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Cu(II) and Fe(III) Complexes Derived from *N*-Acetylpyrazine-2-Carbohydrazide as Efficient Catalysts Towards Neat Microwave Assisted Oxidation of Alcohols

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Abstract: The mononuclear Cu(II) complex [Cu((k*NN*′*O*-HL)(H_2O)$_2$] (**1**) was synthesized using *N*-acetylpyrazine-2-carbohydrazide (H_2L) and characterized by elemental analysis, IR spectroscopy, ESI-MS and single crystal X-ray crystallography. Two Fe(III) complexes derived from the same ligand viz, mononuclear [Fe((k*NN*′*O*-HL)Cl_2] (**2**) and the binuclear [Fe(k*NN*′*O*-HL)Cl(μ-OMe)]$_2$ (**3**) (synthesized as reported earlier), were also used in this study. The catalytic activity of these three complexes (**1**–**3**) was examined towards the oxidation of alcohols using *tert*-butyl hydroperoxide (TBHP) as oxidising agent under solvent-free microwave irradiation conditions. Primary and secondary benzyl alcohols (benzyl alcohol and 1-phenylethanol), and secondary aliphatic alcohols (cyclohexanol) were used as model substrates for this study. A comparison of their catalytic efficiency was performed. Complex **1** exhibited the highest activity in the presence of TEMPO as promoter for the oxidation of 1-phenylethanol with a maximum yield of 91.3% of acetophenone.

Keywords: Cu(II) complex; carbohydrazide; X-ray structure; alcohol oxidation; microwave assisted

1. Introduction

Transition metal complexes play a crucial role as catalysts or catalytic precursors in various organic transformations. The designing of new metal complexes with suitable multidentate ligands is a challenging research area aiming at finding better catalytic efficiency. Several transition metal complexes have already exhibited high catalytic activity in different organic oxidative transformations, such as oxidation of alkanes or alcohols, epoxidation, carboxylation, hydrocarboxylation, in C–C couplings, CO_2 reduction, etc. [1–14]. The efficiency of metal complexes in catalysis is highly dependent on their structural configuration and electronic properties [10,11,15–18]. The ligands also play a supporting role towards the promising catalytic performance of the metal complexes. Therefore, selection of appropriate ligands for the synthesis of new metal complex catalysts is crucial.

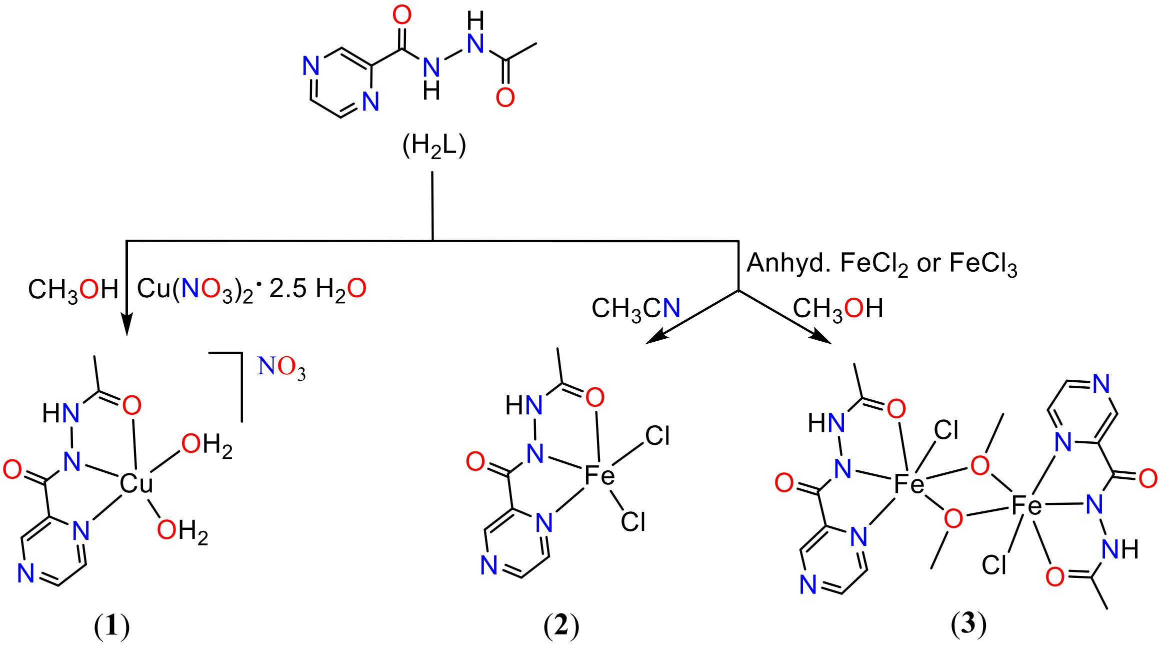
In this study, we mainly focused on the selective oxidation of alcohols to the corresponding carbonyl compounds [18–21]. The products of oxidation of alcohols such as aldehydes and ketones are building blocks for many organic compounds [22–25] and show diverse applications, such as pharmaceuticals, agrochemicals, fragrances, fine chemicals and polymers [26,27]. The commencement of clean synthetic catalytic routes can be implemented by using green oxidants, green solvents or solvent free processes, energy saving beneficial techniques and involves the design of efficient catalysts from environmental and economic perspectives [28–30]. Based on the nature of the catalyst precursors, both homogeneous and heterogeneous (supported) catalysts have been reported by us towards oxidative catalytic reactions [3–9,29–40]. Although many catalysts have been developed to overcome ecological drawbacks, namely those using cheap and abundant metals, like copper and iron, metal catalytic systems operating under sustainable conditions are still challenging.

Considering all the above mentioned points herein we present the synthesis of a new mononuclear Cu(II) complex, [Cu((k*NN′O*-HL)(H_2O)$_2$] (**1**), derived from the *N*-acetylpyrazine-2-carbohydrazide (H_2L) ligand. Two Fe(III) complexes, the mononuclear [Fe((k*NN′O*-HL)Cl_2] (**2**) and the binuclear [Fe(k*NN′O*-HL)Cl(μ-OMe)]$_2$ (**3**), have also been synthesized using the same ligand as reported earlier [41]. The three complexes (**1–3**) were screened as catalytic precursors to assess their catalytic performances in the oxidation of alcohols. In the present investigation, we chose primary or secondary benzyl alcohols (benzyl alcohol, 1-phenyl alcohol) and secondary aliphatic alcohols (cyclohexanol) as model substrates and *tert*-butyl hydroperoxide (TBHP) as oxidising agent under microwave irradiation. MW irradiation acts as an alternative technique due to its simplicity and energy saving characteristics [6], usually leading to higher product yields and selectivities. In this investigation, the best catalytic conditions were optimized by comparing several cofactors like temperature, reaction time, influence of the presence of additives, etc.

2. Results and Discussion

2.1. Synthesis and Characterizations

The pro-ligand *N*-acetylpyrazine-2-carbohydrazide (H_2L) was used to synthesize the mononuclear Cu(II) complex [Cu(k*NN′O*-HL)(H_2O)$_2$] (**1**) (Scheme 1). The Fe(III) complexes [Fe(kNN′O-HL)Cl_2] (**2**) and [Fe(kNN′O-HL)Cl(μ-OMe)]$_2$ (**3**) derived from the same pro-ligand were obtained by a method from the literature [41]. As previously observed, in this case, the *N*-acetylpyrazine-2-carbohydrazide also acts as a mononegative tridentate *N,N,O* donor (HL^-) towards the metal centre [41] and shows different coordination behaviour from a related one derived from *N*-acetylsalicylhydrazide [42–44]. In this case, the –CONH– group attached to the pyrazine ring only deprotonates and favours the formation of two stable five-member chelate rings around the metal centre. In the case of *N*-acetylsalicylhydrazide, the ligand prefers to coordinate simultaneously with two metal ions in its two chelate pockets [42–44].



Scheme 1. Syntheses of [Cu((k*NN′O*-HL)(H_2O)$_2$] (**1**), [Fe(kNN′O-HL)Cl_2] (**2**) and [Fe(kNN′O-HL)Cl(μ-OMe)]$_2$ (**3**).

Characterizations of **1–3** were carried out by elemental analysis, spectroscopic (IR spectroscopy and ESI-MS) methods, and single-crystal X-ray diffraction techniques. In addition to the other characteristic stretching bands of the ligand, a blue shift was observed for the C=O stretching frequency at 1662 cm^{-1} (which is coordinated to the Cu(II) centre) and the presence of nitrate ion at 1384 cm^{-1} [33]. The *m*/*z* value of **1** indicates the loss of non-coordinate nitrate ion present in **1** (see Experimental).

The catalytic properties of **1–3** were investigated towards neat microwave assisted oxidation of alcohols (benzyl alcohol, 1-phenylethanol and cyclohexanol), and their catalytic activities were compared.

2.2. General Description of the Crystal Structure

Green single crystals suitable for the X-ray analysis of **1** (Supplementary Materials: CCDC 1962610) were obtained from methanol upon slow evaporation (in open air) at room temperature. The molecular structure of **1** obtained by X-ray analysis is presented in Figure 1. The crystallographic data and other processing parameters are summarized in Table 1, and selected dimensions (bond lengths and angles) are provided in Table 2.

Complex **1** crystallizes in the monoclinic *C*2/*c* space group and its asymmetric unit comprises the Cu(II) cation with one coordinated ligand, two water molecules, and a non-coordinate nitrate anion. The copper centre of **1** is five-coordinated with two nitrogen atoms (amido and pyrazine) and one *keto* oxygen atom from the HL^- ligand and two water molecules. The metal cation in **1** exhibits N_2O_3 coordination environment assuming a distorted square pyramid geometry ($\tau_5 = 0.144$), where $\tau_5 = 0$ for square pyramid and $\tau_5 = 1$ for trigonal bipyramid geometries [45]. The tridentate HL^- ligand and one water molecule occupy the square plane (N1N9O12O14). The axial position is occupied by another water molecule (O15). The central Cu(II) ion is located 0.214 Å above from the above-mentioned square plane towards apical oxygen O15.

Table 1. Crystal data and structure refinement details for complex **1**.

	1
Empirical formula	$C_7H_{11}CuN_5O_7$
Formula Weight	340.75
Crystal system	Monoclinic
Space group	*C*2/*c*
Temperature/K	297 (2)
a/Å	13.8799 (9)
b/Å	16.9433 (10)
c/Å	11.9900 (7)
α/°	90
β/°	117.763 (2)
γ/°	90
V ($Å^3$)	2495.1 (3)
Z	8
D_{calc} (g cm^{-3})	1.814
μ(Mo Kα) (mm^{-1})	1.79
Rfls. collected/unique/observed	15921/2292/1997
R_{int}	0.029
Final $R1^a$, $wR2^b$ ($I \geq 2\sigma$)	0.027, 0.072
Goodness-of-fit on F^2	1.07

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; ^{b} $wR(F^2) = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^4]^{\frac{1}{2}}$

Table 2. Selected bond distances (Å) and angles (°) in complex **1**.

Cu1—N9	1.8900 (18)
Cu1—O14	1.9066 (17)
Cu1—O12	2.0111 (15)
Cu1—N1	2.0813 (18)
Cu1—O15	2.260 (2)
N9—Cu1—O14	166.20 (10)
N9—Cu1—O12	80.33 (7)
O14—Cu1—O12	94.01 (7)
N9—Cu1—N1	79.43 (7)
O14—Cu1—N1	103.48 (8)
O12—Cu1—N1	157.54 (7)
N9—Cu1—O15	97.24 (8)
O14—Cu1—O15	96.11 (9)
O12—Cu1—O15	99.49 (7)
N1—Cu1—O15	92.63 (7)

Extensive inter- and intra-molecular hydrogen bond interactions were found in **1**. A hydrogen bond 2D network (Figure 2) results from the contacts involving the water ligands, amine nitrogen of the ligand and nitrate anions.

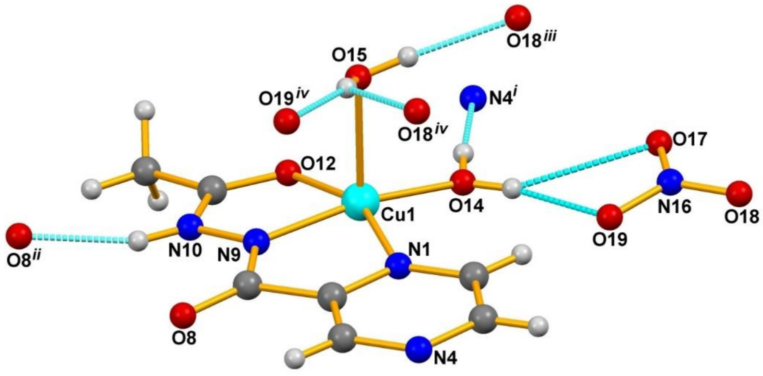


Figure 1. Structural representation (obtained by single crystal X-ray analysis) of **1** with partial atom labelling scheme. H-bond interactions are represented in dotted lines in light blue colour. Symmetry codes for generating equivalent atoms: (i) 1.5 − x,1/2 + y,1/2 − z; (ii) 1 − x,1 − y,1 − z; (iii) 2 − x, y,1/2 − z; (iv) x,1 − y,1/2 + z.

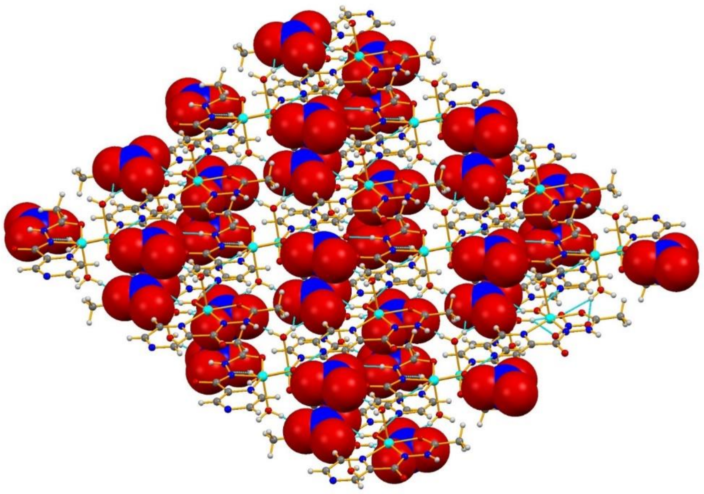
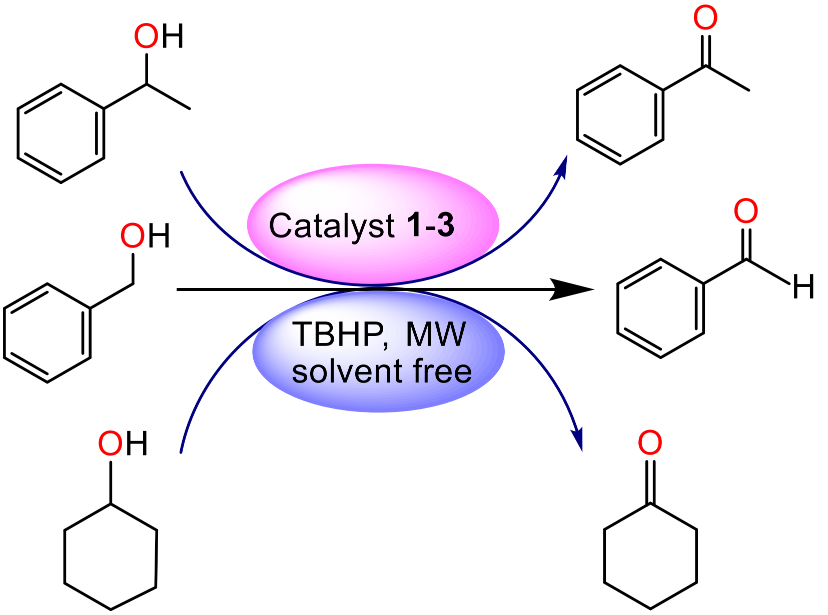


Figure 2. Hydrogen-bonded 2D network of **1**, viewed along the crystallographic *b* axis. The nitrate ions are drawn by the space-filled model.

2.3. Catalytic Studies

Complexes **1–3** were tested as catalyst precursors for the neat microwave (MW)-assisted oxidation of primary or secondary benzyl alcohols (benzyl alcohol, 1-phenylethanol) and secondary aliphatic alcohols (cyclohexanol) to the corresponding aldehydes (for primary alcohols), or ketones (for secondary alcohols), using aqueous *tert*-butyl hydroperoxide (TBHP) as oxidizing agent, under low-power (5–10 W) MW irradiation (Scheme 2). A high selectivity (towards the formation of acetophenone, benzaldehyde and cyclohexanone from their corresponding 1-phenylethanol, benzyl alcohol and cyclohexanol) was observed from the MW-assisted transformations, since no traces of by-products were detected by GC-MS analysis of the final reaction mixtures (only the unreacted alcohol was found, apart from the products). All three complexes of Cu(II) and Fe(III) (**1–3**) act as homogeneous catalyst precursors in neat conditions.



Scheme 2. Microwave-assisted neat oxidation of 1-phenylethanol, benzyl alcohol and cyclohexanol to acetophenone, benzaldehyde and cyclohexanone, respectively, in presence of catalyst precursors (**1–3**) using aq. *tert*-butyl hydroperoxide (Bu^tOOH, TBHP, 70% aq. solution) as oxidant.

The influence of temperature and time was optimized using 1-phenylethanol as a model substrate. With a temperature increase from 80 °C to 120 °C, the catalytic performance of **1–3** was enhanced, exhibiting the highest activity (51.4% yield of acetophenone, entry 3, Table 2) after 30 min, with a corresponding TON (moles of product per mol of catalyst precursor) value of 512 in the presence of **1** under MW irradiation in the absence of any solvent (Figure 3). Analysing the yields of the peroxidative selective oxidation of 1-phenylethanol by complexes **1–3**, it can clearly be seen that the catalytic activity of mononuclear Cu(II) complex **1** is higher than the other two mono and dinuclear Fe(III) complexes (**2** and **3**).

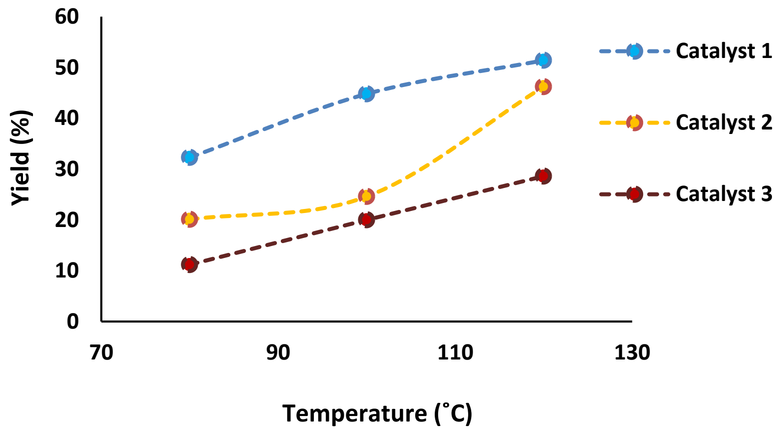


Figure 3. Dependence on the temperature for MW-assisted neat oxidation of 1-phenylethanol using **1**–**3** as catalyst precursors. Reaction conditions: 5 mmol of substrate, 10 µmol (0.2 mol% vs. substrate) of **1**–**3**, 10 mmol of TBHP (2 eq., 70% in H_2O), 30 min reaction time, MW irradiation (5–10 W).

It was found that 1 h of MW irradiation provided the best catalytic conditions for yielding acetophenone, reaching a maximum in the presence of **1**–**3** and then slightly decreasing, conceivably due to overoxidation (Figure 4). Complexes **1**, **2** and **3** exhibited maximum yields of 86.4%, 77.7% and 65.2% [Table 3, entries 4, 23 and 33, respectively].

The other heating technique, the conventional heating (oil bath) mode, was applied under the same optimized reaction conditions on catalytic system **1** to compare the product yield obtained by the MW-assisted selective oxidation of the chosen model substrate, 1-phenylethanol. From the conventional heating, using same conditions, 67.6% yield of acetophenone was achieved after 1 h, whereas 86.4% of acetophenone was obtained with MW irradiation. This clearly indicates the credibility of microwave irradiation as a beneficial technique. After 4 h of heating, the yield enhanced and reached from 67.6% to 87.2% [Table 3, entries 7 and 8]. Therefore, microwave irradiation reduces the reaction time required to achieve similar yields to one quarter of those obtained under conventional heating, which requires more energy.

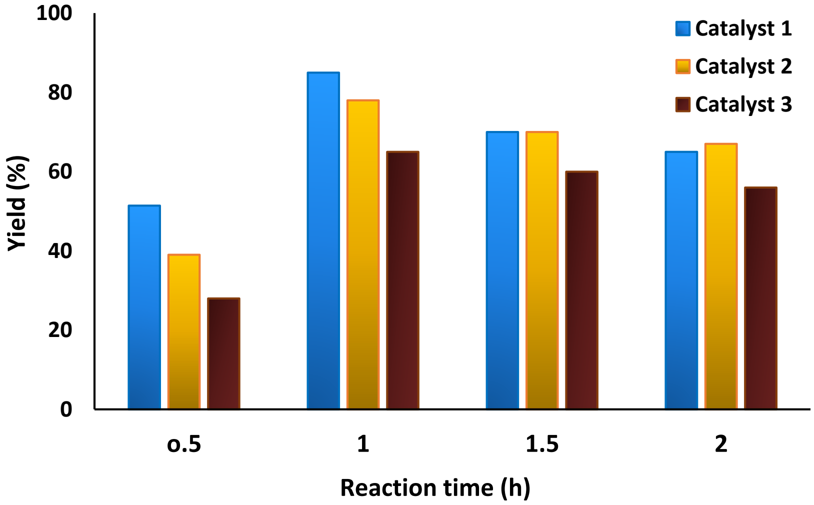


Figure 4. Yield analysis of MW-assisted neat peroxidative oxidation of 1-phenylethanol using **1**–**3** as catalyst precursors with respect to time. Reaction conditions: 5 mmol of substrate, 10 µmol (0.2 mol% vs. substrate) of **1**–**3**, 10 mmol of TBHP (2 eq., 70% in H_2O), 120 °C, MW irradiation (5–10 W).

The influence of various additives was explored in this study. Cu(II) complex **1** was chosen as a benchmark catalyst and its performance investigated, in the presence of nitric acid (HNO_3), 2-pyrazinecarboxylic acid (HPCA), 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) and an oxygen-radical trap such as diphenyl amine (Ph_2NH) towards neat microwave-assisted peroxidative oxidation of 1-phenylethanol at optimized conditions (Figure 5). In the presence of HNO_3, the yield decreased dramatically from 86.4% to 25.6% [Table 3, entry 9]. The heteroaromatic acid HPCA also led to lower yields of acetophenone (51.8%) [Table 3, entry 8]. A highly favourable effect of additive was observed in presence of TEMPO for the MW-oxidation of 1-phenylethanol by 1–3 [Table 3, entries 10, 26 and 36]. The highest yield of 91.3% [TON (TOF) value of 457 (457)] was obtained for the Cu(II) complex **1**, whereas Fe(III) complexes **2** and **3** accounted for 83.8% and 71.3%, respectively.

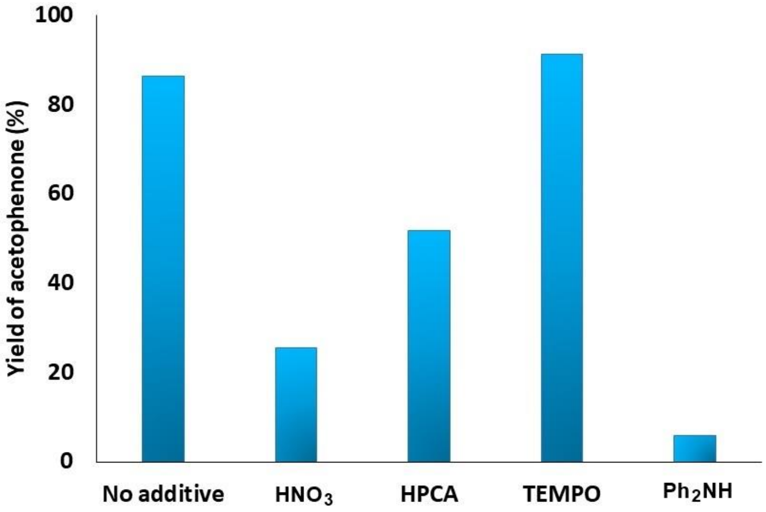


Figure 5. Influence of different additives on the yield of acetophenone, obtained from MW-assisted neat peroxidative oxidation of 1-phenylethanol in presence of catalyst precursor **1**. Reaction conditions: 5 mmol of substrate, 10 µmol (0.2 mol% vs. substrate) of **1**, 10 mmol of TBHP (2 eq., 70% in H_2O), additives [n(additive)/n(catalyst) = 25], 120 °C, MW irradiation (5–10 W).

In contrast, a strong inhibitor effect of the catalytic activity of **1–3** was observed [Table 3, entries 11, 15 and 27] for the reactions carried out in the presence of Ph_2NH. The addition of Ph_2NH to the reaction mixture, a well-known oxygen radical trap [46], resulted in a significant yield drop compared to the reaction carried out under the same conditions but in the absence of such a radical trap. This suggests that oxygen radicals are generated during the reaction, which are trapped by the radical scavenger. The mechanism may involve the coordination of 1-phenylethanol followed by metal-centred dehydrogenation and oxidation of the alcohol through hydrogen abstraction or one-electron oxidation processes [47,48].

Table 3. Data [a] for the selective peroxidative oxidation of cyclohexane with TBHP (70% aq.) using complexes **1–3** as catalyst precursors.

Entry	Catalyst	Substrate	Temperature (°C)	Reaction Time (h)	Additive	Yield (%) [b]	TON (TOF (h^{-1})) [c]
1	**1**	1-phenyl ethanol	80	0.5	-	32.3	162 (324)
2			100	0.5	-	44.8	224 (448)
3			120	0.5	-	51.4	257 (514)
4			120	1.0	-	86.4	432 (432)
5			120	1.5	-	69.8	349 (233)
6			120	2.0	-	65.4	327 (164)
7 [d]			120	1	-	67.6	338 (338)
8 [d]			120	4		87.2	436 (109)
8 [e]			120	1	HPCA	51.8	259 (259)
9 [f]			120	1	HNO_3	25.6	128 (128)
10 [g]			120	1	TEMPO	91.3	457 (457)
11 [h]			120	1	Ph_2NH	5.9	30 (30)
12		benzyl alcohol	120	1	-	33.4	167 (167)
13 [d]			120	1	-	19.5	98 (98)
14 [g]			120	1	TEMPO	41.2	206 (206)
15 [h]			120	1	Ph_2NH	3.6	18 (18)
16		cyclohexanol	120	1	-	65.6	328 (328)
17 [d]			120	1	-	23.9	120 (120)
18 [g]			120	1	TEMPO	67.9	274 (274)
19 [h]			120	1	Ph_2NH	3.9	20 (20)
20	**2**	1-phenyl ethanol	80	0.5	-	20.1	101 (101)
21			100	0.5	-	24.6	123 (123)
22			120	0.5	-	46.2	193 (385)
23			120	1.0	-	77.7	389 (389)
24			120	1.5	-	69.3	347 (231)
25			120	2.0	-	66.9	335 (167)
26 [g]			120	1.0	TEMPO	83.8	419 (419)
27 [h]			120	1.0	Ph_2NH	4.7	24 (24)
28		benzyl alcohol	120	1.0	-	26.7	133 (133)
29		cyclohexanol	120	1.0	-	35.8	179 (179)
30	**3**	1-phenyl ethanol	80	0.5	-	11.2	56 (112)
31			100	0.5	-	20.3	102 (204)
32			120	0.5	-	28.6	143 (286)
33			120	1.0	-	65.2	326 (326)
34			120	1.5	-	60.4	302 (201)
35			120	2.0	-	56.8	284 (142)
36 [g]			120	1.0	TEMPO	71.3	377 (377)
37 [h]			120	1.0	Ph_2NH	2.8	14 (14)
38		benzyl alcohol	120	1.0	-	18.9	95 (95)
39		cyclohexanol	120	1.0	-	36.7	184 (184)

Table 3. *Cont.*

Entry	Catalyst	Substrate	Temperature (°C)	Reaction Time (h)	Additive	Yield (%) [b]	TON (TOF (h^{-1})) [c]
40	$Cu(NO_3).2.5$ H_2O	1-phenyl ethanol	120	1.0	-	6.2	31 (31)
41		benzyl alcohol	120	1.0	-	2.7	14 (14)
42		cyclohexanol	120	1.0	-	4.3	22 (22)
43	$FeCl_3$	1-phenyl ethanol	120	1.0	-	4.9	25 (25)
44		benzyl alcohol	120	1.0	-	2.2	11 (11)
45		cyclohexanol	120	1.0	-	3.4	17 (17)

[a] Reaction conditions: 5 mmol of substrate, 10 µmol (0.2 mol% vs. substrate) of catalyst precursor **1**–**3**, 10 mmol of TBHP (2 eq., 70% in H_2O), MW irradiation (5 W). [b] Moles of ketone product per 100 moles of alcohol. [c] Turnover number = number of moles of product per mol of catalyst precursor; TOF = TON per hour (values in brackets). [d] Conventional heating. [e] n(HPCA)/n(catalyst) = 25. [f] n(HNO_3)/n(catalyst) = 25. [g] n(TEMPO)/n(catalyst) = 25. [h] n(Ph_2NH)/n(catalyst) = 25. MW irradiation (5–10 W).

Since the best catalytic performances were obtained in the presence of **1**–**3** at 120 °C and 1 h MW irradiation, the oxidation of other alcohol substrates was tested under the same optimized reaction parameters. Oxidation of aromatic primary alcohol (benzyl alcohol) and aliphatic alcohol (cyclohexanol) using aq. *tert*-butyl hydroperoxide (Bu^tOOH, TBHP, 70% aq. solution) as oxidant in the presence of catalyst precursors **1**–**3** under neat conditions yielded in lower value than secondary alcohol (1-phenylethanol) (Figure 6). In presence of **1**, we found 33.4% of benzaldehyde after 1 h at 120 °C which increased up to maximum 41.2% yield in presence of TEMPO [Table 3, entries 12 and 14]. In the presence of **1**, using optimized conditions, the oxidation of cyclohexanol, in the presence of TEMPO, exhibited the highest yield (67.9%) of cyclohexanone [Table 3, entry 18]. The oxidation of alcohol by TEMPO-free Cu(II) catalysts is also reported in the literature [49]. From the yield analysis of benzaldehyde and cyclohexanone for **1**–**3** catalytic systems, it was found that the Cu(II) complex acts as a more efficient catalyst precursor than Fe(III) complexes **2** and **3**.

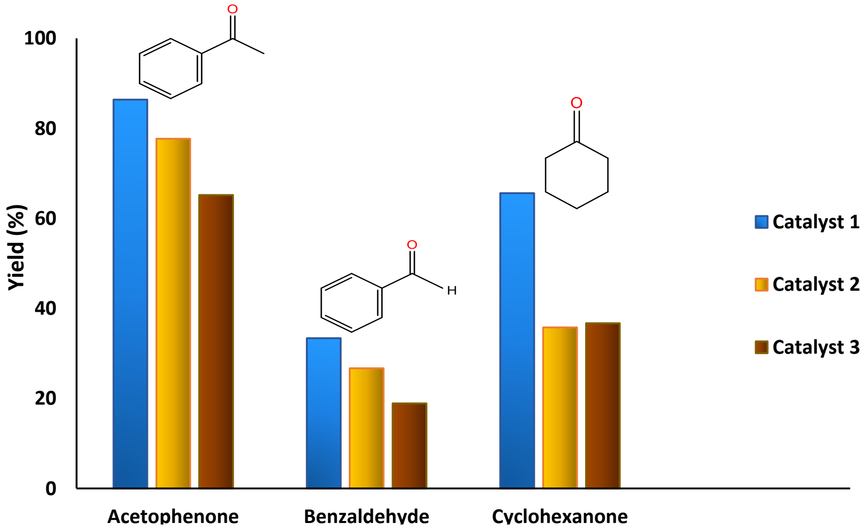


Figure 6. Yield analysis of MW-assisted neat peroxidative oxidation of 1-phenylethanol, benzyl alcohol and cyclohexanol in presence of catalyst precursors **1**–**3**. Reaction conditions: 5 mmol of substrate, 10 µmol (0.2 mol% vs. substrate) of **1**–**3**, 10 mmol of TBHP (2 eq., 70% in H_2O), 120 °C, 1 h reaction time, MW irradiation (5–10 W).

The isolated yield was determined by column chromatography using a mixture of ethylacetate and n-hexane (1:3) as eluent, and the purity of the product was verified by ^1H NMR (SI Figures S1–S3). The catalytic reactions were performed with 10 mmol of each substrate (1-phenyl ethanol, benzyl alcohol and cyclohexanol) under optimized conditions and the isolated yield has been determined from the reaction products. The isolated yields found were 83.6% (for 1-phenyl ethanol to acetophenone), 32.3% (for benzyl alcohol to benzophenone) and 59.7% (for cyclohexanol to cyclohexanone), respectively. The isolated yields were found to be almost 8–9% lower than the yield obtained by GC-MS. This is probably due to the loss of product during the process of column chromatography.

For comparative purposes, the starting salts used in the synthesis of the complexes **1**–**3** were also tested [Table 3, entries 41–45].

The catalytic performance of **1** was also compared with some recent literature reports (Table 4) [50–53]. It is clear from Table 4 that complex **1** exhibits a good catalytic efficiency (a maximum yield of 91.3% was achieved in 1 h) in comparison to the reported ones.

Table 4. Comparison of catalytic activity of **1** with other known compounds.

Catalyst	Amount (mol%)	Substrate	Oxidant	Temp (°C)	Time (h)	Yield (%)	Ref
$[Cu(II)L^1(H_2O)]I_2$	0.25	Benzyl alcohol	H_2O_2 (in the presence of TEMPO and K_2CO_3)	60	24	99	51
$[Cu(im)(\mu\text{-}HL^2\text{-}1\kappa O{:}2\kappa NOO')]_2$	0.15	1-phenylethanol	H_2O_2 (in the presence of TEMPO)	80 (MW irradiation)	1	74	52
$Fe(OTs)_3{\cdot}6H_2O$	0.1	Benzyl alcohol	H_2O_2	60	16	85.6	53
ZnL^3Cl_2	5	Benzyl alcohol	O_2 (in the presence of K^tBuO, Zn dust)	60	24	76	54
$[Cu(kNN'O\text{-}HL)(H_2O)_2]$	0.2	Benzyl alcohol	TBHP (in the presence of TEMPO)	120 (MW irradiation)	1	91.3	This work

H_4L^1 = 5,11,17,23-tetrakis(trimethylammonium)-25,26,27,28-tetrahydroxycalix[4]arene. HL^2 = 2-[2-(2,4-dioxopentan-3-ylidene)hydrazinyl]terephthalic acid. TsOH = Tosyl alcohol. L^3 = 2,6-bis(phenylazo)pyridine.

3. Materials and Methods

Synthesis of the pro-ligand and metal complexes for this study was performed in open air. Reagents and solvents were used as commercially received, without further purification or drying. $Cu(NO_3)_2{\cdot}2.5H_2O$ was used as metal precursor for the synthesis of complex **1**. Elemental analyses (C, H and N) were carried out by the Microanalytical Service of the Instituto Superior Técnico. Bruker Vertex 70 instrument (Bruker Corporation, Ettlingen, Germany) was used for Infrared spectra (4000–400 cm^{-1}) analysis in KBr pellets; wavenumbers are in cm^{-1}. The ^1H NMR spectrum of the ligand was recorded on a Bruker Avance II + 400.13 MHz (UltraShield^{TM} Magnet, Rheinstetten, Germany) spectrometer at room temperature. The internal reference was tetramethylsilane and the chemical shifts are reported in ppm in the ^1H NMR spectrum. Mass spectra were recorded in a Varian 500-MS LC Ion Trap Mass Spectrometer (Agilent Technologies, Amstelveen, The Netherlands) equipped with an electrospray (ESI) ion source. The electrospray ionization was carried out with a flow rate and a drying gas optimized according to the particular sample with 35 p.s.i. nebulizer pressure. Scanning was performed in methanol solution from *m*/z 100 to 1200. The samples were analysed in the positive mode (capillary voltage = 80–105 V).

3.1. Synthesis of the Pro-Ligand H_2L

The pro-ligand *N*-acetylpyrazine-2-carbohydrazide (H_2L) was prepared according to the literature [41] upon acetylation of the pyrazine-2-carbohydrazide.

Yield: 84.0%. Anal. calc. for $C_7H_8N_4O_2$: C, 46.67; H, 4.48; N, 31.10. Found: C, 46.61; H, 4.53; N, 31.08. IR (KBr pellet, cm^{-1}): 3336 ν(NH), 3223 ν(NH), 1698 ν(C=O), 1672 ν(C=O). ^{1}H NMR (DMSO-d_6, δ): 9.16–8.87 (m, 3H, $C_4H_3N_2$), 8.75 (s, 2H, NH), 1.92 (s, 3H, CH_3).

3.2. Synthesis of [Cu(kNN'O-HL)(H_2O)$_2$] (**1**)

The pro-ligand H_2L (0.368 g, 1.00 mmol) was dissolved in 20 mL methanol solution and 0.245 g, 1.05 mmol $Cu(NO_3)_2\cdot 2.5H_2O$ was added to it. The reaction mixture was stirred for 30 min at a temperature of 50 °C. The resultant dark green solution was filtered, and the filtrate was kept in open air for crystallization. Green single crystals were isolated after 2 days, suitable for X-ray diffraction analysis.

Yield: 0.245 g (72%, with respect to Cu). Anal. Calcd for $C_7H_{11}CuN_5O_7$ (**1**): C, 24.67; H, 3.25; N, 20.55. IR (KBr pellet, cm^{-1}): 3126 ν(NH), 1384 ν(NO_3)$^-$, 1700 ν(C=O), 1662 ν(C=O), 1034 ν(N–N). ESI-MS(+): *m/z* 278 [M-(NO_3)]$^+$ (100%).

3.3. Synthesis of [Fe(kNN'O-HL)Cl_2] (**2**) and [Fe(kNN'O-HL)Cl(μ-OMe)]$_2$ (**3**)

The mononuclear 2 and dinuclear Fe(III) complexes were synthesized as described in the literature [41].

[Fe(kNN'O-HL)Cl_2] (**2**): Yield 70%, 0.21 g. Anal. Calcd for $C_7H_7Cl_2FeN_4O_2$: C, 27.48; H, 2.31; N, 18.31. Found: C, 27.43; H, 2.28; N, 18.28. IR (KBr pellet, cm^{-1}): 3130 ν(NH), 1702 ν(C=O), 1666 ν(C=O), 1037 ν(N–N). ESI-MS(+): *m/z* 306 [M+H]$^+$ (100%).

[Fe(kNN'O-HL)Cl(μ-OMe)]$_2$ (**3**): Yield 66 %, 0.19 g. Anal. Calcd for $C_{16}H_{20}Cl_2Fe_2N_8O_6$: C, 31.87; H, 3.34; N, 18.58. Found: C, 31.82; H, 3.32; N, 18.53. IR (KBr; cm^{-1}): 3127 ν(NH), 1664 ν(C=O), 1638 ν(C=O), 1036 ν(N–N). ESI-MS(+): *m/z* 604 [M+H]$^+$ (100%).

3.4. X-Ray Measurements

A single crystal of complex **1** of appropriate quality for X-ray diffraction analysis was chosen and immersed in cryo-oil, mounted in Nylon loops and measured at 297 K. Intensity data were collected using a Bruker AXS PHOTON 100 diffractometer with graphite monochromated Mo-Kα (λ 0.71073) radiation. Data collections were recorded using omega scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART [54] software, and the data were refined using Bruker SAINT [54] on all the observed reflections. Absorption corrections were applied using SADABS [54]. Structures were solved by direct methods by using SIR97 [55] and refined with SHELXL2014 [56]. Calculations were performed using WinGX v2014.1 [57]. Those H-atoms bonded to carbon were included in the model at geometrically calculated positions and refined using a riding model. U_{iso}(H) were defined as 1.2U_{eq} of the parent carbon atoms for aromatic residues and 1.5U_{eq} for the methyl groups. The other hydrogen atoms (N–H) were in calculated positions as aromatic located in the difference Fourier synthesis and refined. Least square refinements with anisotropic thermal motion parameters were applied for all the non-hydrogen atoms and isotropic for the remaining atoms.

3.5. Catalytic Studies

The catalytic experiments were carried out under microwave irradiation in a focused microwave Anton Paar Monowave 300 (Anton Paar GmbH, Graz, Austria) discover reactor fitted with a rotational system and an IR temperature detector. 10 mL capacity cylindrical Pyrex tubes with a 13 mm internal diameter were used. Gas chromatographic (GC) measurements were carried out using a FISONS Instruments GC 8000 series gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) with a DB-624 (J&W) capillary column (FID detector) and the Jasco-Borwin v.1.50 software (Jasco, Tokyo, Japan). The temperature of injection was 240 °C. The initial temperature, 120 °C, was maintained for 1 min, then raised 10 °C/min to 200 °C and held at 200 °C for 1 min. The carrier gas used was helium. GC-MS analyses were conducted using a Perkin-Elmer Clarus 600 C (Shelton, CT, USA) instrument (with He as the carrier gas) with an ionization voltage of 70 eV and a SGE BPX5 column (30 m × 0.25 mm

× 0.25 μm). The comparison of the products retention times with those of known reference compounds enabled their identification. Moreover, their mass spectra to fragmentation patterns were compared with those obtained from the NIST spectral library of the computer software of the spectrometer.

Typical Procedures for the Catalytic Oxidation of Alcohols and Product Analysis

The oxidation reactions of the alcohol substrates were performed in the above-mentioned Pyrex tubes under focused microwave irradiation as follows: alcohol (5 mmol), catalyst precursor **1–3** (10 μmol, 0.2 mol% vs. substrate) and a 70% aqueous solution of ^{t}BuOOH (10 mmol) were introduced in the tube. This was then placed in the microwave reactor and the system was stirred and irradiated (5–10 W) for 0.5–2 h at 80–120 °C. After the reaction, the mixture was allowed to cool down to room temperature. In the case of 1-phenylethanol and cyclohexanol, 300 μL of benzaldehyde (internal standard) and 5 mL of NCMe (to extract the substrate and the organic products from the reaction mixture) were added. For benzyl alcohol, 90 μL cycloheptanone (internal standard) was added and 10 mL of diethyl ether (to extract the substrate and the organic products from the reaction mixture) was added. The mixture was stirred for 10 min. Then, a 1 μL sample was taken from the organic layer and analysed by gas chromatography. The product quantification used the internal standard method. The performed blank experiments indicated that only traces (<0.7%) of ketones (cyclohexanone or acetophenone or) are formed in a catalyst-free system. Flash column chromatography was performed on silica gel 60, 63–200 microns from Panreac; ethyl acetate/hexane as eluent to obtain the desired product.

4. Conclusions

In this work we successfully explored the catalytic activities of a mononuclear Cu(II) complex $[Cu(kNN'O\text{-}HL)(H_2O)_2]$ (**1**) and two Fe(III) complexes mononuclear $[Fe(kNN'O\text{-}HL)Cl_2]$ (**2**) and the binuclear $[Fe(kNN'O\text{-}HL)Cl(\mu\text{-}OMe)]_2$ (**3**) towards the oxidation of alcohols using *tert*-butyl hydroperoxide as oxidising agent under solvent-free microwave irradiation conditions. Three different alcohol substrates (benzyl alcohol, 1-phenylethanol and cyclohexanol) were used for this study to compare the catalytic performance of the catalytic precursors **1–3**. All the catalyst precursors led to very good yields and selectivity towards the oxidation of alcohols. Complex **1** was found to be more efficient than the other two Fe(III) complexes, and the promotor TEMPO had an accelerating effect on the catalytic oxidation of alcohols. The regioselectivity of the catalytic system and the use of neat systems under low power MW irradiation were significant factors for energy saving and the sustainability of greener environments; therefore, the catalytic system could be useful for the future.

Supplementary Materials: CCDC 1962610 for **1** contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data to this article can be found online at http://www.mdpi.com/2073-4344/9/12/1053/s1.

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