

Trinuclear Triangular Copper(II) Clusters – Synthesis, Electrochemical Studies and Catalytic Peroxidative Oxidation of Cycloalkanes

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The reactions of Cu^{II} carboxylates (valerate, 2-methylbutyrate, hexanoate, heptanoate) with pyrazole (Hpz) in EtOH or EtOH/water solutions easily afford the triangular trinuclear copper derivatives [Cu₃(μ₃-OH)(μ-pz)₃(RCOO)₂(L)_x] [R = CH₃(CH₂)₃, L = H₂O, x = 1 for **5**; R = CH₃CH₂CH(CH₃), L = EtOH, x = 2 for **6**; R = CH₃(CH₂)₄, L = EtOH, x = 1 for **7**; R = CH₃(CH₂)₅, L = EtOH, x = 1 for **8**] as it has been previously found for R = H, L = Hpz, x = 2, (**1**); R = CH₃, L = Hpz, x = 1, (**2**); R = CH₃CH₂, L = EtOH, x = 1, (**3**) and [Cu₃(μ₃-OH)(μ-pz)₃-(CH₃(CH₂)₂COO)₂(MeOH)(H₂O)], (**4**). The trinuclear structure common to **5–8** has been assigned on the basis of magnetic susceptibility studies, ESI MS, IR and UV/Vis spectroscopy as well as ¹H NMR measurements. The room temp. magnetic susceptibilities of **5–8** almost correspond to the presence of a single unpaired electron for each trinuclear unit. The IR spectra exhibit signals due to the bridging μ₃-OH in accordance with what was observed in the spectra of **1–4**. Solid-state and MeOH solution UV/Vis spectra show the

same features previously reported for **1–4** and ¹H NMR spectra of **1–8** show almost identical low field signals that can be assigned to pz[−] hydrogens. A detailed investigation of the supramolecular structures of **1** and **4** and the single-crystal X-ray study of the polymeric *paddlewheel* Cu(2-methylbutyrate)₂, **A**, are also reported. Electrochemical experiments show that in **1–8** the Cu^{II} ions can be reduced, in distinct steps, to Cu^I and Cu⁰. All the complexes act as catalysts or catalyst precursors for the efficient peroxidative oxidation, by aqueous hydrogen peroxide in acetonitrile and at room temp., of cycloalkanes RH (cyclohexane and cyclopentane) to the corresponding cyclic alcohols and ketones, with overall yields of up to 34 % and TONs up to 42. Radical pathways involving the formation of alkyl hydroperoxides (ROOH) are involved.

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Introduction

Oligonuclear transition metal complexes have drawn a significant amount of attention due to their magnetic properties, redox characteristics and relevance in numerous catalytic industrial and biological processes.^[1] The strong interest in di-, tri- and polynuclear copper(II) complexes mainly

stems from the fact that copper has been recognised as a fundamental element in biological systems. As an example, copper species are present in numerous enzymes that selectively catalyse various oxidation reactions,^[1g–l,2] including those performed by the still poorly characterised particulate methane monooxygenase (pMMO) present in methanotrophs, in which a Cu cluster catalyses alkane hydroxylation and alkene epoxidation.^[2c,f,g] Moreover, trinuclear arrays of copper(II) have been indicated as the essential functional units in numerous multicopper blue oxidases such as laccase and ascorbate oxidases.^[3]

In past years we have successfully synthesised di-, tri-, tetra- and polynuclear triethanolamine copper(II) complexes,^[4] as well as trinuclear triangular copper(II) complexes with carboxylate ligands^[5] and shown^[4,5c] that they can act as remarkably active and selective catalysts or catalyst precursors for peroxidative oxidation of cycloalkanes to the corresponding alcohols and ketones.

Continuing our studies on these compounds, we have synthesised and characterised four new trinuclear triangular Cu^{II} compounds, [Cu₃(μ₃-OH)(μ-pz)₃(RCOO)₂L_x] [pz = pyr-

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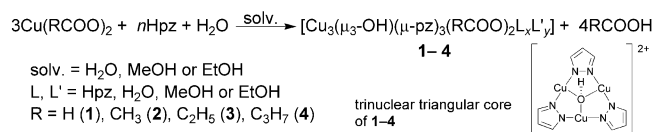
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azolate; L = EtOH, H₂O; R = CH₃(CH₂)₃ (valerate), CH₃CH₂CH(CH₃) (2-methylbutyrate), CH₃(CH₂)₄ (hexanoate), CH₃(CH₂)₅ (heptanoate)]. For these compounds, as well as for the related previously reported derivatives with R = H (formate),^[5b] CH₃ (acetate)^[5a] or CH₃(CH₂)₂ (butyrate),^[5b] we report the catalytic properties for the peroxidative oxidation of cycloalkanes. Moreover, the electrochemical behaviour of such compounds and of an analogous derivative with R = CH₃CH₂ (propionate) is presented. Finally, the crystal structure of Cu(2-methylbutyrate)₂ and the supramolecular H-bonding features of trinuclear triangular derivatives [with R = H and CH₃(CH₂)₂] are briefly outlined.

Results and Discussion

Recently, we established a synthetic procedure for obtaining trinuclear triangular copper(II) derivatives simply by treating Cu^{II} carboxylates with Hpz in the presence of water, according to the reaction reported in Scheme 1.^[5]



Scheme 1. General procedure for the synthesis of trinuclear copper complexes [Cu₃(μ₃-OH)(μ-pz)₃(RCOO)₂L_xL'_y].

The single-crystal X-ray diffraction molecular structures of compounds **1–4**^[5] indicated the formation of a trinuclear triangular core [Cu₃(μ₃-OH)(μ-pz)₃]²⁺, the three Cu^{II} ions also being coordinated by two carboxylate groups, neutral azoles and/or solvent molecules.^[6]

Moreover, these trinuclear triangular clusters act as secondary building units (SBUs) forming 1D (**3**) or 2D (**1**, **2**) metal organic frameworks (MOFs) or a hexanuclear cluster (**4**) through bridging carboxylates. Since a deep examination of other relevant supramolecular interactions, such as H-bonds, was in some cases explicitly omitted,^[5a,5b] we have hereby taken opportunity to briefly describe these features which are involved in the supramolecular assembly of **1** and **4**.^[7]

In [Cu₃(μ₃-OH)(μ-pz)₃(HCOO)₂(Hpz)₂]·H₂O (**1**), the most relevant supramolecular interactions are due to formate bridges generating a “fishing net” 2D MOF^[5b] but a relevant role is also played by H-bonds which involve the crystallisation water molecules, the two formate groups and the μ₃-OH unit (see Figure S1). In particular, each crystallisation water molecule behaves as an H donor in two strong H-bonds, the first one with μ₃-OH [O(1w)···O(1) 2.710(4) Å, O(1w)···H(1)–O(1) 163(5)°] from the complex in the same asymmetric unit, while the second one is with the

uncoordinated carboxylate oxygen [O(5')] of another trinuclear unit [O(5')···O(1w) 2.780(5) Å, O(5')···H(1w)–O(1w) 130(4)°; symmetry code: (I) $-x, y - 0.5, -z + 1$]. Moreover, compound **1** forms two relatively strong intermolecular H-bonds between: i) the pyrazolic hydrogen bound to N(10) and the coordinated oxygen [O(4')] of the formate group belonging to the adjacent trinuclear unit [O(4')···N(10) 2.828(4) Å, O(4')···H(10N)–N(10) 168°] and ii) the pyrazolic hydrogen H(8N) of the second terminally bound pyrazole and a formate oxygen O(2'') of a third trinuclear unit [O(2'')···N(8) 2.677(4) Å, O(2'')···H(8N)–N(8) 167°; symmetry code: (II) $x + 1, y, z$]. In both cases the 2D MOFs generated through formate bridges are reinforced.

In compound **4** the most striking structural feature is the presence, in contrast to **1**, of hexanuclear units located around inversion centres and generated by two monodentate carboxylate bridges (see Scheme S1 in the Supporting Information).^[5b] Two intramolecular H-bonds can also be detected, those involving the carboxylate oxygen O(3) with the proton of the central μ₃-OH group [O(3)···O(1) 2.763(4) Å, O(3)···H–O(1) 162(4)°] and two interactions involving the carboxylate O(5) with the hydrogen of coordinated methanol [O(5)···O(6) 2.815(4) Å, O(5)···H(61)–O(6) 171(6)°] (see Figure S2a). O(5) is also engaged in an intermolecular H-bond with the coordinated water of another hexanuclear unit [O(5)···O(7'') 2.694(4) Å, O(5)···H(8w'')–O(7'') 166(5)°; symmetry code: (II) $-x + 1, -y + 1, -z$] thus generating a 1D supramolecular network running along the *ab* diagonal (see Figure S2b). Moreover, the carboxylate oxygens O(3) pertaining to these parallel networks are also involved in another series of intermolecular H-bonds with coordinated water molecules of neighbouring units [O(3)···O(7'') 2.947(4) Å, O(3)···H(7w'')–O(7'') 151(5)°; symmetry code: (III) $x, y + 1, z$] with formation of a 2D supramolecular network (see Figure S3).

Continuing our studies, we examined the reactions of Hpz with other Cu^{II} carboxylates, namely valerate, 2-methylbutyrate, hexanoate and heptanoate. Incidentally, in the course of the synthesis of copper(II) 2-methylbutyrate, **A**, we isolated well formed crystals of this compound. A single-crystal X-ray diffraction study showed that compound **A** has the typical paddlewheel structure which behaves as a secondary building unit (SBU) to form a 1D MOF in a manner similar to what can be observed in other copper(II) carboxylates.^[8]

The molecular structure of **A**,^[9] which is based on a crystallographic inversion centre located midway along the Cu–Cu vector, is shown in Figure 1. The paddlewheel motif of **A** is generated by two different types of carboxylate anions almost symmetrically bridging two copper(II) ions. The Cu(1)–O bond lengths are very similar, falling in the range 1.927–1.966(3) Å with the exception of the Cu(1')–O(4) distance which is slightly longer [2.004(3) Å]. In addition, O(4) is also coordinated to the copper Cu(1'') of another paddlewheel unit [O(4)–Cu(1'') 2.216(2) Å] thus generating a 1D MOF running down the crystallographic *a* axis (see Figure S4). Finally, the Cu(1)···Cu(1') separation in the carboxylate bridged complex is 2.5820(8) Å [symmetry code (I):

$-x + 1, -y, -z]$ which is substantially shorter than the inter-paddlewheel distance $[\text{Cu}(\text{I}) \cdots \text{Cu}(\text{I}')]$ 3.2438(8) Å, symmetry code (II): $-x, -y, -z]$.

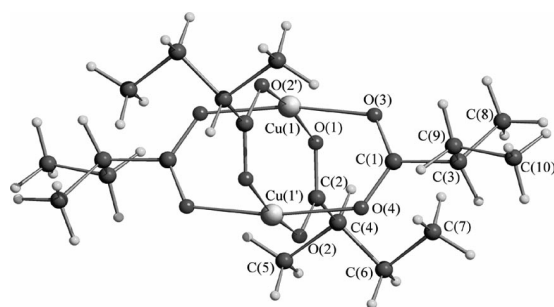


Figure 1. Molecular structure of **A** showing the typical paddlewheel arrangement. Relevant bond lengths [Å]: Cu(1)–O(1) 1.937, Cu(1)–O(2) 1.927, Cu(1)–O(3) 1.966, Cu(1')–O(4) 2.004(3), Cu(1)⋯Cu(1') 2.5820(8).

The reaction of Hpz with Cu^{II} valerate, 2-methylbutyrate, hexanoate or heptanoate yielded compounds **5–8**, respectively. Unfortunately, we were unable to obtain crystals suitable for X-ray diffraction but we inferred their structures from analytical and spectroscopic data all of which suggest that they have the same trinuclear triangular $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3]^{2+}$ core sketched in Scheme 1.

First of all, the formation in each synthesis of the corresponding carboxylic acid (see Experimental Section) indicates that the carboxylates have deprotonated water and Hpz generating OH^- and pz^- ions which build up the Cu^{II} trinuclear triangular core.

IR spectra are in accordance with the proposed structure for **5–8**. The IR spectra of **5**, **7** and **8** in fact show two strong bands corresponding to $\nu_{\text{asym}}(\text{COO})$ (ca 1570 cm^{-1}) and $\nu_{\text{s}}(\text{COO})$ (1430 cm^{-1}). The Δ values [$\nu_{\text{asym}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$] are in agreement with a nearly symmetric bridging bidentate coordination for the carboxylates, analogous to that found in derivative **4**.^[5b] On the other hand, the spectrum of **6** is very similar to that of derivative **3**:^[5b] two sets of absorptions of very different intensities, due to carboxylates, are actually present. Both sets exhibit a Δ value of ca. 120 cm^{-1} and could be assigned to methylbutyrate symmetrically bridging two Cu^{II} centres in a mono- or bidentate fashion.^[16] The IR spectra of **5–8** always show a signal at ca. 750 cm^{-1} [$\delta(\text{CH})_{\text{oop}}$] which corresponds to bridging pyrazolate ligands.^[17] No absorption assignable to $\nu(\text{N-H})$ could be observed. Besides the expected band over 3000 cm^{-1} , due to $\nu(\text{C-H})$ of the pyrazolate,^[18] a broad absorption between 3300–2800 cm^{-1} , most likely due to hydrogen-bonded OH from alcohol or water, is present. Very small absorptions, sometimes found at ca. 1715 cm^{-1} , are due to traces of RCOOH formed during the synthesis.

^1H NMR measurements carried out on CD_3OD solutions of **1–8** show, besides relatively high-field signals due to carboxylate hydrogens, two low-field broad peaks at ca. 37 ppm (δ_1) and ca. 41 ppm (δ_2), integrating in a 2:1 ratio.

These can be assigned to the two equivalent H(3) and H(5) (δ_1) and H(4) (δ_2) pyrazolate hydrogens as already reported for some similar Cu^{II} trinuclear triangular derivatives.^[19]

The room temperature magnetic susceptibilities of compounds **5–8** are consistent with the proposed trinuclear arrangement. The observed μ values, ranging between 2.45 and 2.73 BM, although a little bit larger than those found for **1–4**,^[5a,5b] are too low for three independent Cu^{II} ions, suggesting some kind of exchange coupling in these cases as well.

ESI MS data further support the presence, in **5–8**, of the $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3]^{2+}$ core with positive charges balanced by two carboxylate ions. In detail, most relevant signals (Table 1) can be attributed to trinuclear and hexanuclear moieties, analogous to what was previously observed for compounds **1–4**.^[5] Even though the ESI MS data are not an exhaustive proof of the presence, in the solid-state, of trinuclear or hexanuclear Cu^{II} clusters,^[20] they certainly strongly suggest this feature, particularly if we take into account that peaks attributable to mononuclear Cu^{II} species are generally not observed (see Figures S5–S8).

Table 1. Most relevant signals in the ESI mass spectra of compounds **5–8**.

	Signal ^[a]	Rel. ab. ^[b]	Assignment ^[c]
5	684.8	63	$[\text{Cu}_3(\text{OH})(\text{pz})_3(\text{RCOO})_2(\text{MeOH})(\text{S})] + \text{H}^+$
	1112.8	100	$[\text{Cu}_6(\text{OH})_4(\text{pz})_6(\text{RCOO})(\text{MeOH})_3]^+$
	1148.8	96	$[\text{Cu}_6(\text{OH})_4(\text{pz})_6(\text{RCOO})(\text{H}_2\text{O})_2(\text{MeOH})_3]^+$
6	752.7	16	$[\text{Cu}_3(\text{OH})(\text{pz})_3(\text{RCOO})_2(\text{H}_2\text{O})_2(\text{MeOH})_2(\text{S})] + \text{H}^+$
	1112.6	40	$[\text{Cu}_6(\text{OH})_4(\text{pz})_6(\text{RCOO})(\text{MeOH})_3]^+$
	1148.5	100	$[\text{Cu}_6(\text{OH})_4(\text{pz})_6(\text{RCOO})(\text{H}_2\text{O})_2(\text{MeOH})_3]^+$
7	698.8	52	$[\text{Cu}_3(\text{OH})(\text{pz})_3(\text{RCOO})_2(\text{H}_2\text{O})(\text{S})] + \text{H}^+$
	1154.8	83	$[\text{Cu}_6(\text{OH})_3(\text{pz})_6(\text{RCOO})_2(\text{H}_2\text{O})_3]^+$
	1190.8	100	$[\text{Cu}_6(\text{OH})_3(\text{pz})_6(\text{RCOO})_2(\text{H}_2\text{O})_7]^+$
8	619.9	25	$[\text{Cu}_3(\text{OH})(\text{pz})_3(\text{RCOO})(\text{MeOH})_2(\text{H}_2\text{O})]^+$
	1196.8	35	$[\text{Cu}_6(\text{OH})_3(\text{C}_3\text{H}_3\text{N}_2)_6(\text{RCOO})_2(\text{H}_2\text{O})_4(\text{MeOH})]^+$
	1232.8	100	$[\text{Cu}_6(\text{OH})_3(\text{C}_3\text{H}_3\text{N}_2)_6(\text{RCOO})_2(\text{H}_2\text{O})_6(\text{MeOH})]^+$

[a] Values corresponding to the higher signals of the isotopic clusters. All isotopic clusters fit satisfactorily with calculated ones.^[21]

[b] Relative abundance of the higher signal of the isotopic cluster.

[c] S = MeCN; R = $\text{CH}_3(\text{CH}_2)_3$, (**5**), $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)$, (**6**), $\text{CH}_3(\text{CH}_2)_4$, (**7**), $\text{CH}_3(\text{CH}_2)_5$, (**8**).

Finally, the trinuclear triangular structure of **5–8** is supported by their solid-state reflectance and MeOH solution electronic spectra (400–800 nm) (Figure 2).

The solid-state spectra of **5–8** (Figure 2a) show almost identical patterns. In detail, besides two shoulders around 520 and 720 nm, they display a complex absorption band where two maxima positioned at ca. 610 and 650 nm are evident. These spectroscopic patterns are only slightly different in MeOH solutions (Figure 2b) and the two low energy maxima observed in the solid-state mediate into broad asymmetric signals centred around 620–625 nm. The observed patterns are almost identical to those shown by **1–4**^[5] and other closely related species with Cl^- ,^[22] SO_4^{2-} , ClO_4^- , CF_3COO^- , CF_3SO_3^- and NO_3^- counter anions^[23] and trinuclear triangular structures ascertained by single-crystal X-ray determinations. Moreover, these patterns differ greatly from the UV/Vis spectra of MeOH solutions of the mononuclear species $\text{Cu}(\text{Hpz})_4(\text{X})_2$ ($\text{X} = \text{Cl}^-$, NO_3^- ,

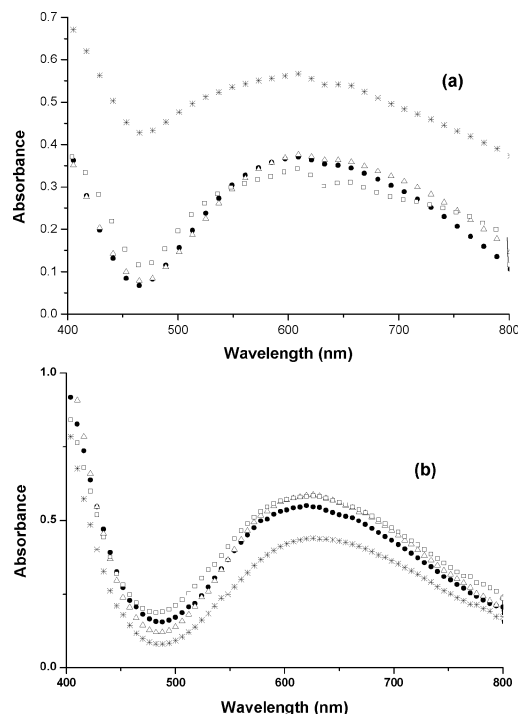


Figure 2. Solid-state reflectance (a) and MeOH solution (b) electronic spectra of **5** (squares), **6** (stars), **7** (solid circles) and **8** (triangles).

H_2PO_4^- , ClO_4^- , CF_3COO^- , CF_3SO_3^- ; $\text{X}_2 = \text{SO}_4^{2-}$), which exhibit a characteristic broad signal in the range 710–720 nm.^[22,23]

Electrochemical Behaviour of 1–8

The redox properties of compounds **1–8** have been investigated by cyclic voltammetry using a Pt electrode in a 0.2 M $[\text{nBu}_4\text{N}][\text{BF}_4]/\text{DMSO}$ solution at 25 °C. All compounds exhibit similar voltammograms, showing two single-electron (per metal atom) irreversible reduction waves, (Figure 3 shows the voltammogram of **2**) assigned to the $\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}}$ (wave I) and $\text{Cu}^{\text{I}} \rightarrow \text{Cu}^0$ (wave II) reductions, at the reduction peak potential values given in Table 2 ($^{\text{I}}E_{\text{p}}^{\text{red}}$ in the range from –0.38 to –0.45 V vs. SCE and $^{\text{II}}E_{\text{p}}^{\text{red}}$ between –1.31 and –1.52 V vs. SCE). In addition, a new irreversible oxidation wave (wave *a*) in the range 0.2–0.5 V vs. SCE (Table 2, Figure 3) can be observed upon scan reversal following the first reduction wave. It corresponds to the oxidation of the Cu^{I} species formed at the first reduction process.

The occurrence of a single-electron reduction per Cu^{II} (or Cu^{I}) ion was confirmed by exhaustive controlled potential electrolysis (CPE) at a potential slightly more cathodic to that of the peak potential of wave I (or II). This corresponds to a charge consumption of 3 F mol^{–1} of complex. The reduced Cu^{I} compounds appear to be stable in the solvent/electrolyte medium along the CPE and the corresponding $\text{Cu}^{\text{I/II}}$ oxidation (wave *a*) and $\text{Cu}^{\text{I/0}}$ reduction (wave II) can be observed at the end of the electrolysis

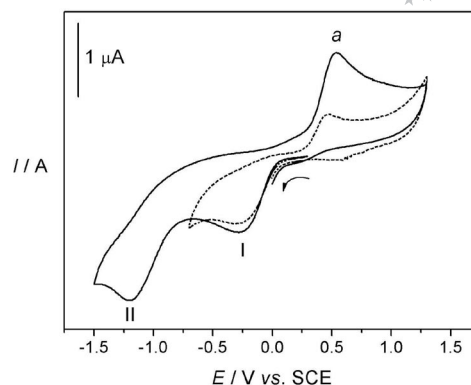


Figure 3. Cyclic voltammogram of $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{CH}_3\text{COO})_2](\text{Hpz})$, **2**, in a 0.2 M $[\text{nBu}_4\text{N}][\text{BF}_4]/\text{DMSO}$ solution ($c = 2.41 \text{ mM}$), at a Pt disk working electrode ($d = 0.5 \text{ mm}$) at 200 mV s^{–1}.

Table 2. Cyclic voltammetric data^[a] for complexes **1–8**.

Complex	Cathodic waves $^{\text{I}}E_{\text{p}}^{\text{red}}$	$^{\text{II}}E_{\text{p}}^{\text{red}}$	Anodic wave ^[b] E_{p}^{ox}
1	–0.40	–1.40	0.28
2	–0.44	–1.31	0.19
3	–0.38	–1.42	0.35
4	–0.38	–1.51	0.33
5	–0.45	–1.44	0.47
6 ^[c]	–0.45	–1.49	0.28
7 ^[c]	–0.45	–1.44	0.54
8	–0.42	–1.52	0.39

[a] Potential values in volts ± 0.02 vs. SCE in a 0.2 M $[\text{nBu}_4\text{N}][\text{BF}_4]/\text{DMSO}$ solution with a Pt disk working electrode, determined by using the $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^{0/+}$ redox couple ($E_{1/2}^{\text{ox}} = 0.44 \text{ V}$ vs. SCE) as internal standard and a scan rate of 200 mV s^{–1}. [b] Anodic wave (*a*) generated upon scan reversal following the first reduction wave. [c] An oxidation wave at $E_{\text{p}}^{\text{ox}} = -0.10 \text{ V}$ is generated upon scan reversal following the second reduction wave.

(Table 2). The CPE performed at the second reduction wave leads to the deposition of metallic copper which can be clearly observed by its sharp oxidation (with desorption) wave at $E_{\text{p}}^{\text{ox}} = -0.11 \text{ V}$, as shown in Figure 4 for compound **2**.

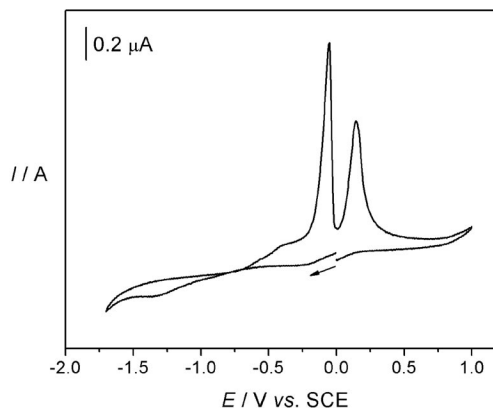


Figure 4. Cyclic voltammogram after CPE at the reduction wave II of $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3(\text{CH}_3\text{COO})_2](\text{Hpz})$, **2**, in a 0.2 M $[\text{nBu}_4\text{N}][\text{BF}_4]/\text{DMSO}$ solution with a Pt disk working electrode ($d = 0.5 \text{ mm}$) at 20 mV s^{–1}.

No oxidation wave has been detected for any of the complexes by a first anodic sweep without a previous reduction scan, indicating that neither a metal centred nor a ligand centred oxidation occurs. Since any of the cathodic waves involve the reduction of the three metal atoms without differentiation of distinct waves at different potentials, no metal–metal electronic communication was detected. Nevertheless, the occurrence of such an interaction, to a limited extent, cannot be ruled out in view of the considerable broadness of the reduction waves which can result from the overlap of other waves at close but distinct reduction potentials, corresponding to the sequential metal reductions, i.e. $\text{Cu}^{\text{II}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}}\text{Cu}^{\text{II}}\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{Cu}^{\text{II}} \rightarrow \text{Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}$ for wave I and, similarly, for the further reductions to Cu^0 at wave II. The values of the reduction potentials of our complexes could reflect the electron-donor character of their ligands but the narrow range and the broadness of the waves prevent reliable comparisons.

All the above indicated characterisations made us fully confident of the trinuclear triangular nature of compounds **5–8**. We therefore tested them (as well as compounds **1**, **2** and **4**) as catalysts for the peroxidative oxidation of cycloalkanes in order to compare their behaviour with that shown by compound **3**.^[5c]

Catalytic Peroxidative Oxidation of Cycloalkanes (Compounds **1**, **2** and **4–8**)

All the new trinuclear triangular copper(II) complexes behave as catalysts or catalyst precursors for the mild peroxidative oxidation of cyclohexane and cyclopentane with aqueous H_2O_2 , at room temperature and atmospheric pressure, to the corresponding cyclic alcohols (i.e. cyclohexanol or cyclopentanol) and cyclic ketones (i.e. cyclohexanone or cyclopentanone). The reactions were carried out in a liquid biphasic ($\text{MeCN}/\text{H}_2\text{O}$) medium in the presence of nitric acid. The activity and selectivity depend on a variety of factors such as the relative amounts of the reagents and solvent which can be varied for the optimisation of the reaction conditions as we have reported^[4b,24–28] for other alkane functionalisation catalytic systems. Moreover, the addition of nitric acid to the reaction mixture strongly enhances the activity as reported^[29–31] for other metal catalysts with N,O ligands, since it can activate the catalyst by promoting unsaturation of the metal centre upon ligand protonation, stabilises peroxo intermediate species^[4a] and prevents the decomposition of hydrogen peroxide. According to our previous observations,^[5c] the maximum activity for the trinuclear copper(II) complexes was reached for the acid-to-catalyst and H_2O_2 -to-catalyst molar ratios of ca. 10:1 and ca. 500–1000, respectively, values that were chosen as typical for the experiments. An increase in the temperature leads to a yield drop (Table 3, entry 18), probably due to the decomposition of hydrogen peroxide.

The use of such catalysts precursors led, in a single batch, to overall yields (based on the cycloalkane) of up to 34% and turnover numbers (TONs) of up to 42 mol of products

per mol of catalyst (see Tables 3, 4, and 5 and Figures 5, 6, and 7). Simple salts of copper(II), such as basic copper(II) carbonate and copper(II) 2-methylbutyrate, exhibit much lower catalytic activities under similar reaction conditions (Tables 3, entries 19, 20 and 5, entries 7, 8). Only traces of cycloalkane oxidation products are obtained in the absence of the copper(II) catalyst.

Table 3. Peroxidative oxidation of cyclohexane to cyclohexanol and cyclohexanone catalysed by compounds **1–8**.^[a]

Entry	Cat ^[b]	$n(\text{H}_2\text{O}_2)/n(\text{Cat})$	% Yield ^[c] of alcohol	% Yield ^[c] of ketone	total ^[d]	A/K ^[e]	TON ^[f]
1	1	500	26.5	4.9	31.4	5.6	31.4
2	2	500	26.4	4.6	31.0	5.9	31.0
3	3 ^[g]	500	23.0	2.6	25.6	9.1	25.6
4	4	500	23.8	4.3	28.1	5.6	28.1
5	5	500	23.3	3.3	26.6	7.1	26.6
6	6	1000	25.2	6.4	31.6	4.0	31.6
7	7	1000	25.2	6.8	32.0	3.7	32.0
8	8	1000	24.1	6.1	30.2	4.0	30.2
9	1	250	23.9	3.1	27.1	7.7	27.1
10	1	750	26.3	7.9	34.2	3.3	34.2
11	1	1000	23.4	9.0	32.4	2.6	32.4
12	4	250	20.2	2.8	23.0	7.1	23.0
13	4	750	25.0	8.2	33.2	7.1	23.0
14	4	1000	19.8	9.7	29.5	2.0	29.5
15	5	250	21.2	3.6	24.8	5.9	24.8
16	5	750	24.7	8.2	32.9	3.0	32.9
17	5	1000	21.2	11.4	32.6	1.9	32.6
18 ^[h]	1	1000	5.5	7.2	12.7	0.8	12.7
19	^[i]	1000	8.0	8.0	16.0	1.0	16.0
20	^[j]	1000	–	7.9	7.9	–	7.9

[a] Selected data; reaction conditions: C_6H_{12} (1 mmol), catalyst precursor (10 μmol), MeCN (4 mL), HNO_3 (0.10 mmol), H_2O_2 (2.5–10 mmol, added as a 30% aqueous solution), 6 h reaction time, room temperature. [b] Cat = catalyst. [c] Mol of product/100 mol of C_6H_{12} , measured upon reduction of ROOH to the alcohol by PPh_3 . [d] Cyclohexanol + cyclohexanone. [e] Alcohol (cyclohexanol)/ketone (cyclohexanone) molar ratio, upon reduction of ROOH to the alcohol by PPh_3 . [f] Overall TON values (mol of products/mol of catalyst). [g] Included^[5c] for comparative purposes. [h] At 50 °C. [i] $\text{CuCO}_3\cdot\text{Cu}(\text{OH})_2$ as catalyst, for comparative purposes. [j] $\text{Cu}\{\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{COO}\}_2$ as catalyst, for comparative purposes.

The complexes **1**, **2** and **4**, in the peroxidative oxidation of cyclohexane under the same reaction conditions (Table 3, entries 1–5), exhibit similar catalytic activities which are slightly higher than those of **5** or **3** (the latter has already been investigated^[5c] and is included for comparative purposes).

An increase in the peroxide-to-catalyst molar ratio results in a yield increase, e.g., for complexes **1**, **4** and **5**, from 24–27 to 33–34% on changing that ratio from 250 to 750 (H_2O_2 amount increase from 2.5 to 7.5 mmol) whereupon the maximum yields are reached (Figure 5). A further rise of the oxidant amount (up to 10 mmol) does not lead to a better yield.

The relative amounts of the products are also dependent on the hydrogen peroxide amount. In fact, although for the H_2O_2 /catalyst molar ratio in the 250–500 range the cyclohexanol-to-cyclohexanone molar ratio (A/K) remains grossly invariant (close to 6–8 for catalysts **1**, **4** and **5**)

Table 4. Effect of the catalyst amount in the peroxidative oxidation of cyclohexane catalysed by compound **4**.^[a]

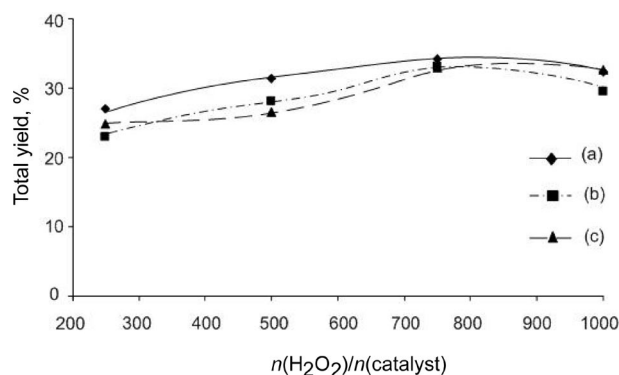
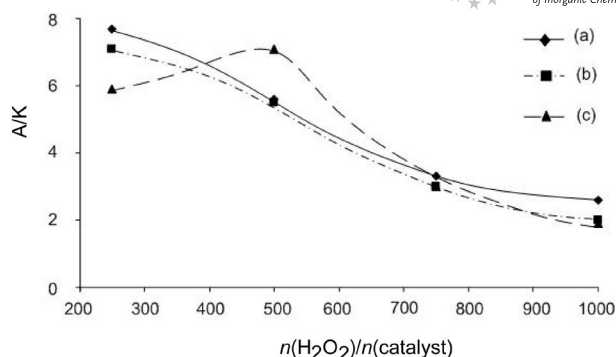
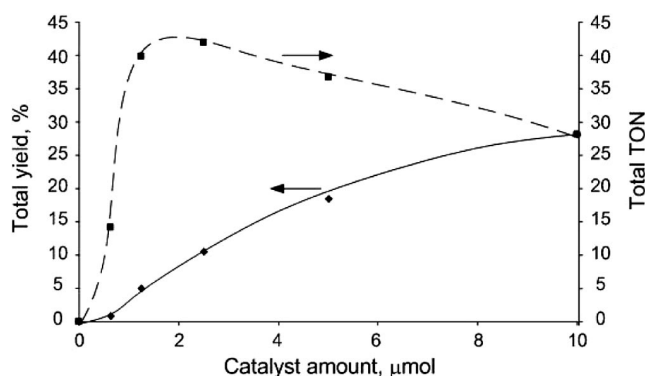
Entry	Catalyst amount μmol	% Yield ^[b] alcohol	% Yield ^[b] ketone	% Yield ^[b] total ^[c]	A/K ^[d]	Overall TON ^[e]
1	0.0	0.1	0.0	0.1	—	—
2	0.63	0.9	0.0	0.9	—	14.1
3	1.25	4.5	0.5	5.0	9.1	39.8
4	2.50	9.6	0.9	10.5	11	41.9
5	5.0	16.7	1.7	18.4	10	36.8
6	10.0	23.8	4.3	28.1	5.6	28.1

[a] Selected data; reaction conditions: C_6H_{12} (1 mmol), MeCN 4 mL, HNO_3 (0.10 mmol), H_2O_2 (5 mmol, added as a 30% aqueous solution), 6 h reaction time, room temperature. [b] Mol of product/100 mol of C_6H_{12} , measured upon reduction of ROOH to the alcohol by PPh_3 . [c] Cyclohexanol + cyclohexanone. [d] Alcohol (cyclohexanol)/ketone (cyclohexanone) molar ratio, upon reduction of ROOH to the alcohol by PPh_3 . [e] Overall TON values (mol of products/mol of catalyst).

Table 5. Peroxidative oxidation of cyclopentane to cyclopentanol and cyclopentanone catalysed by compounds **1–5**.^[a]

Entry	Cat ^[b]	$n(\text{H}_2\text{O}_2)/n(\text{Cat})$	% Yield ^[c] alcohol	% Yield ^[c] ketone	% Yield ^[c] total ^[d]	A/K ^[e]	TON ^[f]
1	—	500	0.0	0.0	—	—	—
2	1	500	16.5	9.4	25.9	1.8	25.9
3	2	500	22.2	7.8	30.0	2.9	30.0
4	3 ^[g]	500	22.6	8.4	31.0	2.7	31.0
5	4	500	18.5	11.1	29.6	1.7	29.6
6	5	500	21.6	9.8	31.4	2.2	31.4
7	^[h]	1000	6.9	8.9	15.8	0.8	15.8
8	^[i]	1000	3.3	5.1	8.4	0.8	8.4

[a] Selected data; reaction conditions: C_5H_{10} (1 mmol), catalyst precursor (10 μmol), MeCN 4 mL, HNO_3 (0.10 mmol), H_2O_2 (5 or 10 mmol, added as an aqueous 30% solution), 6 h reaction time, room temperature. [b] Cat = Catalyst. [c] Mol of product/100 mol of C_5H_{10} , measured upon reduction of ROOH to the alcohol by PPh_3 . [d] Cyclopentanol + cyclopentanone. [e] Alcohol (cyclopentanol)/ketone (cyclopentanone) molar ratio, upon reduction of ROOH to the alcohol by PPh_3 . [f] Overall TON values (mols of products/mol of catalyst). [g] Included^[5c] for comparative purposes. [h] $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ as catalyst, for comparative purposes. [i] $\text{Cu}\{\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{COO}\}_2$ as catalyst, for comparative purposes.

Figure 5. Effect of the peroxide-to-catalyst molar ratio on the overall yield of cyclohexanol and cyclohexanone in the cyclohexane oxidation catalysed by **1** (a), **4** (b) or **5** (c).Figure 6. Effect of the peroxide-to-catalyst molar ratio on the cyclohexanol-to-cyclohexanone molar ratio (A/K), in the cyclohexane oxidation catalysed by **1** (a), **4** (b) or **5** (c).Figure 7. Effect of the amount of catalyst **4** on the total yield and turnover number (TON).

(Figure 6), a further increase of the oxidant amount leads to higher yields of cyclohexanone with rough preservation of the cyclohexanol yields (Table 3) [e.g. A/K decreases from 7.1 to 1.9 and K/A increases correspondingly from 0.14 to 0.54 in the case of catalyst **5**, for the H_2O_2 /catalyst molar ratio change from 500 to 1000]. Hence, the growth of the overall yield with $n(\text{H}_2\text{O}_2)/n(\text{catalyst})$ (250–750 range) is essentially due to the enhanced formation of cyclohexanone for higher oxidant amounts.

The catalyst amount also plays a role and, as expected, its increase leads to a yield enhancement (Table 4, Figure 7), e.g., from 0.9% to 28% for the respective amounts of 0.63 and 10 μmol of catalyst **4** (which correspond to a substrate/catalyst molar ratio decrease from 1.59×10^3 to 100, respectively). On the other hand, a decrease of the catalyst amount below the typical value of 10 μmol results in enhancements of the overall TON from 28 up to 42 and of the A/K ratio from 5.6 up to 11 (Table 4, Figure 7, for catalyst **4**), the maximum TON corresponding to the catalyst amount of 2.5 μmol (substrate/catalyst molar ratio of 400) (entry 4). A further decrease of the amount of catalyst (below ca. 2 μmol , Figure 7) leads to lower TON values.

Our complexes also behave as efficient catalysts or catalyst precursors for the peroxidative oxidation of cyclopentane to cyclopentanol and cyclopentanone, leading to over-

all yields and TONs (Table 5) that are comparable to those observed in the case of cyclohexane oxidation under similar experimental conditions. Typical yields and TONs of ca. 30% and ca. 30, respectively, have been achieved for catalysts **2–5** with **1** being slightly less active. A significant reduction of the relative amount of the alcohol is observed in the cyclopentane oxidation (typical A/K values in the 2–3 range, Table 5) in comparison with the case of cyclohexane (typical A/K values, under identical experimental conditions, within the 6–9 range, Table 3).

The high overall yields (up to 34% in a single batch, in the case of cyclohexane oxidation) achieved with our catalysts (including **3**, already studied previously^[5c]) are comparable with those obtained by other valuable catalysts based on multicopper triethanolamine complexes^[4] or on iron(III)–chromium(III) hydroxides,^[32] a bit lower than that (up to 45%) of a heterotrimetallic Fe/Cu/Co complex with a *N,O*-coordination environment^[33a] and are markedly higher than those with half-sandwich scorpionate tripyrazolylmethane complexes of copper, iron or vanadium^[27a] as well as some pyrazole and trispyrazolylmethane rhenium complexes.^[27b] They are also better than that reported very recently^[27c] for a dipicolinate-Cu/Na coordination polymer (which, however, has the advantages of being water soluble and operating in the absence of acid) and those shown by other Cu catalytic systems,^[33b–33d] namely with salen, acetonitrile or phthalocyanine ligands.

Although the detailed mechanisms of the reactions are unknown, we believe they proceed by means of a radical pathway involving both C- and O-centred radicals since, as observed in other cases,^[4b,5c,28a,28c,28d] the oxidations of the cycloalkanes are essentially suppressed in the presence of radical trapping agents such as bromotrichloromethane, diphenylamine and 2,6-di-*tert*-butyl-4-methylphenol (BHT).

The formation of the ketone does not appear to proceed significantly by oxidation of the alcohol, since by using cyclohexanol as the substrate, instead of the cycloalkane, only very low conversions (2–4%) of cyclohexanol to cyclohexanone were detected (for the H₂O₂/catalyst molar ratio in the 500–1000 range). Hence, the fall in the A/K ratio for high values of the H₂O₂/catalyst molar ratio cannot be explained by further oxidation of cyclohexanol (CyOH) to cyclohexanone but may be accounted for by metal-assisted decomposition of cyclohexyl hydroperoxide (CyOOH) to the ketone.^[28c]

The involvement of CyOOH in the process is indicated by the marked increase of the amount of CyOH (by ca. 70–50%, for the conditions indicated by entries 1 and 11 in Table 3) with the corresponding decrease in the amount of the cycloketone upon treatment of the final reaction solution with an excess of PPh₃ prior to the GC analysis (see Exp. Sect.), following the method reported by Shul'pin.^[34] Reduction of CyOOH by PPh₃ gives CyOH (with formation of phosphane oxide), thus eliminating the decomposition of CyOOH to both CyOH and the cycloketone in the gas chromatograph. The method^[34] also allows the estimation of the amount of CyOOH present at the end of the reaction. This organohydroperoxide is then the main product

(e.g. 67% or 47% of the total of all products, for the conditions indicated by entry 1 or 11, respectively, in Table 3).

The reduction in the amount of CyOOH still present at the end of the reaction, upon increasing the H₂O₂/catalyst molar ratio, suggests that the higher concentrations of H₂O₂ favour the decomposition of CyOOH to the products during the reaction.

The formation of the cycloalkyl hydroperoxide (ROOH) can result from the reaction of a metal-peroxo intermediate, e.g. bearing a Cu^{II}-OOH type moiety, with the organoradical R[•] to form ROOH (and Cu^I).^[27a,35,36] The organohydroperoxide ROOH can undergo metal-assisted homolytic decomposition to alkoxyl (RO[•], upon O–O bond cleavage) and alkylperoxyl (ROO[•], upon O–H bond rupture) radicals from which the final oxygenates can be formed,^[34a,27a,37,38] i.e. cycloalcohol (ROH) upon H-abstraction from the alkane (RH) by RO[•] or upon decomposition of ROO[•] to both ROH and the cycloketone. In addition, the pyrazole and carboxylate ligands of our catalysts can be involved in proton-transfer steps, e.g., among H₂O₂, oxo and/or peroxo species, as suggested^[33c,34a,38b,39] for some V-catalysts with N,O-ligands.

Conclusions

The reactions of Hpz with some copper(II) carboxylates (namely valerate, 2-methylbutyrate, hexanoate and heptanoate) yield Cu^{II} derivatives **5–8** the structures of which, in the absence of XRD data, were inferred on the basis of physico-chemical measurements (magnetic susceptibility, ESI MS, IR and UV/Vis spectroscopy and ¹H NMR spectroscopy). In all cases, the triangular trinuclear skeleton [Cu₃(μ₃-OH)(μ-pz)₃]²⁺ is present, analogous to compounds **1–4**.^[5] The compounds **1–8** exhibit, by cyclic voltammetry, irreversible Cu^{II} → Cu^I and Cu^I → Cu⁰ reduction waves which did not clearly reflect any electronic communication between the metals.

All the compounds **1**, **2** and **4–8** behave as catalyst precursors for the efficient peroxidative oxidation of cycloalkanes by aqueous hydrogen peroxide, in acetonitrile at room temperature, similar to the previously reported compound **3**. Cyclo-alcohols and -ketones are the products of oxidation obtained in markedly high yields, by formation of the corresponding cycloalkyl hydrogen peroxide intermediates (ROOH), following radical mechanisms which were substantiated by radical trap experiments.

Experimental Section

Materials and Methods: All reaction and manipulations were carried out in air. Excluding formate and acetate (Aldrich), copper(II) carboxylates were prepared according to previously reported procedures^[40] that were slightly modified. Trinuclear triangular Cu^{II} derivatives of the type [Cu₃(μ₃-OH)(μ-pz)₃(RCOO)₂L_x] with R = H, [Cu₃(μ₃-OH)(μ-pz)₃(HCOO)₂(Hpz)₂] (**1**)^[5b] R = CH₃, [Cu₃(μ₃-OH)(μ-pz)₃(CH₃COO)₂(Hpz)₂] (**2**)^[5a] R = CH₃CH₂, [Cu₃(μ₃-OH)(μ-pz)₃(CH₃CH₂COO)₂(EtOH)] (**3**)^[5b] and R = CH₃(CH₂)₂, [Cu₃(μ₃-

OH)(μ -pz)₃(CH₃(CH₂)₂COO)₂(MeOH)(H₂O)] (**4**)^[5b] were synthesised as previously reported. All other chemicals were purchased from Aldrich and used without further purification. Elemental analyses (C,H,N) were performed with a Fisons Instruments 1108 CHNS-O Elemental Analyser. IR spectra were recorded from 4000 to 100 cm⁻¹ with a Perkin–Elmer System 2000 FTIR instrument. Positive electrospray mass spectra were obtained with a Series 1100 MSI detector HP spectrometer by using MeOH as mobile phase. Solutions for electrospray ionisation mass spectrometry (ESI-MS) were prepared using reagent grade methanol and acetonitrile and the obtained data (masses and intensities) were compared with those calculated by using the IsoPro isotopic abundance simulator.^[21] Peaks containing copper(II) ions were identified as the centres of isotopic clusters. The magnetic susceptibilities were measured at room temperature (20–28 °C) by the Gouy method with a Sherwood Scientific Magnetic Balance MSB-Auto, using HgCo(NCS)₄ as a calibrating agent and data were corrected for diamagnetism with the appropriate Pascal constants. The magnetic moments (in BM) were calculated from the equation $\mu_{\text{eff}} = 2.84 (X_{\text{m}}^{\text{corr}} T)^{1/2}$. Reflectance solid-state and MeOH solution UV/Vis spectra were recorded on a Varian Cary 5E spectrophotometer, equipped with a device for reflectance measurements. ¹H NMR spectra were obtained with a Bruker Avance 300 instrument. Valeric, 2-methylbutyric, hexanoic and heptanoic acids, formed in the reactions of corresponding copper(II) carboxylates with Hpz, were detected by GC analyses carried out on a Thermo Electron Trace DSQ instrument equipped with a 30 m × 0.25 mm, 0.25 μ Thermo TR 5MS column.

Syntheses

Basic Copper(II) Carbonate: To a water solution (ca. 100 mL) of copper(II) sulfate pentahydrate (10 g) (40 mmol) was added a water solution (75 mL) of K₂CO₃ (5.54 g, 40 mmol) whilst stirring in 1 mL portions. The resultant light-blue basic copper carbonate [CuCO₃·Cu(OH)₂] was filtered off and washed with water until SO₄²⁻ ions were completely eliminated. Wet CuCO₃·Cu(OH)₂ was used to prepare some copper(II) carboxylates.

Copper(II) Valerate: To a valeric acid (12 mL, 11.27 g, 110 mmol) solution in water (400 mL) was added the freshly prepared wet CuCO₃·Cu(OH)₂ in small portions, leading to the formation of a green solid. The suspension was stirred for 48 h and the solid filtered off, washed with water and dried under vacuum in the presence of solid KOH. Yield 6.25 g, 24 mmol, 60%, based on starting copper(II) sulfate. C₁₀H₁₈CuO₄ (265.79): calcd. C 45.19, H 6.83; found C 44.61, H 6.85. IR (KBr): $\tilde{\nu}$ = 1589 (s), 1449 (m), 1433 [m v(COO)] cm⁻¹.

Copper(II) 2-Methylbutyrate, A: The synthesis was carried out as for copper(II) valerate. Yield 60%, based on starting copper(II) sulfate. Recrystallisation from hot EtOH yielded crystals suitable for single crystal XRD determination. C₁₀H₁₈CuO₄ (265.79): calcd. C 45.19, H 6.83; found C 45.19, H 6.85. IR (KBr): $\tilde{\nu}$ = 1589 (s), 1467 (m), 1422 [s v(COO)] cm⁻¹.

Copper(II) Hexanoate: Commercial basic copper(II) carbonate (1.91 g, 8.5 mmol) was suspended in a little excess of hexanoic acid (5 mL, 4.64 g, 40 mmol). The green suspension was stirred overnight, filtered and washed with cold acetone to remove the excess hexanoic acid. The solid was dried under vacuum and extracted with acetone (Soxhlet). The resultant solution was concentrated under vacuum, yielding a green solid that was filtered off, washed with cold acetone and dried under vacuum. Yield 3.0 g, 9.3 mmol, 57%, based on basic copper carbonate. C₁₂H₂₂CuO₄ (293.85): calcd. C 49.05, H 7.55; found C 49.42, H 7.86. IR (KBr): $\tilde{\nu}$ = 1590 (s), 1417 [m v(COO)] cm⁻¹.

Copper(II) Heptanoate: The synthesis was carried out as for copper(II) hexanoate. Yield 63%, based on basic copper carbonate. C₁₄H₂₆CuO₄ (321.90): calcd. C 52.24, H 8.14; found C 52.46, H 8.05. IR (KBr): $\tilde{\nu}$ = 1596 (s), 1433 (m), 1417 [m v(COO)] cm⁻¹.

[Cu₃(μ -OH)(μ -pz)₃(CH₃(CH₂)₃COO)₂(H₂O)] (5**):** To a solution of copper(II) valerate (500 mg, 1.88 mmol) dissolved in EtOH (50 mL), was added Hpz (140 mg, 2.08 mmol) dissolved in EtOH (10 mL) and H₂O (1 mL). The solution immediately turned deep blue and was stirred overnight to give a blue solid that was filtered off, washed with ethanol and dried under vacuum. Yield 350 mg, 0.57 mmol, 89%. The presence of valeric acid was ascertained in the mother liquor.

5: M.p. above 200 °C. C₁₉H₃₀Cu₃N₆O₆ (629.12): calcd. C 36.27, H 4.81, N 13.36; found C 36.87, H 4.13, N 13.22. IR (KBr): $\tilde{\nu}$ = 1570 (s), 1540 [s v(COO)], 1444 (m), 1398 [m v(COO)], 2101 (w) cm⁻¹. MS (ESI+, MeOH, MeCN): *m/z* (%) = 684.8 (63) [Cu₃(OH)(pz)₃(C₄H₉COO)₂(MeOH)(MeCN)]+H⁺; 1076.7 (28) [Cu₆(OH)₄(pz)₆(C₄H₉COO)₂]+Na⁺; 1112.8 (100) [Cu₆(OH)₄(pz)₆(C₄H₉COO)(MeOH)₅]⁺; 1148.8 (96) [Cu₆(OH)₄(pz)₆(C₄H₉COO)(H₂O)₂(MeOH)₅]⁺. μ_{eff} (295 K) = 2.58 BM. λ_{max} /nm (reflectance): 607, 651. λ_{max} /nm (MeOH solution): 626 (ϵ = 191). ¹H NMR (CD₃OD, 298 K): δ = 37.78 (2 H), 40.88 (1 H) ppm.

[Cu₃(μ -OH)(μ -pz)₃(CH₃CH₂CH(CH₃)COO)₂(EtOH)₂] (6**):** To a solution of copper(II) 2-methylbutyrate (550 mg, 2.06 mmol) in EtOH (30 mL) was added Hpz (150 mg, 2.19 mmol) dissolved in EtOH (10 mL). The deep blue solution was stirred overnight and then evaporated to dryness under vacuum. Collected vapours revealed the presence of 2-methylbutyric acid. The deep blue solid was washed with hexane to remove the 2-methylbutyric acid and dried under vacuum. Yield 420 mg, 0.597 mmol, 87%.

6: M.p. above 200 °C. C₂₃H₄₀Cu₃N₆O₇ (703.24): calcd. C 39.28, H 5.73, N 11.9; found C 38.71, H 5.29, N 11.48. IR (Nujol): $\tilde{\nu}$ = 1584 (s), 1548 [s v(COO)], 1465 (s), 1420 [s v(COO)] cm⁻¹. MS (ESI+, MeOH, MeCN): *m/z* (%) = 591.8 (13) [Cu₃(OH)(pz)₃(C₄H₉COO)(MeOH)₂(H₂O)]⁺; 625.8 (20) [Cu₃(pz)₃(C₄H₉COO)₂(MeOH)]⁺; 752.7 (16) [Cu₃(OH)(pz)₃(C₄H₉COO)₂(H₂O)₂(MeOH)₂(MeCN)]+H⁺; 1076.6 (10) [Cu₆(OH)₄(pz)₆(C₄H₉COO)₂]+Na⁺; 1112.6 (40) [Cu₆(OH)₄(pz)₆(C₄H₉COO)(MeOH)₅]⁺; 1148.5 (100) [Cu₆(OH)₄(pz)₆(C₄H₉COO)(H₂O)₂(MeOH)₅]⁺; 1182.4 (19) [Cu₆(OH)₃(pz)₆(C₄H₉COO)₂(H₂O)(MeOH)₄]⁺. μ_{eff} (295 K) = 2.45 BM. λ_{max} /nm (reflectance): 609, 647, 551 (shoulder). λ_{max} /nm (MeOH solution): 626 (ϵ = 179). ¹H NMR (CD₃OD, 298 K): δ = 37.77 (2 H), 40.87 (1 H) ppm.

[Cu₃(μ -OH)(μ -pz)₃(CH₃(CH₂)₄COO)₂(EtOH)] (7**):** To a solution of copper(II) hexanoate (530 mg, 1.81 mmol) in EtOH (20 mL) was added Hpz (130 mg, 1.84 mmol) dissolved in EtOH (5 mL). The deep blue solution was stirred overnight and then evaporated to dryness under vacuum. Collected vapours revealed the presence of hexanoic acid. The blue solid obtained was washed with cyclohexane to eliminate hexanoic acid and dried under vacuum. Yield 400 mg, 0.58 mmol, 96%.

7: M.p. 195–198 °C (dec., blue colour turns to grey). C₂₃H₃₈Cu₃N₆O₆ (685.22): calcd. C 40.31, H 5.59, N 12.26; found C 40.00, H 4.96, N 12.92. IR (Nujol): $\tilde{\nu}$ = 1569 (s), 1542 [s v(COO)], 1430 (m), 1398 [w v(COO)], 2096 (w) cm⁻¹. MS (ESI+, MeOH, MeCN): *m/z* (%) = 536 (15) [Cu₃(OH)₂(pz)₃(H₂O)(EtOH)₂]⁺; 698.8 (52) [Cu₃(OH)(pz)₃(C₅H₁₁COO)₂(H₂O)(MeCN)]+H⁺; 748.8 (14) [Cu₃(OH)(pz)₃(C₅H₁₁COO)₂(H₂O)₂(MeOH)(MeCN)]+H⁺; 1118.8 (17) [Cu₆(OH)₃(pz)₆(C₅H₁₁COO)₂(H₂O)₃]⁺; 1154.8 (83) [Cu₆(OH)₃(pz)₆(C₅H₁₁COO)₂(H₂O)₅]⁺; 1190.8 (100) [Cu₆(OH)₃(pz)₆(C₅H₁₁COO)₂(H₂O)₇]⁺; 1238.8 (10) [Cu₆(OH)₃(pz)₅(C₅H₁₁COO)₃

(H₂O)₇)⁺. μ_{eff} (295 K) = 2.73 BM. λ_{max} (reflectance): 611 nm, 645 nm (shoulder). $\lambda_{\text{max}}/\text{nm}$ (MeOH solution): 621 (ϵ = 181). ¹H NMR (CD₃OD, 298 K): δ = 37.74 (2 H), 40.89 (1 H) ppm.

[Cu₃(μ_3 -OH)(μ -pz)₃(CH₃(CH₂)₅COO)₂(EtOH)] (8): To a solution of copper(II) heptanoate (540 mg, 1.68 mmol) dissolved in EtOH (50 mL) was added Hpz (120 mg, 1.70 mmol) dissolved in EtOH (10 mL). The deep blue solution was stirred for 3 h and then the addition of ca. 80 mL of water produced the precipitation of a clear-blue solid that was filtered off, washed with water and dried under vacuum. Yield 370 mg, 0.52 mmol, 92%. Heptanoic acid was detected in the mother liquor.

8: M.p. 190–195 °C (dec., blue colour fades). C₂₅H₄₂Cu₃N₆O₆ (713.28): calcd. C 42.10, H 5.94, N 11.78; found C 42.05, H 5.47, N 11.96. IR (Nujol): $\tilde{\nu}$ = 1569 (s), 1539 [s ν (COO)], 1456 (w), 1430 [m ν (COO)], 2095 (w) cm⁻¹. MS (ESI⁺, MeOH, MeCN): m/z (%) = 588 (12) [Cu₃(OH)(pz)₃(C₆H₁₃COO)(MeOH)(H₂O)]⁺; 619.9 (25) [Cu₃(OH)(pz)₃(C₆H₁₃COO)(MeOH)₂(H₂O)]⁺; 650 (10) [Cu₃(pz)₃(C₆H₁₃COO)₂]⁺; 682 (15) [Cu₃(pz)₃(C₆H₁₃COO)₂MeOH]⁺; 712.8 (50) [Cu₃(OH)(pz)₄(Hpz)(MeOH)₄(MeCN)]⁺; 1196.8 (35) Cu₆(OH)₃-(C₃H₃N₂)₆(C₆H₁₃COO)₂(H₂O)₄(CH₃OH); 1232.8 (100) Cu₆(OH)₃-(C₃H₃N₂)₆(C₆H₁₃COO)₂(H₂O)₆(CH₃OH); 1294.8 (18) [Cu₆(OH)₂-(pz)₆(C₆H₁₃COO)₃(H₂O)₅]⁺. μ_{eff} (295 K) = 2.56 BM. λ_{max} (reflectance): 611 nm, 643 nm. $\lambda_{\text{max}}/\text{nm}$ (MeOH solution): 626 (ϵ = 191). ¹H NMR (CD₃OD, 298 K): δ = 37.76 (2 H), 40.83 (1 H) ppm.

¹H NMR Spectroscopic Data of 1–4

¹H NMR spectra of compounds 1–4 were recorded at 298 K from CD₃OD solutions.

[Cu₃(μ_3 -OH)(μ -pz)₃(HCOO)₂(HPz)₂] (1): δ = 36.71 (2H), 41.09 (1 H) ppm.

[Cu₃(μ_3 -OH)(μ -pz)₃(CH₃COO)₂(HPz)] (2): δ = 37.48 (2H), 40.94 (1 H) ppm.

[Cu₃(μ_3 -OH)(μ -pz)₃(CH₃CH₂COO)₂(EtOH)] (3): δ = 37.84 (2H), 40.82 (1 H) ppm.

[Cu₃(μ_3 -OH)(μ -pz)₃(CH₃(CH₂)₂COO)₂(MeOH)(H₂O)] (4): δ = 37.77 (2H), 40.82 (1 H) ppm.

Electrochemical Studies: The electrochemical experiments were performed on an EG&G PAR 273A potentiostat/galvanostat connected to a personal computer through a GPIB interface. Cyclic voltammograms were obtained in 0.2 M [*n*Bu₄N][BF₄]/DMSO at a platinum disc working electrode (d = 0.5 mm) and at 25 °C. Controlled-potential electrolyses (CPE) were carried out in electrolyte solutions with the above-mentioned composition in a three-electrode H-type cell. The compartments were separated by a sintered glass frit and equipped with platinum gauze working and counter electrodes. For both CV and CPE experiments, a Luggin capillary connected to a silver wire pseudo-reference electrode was used to control the working electrode potential and a Pt wire was employed as the counter-electrode for the CV cell. The CPE experiments were monitored regularly by cyclic voltammetry, thus assuring no significant potential drift occurred along the electrolyses. The redox potentials of the complexes were measured by CV in the presence of ferrocene as the internal standard and their values are quoted relative to the SCE by using the [Fe(η^5 -C₅H₅)₂]^{0/+} redox couple ($E_{1/2}^{\text{ox}}$ = 0.44 V vs. SCE^[41]).

Catalytic Activity Studies: The reaction mixtures were prepared as follows: to 0.63–10.0 μmol (typically 10.0 μmol) of catalyst precursor contained in the reaction flask were added MeCN (4 mL), HNO₃ (0.1 mmol), C₆H₁₂ (or C₅H₁₀, 1.0 mmol) and H₂O₂ (30% in H₂O, 2.5–10.0 mmol), in that order. The reaction mixture was stirred for 6 h at room temperature (ca. 25 °C) and atmospheric

pressure, thereafter cycloheptanone (as internal standard, 90 μL), diethyl ether (to extract the substrate and the products from the reaction mixture, typically 9.0 mL) and PPh₃ (0.5 g, to reduce the organohydroperoxides, if formed, according to a method developed by Shul'pin^[34]) were added. The resultant mixture was stirred for 15 min and then a sample taken from the organic phase was analysed by GC using a Fisons Instruments GC 8000 series gas chromatograph with a DB WAX fused silica capillary column and the Jasco-Borwin v.1.50 software. The GC analyses of the aqueous phase showed the presence of only traces (less than 0.05%) of oxidation products.

Supporting Information (see also the footnote on the first page of this article): Structures of 1, 4, copper(II) butyrate; ESI-MS spectra and XRPD patterns for 5, 6, 7, 8.

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