O41–Cu1–O43	93.21(12)
For Cu2			
Cu2–N2	2.032(3)	N2–Cu2–O44	169.76(12)
Cu2–N4	2.006(3)	N4–Cu2–O21	152.79(13)
Cu2–O21	1.978(3)	O42–Cu2–N2	87.26(12)
Cu2–O44	1.922(2)	O42–Cu2–N4	96.32(13)
Cu2–O42	2.127(3)	O42–Cu2–O21	109.28(12)
		O42–Cu2–O44	99.61(11)
		N2–Cu2–N4	80.98(14)
		N2–Cu2–O21	90.90(12)
		N4–Cu2–O44	90.67(13)
		O21–Cu2–O44	93.93(11)

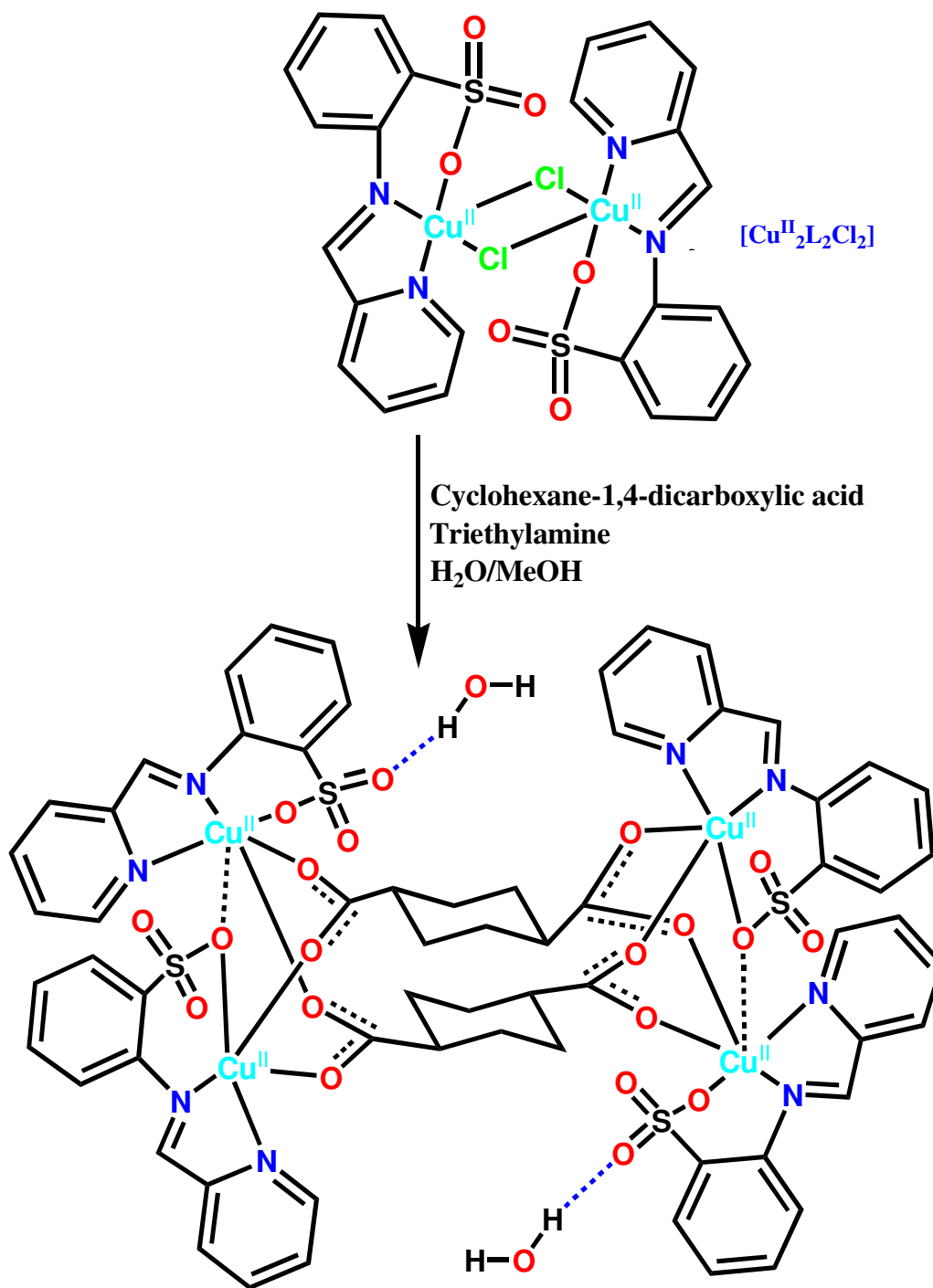
**Table 3.** Geometries [distances in (Å) and angles in (°)] of the hydrogen bonds in [(CuL)<sub>2</sub>(μ<sub>4</sub>-O,O',O'',O''''-CDC)]<sub>2</sub>·2H<sub>2</sub>O (1). Symmetry: *ii*), 1-x, -y, 1-z; *iii*), 1-x, 1-y, 1-z; *iv*) x, y, -1+z.

D–H···A	D···A	H···A	D–H···A
O10–H10B···O13	2.790	1.992	155.07
O10 <sup><i>iii</i></sup> –H10A <sup><i>iii</i></sup> ···O13	3.042	2.454	122.10
C34 <sup><i>iv</i></sup> –H34 <sup><i>iv</i></sup> ···O12	3.222	2.319	163.77
C15 <sup><i>ii</i></sup> –H15 <sup><i>ii</i></sup> ···O12	3.082	2.370	133.28

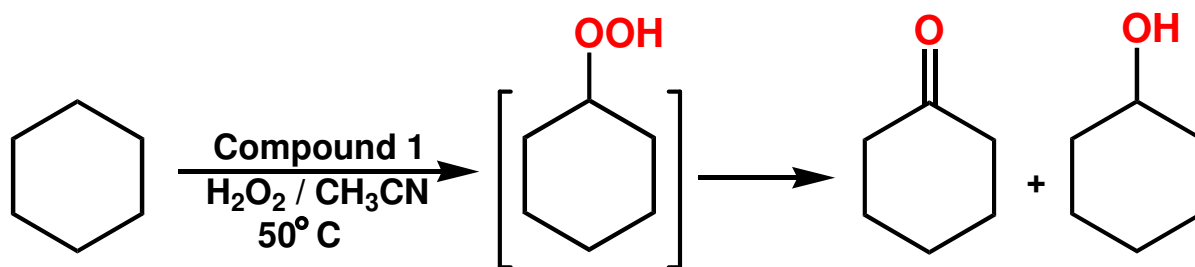
**Table 4.** Oxidation<sup>a</sup> of cyclohexane catalyzed by **1**.

Entry	Oxidant used	Additives used	Radical scavenger used	Yield [%] <sup>b</sup>			TON <sup>c</sup>	Yield drop with trap (%) <sup>d</sup>
				Cyclohexanol	Cyclohexanone	Total		
1	H <sub>2</sub> O <sub>2</sub>	-	-	13.7	15.7	29.4	240	-
2	TBHP	-	-	2.5	1.5	4.0	33	-
3	H <sub>2</sub> O <sub>2</sub>	TFA <sup>e</sup>	-	17.1	13.5	30.6	250	-
4	H <sub>2</sub> O <sub>2</sub>	Pyridine <sup>f</sup>	-	15.7	16.5	32.2	263	-
5	H <sub>2</sub> O <sub>2</sub>	-	BHT <sup>g</sup>	1.8	2.4	4.2	34	87
6	H <sub>2</sub> O <sub>2</sub>	-	CBrCl <sub>3</sub>	1.2	1.4	2.6	21	91
7	H <sub>2</sub> O <sub>2</sub> <sup>h</sup>	-	Ph <sub>2</sub> NH <sup>i</sup>	1.3	1.4	2.7	22	84
8 <sup>j</sup>	H <sub>2</sub> O <sub>2</sub>	-	-	14.5	16.2	30.7	125	-
9 <sup>k</sup>	H <sub>2</sub> O <sub>2</sub>	-	-	15.6	18.8	34.6	57	-
10	H <sub>2</sub> O <sub>2</sub> <sup>h</sup>	-	-	3.7	4.2	7.9	65	-
11	H <sub>2</sub> O <sub>2</sub> <sup>l</sup>	-	-	7.4	8.2	15.6	127	-
12	H <sub>2</sub> O <sub>2</sub> <sup>m</sup>	-	-	8.9	9.8	18.7	153	-
13 <sup>n</sup>	H <sub>2</sub> O <sub>2</sub>	-	-	<0.3	<0.3	-	-	-

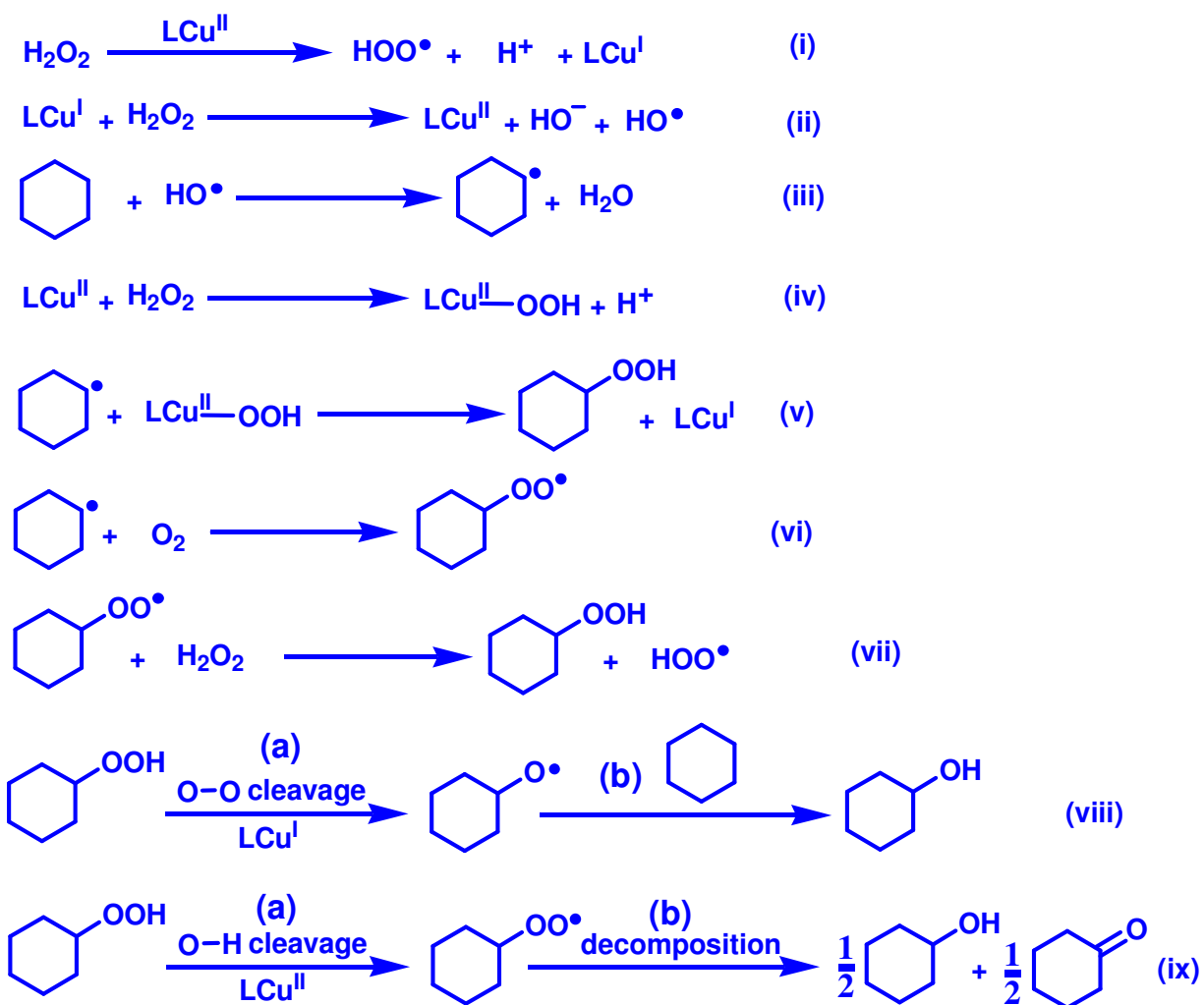
<sup>a</sup> Reaction conditions, unless stated otherwise: cyclohexane (0.49 M), catalyst ( $0.6 \times 10^{-3}$  M), H<sub>2</sub>O<sub>2</sub> (50% aqueous, 2.0 M) or tert-butylhydroperoxide (TBHP, 70% aqueous, 2.0 M), CH<sub>3</sub>CN (up to 5.0 mL total volume), 50°C; <sup>b</sup> Based on cyclohexane, calculated from GC analysis after treatment of the reaction mixture with PPh<sub>3</sub>; reaction time was 4 h; <sup>c</sup> Total TON corresponds to moles of products (cyclohexanol + cyclohexanone) per mole of catalyst; <sup>d</sup>  $(1 - \text{total yield with radical trap} / \text{total yield without radical trap}) \times 100$ ; <sup>e</sup> TFA (trifluoroacetic acid, 0.005 M); <sup>f</sup> Pyridine (0.005 M); <sup>g</sup> BHT (2,6-di-tert-butyl-4-methylphenol); <sup>h</sup> Concentration of H<sub>2</sub>O<sub>2</sub> (50% aqueous) as 0.3 M; <sup>i</sup> Diphenyl amine (0.3 M, equivalent to H<sub>2</sub>O<sub>2</sub> concentration); <sup>j</sup> [Catalyst] =  $1.2 \times 10^{-3}$  M; <sup>k</sup> [Catalyst] =  $3.0 \times 10^{-3}$  M; <sup>l</sup> Concentration of H<sub>2</sub>O<sub>2</sub> (50% aqueous) as 0.8 M; <sup>m</sup> Concentration of H<sub>2</sub>O<sub>2</sub> (50% aqueous) as 1.5 M; <sup>n</sup> Without metal catalyst.



**Scheme 1.** Synthesis of  $[(\text{CuL})_2(\mu_4\text{-O},\text{O}',\text{O}'',\text{O}''')\text{-CDC}]_2 \cdot 2\text{H}_2\text{O}$  (**1**).

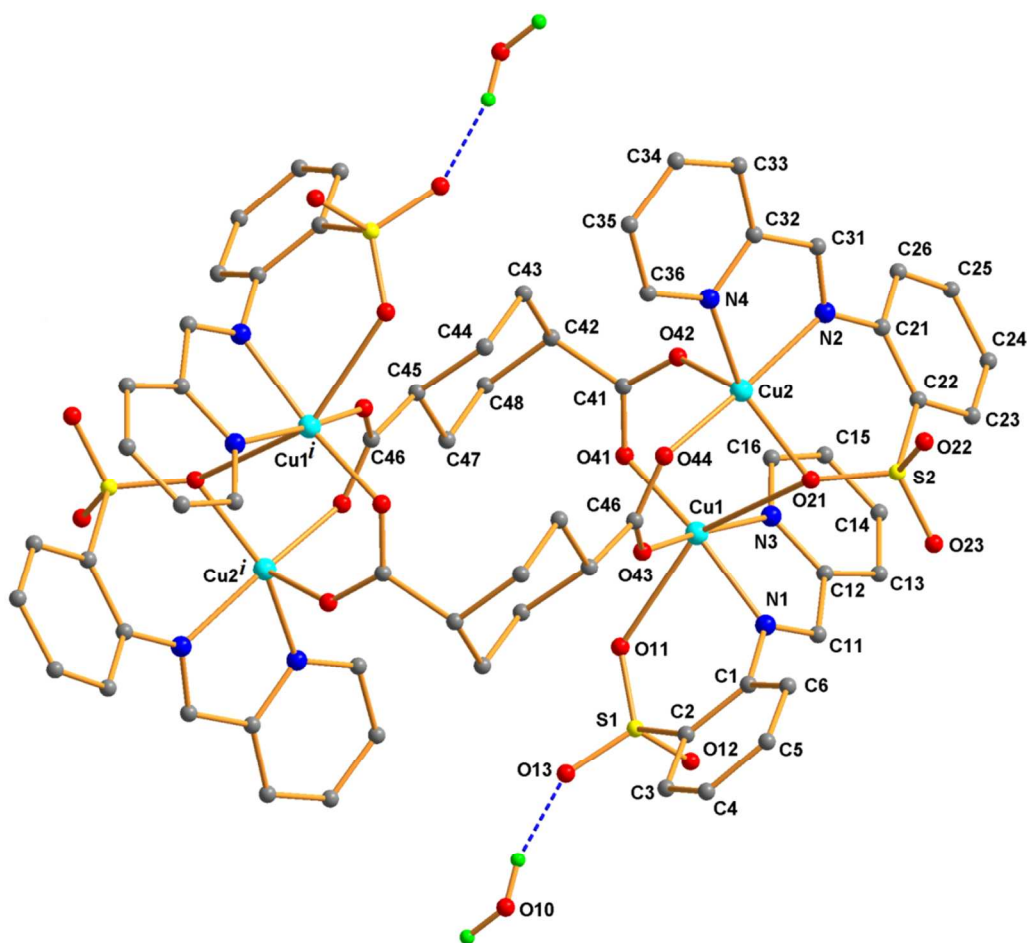


**Scheme 2.** Cyclohexane oxidation reaction catalyzed by **1**.

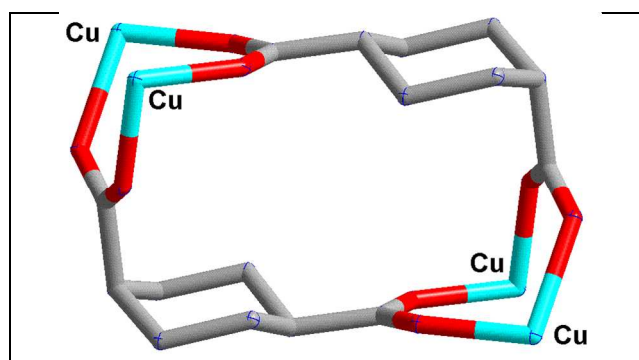


**Scheme 3.** Possible mechanistic pathways of cyclohexane oxidation catalyzed by **1**.

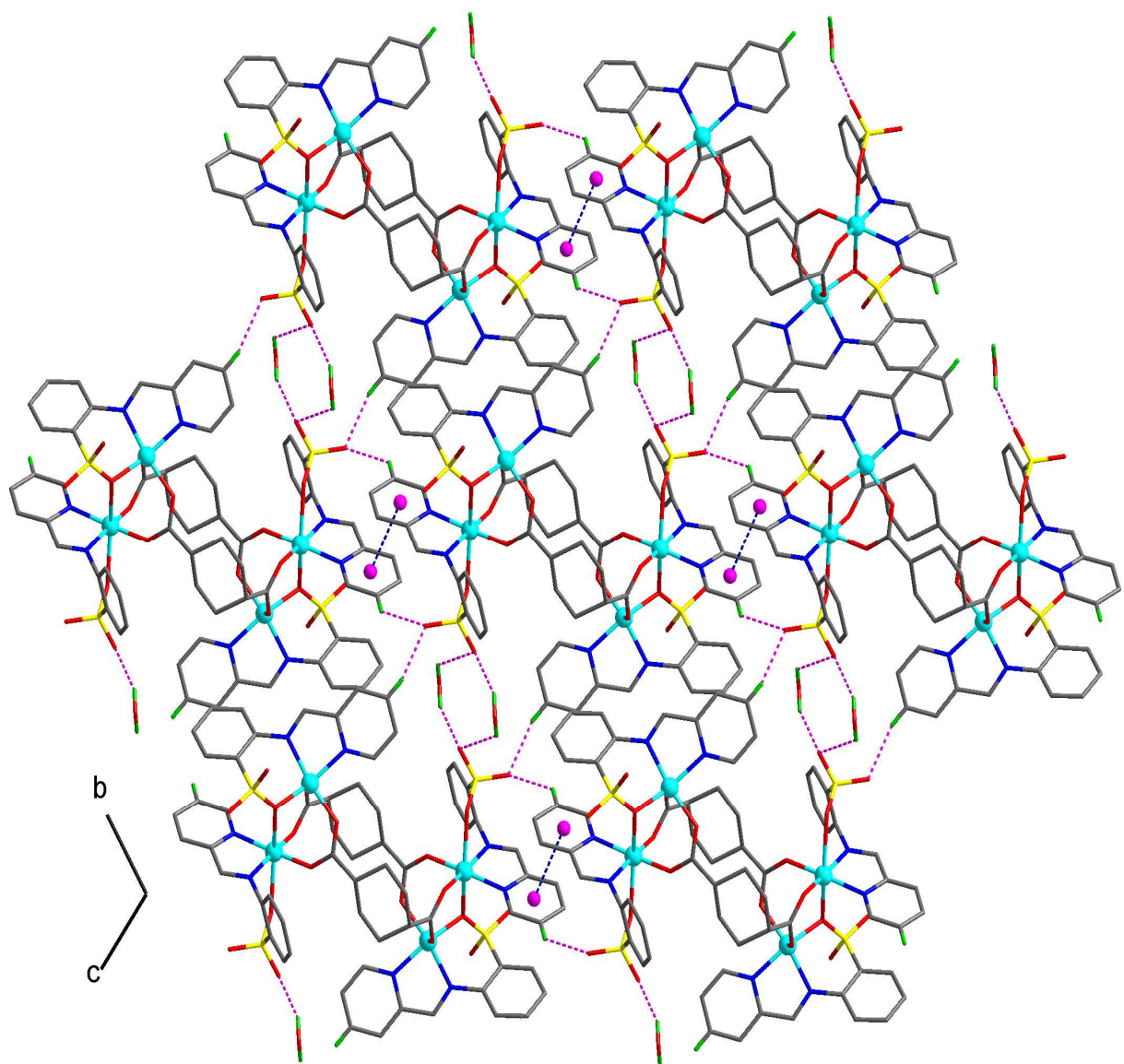




**Fig. 1.** Idealized ball and stick presentation of  $[(\text{CuL})_2(\mu_4\text{-O},\text{O}',\text{O}'',\text{O}''''\text{-CDC})]_2 \cdot 2\text{H}_2\text{O}$  (**1**). Symmetry:  $i$ )  $1-x$ ,  $1-y$ ,  $2-z$ .



**Fig. 2.** Capped stick presentation of metal-carboxylate *cuboid* formed by alternative interconnection of the six member rings (cyclohexane) and the eight member rings in  $[(\text{CuL})_2(\mu_4\text{-O},\text{O}',\text{O}'',\text{O}''''\text{-CDC})]_2 \cdot 2\text{H}_2\text{O}$  (**1**).



**Fig. 3.** Capped stick presentation of the two-dimensional supramolecular structure of  $[(\text{CuL})_2(\mu_4\text{-O},\text{O}',\text{O}'',\text{O}''''\text{-CDC})]_2 \cdot 2\text{H}_2\text{O}$  (**1**) viewed down the crystallographic  $a$ -axis. Metal cations are drawn as cyan balls.  $\pi \cdots \pi$  interactions (*centroid* $\cdots$ *centroid* distance of 3.694 Å) between the N3-pyridyl rings are shown. All H-atoms except those participating in H-bond interactions are omitted for clarity.

## Graphical Abstract

**A Cyclic Tetranuclear Cuboid Type Copper(II) Complex Doubly Supported by Cyclohexane-1,4-Dicarboxylate: Molecular and Supramolecular Structure and Cyclohexane Oxidation Activity**

Susanta Hazra, Sanghamitra Mukherjee, M. Fátima C. Guedes da Silva and Armando J. L. Pombeiro\*

The new bis( $\mu_4$ -(*ae*)-cyclohexane-1,4-dicarboxylato-O,O',O'',O''')-tetracopper(II) complex  $[(\text{CuL})_2(\mu_4\text{-O,O',O'',O'''}\text{-CDC})]_2 \cdot 2\text{H}_2\text{O}$  (**1**) provides the first example of an isolated tetranuclear 3d-system with a single metal CDC *cuboid* cage. It efficiently catalyzes the cyclohexane peroxidative oxidation with aqueous  $\text{H}_2\text{O}_2$  and without any promoter.

