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### New Tetracopper(II) Cubane Cores Driven by a Diamino Alcohol: Selfassembly Synthesis, Structural and Topological Features, and Magnetic and Catalytic Oxidation Properties

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Supporting Information

ABSTRACT: Two new coordination compounds with tetracopper(II) cores, namely, a 1D coordination polymer,  $[Cu_4(\mu_4-H_2edte)(\mu_5-H_2edte)(sal)_2]_n$ .  $10nH_2O(1)$ , and a discrete 0D tetramer,  $[Cu_4(\mu_4-Hedte)_2(Hpmal)_2(H_2O)]$ .  $7.5H_2O(2)$ , were easily self-assembled from aqueous solutions of copper(II) nitrate, N, N, N', N'-tetrakis(2-hydroxyethyl)ethylenediamine (H<sub>4</sub>edte), salicylic acid  $(H_2 sal)$ , or phenylmalonic acid  $(H_2 pma)$ . The obtained compounds were characterized by IR and electron paramagnetic resonance spectroscopy, thermogravimetric and elemental analysis, and single-crystal X-ray diffraction. In addition to different dimensionalities, their structures reveal distinct singleopen  $[Cu_4(\mu_2-O)(\mu_3-O)_3]$  (in 1) or double-open  $[Cu_4(\mu_2-O)_2(\mu_3-O)_2]$  (in 2) cubane cores with 3M4-1 topology. In crystal structures, numerous crystallization water molecules are arranged into the intricate infinite 1D  $\{(H_2O)_{18}\}_n$  water tapes (in 1) or discrete  $(H_2O)_9$  clusters (in 2) that participate in multiple hydrogen-bonding interactions with the metal-organic



hosts, thus extending the overall structures into very complex 3D supramolecular networks. After simplification, their topological analysis revealed the binodal 6,10- or 6,8-connected underlying 3D nets with unique or rare 6,8T2 topology in 1 and 2, respectively. The magnetic properties of 1 and 2 were investigated in the 1.8-300 K temperature range, indicating overall antiferromagnetic interactions between the adjacent  $Cu^{II}$  ions within the  $[Cu_4O_4]$  cores. The obtained compounds also act as bioinspired precatalysts for mild homogeneous oxidation, by aqueous hydrogen peroxide at 50 °C in an acidic MeCN/H2O medium, of various cyclic and linear  $C_5-C_8$  alkanes to the corresponding alcohols and ketones. Overall product yields of up to 21% (based on alkane) were achieved, and the effects of various reaction parameters were studied.

#### INTRODUCTION

Amino alcohols are recognized N,O building blocks for the design of coordination compounds that include a diversity of discrete multinuclear metal complexes, clusters, and molecular wheels, as well as various coordination polymers and metalorganic frameworks.<sup>1-3</sup> Owing to their different functional properties, these amino alcohol driven compounds have found notable applications in areas ranging from molecular magnetism and catalysis to supramolecular chemistry and crystal engineering.3-7

Among the variety of simple amino alcohols (e.g., N,Ndimethylethanolamine, diethanolamine, and triethanolamine), N, N, N', N'-tetrakis(2-hydroxyethyl)ethylenediamine (H<sub>4</sub>edte) represents an interesting multidentate diamine with four ethyl alcohol groups. However, in spite of its low cost and commercial availability, water solubility and stability, potential coordination flexibility and versatility, the application of H<sub>4</sub>edte toward the design of multinuclear metal complexes and, in particular, coordination polymers has remained underexplored.<sup>1,6,7</sup> Although some notable examples of high-nuclearity

 $Mn^6$  and  $Fe^7$  clusters driven by H<sub>4</sub>edte have been reported, the coordination chemistry of H<sub>4</sub>edte toward Cu is still limited to single mono- or dicopper(II) complexes, 5a,8 as attested by a search of the Cambridge Structural Database.<sup>1</sup>

Bearing these points in mind and following our general interest in the exploration of various amino alcohol building blocks for the generation, by a simple aqueous medium selfassembly method, of diverse functional multicopper(II) complexes and coordination polymers,<sup>3,5</sup> the principal objectives of the current work consisted of (i) opening up the application of H<sub>4</sub>edte for the preparation of new discrete and polymeric multicopper(II) derivatives, (ii) identifying their structural and topological features, and (iii) studying their magnetic and catalytic behavior.

Hence, we report herein the aqueous medium self-assembly generation, full characterization, crystal structures, topological analysis, and magnetic and oxidation catalytic properties of two

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novel H<sub>4</sub>edte-driven tetracopper(II) compounds, namely, a 1D coordination polymer,  $[Cu_4(\mu_4-H_2edte)(\mu_5-H_2edte)(sal)_2]_n$ . 10*n*H<sub>2</sub>O (1), and a discrete 0D tetramer,  $[Cu_4(\mu_4-Hedte)_2(Hpmal)_2(H_2O)]\cdot7.5H_2O$  (2). Apart from representing the first multicopper clusters derived from H<sub>4</sub>edte,<sup>1</sup> both compounds also display distinct single- or double-open  $[Cu_4O_4]$  cubane cores, act as metal—organic matrixes to store intricate water clusters, reveal the formation of complex 3D supramolecular networks with undocumented or rare topologies, and function as promising bioinspired precatalysts for the mild oxidation of different cyclic and linear  $C_5-C_8$  alkanes to produce the corresponding alcohols and ketones.

#### EXPERIMENTAL SECTION

General Synthetic Procedure and Characterization for 1 and 2. To an aqueous 0.1 M solution of  $Cu(NO_3)_2$ ·3H<sub>2</sub>O (10 mL, 1 mmol) was added an aqueous 1 M solution of  $N_iN_iN'_iN'$ -tetrakis(2-hydroxyethyl)ethylenediamine (H<sub>4</sub>edte; 0.5 mL, 0.5 mmol) with continuous stirring at room temperature. Then, salicylic acid (H<sub>2</sub>sal; 138 mg, 1 mmol) for 1 or phenylmalonic acid (H<sub>2</sub>pmal; 90 mg, 0.5 mmol) for 2 and an aqueous 1 M solution of NaOH (3 mL, 3 mmol; up to pH ~8) were added to the reaction mixture. The resulting solution was stirred for 1 day and then filtered off. The filtrate was left to evaporate in a beaker at room temperature. Green crystals (including those suitable for single-crystal X-ray diffraction) were formed in 1 month, then collected, and dried in air to furnish compounds 1 and 2 in ~50% yield, based on copper(II) nitrate.

 $[Cu_4(\mu_4-H_2edte)(\mu_5-H_2edte)(sal)_2]_n \cdot 10nH_2O (1). Anal. Calcd for 1 - 3H_2O (Cu_4C_{34}H_{66}N_4O_{21}; MW 1121.1): C, 36.43; H, 5.93; N, 5.00. Found: C, 36.11; H, 5.67; N, 4.87. IR (KBr, cm<sup>-1</sup>): <math>\nu$ (OH) 3362 (s br),  $\nu$ (CH) 2864 (s br),  $\nu$ <sub>as</sub>(COO) 1602 (s), 1566 (s), and 1528 (s),  $\nu$ <sub>s</sub>(COO) 1453 (s) and 1377 (s), 1320 (m),  $\nu$ (C-X) (X = C, N, O) 1253 (s), 1142 (m), and 1066 (s br), 887 (m br), 834 (w), 768 (m), 712 (w), 639 (w), 585 (w), 494 (w). ESI-MS(±) (MeCN/H\_2O): selected fragments with relative abundance >5%. MS(-): m/z 994 (100%) [Cu<sub>4</sub>(H<sub>2</sub>edte)<sub>2</sub>(sal)<sub>2</sub> - H]<sup>-</sup>, 949 (15%) [Cu<sub>4</sub>(H<sub>2</sub>edte)<sub>2</sub>(sal)<sub>2</sub>]<sup>+</sup>, 796 (15%) [Cu<sub>3</sub>(H<sub>2</sub>edte)<sub>2</sub>(Hsal)]<sup>+</sup>, 641 [Cu<sub>4</sub>(Hedte)(sal)(H<sub>2</sub>O)]<sup>+</sup>, 597 (100%) [Cu<sub>4</sub>(Hedte)(sal)(H<sub>2</sub>O) - CH<sub>2</sub>CH<sub>2</sub>OH]<sup>+</sup>.

 $[Cu_4(\mu_4\text{-Hedte})_2(Hpmal)_2(H_2O)]\cdot 7.5H_2O$  (2). Anal. Calcd for 2 (Cu<sub>4</sub>C<sub>38</sub>H<sub>73</sub>N<sub>4</sub>O<sub>24.5</sub>, MW 1232.2): C, 37.04; H, 5.97; N, 4.55. Found: C, 37.03; H, 5.50; N, 4.54. IR (KBr):  $\nu$ (OH) 3419 (s br),  $\nu$ (CH) 2856 (m),  $\nu_{as}$ (COO) 1624 (s br) and 1597 (s),  $\nu_s$ (COO) 1409 (m) and 1395 (m),  $\nu$ (C-X) (X = C, N, O) 1274 (w), 1059 (m), and 1034 (w), 906 (w), 730 (m), 637 (w), 504 (w).

X-ray Crystallography. Crystals of 1 and 2 suitable for X-ray diffraction study were mounted with Fomblin in a cryoloop. Data were collected on a Bruker AXS-Kappa APEX II diffractometer with graphite-monochromated radiation (Mo K $\alpha$ ,  $\lambda$  = 0.17073 Å). The Xray generator was operated at 50 kV and 30 mA, and the X-ray data collection was monitored by the APEX2 program.9 All data were corrected for Lorentzian, polarization, and absorption effects with the SAINT and SADABS programs.<sup>9</sup> SIR97<sup>10</sup> and SHELXS-97<sup>11</sup> were used for structure solution, and SHELXL-97<sup>11</sup> was applied for full-matrix least-squares refinement on  $F^2$ . These three programs are included in the package of programs WINGX, version 1.80.05.12 Non-H atoms were refined anisotropically. A full-matrix least-squares refinement was used for the non-H atoms with anisotropic thermal parameters. All of the H atoms were inserted in idealized positions and allowed to refine in the parent C or O atom, except for the hydroxide H atoms in the amino alcohol ligands, which were located from the electron density map. It was not possible to locate the water H atoms. In both structures, there are disordered water molecules (O9w, O10w, O11w, and O12w in compound 1 and O8w in compound 2) with 0.5 occupancy factors; in the specific case of compound 2, O8w resides near special positions, and thus both positions are nearby. TOPOS 4.0<sup>13</sup> and PLATON<sup>14</sup> were used for topological analysis and hydrogenbonding interactions, respectively. Crystal data and details of data collection for 1 and 2 are reported in Table 1.

## Table 1. Crystal Data and Structure Refinement Details for Compounds 1 and 2

	1	2
formula	Cu <sub>4</sub> C <sub>34</sub> H <sub>52</sub> N <sub>4</sub> O <sub>23</sub>	Cu4C38H56N4O23.5
fw	1139	1199
cryst form, color	plate, green	plate, blue
cryst size (mm)	$0.2 \times 0.1 \times 0.02$	$0.2 \times 0.15 \times 0.04$
cryst syst	orthorhombic	triclinic
space group	Pbca	$P\overline{1}$
a, Å	17.7705(9)	12.838(6)
<i>b,</i> Å	22.3871(12)	13.677(4)
<i>c,</i> Å	23.5210(13)	15.199(3)
$\alpha$ , deg	90	85.959(5)
$\beta$ , deg	90	83.915(6)
γ, deg	90	69.114(4)
Ζ	8	2
<i>V,</i> Å	9357.4(9)	2477.8(15)
Т, К	150(2)	293(2)
$D_{cr}$ g cm <sup>-3</sup>	1.617	1.607
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	1.878	1.779
$\theta$ range (deg)	2.27-26.37	2.26-26.35
reflns collected	63901	42251
indep reflns	9487	10015
$R_{\rm int}$	0.1308	0.0669
R1, <sup><i>a</i></sup> wR2 <sup><i>b</i></sup> $[I \ge 2\sigma(I)]$	0.0943, 0.1671	0.0558, 0.1511
GOF on $F^2$	1.105	1.010
${}^{a}\mathrm{R1} = \sum_{v}   F_{o}  -  F_{c}   / \sum_{v} [w(F_{o}^{2})^{2}]^{1/2}.$	$\sum  F_{o} .  {}^{b} wR2 = []$	$\sum [w(F_{o}^{2} - F_{c}^{2})^{2}]/$

**Magnetic Studies.** The magnetization of powdered samples 1 and 2 was measured over the 1.8–300 K temperature range using a Quantum Design SQUID-based MPMSXL-5-type magnetometer. The superconducting magnet was generally operated at a field strength ranging from 0 to 5 T. Sample measurements were made at a magnetic field of 0.5 T. The SQUID magnetometer was calibrated with the palladium rod sample. Corrections are based on subtraction of the sample-holder signal, and the  $\chi_{\rm D}$  contribution was estimated from Pascal's constants.<sup>15</sup>

Catalytic Studies. The alkane oxidations were carried out in an air atmosphere in thermostated Pyrex reactors equipped with a condenser, under vigorous stirring at 50 °C, and using acetonitrile (MeCN) as the solvent (up to 5.0 mL total volume). In a typical experiment, a solid precatalyst, 1 or 2 (0.01 mmol), and gas chromatography (GC) internal standard (MeNO<sub>2</sub>, 50  $\mu$ L) were introduced into a MeCN solution, followed by the addition of an acid promoter (0.01-0.20 mmol) used as a stock solution in MeCN. The alkane substrate (2 mmol) was then introduced, and the reaction started upon the addition of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>; 50% in water, 10 mmol) in one portion. The reactions were monitored by withdrawing small aliquots after different periods of time, which were treated with PPh<sub>3</sub> (following a method developed by Shul'pin)<sup>16</sup> for reduction of the remaining H<sub>2</sub>O<sub>2</sub> and alkyl hydroperoxides that are typically formed as major primary products in alkane oxidation. The samples were analyzed by GC using nitromethane as an internal standard. Attribution of the peaks was made by a comparison with the chromatograms of authentic samples. Chromatographic analyses were run on an Agilent Technologies 7820A series gas chromatograph (helium as the carrier gas) equipped with a flame ionization detector and a BP20/SGE (30 m  $\times$  0.22 mm  $\times$  0.25  $\mu$ m) capillary column. Blank tests confirmed that alkane oxidation does not proceed in the absence of a copper precatalyst. Given a possibility of alkane oxidation by Cu ions in the presence of trifluoroacetic acid (TFA),<sup>17</sup> control tests were also performed for the oxidation of cyclohexane by  $H_2O_2$ 

with copper(II) nitrate as a precatalyst (reaction conditions were those of Table 2), either in the absence or in the presence of a TFA

## Table 2. Mild Oxidation of Different $C_5-C_8$ Alkanes by the 1/TFA/H<sub>2</sub>O<sub>2</sub> and 2/TFA/H<sub>2</sub>O<sub>2</sub> Systems<sup>*a*</sup>

 $R-H \xrightarrow[MecN/H_2O_2 (50\% \text{ aq.})]{Cu \text{ pre-catalyst,}} R-OH + R'=O$ 

	total yield of oxidation products, $\%^b$	
alkane (R–H)	1/TFA/H <sub>2</sub> O <sub>2</sub>	$2/TFA/H_2O_2$
cyclopentane	7.2	8.9
cyclohexane	13.5	16.2
cycloheptane	21.2	19.8
cyclooctane	16.0	19.3
<i>n</i> -pentane	3.1	2.8
<i>n</i> -hexane	4.2	6.1
n-heptane	10.2	9.4
<i>n</i> -octane	4.4	4.5

<sup>*a*</sup>Reaction conditions: precatalyst 1 or 2 (0.01 mmol), TFA (0.05 mmol), alkane (1.0 mmol),  $H_2O_2$  (50% aq, 5.0 mmol), MeCN (up to 5 mL total volume), 50 °C, 3 h. <sup>*b*</sup>Based on an alkane substrate, calculated from GC analysis after treatment of the reaction mixture with PPh<sub>3</sub>; total yields [(moles of products per mole of substrate) × 100%] correspond to the sum of yields of cyclic alcohols and ketones in the case of cycloalkane oxidation or to the sum of yields of various isomeric alcohols and ketones (aldehydes) in the case of *n*-alkane oxidation; for yields of each product, see Table S1 in the SI.

promoter, resulting in 3.0 or 3.1% total product yield, respectively. These yields are significantly inferior to those achieved in the 1/TFA/ $H_2O_2$  (13.5%) or 2/TFA/ $H_2O_2$  (16.2%) systems (Table 2), thus confirming the influence of ligands and their structural arrangement in the precatalysts 1 and 2 on the observed catalytic behavior.

#### RESULTS AND DISCUSSION

**Synthesis.** To probe the use of  $H_4$ edte as a multidentate amino alcohol building block for the synthesis of multicopper(II) coordination compounds, we applied an aqueous medium self-assembly method. Thus, a simple combination, in a water solution at ~25 °C in air, of copper(II) nitrate with  $H_4$ edte as a main building block, salicylic ( $H_2$ sal) or phenylmalonic ( $H_2$ pmal) acid as an ancillary ligand (Scheme 1), and sodium hydroxide as a pH regulator resulted in the self-





assembly generation of two new coordination compounds bearing tetracopper(II) cubane cores, namely, a 1D coordination polymer,  $[Cu_4(\mu_4-H_2edte)(\mu_5-H_2edte)(sal)_2]_n\cdot10nH_2O$ (1), and a discrete 0D tetramer,  $[Cu_4(\mu_4-Hedte)_2 \times (Hpmal)_2(H_2O)]\cdot7.5H_2O$  (2). The choice of  $H_2sal$  was governed by its recognized application as a simple ancillary ligand to stabilize multicopper(II) cores,<sup>1</sup> whereas  $H_2pmal$  was selected because of its little explored use in copper(II) coordination chemistry,<sup>18</sup> as well as to find out whether the presence of two aliphatic carboxylic groups in addition to a phenyl ring can affect the structure of the resulting product. However, the self-assembly of 1 and 2 appeared to be primarily guided by  $H_4$ edte as a main building block, with both ancillary acids acting as terminal ligands. The obtained products were isolated as air-stable microcrystalline materials and characterized by IR and EPR spectroscopy, thermogravimetric and elemental analysis, and single-crystal X-ray diffraction (for discussion of the spectral and thermogravimetric data, see the Supporting Information, SI).

Structural and Topological Description. Compound 1 is a 1D coordination polymer, the structure of which is composed of the repeating tetracopper(II)  $[Cu_4(\mu_4-H_2edte)(\mu_5-H_2edte)-$ (sal)<sub>2</sub> units (Figure 1a) and 10 crystallization water molecules. The adjacent Cu<sub>4</sub> blocks reveal a single-open  $[Cu_4(\mu_2-O)(\mu_3-$ O),] cubane core and are interconnected via one of the hydroxyethyl arms of the  $\mu_5$ -H<sub>2</sub>edte ligand, forming an infinite metal-organic chain (Figure 1b). The tetracopper(II) blocks consist of four symmetry-nonequivalent Cu atoms, two chelating salicylate(2–) ligands, one  $\mu_4$ -H<sub>2</sub>edte(2–) moiety, and one  $\mu_5$ -H<sub>2</sub>edte(2–) moiety. The five-coordinate Cu1 atom shows a distorted square-pyramidal {CuO<sub>5</sub>} environment ( $\tau_5$  = 0.18 in 1;  $\tau_5 = 0$  for an idealized square-pyramidal geometry),<sup>19a,b</sup> filled by the salicylate O1 and O2 atoms and the amino alcohol O7 and O14 atoms [Cu1-O1 1.927(6) Å; Cu1-O2 1.890(6) Å; Cu1-O7 1.956(5) Å] in equatorial positions, whereas an axial site is taken by the O8<sup>i</sup> atom [Cu1- $O8^{i} 2.432(6)$  Å]. The five-coordinate Cu2 center is very similar to Cu1 in geometrical terms, with its square-pyramidal  $\{CuO_5\}$ environment ( $\tau_5 = 0.15$ ) occupied by two sal and three H<sub>2</sub>edte O atoms; the Cu2–O distances are in the 1.902(6)-2.404(6)Å range. The six-coordinate Cu3 atom exhibits a distorted octahedral { $CuN_2O_4$ } geometry, filled by the N1, N2, O9, and O13 atoms in the equatorial sites [Cu3–N1 2.099(6) Å; Cu3– N2 1.990(8) Å; Cu3–O10 1.943(6) Å; Cu3–O13 1.941(6) Å], whereas the apical positions are taken by the remaining O7 and O9 atoms of the  $\mu_4$ -H<sub>2</sub>edte moiety [Cu3-O7 2.395(5) Å; Cu3-O9 2.648(8) Å]. The six-coordinate Cu4 atom is essentially similar to Cu3, revealing even a more distorted octahedral { $CuN_2O_4$ } environment filled by the equatorial N3, N4, O13, and O14 atoms [Cu4-N3 2.009(8) Å; Cu4-N4 2.071(7) Å; Cu4-O13 1.901(6) Å; Cu4-O14 1.988(6) Å] and the axial O10 and O12 atoms [Cu4–O10 2.900(6) Å; Cu4– O12 2.428(8) Å] of the  $\mu_5$ -H<sub>2</sub>edte ligand, which possesses one hydroxyethyl arm connected to the Cu1 atom of an adjacent tetracopper(II) block. Although some of the Cu–O bonds [i.e., Cu3-O9 2.648(8) Å and Cu4-O10 2.900(6) Å] are rather long, these are still inferior to the sum of the van der Waals radii of the Cu and O atoms ( $\sim$ 2.92 Å).<sup>19c</sup> The four Cu centers are mutually interconnected via three  $\mu_3$ -O and one  $\mu_2$ -O atoms of two H<sub>2</sub>edte moieties to generate a distorted single-open  $[Cu_4(\mu_2-O)(\mu_3-O)_3]$  cubane core (Scheme 2b,e) with the Cu··· Cu separations in the 3.129(2)-3.624(1) Å range (avg 3.329 Å). From the topological viewpoint, <sup>13a,b</sup> both regular and open [Cu<sub>4</sub>O<sub>4</sub>] cubane cores (Scheme 2) can be classified as uninodal 3-connected motifs with 3M4-1 topology and a point symbol of  $(3^3)$ . Scheme 2d shows a graph of the Cu<sub>4</sub> skeleton obtained after transforming the  $\mu$ -O atoms in the  $[Cu_4(\mu_2-O)(\mu_3-O)_3]$ core to Cu–Cu edges, by applying a method developed for the topological analysis of coordination clusters.  $^{\rm 13a,b,19,20}$ 

A notable feature of 1 consists of the presence of numerous crystallization water molecules that are arranged into intricate



Figure 1. Structural fragments of 1 showing (a) a tetracopper(II)  $[Cu_4(\mu_4-H_2edte)(\mu_5-H_2edte)(sal)_2]$  unit with an atom numbering scheme, (b) a 1D metal-organic chain with polyhedral representation of the coordination environments around Cu atoms, and (c) a topological representation of the underlying binodal 6,10-connected 3D supramolecular network. Further details: (a and b) H atoms omitted for clarity [Cu, green; O, red; N, blue; C, gray]; (c) view along the *a* axis, centroids of 6-connected  $[Cu_4(H_2edte)_2(sal)_2]$  (green balls) and 10-connected  $(H_2O)_{18}$  (gray) nodes. Selected distances (Å): Cu1-O1 1.927(6), Cu1-O2 1.890(6), Cu1-O7 1.956(5), Cu1-O8<sup>i</sup> 2.432(6), Cu1-O14 1.970(6), Cu2-O4 1.902(6), Cu2-O5 1.908(7), Cu2-O7 1.975(6), Cu2-O10 1.921(5), Cu2-O14 2.404(6), Cu3-O7 2.395(5), Cu3-O9 2.648(8), Cu3-O10 1.943(6), Cu3-O13 1.941(6), Cu3-N1 2.099(6), Cu3-N2 1.990(8), Cu4-O10 2.900(6), Cu4-O12 2.428(8), Cu4-O13 1.901(6), Cu4-O14 1.988(6), Cu4-N3 2.009(8), Cu4-N4 2.071(7), Cu1--Cu2 3.129(2), Cu1--Cu3 3.624(1), Cu1…Cu4 3.453(1), Cu2…Cu3 3.156(2), Cu2…Cu4 3.387(2), Cu3…Cu4 3.322(2). Symmetry code: (i)  $x + \frac{1}{2}$ , y,  $-z + \frac{3}{2}$ .

infinite 1D { $(H_2O)_{18}$ }, water tapes (Figure S3a in the SI), built from cyclic  $(H_2O)_n$  (n = 8, 3) associates. Given the presence of some disorder, these water tapes can be roughly classified within the T8 general type according to the systematization introduced by Infantes and Motherwell.<sup>21</sup> These water tapes participate in multiple intermolecular hydrogen-bonding interactions with the host 1D metal–organic chains, thus extending the structure into a very complex 3D supramolecular network (Figure S4a in the SI). To gain further insight into this network, we have performed its topological analysis by following the concept of a simplified underlying net.<sup>13</sup> The structure of 1 underwent a significant simplification, namely involving the contraction of the [ $Cu_4(H_2edte)_2(sal)_2$ ] units and the ( $H_2O$ )<sub>18</sub> fragments of water tapes to the centroids that correspond to the 6- and 10-connected nodes, respectively. The Scheme 2. Schematic Representation of (a) Regular, (b) Single-Open, and (c) Double-Open  $[Cu_4O_4]$  Cubane Cores and (d) Their Simplified Topological Graph Showing a Uninodal 3-Connected Motif with 3M4-1 Topology and a Point Symbol of (3<sup>3</sup>) and Ball-and-Stick Representation of Distorted (e) Single-Open  $[Cu_4(\mu_2-O)(\mu_3-O)_3]$  and (f) Double-Open  $[Cu_4(\mu_2-O)_2(\mu_3-O)_2]$  Cubane Cores in 1 and 2, Respectively<sup>*a*</sup>



<sup>*a*</sup>Color code: Cu centers, green balls; O atoms, red balls.

resulting binodal 6,10-connected net (Figure 1c) has a point symbol of  $(3^5.4^7.5^2.6)_2(3^8.4^{12}.5^{20}.6^4.7)$  and is topologically unique, as confirmed by a search of various databases.<sup>1,13,22a</sup>

The discrete 0D structure of **2** bears a neutral tetracopper(II)  $[Cu_4(\mu_4-Hedte)_2(Hpmal)_2(H_2O)]$  unit (Figure 2a) and 7.5 crystallization water molecules. Although this Cu<sub>4</sub> unit resembles that of 1, there are a few differences, which consist of (i) the compound's dimensionality (0D in 2 vs 1D in 1), (ii) the presence of two monoprotonated  $\mu_4$ -Hedte ligands in 2 versus  $\mu_4$ - and  $\mu_5$ -H<sub>2</sub>edte in 1, and (iii) the existence of three five-coordinate (Cu1, Cu3, and Cu4) and one six-coordinate (Cu2) Cu atoms in 2 versus a pair of five- and six-coordinate Cu centers in 1. These differences lead to the formation of a slightly distinct double-open cubane  $[Cu_4(\mu_2-O)_2(\mu_3-O)_2]$  core in 2 (Scheme 2c,f) with the Cu…Cu separations ranging from 3.102(1) to 3.548(2) Å (avg 3.309 Å). This core also has 3M4-1 topology (Scheme 2d). In 2, the Cu1 and Cu4 centers show resembling distorted square-pyramidal {CuO<sub>5</sub>} environments ( $\tau_5 = 0.16$  and 0.12, respectively),<sup>19a,b</sup> which are filled by two O atoms of the chelating monoprotonated phenylmalonate(-)ligands [Cu1-O1 1.952(3) Å; Cu1-O3 1.937(3) Å; Cu4-O7 1.931(3) Å; Cu4–O8 1.923(3) Å] and the remaining O atoms coming from the Hedte moieties [Cu1–O4 1.966(3) Å; Cu1– O5 1.924(3) Å; Cu1–O12 2.303(3) Å; Cu4–O4 1.942(3) Å; Cu4–O12 1.946(3) Å] as well as a coordinated water molecule [only at the Cu4 center, Cu4–O7w 2.498(5) Å]. In contrast, the Cu3 atom features a  $\{CuN_2O_3\}$  geometry that is better considered as a highly distorted trigonal-bipyramidal ( $\tau_5 = 0.65$ in 2;  $\tau_5 = 1$  for idealized trigonal-bipyramidal geometry),<sup>19a,b</sup> which is filled by the equatorial N4, O6, and O12 atoms and the axial N3 and O11 atoms of Hedte moieties [Cu3-N4 2.021(4) Å; Cu3-O6 1.917(3) Å; Cu3-O12 2.012(3) Å; Cu3-N3 2.098(4) Å; Cu3-O11 2.292(3) Å]. The sixcoordinate Cu2 atom exhibits a distorted octahedral  ${CuN_2O_4}$  environment filled by the basal N1, N2, O5, and O6 atoms and the apical O4 and O14 atoms of Hedte ligands [Cu2-N1 2.088(4) Å; Cu2-N2 1.990(5) Å; Cu2-O5 1.932(3) Å; Cu2-O6 1.936(3) Å; Cu2-O4 2.439(3) Å;



Figure 2. Structural fragments of 2 showing (a) a tetracopper(II)  $[Cu_4(\mu_4-Hedte)_2(Hpmal)_2(H_2O)]$  unit with atom numbering scheme and (b) a topological representation of the underlying binodal 6,8connected 3D supramolecular network with 6,8T2 topology. Further details: (a) H atoms omitted for clarity [Cu, green; O, red; N, blue; C, gray]; (b) view along the b axis, centroids of 8-connected [Cu<sub>4</sub>(Hedte)<sub>2</sub>(Hpmal)<sub>2</sub>(H<sub>2</sub>O)] (green balls) and 6-connected  $(H_2O)_9$  (gray) nodes. Selected distances (Å): Cu1-O1 1.952(3), Cu1-O3 1.937(3), Cu1-O4 1.966(3), Cu1-O5 1.924(3), Cu1-O12 2.303(3), Cu2-N1 2.088(4), Cu2-N2 1.990(5), Cu2-O4 2.439(3), Cu2-O5 1.932(3), Cu2-O6 1.936(3), Cu2-O14 2.576(8), Cu3-N3 2.098(4), Cu3-N4 2.021(4), Cu3-O6 1.917(3), Cu3-O11 2.292(3), Cu3-O12 2.012(3), Cu4-O4 1.942(3), Cu4-O7 1.931(3), Cu4-O7w 2.498(5), Cu4-O8 1.923(3), Cu4-O12 1.946(3), Cu1-Cu2 3.159(1), Cu1···Cu3 3.423(1), Cu1···Cu4 3.102(1), Cu2···Cu3 3.352(1), Cu2…Cu4 3.548(2), Cu3…Cu4 3.269(1).

Cu2–O14 2.576(8) Å]. In 2, most of the bonding parameters are comparable to those found in 1 and other Cu compounds derived from  $H_4$ edte.<sup>5a,8</sup> Because the reported Cu-edte derivatives are limited to a few mono- and dinuclear complexes,<sup>5a,8</sup> both compounds 1 and 2 not only represent the first examples of polynuclear copper clusters derived from  $H_4$ edte but also bear the first [ $M_4O_4$ ] cubane cores (Scheme 2) encountered in other transition-metal  $H_4$ edte-driven compounds.<sup>1</sup> Hence, the present work opens up the application of  $H_4$ edte toward the design of copper clusters.

Furthermore, several crystallization water molecules in 2 are assembled into discrete  $(H_2O)_9$  clusters that comprise a linear  $(H_2O)_7$  motif with two branched water groups (Figure S3b in the SI). These clusters can be classified within the D7 type.<sup>21</sup> An intense pattern of intermolecular hydrogen-bonding interactions involving such water clusters, discrete water

(O4w and O6w) molecules, and tetracopper(II) units leads to the generation of an intricate 3D supramolecular network (Figure S4b in the SI). For topological analysis,<sup>13</sup> this network has been simplified by reducing the 8-connected  $[Cu_4(Hedte)_2(Hpmal)_2(H_2O)]$  and 6-connected  $(H_2O)_9$  moieties to their centroids and eliminating discrete water molecules. The resulting binodal 6,8-connected net (Figure 2b) features 6,8T2 topology<sup>13,22</sup> with a point symbol of  $(3^2.4^{12}.5^{10}.6^4)(3^2.4^6.5^6.6)_2$ . This topological type is rare and was only identified in one compound.<sup>22b</sup>

**Magnetic Studies.** The magnetic properties of 1 and 2 were investigated over the temperature range of 1.8-300 K. Plots of the magnetic susceptibility  $\chi_m$  and  $\chi_m T$  product versus T ( $\chi_m$  is the molar magnetic susceptibility for four Cu<sup>II</sup> ions) are given in Figures S5 in the SI and 3a, respectively. At room



**Figure 3.** (a) Temperature dependence of experimental  $\chi_m T$  ( $\chi_m$  per 4 Cu<sup>II</sup> atoms) for 1 and 2. The solid lines (for 1 and 2) are the calculated curves derived from eq 1. (b) Schematic representation of the exchange coupling pattern in the model 2 + 4 [Cu<sub>4</sub>O<sub>4</sub>] cubane core.

temperature,  $\chi_m T$  is 1.52 and 1.59 cm<sup>3</sup> K mol<sup>-1</sup> for 1 and 2, respectively; these values are consistent with the presence of four uncoupled Cu<sup>II</sup> ions  $[\chi_m T = 4(N\beta^2 g^2/3k)S(S + 1) = 1.5]$ cm<sup>3</sup> K mol<sup>-1</sup>, assuming g = 2.1 and S = 1/2, where N,  $\beta$ , g, k, S, and T have their usual meaning].<sup>23</sup> Upon cooling,  $\chi_m T$ continuously decreases, reaching almost zero at 1.8 K in 1. These features are characteristic of an overall antiferromagnetic coupling in 1, which leads to a low-lying spin state (S = 0). Additionally, the maximum of the magnetic susceptibility is observed in the  $\chi_m$  versus T plot for 1 at 45 K (Figure S5 in the SI). The increase of  $\chi_m$  at low temperature indicates the presence of a small amount of paramagnetic impurities (S = 1/2). The absence of a maximum in the  $\chi_m$  curve of 2 may indicate that the possible coupling is weaker in this compound.



**Figure 4.** Oxidation of cyclohexane to cyclohexanol and cyclohexanone by  $H_2O_2$  in the presence of precatalyst **1**. (a) Evolution of the total product yield with time in the absence and in the presence of different acid promoters (TFA, HNO<sub>3</sub>,  $H_2SO_4$ , or HCl; 0.1 mmol). (b) Effect of the TFA amount on the evolution of the total product yield with time (1/TFA molar ratios: 1:0, 1:1, 1:2, 1:5, 1:10, and 1:20). General conditions:  $C_6H_{12}$  (2 mmol),  $H_2O_2$  (50% aqueous, 10 mmol), **1** (0.01 mmol), TFA (0–0.2 mmol), 50 °C, MeCN (up to 5 mL). For similar data with precatalyst **2**, see Figure S8 in the SI.

To confirm the nature of the ground state of 1 and 2, we have investigated variation of the magnetization (M) with respect to the field (H) at 2 K. The results are shown in Figure S6 in the SI, where the molar magnetization M (per Cu<sub>4</sub> entity) is expressed in  $\mu_{\rm B}$  units. The magnetization curves for 1 and 2 were reproduced by the equation  $M = g\beta SNB_s(x)$  ( $S = 4S_{\rm Cu}$ ), where  $B_s(x)$  is the Brillouin function and  $x = g\beta H/kT.^{23}$  The experimental values for 1 and 2 are much lower than those calculated using the Brillouin function for four noninteracting Cu<sup>II</sup> ions. This feature agrees with the global antiferromagnetic coupling within the four Cu<sup>II</sup> ions in 1 and 2.

In compounds 1 and 2, four  $Cu^{II}$  ions ( $Cu_a$ ,  $Cu_b$ ,  $Cu_c$ , and  $Cu_d$ ) occupy alternating cubane vertices and have six Cu...Cu exchange interactions. Considering the presence of two short (3.102–3.159 Å) and four rather long (3.269–3.624 Å) Cu... Cu separations in 1 and 2, their [ $Cu_4O_4$ ] cubane cores can be classified within the 2 + 4 type<sup>24</sup> and analyzed using the spin Hamiltonian given in eq 1:<sup>23</sup>

$$H = -J_1(\hat{S}_a\hat{S}_b + \hat{S}_c\hat{S}_d) - J_2(\hat{S}_a\hat{S}_c + \hat{S}_a\hat{S}_d + \hat{S}_b\hat{S}_c + \hat{S}_b\hat{S}_d)$$
(1)

where  $J_1$  and  $J_2$  are the intra- and interdinuclear exchange coupling constants between the local spins within the  $[Cu_4O_4]$ cubane core (Figure 3b). The molar magnetic susceptibility for 1 and 2 is given in the SI. A least-squares fitting of the experimental data leads to the following values:  $J_1 = -53.3(3)$ cm<sup>-1</sup>,  $J_2 = -23.7(5)$  cm<sup>-1</sup>, g = 2.09(1), and  $\rho = 5.4\%$  ( $R = 2.5 \times 10^{-4}$ ) for 1 and  $J_1 = -48.3(4)$  cm<sup>-1</sup>,  $J_2 = -1.2(1)$  cm<sup>-1</sup>, g = 2.24(2), and  $\rho = 3.4\%$  ( $R = 2.2 \times 10^{-4}$ ) for 2. The criterion applied to determine the best fit was based on the minimization of the sum of squares of the deviation,  $R = \sum (\chi_{exp}T - \chi_{calc}T)^2 / \sum (\chi_{exp}T)^2$ . The calculated curves for 1 and 2 (solid lines in Figure 3a) match very well with the experimental magnetic data in the whole temperature range. The obtained values of  $J_1$  and  $J_2$  indicate an antiferromagnetic coupling between the Cu<sup>II</sup> ions within the tetracopper(II) clusters in 1 and 2.

Magnetostructural correlations for the hydroxo- and alkoxobridged copper(II) compounds were proposed by Hatfield and co-workers.<sup>25</sup> They found that the nature and strength of the magnetic exchange coupling are mainly affected by the Cu···Cu distance and the Cu–O–Cu bridging angle ( $\alpha$ ). In general, the antiferromagnetic coupling is observed for large Cu-O-Cu bond angles and long Cu…Cu separations, whereas the ferromagnetic interaction is favored for small Cu-O-Cu bond angles (<97.5°), which usually imply shorter Cu…Cu distances. Although the Cu-O-Cu angles and Cu-Cu distances are the most crucial geometrical parameters, the coupling constants can also be modulated by other structural features. The values of  $J_1$  obtained for 1 and 2 are roughly in agreement with the earlier reported figures for this parameter in alkoxo-bridged  $[Cu_4O_4]$  cubanes.<sup>24,26–28</sup> The presence of antiferromagnetic interactions in 1 and 2 is certainly attributed to the relatively large Cu-O-Cu angles (mean value above 100°) and rather long Cu…Cu separations (avg 3.329 or 3.309 Å for 1 or 2, respectively). However, the calculated  $J_2$ parameters for 1 and 2 have negative values in contrast to the weakly ferromagnetic interactions generally found in the literature.<sup>27</sup> It was proposed that these interactions are practically independent of the geometrical parameters.<sup>24c</sup> In general, the magnetic behavior of 1 and 2 is in agreement with the majority of alkoxo-bridged tetranuclear copper(II) compounds. Although 1 and 2 show rather similar magnetic features, some distinction in their behavior may be caused by the 1D chain structure of 1 and the different coordination geometries of Cu atoms in these compounds.

**Mild Catalytic Oxidation of Alkanes.** Following our interest in the oxidative functionalization of alkanes under mild conditions catalyzed by multicopper(II) complexes, <sup>3,5b-e,29</sup> we probed both compounds 1 and 2 as precatalysts for the oxidation by  $H_2O_2$  of various cyclic and linear  $C_5-C_8$  alkanes to the corresponding alcohols and ketones. The oxidation reactions were carried out in an aqueous MeCN medium at 50 °C and in the presence of an acid promoter (Table 2). Cyclohexane was studied in detail as a recognized model substrate<sup>30</sup> (Figures 4 and S8–S10 in the SI), whereas other alkanes were oxidized under optimized conditions.

In the oxidation of cyclohexane to cyclohexanol and cyclohexanone, both compounds 1 and 2 exhibit rather low activity (2–4% total yields) unless a small amount of acid promoter is added (Figures 4 and S9 in the SI), leading to a pronounced yield growth. To examine whether the type of acid promoter affects the efficiency of cyclohexane oxidation,<sup>3,31</sup> we

tested the activity of precatalysts 1 (Figure 4a) and 2 (Figure S9a in the SI) in the presence of various acid promoters, namely, trifluoroacetic (TFA), nitric (HNO<sub>3</sub>), sulfuric  $(H_2SO_4)$ , and hydrochloric (HCl) acids. Compounds 1 and 2 show rather similar behavior. Although the type of promoter affects significantly the reaction rate of cyclohexane oxidation, the final product yields are comparable when using different acids. In the  $C_6H_{12}$  oxidation, the 1/TFA and 2/TFA systems result in total yields of 17 and 18% after 120 min, respectively. The kinetic curves of product accumulation in the 1/HNO<sub>3</sub> and  $2/HNO_3$  systems are very close to those in the presence of TFA promoter, leading to  $\sim$ 15% yields. Although the oxidation of cyclohexane is slower when using  $H_2SO_4$  as a promoter, total yields of 14 and 18% are achieved with precatalysts 1 and 2, respectively. Interestingly, the oxidation of C<sub>6</sub>H<sub>12</sub> is extremely fast in the presence of HCl and the reaction is completed in 3 min but results in inferior product yields (13%) in both systems containing 1 or 2. According to the literature background,<sup>3,29,31</sup> the role of an acid promoter consists of its participation in proton-transfer steps, activation of the precatalyst by protonation of ligands and unsaturation of the metal centers, and augmentation of the oxidative properties of H<sub>2</sub>O<sub>2</sub> and prevention of its decomposition (i.e., catalase activity).

Given the good promoting behavior of TFA, the effect of its amount was investigated in the cyclohexane oxidation with precatalysts 1 (Figure 4b) and 2 (Figure S9b in the SI). A very small amount of TFA (1-2 equiv relative to the precatalyst) is enough to promote the activity of both tetracopper(II) compounds and increase the reaction rate of  $C_6H_{12}$  oxidation (Figure S10 in the SI). In the case of 1, the maximum value of the initial reaction rate  $(W_0)$  was achieved at a 1/TFA molar ratio of 1:2, corresponding to a total product yield of 14%. A further increase of the TFA amount up to 10 and 20 equiv results in a decrease of  $W_0$  (Figure S10a in the SI), without significantly affecting the efficiency of the precatalyst and leading to comparable total product yields of 17 and 15%, respectively (Figure 4b). In the cyclohexane oxidation by the 2/ $TFA/H_2O_2$  system, the maximum initial rate  $W_0$  is attained at a 2/TFA molar ratio of 1:5 (Figure S10b in the SI), corresponding to a total product yield of 10%. A further increase of the TFA loading has almost no effect on  $W_0$  but gives a higher product yield (18% at a 2/TFA molar ratio of 1:10; Figure S9b in the SI).

It should be mentioned that precatalysts 1 and 2 are not intact during the catalytic experiments and in the presence of an acid promoter and H<sub>2</sub>O<sub>2</sub> lead to the formation of homogeneous catalytically active species, eventually via the additional protonation and partial decoordination of amino alcohol or aromatic carboxylate ligands.<sup>3,16,29,31</sup> Although a detailed investigation of catalytic intermediates was out of the main scope of the current work, we performed an electrospray ionization mass spectrometry (ESI-MS) study of precatalyst 1 in a MeCN/H2O medium before and after its treatment with TFA promoter and H<sub>2</sub>O<sub>2</sub> oxidant, using conditions equal to those of the catalytic tests. The most characteristic peaks observed in the ESI-MS(-) spectrum of 1 are due to the tetracopper  $[Cu_4(H_2edte)_2(sal)_2 - H]^-$  (m/z 994) and  $[Cu_4(H_2edte)_2(sal)_2 - CH_2CH_2OH]^-$  (m/z 949) fragments, with the latter corresponding to an ESI-induced cleavage of one hydroxyethyl group in  $H_2$ edte. The ESI-MS(+) plot of 1 also reveals tetracopper fragments, namely, [Cu<sub>4</sub>(Hedte)<sub>2</sub>(Hsal)]<sup>+</sup> (m/z 858) and  $[Cu_4(Hedte)(sal)(H_2O) - CH_2CH_2OH]^+ (m/z)^+$ z 597), corresponding to fragmentations with the elimination of one carboxylate or one carboxylate along with one amino alcohol ligand. After the treatment of 1 with TFA and  $H_2O_2$ , the obtained ESI-MS( $\pm$ ) patterns still display all of the abovementioned fragments, although their intensity has decreased with the exception of  $[Cu_4(Hedte)(sal)(H_2O) - CH_2CH_2OH]^+$  (m/z 597), which continues to be the most intense peak in a positive mode. In addition, new  $[Cu_4(edte)-(sal)(H_2O)_2(MeCN)]^-$  (m/z 699) and  $[Cu_4(Hedte)_2(H_2O) - CH_2CH_2OH]^-$  (m/z 649) fragments have emerged in the ESI-MS(-) spectrum. These data suggest that various tetracopper species derived from the parent precatalyst 1 upon decoordination of one H<sub>2</sub>edte and one sal ligands or a pair of salicylate moieties can potentially constitute the catalytically active species.

The  $1/\text{TFA}/\text{H}_2\text{O}_2$  and  $2/\text{TFA}/\text{H}_2\text{O}_2$  systems can also be applied for the oxidation of other alkanes, including various cyclic and linear  $\text{C}_5-\text{C}_8$  hydrocarbons (Table 2). Among cyclic alkanes, the oxidation of cycloheptane appears to be the most efficient, resulting in up to 20-21% total yields of cycloheptanol and cycloheptanone. Cyclooctane and cyclohexane are slightly less reactive substrates (14–19% total product yields), followed by cyclopentane, which is the least active cycloalkane (7–9% total product yield). In contrast to cycloalkanes, linear C<sub>5</sub>-C<sub>8</sub> alkanes are less reactive, showing the maximum total yields of oxidation products (isomeric alcohols and ketones) of 9–10% in the case of *n*-heptane, followed by *n*-hexane (4–6%), *n*-octane (4–5%), and *n*-pentane (3%).

By analogy with other multicopper(II) precatalysts for alkane oxidation by H2O2, the determined regioselectivity, bondselectivity, and stereoselectivity parameters (see Table S2 and additional discussion in the SI) are comparable to those previously reported<sup>3,29</sup> for copper-based catalytic systems operating with hydroxyl radicals, thus suggesting their involvement as principal oxidizing species. Considering the related literature background,<sup>3,29,31</sup> it is possible to assume the following mechanistic steps for alkane oxidation. Thus, an acid promoter interacts with a copper precatalyst, causing the formation of labile sites (via an additional protonation and partial decoordination of amino alcohol and/or carboxylate ligands) and the generation of active copper(II) species. These participate in the formation of HO<sup>•</sup> radicals from  $H_2O_{23}^{3,29c}$ which then abstract H atoms from an alkane, generating the alkyl radicals ( $\mathbb{R}^{\bullet}$ ). These react further with  $O_2$  (e.g., from air), giving rise to the ROO<sup>•</sup> radicals, which are transformed to alkyl hydroperoxides (ROOH) as primary intermediate products. Alkyl hydroperoxides rapidly decompose to furnish the corresponding alcohols and ketones as final products.<sup>3,29,31,32</sup>

#### CONCLUSIONS

The current study has widened a still very limited application of  $H_4$ edte as an aqua-soluble, commercially available, and versatile multidentate building block for the design of new multicopper compounds, namely resulting in the aqueous medium self-assembly generation of two tetracopper(II) products, **1** and **2**. The type of ancillary aromatic carboxylate ligand plays an important structure-driven role in defining the dimensionality and kind of the tetracopper(II) cubane core in the obtained compounds. Apart from representing the first polynuclear copper clusters derived from  $H_4$ edte, both **1** and **2** also reveal the first examples of transition-metal  $[M_4O_4]$  cubane cores driven by this amino alcohol.<sup>1</sup>

Another structural feature concerns the fact that the metalorganic chains in 1 or discrete clusters in 2 also act as matrixes to host numerous crystallization water molecules, which are assembled into the intricate  $\{(H_2O)_{18}\}_n$  water tapes or discrete  $(H_2O)_9$  clusters, respectively. These water aggregates play a key role in sewing the metal—organic hosts into very complex 3D supramolecular frameworks. Their topological analysis has disclosed either binodal 6,10- or 6,8-connected underlying 3D nets with the hitherto undocumented or rare topologies in 1 or 2, respectively. Thus, the present work not only widens the growing family of water assemblies detected in coordination compounds<sup>35,36</sup> but also contributes toward the identification of novel topological networks, which is currently a sweeping research direction in crystal engineering.<sup>13,22</sup>

The magnetic properties of the obtained compounds were investigated, indicating a predominant antiferromagnetic coupling between Cu<sup>II</sup> centers within the  $[Cu_4O_4]$  cores. Although these cores in 1 and 2 reveal a number of structural differences, both compounds show essentially similar magnetic behavior, which is also in good agreement with other alkoxobridged tetranuclear copper(II) derivatives.

Besides, the present work showed that the obtained copper(II) derivatives can act as bioinspired oxidation precatalysts<sup>33</sup> with some relevance to particulate methane monooxygenase (a unique copper enzyme that contains an active site based on a multicopper cluster with an N,O environment capable of hydroxylating alkanes).<sup>34</sup> In fact, both compounds **1** and **2** are precatalysts in the mild oxidation, by aqueous  $H_2O_2$  in acidic MeCN/H<sub>2</sub>O media, of different cyclic and linear  $C_5-C_8$  alkanes to produce the corresponding alcohols and ketones. Because these reactions also require the presence of an acid cocatalyst, the promoting influence of different acids (TFA, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and HCl) was studied, revealing the highest activity in the systems containing TFA. The substrate versatility and different selectivity parameters were also investigated.

Further research will be pursued toward the exploration of  $H_4$ edte and related amino alcohol building blocks in the design of novel multicopper(II) cores, their incorporation into metal–organic frameworks, and the study of the magnetic and catalytic properties of the obtained materials. These and other research directions are currently in progress.

#### ASSOCIATED CONTENT

#### Supporting Information

Materials and methods, additional discussion of IR and EPR spectra, thermogravimetric analyses, magnetic and catalytic studies, as well as thermogravimetric–differential thermal analysis plots (Figures S1 and S2), structural representations of water clusters (Figure S3), 3D supramolecular networks (Figure S4), molar magnetic susceptibility plots (Figure S5), field dependence of the magnetization (Figure S6), EPR spectra (Figure S7), additional catalytic results (Table S1 and Figures S8–S10), selectivity parameters (Table S2), and crystallographic files for 1 and 2 in CIF format (CCDC 1042427–1042428). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b00048.

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#### Notes

The authors declare no competing financial interest.

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