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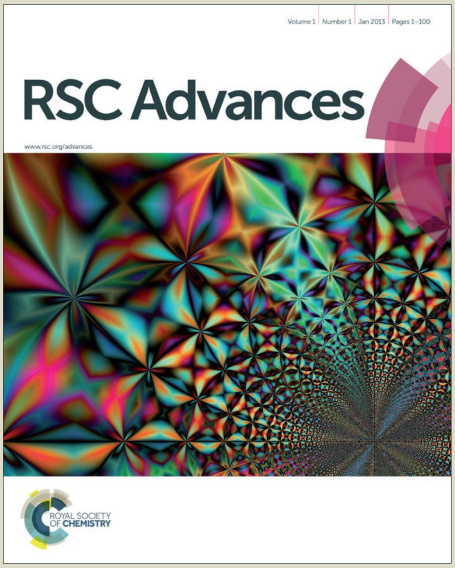

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Sulfonated Schiff Base Copper(II) Complexes as Efficient and Selective Catalysts in Alcohol Oxidation: Syntheses and Crystal Structures†

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†Electronic Supplementary Information (ESI) available: Figures S1 and S2. Tables S1 and S2. CCDC 1411065 – 1411069 for **1** – **5**, respectively, contain the supplementary crystallographic data for this paper. These CIF data can also be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found in the online version.

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Abstract

The reaction between 2-aminobenzenesulfonic acid and 2-hydroxy-3-methoxybenzaldehyde produces the acyclic Schiff base 2-[(2-hydroxy-3-methoxyphenyl)methylideneamino]benzenesulfonic acid (H_2L) (**1**). *In situ* reactions of this compound with Cu(II) salts and, eventually, in the presence of pyridine (py) or 2,2'-bipyridine (2,2'-bipy) lead to the formation of the mononuclear complexes $[CuL(H_2O)_2]$ (**2**) and [CuL(2,2'-bipy)].DMF.H_2O (**3**) and the diphenoxo-bridged dicopper compounds $[CuL(py)]_2$ (**4**) and $[CuL(EtOH)]_2.2H_2O$ (**5**). In **2 – 5** the L^{2-} ligand acts as a tridentate chelating species by means of one of the O-sulfonate atoms, the O-phenoxo and the N-atoms. The remaining coordination sites are then occupied by H_2O (in **2**), 2,2'-bipyridine (in **3**), pyridine (in **4**) or EtOH (in **5**). Hydrogen bond interactions resulted in $R_2^2(14)$ and in $R_4^4(12)$ graph sets leading to dimeric species (in **2** and **3**, respectively), to 1D chain associations (in **2** and **5**) or to a 2D network (**1**). Complexes **2 – 5** are applied as selective catalysts for the homogeneous peroxidative (with *tert*-butylhydroperoxide, TBHP) oxidation of primary and secondary alcohols, under solvent- and additive-free conditions and under low power microwave (MW) irradiation. A quantitative yield of acetophenone was obtained by oxidation of 1-phenylethanol with compound **4** [TOFs up to 7.6×10^3 h^{-1}] after 20 min of MW irradiation, whereas the oxidation of benzyl alcohol to benzaldehyde is less effective (TOF 992 h^{-1}). The selectivity of **4** to oxidize the alcohol relative to the ene function is demonstrated when using cinnamyl alcohol as substrate.

Keywords: Sulfonated Schiff base/Mononuclear/Dinuclear/Pyridine/2,2'-Bipyridine/Alcohol Oxidation/Microwave.

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Introduction

Over the past few decades there has been a marked development in the coordination chemistry of Schiff base metal complexes,[1] encouraged by the variety of their solid state structures,[2] magnetic,[3,4] fluorescence[5] and catalytic[6] properties. Though a large number of Schiff bases of various types,[1–7] including those containing the carboxylic acid group,[7] have been reported, sulfonated Schiff bases are rare and only a few metal complexes are known,[8] although covalent or non-covalent (H-bonding) interactions *via* sulfonate oxygen atoms could generate interesting multinuclear[8a–e] or supramolecular structures.[8a–c] Catalytic properties of sulfonated Schiff base metal complexes have also been rarely investigated.[8a,b,e] Thus, the syntheses of a new sulfonated Schiff base and their copper complexes which could be useful for further catalytic studies, deserve to be explored and constitute a general aim of the current study.

The oxidation of alcohols to carbonyl compounds is one of the most important reactions in synthetic organic chemistry as well as in chemical industry.[9,10] Moreover, it is of interest for the development of environmentally benign production processes of new materials and energy sources.[9e,10a]

Many catalytic methods have been developed for the oxidation of alcohols.[10] A recent environmentally compatible approach concerns oxidations with copper catalysts and dioxygen, hydrogen peroxide or *tert*-butylhydroperoxide (TBHP) as oxidants.[10c,10g,11] Hence, inspired by our previous catalytic applications of a few sulfonated Schiff base copper complexes in the peroxidative oxidation of cyclohexane[8a,e] and in the nitro-aldol reaction,[8b] we have anticipated that the new copper(II) complexes bearing a sulfonated Schiff base could be active in alcohol oxidation catalysis.

In accord, the new sulfonated Schiff base 2-[(2-hydroxy-3-methoxyphenyl)methylideneamino]benzenesulfonic acid H_2L (**1**) (Scheme 1) is prepared from the condensation reaction of 2-hydroxy-3-methoxybenzaldehyde and 2-aminobenzenesulfonic acid. Addition of Cu(II) salt(s) to the same reactant mixtures in different solvents (MeOH, EtOH or DMF) and in the absence or in the presence of an N-heterocycle [pyridine (py) or 2,2'-bipyridine (2,2'-bipy)] produces the mononuclear copper complexes $[CuL(H_2O)_2]$ (**2**) and $[CuL(2,2'\text{-bipy})].DMF.H_2O$ (**3**) and the diphenoxo-bridged dicopper complexes $[CuL(py)]_2$ (**4**)

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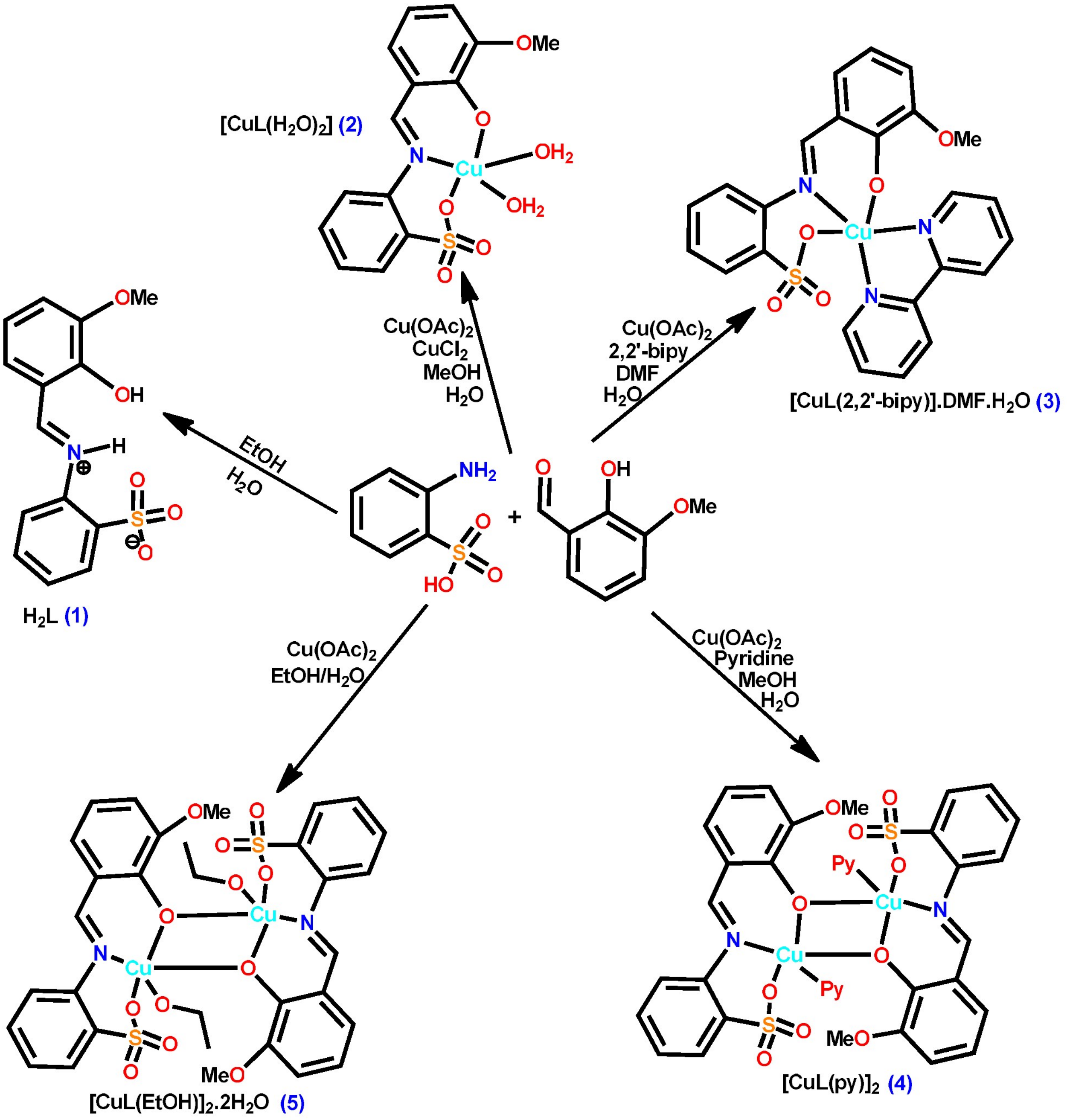
and $[CuL(EtOH)]_2.2H_2O$ (**5**). Hence, herein we report the syntheses, crystal structures and catalytic alcohol oxidation studies of these four new copper(II) complexes (**2** – **5**).



Scheme 1. Syntheses of **1** – **5**.

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Results and Discussion

Syntheses and Characterization

The [1+1] condensation of 2-hydroxy-3-methoxybenzaldehyde and 2-aminobenzenesulfonic acid in aqueous ethanol leads to the formation of the Schiff base H_2L (**1**) (Scheme 1), which can be isolated or used *in situ* for further syntheses of copper(II) complexes (Scheme 1). Hence, addition of an aqueous methanol (1:1) solution of $Cu(OAc)_2.H_2O$ and $CuCl_2{\cdot}2H_2O$ (in 1:1 molar ratio) to that solution of H_2L (**1**) prepared *in situ* produces the mononuclear copper(II) complex $[CuL(H_2O)_2]$ (**2**). When the reaction is performed in aqueous ethanol (1:1) and only with $Cu(OAc)_2.H_2O$ as the copper(II) salt, the diphenoxo bridged dicopper(II) complex $[CuL(EtOH)]_2.2H_2O$ (**5**) is obtained. The mononuclear complex [CuL(2,2′-bipy)].DMF.H_2O (**3**) is synthesized similarly from the *in situ* reaction of **1**, $Cu(OAc)_2.H_2O$ and 2,2′-bipyridine (2,2′-bipy) in aqueous DMF (1:1) solution, while the analogous reaction with pyridine (py) instead of 2,2′-bipy using aqueous methanol solution generates the diphenoxo bridged dicopper(II) complex $[CuL(py)]_2$ (**4**). As no product was isolated from the attempted distinct *in situ* reactions of **1** with either $Cu(OAc)_2.H_2O$ or $CuCl_2{\cdot}2H_2O$ in aqueous methanol, we tried the reaction with both salts together in this solvent and thus compound **2** was isolated.

All the compounds (**1** – **5**) were characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction study. The Schiff base **1** was also characterized by the ^{1}H NMR spectrum. They were isolated in moderate to good yields (69–82%).

The IR spectrum of the Schiff base H_2L (**1**) exhibits the expected bands at 1629 and 1375 cm^{-1} which are indicative of the C=N bond and the sulfonate group, respectively. In the IR spectra of the metal complexes (**2** – **5**), ν(C=N) is observed in the range of 1609–1618 cm^{-1}, whereas the sulfonate groups are evidenced by the medium intense bands at the 1375–1386 cm^{-1} range.[8a–d]

Description of the Crystal Structures

The crystal structures of the Schiff base and its mono- or dicopper derivatives (**1** – **5**) are shown in Figure 1. Important bond distances and angles are presented in Table 1. Compound **1** is approximately planar as measured by the angle between the least square planes of the aromatic

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rings (4.77º, Table 1). Upon O_2N chelation to the metal cation by means of the phenolic O-, the imine N- and a sulfonate O-atoms, the basic form of **1** (L^{2-}) becomes highly distorted as evidenced by the angle values (30.25–61.63º, Table 1) of those l.s. planes, following the order **2** < **5** < **4** < **3**. Such a distortion is also envisaged through the N–C–C–S and C–N–C–C_{SO3} torsion angles which, however, trail in a different way (Table 1; **5** < **4** < **2** < **3** for the former, and **3** < **5** < **4** < **2** for the latter). Despite all these variances, the N_{imine}–C_{sp2} bond distances in **1** – **5** are similar and vary in the 1.290(4) – 1.315(4) Å range.

To accomplish the pentacoordination sphere of the metal, the copper cations in **2** – **5** are then bound to two water molecules (in **2**), one 2,2′-bipy chelator (in **3**), one py (in **4**) and one ethanol molecule (in **5**). Probably as a result of the chelating mode of bipyridine, the L^{2-} ligand in **3** occupies both equatorial (O-phenoxo and N-imine atoms) and apical (O-sulfonate) sites, thus contrasting with the other complexes (**2**, **4** and **5**) in which it occupies three of the equatorial positions. The τ5 descriptor values,[12] between 0.08 (in **2**) and 0.36 (in **3**), may be a result of steric interferences involving the ligands. Compounds **2** and **3** are mononuclear, while **4** and **5** are dinuclear species with an inversion centre in the middle of the Cu_2O_2 core. Consequently, the copper cation in the complexes are involved in 4-membered (in **4** and **5**), 5-membered (in **3**) and 6-membered (in all cases) metallacycles.

The Cu–N_L bond distances lie in the 1.956(3) – 2.012(3) Å range (Table 1) and are slightly shorter than those involving the other N-ligands [2.019(2) – 2.075(2) Å]. The equatorial Cu–$O_{phenoxo}$ distances [1.876(2) – 1.910(2) Å] are shorter than the axial [2.352(2) and 2.5057(15) Å in **4** and **5**, respectively] and the Cu–$O_{sulfonate}$ ones [1.931(2) – 2.359(2) Å]. Although the Cu–O_{water} bond distance of 2.932(4) Å in **2** is the longest found in this work, and slightly longer than the sum of the Van der Waals radii of copper and oxygen atoms (2.92 Å), all the parameters are comparable to those found in the literature.[8a–d]

Several H-bond interactions stabilize structures **1** – **3** and **5**. The molecule of **1** is involved in two intramolecular H-bond cycles (Table S2) with graph set $S_1^1(6)$ linking the imino nitrogen atom (as donor) and both the phenolic and sulfonate oxygen atoms (as acceptors). However, the most interesting feature of the crystal structure of **1** is the extensive H-bond interactions of the crystallization water molecules leading to the formation of infinite chains along the crystallographic *b* axis (Figure 2A). These are further interlinked by H-bonds to the Schiff base, generating 2D layers (Figure 2B) which are stabilized by π⋯π stacking

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interactions. Also resulting from the presence of crystallization water molecules, compounds **2** and **3** form ring graph sets of type $R_2^2(14)$ and $R_4^4(12)$, respectively, the former involving one of the H-atoms of the water molecule (as donor) and an O-methoxide (as acceptor), and the latter linking both H-atoms of water to two O-sulfonate atoms of the same moiety (Figure S1). The structure of **2** further generates infinite 1D double chains involving the coordinated water molecules and vicinal sulfonate O-atoms (Figure 3). The strongest H-interactions in **5** include the crystallization water molecule, both as donor and as acceptor, and the coordinated ethanol molecule (as donor), giving rise to $R_2^2(9)$ graph sets. Overall a 1D chain is formed in the crystal packing of **5** (Figure S2).

Table 1. Selected bond distances (Å), bond angles and torsion angles (°) for H_2L (**1**) and the metal complexes **2 – 5**.

	1	**2**	**3**	**4**	**5**
Involving the anionic ligand L^{2-}					
N–C_{sp2}	1.290(4)	1.315(4)	1.295(3)	1.289(4)	1.299(2)
N–C_{Ar}	1.432(4)	1.432(4)	1.430(3)	1.440(4)	1.432(2)
∠ N–C–C–S	-0.8(4)	-3.4(5)	-11.7(3)	-1.0(4)	-0.3(2)
∠ C–N–C–C_{SO3}	-172.9(3)	145.9(3)	119.9(3)	141.6(3)	137.6(2)
∠ l. s. planes of aromatic rings	4.77	39.25	61.63	53.21	52.48
Involving the metal					
Cu coordination sphere	-	O_4N_1	O_2N_3	O_2N_3	O_4N_1
τ_5 descriptor		0.08	0.36	0.15	0.14
M–O_{SO3}	-	1.931(2)	2.359(2)	1.951(2)	1.9573(15)
M–$O_{phenoxo\ (equatorial)}$	-	1.876(2)	1.893(2)	1.910(2)	1.9085(14)
M–$O_{phenoxo\ (axial)}$	-	-	-	2.352(2)	2.5057(15)
M–O_{other}	-	1.974(3) 2.932(3)	-	-	1.9912(14)
M–N_L	-	1.956(3)	1.995(2)	2.012(3)	1.9841(16)
M–N_{other}	-	-	2.019(2) 2.075(2)	2.032(3)	-
O_{SO3}–M–$O_{phenoxo}$	-	161.87(12)	116.12(8)	175.55(10)	169.37(7)
N_L–M–O(N)	-	156.90(12)	175.05(9)	166.69(11)	177.79(6)
∠ Cu–N–C–C_{SO3}	-	-37.3(4)	-58.6(3)	-39.5(4)	42.9(2)
$M\cdots M$ (intramolecular)	-	-	-	3.2720(11)	3.3606(6)
$M\cdots M$ (intermolecular)	-	5.188	7.8678(5)	6.534(2)	6.0889(8)

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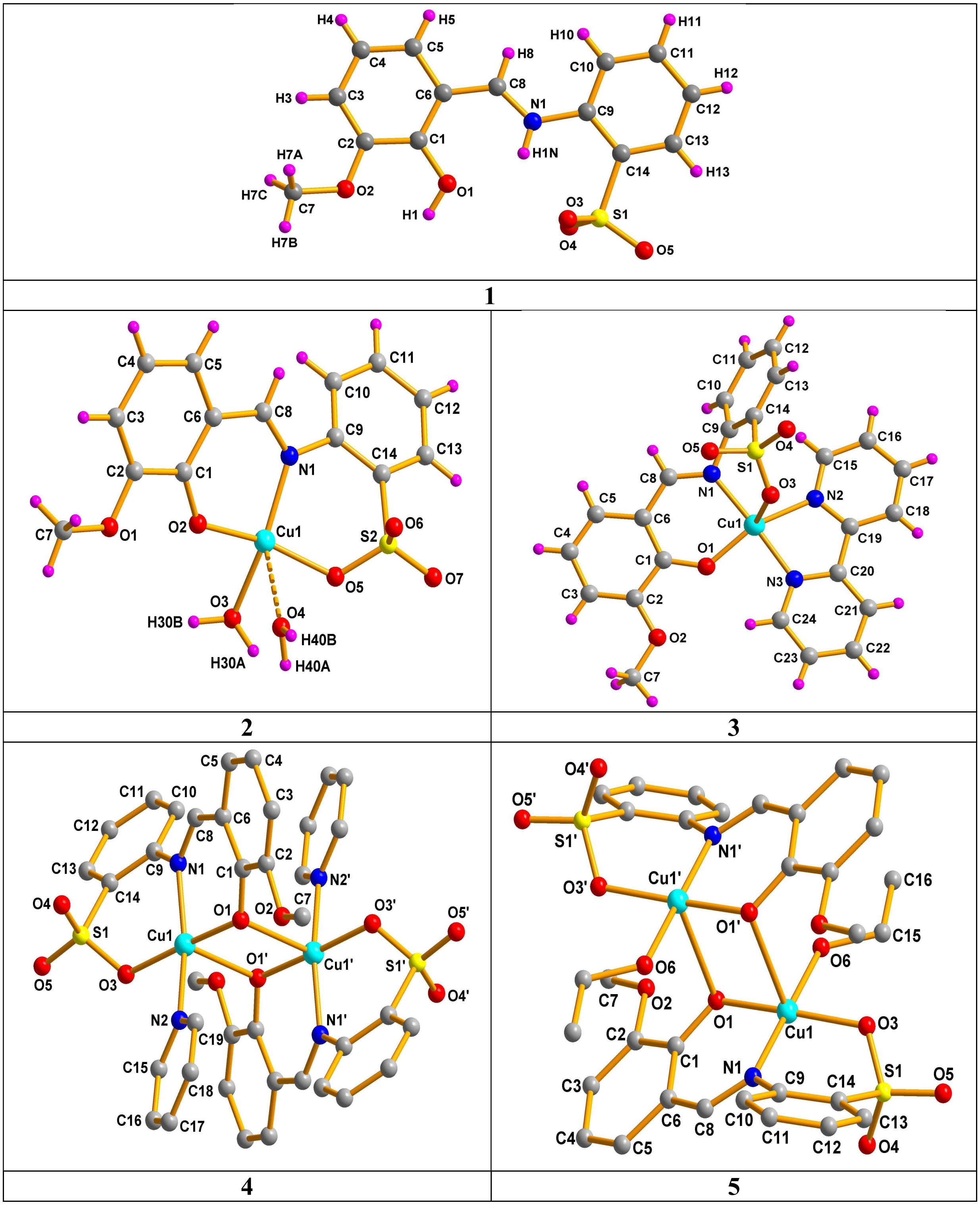

1

2 **3**

4 **5**

Figure 1. Idealized ball and stick presentation of the crystal structure of **1**–**5** with atom labeling schemes. Crystallization solvent molecules in **1**, **3** and **5** as well as hydrogen atoms in **4** and **5** are omitted for clarity. Symmetry codes to generate equivalent atoms: 1–x,1–y,1–z (**4**) and –x, 2–y, 2–z (**5**).

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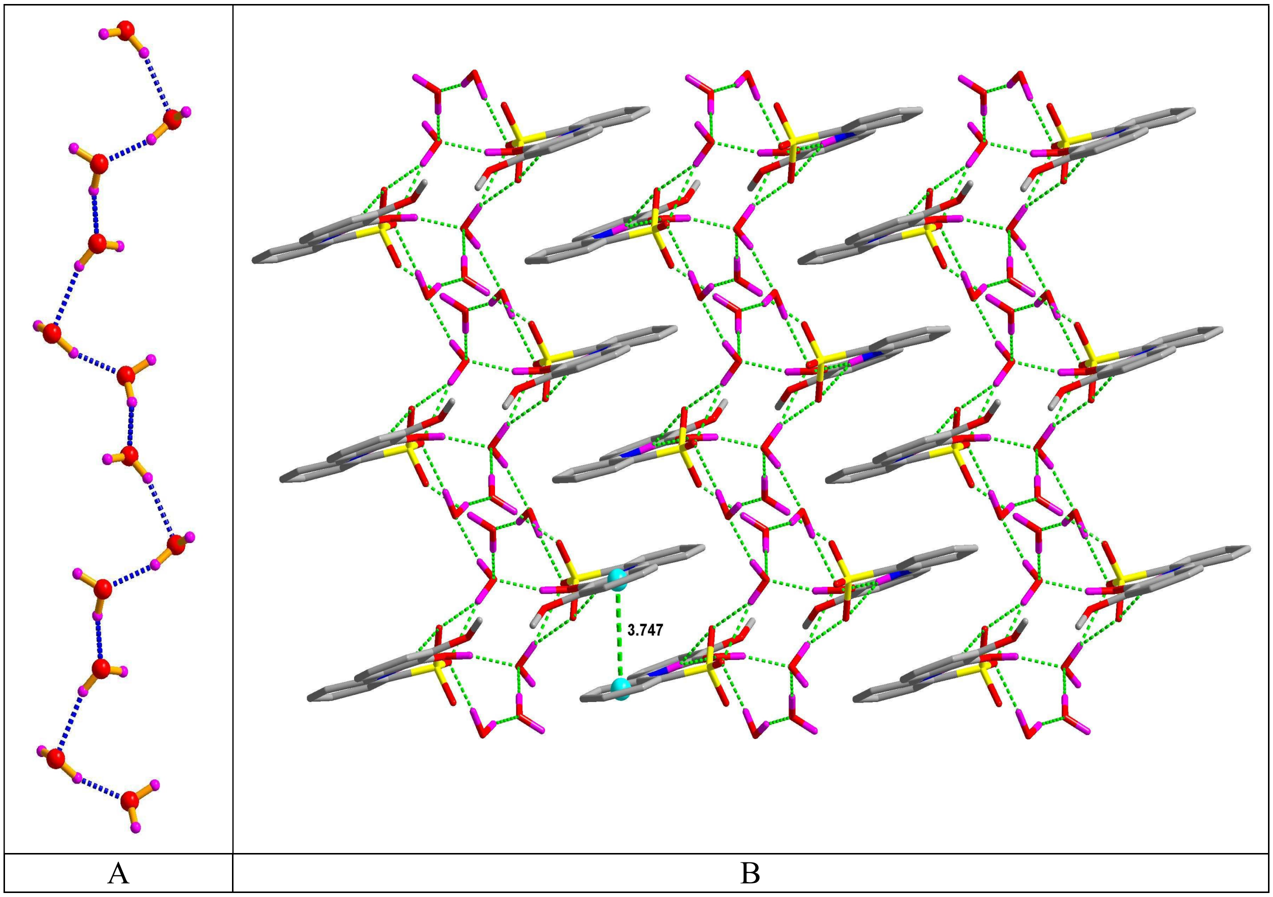

Figure 2. (A) Representation (along the crystallographic *b* axis) of an infinite chain of hydrogen-bonded (dotted lines) water molecules in the structure of **1**, and (B) fragment of the 2D supramolecular packing diagram of **1** constructed by hydrogen bonds between the Schiff base and the lattice water molecules, also evidencing the π···π stacking between adjacent aromatic rings.

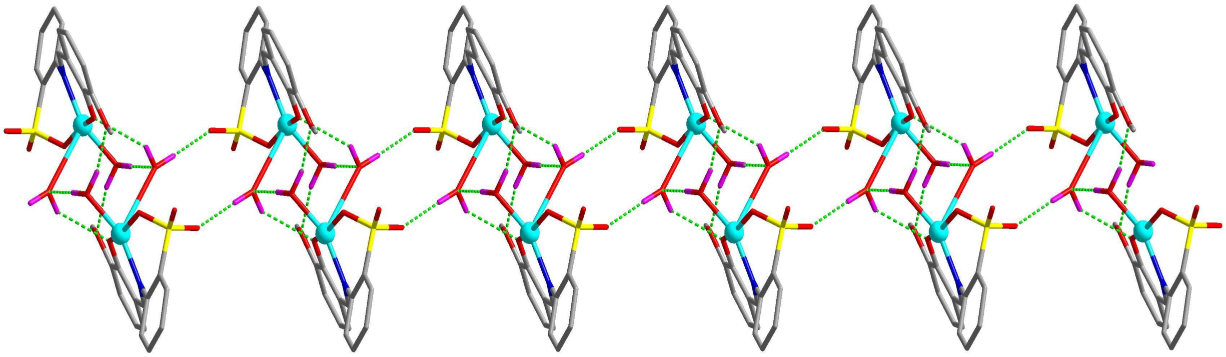

Figure 3. H-bond supported double chain 1D association in **2**.

It is worthwhile mentioning that sulfonated Schiff bases are of great interest due to their versatile complex formation abilities; they can form monomers, dimers, tetramers and polymers (both 1D and 2D).[8] In one of our earlier studies we have reported that the Schiff base 2-[(2-hydroxyphenyl)methylideneamino]benzenesulfonic acid can form solvatomorphs which have identical basic structure but with different non-coordinated solvents.[8d] We have also introduced a bis(μ_4-(*ae*)-cyclohexane-1,4-dicarboxylato-O,O',O'',O''')-tetracopper[8a,e] and three pseudohalide bridged copper complexes[8b] containing 2-(2-pyridylmethyleneamino)benzenesulfonate. The tetracopper complex was an efficient catalyst for the cyclohexane oxidation in both conventional (CH_3CN/H_2O)[8a] and non-conventional (ionic liquid) solvents,[8e] while pseudohalide complexes[8b] were found to catalyze the Henry reaction in aqueous medium.

The interesting molecular structures and catalytic properties of such compounds inspired us (i) to synthesize copper complexes of the new sulfonated Schiff base ligand 2-[(2-hydroxy-3-methoxyphenyl)methylideneamino]benzenesulfonate (L^{2-}), as described above, and (ii) to apply them in alcohol oxidation studies (see below).

Alcohol Oxidation Catalyzed by Copper Complexes 2 – 5

Complexes **2** – **5**, as well as their salt precursors $Cu(OAc)_2.H_2O$ and $CuCl_2.2H_2O$, were tested as catalysts for the homogeneous oxidation of 1-phenylethanol and benzyl alcohol (chosen as models) to acetophenone or benzaldehyde, respectively, using aqueous *tert*-butyl hydroperoxide (Bu^tOOH, TBHP) as oxidizing agent, under optimized conditions of 100 ºC, low power (10 W) microwave irradiation (MW), 20 (or 150 for benzaldehyde) min reaction time and in a solvent- and additive-free medium (Scheme 2, Table 2). The eventual organocatalytic ability of the Schiff base H_2L (**1**) was also evaluated (entries 1 and 9, Table 2). Under the assayed conditions, acetophenone or benzaldehyde for the oxidation of 1-phenylethanol or benzyl alcohol, respectively, were the only products detected by GC–MS analysis, thus revealing a very selective oxidation system.

The copper(II) complex catalysts **2** – **5** exhibit good performance (best TOF value of 7.60 x 10^3 h^{-1} with **4**, entry 4 of Table 2) leading to yields (based on the alcohol) of acetophenone or benzaldehyde in the 52.3 – 99.6% or 57.6 – 99.2% ranges, respectively (Table 2, Figure 4). However, the oxidation of benzyl alcohol was significantly slower as shown by the lower TOF

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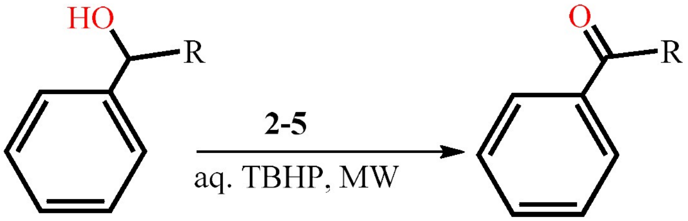
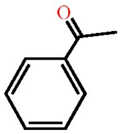
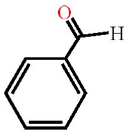
values obtained (Table 2). For example, in the presence of **4**, 2.5 h are needed to achieve the quantitative conversion of the said alcohol into benzaldehyde whereas acetophenone is obtained in a 99.6% yield after only 20 min of MW irradiation on 1-phenylethanol.



Scheme 2. Neat homogeneous oxidation of 1-phenylethanol (R = CH_3) or benzyl alcohol (R = H), by the **2**–**5**/TBHP/MW system.

Table 2. Selected data for the optimized MW-assisted solvent- and additive-free homogeneous oxidation of 1-phenylethanol (entries 1–8) or benzyl alcohol (entries 9–16) using **1** – **5**, $Cu(OAc)_2.H_2O$ or $CuCl_2.2H_2O$.[a]

Entry	Catalyst	Product	Yield[b] (%)	TOF (h^{-1})[c]	Selectivity (%)[d]
1	**1**		5.2	394	67
2	**2**		64.0	4.9×10^3	98
3	**3**		52.3	4.0×10^3	99
4	**4**		99.6	7.6×10^3	>99
5	**5**		94.3	7.1×10^3	98
6	$Cu(OAc)_2.H_2O$		18.7	1.4×10^3	51
7	$CuCl_2.2H_2O$		16.4	1.2×10^3	42
8	-		4.9	-	83
9	**1**		4.1	41	80
10	**2**		57.6	576	99
11	**3**		78.8	788	97
12	**4**		99.2	922	98
13	**5**		91.7	917	>99
14	$Cu(OAc)_2.H_2O$		16.3	163	63
15	$CuCl_2.2H_2O$		12.1	121	70
16	-		2.3	-	76

[a] Reaction conditions unless stated otherwise: 2.5 mmol of alcohol, 1 μmol (0.04 mol% *vs*. substrate) of catalyst, 5 mmol of TBHP (2 eq., 70% in H_2O), 100 °C, 20 min (1-phenylthanol) or 150 min (benzyl alcohol) of MW irradiation (10 W). [b] Moles of ketone or aldehyde per 100 moles of alcohol. [c] TOF = number of moles of ketone or aldehyde per mol of catalyst (TON) per hour. [d] Moles of ketone or aldehyde per mole of converted alcohol.

As shown in Table 2 and Figure 4, the best results, both for acetophenone and benzaldehyde, under the above ecofriendly conditions, were obtained with the diphenoxo bridged dicopper compounds **4** and **5**. The presence of pyridine in the coordination sphere of Cu(II) (in **4**), when

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compared to the EtOH ligand (in **5**), appears to slightly enhance the catalytic activity (compare entries 4 and 5 or 12 and 13 of Table 2), as observed in other cases.[11e,k]

The reactions performed under the same conditions but in the presence of the mononuclear complexes (**2** and **3**) resulted in lower yields in acetophenone, between 52.3 and 64.0% (entries 2 and 3, Table 2), and also in benzaldehyde, between 57.6 and 78.8% (entries 10 and 11, Table 2). However, if nuclearities are considered, the mononuclear compounds **2** and **3** become the most effective ones (higher TOFs per metal atom) under the used conditions.

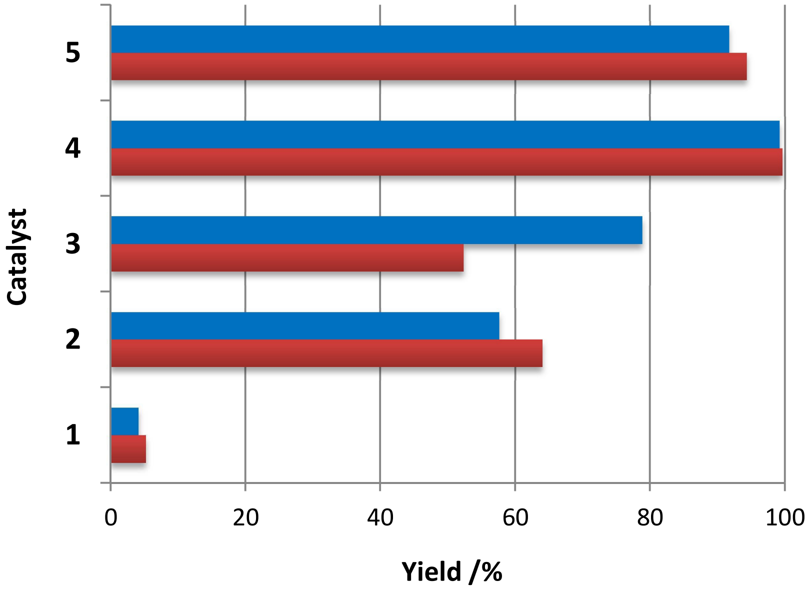

Figure 4. MW-assisted, solvent- and additive-free acetophenone (🟥) or benzaldehyde (🟦) production (see Table 2) by oxidation of 1-phenylethanol or benzyl alcohol, respectively, catalyzed by **1** – **5**.

Blank tests were performed under the same reaction conditions but in the absence of the copper compounds: no significant conversion of 1-phenylethanol or benzyl alcohol was observed (entry 8 or 16, Table 2). Moreover, the replacement of the copper(II) complexes (**2** – **5**) by their inorganic salt precursors resulted in a drastic decrease of activity (compare *e.g.,* entries 6 or 7 with entries 5 or 2, respectively, Table 2).

The used low power (10 W) MW irradiation provides a much more efficient synthetic method than conventional heating (open atmosphere or non-pressurized refluxing, see Experimental Section below), allowing the attainment of similar or better yields in much shorter

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times (Figure 5, for the oxidation of 1-phenylethanol in the presence of **4**). The promoting effect of MW methods was observed in other cases.[11c–g,11k,m,n,13] At 100 ºC, the MW-assisted method with **4** leads to the almost quantitative oxidation of 1-phenylethanol to acetophenone in only 20 mins, whereas by the conventional method of heating, even at the higher temperature of 150 ºC, the quantitative conversion was not yet approached after 3.5 h. Attempts to perform the oxidation at room temperature (without MW or conventional heating) failed, and the minimum required temperature is 50 ºC. The overall temperature coefficient (in the 50–100 ºC range) of the MW oxidations is *ca.* 1.2.

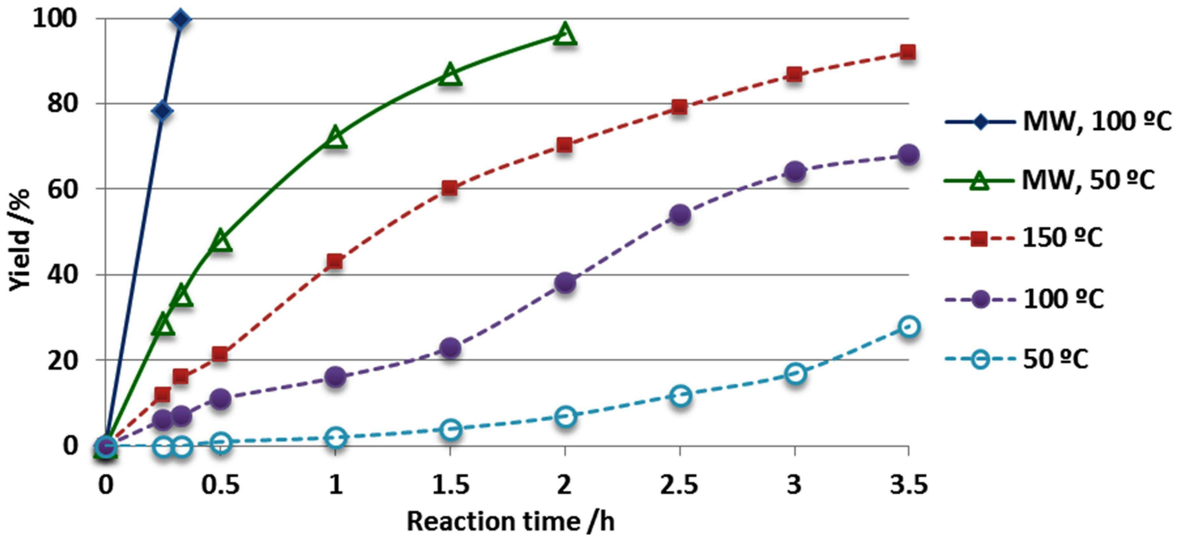

Figure 5. Influence of the temperature and reaction time on the yield of acetophenone obtained by MW-assisted (−) or conventional (--) oxidation of 1-phenylethanol in the presence of **4**.

Our system affords acetophenone upon oxidation of 1-phenylethanol, in the presence of **4** or **5**, in comparable yields with those of other successful MW-assisted oxidations of secondary alcohols involving a Cu(II) complex with a Schiff base and diethanolamine ligands (yields up to 85%, TON = 850),[11c] alkoxy-1,3,5-triazapentadienate Cu(II) complexes (yields up to 100%, TON = 500),[11f,j] but in much higher yields than in the presence of various mononuclear Cu(II) complexes bearing azathia macrocycles (yields up to 30%, TON = 150)[11g,k] or aryhydrazones (yields up to 40%, TON = 98),[11m] copper-containing metal-organic frameworks (MOFs) based on 5-(4-pyridyl)tetrazole building blocks (yields up to 79%, TON = 397)[11d] or coordination polymers with pyrazolato-based tectons (yields up to 43%, TON = 680).[11n] Similar yields are

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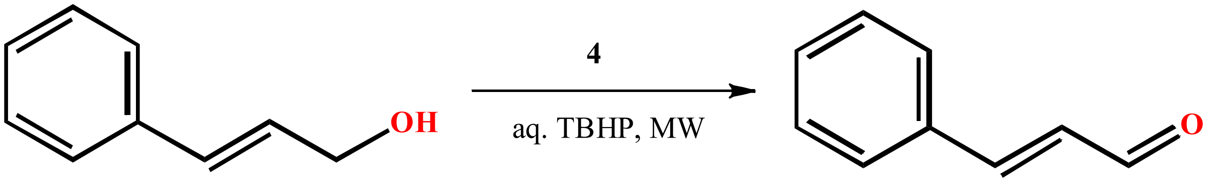
also observed with bi- or tetranuclear cage-like Cu(II) silsesquioxanes (yields up to 100%, TON = 475)[11i,l] with conventional heating.

Moreover, the almost quantitative conversion of benzyl alcohol to benzaldehyde, obtained with the **4**/TBHP/MW system (entry 12, Table 2), is also noticeable, since previous Cu(II) catalyst/ TBHP/ MW methods led to lower benzaldehyde yields (up to 75%)[11n] and also needed higher reaction temperatures (120 ºC[11n] or 150 ºC[11m]). Thus, our system could constitute a faster and eco-friendly alternative to the usually preferred aerobic oxidation in the presence of the additive nitrosyl TEMPO (2,2,6,6-tetramethyl-piperidinyloxyl) radical and using conventional heating.[10a,11b,13]

The selectivity of our best catalytic system **4**/TBHP/MW was further investigated by using cinnamyl alcohol as substrate and water as solvent, under the above optimized conditions (100 ºC, 150 min reaction time, 10 W MW irradiation). Cinnamaldehyde (85% yield, TOF of 851 h^{-1}) was the unique product detected (Scheme 3), clearly revealing the preference of our oxidation system for the alcohol function. Moreover, the reported yield in the present work is considerably higher than the previously obtained (66%)[11o] by H_5IO_6, in water, in the presence of Ru(III) compounds immobilized on silica, at room temperature.



Scheme 3. Homogeneous oxidation of cinnamyl alcohol, by the **4**/TBHP/MW system in water.

The alcohol peroxidative oxidation is believed to proceed mainly *via* a radical mechanism as proposed for other copper complexes,[11] which involves both carbon- and oxygen-centred radicals.[9a,11b,14] In fact, a strong inhibition effect was observed when it is carried out in the presence of either the carbon-radical trap $CBrCl_3$ or the oxygen-radical trap Ph_2NH (*e.g.*, acetophenone yield decreases to 5.8 and 4.9%, respectively). It may involve *e.g.*, ^{t}BuO$^\cdot$ and ^{t}BuOO$^\cdot$ radicals produced in the Cu promoted decomposition of TBHP[11i,15] according to the following equations (1) – (6):

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$$\mathrm{Cu^{II}} + {}^t\mathrm{BuOOH} \rightarrow \mathrm{Cu^{I}} + {}^t\mathrm{BuOO^{\cdot}} + \mathrm{H^+} \qquad (1)$$

$$\mathrm{Cu^{I}} + {}^t\mathrm{BuOOH} \rightarrow \mathrm{Cu^{II}}\text{–}\mathrm{OH} + {}^t\mathrm{BuO^{\cdot}} \qquad (2)$$

$$\mathrm{Cu^{II}}\text{–}\mathrm{OH} + {}^t\mathrm{BuOOH} \rightarrow \mathrm{Cu^{II}}\text{–}\mathrm{OO}\text{–}{}^t\mathrm{Bu} + \mathrm{H_2O} \qquad (3)$$

$${}^t\mathrm{BuO^{\cdot}} + \mathrm{R_2CHOH} \rightarrow {}^t\mathrm{BuOH} + \mathrm{R_2C^{\cdot}}\text{–}\mathrm{OH} \qquad (4)$$

$${}^t\mathrm{BuOO^{\cdot}} + \mathrm{R_2CHOH} \rightarrow {}^t\mathrm{BuOOH} + \mathrm{R_2C^{\cdot}}\text{–}\mathrm{OH} \qquad (5)$$

$$\mathrm{Cu^{II}}\text{–}\mathrm{OO}\text{–}{}^t\mathrm{Bu} + \mathrm{R_2C^{\cdot}}\text{–}\mathrm{OH} \rightarrow \mathrm{R_2C{=}O} + {}^t\mathrm{BuOOH} + \mathrm{Cu^{I}} \qquad (6)$$

However, it was not possible to detect any oxygenated intermediate species, conceivably due to their high reactivity.

It is worth to mention that, to our knowledge, the present **4**/TBHP/MW and **5**/TBHP/MW catalytic systems are among the fastest and most effective copper catalyzed MW-assisted, solvent- and additive-free oxidations of 1-phenylethanol and benzylalcohol and this type of sulfonated Schiff base copper systems has been applied in alcohol oxidation only for the second time after a mononuclear copper complex containing 2-(((1-hydroxynaphthalen-2-yl)methylene)amino)benzenesulfonate.[11c]

In view of the achieved results, the heterogenization of compounds **4** and **5** at different supports (carbon and zeolitic materials) in order to render them heterogeneous, and therefore reusable catalysts, is envisaged.

Conclusions

By taking advantage of the coordinating ability of the sulfonate group of the acyclic Schiff base 2-[(2-hydroxy-3-methoxyphenyl)methylideneamino]benzenesulfonic acid H_2L (**1**), two mononuclear copper complexes $[CuL(H_2O)_2]$ (**2**), [CuL(2,2'-bipy)].DMF.H_2O (**3**) and two diphenoxo-bridged dicopper compounds $[CuL(py)]_2$ (**4**) and $[CuL(EtOH)]_2.2H_2O$ (**5**) have been synthesized. The crystal lattices of all compounds are stabilized by non-covalent H-bond and $\pi\cdots\pi$ stackings interactions that generated 2D polymeric networks (in **1**) and a 1D double chain (in **2**).

These metal complexes (**2** – **5**) efficiently catalyze the neat microwave assisted 1-phenylethanol oxidation reaction to acetophenone, under mild conditions and in the absence of any additive. Overall 99.6 and 94.3% yields were obtained with the catalysts **4** and **5**, respectively. To our knowledge, the catalytic systems **4**/THBP/MW and **5**/THBP/MW are among the fastest and most effective copper catalyzed MW-assisted, solvent- and additive-free oxidations of secondary alcohols and this type of sulfonated Schiff base systems has been investigated in alcohol oxidation only for the second time.

The *in situ* synthetic methodology for the copper(II) complexes **2** – **5** in different solvents is quite easy.

In summary, a simple and efficient protocol for the synthesis of four effective and selective copper(II) catalysts for alcohol oxidation is presented and the extension of this study to the preparation of further copper complexes with these types of ligands and to their applications in oxidation catalysis deserves to be explored.

Experimental Section

Materials and Physical Methods

All the reagents and solvents were purchased from commercial sources and used as received. The water used for all preparations and analyses was double-distilled and de-ionised. Elemental analyses were performed by the Microanalytical Service of the Instituto Superior Técnico. FT-IR spectra were recorded in the region 400–4000 cm^{-1} on a Bruker Vertex 70 spectrophotometer with samples as KBr disks. The ^{1}H NMR spectrum was recorded at ambient temperature on a Bruker 400 UltraShield^{TM} spectrometer. The chemical shifts are reported in ppm using tetramethylsilane as an internal reference.

Syntheses

$H_2L.3H_2O$ (1). To a hot and stirred water solution (10 mL) of 2-aminobenzenesulfonic acid (0.692 g, 4.0 mmol) was added dropwise an ethanol solution (20 mL) of 2-hydroxy-3-methoxybenzaldehyde (0.608 g, 4.0 mmol). The resulted yellow solution was filtered and kept at room temperature overnight. After 1 day, yellow crystals, suitable for X-ray diffraction analysis, formed which were collected by filtration and washed with ethanol. Yield 1.185 g (82%). Anal.

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calcd. for $C_{14}H_{19}NO_8S$ (361.36): C 46.53, H 5.30, N 3.88%; found: C 46.63, H 5.27, N 3.84%. FT-IR (cm^{-1}, KBr): ν(OH), 3449br; ν(N–H), 2923br; ν(C=N), 1629s; ν(C–O), 1228s; ν(sulfonate), 1375s, 1173s. ^{1}H NMR (DMSO-D_6) δ (ppm): 10.29 (s, Ar-OH); 9.33 (s, CH=N); 6.92 – 7.79 (m, 7-Ar-H); 5.90 (br, N–H); 3.85 (s, O–CH_3).

[CuL(H_2O)$_2$] (**2**). To a hot and stirred aqueous methanol (1:1) solution (10 mL) of 2-aminobenzenesulfonic acid (0.173 g, 1.0 mmol) and 2-hydroxy-3-methoxybenzaldehyde (0.152 g, 1.0 mmol), an aqueous methanol (1:1) solution (10 mL) of $Cu(OAc)_2.H_2O$ (0.100 g, 0.5 mmol) and $CuCl_2.2H_2O$ (0.085 g, 0.5 mmol) was added dropwise to obtain a brown solution. The solution was filtered and kept at room temperature. After 2 days brown crystals, suitable for X-ray diffraction analysis, formed which were collected by filtration and washed with cold aqueous methanol solution (1:1). Yield: 0.292 g (72%). Anal. calcd. for $C_{14}H_{15}CuNO_7S$ (404.89): C 41.53, H 3.73, N 3.46%; found C 41.63, H 3.76, N 3.42%. FT-IR (cm^{-1}, KBr): ν(OH), 3449br; ν(C=N), 1618; ν(C–O), 1283s; ν(sulfonate), 1383m, 1174s.

[CuL(2,2′-bipy)].DMF.H_2O (**3**). To a hot and stirred aqueous DMF (1:1) solution (10 mL) of 2-aminobenzenesulfonic acid (0.173 g, 1.0 mmol) and 2-hydroxy-3-methoxybenzaldehyde (0.152 g, 1.0 mmol), was added dropwise a DMF solution (5 mL) of $Cu(OAc)_2.H_2O$ (0.199 g, 1.0 mmol). After 30 mins, to the resulted green solution was added dropwise a DMF solution (5 mL) of 2,2’-bipyridine (0.234 g, 1.5 mmol) affording a dark green solution. After one hour, the solution was filtered and kept at room temperature. After a few days dark green crystalline compounds, suitable for X-ray diffraction analysis, formed which were collected by filtration. Yield: 0.468 g (76%). Anal. calcd. for $C_{27}H_{28}CuN_4O_7S$ (616.14): C 52.63, H 4.58, N 9.09%; found C 52.69, H 4.62, N 9.04%. FT-IR (cm^{-1}, KBr): ν(OH), 3440br; ν(C=N), 1614; ν(C–O), 1274m; ν(sulfonate), 1386m, 1171s.

[CuL(py)]$_2$ (**4**). To a hot and stirred aqueous methanol (1:1) solution (15 mL) of 2-aminobenzenesulfonic acid (0.173 g, 1.0 mmol) and 2-hydroxy-3-methoxybenzaldehyde (0.152 g, 1.0 mmol) was added dropwise a methanol solution (2 mL) of pyridine (0.316 g, 4.0 mmol). After 2 h, was added dropwise an aqueous methanol (1:1) solution (10 mL) of $Cu(OAc)_2.H_2O$ (0.199 g, 1.0 mmol) to obtain a green solution. The solution was filtered and kept at room temperature. After one day green crystals, suitable for X-ray diffraction analysis, formed which were collected by filtration and washed with cold methanol. Yield: 0.309 g (69%). Anal. calcd.

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for $C_{38}H_{32}Cu_2N_4O_{10}S_2$ (895.90): C 50.94, H 3.60, N 6.25%; found C 50.99, H 3.65, N 6.21%. FT-IR (cm^{-1}, KBr): ν(C=N), 1609; ν(C–O), 1279s; ν(sulfonate), 1381m, 1170s.

$[CuL(EtOH)]_2.2H_2O$ (**5**). To a hot and stirred aqueous ethanol (1:1) solution (10 mL) of 2-aminobenzenesulfonic acid (0.173 g, 1.0 mmol) and 2-hydroxy-3-methoxybenzaldehyde (0.152 g, 1.0 mmol) was added dropwise an aqueous ethanol (1:1) solution (10 mL) of $Cu(OAc)_2.H_2O$ (0.199 g, 1.0 mmol) to obtain a green solution. After two hours, the solution was filtered and kept at room temperature. After 1 day green crystals, suitable for X-ray diffraction analysis, formed which were collected by filtration and washed with cold ethanol. Yield: 0.311 g (75%). Anal. calcd. for $C_{32}H_{38}Cu_2N_4O_{10}S_2$ (829.89): C 46.31, H 4.62, N 6.75%; found C 46.37, H 4.66, N 6.71%. FT-IR (cm^{-1}, KBr): ν(OH), 3445br; ν(C=N), 1612s; ν(C–O), 1278m; ν(sulfonate), 1385m, 1176s.

Crystal Structure Determinations

X-ray quality single crystals of the compounds were immersed in cryo-oil, mounted in a nylon loop and measured at room temperature (**1** – **5**). Intensity data were collected using a Bruker APEX-II PHOTON 100 diffractometer with graphite monochromated Mo-Kα (λ 0.71069) radiation. Data were collected using phi and omega scans of 0.5° per frame and a full sphere of data was obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT[16a] on all the observed reflections. Absorption corrections were applied using SADABS.[16a] Structures were solved by direct methods by using the SHELXS-97 package[16b,c] and refined with SHELXL-2014.[16b,c] Calculations were performed using the WinGX System–Version 1.80.03.[16d] The hydrogen atoms attached to carbon atoms and to the nitrogen atoms were inserted at geometrically calculated positions and included in the refinement using the riding-model approximation; Uiso(H) were defined as 1.2Ueq of the parent nitrogen atoms or the carbon atoms for phenyl and methylene residues, and 1.5Ueq of the parent carbon atoms for the methyl groups. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic ones for the remaining atoms were employed. Crystallographic data are summarized in Table S1 (Supplementary Information file) and selected bond distances and angles are presented in Table 1. CCDC 1411065–1411069 for **1–5**, respectively, contain the supplementary crystallographic data for this paper.

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General Procedures for the Oxidation of Alcohols

MW-assisted method: The catalytic tests under microwave irradiation (MW) were performed in a focused Anton Paar Monowave 300 microwave reactor using a sealed 5 mL capacity cylindrical Pyrex reaction tube with a 10 mm internal diameter, fitted with a rotational system and an IR temperature detector. The alcohol (2.5 mmol), TBHP (70 % aqueous solution, 5.0 mmol) and catalyst precursor (1 – 10 μmol, 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. The system was stirred and irradiated (5 – 25 W) for 0.15 – 1.5 h at 50 – 150 ºC.

Conventional heating method: The catalytic assays were carried out with conventional heating (oil bath) in air, using 25 mL round-bottomed flaks equipped with a reflux condenser. The alcohol (2.5 mmol), TBHP (70% aqueous solution, 5.0 mmol) and the catalyst (1 μmol, 0.04 mol% *vs*. substrate) were introduced in the flask and vigorous stirred during the desired reaction time.

Products extraction and analysis: After the reaction, the mixture was allowed to cool down to room temperature. 150 μL 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 *ca.* 10 min and then a sample (1 μL) was taken from the organic phase and analysed by GC or GC-MS. The internal standard method was used to quantify the organic products.

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 ºC. The initial temperature was maintained at 140 ºC for 1 min, then raised 10 ºC/min to 220 ºC and held at this temperature for 1 min. Helium was used as the carrier gas. The products were identified by comparison of their retention times with those of known reference compounds.

GC-MS analyses were performed using a Perkin Elmer Clarus 600 C instrument (He as the carrier gas). The ionization voltage was 70 eV. Gas chromatography was conducted in the temperature-programming mode, using a SGE BPX5 column (30 m × 0.25 mm × 0.25 μm). Reaction products were identified by comparison of their retention times with those of known reference compounds, and by comparing their mass spectra to fragmentation patterns obtained from the NIST spectral library stored in the computer software of the mass spectrometer.

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Graphical Abstract
for
Sulfonated Schiff Base Copper(II) Complexes as Efficient and Selective Catalysts in Alcohol Oxidation: Syntheses and Crystal Structures

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Crystal structure and alcohol oxidation activities of the monomeric complexes [CuL(H_2O)$_2$] (**2**) and [CuL(2,2'-bipy)].DMF.H_2O (**3**) and the dicopper compounds [CuL(py)]$_2$ (**4**) and [CuL(EtOH)]$_2$.2H_2O (**5**) derived from the sulfonated Schiff base H_2L (**1**) are described. A quantitative yield of acetophenone was obtained by the oxidation of 1-phenylethanol with **4** [TOFs up to 7.6 × 10^3 h^{-1}] within 20 min of low power MW irradiation (10 W) which is found to be more efficient than conventional heating. The selectivity of **4** to oxidize the alcohol relative to the ene function is demonstrated with cinnamyl alcohol.