Copper(II) Coordination Polymers and Complexes Derived from Aminoalcohols and Aromatic Carboxylic Acids: Synthesis, Structural Characteristics and Applications

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Abstract

This work describes the self-assembly synthesis, characterization and applications of eight new complex compounds, namely [Cu₂(µ-dmea)(µ-n-da)(H₂O)]₂·2nH₂O (1), [Cu₂(µ-Hmdea)(µ-n-da)]₂·2nH₂O (2), [Cu₂(µ-Hbdea)(µ-n-da)]₂·2nH₂O (3), [Cu₂(H₂etda)(µ-n-da)]·nda·4H₂O (4), [Cu₂(µ₂-H₁bis-tris)(µ₂-Hhpa)]·H₂O (5), [Cu₂(µ₂-H₂tea)(µ₂-hpa)(µ₂-hpa)]₄ (6), [Cu₆(µ₄-H₂etda)(µ₃-H₂etda)(sal)₂]₄·10H₂O (7) and [Cu₆(µ₄-Hetda)(Hpma)₃·H₂O]·7.5H₂O (8) derived from various aminoalcohols [N,N-dimethylethanolamine (Hdmea), N-methylidethanolamine (H₂mdea), N-butylidethanolamine (H₂bdea), N,N,N',N'-tetraakis(2-hydroxyethyl)ethylenediamine (H2etda), bis(2-hydroxyethyl)amino-tris(hydroxymethyl)methane (H₂bis-tris) or triethanolamine (H₂tea)] and 2,6-naphthalenedicarboxylic (H₂nda), homophthalic (H₂hpa), salicylic (H₂sal) or phenylmalonic (H₂pmal) acids. The obtained products were characterised by IR, ESI-MS(±), thermogravimetric, elemental and single crystal X-ray diffraction analysis. Structural elucidation of the compounds gave rise to the following conclusions: 1–3 are 1D coordination polymers assembled from dicopper(II) aminoalcohol blocks and µ-n-da linkers, 4 is a discrete 0D dimer composed of two [Cu(H₂etda)]²⁺ fragments interlinked by the µ-n-da moiety, 5 is a discrete 0D trimer with symmetric [Cu₆(µ₂-O)(µ₂-COO)]₂ core, 6 is a zigzag 1D coordination polymer with asymmetric [Cu₆(µ₂-O)(µ₂-COO)]₂ core, 7 is a 1D coordination polymer with single-open cubane [Cu₆(µ₂-O)(µ₂-O)₃] core and 8 is a 0D tetramer with double-open cubane [Cu₆(µ₂-O)(µ₂-O)₃] core. An intense pattern of intermolecular (O–H···O) hydrogen bonds provides the extension of the structures into distinct supramolecular networks [1D → 3D (1, 2, 7), 1D → 2D (3, 6) and 0D → 3D (4, 5, 8)]. Their topological analysis was performed, disclosing some rare (1, 3, 5 and 6) or even undocumented (2, 4, 7 and 8) topological types. The magnetic susceptibility studies of 1–3 indicate a strong antiferromagnetic coupling between the Cu(II) atoms through the µ-alcoxo bridges [J ≈ −470(2), −100(2) and −590(1) cm⁻¹, respectively] and a predominant ferromagnetic coupling [J = 39.1(1) and 29.5(1) cm⁻¹, respectively] within the mixed-bridged tricopper(II) cores in 5 and 6. In contrast, 4 is devoid of any significant magnetic interaction within the dicopper(II) units. Finally, compounds 5–8 were also applied as rather efficient bio-inspired pre-catalysts for the mild homogeneous oxidation, by aqueous H₂O₂ at 50°C in acidic MeCN/H₂O medium, of cyclohexane to cyclohexanol and cyclohexanone with overall yields up to 27% based on the alkane.

Keywords: coordination polymers, copper(II) complexes, crystal structures, catalysis, magnetism.
**Introduction**

Within the vast development of crystal engineering research in recent years, the design of novel molecular materials bearing diverse multicopper(II) cores with promising functional properties has attracted an increased attention in view of the versatile redox, magnetic, biological, catalytic and coordination behavior of copper ions.\(^1\) In many cases, rather unusual multicopper(II) aggregates of diverse nuclearity can be constructed via simple self-assembly protocols employing a variety of organic building blocks.\(^2,3\) Aiming at searching for such organic molecules, we have focused our attention on some aminoalcohols as main building blocks, namely, \(\text{H}_5\text{bis-tris}, \text{H}_3\text{tea}, \text{H}_4\text{mdea}, \text{H}_2\text{bdea}, \text{Hdmae} \) and \(\text{H}_4\text{etda};\) some of them are commonly applied as buffers in biochemistry and molecular biology (Figure 1).\(^4\) As potential linkers, we have chosen aromatic carboxylic acids, namely \(\text{H}_2\text{nda}, \text{H}_2\text{sal}, \text{H}_2\text{pma} \) and \(\text{H}_2\text{hpa} \) (Figure 2). In spite of their commercial availability, aqueous solubility and coordination versatility, the application of some of these aminoalcohols and carboxylic acids as potentially multidentate building blocks in crystal engineering of mixed-ligand multicopper materials has remained underexplored.\(^5\)

**Figure 1.** Structural formulae of aminoalcohol building blocks.

However, some notable examples of polynuclear Cu(II) compounds derived from \(\text{H}_3\text{tea}, \text{Hdmae} \) and carboxylic acids have been documented\(^6-8\). We report herein the aqueous medium self-assembly synthesis (Scheme 1) of compounds 1–8 that comprise di-, tri- or tetracopper(II) aminoalcohol cores (Scheme 2), their spectral characteristics, crystal structures, thermogravimetric, magnetic and catalytic properties.

**Scheme 1.** Synthesis of 1–8 by aqueous medium self-assembly.

**Scheme 2.** Structural formulae of 1–8.
Experimental section

Materials and Methods

All synthetic work was performed in air and at room temperature (~25°C). C, H and N elemental analyses were carried out by the Microanalytical Service of the IST. Infrared spectra (4000–400 cm⁻¹) were recorded on a JASCO FT/IR-4100 instrument in KBr pellets. 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. The thermogravimetric analyses (TGA) were carried out on a Setaram Setsys TG–DTA 16 instrument by heating the crystalline samples (8–12 mg) of 1–6 under N₂ at the 10 °C/min rate in the 30–750 °C temperature range. The crystal structures data were collected on a Bruker AXS-KAPPA APEX II diffractometer with graphite-monochromated radiation (Mo Kα, λ=0.17073 Å) at 273-303 K (1–4, 8) or 150 K (5–7). The magnetization of the powdered samples 1–6 were measured over the 1.8–300 K temperature range using a Quantum Design SQUID–based MPMSXL–5-type magnetometer.

Synthesis and Characterisation of 1–8

To 10 mL of an aqueous 0.1 M solution of Cu(NO₃)₂·3H₂O (1 mmol) was added 1 mmol of an aqueous 1 M solution of aminoalcohol (Hdmea for 1, H₂mdea for 2, H₂bdea for 3, H₆bis-tris for 5 and H₆tea for 6) and 0.5 mmol of H₂etda for 4, 7 and 8 with continuous stirring at r.t. Then, an organic linker, 0.5 mmol of (H₂nda for 1–4 and H₂pmal for 8) and 1 mmol of (H₂lpa for 5, 6 or H₂sal for 7), and finally an aqueous 1 M solution of NaOH (3 mmol; up to pH ~8) for 1–8 was 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 r.t. Grayish blue (1), blue (2, 4, 6), cyan-blue (3, 5) and green (7, 8) crystals (including those of X-ray quality) were formed in 1–3 weeks, then collected and dried in air to furnish the compounds 1–8 in ~50% yield, based on copper(II) nitrate.

[Cu₂(μ-dmea)₂(μ-nda)(H₂O)]₂·2nH₂O (1). Anal. calcd for 1+0.5H₂O: Cu₂C₂H₂N₂O₀·0.5H₂O (MW 598.6): C 40.13, H 5.89, N 4.68; found: C 40.02, H 5.61, N 4.48. Compound 1 is barely soluble in MeCN, Me₂CO and DMSO. IR (KBr, cm⁻¹): 3379 (vs) ν(H₂O), 3003 (w) and 2967 (w) ν₃(CH), 2886 (w) and 2858 (w) ν₂(CH), 1617 (vs) and 1585 (s) ν₃(COO), 1392 (vs) and 1362 (vs) ν₁(COO), 1497 (w), 1469 (w), 1326 (w), 1275 (w), 1247 (w), 1187 (m) and 1140 (w) ν(C−X) (X = C, N), 1085 (s) and 1071 (s) ν(C−O), 1023 (w), 1016 (w), 978 (w), 948 (m), 904 (m), 847 (w), 799 (s), 789 (s), 661 (w), 644 (w), 589 (w), 526 (w), 488 (w), 476 (w), 427 (w), 418 (w). ESI–MS(±) (MeCN), selected fragments with relative abundance >20%. MS(±): m/z: 373 (30%) [Cu₂(dmea)₂(H₂O)₂ + 2H₂O + H]⁺, 330 (100%) [Cu₂(dmea)₂ + 5H₂O + H]⁺, 282 (60%) [Cu₂(dmea)₂ + CH₃CN + H]⁺ 152 (20%) [Cu₂(Hdmea)]⁺; MS(−): m/z: 295 (30%) [Cu(H₂O)(nda) – H]⁻, 251 (100%) [Hnda + 2H₂O]⁻.

[Cu₂(μ-Hmdea)₂(μ-nda)]₂·2nH₂O (2). Anal. calcd for 2: Cu₂C₂H₁₂N₂O₁₀ (MW 613.6): C 43.06, H 5.59, N 4.57; found: C 43.51, H 5.67, N 4.50. Compound 2 is barely soluble in MeOH and EtOH. IR (KBr, cm⁻¹): 3510 (m), 3408 (s br.) and 3189 (s), 251 (100%) [Hnda + 2H₂O]⁻. ESI–MS(±) (MeOH), selected fragments with relative abundance >20%, MS(±): m/z: 361 (20%) [Cu₂(Hmdea)₂ + H]⁺, 274 (25%) [Cu₂(dmea)₂ + MeO]⁺, 120 (40%) [H₂mdea + H]⁺; MS(−): m/z: 215 (100%) [Hnda]⁻.
[Cu$_2$(µ-Hbdea)$_2$(µ-nda)]$_n$.2nH$_2$O (3). Anal. calcd for 3: Cu$_5$C$_{24}$H$_{46}$N$_{30}$O$_{10}$ (MW 697.8): C 48.20, H 6.64, N 4.01; found: C 48.34, H 6.60, N 3.97. Compound 3 is barely soluble in MeOH and MeCN. IR (KBr, cm$^{-1}$): 3449 (s br), 3370 (sh.) and 3188 (m br) ν$_{H_2O/OH}$, 2953 (m) and 2922 (w) ν$_{as}$(CH), 2848 (m) ν$_s$(CH), 1609 (s) and 1582 (s) ν$_{as}$(COO), 1385 (vs) and 1352 (s) ν$_s$(COO), 1490 (w), 1462 (w), 1191 (w) ν(C–X) (X = C, N), 1088 (m) ν(C–O), 1035 (w), 979 (w), 900 (w), 783 (m), 662 (w), 582 (w), 559 (w), 481 (w). ESI–MS(+) (MeOH), selected fragments with relative abundance >20%. MS(−): m/z: 445 (100%) [Cu$_2$(Hbdea)$_2$ + H]$,^+$, 384 (10%) [Cu(Hbdea)$_2$ + H]$^+$, 162 (100%) [H$_2$bdea + H]$^+$; MS(−): m/z: 215 (100%) [Hnda]$^−$.

[Cu$_2$(H2etda)$_2$(µ-nda)]$^+$-nda-4H$_2$O (4). Anal. calcd for 4: Cu$_5$C$_{22}$H$_{30}$N$_{20}$O$_{10}$ (MW 1100.1): C 48.04, H 6.23, N 5.09; found: C 48.34, H 6.23, N 5.06. Compound 4 is barely soluble in MeCN, Me$_2$CO and DMSO. IR (KBr, cm$^{-1}$): 3457 (vs br) ν$_{H_2O/OH}$, 2975 (w) ν$_{as}$(CH), 2902 (w) ν$_s$(CH), 1605 (s) and 1574 (s) ν$_{as}$(COO), 1395 (vs) and 1356 (s) ν$_s$(COO), 1494 (w), 1456 (w), 1195 (m) and 1262 (w) ν(C–X) (X = C, N), 1061 (s) ν(C–O), 1148 (w), 926 (w), 875 (w), 797 (m), 763 (w), 737 (w), 646 (w), 487 (w). ESI–MS(+) (MeCN), selected fragments with relative abundance >20%. MS(−): m/z: 362 (10%) [Cu$_2$(H2etda)$_2$]$^+$, 278 (100%) [Cu(nnda) + H]$^+$, 237 (35%) [H$_2$etda + H]$^+$; MS(−): m/z: 251 (100%) [Hnda + 2H$_2$O]$^−$.

[Cu$_6$(µ$_2$-Hbdea)$_3$(µ$_2$-tris)]$_2$.4H$_2$O (5). Anal. calcd for 5: Cu$_{34}$C$_{16}$H$_{36}$N$_{10}$O$_{10}$ (MW 951.4): C 41.61, H 5.14, N 2.85; found: C 40.98, H 5.34, N 2.71. IR (KBr): 3445 (m br) and 3176 (w br) ν$_{H_2O/OH}$, 2985 (w) ν$_{as}$(CH), 2929 (w) ν$_s$(CH), 1603 (m sh) and 1562 (vs) ν$_{as}$(COO), 1418 (m sh) and 1388 (s br) ν$_s$(COO), 1486 (m), 1236 (w), 1187 (w), 1140 (w), 1089 (w), 1049 (w), 1038 (s) 1006 (w), 931 (w), 906 (w), 860 (w), 816 (w), 770 (w), 736 (m), 675 (m), 636 (w), 587 (w), 553 (w), 497 (w), 468 (w), 437 (w), 423 (w).

[Cu$_5$(µ$_2$-H2tea)$_2$(µ$_2$-hpa)(µ$_2$-hpa)]$_n$.10H$_2$O (6). Anal. calcd for 6: Cu$_5$C$_{30}$H$_{40}$N$_{24}$O$_{14}$ (MM 843.3): C 42.73, H 4.78, N 3.32; found: C 42.58, H 4.80, N 3.31. IR (KBr): 3330 (m br) ν(OH), 3013 (w) and 2975 (w) ν$_{as}$(CH), 2915 (w), 2871 (w) and 2838 (w) ν$_s$(CH), 1605 (s sh) and 1569 (vs) ν$_{as}$(COO), 1414 (s sh) and 1396 (vs) ν$_s$(COO), 1485 (w), 1466 (w), 1455 (w), 1312 (w), 1270 (m), 1228 (w), 1153 (w), 1140 (w), 1085 (s), 1067 (m), 1022 (w), 1006 (w), 963 (w), 932 (w, 894 (m), 859 (w), 809 (w), 768 (w), 742 (m), 730 (m sh), 703 (w), 670 (w), 647 (w), 603 (w), 574 (w), 554 (w), 516 (w), 451 (w), 420 (w), 407 (w).

[Cu$_5$(µ$_3$-H2etda)(µ$_4$-H2etda)(sal)$_2$]$_2$.10H$_2$O (7). Anal. calcd for 7-3H$_2$O: Cu$_5$C$_{56}$H$_{66}$N$_{39}$O$_{21}$ (MW 1121.1): C 36.42, H 5.93, N 5.00; found: C 36.11, H 5.67, N 4.87. Compound 7 is slightly soluble in H$_2$O, MeOH, EtOH and MeCN. IR (KBr): 3362 (s br) ν(OH), 2864 (m) ν$_s$(CH), 1602 (s) ν$_s$(COO), 1566 (s), 1528 (s) and 1453 (s) ν$_s$(COO), 1377 (s), 1320 (m), 1253 (s), 1142 (m) and 1066 (s) ν(C–X) (X = C, N, O), 887 (m), 834 (w), 768 (m), 712 (w), 639 (w), 585 (w).

[Cu$_6$(µ$_2$-H2etda)(Hpmal)(H$_2$O)]-7.5H$_2$O (8) Anal. calcd for 8: Cu$_3$C$_{9}$H$_{13}$N$_{2}$O$_{2.5}$ (MW 1232.2): C 37.04, H 5.97, N 4.55; found: C 37.03, H 5.50, N 4.54. Compound 8 is slightly soluble in H$_2$O, MeOH and EtOH. IR (KBr): 3419 (s br) ν(OH), 2856 (m) ν$_s$(CH), 1624 (s) and 1597 (s) ν$_s$(COO), 1409 (m) ν$_s$(COO), 1274 (w), 1059 (m) ν(C–X) (X = C, N, O), 906 (w), 730 (m), 637 (w), 504 (w).

**Catalytic studies**

The cyclohexane oxidation was typically carried out in air atmosphere in round flasks equipped with a condenser, under stirring at 50 °C and using MeCN as solvent (up to 5.0 mL total volume). In a typical experiment, a solid pre-catalyst 5–8 was introduced (0.01 mmol) into the reaction mixture,
followed by the addition of an acid co-catalyst (0.1 mmol). Finally, cyclohexane (2 mmol) was introduced and the reaction started after the addition of hydrogen peroxide (50% in H₂O, 10 mmol).

The reactions were monitored by removing small aliquots after different periods of time, which were treated with PPh₃. The samples were analyzed by gas chromatography (GC) using nitromethane as an internal standard. Attribution of peaks was made by comparison with chromatograms of authentic samples. GC analyses were run on an Agilent Technologies 7820A series gas chromatograph (He as carrier gas) equipped with FID detector and BP20/SGE (30 m × 0.22 mm × 0.25 μm) capillary column.

Results and Discussion

Spectroscopic characterization

The IR spectra of 1–8 show comparable features due to the presence of copper(II) aminoalcohol blocks, aromatic carboxylate ligands and water molecules. Hence, the characteristic vibrations include one or two ν(H₂O)/ν(OH) bands with maxima in the 3510–3185 cm⁻¹ range due to H₂O molecules and OH groups of aminoalcohol ligands, the broad character of which is indicative of intensive hydrogen bonding. The νₘ and νₛ CH vibrations are observed as two to four typically weak bands in the 3020–2830 cm⁻¹ range. Besides, the spectra of 1–8 also reveal the two pairs of strong νₛ(COO) [1617–1600 and 1585–1560 cm⁻¹] and νₘ(COO) [1395–1385 and 1352–1362 cm⁻¹] bands of the carboxylic linkers. The ESI–MS(+) plots of 1–3 show several Cu-aminoalcohol fragments obtained upon removal of nda ligands. Thus, the heaviest [Cu₂(dmea)₂(H₂O)₂ + 2H₂O − H]⁺ (m/z 373), [Cu₂(Hmdea)₂ − H]⁺ (m/z 361) and [Cu₂(Hbdea)₂ − H]⁺ (m/z 445) fragments with the expected isotopic distribution pattern were detected in 1–3, respectively. In these compounds, other characteristic peaks correspond to further fragmentation with the loss of one aminoalcohol moiety and/or one Cu atom. The ESI–MS(+) spectrum of 4 exhibits the characteristic [Cu₂(Hetda)]⁺ (m/z 362) and [Cu(nda) + H]⁺ (m/z 278) peaks. The ESI–MS(−) plots of all compounds are less informative, showing the highly intense peaks due to the [Hnda + 2H₂O]⁻ (m/z 251 in 1 and 4) or [Hnda]⁻ (m/z 215 in 2 and 3) fragments.

Thermogravimetric analysis

The TGA analyses have been performed under a N₂ atmosphere in the 30–750 °C range to evaluate the thermal behaviour of 1–6. The compounds 2 and 3 showed similar characteristics within the 80–410 °C temperature range. The first endothermic effect of 2–4 corresponded to the elimination of crystallization water molecules, namely two for 2 and 3 and 2.5 for 4 and it occurred within the 80–200 °C temperature range, whereas for compound 1 the elimination of two crystallization H₂O molecules was initiated only at 220 °C. The decomposition of the aminoalcohol in 1–4 was observed in the 200–340 °C temperature range. Further thermal effects with maxima at 370 °C (in 1), 300°C and 390 °C (in 2), 320°C (in 3) and 445 °C (in 4) are due to the multistep elimination of nda fragments. In 5 the elimination of one crystallization H₂O molecule is observed during the endothermic effect that occurred in the 50–140 °C temperature range. The removal of the one H₂bis-tris moiety in 5 and two H₂tea moieties in 6 was observed in the 215–270 °C temperature range. The second H₂bis-tris fragment and two Hhpa ligands in 5 decompose in the 240–450 °C range whereas in 6 the complete removal of two hpa fragments occurred in the 270–450 °C temperature range.

Description of crystal structures

The crystal structure of the linear 1D coordination polymer 1 is based on a dicopper(II) [Cu₂(µ-dmea)₂(H₂O)₂]₂⁺ block, a µ-nda(2−) linker and two
crystallization H₂O molecules (Figure 3a). Similarly to 1, the structures of 2 (Figure 3b) and 3 also feature the 1D metal-organic chains assembled from the related [Cu₂(µ-Hmdea)₂]²⁺ or [Cu₂(µ-Hbdea)₂]²⁺ blocks and µ-nda linkers. However, in these dicopper(II) blocks the axial site around the Cu atom is not occupied by the H₂O ligand, but by the OH group from an additional CH₂CH₂OH arm of the aminoalcohol moiety.

Similarly to 1, the structures of 2 (Figure 3b) and 3 also feature the 1D metal-organic chains assembled from the related [Cu₂(µ-Hmdea)₂]²⁺ or [Cu₂(µ-Hbdea)₂]²⁺ blocks and µ-nda linkers. However, in these dicopper(II) blocks the axial site around the Cu atom is not occupied by the H₂O ligand, but by the OH group from an additional CH₂CH₂OH arm of the aminoalcohol moiety.

Compound 4 reveals a discrete 0D structure composed of dicopper(II) [Cu₂(H₂etda)₂(µ-nda)]²⁺ cation, nda(2–) anion and four crystallization H₂O molecules (Figure 4).

The cation bears two symmetric equivalent {Cu(H₂etda)}²⁺ blocks that are interconnected by the bridging 2,6-naphthalenedicarboxylate. The discrete 0D structure of 5 consists of the neutral tricopper(II) [Cu₃(µ₂-H₂tea)(µ₂-Hp)(µ₃-Hp)] unit and a half crystallization water molecule. It has a symmetric linear [Cu₃(µ-O)₃(µ-COO)]₂⁻ core (Figure 5).

The crystal structure of 6 discloses a zigzag 1D coordination polymer assembled from the repeating tricopper(II) [Cu₃(µ₂-H₂tea)(µ₂-Hp)(µ₃-Hp)] units with an asymmetric [Cu₃(µ-O)₃(µ-COO)]₂⁻ core (Figure 6). The compound 7 is a 1D coordination polymer, the structure of which is composed of the repeating tetracopper(II) [Cu₄(H₂etda)(sal)]₂⁻ units (Figure 7a) and ten crystallization water molecules. The adjacent Cu₄ blocks reveal a single-open cubane [Cu₄(µ₂-O)(µ₁-O)]₃ core and are interconnected via one of the hydroxyethyl arms of the H₂etda ligand, forming an infinite metal-organic chain (Figure 7a,b).
7. (c) tetracopper block of compound 8 with coordination polyhedra around the copper atom, (d) distorted double-open cubane [Cu₄(μ₂-O)₂(μ₂-O)₂] core of 8.

The discrete 0D structure of 8 bears the neutral tetracopper(II) [Cu₄(Hetda)₂(Hpmal)₂(H₂O)] unit (Figure 7c). Although this Cu₄ unit resembles that of 7, there are a few differences that consist in: (i) the compound dimensionality (0D in 8 vs. 1D in 7), (ii) the presence of two monoprotonated μ₄-Hetda ligands in 8 vs. μ₄- and μ₃-Hetda in 7 and (iii) the existence of three five-coordinate (Cu₁, Cu₃, Cu₄) and one six-coordinate (Cu₂) copper atoms in 8 vs. a pair of five- and six-coordinate copper atoms in 7. These differences lead to the formation of a distinct double-open cubane [Cu₄(μ₂-O)₂(μ₂-O)₂] core in 8 (Figure 7d).

**Topological analysis of H-bonded networks of 1–8**

An intense pattern of intermolecular (O–H···O) hydrogen bonds provides the extension of the structures into distinct supramolecular networks [1D → 3D (1, 2, 7), 1D → 2D (3, 6) and 0D → 3D (4, 5, 8)]. The topological analysis was performed after simplification of the supramolecular networks following the concept of underlying net, revealing some rare (1, 3, 5, 6) or even undocumented (2, 4, 7 and 8) topological types.

**Magnetic properties of 1–6**

The magnetic properties of 1–4 (Figure 8), 5 and 6 (Figure 9) were investigated over the temperature range of 1.8–300 K. For that purpose the magnetic susceptibility χₘT vs. T was studied.

**Figure 8.** Temperature dependence of experimental χₘT (χₘ per 2 Cu²⁺ atoms) for 1–4.

**Figure 9.** Temperature dependence of experimental χₘT (χₘ per 3 Cu²⁺ atoms) for 5 and 6.

The magnetic susceptibility studies of 1–3 indicate a strong antiferromagnetic coupling between the Cu(II) atoms through the μ-alkoxy bridges, so the compounds behave as antiferromagnetically coupled dicopper(II) derivatives [J = −470(2), −100(2) and −590(1) cm⁻¹, respectively] whereas 5 and 6 showed a predominant ferromagnetic coupling [J = 39.1(1) and 29.5(1) cm⁻¹, respectively] within the mixed-bridged tricopper(II) cores. However, 4 has no significant magnetic interaction within the dicopper(II) units.

**Mild catalytic oxidation of cyclohexane of 5–8**

The compounds 5–8 have been applied as pre-catalysts for the mild homogeneous oxidation of cyclohexane by aqueous H₂O₂ in acetonitrile solution and in the presence of an acid promoter (co-catalyst), resulting in the formation of the corresponding alcohol and ketone. It was observed that the C₆H₁₂ oxidations catalyzed by the 5–8/TFA systems (TFA = trifluoroacetic acid) achieve 27% of the maximum total product yield, based on substrate.

We have observed that pre-catalysts 5–8 are almost inactive unless a small amount of an acid is added. Aiming at verifying whether the type of acid (co-catalyst) has an influence on the efficiency of the catalytic system, we have tested different acids (TFA, HCl, H₂SO₄ and HNO₃) in the oxidation of C₆H₁₂ with 5 (Figure 11a), 7 (Figure 11b) and 8 (Figure 11c) as pre-catalysts. Despite the addition of TFA or H₂SO₄ leads to the maximum total product yields, the oxidation is exceptionally quick.
in the presence of HCl. The oxidation of C₆H₁₂ also proceeds with HNO₃ as co-catalyst despite being slower than in the system with TFA.

![Graph a](image1)

![Graph b](image2)

![Graph c](image3)

**Figure 11.** Oxidation of cyclohexane to cyclohexanol and cyclohexanone by H₂O₂ catalysed by (a) 5¹⁄₂, (b) 7 and (c) 8. Evolution of the total product yield with time in the absence and in the presence of different acid co-catalysts (HNO₃, H₂SO₄, HCl, TFA; 0.1 mmol).

Although addition of TFA provided the maximum total products yield of 20% for 5–8, the oxidation is exceptionally quick in the presence of HCl resulting in a comparable maximum total yield of 18% for 5 achieved in only 5 min reaction time¹¹. The oxidation of C₆H₁₂ also proceeds with H₂SO₄ as a co-catalyst providing a maximum total yield of 18% for 5 and 8. Surprisingly, H₂SO₄ was the most efficient co-catalyst for 8 (Figure 11c). In contrast, HNO₃ showed a weaker promoting behavior with maximum total yield of 12–16% for 5, 6 and 8. However, for 7 HNO₃ showed a similar promoting behavior as TFA until 60 min reaction time. Furthermore, we have studied the effect of TFA amount on the total product yield. Different optimum TFA amounts were observed for each pre-catalyst. Thus, the maximum total products yield corresponded to the molar ratio of 1:10 in 5¹⁄₂, 1:2 in 7 and 1:5 in 8. The maximum yield achieved (27%) was in the system in which we used TFA as co-catalyst. Such an observation suggests that TFA is necessary to activate the pre-catalyst, presumably via additional protonation and partial decoordination of aminoalcohol and carboxylate moieties.¹³

**Conclusions**

Herein we described the self-assembly synthesis of new complexes and/or coordination polymers. They were characterized by IR spectroscopy, ESI(-)MS, TGA, elemental and single crystal X-ray diffraction analyses. It was found that compounds 1–3 are 1D coordination polymers assembled from dicopper(II) aminoalcohol blocks and μ-nda linkers, 4 is a discrete 0D dimer composed of two [Cu(HΔeta)]²⁺ fragments interlinked by the μ-nda moiety, 5 is a discrete 0D trimer with symmetric [Cu₃(μ⁴-O)₃(μ-CoO)₃] core, 6 is a zigzag 1D coordination polymer with asymmetric [Cu₃(μ⁴-O)₃(μ-CoO)₃] core, 7 is a 1D coordination polymer, with a single-open cubane [Cu₃(μ₂-O)(μ₃-O)₃] core and 8 is a 0D tetramer with a double-open cubane [Cu₃(μ₂-O)(μ₃-O)₃] core.

An intense pattern of intermolecular (O–H⁻O) hydrogen bonds provided the extension of the structures into distinct supramolecular networks [1D → 3D (1, 2, 7), 1D → 2D (3, 6) and 0D → 3D (4, 5, 8)] which were topologically analysed. The magnetic susceptibility studies revealed a strong antiferromagnetic coupling between the Cu(II) atoms through the μ-alkoxo bridges in 1–3 and a predominant ferromagnetic coupling within the
mixed-bridged tricopper(II) cores in 5 and 6. Finally, it was confirmed that compounds 5–8 can act as rather efficient bio-inspired pre-catalysts for the mild homogeneous oxidation of cyclohexane to the corresponding alcohol and ketone, by aqueous H$_2$O$_2$ at 50°C in acidic MeCN/H$_2$O medium, with overall yields up to 27% based on the alkane. This work was important to: (i) extend the diversity of copper(II) coordination polymers and multinuclear complexes assembled from aminoalcohols and aromatic carboxylate ligands, (ii) give new insights on the topological studies, resulting on the discovery of unreported topological types, (iii) study their magnetic properties and (iv) evaluate their catalytic efficiency for the mild oxidation of cyclohexane. Further research on broadening the types of self-assembled copper(II) coordination polymers and multinuclear complexes derived from various aminoalcohols and search for their applications in molecular magnetism and in oxidation catalysis is underway.

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