



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 $[\text{Cu}(\text{H}_3\text{L}^1)(\text{NCS})]$ (**1**) and $[\text{Cu}_2(\mu\text{-HL}^2)_2(\text{NCS})_2]$ (**2**) were easily self-assembled from $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$, 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(\pm), 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 $\text{K}_2\text{S}_2\text{O}_8$, of various linear and cyclic C_n ($n = 5\text{--}8$) 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.

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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.

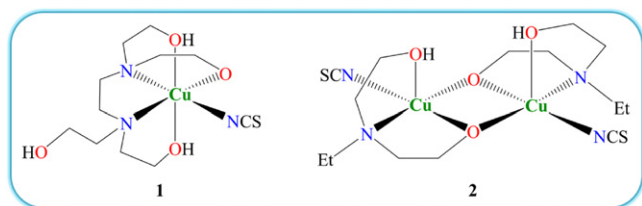
Following our general research line focused on the development of new catalytic systems for the oxidative functionalization of hydrocarbons [16–22] and alcohols [23–25], we have obtained a series of multicopper(II) compounds bearing aminopolyalcoholate ligands and applied them as valuable and versatile 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 $[\text{Cu}(\text{H}_3\text{L}^1)(\text{NCS})]$ (**1**) and $[\text{Cu}_2(\mu\text{-HL}^2)_2(\text{NCS})_2]$ (**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, H₂O and K₂S₂O₈, of various linear and cyclic C_n (n=5–8) alkanes into the corresponding C_{n+1} carboxylic acids (Scheme 2).

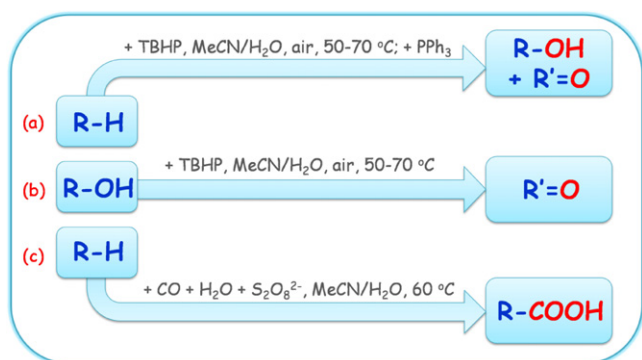
2. Experimental

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(CH₃COO)₂·H₂O (100 mg, 0.50 mmol) was added N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine (107 μL, 0.50 mmol; for **1**) or N-ethyl-diethanolamine (66 μL, 0.50 mmol; for **2**) with continuous stirring at room temperature (ca. 25 °C). Sodium thiocyanate



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) C₅–C₈ linear and cyclic alkanes.

(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.

[Cu(H₃L¹)(NCS)] (1). Anal. calcd for C₁₁H₂₃CuN₃NaO₄S (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%) [Cu₂(H₃L¹)₂-H]⁺, 298 (25%) [Cu(H₃L¹)]⁺; MS(-), *m/z*: 478 (10%) [Cu₂(H₃L¹)(NCS)₂]⁻, 298 (10%) [Cu(H₂L¹)]⁻, 180 (100%) [Cu(NCS)₂]⁻.

[Cu₂(μ-HL²)₂(NCS)₂] (2). Anal. calcd for C₁₄H₂₈Cu₂N₄O₄S₂ (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%) [Cu₄(HL²)₄(NCS)₂-H]⁺, 780 (100%) [Cu₄(L²)₄+H]⁺; MS(-), *m/z*: 822 (40%) [Cu₄(L²)₃(NCS)₃]⁻, 300 (15%) [Cu₂(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**: C₁₁H₂₃CuN₃O₄S, M = 356.92, λ = 0.71073 Å (Mo-Kα), T = 120(2) K, orthorhombic, space group P2₁2₁2₁, a = 8.0796(2), b = 13.5380(7), c = 13.8637(7) Å, V = 1516.43(12) Å³, Z = 4, D_c = 1.563 g/cm³, F₀₀₀ = 748, μ = 1.594 mm⁻¹, 19,574 reflections collected, 3480 unique, I > 2σ(I) (R_{int} = 0.0599), R₁ = 0.0344, wR₂ = 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**: C₁₄H₂₈Cu₂N₄O₄S₂, 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) Å³, Z = 16, D_c = 1.580 g/cm³, F₀₀₀ = 4192, μ = 2.219 mm⁻¹, 35,634

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