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Mild oxidative functionalization of alkanes and alcohols catalyzed by new mono- and dicopper(II) aminopolyalcoholates

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ABSTRACT

The new mono- and dicopper(II) complexes $[Cu(H_3L^1)(NCS)]$ (**1**) and $[Cu_2(\mu\text{-}HL^2)_2(NCS)_2]$ (**2**) were easily self-assembled from $Cu(CH_3COO)_2{\cdot}H_2O$, NaNCS, NaOH and N,N,N′,N′-tetrakis(2-hydroxyethyl)ethylenediamine (H_4L^1) or N-ethyldiethanolamine (H_2L^2), respectively. They were fully characterized by IR spectroscopy, ESI-MS(±), elemental and single-crystal X-ray diffraction analyses, and applied as homogeneous catalysts for (i) the oxidation of alkanes by *t*-BuOOH in air to alkyl peroxides, alcohols and ketones, and in turn the oxidation of alcohols to ketones, and (ii) the single-pot aqueous medium hydrocarboxylation, by CO, H_2O and $K_2S_2O_8$, of various linear and cyclic C_n (n = 5–8) alkanes into the corresponding C_{n+1} carboxylic acids. Compound **1** was significantly more active in the oxygenation of alkanes and oxidation of alcohols, allowing to achieve 18% yield (TON = 800) of oxygenates in the oxidation of cyclohexane, and 78% yield (TON = 780) of cyclohexanone in the oxidation of cyclohexanol. In alkane hydrocarboxylations, **1** and **2** exhibited comparable activities with the total yields (based on alkane) of carboxylic acids attaining 39%. The selectivity parameters for oxidative transformations were measured and discussed, supporting free-radical mechanisms.

1. Introduction

The development of new transition metal catalysts and single-pot methods for the selective oxidative functionalization of alkanes is a topic of high interest in the fields of homogeneous catalysis, organic and green chemistry [1–9]. As naturally abundant and potentially cheap carbon raw materials, alkanes are attractive substrates for added value organic chemicals (alcohols, ketones, aldehydes and carboxylic acids) [1–15]. Unfortunately, the high inertness of these hydrocarbons constitutes a considerable limitation towards their broad application for direct syntheses of oxygenated products under relatively mild conditions. However, the selection of an appropriate metal catalyst and a suitable oxidizing agent, along with thoroughly tuned reaction conditions, can open up an entry towards mild and atom efficient oxidative transformations of alkanes.

Following our general research line focused on the development of new catalytic systems for the oxidative functionalization of hydrocarbons [16–22] and alcohols [23–25], we have obtained a series of multicopper(II) compounds bearing aminopolyalcoholate ligands and applied them as valuable and versatile catalysts or catalyst precursors for the oxidation and hydrocarboxylation of alkanes and other substrates [24–29]. As a further extension of these synthetic and catalytic directions, the present work aims at the preparation of new copper(II) complexes derived from related aminopolyalcohols, N,N,N′,N′-tetrakis(2-hydroxyethyl)ethylenediamine (H_4L^1) and N-ethyldiethanolamine (H_2L^2), and at probing their catalytic potential in mild oxidative transformations of different substrates. The choice of H_4L^1 and H_2L^2 as N,O-ligands is governed by their aqueous solubility and rather limited use in coordination chemistry [24,30,31], whereas different Cu complexes with N,O-environment are recognized bio-inspired catalysts [32–34] with relevance to the active sites of various metalloenzymes (e.g. particulate methane monooxygenase [35,36]).

Hence, we report herein the simple self-assembly generation and full characterization of the two new complexes $[Cu(H_3L^1)(NCS)]$ (**1**) and $[Cu_2(\mu\text{-}HL^2)_2(NCS)_2]$ (**2**) (Scheme 1), which exhibit catalytic activity in the following types of

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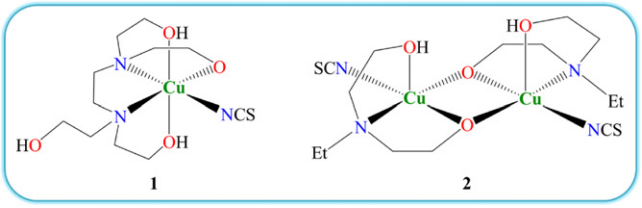


Scheme 1. Structural formulae of complexes **1** and **2**.

oxidative transformations: (i) the oxidation of alkanes (cyclohexane, cyclooctane) by *tert*-butyl hydroperoxide (TBHP) to alkyl peroxides, alcohols and ketones, and in turn further oxidation of alcohols (using cyclohexanol as a representative of this class) by TBHP to ketones, and (ii) the hydrocarboxylation, by CO, H_2O and $K_2S_2O_8$, of various linear and cyclic C_n (n = 5–8) alkanes into the corresponding C_{n+1} carboxylic acids (Scheme 2).

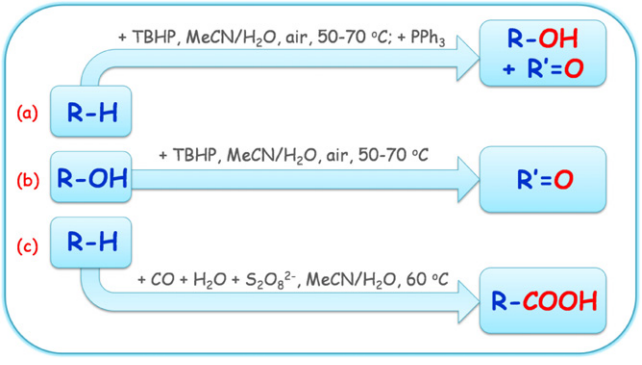
2. Experimental

2.1. Materials and methods

All synthetic work was performed in air, at ambient temperature (ca. 25 °C) and in aqueous medium (bidistilled water). All chemicals were obtained from commercial sources and used as received. C, H, N and S elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets (abbreviations: vs, very strong; s, strong; m, medium; w, weak; br., broad; sh., shoulder). ESI-MS(±) spectra were run on a 500-MS LC Ion Trap instrument (Varian Inc, Alto Palo, CA, USA) equipped with an electrospray (ESI) ion source, using ca. 10^{-3} M solutions of **1** and **2** in methanol. Gas chromatography (GC) analyses were performed on a Fisons Instruments GC 8000 series gas chromatograph with a DB WAX (J&W) capillary column (30 m × 0.25 mm × 0.25 μm; helium carrier gas) and by using Jasco-Borwin v.1.50 software.

2.2. Synthesis and characterization of *1* and *2*

To an aqueous solution (5.0 mL) of $Cu(CH_3COO)_2{\cdot}H_2O$ (100 mg, 0.50 mmol) was added N,N,N′,N′-tetrakis(2-hydroxyethyl)ethylenediamine (107 μL, 0.50 mmol; for **1**) or N-ethyldiethanolamine (66 μL, 0.50 mmol; for **2**) with continuous stirring at room temperature (ca. 25 °C). Sodium thiocyanate (41 mg, 0.50 mmol) was dissolved in an aqueous 1 M solution of NaOH (1.5 mL, 1.50 mmol) and added to the reaction mixture. The resulting deep blue solution was stirred overnight and then filtered. The filtrate was left to evaporate in a beaker at ambient temperature. Greenish blue crystals (including those of X-ray quality) were formed in 1–2 weeks, then collected and dried in air to give compounds **1** and **2** in ~70% yields, based on copper(II) acetate.



Scheme 2. Cu-catalyzed (by **1** or **2**) transformations: (a) oxidation of alkanes to alcohols and ketones, (b) oxidation of alcohols to ketones, and (c) hydrocarboxylation of alkanes to carboxylic acids; only major products are shown in scheme. Substrates tested: (a) cyclohexane, cyclooctane, *n*-heptane, *n*-octane, methylcyclohexane, *cis*- and *trans*-1,2-dimethylcyclohexane; (b) cyclohexanol; and (c) C_5–C_8 linear and cyclic alkanes.

[Cu(H_3L^1)(NCS)] (**1**). Anal. calcd for $C_{11}H_{23}CuN_3NaO_4S$ (MW 356.9): C 37.02, H 6.50, N 11.77, S 8.98; found: C 36.98, H 6.69, N 11.65, S 9.07. IR (KBr): 3534 w br. and 3437 m br. ν(OH), 2940 w and 2855 w ν(CH), 2113 s br. ν(CN), 1638 m br. δ(OH), 1460 m, 1365 m, 1322 w, 1264 m, 1161 w, 1093 s, 1063 s, 1017 s, 914 s br. ν(CS), 801 s, 760 w, 735 s, 625 m, 569 s, 526 w, 505 w and 468 m cm^{-1}. ESI-MS(±) (MeOH), selected fragments with relative abundance >10%: MS(+), *m/z*: 595 (100%) $[Cu_2(H_3L^1)_2{-}H]^+$, 298 (25%) $[Cu(H_3L^1)]^+$; MS(−), *m/z*: 478 (10%) $[Cu_2(H_3L^1)(NCS)_2]^-$, 298 (10%) $[Cu(H_2L^1)]^-$, 180 (100%) $[Cu(NCS)_2]^-$.

[Cu_2(μ-HL^2)$_2$($NCS)_2$] (**2**). Anal. calcd for $C_{14}H_{28}Cu_2N_4O_4S_2$ (MW 507.6): C 33.13, H 5.56, N 11.04, S 12.63; found: C 33.17, H 5.62, N 11.02, S 12.69. IR (KBr): 3150 m br. ν(OH), 2974 m and 2926 m ν_{as}(CH), 2878 m and 2848 w ν_s(CH), 2110 sh. and 2087 vs ν(CN), 1640 w br. δ(OH), 1475 w, 1460 m, 1385 m, 1345 m, 1327 w, 1254 w, 1232 w, 1179 w, 1150 w, 1075 s, 1050 s, 1020 s, 914 m and 891 m ν(CS), 738 w, 614 m, 582 w, 455 w, 431 w and 414 w cm^{-1}. ESI-MS(±) (MeOH), selected fragments with relative abundance >10%: MS(+), *m/z*: 899 (15%) $[Cu_4(HL^2)_4(NCS)_2{-}H]^+$, 780 (100%) $[Cu_4(L^2)_4{+}H]^+$; MS(−), *m/z*: 822 (40%) $[Cu_4(L^2)_3(NCS)_3]^-$, 300 (15%) $[Cu_2(NCS)_3]^-$, 180 (100%) $[Cu(NCS)_2]^-$.

2.3. X-ray crystallography

The X-ray diffraction data for **1** were collected with a Nonius Kappa CCD diffractometer using Mo-Kα radiation. The Denzo-Scalepack [37] program package was used for cell refinements and data reductions. The structure was solved by direct methods using the SHELXS-97 program [38] with the WinGX [39] graphical user interface. An absorption correction was applied using SADABS [38]. Structural refinement was carried out with SHELXL-97 [38]. The OH hydrogen atoms were located from the difference Fourier map but constrained to ride on their parent atom, with U_{iso} = 1.5 U_{eq}(parent atom). Other H atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H = 0.99 Å and U_{iso} = 1.2 U_{eq}(parent atom). Crystal data for **1**: $C_{11}H_{23}CuN_3O_4S$, M = 356.92, λ = 0.71073 Å (Mo-Kα), T = 120(2) K, orthorhombic, space group $P2_12_12_1$, a = 8.0796(2), b = 13.5380(7), c = 13.8637(7) Å, V = 1516.43(12) $Å^3$, Z = 4, D_c = 1.563 g/cm^3, F_{000} = 748, μ = 1.594 mm^{-1}, 19,574 reflections collected, 3480 unique, $I > 2\sigma(I)$ (R_{int} = 0.0599), R_1 = 0.0344, wR_2 = 0.0698, *GOF* 1.052, Flack parameter 0.006(15).

The X-ray diffraction data of **2** were collected using a Bruker AXS KAPPA APEX II diffractometer with graphite-monochromated Mo-Kα radiation. Data were collected using omega scans of 0.5° per frame, and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT on all the observed reflections [40]. Absorption corrections were applied using SADABS [40]. The structure was solved using SHELXS-97 and refined with SHELXL-97 [38]. Calculations were performed using the WinGX System-Version 1.80.03 [39]. All hydrogen atoms were inserted in calculated positions. Crystal data for **2**: $C_{14}H_{28}Cu_2N_4O_4S_2$, M = 507.60, λ = 0.71073 Å (Mo-Kα), T = 150(2) K, monoclinic, space group $C2/c$, a = 25.771(3), b = 20.290(2), c = 17.8787(19) Å, β = 114.349(5)°, V = 8517.3(17) $Å^3$, Z = 16, D_c = 1.580 g/cm^3, F_{000} = 4192, μ = 2.219 mm^{-1}, 35,634

reflections collected, 8428 unique, $I > 2\sigma(I)$ ($R_{int} = 0.0945$), $R_1 = 0.0521$, $wR_2 = 0.1207$, *GOF* 0.981.

CCDC 833514 and 833515 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/datarequest/cif.

2.4. Oxidation of alkanes and alcohols with TBHP

The oxidation reactions of alkanes and cyclohexanol were typically carried out in air in thermostated Pyrex cylindrical vessels or round-bottom flasks with vigorous stirring and using MeCN as solvent. In a typical experiment, the copper compound **1** or **2** was added into the reaction mixture in the form of a stock solution in MeCN. The substrate (alkane or alcohol) and GC internal standard ($MeNO_2$, 0.05 mL) were then introduced and the reaction started upon addition of TBHP (70% in H_2O) in one portion. The reaction mixtures were vigorously stirred for 0.5–12 h. *Caution*: the combination of air or molecular oxygen and a peroxide with organic compounds at elevated temperatures may be explosive! The oxidations were monitored by withdrawing small aliquots after different periods of time, which were then treated with PPh_3 (for reduction of remaining TBHP and alkyl peroxides that are formed as major primary products in alkane oxidations [4,41,42]) followed by GC analyses. Attribution of peaks was made by comparison with chromatograms of authentic samples and, in some cases, by GC–MS analyses using a Shimadzu QP-2010 Plus instrument (He as the carrier gas), equipped with a capillary column (BP-20, SGE). Blank tests indicated that only traces of products can be formed in the absence of the copper catalyst.

2.5. Hydrocarboxylation of alkanes

In a typical experiment, the reaction mixtures were prepared as follows: H_2O (2.0 mL), MeCN (4.0 mL) (total solvent volume was 6.0 mL), $K_2S_2O_8$ (1.5 mmol) and an alkane (1.0 mmol) were added to the Cu catalyst **1** or **2** (8.0 μmol) contained in a 13.0 mL stainless steel autoclave, equipped with a Teflon-coated magnetic stirring bar. The autoclave was closed and flushed with CO three times to remove the air, and finally pressurized with 20 atm (5.32 mmol) of CO. *Caution*: due to the high toxicity of CO, all the manipulations should be performed with due care! The reaction mixture was stirred for 4 h at 60 °C using a magnetic stirrer and an oil bath, whereupon it was cooled in an ice bath, degassed, opened and transferred to a flask. Diethyl ether (9.0 mL) and 90 μL of cycloheptanone (GC internal standard) were added. The obtained mixture was vigorously stirred for 10 min, and the organic layer was analyzed by gas chromatography (internal standard method), revealing the formation of isomeric monocarboxylic acids as the dominant products.

In the reactions with cycloalkane substrates, cyclic ketones and alcohols were also formed as by-products of partial alkane oxidation, whereas in the transformations of linear alkanes the generation of the corresponding oxygenates was negligible (their overall yields were not exceeding 1.0%). Blank tests indicated that the hydrocarboxylations also proceed in the metal-free systems, although typically leading to 2–5 times inferior yields of carboxylic acids in comparison with the Cu-catalyzed transformations [29,43–45]. The alkane hydrocarboxylations do not undergo either in sole H_2O or MeCN solvent. The formation of dicarboxylic acids was also not observed.

3. Results and discussion

3.1. Synthesis and characterization of **1** and **2**

The copper(II) complexes **1** and **2** have been synthesized by modifying our previously developed self-assembly protocol in aqueous medium [46–49]. Hence, the reactions of copper(II) acetate, in water at ambient temperature, with either N,N,N′,N′-tetrakis(2-hydroxyethyl)ethylenediamine (H_4L^1) or N-ethyldiethanolamine (H_2L^2) as a main ligand source, followed by the addition of sodium hydroxide as a pH-regulator and sodium thiocyanate as an auxiliary ligand source, result in the self-assembly of the new products $[Cu(H_3L^1)(NCS)]$ (**1**) and $[Cu_2(\mu\text{-}HL^2)_2(NCS)_2]$ (**2**). The use of $Cu(CH_3COO)_2{\cdot}H_2O$, H_4L^1/H_2L^2 and NaNCS in a stoichiometric ratio (1:1:1) was more favourable for the crystallization of analytically pure complexes **1** and **2**. These compounds have been isolated as greenish blue air-stable crystalline solids in ~70% yields (based on Cu(II) acetate) and characterized by IR spectroscopy, ESI-MS(±), elemental and single-crystal X-ray diffraction analyses.

The IR spectra of **1** and **2** are rather similar and show typical ν(OH) bands with maxima at 3437 (**1**) and 3150 (**2**) cm^{-1}, ν_{as} and ν_s(CH) vibrations detected as two to four bands in the 2975–2845 cm^{-1} range, as well as a number of strong bands (1100–1000 cm^{-1}) associated to ν(C–X) (X = C, N, O) vibrations of the H_3L^1 and HL^2 ligands. The most characteristic feature concerns an intense ν(CN) band at 2113 cm^{-1} in **1**, or at 2087 cm^{-1} with a shoulder at 2110 cm^{-1} in **2**, which is typical for the terminal N-bound thiocyanate ligand [50]. In addition, there are characteristic bands in the 914–891 cm^{-1} range due to ν(CS) vibrations.

The ESI-MS(±) spectra of the solutions of **1** and **2** in methanol exhibit a number of interesting features associated to the aggregation of mono- and dicopper units into fragments of higher nuclearity. In fact, the ESI-MS(+) plots of **1** and **2** reveal the presence of the respective dicopper $[Cu_2(H_3L^1)_2{-}H]^+$ ($m/z = 595$) and tetracopper $[Cu_4(L^2)_4{+}H]^+$ ($m/z = 780$) fragments with the highest relative intensity (100%) and the expected isotopic distribution patterns. Although these aggregations mainly proceed with concomitant decoordination of auxiliary thiocyanate ligands, other lower intensity fragments containing NCS moieties have also been detected in the ESI-MS(−) spectra, namely $[Cu_2(H_3L^1)(NCS)_2]^-$ ($m/z = 478$, 10%) in **1** and $[Cu_4(L^2)_3(NCS)_3]^-$ ($m/z = 822$, 40%) in **2**. These aggregations can possibly derive from strong H-bonding interactions as confirmed by the solid-state structures of **1** and **2**.

The molecular structure of **1** (Fig. 1a) is composed of discrete monomeric $[Cu(H_3L^1)(NCS)]$ units in which the six-coordinate Cu1 atoms exhibit a distorted octahedral $\{N_3O_3\}$ coordination geometry. The H_3L^1 acts as a pentadentate N_2O_3-ligand with one of the hydroxyethyl arms (O4) remaining uncoordinated, whereas thiocyanate acts as a linear N-bound ligand [N1–C1–S1 179.2(3)°]. The equatorial positions around the Cu1 centre are occupied by the O1, N2 and N3 atoms of H_3L^1 and the N1 atom of NCS, with the bonding distances ranging from 1.951(2) Å [Cu1–N1] to 2.104(2) Å [Cu1–N3]. The apical sites are taken by the O2 and O3 atoms of H_3L^1 with the elongated Cu1–O2 and Cu1–O3 bonds of 2.370(2) and 2.342(2) Å, respectively. The O3–Cu1–N3 (77.18(8)°) and O1–Cu1–N3 (165.76(8)°) angles represent major deviations from the octahedral geometry around the Cu1 atom. In general, the bonding parameters in **1** are comparable to those of other reported Cu(II) aminopolyalcoholate complexes [27,31,51]. Two strong O–H···O hydrogen bonds involving the O1, O2 and O3 atoms of H_3L^1 lead to the assembly of $[Cu(H_3L^1)(NCS)]$ units into zig-zag 1D H-bonded chains (running along the *a* axis), which are further interlinked by the intermolecular O4–H4O···S1^i [(*i*) $2-x$, $-0.5+y$, $0.5-z$] interactions into a 3D supramolecular network. Besides, an important point concerning **1** consists in the fact that it represents the first structurally characterized monocopper compound derived

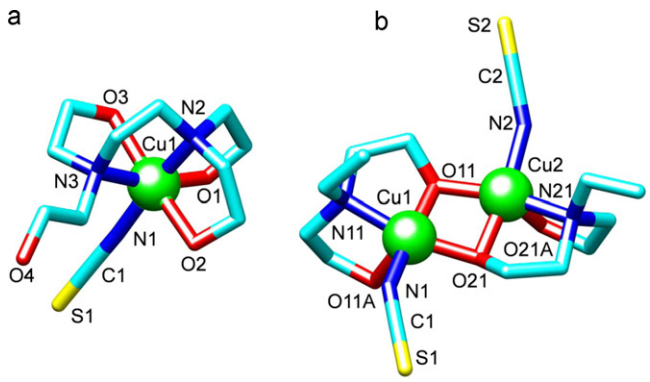


Fig. 1. X-ray crystal structures of **1** (a) and **2** (b) with atom numbering scheme. H atoms (in **1** and **2**) and an additional dicopper unit (in **2**) are omitted for clarity. Selected distances (Å) and angles (°): **1**: Cu1–N1 1.951(2), Cu1–N2 2.027(2), Cu1–N3 2.104(2), Cu1–O1 1.957(2), Cu1–O2 2.370(2), Cu1–O3 2.342(2), N2–Cu1–N3 86.06(9), O3–Cu1–N3 77.18(8), N1–Cu1–O1 95.56(9), O1–Cu1–N3 165.76(8), N1–C1–S1 179.2(3); **2**: Cu1–N1 1.935(6), Cu1–N11 2.026(5), Cu1–O11A 2.303(5), Cu1–O11 1.948(4), Cu1–O21 1.945(4), Cu1···Cu2 2.9018(11), N1–Cu1–N11 97.4(2), O21–Cu1–O11 81.41(16), N1–C1–S1 178.0(7), Cu1–O11–Cu2 95.62(17), Cu1–O21–Cu2 96.23(17).

from H_4L^1 [30], albeit a related dicopper(II) derivative $[Cu_2(\mu\text{-}H_3L^1)](ClO_4)_2$ was reported earlier [31a].

In contrast to **1**, the crystal structure of **2** (Fig. 1b) bears dimeric $[Cu_2(\mu\text{-}HL^2)_2(NCS)_2]$ units (two per unit cell). The five-coordinate Cu1 and Cu2 atoms exhibit distorted square-pyramidal $\{N_2O_3\}$ geometries filled by the N,O,O-tridentate μ-HL^2 ligands and terminal N-bound thiocyanate moieties. The basal positions around the Cu centres are occupied by the μ-oxygen (O11 and O21) and the amino nitrogen (N11 and N21) atoms of μ-HL^2, along with the nitrogen (N1 and N2) atoms of the NCS ligands. The two remaining oxygen atoms (O11A and O21A) of μ-HL^2 are located in apical sites, being also spatially oriented in the same direction. Their binding involves the Cu1–O11A (2.303(5) Å) and Cu2–O21A (2.231(4) Å) bonds, which are lengthened in comparison to basal Cu–O and Cu–N bonds that have distances in the 1.929(6)–2.056(5) Å range. The NCS ligands adopt the linear geometry with the N–C–S angles of 178.0(7) and 179.7(6)°. The $\{Cu_2(\mu_2\text{-}O)_2\}$ core is nonplanar and features a rather short Cu1···Cu2 separation of 2.9018(11) Å. The bonding parameters in **2** are in agreement with those encountered in other structurally related Cu(II) complexes with $\{Cu_2(\mu_2\text{-}O)_2\}$ cores [24,27,48,52]. A noteworthy feature of **2** consists in the formation of tetracopper aggregates via four strong intermolecular O–H···O hydrogen bonds between two vicinal dimeric $[Cu_2(\mu\text{-}HL^2)_2(NCS)_2]$ units.

3.2. Oxidation of alkanes and alcohols with TBHP

We have found that complex **1** efficiently catalyzes the oxidation of alkanes with TBHP in acetonitrile solution (Scheme 2, reaction a) under relatively mild conditions (temperature 50–70 °C, under normal pressure of air). Two examples of the kinetic curves are shown in Figs. 2 and 3. Concentrations of the final products (alcohols and ketones) were measured after treatment of the samples with PPh_3 which leads to the reduction of formed peroxides (primary products) to the corresponding alcohols [4,41,42,53,54]. It can be seen that the oxidation of cyclohexane gives after 8.5 h cyclohexanol and cyclohexanone in 17% yield, and the turnover number (TON) attains 800. The accumulation of cyclohexanone occurs with some autoacceleration, which can be due to the gradual decomposition of the formed alkyl peroxides to the corresponding ketone [53,54] and the oxidation of cyclohexanol in the course of the reaction. Cyclooctane is oxidized less efficiently, leading to TON of 460 after 11 h. It is

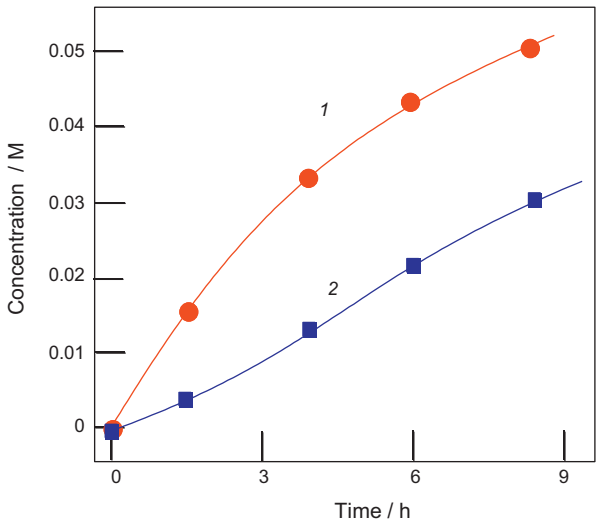


Fig. 2. Accumulation of oxygenates (cyclohexanol, curve *1*; cyclohexanone, curve *2*) with time in cyclohexane (0.46 M) oxidation with TBHP (0.56 M, 70% aqueous) catalyzed by complex **1** (1×10^{-4} M) in acetonitrile (total volume of the reaction solution was 5 mL), 50 °C. Concentrations of the products were measured after reduction of the samples with PPh_3.

interesting that in the case of this alkane, the concentration of the ketone product is higher than that of the alcohol.

Complex **2** does not exhibit catalytic activity in the oxidation of alkanes with TBHP, what can be associated with its relatively rapid decomposition or transformation into a catalytically inactive species under the reaction conditions. This leads to the formation of a mixture composed of copper oxide derivatives and brown oil, the detailed analysis of which could not be performed. In contrast, both **1** and **2** are good catalysts for the oxidation of cyclohexanol to cyclohexanone in acetonitrile by TBHP (Scheme 2, reaction b). Examples of the kinetic curves are presented in Figs. 4 and 5. The maximum values of TON and yield of cyclohexanone achieve 820 (Fig. 4) and 78% (Fig. 5), respectively. Complex **2** is less effective than complex **1** (compare curves 2 and 3 in Fig. 4).

To understand the nature of the oxidizing species in oxidations catalyzed by complex **1**, we determined the selectivity parameters in the reactions with certain linear (*n*-heptane, *n*-octane), branched and cyclic (methylcyclohexane, *cis*- and *trans*-1,2-dimethylcyclohexanes) saturated hydrocarbons. The results are summarized in Tables 1 (entry 1) and 2. For comparative

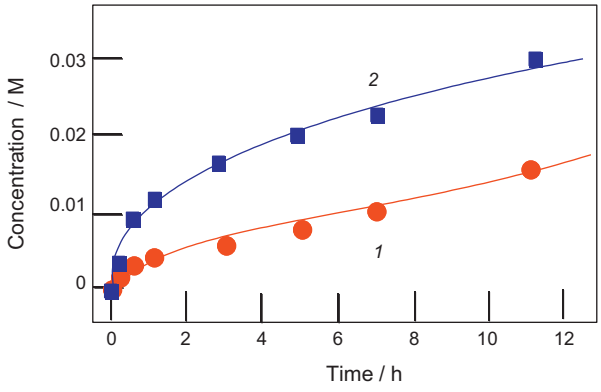


Fig. 3. Accumulation of oxygenates (cyclooctanol, curve *1*; cyclooctanone, curve *2*) with time in cyclooctane (0.25 M) oxidation with TBHP (0.56 M, 70% aqueous) catalyzed by complex **1** (1×10^{-4} M) in acetonitrile (total volume of the reaction solution was 5 mL), 70 °C. Concentrations of the products were measured after reduction of the samples with PPh_3.

Table 1
Selectivity parameters in alkane oxidations by certain catalytic systems.[a]

Entry	System [reference]	C(1):C(2):C(3):C(4)		1°:2°:3°	*trans*/*cis*	
		n-Heptane	*n*-Octane	MCH	*cis*-DMCH	*trans*-DMCH
1	**1**/TBHP [this work]	1:10:8:11	1:12:8:7	1:15:170	0.6	0.1
2	$FeSO_4/H_2O_2$ [55]	1:5:5:4.5		1:3:6	1.3	1.2
3[b]	$VO_3^-/PCA/H_2O_2$ [56]	1:6:7:5		1:9:37	0.75	0.8
4	$VO_3^-/H_2SO_4/H_2O_2$ [57]	1:7:7:6		1:7:26	0.85	0.9
5[c]	Fe_2(HPTB)/PCA/H_2O_2 [58]	1:6:6:5		1:6:13		
6	$Cp^*_2Os/py/H_2O_2$ [59]	1:7:7:7		1:8:23	1.0	0.9
7[d]	TS-1/NaOH/MeCN/H_2O_2 [60]	1:8:8:8		1:6:21	0.86	0.95
8	$Cu(NO_3)_2/HNO_3/H_2O_2$ [26]	1:7:6:5			0.9	0.7
9[e]	**3**/CF_3COOH/H_2O_2 [26]	1:8:7:5	1:5:5:4	1:5:14	0.8	0.8
10[e]	**3**/TBHP [23]	1:34:23:21	1:65:32:30	1:16:128	0.4	0.1
11[f]	**4**/$MeCO_2H/H_2O_2$ [61]	1:46:35:34	1:29:25:24	1:26:200	0.3	4.1
12[f]	**4**/$(COOH)_2$/TBHP [62]	1:14:13:12	1:17:12:11	1:0.3:0.6	0.2	7.3

[a] All parameters were measured after reduction of the reaction mixtures with PPh_3 before GC analysis and calculated based on the ratios of isomeric alcohols. Parameters C(1):C(2):C(3):C(4) are relative normalized reactivities of H atoms at carbon atoms C(1), C(2), C(3) and C(4) of *n*-heptane or *n*-octane chain. Parameters 1°:2°:3° are relative normalized (taking into account the number of H atoms at each carbon atom) reactivities of hydrogen atoms at primary, secondary and tertiary carbon atoms of branched alkanes. Parameter *trans*/*cis* is determined as the ratio of the formed tertiary alcohol isomers with mutual *trans* and *cis* orientation of the methyl groups. MCH, methylcyclohexane; DMCH, 1,2-dimethylcyclohexane.
[b] PCA is pyrazine-2-carboxylic acid.
[c] Catalyst $[Fe_2(HPTB)(\mu\text{-}OH)(NO_3)_2](NO_3)_2\cdot CH_3OH\cdot 2H_2O$, in which HPTB is N,N,N′,N′-tetrakis(2-benzimidazolylmethyl)-2-hydroxo-1,3-diaminopropane.
[d] TS-1 is microporous titanosilicalite.
[e] Complex **3** is $[O\subset Cu_4\{N(CH_2CH_2O)_3\}_4(BOH)_4][BF_4]_2$.
[f] Complex **4** is $[Mn_2L_2(O)_3]^{2+}$, where L is 1,4,7-trimethyl-1,4,7-triazacyclononane.

purposes, Table 1 also lists the data for some other oxidizing systems [23,26,55–62]. The regio- and bond selectivity parameters are higher than those observed for the oxidation by the systems operating with the participation of hydroxyl radicals (Table 1, entries 2–9), thus suggesting the possible involvement of different types of active oxidizing species. Other Cu-containing systems [26] based on H_2O_2 (Table 1, entries 8 and 9) operate with the involvement of hydroxyl radicals.

The oxygenation of methylcyclohexane (MCH) proceeds predominantly at the tertiary carbon atom with formation of 1-methylcyclohexanol (Table 2, **P4**, Supplementary material, Scheme S1, Fig. S1). It is interesting that the position 2 (**P5** and **P6**) relatively to the methyl group of the substrate is noticeably less reactive than the corresponding positions 3 (**P7** and **P9**) and 4 (**P8** and **P10**) regarding the formation of alcohol products. This can be explained by the substantial sterical hindrance which is apparently due to the involvement of a bulky oxidizing species. Comparable parameters of bond selectivity 1°:2°:3° have been reported for the systems based on a dinuclear Mn(IV) complex **4** [61,62] with a sterically hindered reaction centre (Table 1, entries 11 and 12). The oxidations of linear alkanes (heptane and octane) catalyzed by complex **1** exhibit much lower regio-selectivity in comparison with that of the system containing a sterically hindered tetracopper(II) triethanolaminate complex $[O\subset Cu_4\{N(CH_2CH_2O)_3\}_4(BOH)_4][BF_4]_2$ (**3**) (Table 1, entry 10), wherein the reaction occurs in a cleft [23].

It is noteworthy that the oxidation of *cis*- and *trans*-1,2-dimethylcyclohexanes (DMCH) by the **1**/TBHP system (Table 1, entry 1) proceeds with a substantial retention of configuration in the case of *cis*-DMCH (parameter *trans*/*cis* < 1) and with inversion of configuration in the case of *trans*-DMCH (parameter *trans*/*cis* < 1 as well). These values are essentially different from those (ca. 0.7–1.0) typical for the reactions involving HO• radicals (Table 1, entries 2–9). The *trans*/*cis* value obtained in the oxidation of *cis*-DMCH is comparable to those (ca. 0.2–0.3) observed in the oxidations with **4** (entries 11 and 12) which, in contrast to the **1**/TBHP system (*trans*/*cis* = 0.1), do not lead to inversion of the configuration

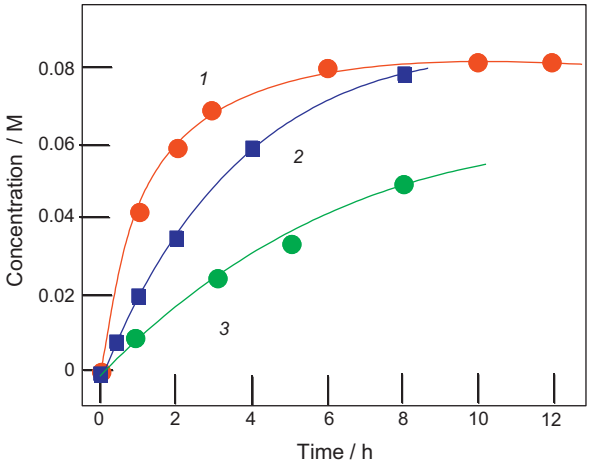


Fig. 4. Accumulation of cyclohexanone with time in cyclohexanol (0.25 M) oxidation with TBHP (0.56 M, 70% aqueous) in acetonitrile (total volume of the reaction solution was 5 mL). Catalysis by complex **1** (1×10^{-4} M) at 70 (curve *1*) and 50 °C (curve *2*), and by complex **2** (1×10^{-3} M) at 50 °C (curve *3*). Concentration of cyclohexanone was measured after reduction of the samples with PPh_3.

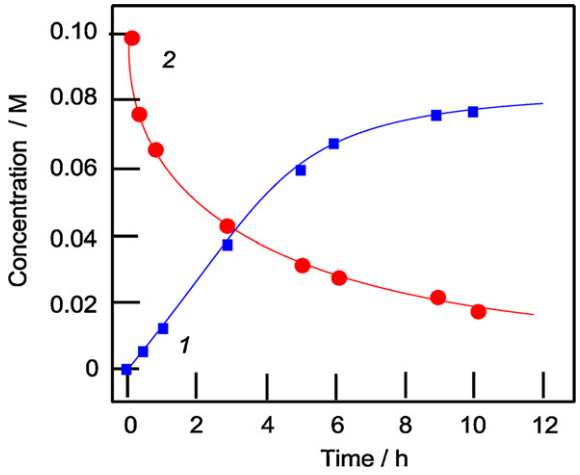


Fig. 5. Accumulation of cyclohexanone (curve *1*) and consumption of cyclohexanol (curve *2*) with time in cyclohexanol (0.10 M) oxidation with TBHP (1.12 M, 70% aqueous) catalyzed by complex **1** (1×10^{-4} M) at 70 °C in acetonitrile (total volume of the reaction solution was 5 mL). Concentration of cyclohexanone was measured after reduction of the samples with PPh_3.

Table 2
Accumulation of oxygenates in the oxidation of methylcyclohexane (MCH) with TBHP catalyzed by complex **1**.[a]

Products (concentration, mM)[b]											
Time (h)	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**	**P8**	**P9 + P10**	**P11**	1°:2°:3°
1	0.2	0.3	0.07	1.7	0.04	0.1	0.45	0.15	0.7	0.03	1:15:170
2	0.8	0.8	0.6	4.8	0.05	0.2	1.0	0.6	2.3	0.10	1:13:150
3	0.9	2.4	0.9	4.0	0.08	0.2	0.6	0.3	2.4	0.08	1:13:150
4	2.0	3.0	2.0	6.5	0.09	0.3	1.1	1.3	3.7	0.10	1:20:200
7	1.1	3.4	1.3	3.4	0.1	0.2	0.6	0.7	2.3	0.07	1:17:150

[a] Reaction conditions: $[\mathbf{1}]_0 = 0.1$ mM, $[TBHP]_0 = 1.3$ M, $[MCH]_0 = 0.25$ M, MeCN up to 5 mL total volume, 70 °C.
[b] Concentrations of isomers (after reduction with PPh_3) are given. Products: 2-methylcyclohexanone (**P1**), 3-methylcyclohexanone (**P2**), 4-methylcyclohexanone (**P3**), 1-methylcyclohexanol (**P4**), *trans*-2-methylcyclohexanol (**P5**), *cis*-2-methylcyclohexanol (**P6**), *trans*-3-methylcyclohexanol (**P7**), *trans*-4-methylcyclohexanol (**P8**), *cis*-3-methylcyclohexanol (**P9**), *cis*-4-methylcyclohexanol (**P10**), cyclohexylmethanol (**P11**). The formulae of the oxygenates and an example of chromatogram are shown in Scheme S1 and Fig. S1 (see Supplementary data).

when oxidizing *trans*-DMCH, as shown by the very high *trans*/*cis* values in the 4.1–7.3 range.

Based on the abovementioned features regarding product distribution patterns and selectivity parameters in alkane oxygenations, we can conclude that the oxidation by the **1**/TBHP system occurs with the participation of *t*-BuO• radicals generated from TBHP under the action of complex **1** [21,23]. The first stage of the process can be the reduction of Cu(II) by TBHP, possibly forming an adduct of TBHP with the Cu(II) complex:

$$Cu(II) + t\text{-BuOOH} \rightarrow Cu(I) + t\text{-BuOO}^{\bullet} + H^{+}$$

Low-valent Cu(I) derivative reacts further with the second molecule of TBHP to produce reactive radical *t*-BuO•:

$$Cu(I) + t\text{-BuOOH} \rightarrow Cu(II) + t\text{-BuO}^{\bullet} + HO^{-}$$

We cannot exclude also the formation of some amount of hydroxyl radicals via the following route:

$$Cu(I) + t\text{-BuOOH} \rightarrow Cu(II) + t\text{-BuO}^{-} + HO^{\bullet}$$

These oxygen-centred radicals attack C–H bonds of the alkane, RH, to produce alkyl radicals (R•) that rapidly add molecular oxygen from the atmosphere. Further transformations of alkyl peroxy radicals ROO• lead to the formation of alkyl peroxides, ketones and alcohols.

$$t\text{-BuO}^{\bullet} + RH \rightarrow t\text{-BuOH} + R^{\bullet}$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + Cu(I) \rightarrow ROO^{-} + Cu(II)$$

$$ROO^{-} + H^{+} \rightarrow ROOH$$

High concentrations of ketones after reduction of the reaction solutions with PPh_3 (see Figs. 2 and 3) indicate that the substantial portions of initially formed alkyl peroxides are transformed into the corresponding ketones and alcohols in the course of the oxidation reaction rather than in the chromatograph [4,41,42,53,54].

3.3. Hydrocarboxylation of alkanes to carboxylic acids

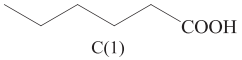
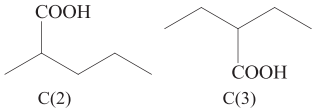
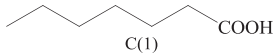
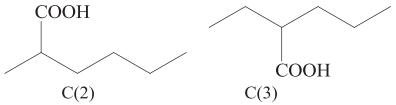
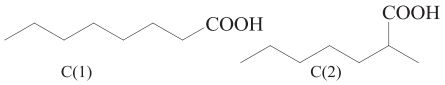
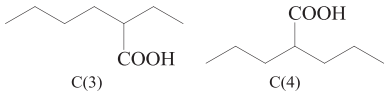
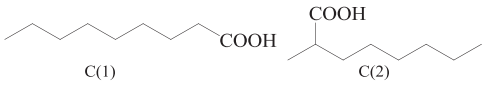
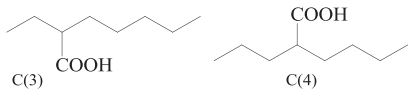
Following our recently developed protocol for the mild hydrocarboxylation of C_n alkanes into C_{n+1} carboxylic acids [29,43–45], we have tested the catalytic activity of **1** and **2** in this type of transformations using different C_5–C_8 cyclic and linear alkanes as

Table 3
Cu-catalyzed (by **1** or **2**) single-pot hydrocarboxylation of C_n cycloalkanes into the corresponding C_{n+1} cycloalkanecarboxylic acids.[a]

Entry	Cycloalkane	Catalyst	Yield of products (%)[b]			
			Carboxylic acid	Ketone	Alcohol	Total[c]
1	 cyclopentane	**1**	21.4	2.0	0.1	23.5
2		**2**	15.4	1.5	0.1	17.0
3[d]	 cyclohexane	**1**	34.1	0.9	0.5	35.5
4[d]		**2**	23.5	0.9	0.1	24.5
5	 cycloheptane	**1**	16.4	4.8	1.4	22.6
6		**2**	15.2	7.0	2.0	24.2
7	 cyclooctane	**1**	11.4	9.6	5.2	26.2
8		**2**	9.8	9.5	4.2	23.5

[a] Cyclic ketones and alcohols are also formed as products of cycloalkane oxidations. Reaction conditions (unless stated otherwise): cycloalkane (1.00 mmol), Cu catalyst (8.0 μmol), $p(CO) = 20$ atm, $K_2S_2O_8$ (1.50 mmol), H_2O (2.0 mL)/MeCN (4.0 mL), 60 °C, 4 h in an autoclave (13.0 mL capacity).
[b] Moles of product/100 mole of cycloalkane.
[c] Yield of all products.
[d] H_2O (3.0 mL)/MeCN (3.0 mL), 50 °C.

Table 4
Cu-catalyzed (by **1** or **2**) single-pot hydrocarboxylation of linear C_n alkanes into the corresponding C_{n+1} carboxylic acids.[a]

Entry	Alkane	Carboxylic acid product	Catalyst	Product yield[b]					Regioselectivity[d]
				C(1)	C(2)	C(3)	C(4)	Total[c]	C(1):C(2):C(3):C(4)
1			**1**	1.7	24.6	10.2	–	36.5	1:22:18
2	*n*-pentane	C(1)	**2**	1.6	26.0	10.9	–	38.5	1:24:20
		 C(2) C(3)							
3			**1**	1.5	14.9	14.9	–	31.3	1:15:15
4	*n*-hexane	C(1)	**2**	1.3	17.3	17.4	–	36.0	1:19:19
		 C(2) C(3)							
5			**1**	0.7	6.8	7.7	3.6	18.8	1:15:17:16
6	*n*-heptane	C(1) C(2)	**2**	1.1	10.0	9.6	4.1	24.8	1:14:14:12
		 C(3) C(4)							
7			**1**	0.6	7.0	6.2	5.7	19.5	1:17:15:14
8	*n*-octane	C(1) C(2)	**2**	0.7	7.6	7.0	6.9	22.2	1:16:15:15
		 C(3) C(4)							

[a] Reaction conditions: alkane (1.00 mmol), Cu catalyst (8.0 μmol), $p(CO) = 20$ atm, $K_2S_2O_8$ (1.50 mmol), H_2O (2.0 mL)/MeCN (4.0 mL), 60 °C, 4 h in an autoclave (13.0 mL capacity).
[b] Moles of product/100 mole of cycloalkane.
[c] Yield of all products; the yields of ketones and alcohols are negligible (<1%) and thus are not indicated herein.
[d] Regioselectivity parameters C(1):C(2):C(3) and C(1):C(2):C(3):C(4) mean the normalized (for the relative number of H atoms) reactivities of hydrogen atoms at different positions of linear alkane chains, respectively.

substrates. These reactions were run in stainless steel autoclaves by reacting, in H_2O/MeCN medium at 60 °C, an alkane with carbon monoxide, water and potassium peroxodisulfate, in the presence of the copper catalyst **1** or **2** (Scheme 2, reaction c). As typical conditions, the previously optimized [43,44] reaction parameters were applied. The obtained results are summarized in Tables 3 and 4. All the product yields along the discussion below are given in molar% based on alkanes.

Both compounds **1** and **2** catalyze the hydrocarboxylation of cycloalkanes (Table 3) to the corresponding cycloalkanecarboxylic acids (major products). Owing to the presence of a single type of carbon atoms in cycloalkane, the formation of only one carboxylic acid product is detected. Hence, cyclopentanecarboxylic (15–21%, entries 1 and 2), cyclohexanecarboxylic (24–34%, entries 3 and 4), cycloheptanecarboxylic (15–16%, entries 5 and 6) and cyclooctanecarboxylic (10–11%, entries 7 and 8) acids are generated in the 34–10% yields upon hydrocarboxylation of C_5H_{10}, C_6H_{12}, C_7H_{14} and C_8H_{18}, respectively. In all cases, catalyst **1** shows a slightly higher activity over the dicopper(II) complex **2**. The formation of the oxidation products (cyclic ketones and alcohols) also takes place. Although the total yields of these oxidation products are rather low (1–2%) in the reactions when using cyclopentane and cyclohexane as substrates, they reach values of 9–15% in the reactions with cycloheptane and cyclooctane.

In contrast to cycloalkanes, the hydrocarboxylations of linear C_5–C_8 alkanes (Table 4) generate three or four isomeric carboxylic acid products owing to the presence of primary C(1) and different secondary C(2), C(3) and C(4) carbon atoms within the hydrocarbon chain. As expected for free-radical processes, the branched acids derived from the carboxylations at secondary C atoms always constitute the major products, whereas the yields of linear (fatty) acids lie in the 1–2% range. Hence, isomeric carboxylic acids obtained from linear alkanes include: (i) 2-methylpentanoic, 2-ethylbutanoic and hexanoic acids from *n*-C_5H_{12}, (ii) 2-methylhexanoic, 2-ethylpentanoic and heptanoic acids from *n*-C_6H_{14}, (iii) 2-methylheptanoic, 2-ethylhexanoic, 2-propylpentanoic and octanoic acids from *n*-C_7H_{16}, and (iv) 2-methyloctanoic, 2-ethylheptanoic, 2-propylhexanoic and nonanoic acids from *n*-C_8H_{18} (see Table 4 for structural formulae).

The maximum total yields of carboxylic acids (Table 4) are achieved in the hydrocarboxylations of *n*-C_5H_{12} (37–39%), *n*-C_6H_{14} (31–36%), *n*-C_7H_{16} (19–25%) and *n*-C_8H_{18} (20–22%). Interestingly, in these systems the dicopper(II) complex **2** is slightly more active in comparison with the monocopper(II) derivative **1**. In contrast to reactions with cycloalkanes, the formation of ketones and alcohols as products of partial oxidation is negligible (less than 1% in total) in the hydrocarboxylations of linear alkanes.

Although a somewhat preferable carboxylation at the C(2) atom is observed in *n*-C_5H_{12} with the regioselectivity [63] (normalized for the relative number of H atoms) parameters C(1):C(2):C(3) of 1:(22–24):(18–20) (Table 4, entries 1 and 2), in other tested linear alkanes all the secondary carbon atoms are carboxylated without considerable preference to a particular C atom, as attested by the regioselectivities C(1):C(2):C(3) = 1:19:19 (for *n*-C_6H_{14}, entry 4) and C(1):C(2):C(3):C(4) = 1:16:15:15 (for *n*-C_8H_{18}, entry 8). These regioselectivities resemble those previously observed by us in the related hydrocarboxylations catalyzed by tetra- [44] and tricopper(II) [46] aminopolyalcoholate complexes, thus suggesting the involvement of the sulfate radical $SO_4^{\bullet -}$ as an active species [29,64].

On the basis of the previous background [29,43–45,65] and experimental data, the present hydrocarboxylations of both cyclic and linear alkanes (RH) apparently proceed via a free-radical mechanism that involves the following main steps: (1) formation of the alkyl radical R• from an alkane [generated via H abstraction by sulfate radical $SO_4^{\bullet -}$ derived from $K_2S_2O_8$], (2) carbonylation of R• by CO to give the acyl radical RCO•, (3) oxidation of RCO• by copper(II) species to the acyl cation RCO^+ [via the Cu^{II}/Cu^{I} redox couple], (3′) regeneration of the Cu^{II} form upon oxidation of Cu^+ by $K_2S_2O_8$, and (4) hydrolysis of RCO^+ to yield the carboxylic acid product [29]. The latter step has been previously confirmed by experiments with ^{18}O-labeled H_2O and theoretical calculations [29].

The obtained total yields of carboxylic acid products (Tables 3 and 4) in the systems catalyzed by **1** or **2** are comparable or even higher than those achieved earlier in (i) the V- or Re-catalyzed carboxylations of C_5–C_6 cyclic and linear alkanes in concentrated trifluoracetic acid (TFA) as reaction medium [18,66], and (ii) in the other Cu-catalyzed hydrocarboxylations of various alkanes in aqueous medium [29,43,44,46]. A noteworthy feature also concerns the possibility of generating, in a single step from linear alkanes, a variety of isomeric carboxylic acids as a mixture of reaction products, thus allowing its use, without the need for isolation of each isomer, in antibacterial, anti-fungicide and sanitizing compositions [44]. Besides, the achieved herein yields of carboxylic acids are very high considering the exceptional inertness of alkanes [1–9] and the fact that the present hydrocarboxylations involve C–C bond formation, and undergo in aqueous acid-solvent-free medium and at a very mild temperature (60 °C). These reactions also contrast with many state-of-the-art processes for the considerably mild transformations of alkanes that require the use of strongly acidic reaction media (concentrated trifluoroacetic or sulfuric acid or a superacid) [1–9,67].

4. Conclusions

The present study has further extended the scope of our aqueous medium self-assembly synthetic method [46–49] to different types of aminopolyalcoholate ligands, a slight modification of which appears to provide a driving force in the formation of copper(II) complexes **1** and **2** that feature distinct nuclearities. These compounds not only widen the underexplored coordination chemistry [30] of aqua-soluble and commercially available aminopolyalcohols H_4L^1 and H_2L^1, but also represent rare examples of such derivatives that find a noteworthy application in homogeneous oxidation catalysis.

In fact, the work has shown that **1** and/or **2** can act as versatile and efficient homogeneous catalysts for (i) the oxygenation of alkanes to alkyl peroxides, alcohols and ketones, (ii) the oxidation of alcohols to ketones, and (iii) the single-pot hydrocarboxylation of various cyclic and linear alkanes to the corresponding carboxylic acids bearing one more carbon atom. All these transformations proceed rather selectively, under mild conditions (50–70 °C) and in MeCN/H_2O medium, without the need for any co-catalysts or additives.

Future research should focus on the extension of both synthetic and catalytic directions, by widening the type of metal complex catalysts and by broadening the substrate versatility of the catalytic transformations, also searching for more favourable reaction conditions.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.08.028.

References

[1] A.E. Shilov, G.B. Shul'pin, Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes, Kluwer Acad. Publ., Dordrecht, 2000.
[2] G.A. Olah, Á. Molnár, Hydrocarbon Chemistry, Wiley, Hoboken, NJ, 2003.
[3] G.B. Shul'pin, in: M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, vol. 2, second ed., Wiley-VCH, Weinheim/New York, 2004, pp. 215–242.
[4] G.B. Shul'pin, Mini-Rev. Org. Chem. 6 (2009) 95–104.
[5] J.A. Labinger, J.E. Bercaw, Nature 417 (2002) 507–514.
[6] R.H. Crabtree, J. Organomet. Chem. 689 (2004) 4083–4091.
[7] A.A. Fokin, P.R. Schreiner, Chem. Rev. 102 (2002) 1551–1593.
[8] A. Sen, Acc. Chem. Res. 31 (1998) 550–557.
[9] A.E. Shilov, G.B. Shul'pin, Chem. Rev. 97 (1997) 2879–2932.
[10] Ullmann's Encyclopedia of Industrial Chemistry, 6th ed., Wiley-VCH, Weinheim, 2002.
[11] Encyclopedia of Chemical Technology, 5th ed., Kirk-Othmer, Wiley, New York, 2004.
[12] H. Wittcoff, B.G. Reuben, J.S. Plotkin, Industrial Organic Chemicals, 2nd ed., Wiley, 2004.
[13] Carboxylic Acids: Carboxylic Acid, Formic Acid, Niacin, Valproic Acid, Essential Fatty Acid, Acetoacetic Acid, Pcaa, Ibuprofen, Lipoic Acid, General Books LLC, 2010.
[14] H.M. Colquhoun, D.J. Thompson, M.V. Twigg, Carbonylation: Direct Synthesis of Carbonyl Compounds, Springer, 1991.
[15] G. Tojo, M. Fernández, Oxidation of Alcohols to Aldehydes and Ketones: A Guide to Current Common Practice, Springer, New York, 2006.
[16] Y.Y. Karabach, M.F.C. Guedes da Silva, M.N. Kopylovich, B. Gil-Hernández, J. Sanchiz, A.M. Kirillov, A.J.L. Pombeiro, Inorg. Chem. 49 (2010) 11096–11105.
[17] M.V. Kirillova, A.M. Kirillov, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Eur. J. Inorg. Chem. (2008) 3423–3427.
[18] M.V. Kirillova, A.M. Kirillov, P.M. Reis, J.A.L. Silva, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, J. Catal. 248 (2007) 130–136.
[19] D.S. Nesterov, V.N. Kokozay, V.V. Dyakonenko, O.V. Shishkin, J. Jezierska, A. Ozarowski, A.M. Kirillov, M.N. Kopylovich, A.J.L. Pombeiro, Chem. Commun. (2006) 4605–4607.
[20] M.N. Kopylovich, A.M. Kirillov, A.K. Baev, A.J.L. Pombeiro, J. Mol. Catal. A: Chem. 206 (2003) 163–178.
[21] G.B. Shul'pin, J. Gradinaru, Y.N. Kozlov, Org. Biomol. Chem. 1 (2003) 3611–3617.
[22] L.S. Shul'pina, K. Takaki, T.V. Strelkova, G.B. Shul'pin, Petrol. Chem. 48 (2008) 219–222.
[23] M.V. Kirillova, A.M. Kirillov, D. Mandelli, W.A. Carvalho, A.J.L. Pombeiro, G.B. Shul'pin, J. Catal. 272 (2010) 9–17.
[24] P.J. Figiel, A.M. Kirillov, M.F.C. Guedes da Silva, J. Lasri, A.J.L. Pombeiro, Dalton Trans. 39 (2010) 9879–9888.
[25] P.J. Figiel, A.M. Kirillov, Y.Y. Karabach, M.N. Kopylovich, A.J.L. Pombeiro, J. Mol. Catal. A: Chem. 305 (2009) 178–182.
[26] M.V. Kirillova, Y.N. Kozlov, L.S. Shul'pina, O.Y. Lyakin, A.M. Kirillov, E.P. Talsi, A.J.L. Pombeiro, G.B. Shul'pin, J. Catal. 268 (2009) 26–38.
[27] K.R. Gruenwald, A.M. Kirillov, M. Haukka, J. Sanchiz, A.J.L. Pombeiro, Dalton Trans. (2009) 2109–2120.
[28] Y.Y. Karabach, A.M. Kirillov, M. Haukka, M.N. Kopylovich, A.J.L. Pombeiro, J. Inorg. Biochem. 102 (2008) 1190–1194.
[29] M.V. Kirillova, A.M. Kirillov, M.L. Kuznetsov, J.A.L. Silva, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, Chem. Commun. (2009) 2353–2355.
[30] See the Cambridge Structural Database (CSD, version 5.32, Feb. 2011): F.H. Allen, Acta Crystallogr. B 58 (2002) 380–388.
[31] (a) A.S. de Sousa, M.A. Fernandes, Polyhedron 21 (2002) 1883–1888; (b) O. Orama, M. Orama, U. Schubert, Finn. Chem. Lett. 1 (1979) 136–139.
[32] L. Que Jr., W.B. Tolman, Nature 455 (2008) 333–340.
[33] E.A. Lewis, W.B. Tolman, Chem. Rev. 104 (2004) 1047–1076.
[34] P. Gamez, P.G. Aubel, W.L. Driessen, J. Reedijk, Chem. Soc. Rev. 30 (2001) 376–385.
[35] R.L. Lieberman, A.C. Rosenzweig, Nature 434 (2005) 177–182.
[36] S.I. Chan, V.C.-C. Wang, J.C.-H. Lai, S.S.-F. Yu, P.P.-Y. Chen, K.H.-C. Chen, C.-L. Chen, M.K. Chan, Angew. Chem. Int. Ed. 46 (2007) 1992–1994.
[37] Z. Otwinowski, W. Minor, in: C.W. Carter, J. Sweet (Eds.), Methods in Enzymology, Volume 276, Macromolecular Crystallography, Part A, Academic Press, New York, USA, 1997, pp. 307–326.
[38] G.M. Sheldrick, Acta Crystallogr. A 64 (2008) 112–122.
[39] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837–838.
[40] Bruker, APEX2 & SAINT, AXS Inc., Madison, WI, 2004.
[41] G.B. Shul'pin, J. Mol. Catal. A: Chem. 189 (2002) 39–66.
[42] G.B. Shul'pin, CR Chimie 6 (2003) 163–178.
[43] M.V. Kirillova, A.M. Kirillov, A.J.L. Pombeiro, Adv. Synth. Catal. 351 (2009) 2936–2948.
[44] M.V. Kirillova, A.M. Kirillov, A.J.L. Pombeiro, Appl. Catal. A: Gen. 401 (2011) 106–113.
[45] M.V. Kirillova, A.M. Kirillov, A.J.L. Pombeiro, Chem. Eur. J. 16 (2010) 9485–9493.
[46] A.M. Kirillov, Y.Y. Karabach, M.V. Kirillova, M. Haukka, A.J.L. Pombeiro, Dalton Trans. 40 (2011) 6378–6381.
[47] A.M. Kirillov, J.A.S. Coelho, M.V. Kirillova, M.F.C. Guedes da Silva, D.S. Nesterov, K.R. Gruenwald, M. Haukka, A.J.L. Pombeiro, Inorg. Chem. 49 (2010) 6390–6392.
[48] A.M. Kirillov, Y.Y. Karabach, M. Haukka, M.F.C. Guedes da Silva, J. Sanchiz, M.N. Kopylovich, A.J.L. Pombeiro, Inorg. Chem. 47 (2008) 162–175.
[49] Y.Y. Karabach, A.M. Kirillov, M. Haukka, J. Sanchiz, M.N. Kopylovich, A.J.L. Pombeiro, Cryst. Growth Des. 8 (2008) 4100–4108.
[50] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th ed., Wiley, New York, 1997.
[51] A.M. Kirillov, M.N. Kopylovich, M.V. Kirillova, E.Y. Karabach, M. Haukka, M.F.C.G. da Silva, A.J.L. Pombeiro, Adv. Synth. Catal. 348 (2006) 159–174.
[52] A.M. Kirillov, M.N. Kopylovich, M.V. Kirillova, M. Haukka, M.F.C.G. da Silva, A.J.L. Pombeiro, Angew. Chem. Int. Ed. 44 (2005) 4345–4349.
[53] G.B. Shul'pin, Y.N. Kozlov, L.S. Shul'pina, A.R. Kudinov, D. Mandelli, Inorg. Chem. 48 (2009) 10480–10482.
[54] G.B. Shul'pin, Y.N. Kozlov, L.S. Shul'pina, P.V. Petrovskiy, Appl. Organomet. Chem. 24 (2010) 464–472.
[55] G.B. Shul'pin, G.V. Nizova, Y.N. Kozlov, L. Gonzalez Cuervo, G. Süss-Fink, Adv. Synth. Catal. 346 (2004) 317–332.
[56] M.V. Kirillova, M.L. Kuznetsov, V.B. Romakh, L.S. Shul'pina, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, G.B. Shul'pin, J. Catal. 267 (2009) 140–157.
[57] L.S. Shul'pina, M.V. Kirillova, A.J.L. Pombeiro, G.B. Shul'pin, Tetrahedron 65 (2009) 2424–2429.
[58] G.V. Nizova, B. Krebs, G. Süss-Fink, S. Schindler, L. Westerheide, L. Gonzalez Cuervo, G.B. Shul'pin, Tetrahedron 58 (2002) 9231–9237.
[59] G.B. Shul'pin, M.V. Kirillova, Y.N. Kozlov, L.S. Shul'pina, A.R. Kudinov, A.J.L. Pombeiro, J. Catal. 277 (2011) 164–172.
[60] G.B. Shul'pin, M.V. Kirillova, T. Sooknoi, A.J.L. Pombeiro, Catal. Lett. 128 (2008) 135–141.
[61] G.B. Shul'pin, G. Süss-Fink, L.S. Shul'pina, J. Mol. Catal. A: Chem. 170 (2001) 17–34.
[62] Y.N. Kozlov, G.V. Nizova, G.B. Shul'pin, J. Phys. Org. Chem. 21 (2008) 119–126.
[63] For a recent review on regioselectivity, see: G.B. Shul'pin, Org. Biomol. Chem. 8 (2010) 4217–4228.
[64] F. Minisci, A. Citterio, C. Giordano, Acc. Chem. Res. 16 (1983) 27–32.
[65] M.V. Kirillova, M.L. Kuznetsov, P.M. Reis, J.A.L. da Silva, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, J. Am. Chem. Soc. 129 (2007) 10531–10545.
[66] P.M. Reis, J.A.L. Silva, A.F. Palavra, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, J. Catal. 235 (2005) 333–340.
[67] G.A. Olah, G.K. Surya Prakash, Á. Molnár, J. Sommer, Superacid Chemistry, 2nd ed., Wiley, New York, 2009.