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Copper(II) complexes with a new carboxylic-functionalized arylhydrazone of β -diketone as effective catalysts for acid-free oxidations[†]

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The aquasoluble [Cu(H₂O)((CH₃)₂NCHO)(HL)] (2) and [Cu₂(CH₃OH)₂(μ -HL)₂] (3) Cu^{II} complexes were prepared by reaction of Cu^{II} nitrate hydrate with the new 3-(2-hydroxy-4carboxyphenylhydrazone)pentane-2,4-dione (H₃L, 1), in the presence (for 2) or absence (for 3) of (*n*-C₄H₉)₂SnO, and characterized by elemental analysis, IR spectroscopy and X-ray single crystal diffraction. Magnetic susceptibility measurements, in compound 3, reveal strong antiferromagnetic coupling between the Cu^{II} ions through the μ_2 -phenoxido-O atoms, J = -203(1) cm⁻¹. Complexes 2 and 3 act as catalyst precursors for the acid-free peroxidative oxidation of cyclohexane to the mixture of cyclohexyl hydroperoxide (primary product), cyclohexanol and cyclohexanone (TONs and yields up to 163 and 14.4%, respectively), as well as for the selective aerobic oxidation of benzyl alcohols to benzaldehydes in aqueous solution, mediated by a TEMPO radical, under mild conditions (TONs and yields up to 390 and 94%, respectively). In the alkane oxidations, 2 and 3 appear to behave as "dual role catalysts" combining, in one molecule, an active metal centre and an acidic promoting group, to provide a high activity of the system even without any acid promoter.

Introduction

Arylhydrazones of β -diketones (AHBD, Scheme 1 for the particular example of this study, see below) are compounds which bear diketo- and hydrazone-moieties in one molecule. One can expect that AHBD would combine the advantages of both the above-mentioned types of species, thus being attractive candidates for a wide range of applications and further chemical transformations.¹ Complexes of AHBD have recently been intensively investigated regarding their structural properties and applications, *e.g.*, in catalysis.² The addition to AHBD of groups other than diketo- and hydrazone-moieties (*e.g.*, hydroxyl or carboxyl moieties) even further expands their coordination ability with possible formation of diverse types of complexes. Moreover, acidic (*e.g.*, carboxylic) groups within the AHBD complexes could be expected to promote catalytic reactions which require specific acidic conditions (see below). On the other hand, the carboxylic groups can significantly improve the solubility of complexes in water media, a property of a great significance for the development of green homogeneous metal catalysis.³ Reactions carried out in water can also provide the opportunity to finely tune the pH, which can lead to changes in reactivity and selectivity. Thus, it would be attractive to prepare new a AHBD bearing those groups (Scheme 1), synthesize derived water-soluble complexes and study their catalytic and magnetic properties. It is known that Cu^{II} is a good candidate for coordination with AHBD, as well as for magnetic and catalytic studies.^{1,2}



Scheme 1 3-(2-Hydroxy-4-carboxyphenylhydrazone)pentane-2,4-dione (H₃L, 1).

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but employed a synthetic strategy different from that described before,² hoping to obtain new complexes with interesting properties.

One of the known applications of copper complexes concerns their use as catalysts in various oxidation reactions, whereas cyclohexane oxidation is an important and widely studied catalytic transformation, which is carried out by industrial chemical processes but with low conversions and poor selectivities.⁴ Therefore, it is of great practical interest to develop a more efficient, as well as easily synthesizable, reusable and environment-friendly catalyst for this oxidation process.

The selective oxidation of alcohols to the corresponding aldehydes or ketones is another fundamental transformation in both laboratory and industrial syntheses, being frequently used *e.g.* for the preparation of pharmaceuticals, flavours and fragrances.⁵ In this case, the development of new catalytic oxidation systems with a high selectivity using cheap and green oxidants (*e.g.*, molecular oxygen) is also very attractive. Hence, we have selected these two oxidation processes for consideration in the current study.

Recent years have also witnessed much interest in moleculebased multifunctional materials, including photomagnetic and magneto-optical materials, and magnetic conductors.^{5a} Great efforts are currently devoted to the development of organic– inorganic hybrid building blocks, in which long-range magnetic coupling involving π -d interactions is expected.^{6b,c} Although the magnetic properties of β -diketonates of transition metals have been investigated,^{6d,e} to our knowledge there are no reported data about magnetic properties of AHBD complexes.

Therefore, the main objectives of this work are as follows: (i) to synthesize a new AHBD bearing both a carboxylic and an hydroxo group, *i.e.*, with an acidic function and a chelating ability, namely 3-(2-hydroxy-4-carboxyphenylhydrazone)pentane-2,4-dione (H₃L, **1**, Scheme 1); (ii) to prepare water soluble Cu^{II} complexes with this species; (iii) to study the magnetic properties of the synthesized Cu^{II} –AHBD complexes; (iv) to evaluate the catalytic activity of such complexes for the mild oxidations of cyclohexane to cyclohexanol and cyclohexanone, and of benzyl alcohols to the corresponding aldehydes.

Results and discussion

Syntheses and characterization of H₃L (1) and its [Cu(H₂O)((CH₃)₂NCHO)(HL)] (2) and [Cu₂(CH₃OH)₂(µ-HL)₂] (3) complexes

3-(2-Hydroxy-4-carboxyphenylhydrazone)pentane-2,4-dione (H₃L, **1**) was synthesized *via* the Japp–Klingemann reaction² between the respective aromatic diazonium salt and pentane-2,4-dione in water solution containing sodium hydroxide, and characterized by IR and NMR spectroscopies and elemental analysis. It is known that AHBD can theoretically exist in three tautomeric forms (enol-azo, keto-azo and hydrazone),^{1,2} but experimentally it has been observed that all the studied arylhydrazones prepared from symmetric β -diketones exist in solution and in the solid state only in the hydrazone form.² In agreement, the ¹H and ¹³C-NMR spectra of **1** support the hydrazone form.² The hydrazo ==N-NH- signal is observed at δ 14.56 in the ¹H-NMR spectrum, while the ¹³C-NMR spectrum

shows two separate singlets for the methyl groups of the pentane-2,4-dione moiety at δ 26.49 and 31.27. These data are consistent with the predominance of the hydrazone form with a sixmembered H-bonded ring involving one of the carbonyl groups and the ==N-NH- of the hydrazone structure (Scheme 1). The IR spectrum of 1 shows ν (OH) and ν (NH) vibrations at 3468 and 3083 cm⁻¹, respectively, while ν (C==O), ν (C==O···H), δ (OH) and ν (C==N) are observed at 1731 and 1669, 1635, 1631 and 1605 cm⁻¹, correspondingly, supporting the existence of the H-bonded hydrazone structure in the solid state.

Upon attempting to prepare a heteronuclear Cu–Sn complex by reaction of Cu^{II} nitrate with **1** and dibutyltin oxide (1:1:1 molar ratios) in dry methanol, the brown solid precipitated during the reaction was recrystallized from *N*,*N*-dimethylformamide (DMF) to give [Cu(H₂O)((CH₃)₂NCHO)(HL)] (**2**) (Fig. 1, Scheme 2, for details see Experimental part). Suitable crystals of **2** for X-ray structural analysis were obtained upon concentration of a DMF solution of the crude precipitate.

The structure of complex 2 shows the Cu atom in a square pyramidal environment formed, in the basal plane, by two O and one N atoms from HL²⁻ [O1, O3 and N1] and the aqua O10 atom; the apical position is taken by O6 of a formamide ligand. However, the linkage of neighbouring units via intermolecular contacts gives rise to the formation of dimeric copper aggregates (Fig. 1b). In such a situation, each copper metal can be considered as taking up an octahedral geometry where the intermolecular Cu1...O2 bond distances assume values of 2.9001(19) Å, which are considerably longer than the other metal-oxygen bond distances of the complex (in the 1.9300(14)-2.5260(16) Å range). In these units the Cu atoms are 6.7305(4) Å apart. Additionally, each monomer of 2 is associated with neighbouring units via intermolecular hydrogen interactions involving the coordinated water molecules as H-donor atoms, the O6 from dmf as an acceptor, and the carboxylate group as both donor and acceptor (Fig. 1a). When the phenolate O1 atoms act as acceptors, planar (Cu1-O10-H10A-O1)₂ rings are generated, leading to a Cu. . . Cu distance of 5.0748(3) Å, the minimum inter-metal distance that could be found in 2; an inversion centre lies in the middle of the thus engendered eightmembered ring. The copper(II) cation belongs to fused six- and five-membered metallacycles. Due to the coordination of O3 and to the hydrogen bonding it is involved in, the C11-O3 bond length is longer than that of the uncoordinated C9-O2 (1.268(2) Å and 1.222(3) Å, respectively). Interestingly, the metal-O bond distances in both metallacycles are quite similar [1.9370(14) and 1.9300(14) Å] and considerably shorter than that involving the aqua ligand (2.5260(16) Å).

The Cu^{II} complex **3** (Scheme 2) was prepared upon refluxing for a short time (5 min) a methanol solution of **1** and Cu^{II} nitrate hydrate, whereafter it was isolated in a good yield (47%) as dark brown crystals formed upon slow solvent evaporation at room temperature. The crystal structure shows that **3** consists of binuclear [Cu₂(CH₃OH)₂(μ -HL)₂] molecules. The copper atoms are bridged by the phenolate oxygen atoms of the chelating ligands HL²⁻ thus giving rise to a Cu₂O₂ core with the Cu···Cu separation of 3.0137(8) Å; an inversion centre lies in the middle of this core. The geometry around the copper atoms is that of basal edge-sharing highly distorted square pyramids ($\tau_5 = 0.40$), the copper atom being shifted



Fig. 1 ORTEP diagrams of complex **2** (a) with atomic numbering scheme and showing the hydrogen bonding interactions, and (b) showing the linkage of neighbouring molecules *via* intermolecular Cu···O contact interactions generating octahedral dinuclear aggregates. Ellipsoids are drawn at 50% probability. Selected bond distances (Å) and angles (°): O1–Cl 1.342(2), O3–Cl1 1.268(2), N1–N2 1.289(2), N2–Cl0 1.353(3), Cu1–O1 1.9370(14), Cu1–O3 1.9300(14), Cu1–O6 2.5260(16), Cu1–O10 1.9712(14), Cu1–N1 1.9153(16), Cu1–O2^{iv} 2.9001(19); O1–Cu1–O3 173.42(6), Cl2–N3–Cl4 121.8(2), O1–Cu1–O6 98.12(6), O1–Cu1–O10 96.35(6), O1–Cu1–N1 85.83(6), O3–Cu1–O6 86.77(6), O3–Cu1–O10 88.45(6), O3–Cu1–N1 89.13(6), O6–Cu1–O10 84.59(6), O6–Cu1–N1 98.29(7), O10–Cu1–N1 176.12(6), O6–Cu1–O2^{iv} 174.04(5). Selected hydrogen bonds [*d*(H···A), \angle (DHA)]: O5–H5···O6 2.666(2), 174°; O10–H10A···O1 2.636(2), 173(3)°; O10–H10B···O4 2.838(2), 176(2)°. Symmetry operations used to generate equivalent atoms: (i) –1 + x, 1 + y, z; (ii) 1 + x, -1 + y, z; (iii) –x, 1 – y, 1 – z; (iv) 1 – x, 1 – y, -z.



Scheme 2 Schematic representations of complexes 2 and 3.

0.284 Å above the fitted basal O1–O1ⁱ–O2–N1 plane towards the apical position occupied by a coordinated methanol molecule (Fig. 2). While the anionic HL^{2-} ligands are nearly planar, they make angles of *ca.* 25.47° with the central Cu₂O₂ core. The β -diketone fragments act as *O,N,O* donors to the Cu^{II} atoms, with the phenolate oxygen bridging between the two metal cations. The copper atoms belong to three different metallacycles: the Cu₂O₂ core, which is the central planar ring of the molecule, and two fused six- and five-membered metallacycles, Cu1–O2–C9–C10–N2–N1 and Cu1–N1–C2–C1–O1, with O2–Cu1–N1 and O1–Cu1–N1 angles of 90.96(12)° and 85.24(12)°, respectively. The [Cu₂(CH₃OH)₂(µ-HL)₂] units form an extended array by hydrogen bonding contacts (Fig. 2) leading to the

formation of a 2D network: one network flows along the [100] direction by means of the interactions between carboxyl groups of vicinal units, and another network runs along the [0-1-1] path and results from the connections between the methanol hydroxyls and the ketone groups. The elemental analysis supports the formulation, while the IR spectrum of **3** displays ν (OH), ν (C=O), δ (OH) and ν (C=N) at 3448, 1672 and 1638, 1629 and 1594 cm⁻¹, respectively, values that are significantly shifted in relation to the corresponding ones of the free ligand.

Both complexes 2 and 3 are soluble in water and in acetonitrile, features that are of significance towards their eventual application in catalysis in water and in aqueous NCMe media (see below).



Fig. 2 ORTEP diagram of complex 3, with atomic numbering scheme and showing the hydrogen bonding interactions. Ellipsoids are drawn at 50% probability. Selected bond distances (Å) and angles (°): N1-N2 1.277(4), N1-Cu1 1.912(3), O1-Cu1 1.939(2), O1-Cu1¹ 2.007(3), O2-Cu1 1.899(3), O20-Cu1 2.204(3), Cu1-O1¹ 2.007(3), Cu1–Cu1¹ 3.0137(10); O2-Cu1-N1 90.96(12), O2-Cu1-O1 O2–Cu1–O1ⁱ 100.44(11), 173.52(12), N1–Cu1–O1 85.24(12), N1-Cu1-O1ⁱ 149.36(13), O1-Cu1-O1ⁱ 80.45(12), O2-Cu1-O20 95.34(11), N1-Cu1-O20 113.43(13), O1-Cu1-O20 90.99(11), O1-Cu1-O20ⁱ 93.88(12), O2-Cu1-Cu1ⁱ 139.47(9), N1-Cu1-Cu1ⁱ 121.31(9). Selected hydrogen bonds $[d(H \cdots A), \angle (DHA)]$: O5-H5···O4 2.618(5), 168.21°; O20-H20O···O3 2.691(5), 165.59°. Symmetry operations used to generate equivalent atoms: (i) -x, -y, 1 - z; (ii) -1 - x, -y, 1 - z; (iii) 1 - x, -y, 1 - z; (iv) -1 - x, 1 - y, 2-z; (v) -1 + x, y, z; (vi) 1 + x, y, z; (vii) 1 + x, -1 + y, -1 + z.

Magnetic properties

The temperature dependence of the molar magnetic susceptibility, χ_M , for compound **3** is shown in Fig. 3. The shape of the plot is typical for a Cu^{II} dinuclear complex displaying a rather strong intramolecular antiferromagnetic coupling. Having in mind the dinuclear structure of compound **3**, the magnetic data were analyzed by means of the Bleaney–Bowers expression for two interacting spin doublets, eqn (1) (where *J* is the intramolecular magnetic exchange coupling constant, *g* is the Landé factor, β is the Bohr magneton and *k* is the Bohtzman's constant), which considers the isotropic spin Hamiltonian $H = -J(S_1S_2)^{.7a}$

$$\chi_{\rm M} = \frac{N\beta^2 g^2}{3kT} \left[\frac{6}{3 + \exp(-J/kT)} \right] \tag{1}$$

The best fit parameters to eqn (1) are g = 2.09(1), $J = -203(1) \text{ cm}^{-1}$ and $R = 7.27 \times 10^{-6}$. *R* is the agreement factor defined as $\sum_{i} [(\chi_{\rm M})_{\rm obs}(i) - (\chi_{\rm M})_{\rm calc}(i)]^2 / \sum_{i} [(\chi_{\rm M})_{\rm obs}(i)]^2$. Paramagnetic impurities as mononuclear species are found to be $\rho = 0.04$.



Fig. 3 Temperature dependence of the molar magnetic susceptibility, χ_M , of compound 3. The solid line is the best fit to the Bleaney–Bowers expression, see text.

The magnetic susceptibility data show a good agreement with the dinuclear model (Fig. 3).

The nature and the strength of the magnetic exchange coupling in alkoxide and hydroxide bridged Cu^{II} dinuclear complexes are mainly affected by the Cu–O–Cu bond angles (Θ) . Generally antiferromagnetic coupling is observed for $\Theta > 98^{\circ}$, whereas ferromagnetic couplings are observed for $\Theta < 98^{\circ}$.^{7b} However, other parameters such as the trigonal distortion of the Cu^{II} environment, the out-of-plane shift of the carbon atom of the alkoxide bridge or the hinge distortion of the Cu₂O₄ core modulate the coupling^{7c} and ferromagnetic couplings can be observed for slightly larger Θ angles.^{7d} Compound **3** conforms this correlation displaying strong antiferromagnetic couplings for large Cu–O–Cu angles and ferromagnetic couplings for angles smaller than 99.8°.

Catalytic activity of the copper complexes

Mild peroxidative oxidation of alkanes. Following the interest of our group in the Cu-catalyzed functionalization of alkanes under mild conditions,^{2,8} we have tested in detail the catalytic behaviour of complexes 2 and 3 in the oxidation of cyclohexane (CyH, model alkane substrate, Scheme 3). A couple of other alkanes (methylcyclohexane and n-heptane) were also tested, in less detail, for particular selectivity studies (see below). The catalytic tests were undertaken by reacting, at 50 °C in MeCN/ H₂O medium, an alkane with aqueous hydrogen peroxide (50%) in the presence of 2 or 3, either in the absence or in the presence of an acid promoter (trifluoroacetic acid, TFA). In some cases (with CyH) the reaction mixture was analyzed twice, before and after addition of PPh₃, and the observed difference in alcohol/ketone compositions allowed us to infer the presence of cyclohexyl hydroperoxide as the primary oxidation product.9 But for the determination of the final oxygenate amounts, only data obtained after treatment of the reaction sample with PPh₃ (in order to reduce CyOOH to CyOH) were usually used.

Both complexes 2 and 3 catalyze the oxidation of cyclohexane (CyH) to cyclohexyl hydroperoxide (CyOOH) as the primary product, which is converted in the course of the reaction to more stable cyclohexanol and cyclohexanone. One can assume that the predominant formation of cyclohexanol over cyclohexanone after the treatment of the reaction mixture with PPh₃ indicates⁹



Scheme 3 Oxidation of cyclohexane catalyzed by 2 and 3.

the formation of CyOOH (Table 1). The catalyst **2** was initially tested in a lower loading $(30 \times 10^{-5} \text{ mol L}^{-1})$ which allowed reaching higher turnover numbers (TONs) (Table 1). These gradually increase from 8 to the maximum of 163 (corresponding to 10.6% yield) on prolonging the reaction time from 15 to 190 min (Table 1, entries 1–6). It is important to highlight that these levels of activity have been reached in the *absence of any acid promoter*, thus constituting a remarkable feature of the present catalytic system. Such a behaviour of **2** contrasts to many of the previously reported Cu-containing catalytic systems,^{8,9} which exhibit a good activity towards the oxidation of alkanes by H₂O₂ only in the presence of an acid additive. However, such Cu-catalyzed oxidations with *tert*-butyl hydroperoxide (TBHP) usually do not require the presence of an acid.^{8d} Nevertheless, we have tested the influence of a trifluoroacetic acid (TFA) additive on the oxidation of cyclohexane. Interestingly, in the presence of **2** the addition of an excess of TFA accelerates to some extent the oxidation, leading to higher TONs within the first 60 min of the reaction (Table 1, entries 7–9 vs. 1–3). However, the final TON of 115 (entry 12) achieved in the presence of an acid promoter is inferior to that of 163 (entry 6) obtained in the acid-free system. A similar behaviour was observed when a higher amount of catalyst **2** (Table 1, entries 13–20, Fig. S1, ESI†) was used, with maximum TONs of 21 and 18 (or 13.4 and 11.8% yields) in acid-free and TFA-promoted systems, respectively (entries 16 and 20). The fact that **2** does not require an acid additive conceivably concerns the presence of uncoordinated acidic COOH groups of the AHBD ligands within the molecule of

Table 1 Oxidation of cyclohexane to cyclohexanol and cyclohexanone catalyzed by complexes 2 and 3^a

Entry	Catalyst amount, mol L ⁻¹	Acid additive (TFA), mol L^{-1}	Time (min)	Products, mmol L ^{-1b} (after PPh ₃)			Total TON ^c
				Cyclo-hexanol	Cyclo-hexanone	Total	[total yield, %]
Catalyst 2							
1	30×10^{-5}	_	15	1.7	0.6	2.3	8
2			30	3.5	0.9	4.4	15
3			60	5.7	2.6	8.3	28
4			90	18.4	3.2	21.6	72
5			140	28.9	7.3	36.2	121
6			190	42.3	5.8	48.1	163 [10.6]
7	30×10^{-5}	0.0035	15	3.4	0.9	4.3	14
8			30	4.0	1.1	5.1	17
9			60	8.8	1.4	10.2	34
10			90	16.4	1.5	17.9	60
11			140	22.3	3.7	26.0	87
12			190	31.3	3.2	34.5	115 [7.5]
13	30×10^{-4e}	_	60	21.7	3.2	24.9	8
14			120	24.6	4.7	29.3	10
15			240	42.3	8.1	50.4	17
16			330	44.2	17.6	61.8	21 [13.4]
17	30×10^{-4e}	0.01	60	40.2	10.1	50.3	17
18			120	44.1	9.3	53.4	18
19			240	49.9	9.5	59.4	20
20			330	33.7	20.7	54.4	18 [11.8]
Catalyst 3	5						[]
21	5×10^{-4e}	_	20	10.1	0.0	10.1	20
22			40	19.0	1.9	20.9	42
23			60	27.1	8.4	35.5	71
24			120	48.9	9.0	57.9	116
25			270	49.0	17.3	66.3	133 [14.4]
26	5×10^{-4e}	0.01	20	6.3	1.1	7.4	15
27			40	23.8	1.1	24.9	50
28			65	34.5	6.8	41.3	83
29			120	33.3	9.7	43.0	86
30			270	35.9	9.5	45.4	91 [9.9]

^{*a*} Reaction conditions, unless stated otherwise: [cyclohexane]₀ = 0.46 mol L⁻¹, [total H₂O₂]₀ = 2.2 mol L⁻¹ (50% aqueous), [total H₂O]₀ = 6.4 mol L⁻¹, MeCN up to 5 mL total volume, 50 °C. TFA = CF₃COOH. ^{*b*} Based on GC analysis, after treatment with PPh₃. ^{*c*} Total TON corresponds to moles of products per mol of catalyst. ^{*d*} Values in square brackets correspond to total yields (moles of products/100 moles of cyclohexane). ^{*e*} [Total H₂O]₀ = 4.2 mol L⁻¹.

Table 2 Selectivity parameters in the oxidation of *n*-heptane and methylcyclohexane (MCH)^a

Entry	Catalytic system	Regioselectivity $(n-C_7H_{16})$ C(1): C(2): C(3): C(4)	Bond selectivity (MCH) 1°:2°:3°
1	$2/H_2O_2/CH_3CN$	1:5:5:5	1:2:6
2	2/TFA/H ₂ O ₂ /CH ₃ CN	1:6:6:5	1:2:7
3	$3/H_2O_2/CH_3CN$	1:5:5:5	1:3:7
4	3/TFA/H2O2/CH2CN	1:6:6:5	1:3:9
5^b	Cu ₄ /TFA/H ₂ O ₂ /CH ₃ CN	1:8:7:5	1:5:14
6 ^b	Cu ₄ /t-BuOOH/CH ₃ CN	1:34:23:21	1:16:128

^{*a*} Reaction conditions: catalyst $[2]_0$ or $[3]_0 = 30$ or 5×10^{-4} mol L⁻¹, $[TFA]_0 = 0.01$ mol L⁻¹, $[substrate]_0 = 0.46$ mol L⁻¹, $[H_2O_2]_0 = 2.2$ mol L⁻¹ (50% aqueous), [total H₂O]_0 = 4.2 mol L⁻¹, MeCN up to 5 mL total volume, 50 °C. All parameters were measured after reduction of the reaction mixtures with PPh3 before GC analysis and calculated based on the ratios of isomeric alcohols. The calculated parameters were normalized, *i.e.*, recalculated taking into account the number of H atoms at each carbon. Parameters C(1): C(2): C(3): C(4) are relative reactivities of hydrogen atoms at carbons 1, 2, 3 and 4 of the *n*-heptane chain. Parameters 1°: 2°: 3° are relative normalized reactivities of the hydrogen atoms at primary, secondary and tertiary carbons of methylcyclohexane. ^{*b*} Compound Cu₄ is the [OCu₄{N(CH₂CH₂O)₃}₄(BOH)₄][BF₄]₂ complex; for this system see ref. 8*a*, 9*d*.

the complex which thus can be considered as a "dual role catalyst". Considering the prior background^{8b,f;9d} on the use of acid co-catalysts in Cu-catalyzed alkane oxidations, one should expect that the role of an acid additive (TFA) or uncoordinated COOH groups of the AHBD ligands consists in participating in proton-transfer steps, activating the catalyst *via* protonation of ligands, promoting unsaturation of the copper centres and enhancing the oxidizing properties of metal complex intermediates and hydrogen peroxide.

The dicopper(II) complex 3 also catalyzes the oxidation of cyclohexane (Table 1, entries 21-30, Fig. S2, ESI⁺), showing (for the complex concentration of 5×10^{-4} mol L⁻¹) a similar catalytic performance to that of the monocopper(II) compound 2, leading to maximum TON and yield values of 133 and 14.4%, respectively, in the acid-free system. This apparently suggests the involvement of analogous types of catalytically active species. Such a possibility was also indicated by the study of the oxidation of *n*-heptane and methylcyclohexane (MCH), with the estimate of the regioselectivity C(1): C(2): C(3): C(4) and bond selectivity $1^{\circ}: 2^{\circ}: 3^{\circ}$ parameters for their respective oxidations (Table 2). Both catalysts 2 and 3 appear to show rather similar regio- and bond selectivity parameters, either in the absence or presence of TFA. Their typical values range from 1:5:5:5 to 1:6:6:5 for regioselectivity, and from 1:2:6 to 1:3:9 for bond selectivity (Table 2, entries 1-4). These rather low selectivity parameters are well comparable to those previously reported for other multicopper(II) catalytic systems (e.g. Table 2, entry 5) that operate with participation of free hydroxyl radicals.9 In fact, alkane oxidations that do not involve hydroxyl radicals are expected to show rather distinct selectivity profiles (for comparison, see entry 6, Table 2). Thus, based on the literature background^{8,9} and the above mentioned features regarding (i) the formation of CyOOH as a primary intermediate product and (ii) the observed selectivity parameters, we can conclude that the

present alkane oxidations proceed *via* a free radical mechanism^{8,9} through the generation of hydroxyl radicals as active oxidizing species.

In summary, the obtained results indicate that in the alkane oxidations with hydrogen peroxide both complexes 2 and 3 behave as "dual role catalysts" which combine the active metal centre with acidic promoting groups in the molecule. This allows achieving rather high values of TONs (up to 163) even without any acid promoter, what constitutes a remarkable and unusual feature of the present catalytic systems.

Aerobic oxidation of alcohols in aqueous solutions. We have recently reported the activity of some Cu^{II} complexes with *N*,*N*- and *N*,*O*-ligands as catalysts for the aerobic oxidation of benzylic alcohols mediated by TEMPO in aqueous media.^{2a,5,10,11} Therefore, as a continuation of these studies, we have now applied the aquasoluble complexes **2** and **3** as catalysts for this reaction (Scheme 4, Table 3), and used previously optimized reaction conditions,^{2a} although now with significantly lower amounts of catalysts.

Thus, aerobic oxidation of benzyl alcohol (1.5 mmol) in basic (0.1 M K₂CO₃) aqueous solution, in the presence of a catalytic amount of complex **2** (0.015 mmol, 1 mol% vs. substrate) and TEMPO (0.075 mmol, 5 mol% vs. substrate) results in 20% yield of benzaldehyde after 4 h of reaction (Table 3, run 1). The reaction under the same conditions but with the dimeric complex **3** results in 9% of the product, the triple increase of the amount of **3** does not rise the yield substantially (runs 2 and 3). Prolongation of the reaction time to 22 h resulted in a very good yield of benzaldehyde in the case of **2** (93%, with TON of *ca*. 93, run 4), but in a lower one for **3** (62%, run 5), while a triple amount of **3** increases slightly the yield to 65% (run 6). Reaction in the presence of **2** but at the lower temperature of 60 °C results in a lower yield (77%, run 7).



Scheme 4 Aerobic oxidation of benzylic alcohols in water.

 Table 3
 Aerobic oxidation of selected alcohols to the corresponding aldehydes^a

Run	Complex	Substrate-to-catalyst ratio	Substrate	Product	Temperature [°C]	Time [h]	Yield ^b [%]	TON
1	2	100	Benzyl alcohol	Benzaldehyde	80	4	20	20
2	3	600	Benzyl alcohol	Benzaldehyde	80	4	9	54
3	3	200	Benzyl alcohol	Benzaldehyde	80	4	13	26
4	2	100	Benzyl alcohol	Benzaldehyde	80	22	93	93
5	3	600	Benzyl alcohol	Benzaldehyde	80	22	62	372
6	3	200	Benzyl alcohol	Benzaldehyde	80	22	65	390
7	2	100	Benzyl alcohol	Benzaldehyde	60	22	77	77
8^c	2	100	Benzyl alcohol	Benzaldehyde	80	22	3	3
9^d	2	100	Benzyl alcohol	Benzaldehyde	80	22	2	2
10	2	100	2-Me-benzyl alcohol	2-Me-benzaldehyde	80	22	43	43
11	2	100	3-Me-benzyl alcohol	3-Me-benzaldehyde	80	22	72	72
12	2	100	4-Me-benzyl alcohol	4-Me-benzaldehyde	80	22	82	82
13	2	100	4-MeO-benzyl alcohol	4-MeO-benzaldehvde	80	22	94	94
14	2	100	4-Cl-benzyl alcohol	4-Cl-benzaldehyde	80	22	70	70

^{*a*} Conditions: 1.5 mmol of the substrate, 0.0025–0.015 mmol (0.17–1.0 mol%) of catalyst and 0.075 mmol (5 mol%) of TEMPO in 5 mL of 0.1 mol L^{-1} K₂CO₃ aqueous solution, 1 atm air. ^{*b*} Yields based on GC analyses, selectivity in all cases >99%. ^{*c*} Reaction without K₂CO₃. ^{*d*} Reaction without TEMPO.

The presence of a base (here K_2CO_3), as well as of a TEMPO radical, is crucial for the efficiency of this process (runs 8 and 9). Substituted benzylic alcohols can also be converted to the corresponding aldehydes with rather good yields. Thus, oxidation of 1-, 2- or 3-methylbenzyl alcohols results in 43, 72 and 82% of the corresponding aldehydes, revealing a hampering effect of the substituents on ortho- and to lesser extent on meta-positions (runs 10-12). 4-Methoxybenzyl alcohol is oxidized to the corresponding aldehyde with identical yield (94%) and TON (564) to those of the unsubstituted alcohol (run 13 vs. 4), whereas 4-methyl and 4-chlorobenzyl alcohols are oxidized less effectively (runs 12 and 14). The catalytic system is expected to involve the coordination of alcohol (and TEMPO) to the copper centre, deprotonation of alcohol by base and β-hydrogen abstraction from the benzyloxide ligand by TEMPO resulting in a radical-TEMPOH-copper species. Intramolecular one-electron transfer from the radical to Cu^{II} leads to the aldehyde, TEMPOH and Cu^I species. The initial Cu^{II} complex is regenerated by the TEMPO-mediated oxidation of Cu^I to Cu^{II}, whereas TEMPO is regenerated by the aerobic oxidation of TEMPOH.^{4,10,11}

Conclusions

A new carboxyl containing arylhydrazone of pentane-2,4-dione, *i.e.* 3-(2-hydroxy-4-carboxyphenylhydrazone)pentane-2,4-dione (H₃L, 1), is shown to display a good synthetic potential towards complex formation with copper(II), acting as a suitable ligand to create water soluble Cu^{II} complexes (2 and 3).

It is established that 2 and 3 act as active catalysts for oxidation processes, particularly for the peroxidative oxidation, in NCMe/H₂O and under mild conditions, of cyclohexane to the mixture of cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone, as well as for the selective oxidation, in water, of benzyl alcohols to the corresponding benzaldehydes. In the alkane peroxidative oxidations, 2 and 3 behave as "dual role catalysts" combining, in one molecule, an active metal centre and an acidic promoting group, thus providing a high activity of the system even without any acid promoter. The magnetic study reveals that the magnetic behaviours of 3 follow the general trend for alkoxo-bridged Cu^{II} complexes, displaying antiferromagnetic couplings for large Cu–O–Cu bridging angles and ferromagnetic couplings for the angles smaller than 99.8°.

The strategy used in this study deserves to be extended to the synthesis of other carboxyl functionalized AHBD and derived water soluble complexes to be applied as convenient "dual role catalyst" precursors in green catalysis, under acid-free aqueous conditions.

Experimental

Materials and instrumentation

1D $[^{1}H, ^{13}C\{^{1}H\}]$ NMR spectra were recorded on Bruker Avance II+ 300.130 (UltraShield[™] Magnet) and Bruker Avance II+ 400 MHz (UltraShield Magnet) spectrometers at ambient temperature using tetramethylsilane as an internal reference. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. Carbon, hydrogen, and nitrogen elemental analyses were carried out by Microanalytical Service of Instituto Superior Técnico. The synthetic work of ligand 1 and copper complex 3 was performed in air and at room temperature, whereas the mononuclear complex 2 was synthesized in flame-dried glassware under a dinitrogen atmosphere by using inert gas flow and vacuum-line techniques. All reagents were obtained from commercial sources (Aldrich), whereas methanol was purified by conventional distillation over magnesium powder. Chromatographic analyses were undertaken by using a Fisons Instruments GC 8000 series gas chromatograph (He as carrier gas) with a DB-624 (J&W) capillary column (FID detector) and the Jasco-Borwin v.1.50 software, or a Perkin Elmer Clarus 500 gas chromatograph (He as carrier gas, FID) with a BP20 capillary column (SGE). Internal standards (nitromethane and acetophenone) were used to quantify the organic products in the catalytic experiments. Magnetic susceptibility measurements on a polycrystalline sample were carried out at the temperature range of 55-310 K, by means of a Quantum Design SQUID magnetometer operating with an applied magnetic field of 10.000 Oe. Diamagnetic corrections of the constituent atoms were estimated from Pascal's constants. Experimental susceptibilities were also corrected for the temperature-independent paramagnetism [$60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \text{ per Cu}^{\text{II}}$] and the magnetization of the sample holder.

Synthesis of H₃L (1)

Diazotization. A 3.825 g, 0.025 mol portion of 2-hydroxy-4carboxyaniline was dissolved in 50 mL of water upon addition of 1.000 g of crystalline NaOH. The solution was cooled in an ice bath to 0 °C and 1.725 g, 0.025 mol of NaNO₂ was added with subsequent addition of 5 mL of 33% HCl in portions of 0.2 mL for 1 h under vigorous stirring. During the reaction the temperature of the mixture must not exceed 278 K. A suspension of the unstable 2-hydroxy-4-carboxyphenyldiazonium chloride $[N \equiv N{CC(OH)CHC(COOH)CHCH}]^+Cl^-$ was obtained which then was used as such for the next stage.

Azocoupling. 1.000 g, 0.025 mol NaOH were added to a mixture of 2.55 mL, 0.025 mol of pentane-2,4-dione with 50 mL of water–ethanol (1:1, v/v). The solution was cooled on an ice bath, and a suspension of 2-hydroxy-4-carboxyphenyl-diazonium chloride was added in two equal portions under vigorous stirring for 1 h. On the next day, the formed precipitate of 3-(2-hydroxy-4-carboxyphenylhydrazone)pentane-2,4-dione (1) was filtered off, washed with water, recrystallized from ethanol and dried in air. The identification of 1 was carried out by IR, element analysis, ¹H and ¹³C NMR spectroscopies.

Yield 87.0% (based on pentane-2,4-dione), dark brown powder, soluble in ethanol, acetone, THF and methanol, and insoluble in water and chloroform. Calcd. for $C_{12}H_{12}N_2O_5$ (M = 264.2): C, 54.55; H, 4.58; N, 10.60; Found: C, 54.52; H, 4.60; N, 10.56%. IR, cm⁻¹: 3537 (s, br) ν (OH), 3468 (s, br) ν (OH), 3083 (s, br) ν (NH), 1731 and 1669 (s) ν (C=O), 1635 (s) ν (C=O···H), 1631 δ (OH), 1605 (s) ν (C=N). ¹H NMR (300 MHz, DMSO- d^6 , Me₄Si): $\delta = 2.27$ (s, 3H, CH₃), 2.45 (s, 3H, CH₃), 7.47–7.64 (m, 3H, Ar–H), 11.81 (s, 1H, OH), 14.56 (s, 1H, NH). ¹³C{¹H} (75.468 MHz, DMSO- d^6 , Me₄Si): $\delta = 26.49$ (CH₃), 31.27 (CH₃), 114.13 (Ar–H), 116.48 (Ar–H), 121.40 (Ar–COOH), 128.84 (Ar–H), 132.72 (C=N), 134.02 (Ar–NH–N), 146.08 (Ar–OH), 167.14 (C=O), 196.36 (C=O), 196.75 (C=O).

Synthesis of [Cu(H₂O)((CH₃)₂NCHO)(HL)] (2)

Addition of solid Cu(NO₃)₂ (159.2 mg, 0.68 mmol) to a stirred suspension of **1** (181.5 mg, 0.68 mmol) in 30 mL of dry methanol at room temperature (20 °C) gave a brown precipitate. The mixture was further stirred under nitrogen for 1 h. Solid Bu₂SnO (170.1 mg, 0.68 mmol) was then added and the reaction mixture was left stirring vigorously overnight at 40 °C in an inert atmosphere. The brown solid that formed was collected by filtration, washed with cold methanol and dried under vacuum. The crystals of **2** suitable for X-ray structural analysis were obtained by slow evaporation of a DMF solution of the crude brown solid. Yield 47% (based on Cu). Calcd. for C₁₅H₁₉CuN₃O₇ (M = 416.87): C, 43.22; H, 4.59; N, 10.08; Found: C, 43.06; H, 4.46; N, 10.04%. MS (ESI): m/z: 418 [M + H⁺]. IR, cm⁻¹: 3259 ν (OH), 1676 ν (C=O), 1645 ν (C=O), 1596 ν (C=N).

Synthesis of [Cu₂(CH₃OH)₂(µ-HL)₂] (3)

To a 50 mL methanol solution of **1** (0.0264 mg, 0.1 mmol), 0.0233 mg (0.1 mmol) of Cu(NO₃)₂·2.5 H₂O was added. The mixture was stirred for 5 min and left for slow evaporation. Dark brown crystals started to form in the reaction mixture after five days at room temperature; they were filtered off and dried in air. Yield 47% (based on Cu). Calcd. for C₂₆H₂₈Cu₂-N₄O₁₂ (M = 715.6): C, 43.64; H, 3.94; N, 7.83; Found: C, 43.36; H, 3.76; N, 7.84%. MS (ESI): m/z: 651 [M – 2CH₃OH + H⁺]. IR, cm⁻¹: 3448 ν (OH), 1672 and 1638 ν (C=O), 1629 δ (OH), 1594 ν (C=N).

X-Ray structure determination

Crystals of 2 and 3 were grown by slow evaporation at room temperature of DMF (2) and methanol (2) solutions, respectively. They were immersed in cryo-oil, mounted in a Nylon loop and measured at a temperature of 150 K. Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo-Ka ($\lambda = 0.71073$) radiation. Data were collected using omega scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT^{12a} on all the observed reflections. Absorption corrections were applied using SADABS.^{12a} Structures were solved by direct methods by using the SHELXS-97 package^{12b} and refined with SHELXL-97.12c Calculations were performed using the WinGX System-Version 1.80.03.^{12d} All hydrogen atoms were inserted at calculated positions. Crystallographic details are listed in Table S1 (ESI).[†]

Catalytic activity studies

Peroxidative oxidation of alkanes. The alkane oxidations were typically carried out in air in thermostated (50 °C) Pyrex cylindrical vessels or round bottom flasks with vigorous stirring and using MeCN as solvent (up to 5.0 mL total volume). Typically, the catalyst precursor 2 or 3 was introduced into the reaction mixture as a solid or in the form of a stock solution in aqueous (10% vol) acetonitrile (7.5 or 1.25×10^{-4} mol L⁻¹, respectively, for 2 or 3). Then TFA (optional) was added in the form of a stock solution in MeCN $(0.44 \text{ mol } \text{L}^{-1})$. The alkane substrate, typically cyclohexane (0.25 mL, 2.3 mmol) was then introduced, and the reaction started when hydrogen peroxide (50% in H₂O, 0.68 mL, 11 mmol) was added in one portion. The final concentrations of the reactants in the reaction mixture were as follows: catalyst precursor **2** or **3** (30 \times 10⁻⁴–5 \times 10⁻⁵ mol L⁻¹), TFA (0-0.01 mol L^{-1}), substrate (0.46 mol L^{-1}) and H₂O₂ (2.2 mol L^{-1}). The reactions were stopped by cooling and analyzed by GC. Attribution of peaks was made by comparison with chromatograms of authentic samples. Nitromethane (0.05 mL) was used as GC internal standard.

Since the oxygenation of alkanes usually gives rise to the formation of the corresponding alkyl hydroperoxides as the main primary products, the quantification was performed by a method developed by Shul'pin.^{9a-c} For precise determination of oxygenate concentrations only data obtained after reduction of the reaction sample with PPh₃ were usually used, taking into account that the original reaction mixture typically contained

the three products: alkyl hydroperoxide (as the primary product), ketone and alcohol.

Aerobic oxidation of alcohols. The reactions were carried out in 50 mL round-bottom flasks equipped with condensers under atmospheric pressure of air. Typically, to a 10 mL of 0.1 mol L⁻¹ aqueous solution of K₂CO₃ were added 3.0 mmol of alcohol, 0.03 mmol (1 mol% vs. substrate) of catalyst **2** or **3**, and 0.15 mmol (5 mol% vs. substrate) of TEMPO. The reaction solutions in all cases were vigorously stirred using magnetic stirrers, and an oil bath was used to achieve the desired reaction temperature. After the oxidation reaction, reaction mixtures were neutralized by 1 mol L⁻¹ HCl, and then extracted with 10 mL of ethylacetate. The organic phase was used for chromatographic analysis using acetophenone as the internal standard.

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