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Mn^{II} and Cu^{II} complexes with arylhydrazones of active methylene compounds as effective heterogeneous catalysts for solvent- and additive-free microwave-assisted peroxidative oxidation of alcohols†

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A one-pot template reaction of sodium 2-(2-(dicyanomethylene)hydrazinyl)benzenesulfonate (NaHL¹) with water and manganese(II) acetate tetrahydrate led to the mononuclear complex [Mn(H₂O)₆](HL^{1a})₂·4H₂O (1), where (HL^{1a})⁻ = 2-(SO₃⁻)C₆H₄(NH)N=C(C≡N) (CONH₂) is the carboxamide species derived from nucleophilic attack of water on a cyano group of (HL¹)⁻. The copper tetramer [Cu₄(H₂O)₁₀-(1κN:κ²O:κO,2κN:κO-L²)₂]·2H₂O (2) was obtained from reaction of Cu(NO₃)₂·2.5H₂O with sodium 5-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)-4-hydroxybenzene-1,3-disulfonate (Na₂H₂L²). Both complexes were characterized by elemental analysis, IR spectroscopy, ESI-MS and single crystal X-ray diffraction. They exhibit a high catalytic activity for the solvent- and additive-free microwave (MW) assisted oxidation of primary and secondary alcohols with *tert*-butylhydroperoxide, leading to yields of the oxidized products up to 85.5% and TOFs up to 1.90 × 10³ h⁻¹ after 1 h under low power (5–10 W) MW irradiation. Moreover, the heterogeneous catalysts are easily recovered and reused, at least for three consecutive cycles, maintaining 89% of the initial activity and a high selectivity.

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1. Introduction

The development of efficient and selective catalysts for the oxidation of alcohols into their corresponding carbonyl compounds is a fundamental issue in organic synthesis, as well as in the chemical industry.^{1,2} Carbonyl compounds, such as aldehydes and ketones, are precursors for the synthesis of many

drugs, ligands, vitamins, *etc.*, and important intermediates for many complex syntheses.^{1–3} A good number of studies has been reported on homogeneous or heterogeneous catalytic oxidation of alcohols with different catalysts and oxidants.^{4,5} Due to several disadvantages of heterogeneous systems, namely difficult catalyst recycling, alcohol oxidation using heterogeneous catalysts is gathering increasing interest.^{2,4} Moreover, oxidation of alcohols with air or peroxides represents an important field of contemporary metal complex catalysis.^{4–6} Galactose oxidase is a copper-containing enzyme that catalyzes the two-electron oxidation of primary alcohols to aldehydes using molecular oxygen as the terminal oxidant.⁴ Synthetic models of galactose oxidase, *i.e.*, copper complexes with different types of organic ligands are also known to be good catalysts in the oxidation of alcohols by molecular oxygen of air or hydrogen peroxide.^{4,5}

Recently, we have found that water-solubility of arylhydrazones of active methylene compounds (AHAMCs) and their copper(II) complexes can be increased by functionalization of ligands with hydrophilic polar groups, such as sulfo, carboxy or nitro, and they can be significantly active catalysts in the aerobic and peroxidative oxidation of alcohols or of unsaturated hydrocarbons to the corresponding organic compounds.^{7–11} The modification of AHAMCs ligands with several sulfonic groups can promote the solubility of the isolated complexes in polar

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† Electronic supplementary information (ESI) available: Analytical data for compounds NaHL¹ and Na₂H₂L². Crystallographic and selected structural details are listed in Tables S1 and S2. CCDC 1023179 and 1023180. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5ra02667a

solvents, but hamper their solubility in solvents with low polarity. Hence, these complexes could act as heterogeneous catalysts for the solvent-free and microwave-assisted oxidation of less polar bulky substituted or long chain alcohols, such as benzyl alcohol, 1-phenylethanol, hexan-1-ol, heptan-1-ol, *etc.* to the corresponding carbonyl compounds. The application of such an approach to the establishment of an heterogeneous catalytic system for alcohol oxidation constitutes the main aim of the current study.

Herein, we report the synthesis and characterization of highly water soluble copper(II) and manganese(II) complexes of AHAMCs, *i.e.*, 2-(2-(dicyanomethylene)hydrazinyl)benzenesulfonate (HL^1)⁻ and 5-(2-(4,4-dimethyl-2,6-dioxocyclohexylidene)hydrazinyl)-4-hydroxybenzene-1,3 disulfonate (L^2)⁴⁻, and their catalytic activity (as heterogeneous catalysts) towards solvent- and additive-free peroxidative oxidation of aromatic and of aliphatic cyclic or long chain alcohols under low power microwave irradiation.

2. Results and discussion

2.1. Synthesis and characterization of 1 and 2

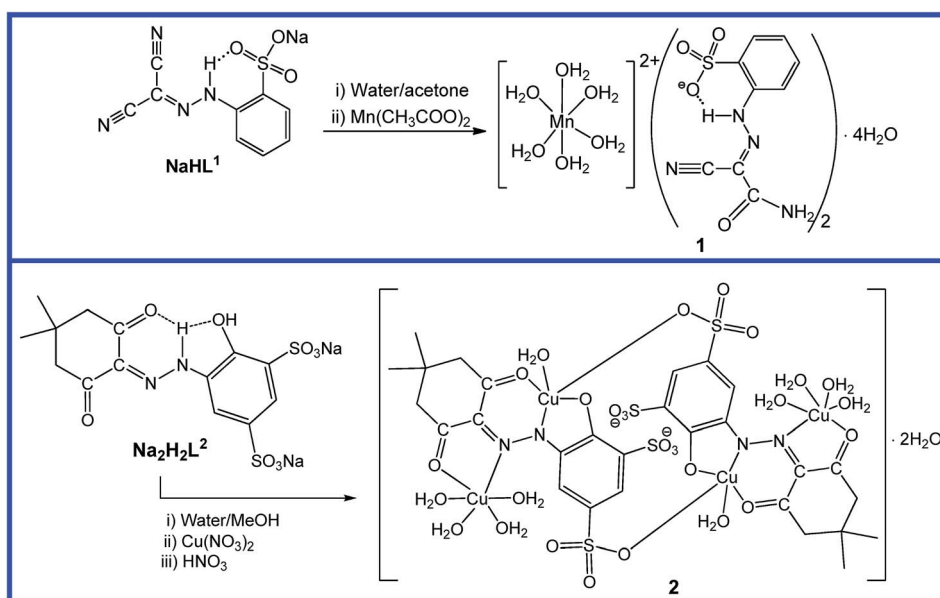
Sodium salts of both ligands, NaHL^1 and $\text{Na}_2\text{H}_2\text{L}^2$, were synthesized by the Japp–Klingemann method^{7b,12} upon reaction between the aromatic diazonium salt of a substituted aniline and malononitrile or 5,5-dimethylcyclohexane-1,3-dione in water solution containing sodium hydroxide (for analytical data see ESI†). They were reported earlier by some of us.^{7b,12}

The reaction of NaHL^1 with $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in water/acetone mixture afforded a deep red precipitate which upon recrystallization from methanol produces deep red crystals of $[\text{Mn}(\text{H}_2\text{O})_6](\text{HL}^{1a})_2 \cdot 4\text{H}_2\text{O}$ (**1**) in 70% yield (Scheme 1). The synthesis involves an *in situ* ligand formation, in which one of the cyano groups of (HL^1)⁻ undergoes hydrolysis by water

resulting in the formation of the carboxamide ($\text{HL}^{1a})^- = 2-(\text{SO}_3^-)\text{C}_6\text{H}_4(\text{NH})\text{N}=\text{C}(\text{C}\equiv\text{N})(\text{CONH}_2)$. A slow evaporation of a mixture of copper(II) nitrate hydrate, $\text{Na}_2\text{H}_2\text{L}^2$ and HNO_3 in water/methanol mixture furnishes greenish-black crystals of the tetranuclear complex $[\text{Cu}(\text{H}_2\text{O})\text{Cu}(\text{H}_2\text{O})_4(\mu\text{-L}^2)]_2 \cdot 2\text{H}_2\text{O}$ (**2**) (Scheme 1).

Both complexes were characterized by elemental analysis, IR spectroscopy, ESI-MS and X-ray analysis. Elemental analysis and the ESI-MS peaks at 81.5 $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, 163.0 $[\text{Mn}(\text{H}_2\text{O})_6]^+$, 267.2 ($\text{HL}^{1a})^-$, and 652.3 $[\text{Cu}_2(\text{H}_2\text{O})_6(\text{L}^2)+\text{H}^+]$ support the formulation. In the IR spectrum of **1**, $\nu(\text{OH})$ and $\nu(\text{NH})$ vibrations are observed at 3436 and 3103 cm^{-1} , respectively, while $\nu(\text{C}\equiv\text{N})$ of the unreacted cyano group appears at 2227 cm^{-1} . A new peak at 1645 cm^{-1} indicates that, in the solid state, **1** exhibits the carboxamide form which is also supported by X-ray data (see below). The IR spectrum of **2** displays peaks at 3307, 3217 and 3129 $\nu(\text{OH})$, 1666 and 1639 $\nu(\text{C}=\text{O})$ and 1582 $\nu(\text{C}=\text{N})$ cm^{-1} , which are significantly shifted in relation to those of the corresponding free ligand at 3287, 3203 and 3105 $\nu(\text{OH})$, 2965 $\nu(\text{NH})$, 1648 and 1622 $\nu(\text{C}=\text{O})$ and 1576 $\nu(\text{C}=\text{N})$ cm^{-1} . No band assignable to $\nu(\text{NH})$ was observed, indicating that (L^2)⁴⁻ is coordinated in the deprotonated hydrazone form (see below).

The molecular structures of complexes **1** and **2** have been established by single-crystal X-ray diffraction (Scheme 1, Fig. 1). The crystal structure of **1** consists of two anionic organic moieties, one cationic Mn centre with an almost perfect octahedral geometry (quadratic elongation of 1.000 and angle variance of 0.52°)¹³ filled with water ligands, and two crystallization water molecules. The asymmetric unit of **2** contains half of the tetranuclear cluster molecule, an inversion centre being located in the middle of the macrocycle. The L^2 ligands act as hexadentate $1\kappa\text{N}:1\kappa\text{O}:2\kappa\text{N}:2\kappa\text{O}$ chelators to the copper cations that present distorted N_1O_4 square pyramidal ($\text{Cu}1$, $\tau_5 = 0.14$)¹⁴ and



Scheme 1 Synthesis and schematic representation of **1** and **2**.

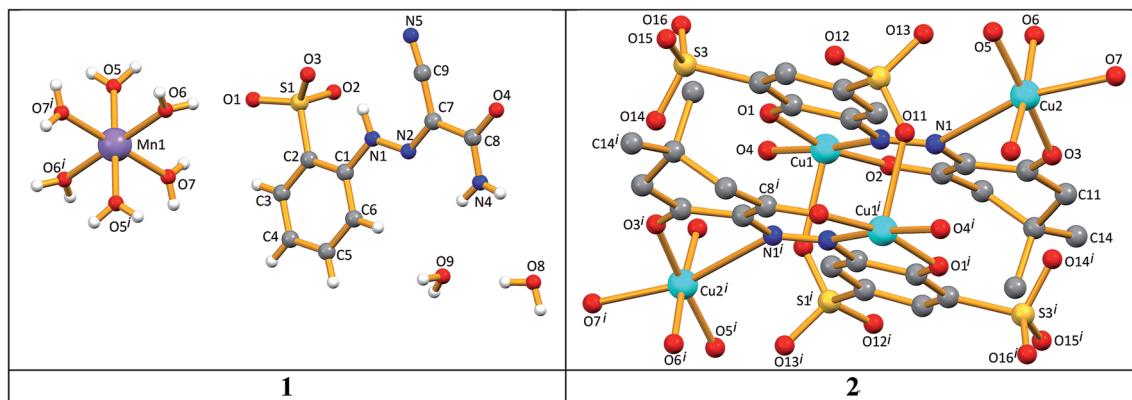


Fig. 1 Crystal structures of **1** and **2**. Hydrogen atoms and crystallization water molecule (in **2**) were omitted for clarity. Symmetry codes to generate equivalent atoms: (i) $1 - x, -y, -z$ (**1**); $1 - x, 1 - y, 1 - z$ (**2**).

N_1O_5 octahedral environments (Cu2, quadratic elongation of 1.058 and angle variance of 591.06°).¹³ Both compounds present extensive hydrogen bond interactions that lead to 3D supramolecular frameworks.

2.2. Catalytic activity of **1** and **2** in alcohol oxidation

Complexes **1** and **2** were tested as catalysts for the oxidation of 1-phenylethanol (model substrate), using aqueous *tert*-butylhydroperoxide (Bu^tOOH, TBHP, aq. 70%, 2 eq.) as oxidizing agent, under typical conditions of 150 °C, low power (10 W) microwave (MW) irradiation, 1 h reaction time and in a solvent- and additive-free medium (Scheme 2). A good catalytic activity was observed under the above conditions, leading to yields of acetophenone up to 76.1% (**1**) or 85.5% (**2**) (Table 1, entries 12 and 10, respectively), and turnover frequencies (TOF, moles of product per mol of catalyst per hour) up to 1.83×10^{-3} (**1**) or $1.90 \times 10^3 \text{ h}^{-1}$ (**2**, *i.e.*, $4.75 \times 10^2 \text{ h}^{-1}$ per Cu atom) for a low catalyst loading (catalyst/substrate molar ratio of 0.04%) after 1 h under MW irradiation (Table 1, entries 11 and 13, respectively).

Moreover, these heterogeneous catalysts could be easily recovered and reused, at least for three consecutive cycles, maintaining 89% of the initial activity and a rather high selectivity (see below).

Complexes **1** and **2** were also tested towards the oxidation of primary (benzyl alcohol) and other secondary alcohols, namely cyclohexanol and the linear 2- and 3-hexanol. The ketones are the only oxidation products obtained (Table 2). As expected, the alicyclic cyclohexanol is less reactive than 1-phenylethanol: in the presence of a catalytic amount of **1** or **2** (0.4 mol% *vs.*

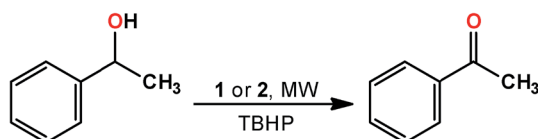
substrate) and in the solvent- and additive-free medium, the systems yield 56.4% and 65.5% of cyclohexanone after 1 h at 150 °C/10 W MW irradiation (Table 2, entries 1 and 2, for **1** and **2**, respectively). The linear aliphatic alcohols 2-hexanol and 3-hexanol lead to similar (**1**) or lower (**2**) yields (Table 2, entries 3–6), under similar reaction conditions, as reported in other cases.^{5,6h–k,15} However, benzyl alcohol leads to the lowest product yield in contrast to what is usually observed,¹⁶ what can be due to the used temperature of 150 °C. In fact, it was previously found^{15a} that temperatures up to 100 °C are preferable for the solvent-free peroxidative MW oxidation of this substrate catalyzed by copper compounds.

While the heterogeneous copper **2**/MW/TBHP oxidation system of the present study yields ketone products in the range of other previously reported copper homogeneous systems,^{5,6h–k} the heterogeneous Mn **1**/MW/TBHP system is much more efficient than other MW/TBHP homogeneous systems with dinuclear Mn(II) complexes with Schiff bases^{15b} in the oxidation of secondary alcohols, since our system operates effectively under additive-free conditions and requires much lower loads of catalyst precursor.

The activity of **1** or **2** in the oxidation of benzyl alcohol is rather modest since only moderated 19% (**1**) or 24% (**2**) yields of benzaldehyde were obtained under the same reaction conditions (Table 2, entries 7 and 8, for **1** and **2**, respectively). The silica-supported manganese dioxide previously applied¹⁶ for the oxidation of benzyl alcohol under MW solvent-free conditions, yielded 88% of benzaldehyde after 20 s irradiation. However, the MW power and the temperature were not indicated and this system required a 5 : 1 molar excess of MnO₂ relatively to the substrate.

The influences of various reaction parameters, such as the amounts of catalyst and oxidant, type of oxidant, time, temperature and presence of additives, were investigated for the most active substrate (1-phenylethanol), and the results are summarized in Table 1 and Fig. 2–4.

The MW-assisted alcohol oxidation depends strongly on the temperature (Fig. 2). The overall temperature coefficient of the oxidations is *ca.* 6.8 for **1** or 4.1 for **2** (temperature range 80–150 °C). For example, a high yield of 85.5% of acetophenone



Scheme 2 MW-assisted oxidation of 1-phenylethanol to acetophenone catalysed by **1** or **2**.

Table 1 Selected results for the solvent-free MW-assisted oxidation of 1-phenylethanol using **1** or **2** as catalysts^a

Entry	Catalyst (amount, mol% vs. substrate)	Reaction time (h)	Temperature (°C)	Additive (mol% vs. substrate)	Yield ^b (%)	TON ^c [TOF (h ⁻¹)]
1	1 (0.4)	0.5	80	—	6.0	15 (30)
2	1 (0.4)	1	80	—	11.1	28 (28)
3	1 (0.4)	2	80	—	14.7	37 (18)
4	2 (0.4)	0.5	80	—	14.4	36 (72)
5	2 (0.4)	1	80	—	21.1	52 (52)
6	2 (0.4)	2	80	—	39.2	98 (49)
7	1 (0.4)	1	120	—	33.1	83 (83)
8	1 (0.4)	1	150	—	75.2	188 (188)
9	2 (0.4)	1	120	—	83.2	208 (208)
10	2 (0.4)	1	150	—	85.5	214 (214)
11	1 (0.04)	1	150	—	73.0	1.83 × 10 ³ (1.83 × 10 ³)
12	1 (0.2)	1	150	—	76.1	381 (381)
13	2 (0.04)	1	150	—	76.0	1.90 × 10 ³ (1.90 × 10 ³)
14	2 (0.2)	1	150	—	78.2	391 (391)
15	1 (0.4)	1	150	K ₂ CO ₃ (2.5)	38.1	95 (95)
16	1 (0.4)	1	150	HNO ₃ (2.5)	34.0	85 (85)
17	1 (0.4)	1	150	TEMPO (2.5)	56.6	142 (142)
18	1 (0.4)	1	150	Ph ₂ NH (100)	9.7	24 (24)
19	1 (0.4)	1	150	CBrCl ₃ (100)	33.1	83 (83)
20	2 (0.4)	1	150	K ₂ CO ₃ (2.5)	19.8	50 (50)
21	2 (0.4)	1	150	HNO ₃ (2.5)	43.7	109 (109)
22	2 (0.4)	1	150	TEMPO (2.5)	58.1	145 (145)
23	2 (0.4)	1	150	Ph ₂ NH (100)	5.6	14 (14)
24	2 (0.4)	1	150	CBrCl ₃ (100)	33.7	84 (84)
25 ^d	1 (0.4)	1	150	—	3.0	8 (8)
26 ^e	Cu(NO ₃) ₂ (0.4)	1	150	—	18.2	46 (46)
27 ^e	Mn(CH ₃ COO) ₂ (0.4)	1	150	—	16.9	42 (42)

^a Reaction conditions unless stated otherwise: 2.5 mmol of 1-phenylethanol, 1–10 μmol (0.04–0.4 mol% vs. substrate) of **1** or **2**, 5 mmol of TBHP (2 eq., 70% in H₂O), 80–150 °C, MW irradiation (5–10 W power). ^b Molar yield (%) based on substrate, *i.e.* moles of acetophenone per 100 mol of 1-phenylethanol determined by GC. ^c Turnover number = number of moles of product per mol of catalyst precursor; TOF = TON per hour (values in brackets). ^d 5 mmol of H₂O₂ (30% aqueous solution) instead of TBHP. ^e Included for comparative purposes.

is achieved after 1 h at 150 °C (5 W) for the copper system **2** without any additive (Table 1, entry 10), which is much higher than the 21.1% yield obtained for the same reaction time but at 80 °C (Table 1, entry 5). Furthermore, at this temperature, only 39.2% (**2**) or 14.7% (**1**) of acetophenone is obtained for the extended reaction time of 2 h (Table 1, entries 6 and 3, respectively).

The influence of the amount of **1** and **2** on the yield and TON (or TOF) is shown in Fig. 3 (entries 8 and 10–14, Table 1). While

an amount increase of **1** does not appear to have a significant effect on the acetophenone yield, the increase of **2** results in a yield enhancement, *e.g.* from 76.0% to 85.5% upon changing the amount of catalyst from 1 μmol (0.04% vs. substrate) to 10 μmol (0.4 mol% vs. substrate). As expected, the increase of the catalysts amounts results in a corresponding TON lowering for both **1** and **2** (Fig. 3).

For **1**, experiments with the cheaper and environmentally friendly hydrogen peroxide (30% aqueous solution) as oxidant

Table 2 Selected results for the solvent-free MW-assisted oxidation of selected C₆ secondary alcohols and of benzylalcohol using **1** and **2** as catalysts^a

Entry	Catalyst	Substrate	Product	Yield ^b (%)	TON ^c [TOF (h ⁻¹)]
1	1	Cyclohexanol	Cyclohexanone	56.4	141 (141)
2	2			65.5	164 (164)
3	1	2-Hexanol	2-Hexanone	60.3	151 (151)
4	2			52.4	131 (131)
5	1	3-Hexanol	3-Hexanone	55.5	139 (139)
6	2			37.1	93 (93)
7	1	Benzylalcohol	Benzaldehyde	24.0	60 (60)
8	2			19.1	48 (48)

^a Reaction conditions: 2.5 mmol of substrate, 5 mmol of TBHP (aq. 70%), 10 μmol (0.4 mol% vs. substrate) of **1** or **2**, 150 °C, 1 h of microwave irradiation (10 W). ^b Molar yield (%) based on substrate, *i.e.* moles of product per 100 mol of substrate determined by GC. ^c Turnover number = number of moles of product per mol of metal catalyst; TOF = TON per hour (values in brackets).

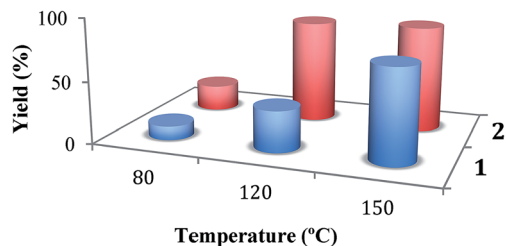


Fig. 2 Influence of the temperature on the yield of acetophenone in the MW-assisted peroxidative oxidation of 1-phenylethanol catalysed by 1 or 2.

are not effective, as attested by the marked yield lowering, *e.g.*, from 85.5% to 3.0% (entries 10 and 25, Table 1), in accord with the expected decomposition of H_2O_2 under the used reaction conditions (150 °C).

The influence of 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO), a nitroxyl radical can be a promoter in aerobic oxidation catalysis of alcohols,^{5,6h,15,17–19} was also investigated. However, a significant yield decrease (Fig. 4) was observed for the 1-phenylethanol oxidation, from 75.2% or 85.5% in the absence of TEMPO (for 1 or 2, respectively, entry 8 or 10, Table 1) to 56.6% (1) or 58.1% (2) in its presence (entry 17 or 22, Table 1). TEMPO is also known to inhibit the further oxidation of aldehydes to carboxylic acids when this reaction occurs *via* a radical mechanism.^{19c} Moreover, the previously recognised promoting effect of basic additives^{5,6a,b,e,17a,20} is also not observed for the present catalytic systems; in contrast, addition of 1 M aqueous solution of K_2CO_3 hampers the catalysis (Table 1, entries 15 and 20; Fig. 4), eventually as a result of reaction with the aqua-metal centres. The presence of HNO_3 also exhibits an inhibitory effect on the acetophenone yield (Table 1, entries 16 and 21, Fig. 4), as found, *e.g.*, for the MW-assisted oxidation of 1-phenylethanol with TBHP catalysed by Cu(II) complexes bearing Schiff base^{6h} or 1,6-bis(2'-pyridyl)-2,5-dithiahexane ligands.^{6e,21} In fact, the mechanism of alcohol oxidation with TBHP does not seem to require the presence of acid as also verified^{6f,g} in the oxidation of 1-phenylethanol with

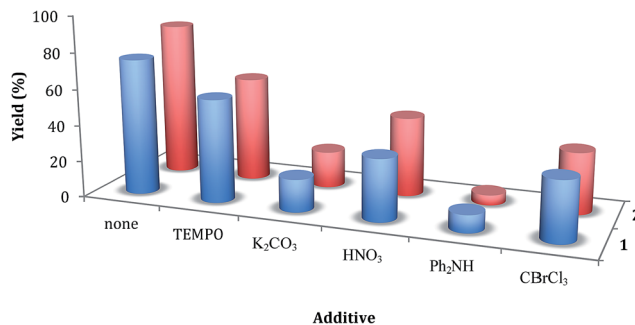


Fig. 4 Influence of different additives (TEMPO, K_2CO_3 , HNO_3 , radical traps) on the yield of acetophenone in the MW-assisted peroxidative oxidation of 1-phenylethanol catalysed by 1 and 2.

TBHP catalysed by bi- or tetra-nuclear cage-like copper(II) silsesquioxanes.

A very strong inhibition effect is observed (Fig. 4) when the peroxidative oxidation of 1-phenylethanol is carried out in the presence of either an oxygen-radical trap such as Ph_2NH (Table 1, entries 18 (1) or 23 (2)) or a carbon-radical trap such as CBRCl_3 (Table 1, entries 19 (1) or 24 (2)). This suggests that the oxidation reaction proceeds mainly *via* a radical mechanism involving both oxygen- and carbon-centred radicals.²² It may involve, *e.g.*, the $t\text{BuO}^\cdot$ radical produced in the Mn or Cu promoted decomposition of TBHP.⁵ It may proceed *via* the coordination of the alcohol substrate to an active site of the catalyst, and its deprotonation to form the alkoxide ligand, followed by a metal-centred dehydrogenation.^{6b,17a,20a,e,d,23}

2.2.1. Catalyst recycling. Catalyst recyclability was investigated for up to three consecutive cycles for both catalysts 1 and 2. On completion of each cycle, the product was analyzed as usual and the solid catalyst was recovered upon filtration of the reaction mixture, thoroughly washed and dried. The subsequent cycle was initiated upon addition of new standard portions of all other reagents. The filtrate was tested in a new reaction (by addition of fresh reagents), and no oxidation products were detected. Fig. 5 shows the recyclability of the systems: in the second cycle, 1 maintains almost (99.5%) the

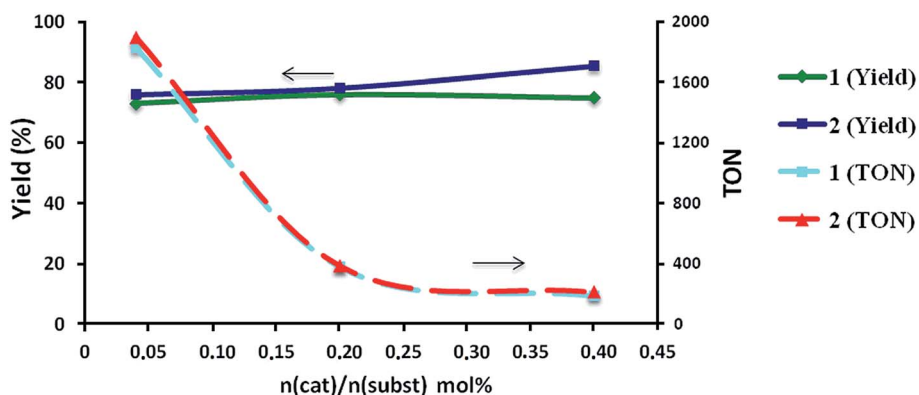


Fig. 3 Effect of the amount of catalysts 1 and 2 on the yield (solid lines) and turnover number (TON) (dashed lines) for the oxidation of 1-phenylethanol to acetophenone.

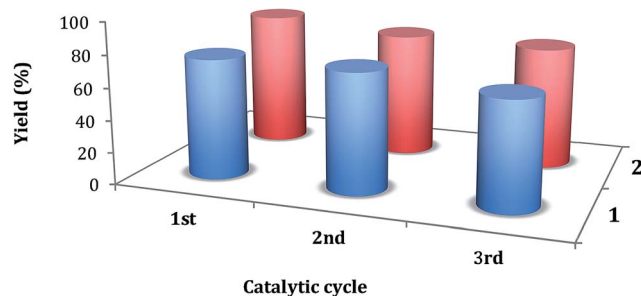


Fig. 5 Effect of the catalyst recycling on the yield of acetophenone from MW-assisted peroxidative oxidation of 1-phenylethanol catalysed by 1 and 2.

original level of activity, and 2 achieves 91.8% of its initial one. In the third consecutive reaction cycle, 89% of the initial activity is still exhibited by both complexes, with a rather high selectivity to acetophenone. Atom absorption analysis (7.1% Mn and 19.5% Cu), IR spectroscopy (Fig. S1 and S2, ESI[†]) and powder X-ray diffraction (Fig. S3 and S4, ESI[†]) for the recovered catalysts 1 and 2 showed that the structural integrity remains unaltered after the catalytic reaction.

3. Conclusions

We have achieved simple and effective syntheses of hydro-soluble mononuclear manganese(II) and tetranuclear copper(II) complexes with AHAMCs ligands, which are not soluble in low polar solvents, thus with a potential for application as heterogeneous catalysts in such media. Their structure and nuclearity are dependent on the active methylene fragment and on substituents in the aromatic part of the AHAMCs ligands, besides the metal ions. The obtained complexes act as efficient and selective heterogeneous catalyst precursors for the mild MW-assisted oxidation of secondary alcohols in solvent- and additive-free systems, thus widening the scope of heterogeneous catalytic systems suitable for MW assisted oxidative transformations of alcohols. A comparative study of their catalytic efficiency has been drawn towards different alcohol substrates.

Moreover, these heterogeneous catalysts are easily recycled without considerable loss of activity. Hence, they show the same advantage, in terms of easy separation and recycling, of supported metal complex catalysts, but without requiring the use of any solid support. The approach followed in this study deserves to be further explored and extended to other oxidation catalyses and to the synthesis and catalytic applications of metal complexes of low solubility in common organic solvents.

4. Experimental

4.1. Materials and methods

All the chemicals were obtained from commercial sources and used as received. The ¹H and ¹³C NMR spectra were recorded at room temperature on a Bruker Avance II 300 (UltraShield™ Magnet) spectrometer operating at 300.130 and 75.468 MHz for

proton and carbon-13, respectively. The chemical shifts are reported in ppm using tetramethylsilane as an internal reference. The infrared spectra (4000–400 cm⁻¹) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. Carbon, hydrogen and nitrogen elemental and atomic absorption (Mn and Cu) analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. All of the synthetic work was performed in air and at room temperature. The catalytic tests under microwave irradiation (MW) were performed in a focused Anton Paar Monowave 300 microwave reactor using a 10 mL capacity reaction tube with a 10 mm internal diameter, fitted with a rotational system and an IR temperature detector. Chromatographic analyses were undertaken by using a Fisons Instruments GC 8000 series gas chromatograph with a DB-624 (J&W) capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm), FID detector, and the Jasco-Borwin v.1.50 software. The temperature of injection was 240 °C. The initial temperature was maintained at 140 °C for 1 min, then raised 10 °C min⁻¹ to 220 °C and held at this temperature for 1 min. Helium was used as the carrier gas. The internal standard method was used to quantify the organic products.

X-ray powder diffraction patterns (XRPD) were recorded in the reflection mode using a D-8 Bruker AXS diffractometer operating at 40 kV and 40 mA, using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$). The XRD patterns were collected at 2θ values ranging from 3° to 70° with step 0.02°. Electrospray mass spectra (ESI-MS) were run with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 p.s.i. nebulizer pressure. Scanning was performed from m/z 50 to 1200 in methanol solution. The compounds were observed in the negative or positive mode (capillary voltage = 80–105 V).

4.2. Synthesis of complexes

4.2.1. Synthesis of 1. Manganese(II) acetate tetrahydrate, Mn(CH₃COO)₂·4H₂O (24.5 mg, 0.1 mmol), was added to a solution of NaHL¹ (27.2 mg, 0.1 mmol) in acetone–water (3 : 1, v/v) mixture (20 mL). The reaction mixture was heated under reflux for 3 h. A deep red precipitate was obtained. The reaction mixture was then filtered and the filtrate was rejected. The residue obtained was washed several times with acetone. The crystals of 1 suitable for X-ray structural analysis were obtained by slow evaporation of a methanol solution of the deep red solid.

Yield, 27 mg, 70%. Anal. calcd for C₁₈H₃₄MnN₈O₁₈S₂ ($M_r = 769.59$): C, 28.09; H, 4.45; N, 14.56. Found: C, 28.42; H, 4.61; N, 14.17%. MS (ESI) m/z : 81.5 [Mn(H₂O)₆]²⁺, 163.0 [Mn(H₂O)₆]⁺ and 267.2 (HL^{1a})⁻. IR, cm⁻¹: 3436 ν (OH), 3103 ν (NH), 2227 ν (C≡N), 1645 ν (C=O), 1630 δ (OH) of H₂O, 1513 ν (C=N).

4.2.2. Synthesis of 2. Copper(II) nitrate pentahemihydrate, Cu(NO₃)₂·2.5H₂O (23.2 mg, 0.1 mmol), and 0.05 mL of HNO₃ (65%, w/w) were added to a solution of Na₂H₂L² (46.4 mg, 0.1 mmol) in MeOH/water (4 : 1 v/v) mixture (16 mL). The

reaction mixture was left to slow evaporation at room temperature. After two days, greenish-black crystals of **2** were obtained.

Yield, 24 mg, 74%. Anal. Calcd for $C_{28}H_{48}Cu_4N_4O_{30}S_4$ ($M_r = 1303.10$) C, 25.81; H, 3.71; N, 4.30. Found: C, 25.75; H, 3.63; N, 4.07. MS (ESI): m/z : 652.3 [$Cu_2(H_2O)_6(L^2)+H^+$]. IR, cm^{-1} : 3307, 3217, 3129 and 2964 $\nu(OH)$, 1666 $\nu(C=O)$, 1639 $\nu(C=O)$, 1628 $\delta(OH)$ of H_2O , 1582 $\nu(C=N)$.

4.3. X-ray measurements

The analyzed crystal was immersed in cryo-oil, mounted in a Nylon loop and measured at a temperature of 296 K. Intensity data were collected using a Bruker APEX II PHOTON 100 diffractometer with graphite monochromatic Mo-K α (λ 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 SAINT²⁴ on all the observed reflections. Absorption corrections were applied using SADABS.²⁵ Structures were solved by direct methods by using the SHELXS-97 package and refined with SHELXL-2013.²⁶ Calculations were performed using the WinGX System-Version 1.80.03.²⁷ The water and the hydrazine hydrogen atoms were located from the difference Fourier map and refined isotropically with the help of distance restraints. The other hydrogen atoms were placed in calculated positions and refined by using a riding model. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms were employed.

4.4. General procedure for the peroxidative oxidation of alcohols

Oxidation reactions of the alcohols were carried out in sealed cylindrical Pyrex tubes under focused microwave irradiation as follows: the alcohol (2.5 mmol), *tert*-butyl hydroperoxide (TBHP) (70% aqueous solution, 5.0 mmol) and the catalyst **1** or **2** (1–10 μ mol, 0.04–0.4 mol% vs. substrate) were introduced in the tube which was then placed in the microwave reactor. In the experiments with radical traps, $CBrCl_3$ (2.5 mmol) or $NHPh_2$ (2.5 mmol) was added to the reaction mixture. In the experiments with other additives (TEMPO, nitric acid 1 M solution, or potassium carbonate 1 M solution), a 2.5% additive/substrate molar ratio was used. The system was stirred and irradiated (5–10 W) for 0.5–2 h at 80–150 °C. After the reaction, the mixture was allowed to cool down to room temperature. 150 μ L of benzaldehyde (internal standard) and 2.5 mL of CH_3CN (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred for 10 min, filtered and then a sample (1 μ L) was taken from the organic phase and analysed by GC using the internal standard method. Blank tests indicate that only traces (<0.8%) of ketone or aldehyde are generated in a metal-free system.

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