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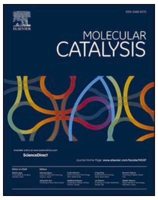

Mild oxidative functionalization of cycloalkanes catalyzed by novel dicopper(II) cores

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ABSTRACT

The search for new transition metal based catalytic systems that are active in the oxidative functionalization of such inert substrates as saturated hydrocarbons continues to be an important research direction in molecular catalysis. In the present study, two new copper(II) coordination compounds, namely a discrete dimer $[Cu_2(\mu\text{-}H_2tea)_2(nfa)_2]\cdot 2H_2O$ (**1**) and a 1D coordination polymer $[Cu_2(\mu\text{-}H_2tea)_2(\mu\text{-}Htma)]_n\cdot 4nH_2O$ (**2**) were synthesized and applied as homogeneous catalysts for the mild oxidative functionalization of cycloalkanes (cyclopentane, cyclohexane, cycloheptane, and cyclooctane). Both products **1** and **2** were self-assembled in aqueous medium from copper(II) nitrate, triethanolamine (H_3tea), sodium hydroxide, and 2-naphthoic (Hnfa) or trimesic (H_3tma) acids, isolated as stable crystalline solids, and fully characterized by standard methods including single-crystal X-ray diffraction. Their structures feature a similar type of dicopper(II) triethanolaminate cores that are decorated by terminal or bridging aromatic carboxylate ligands. Two model catalytic reactions were investigated, namely the oxidation of cycloalkanes by H_2O_2 to produce cycloalkyl hydroperoxides as intermediate products and then a mixture of cyclic alcohols and ketones as final products, and the carboxylation of cycloalkanes with $CO/S_2O_8^{2-}/H_2O$ to form cycloalkanecarboxylic acids as main products. These model reactions undergo under very mild conditions (50–60 °C) and show good efficiency. Substrate scope, selectivity features, and the effects of reaction parameters were investigated and discussed in detail. This study widens the family of multicopper(II) cores capable of catalyzing the oxidative functionalization of saturated hydrocarbons under mild conditions.

1. Introduction

The search for efficient and versatile catalytic systems capable of activating such inert substrates as saturated hydrocarbons continues to be an inspiring research direction in molecular catalysis, especially given an abundance of these hydrocarbons as main components of the petroleum and natural gas feedstocks [1–3]. Although many attractive transition metal based catalytic systems have been proposed for the activation and oxidative functionalization of alkanes, there is still a need for catalytic solutions based on abundant and low-cost metals and relatively simple ligands [4–10].

Among a variety of transition metal coordination compounds commonly applied in alkane functionalization both at laboratory and industrial scales, the catalytic systems incorporating copper are particularly attractive in view of different notable characteristics of this metal. These include the versatile redox behavior and catalytic applications, rich coordination chemistry, natural abundance and low cost [11–14], as well as the presence in many enzymatic active sites, including multicopper oxidases and pMMO (particulate methane monooxygenase) [15–18]. Hence, there is an intense research in the areas of bioinorganic copper chemistry and bioinspired and/or biomimetic catalytic transformations, aiming at the development of new Cu-based catalytic systems for the oxidative functionalization of different substrates including alkanes [15–20]. A recognized inertness of saturated hydrocarbons precludes their wide application as an attractive feedstock for the mild and single-step generation of added value oxidation products with

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alcohol, ketone, aldehyde or carboxylic acid functional groups [1–3]. However, a combination of appropriate ligand types around the redox active copper centers along with the selection of suitable oxidants might result in new molecular catalytic systems for the oxidative functionalization of alkanes, which would proceed efficiently at low temperature and pressure conditions.

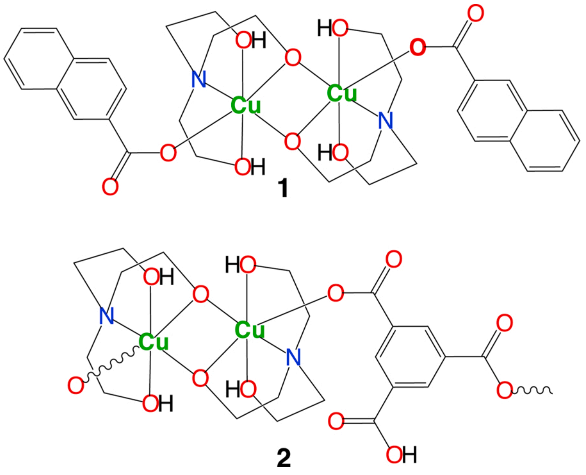
Following our continuing interest in the design and catalytic exploration of copper(II) coordination compounds, including discrete complexes [21,22] and metal-organic networks [23,24], the principal goal of this study has been to synthesize novel dicopper(II) cores stabilized by aminoalcoholate and carboxylate ligands, as well as to probe their catalytic potential in the mild oxidative functionalization of cycloalkanes as model substrates. Herein, triethanolamine (H_3tea) has been selected as a principal *N,O*-ligand given its aqueous solubility, chelating properties, low cost, and capability to stabilize multicopper cores [9]. Simple aromatic carboxylic acids such as 2-naphthoic (Hnfa) and trimesic (H_3tma) acids were chosen as supporting ligands that can also promote the oxidation of alkanes [10]. Besides, carboxylate complexes of redox-active metal centers (e.g., Co, Fe, Cu, Mn) that are soluble in nonpolar systems are widely applied as homogeneous oxidation catalysts in petroleum industry [25]. For example, cobalt(II) naphthenate and related derivatives are classical industrial catalysts for the oxidation of cyclohexane to KA oil (cyclohexanone and cyclohexanol mixture) which, despite proceeding at elevated temperatures and pressures ($T = 150-160$ °C, $P_{air} = 10-15$ atm), shows low KA oil yields not exceeding 5−10 % [25–27]. The remaining substrate is then recycled and returned to an oxidation reactor.

Hence, this work reports on the self-assembly generation, structural features and catalytic application of two new heteroleptic copper(II) derivatives, namely $[Cu_2(\mu\text{-}H_2tea)_2(nfa)_2]\cdot 2H_2O$ (**1**) and $[Cu_2(\mu\text{-}H_2tea)_2(\mu\text{-}Htma)]_n\cdot 4nH_2O$ (**2**) (Scheme 1). These coordination compounds were explored as homogeneous catalysts in two model reactions: (a) the oxidation of cycloalkanes by H_2O_2 to produce a mixture of cyclic alcohols and ketones, and (b) the carboxylation of cycloalkanes with $CO/S_2O_8^{2-}/H_2O$ to form carboxylic acids as main products (Scheme 2). These model reactions proceed under very mild conditions (50–60 °C) and exhibit good efficiency. Substrate scope, selectivity features, and the effects of reaction parameters were investigated.

2. Experimental

2.1. Reagents and methods

All reagents and solvents were obtained from commercial sources. Infrared spectra were measured on a JASCO FT/IR-4100 instrument using KBr discs (abbreviations: vs – very strong, s – strong, m–medium, w–weak, br–broad, sh – shoulder). EA (elemental analyses) were carried out on a Perkin Elmer PE 2400 Series II analyzer (Laboratory of Analyses, IST). ESI-MS(+) studies were performed on a LCQ Fleet mass spectrometer with an ESI source (Thermo Scientific). In catalytic experiments, GC (Gas chromatography) analyses were performed on an Agilent Technologies 7820A series gas chromatograph (carrier gas: helium; detector: flame ionization; capillary column: BP20/SGE, 30m × 0.22mm × 0.25 μm).



Scheme 1. Structural formulae of compounds **1** and **2**.

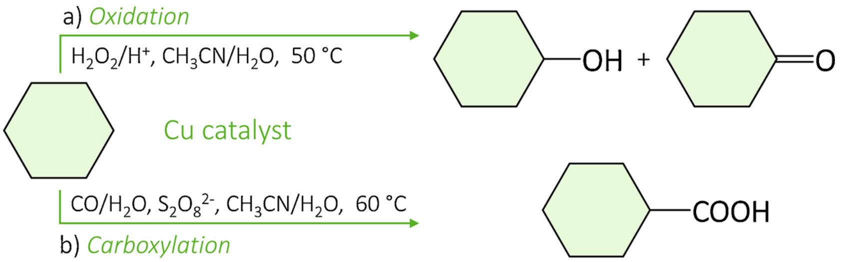
2.2. Synthesis and characterization of 1 and 2

$[Cu_2(\mu\text{-}H_2tea)_2(nfa)_2]\cdot 2H_2O$ (**1**). In a round-bottom 50 mL flask, an aqueous 1 M solution of triethanolamine (H_3tea; 1.0 mmol, 1 mL) was added dropwise to an aqueous solution of $Cu(NO_3)_2\cdot 2.5H_2O$ (10 mL, 1.0 mmol, 233 mg) with continuous stirring (magnetic stirring bar) at room temperature, producing a blue solution. In a separate small vial, 2-naphthoic acid (Hnfa, 1 mmol, 172 mg) was dissolved in an aqueous 1 M solution of NaOH (3.0 mmol, 3 mL). The obtained colorless solution was added dropwise to the main reaction mixture under constant stirring, producing a deep blue solution. This was stirred further for 12 h and then filtered off to remove any traces of precipitate using a filter paper. The deep blue filtrate was left in an open beaker (25 mL) to slowly evaporate in air at room temperature, producing greenish-blue crystals (including those of X-ray quality) in ~2 weeks. The mother liquor was decanted and the crystals of the product were washed with a minimum amount of distilled water and then manually transferred onto a filter paper, followed by their drying in air or in desiccator at room temperature. As a result, crystalline sample of compound **1** was produced in ~65 % yield, based on copper(II) nitrate. Additional crops of **1** can be obtained by further evaporation of the above-mentioned mother liquor. Small portions of crystals of **1** were isolated manually without being washed and dried, and subjected to single-crystal X-ray diffraction. Anal. Calculated for $C_{34}H_{46}Cu_2N_2O_{12}$ (MW 801.8): C 50.93, H 5.78, N 3.49; found: C 50.90, H 5.75, N 3.41. FT-IR (KBr, cm^{-1}): 3363 (s) and 3150 (m) $\nu(OH/H_2O)$, 3051 (w) $\nu_{as}(CH)$, 2870 (w) $\nu_s(CH)$, 1626 (m sh), 1599 (s sh), 1584 (s sh), 1548 (s) $\nu_{as}(COO)$, 1464 (m), 1432 (m), 1391 (s sh), 1377 (s) $\nu_s(COO)$, 1228 (m), 1097 (m), 1027 (w), 1015 (w), 967 (w), 953 (m), 926 (m), 837 (m), 789 (s), 767 (s), 730 (m), 673 (m), 638 (m), 602 (m), 491 (m), 477 (m), 419 (m). ESI-MS(+) ($H_2O/CH_3CN/H^+$), *m/z*: 593 $[Cu_2(H_2tea)_2(nfa)]^+$, 421 $[Cu_2(H_2tea)_2(Htea)]^+$.

$[Cu_2(\mu\text{-}H_2tea)_2(\mu\text{-}Htma)]_n\cdot 4nH_2O$ (**2**). This compound was prepared following a procedure described for **1** but using trimesic acid (Htma, 0.5 mmol, 105 mg) instead of 2-naphthoic acid. Blue crystals of the compound **2** were obtained in ~55 % yield, based on copper(II) nitrate. Small portions of crystals of **2** were isolated manually without being washed and dried, and subjected to single-crystal X-ray diffraction. Anal. Calculated for $C_{21}H_{40}Cu_2N_2O_{16}$ (**2**, MW 703.6): C 35.85, H 5.73, N 3.98; found: C 36.06, H 5.52, N 4.14. FT-IR (KBr, cm^{-1}): 3361 (vs) $\nu(OH/H_2O)$, 2963 (w) $\nu_{as}(CH)$, 2874 (w) $\nu_s(CH)$, 1613 (s) $\nu_{as}(COO)$, 1438 (s), 1383 (s) and 1361 (s sh) $\nu_s(COO)$, 1050 (m), 929 (w), 760 (m), 724 (s), 478 (m), 427 (m). ESI-MS(+) ($H_2O/CH_3CN/H^+$), *m/z*: 631 $[Cu_2(H_2tea)_2(H_2tma)]^+$, 421 $[Cu_2(H_2tea)(Htea)]^+$.

2.3. X-ray crystal structure determination

The single crystals of **1** and **2** were mounted using Fomblin© and a cryoloop. The X-ray data was collected on a BRUKER D8 QUEST diffractometer (graphite-monochromated radiation, Mo Kα, λ = 0.7107 Å). APEX3 program [28] was used for monitoring the collection of data, which was also corrected for Lorentzian, polarization, and absorption effects with SAINT [29] and SADABS [30]. SHELXT [31] and SHELXL-97 [32] software was used for structure solution and full matrix least-squares refinement on F^2, respectively. These programs are a part of the WINGX-Version 2014.1 package [33,34]. Full-matrix least-squares refinement was applied for the non-H atoms with anisotropic thermal parameters. All hydrogen atoms of CH moieties were placed



Scheme 2. Mild Cu-catalyzed oxidation (a) and carboxylation (b) of cyclohexane as a model substrate.

into the idealized positions and refined at a parent C atom. The OH/H_2O hydrogen atoms were located from the electron density map and fixed. In **2**, a squeeze procedure was applied to remove disordered water solvent molecules. CCDC 2,018,678 − 2,018,679.

*Crystal data for **1***: $C_{34}H_{46}Cu_2N_2O_{12}$, $M = 801.81$, $\lambda = 0.71073$ Å (Mo-*K*α), $T = 296(2)$ K, triclinic, space group *P-1*, $a = 7.5163(4)$, $b = 8.0649(4)$, $c = 15.5293(8)$ Å, $\alpha = 95.232(2)$, $\beta = 94.502(2)$, $\gamma = 109.528(2)°$, $V = 877.54(8)$ Å^3, $Z = 1$, $D_c = 1.517$ g/cm^3, $\mu = 1.277$ mm^{-1}, 45,979 reflections collected, 5417 unique, $I > 2\sigma(I)$ ($R_{int} = 0.0333$), $R_1 = 0.0280$, $wR_2 = 0.0661$, GOF on $F^2 = 1.038$. *Crystal data for **2***: $C_{21}H_{32}Cu_2N_2O_{12}\cdot$(solvent), $M = 631.59$, $\lambda = 0.71073$ Å (Mo-*K*α), $T = 296(2)$ K, orthorhombic, space group *Pbcn*, $a = 14.9193(9)$, $b = 18.1974(10)$, $c = 12.4831(6)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 3389.1(3)$ Å^3, $Z = 4$, $D_c = 1.238$ g/cm^3, $\mu = 1.304$ mm^{-1}, 28,125 reflections collected, 3481 unique, $I > 2\sigma(I)$ ($R_{int} = 0.0582$), $R_1 = 0.0401$, $wR_2 = 0.0970$, GOF on $F^2 = 1.044$.

2.4. Catalytic oxidation reactions

Cycloalkane oxidation reactions were run in air atmosphere in thermostated glass vessels equipped with a reflux condenser. The reactions were performed at 50 °C under vigorous stirring in CH_3CN as solvent (up to 5 mL of the total reaction mixture volume). In a typical catalytic test, catalyst **1** or **2** (10 μmol), acid promoter (0.1 mmol as a stock solution in CH_3CN), GC (gas chromatography) internal standard (CH_3NO_2, 50 μL), and cycloalkane substrate (2 mmol) were added into a reaction vessel containing CH_3CN solution. Then, the reaction was initiated by adding H_2O_2 (50 % in H_2O, 10 mmol) in one portion. The reaction progress was monitored by withdrawing small aliquots in regular time periods. Prior to GC analysis, the aliquots were treated with triphenylphosphine for reducing the remaining H_2O_2 and cycloalkyl hydroperoxides that are commonly formed as initial products in the oxidation of cycloalkanes. In several cases, the samples were analyzed by GC two times, before and after the addition of PPh_3, aiming at confirming the formation of cycloalkyl hydroperoxides (Shul'pin's method [35–37]). GC peak allocation was performed by comparing the chromatograms with those of authentic samples. The quantification of products was performed using nitromethane as an internal standard. Blank tests confirmed that cycloalkane oxidations do not proceed in the absence of copper catalyst (only traces of oxidation products can be detected).

2.5. Catalytic carboxylation reactions

The cycloalkane carboxylation reactions were run in stainless steel autoclaves (20.0 mL volume), equipped with a Teflon-coated magnetic stirring bar. In a typical catalytic test, catalyst **1** or **2** (10 μmol) was added to an autoclave, followed by the introduction of $K_2S_2O_8$ (1.50 mmol), H_2O (2.0 mL) and CH_3CN (4.0 mL), and cycloalkane (1.00 mmol). Then the autoclave was sealed, flushed three times with CO, and finally pressurized CO (20 atm). Caution: Due to toxicity of CO, all operations must be carried out in a well-ventilated hood! The reaction was run at 60 °C for 4 h using a magnetic stirrer and an oil bath with temperature control. After this time, the autoclave was cooled down using an ice bath, degassed and opened. The reaction mixture was transferred to a Schlenk flask. Diethyl ether (9.0 mL) and cycloheptanone (45 μL, GC internal standard) were added. In the carboxylation of cycloheptane, cyclohexanone (45 μL) was used instead as a GC standard. The obtained mixture was vigorously stirred for 10 min, and the organic layer was analyzed by GC (internal standard method). Cycloalkane carboxylic acids were formed as principal carboxylation products along with the corresponding cyclic alcohols and ketones (oxidation products). Attribution of GC peaks was made by comparison with chromatograms of authentic samples.

3. Results and discussion

3.1. Synthesis of copper (II) catalysts 1 and 2

The self-assembly reactions, at ~25 °C in water, between copper(II) nitrate (metal source), triethanolmaine (principal ligand), 2-naphthoic or trimesic acid (supporting ligand), and sodium hydroxide (regulator of pH) led to the generation of new copper(II) derivatives $[Cu_2(\mu\text{-}H_2tea)_2(nfa)_2]\cdot 2H_2O$ (**1**) and $[Cu_2(\mu\text{-}H_2tea)_2(\mu\text{-}Htma)]_n\cdot 4nH_2O$ (**2**). These compounds were obtained as stable crystalline solids in good yields and were characterized by FTIR spectroscopy, elemental analysis and single crystal X-ray diffraction. Both compounds feature a similar type of dicopper(II) triethanolaminate $[Cu_2(\mu\text{-}H_2tea)_2]^{2+}$ cores that are stabilized by the terminal nfa$^-$ ligands in **1** or extended by the μ-Htma^{2-} linkers into a 1D metal-organic chain in **2**. These copper(II) derivatives also dissolve in the reaction mixtures typically used for the oxidation ($H_2O/CH_3CN/H_2O_2/H^+$) or carboxylation ($H_2O/CH_3CN/S_2O_8^{2-}$) of cycloalkanes, thus enabling their application as homogeneous catalysts in the cycloalkane functionalization reactions.

3.2. Crystal structures

The structure of $[Cu_2(\mu\text{-}H_2tea)_2(nfa)_2]\cdot 2H_2O$ (**1**) contains a discrete dicopper(II) molecular unit, which is composed of two symmetry equivalent Cu1 centers, two μ-H_2tea$^-$ moieties, and two terminal nfa$^-$ ligands (Fig. 1a). The Cu1 atom is 6-coordinate and adopts a distorted $\{CuNO_5\}$ octahedral environment. This is constructed from one carboxylate O atom from nfa$^-$ [Cu−O 1.9533(1) Å] as well as one N [Cu−N 2.0482(1) Å] and two μ-O [Cu−O 1.9445(1) and 1.9382(1) Å] donors from the μ-H_2tea$^-$ moiety in equatorial sites, while the apical positions are taken by the remaining OH groups of the μ-H_2tea$^-$ ligands [Cu−O 2.4584(1) and 2.5513(1) Å]. These bonding parameters as well as a short Cu…Cu separation of 2.9130(6) Å are comparable with those found in related dicopper(II) cores [38,39].

The crystal structure of $[Cu_2(\mu\text{-}H_2tea)_2(\mu\text{-}Htma)]_n\cdot 4nH_2O$ (**2**) features a dicopper(II) triethanolaminate core (Fig. 1b) that is essentially similar to that of **1**. In **2**, the symmetry equivalent Cu1 centers are also 6-coordinate and show a distorted $\{CuNO_5\}$ octahedral geometry. The main difference lies in the type of aromatic carboxylate ligand which is a μ-bridging in **2** (μ-Htma^{2-}), thus generating a 1D metal-organic chain structure (Fig. 1c). The μ-Htma^{2-} ligand acts as a linker between the adjacent dicopper(II) units with a Cu…Cu separation of 10.7085(9) Å,

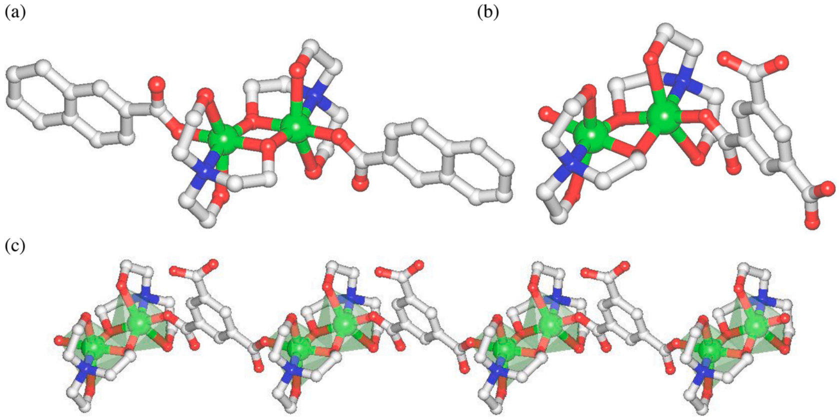


Fig. 1. Ball-and-stick representation of the crystal structures of **1** (a) and **2** (b, c). (a) Molecular [Cu_2(μ-H_2tea)$_2$(nfa)$_2$] unit. (b) [Cu_2(μ-H_2tea)$_2$(μ-Htma)] structural fragment. (c) 1D metal-organic chain with coordination polyhedra around Cu(II) centers. H atoms and crystallization water molecules are omitted; Cu (green), O (red), N (blue), C (gray) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

while the Cu…Cu distance within the Cu_2 core is also rather short [2.8545(7) Å].

3.3. Cu-catalyzed oxidation of cyclohexane

Compounds **1** and **2** were screened as homogeneous catalysts for the mild oxidation of C_5-C_8 cycloalkanes by hydrogen peroxide to give the corresponding cyclic alcohols and ketones as final products (Scheme 2a). Cyclohexane was used as a model substrate due to an industrial relevance of its oxidation products (KA oil) [25–27]. The oxidation reactions undergo in aqueous acetonitrile medium under mild conditions (atmospheric pressure, aqueous H_2O_2 as oxidant, 50 °C).

Given the presence of similar dicopper(II) triethanolaminate cores, the compounds **1** and **2** exhibit the comparable product accumulation patterns (Fig. 2) with the total product yields of 21−22 % after 90 min of the reaction; hereinafter, all the product yields are based on cycloalkane substrate: (moles of products per moles of cycloalkane)×100 %. For both catalytic systems, the cyclohexane oxidation undergoes with a linear increase of product yields in the first 90 min of reaction, resulting in TOF values of 29 and 28 h^{-1} for **1** and **2**, respectively (turnover frequencies, TOFs, were calculated as moles of products formed per mole of catalyst per hour). These oxidation reactions require the presence of a catalytic amount of acid promoter such as sulfuric acid. Cyclohexanol is generated predominantly to cyclohexanone at the beginning of reaction. This observation as well as the fact that the alcohol yields differ if the GC analyses of the reaction mixtures performed before and after the treatment with a reducing agent (PPh_3, Shul'pin's method [35–37]) testify the formation of cyclohexyl hydroperoxide as a primary (intermediate) product in the present cyclohexane oxidation.

As the catalytic systems based on **1** and **2** require the use of an acid promoter, the influence of various acids on the cyclohexane oxidation was investigated (Fig. 3). Prior studies demonstrated [7–10] that the presence of a catalytic amount of strong acid can demonstrate a number of advantages in the reaction system, namely (1) an activation of Cu catalyst via protonation of aminoalcoholate and carboxylate ligands, (2) a facilitation of H^+-transfer steps, and (3) an improvement of the oxidation properties of hydrogen peroxide in acidic medium and preventing its decomposition via catalase activity. In the oxidation of cyclohexane, the product accumulation curves display distinct trends in the presence of sulfuric, nitric, and trifluoroacetic (TFA) acids as promoters (Fig. 3), with the maximum yields observed for both catalysts **1** and **2** when using H_2SO_4. For **1**, a linear trend of product accumulation is seen in the first 90 (H_2SO_4, HNO_3) or 60 (TFA) min with the corresponding TOF values of 29, 25, and 35 h^{-1}, respectively. For **2**, a linear trend is present in the first 90 (H_2SO_4) or 120 (HNO_3, TFA) min with TOFs of 28, 18, and 14 h^{-1}, respectively. After approaching the steady state, the oxidation of cyclohexane stops eventually due to the deactivation of catalyst and/or consumption of oxidant.

Given a good performance of sulfuric acid in terms of both product yields and reaction rates, its loading was also optimized for both catalysts (Fig. 4), resulting in an optimum acid-to-catalyst molar ratio of 10:1 with the total product yields of 21−22 %. The best cyclohexane

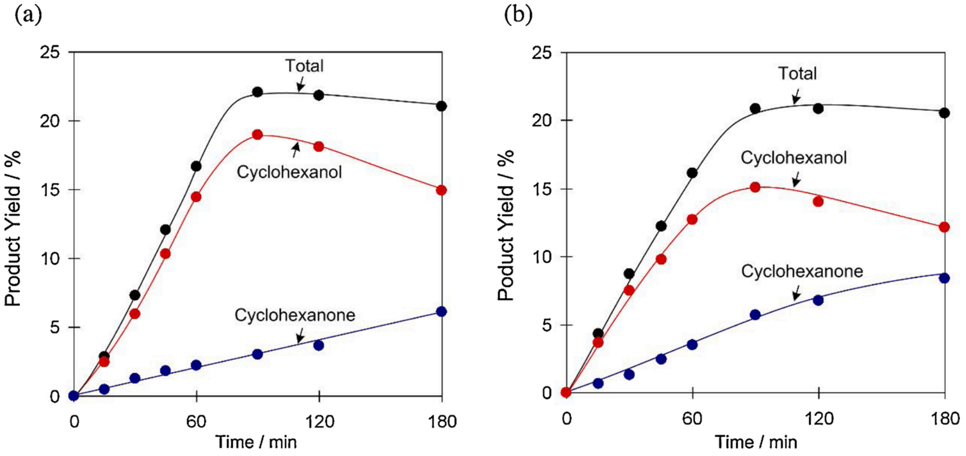


Fig. 2. Product accumulation curves in the oxidation of cyclohexane to cyclohexanol and cyclohexanone catalyzed by **1** (a) and **2** (b). Conditions: catalyst (10 μmol), H_2SO_4 (0.1 mmol), C_6H_{12} (2.0 mmol), H_2O_2 (aq. 50 %, 10.0 mmol), CH_3CN (total reaction volume up to 5 mL), 50 °C.

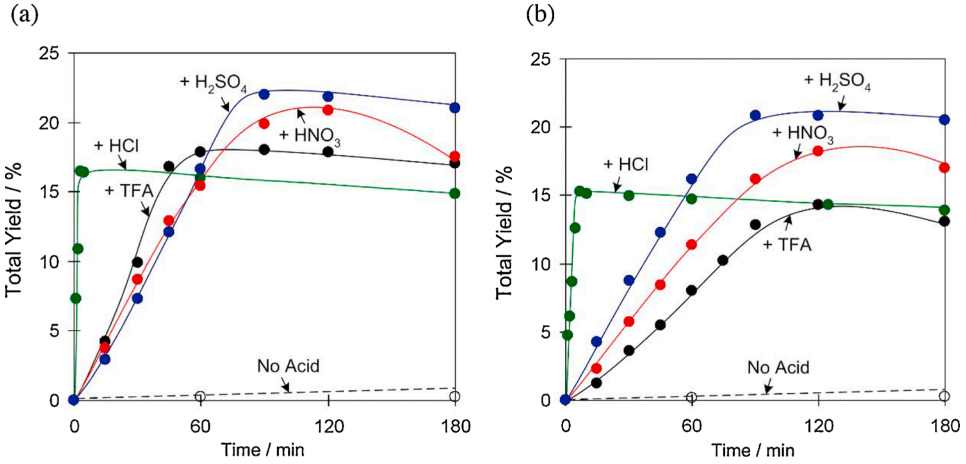


Fig. 3. Effect of the acid promoter in the oxidation of cyclohexane to cyclohexanol and cyclohexanone (total yield vs. time) catalyzed by **1** (a) and **2** (b). Conditions: catalyst (10 μmol), acid promoter (0.1 mmol), C_6H_{12} (2.0 mmol), H_2O_2 (aq. 50 %, 10.0 mmol), CH_3CN (total reaction volume up to 5 mL), 50 °C.

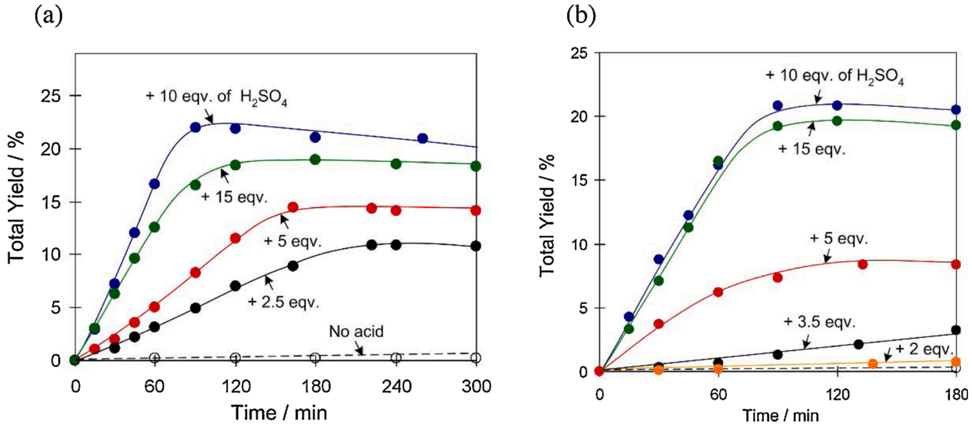


Fig. 4. Effect of the amount of H_2SO_4 on the oxidation of cyclohexane to cyclohexanol and cyclohexanone (total yield vs. time) catalyzed by **1** (a) and **2** (b). Conditions: catalyst (10 μmol), H_2SO_4 promoter (0–0.15 mmol), C_6H_{12} (2.0 mmol), H_2O_2 (aq. 50 %, 10.0 mmol), CH_3CN (total reaction volume up to 5 mL), 50 °C.

oxidation performance obtained when using this acid-to-catalyst ratio suggests the need for an increased concentration of H^+ ions to allow the activation of catalyst and the prevention of an eventual catalase activity (H_2O_2 decomposition) in acidic medium. However, higher amount of acid (acid-to-catalyst molar ratio of 15:1, Fig. 4) is not beneficial as this may provoke full protonation of ligands and their decoordination from copper centers, thus resulting in inferior catalytic activity. In fact, under similar reaction conditions (conditions of Fig. 3, 2 h), various control tests on the cyclohexane oxidation catalyzed by the $Cu(NO_3)_2$ (3.6 %), $Cu(NO_3)_2$/H_3tea/Hnfa (5.7 %), $Cu(NO_3)_2/H_2SO_4$ (5.3 %), $Cu(NO_3)_2$/H_3tea/H_2SO_4 (9.8 %), $Cu(NO_3)_2$/Hnfa/H_2SO_4 (11.1 %), and $Cu(NO_3)_2$/H_3tea/Hnfa/H_2SO_4 (11.4 %) systems resulted in inferior total product yields (% values in brackets) than those obtained in the presence of compounds **1** (21.8 %) and **2** (20.8 %) as catalysts. Despite appreciable product yields attained when using the in-situ generated catalytic systems containing full combination of ligands and acid promoter, the performance of isolated Cu(II) compounds **1** and **2** is significantly superior. This behavior is also in good agreement with the results reported for other copper catalytic systems [9].

Interestingly, a different promoting behavior is detected in the presence of hydrochloric acid with a drastically increased reaction rate of cyclohexane oxidation (Fig. 3). As a result, the reaction is very fast and completes in 3 or 7 min with the total product yields of 17 or 15 % for catalysts **1** and **2**, respectively (TOFs = 680−250 h^{-1}). Although an unusual reaction accelerating role of hydrochloric acid is not clearly implicit if compared to other strong acids, it may be associated to a capability of chloride anions to behave as additional terminal or bridging ligands as well as to stabilize copper(I) species or eventual Cu-peroxo intermediates [39]. It should also be mentioned that the cyclohexane oxidation reactions catalyzed by CuO (0.2 %), CuO/HCl (6.6 %), $CuCl_2$ (6.2 %) and $CuCl_2$/HCl (7.3 %) are less efficient as those in the presence of **1** and **2** (15 − 17 % total yields).

3.4. *Cu-catalyzed oxidation of C_5−C_8 cycloalkanes*

After the above optimization tests, further reactions were run to explore a substrate scope in the Cu-catalyzed cycloalkane oxidations (Fig. 5). The catalysts **1** and **2** behave in a different way concerning the product accumulation patterns and the maximum total yields in the oxidation of C_6−C_8 cycloalkanes. For the catalyst **1**, the highest activity (29 % overall product yield) was detected in the oxidation of cycloheptane, followed by cyclooctane (27 %) and cyclohexane (22 %). In the presence of catalyst **2**, the trend is different with a superior activity observed in the oxidation of cyclohexane (21 % overall product yield), cyclooctane (16 %), and then cycloheptane (13 %). A decreased activity of **2** vs. **1** can be associated with its structural features (presence of a μ-carboxylate linker and 1D coordination polymer structure). Although some overoxidation processes can occur at prolonged reaction times (Fig. 5), good overall selectivities toward main products, i.e. cyclic alcohols and ketones (commonly above 90 % within the first reaction hours), were observed in the present systems catalyzed by **1** and **2**. Both catalysts **1** and **2** reveal a decreased efficacy in the oxidation of

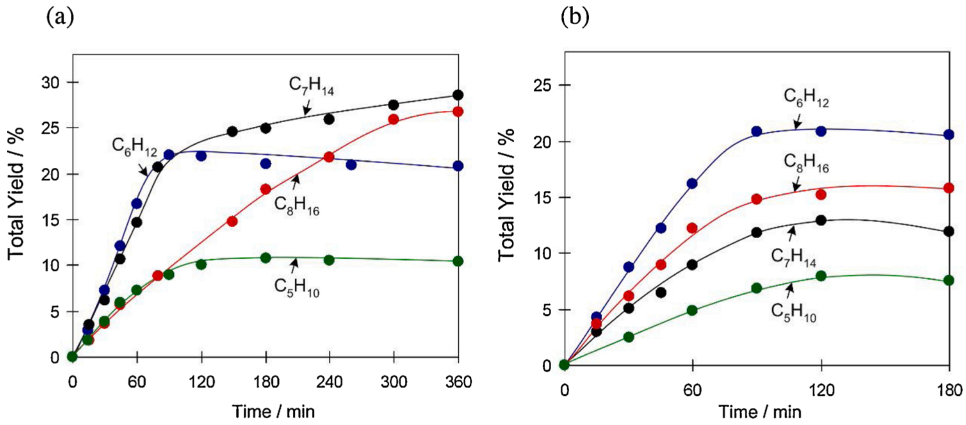


Fig. 5. Oxidation of C_5–C_8 cycloalkanes to the corresponding alcohols and ketones (total yield vs. time) catalyzed by **1** (a) and **2** (b). Conditions: catalyst (10 μmol), H_2SO_4 (0.1 mmol), cycloalkane (2.0 mmol), H_2O_2 (aq. 50 %, 10.0 mmol), CH_3CN (total reaction volume up to 5 mL), 50 °C.

cyclopentane with the overall product yields of 10 and 7%, respectively (Fig. 5). With an exception of cyclopentane, the total 22−29 % yields of cyclic alcohols and ketones obtained in the oxidation of other cycloalkanes (cyclohexane, cycloheptane, and cyclooctane) are significantly higher than those commonly observed in, for example, industrial oxidation of C_6H_{12} to KA oil with a homogeneous Co(II) naphthenate catalyst [25,26]. The attained herein yields of products when using **1** and **2** are also comparable or better than those shown by various catalysts in related cycloalkane oxidation, including the reactions catalyzed by other Cu coordination compounds composed of resembling types of ligands [9,21,22].

3.5. *Selectivity and mechanistic features in Cu-catalyzed oxidation of alkanes*

To get some further details on the nature of oxidizing species in the present Cu-catalyzed reactions, we investigated the oxidation of specific alkane substrates and determined different selectivity parameters (Table 1). Thus, the oxidation of a linear alkane, *n*-heptane, undergoes without specific preference to a particular secondary C atom, as attested by the regioselectivity C(1):C(2):C(3):C(4) parameters of 1:4:5:6 and 1:4:4:5 for the catalysts **1** and **2**, respectively. The oxidation of methylcyclohexane shows the moderate bond selectivity 1°:2°:3° parameters of 1:5:8 (**1**) and 1:4:7 (**2**). The Cu-catalyzed oxidation reactions of *cis*- and *trans*-1,2-dimethylcyclohexane undergo in a non-stereoselective way with the *trans/cis* parameters of 0.8−1.0. All these selectivity features, the formation of cycloalkyl hydroperoxides as intermediate products, and the previous data on Cu-catalyzed alkane oxidation [7–10, 21–24] testify the presence of indiscriminate and potent oxidizing species like hydroxyl radicals.

Hence, having this experimental evidence and considering a prior background for resembling Cu-based homogeneous catalysts [9,10], the following radical type mechanistic steps can occur in the present cycloalkane oxidation reactions: (i) reaction of Cu catalyst with hydrogen peroxide to furnish hydroxyl radicals ($HO^•$); (ii) cycloalkane (CyH) reaction with $HO^•$ to form cycloalkyl radicals ($Cy^•$); (iii) coupling of $Cy^•$ with O_2 to give cycloalkyl peroxo radicals ($CyOO^•$); (iv) conversion of $CyOO^•$ to cycloalkylperoxide anions ($CyOO^−$), (v) generation of cycloalkyl hydroperoxides (CyOOH) as primary products, (vi) decomposition of CyOOH to furnish cyclic alcohols (CyOH) and ketones (Cy'=O) as final products.

Table 1
Regio-, bond- and stereoselectivity parameters in the Cu-catalyzed oxidation of alkanes.[a]

Selectivity (alkane substrate)	1	2
Regioselectivity		
C(1):C(2):C(3):C(4) (*n*-heptane)[b]	1:4:5:6	1:4:4:5
Bond selectivity		
1°:2°:3° (methylcyclohexane)[c]	1:5:8	1:4:7
Stereoselectivity		
trans/cis (*cis*-1,2-dimethylcyclohexane)[d]	1.0	0.8
trans/cis (*trans*-1,2-dimethylcyclohexane)[d]	0.9	0.8

[a] Conditions: catalyst (5 μmol), H_2SO_4 (0.05 mmol), alkane (1.0 mmol), H_2O_2 (aq. 50 %, 5.0 mmol), CH_3CN (total reaction volume up to 2.5 mL), 2 h, 50 °C. Selectivities were calculated on the basis of the molar ratios of isomeric alcohol products; normalization was made considering the number of H atoms at each C atom.

[b] C(1):C(2):C(3):C(4) refers to reactivity of H atoms at C(1), C(2), C(3), and C (4) atoms of *n*-heptane.

[c] 1°:2°:3° stands for reactivity of H atoms at primary, secondary and tertiary C atoms of methylcyclohexane.

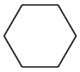
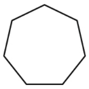
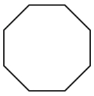
[d] Parameter *trans/cis* refers to the ratio of the tertiary alcohol products with mutual *trans* and *cis* orientation of CH_3 groups.

3.6. *Cu-catalyzed carboxylation of C_5−C_8 cycloalkanes*

Apart from the oxidation of C_5−C_8 cycloalkanes, the compounds **1** and **2** were also tested as catalysts for the single-step carboxylation of these substrates to give the corresponding cycloalkanecarboxylic acids as main carboxylation products along with cyclic alcohols and ketones as oxidation products (Scheme 2b). In these Cu-catalyzed carboxylation reactions, cycloalkane is treated with carbon monoxide (source of carbonyl functionality), water (source of hydroxyl group), and potassium peroxodisulfate (oxidizing agent) at 60 °C in H_2O/CH_3CN medium [9,40–42]. It should be mentioned that there is no need for an acid promoter in the carboxylation reactions. The results are collected in Table 2.

Both catalysts **1** and **2** show a comparable level of activity in the carboxylation of cycloalkanes with the overall product yields attaining 28 and 33 % based on cycloalkane (TOFs 6.9 and 8.2 h^{-1}). For the cyclopentane and cyclohexane substrates, a slightly superior activity was observed when using **1**, resulting in the yields of cyclopentanecarboxylic and cyclohexanecarboxylic acids in the 29−30 % range and TOFs of 8.0−8.2 h^{-1} (Table 2, entries 1, 3). These cycloalkanes are also more prone to undergo the carboxylation in comparison with the oxidation reactions, as attested by rather low yields of cyclic alcohols and ketones (3−4% total yields). However, the carboxylation reactions of cycloheptane and cyclooctane lead to the modest yields of carboxylic acids (14−16 % of cycloheptanecarboxylic acid; 7% of cyclooctanecarboxylic acid) and more pronounced yields of oxidation products (9−16 % total yields). This reactivity of cycloalkanes with regard to carboxylation reactions can be explained by a stability of

Table 2
Single-step carboxylation of cycloalkanes catalyzed by **1** and **2**.[a]

Entry	Cycloalkane (CyH)	Catalyst	Product yield, %[b]				
			Acid (CyCOOH)	Ketone (Cy'=O)	Alcohol (CyOH)	Total	TOF, h^{-1} [c]
1		**1**	29.1	2.4	1.2	32.7	8.2
2		**2**	24.6	2.2	0.8	27.6	6.9
3		**1**	29.8	1.8	0.5	32.1	8.0
4		**2**	24.0	2.2	0.5	26.7	6.7
5		**1**	14.4	6.3	2.8	23.5	5.9
6		**2**	16.0	8.8	2.5	27.3	6.8
7		**1**	6.8	10.8	6.2	23.8	6.0
8		**2**	7.0	11.7	6.0	24.7	6.2

[a] Conditions: cycloalkane (1.00 mmol), Cu catalyst (10 μmol), CO (20 atm), $K_2S_2O_8$ (1.50 mmol), H_2O (2.0 mL)/MeCN (4.0 mL), 60 °C, 4 h in an autoclave (20.0 mL capacity).

[b] (Moles of product per moles cycloalkane)×100 %; CyCOOH are generally the main carboxylation products; Cy'=O and CyOH are also generated as oxidation products.

[c] Moles of products per mol of catalyst per hour.

cycloalkyl radicals, following a reverse trend ($Cy_6 \leq Cy_5 < Cy_7 < Cy_8$) [43]. This means that the carboxylation is not a favorable process for cycloalkyl radicals having higher stability (Cy_7 and Cy_8), which are more susceptible to undergo oxidation reactions thus explaining significantly higher yields of the oxidation products in the reactions of C_7H_{14} and C_8H_{16} (Table 2, entries 5−8). Despite not being very high from a synthetic viewpoint, the overall product yields (up to 33 %) in the present carboxylation reactions are appreciable given the inertness of cycloalkanes and rather mild reaction conditions applied. Attempts to further increase the yields of carboxylic acid products by prolonging the reaction time, augmenting the temperature or using increased amounts of carboxylating agent and oxidant were not successful.

The obtained results on the carboxylation of cycloalkanes as well as prior background for related Cu-catalyzed transformations indicate that the reactions proceed via a free-radical mechanism involving sulfate $SO_4^{\bullet -}$ radical anions as main species [9,40–42]. Hence, the following reaction steps can be present in these carboxylation reactions: (i) generation of sulfate radical anions ($SO_4^{\bullet -}$) via homolysis of $S_2O_8^{2-}$; (ii) reaction of cycloalkane (CyH) with $SO_4^{\bullet -}$ to give cycloalkyl radicals ($Cy^{\bullet}$); (iii) carbonylation of $Cy^{\bullet}$ with CO to form cycloacyl radicals ($CyCO^{\bullet}$); (iv) oxidation of $CyCO^{\bullet}$ to furnish cycloacyl cations ($CyCO^{+}$); (v) hydrolysis of $CyCO^{+}$ to give cycloalkanecarboxylic acid product (CyCOOH). The competitive oxidation processes of $Cy^{\bullet}$ can also occur explaining the formation of cyclic alcohols and ketones as oxidation products.

4. Conclusions

In this work, we showed that new copper(II) coordination compounds with notable catalytic potential in mild oxidative functionalization of cycloalkanes can be easily generated by self-assembly in water and using simple and commercially available chemicals. The obtained $[Cu_2(\mu\text{-}H_2tea)_2(nfa)_2]\cdot 4H_2O$ (**1**) and $[Cu_2(\mu\text{-}H_2tea)_2(\mu\text{-}Htma)]_n\cdot 4nH_2O$ (**2**) products were structurally characterized, revealing a similar type of dicopper(II) triethanolaminate cores but distinct stabilizing or linking carboxylate ligands.

Apart from extending the family of heteroleptic copper(II) derivatives bearing aminoalcoholate and carboxylate ligands, these dicopper(II) cores were also applied as efficient homogeneous catalysts for the oxidation of cycloalkanes leading to the formation of cyclic alcohol and ketone products. Besides, both catalysts are also active for the mild carboxylation of cycloalkanes to give the corresponding cycloalkanecarboxylic acids along with alcohols and ketones in up to 33 % product yields based on the cycloalkane substrate. Given a recognized inertness of saturated hydrocarbons and very mild reaction conditions (50−60 °C, aqueous acetonitrile medium), the achieved herein product yields can be considered as rather high in the field of oxidative functionalization of alkanes [1–5], despite being modest from an organic synthesis perspective. In fact, an industrial oxidation of cyclohexane to a mixture of cyclohexanone and cyclohexanone (KA oil, intermediate in nylon synthesis) utilizes a homogeneous Co(II) naphthenate catalyst and proceeds under harsher reaction conditions (150−160 °C), resulting in significantly lower overall product yields (5−10 %).

Since the compounds **1** and **2** are not only active in the oxidative functionalization of saturated hydrocarbons but also display an *N,O*-donor environment at Cu centers, these can be classified as bioinspired catalysts with a relevance to pMMO (particulate methane monooxygenase) [18], a unique multicopper enzyme capable of oxidizing the CH bonds of inert alkanes. In addition, the reported herein compounds widen the family of multicopper core catalysts applied in various oxidation reactions [9,44–46]. Further research on the synthesis of new types of multicopper catalysts assembled from simple and readily available building blocks, as well as the exploration of such Cu coordination compounds in the mild oxidative functionalization of alkanes and other substrates is underway.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Kiryl I. Trusau: Investigation, Data curation, Validation. **Marina V. Kirillova:** Investigation, Conceptualization, Methodology, Visualization, Writing - original draft, Writing - review & editing. **Vânia André:** Investigation, Data curation, Validation. **Andrew I. Usevich:** Data curation, Supervision, Validation. **Alexander M. Kirillov:** Conceptualization, Visualization, Funding acquisition, Writing - original draft, Writing - review & editing.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2021.111401.

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