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Catalytic activity of a benzoyl hydrazone based dimeric dicopper(II) complex in catechol and alcohol oxidation reactions

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ABSTRACT

The benzoyl hydrazone based dimeric dicopper(II) complex $[Cu_2(R)(CH_3O)(NO_3)]_2(CH_3O)_2$ (**R-Cu^{2+}**), recently reported by us, catalyzes the aerobic oxidation of catechols (catechol (S1), 3,5-ditertiarybutylcatechol (S2) and 3-nitrocatechol (S3)) to the corresponding quinones (catecholase like activity), as shown by UV–Vis absorption spectroscopy in methanol/HEPES buffer (pH 8.2) medium at 25 °C. The highest activity is observed for the substituted catechol (S2) with the electron donor tertiary butyl group, resulting in a turnover frequency (TOF) value of 1.13×10^3 h^{-1}. The complex **R-Cu^{2+}** also exhibits a good catalytic activity in the oxidation (without added solvent) of 1-phenylethanol to acetophenone by Bu^{t}OOH under low power (10 W) microwave (MW) irradiation.

1. Introduction

Biological activities are often mediated by specific proteins or enzymes that usually require one or more metal ions which may provide binding sites to the substrates and function as catalytic centers [1–7]. This has motivated attempts to reproduce, at least partially, the catalytic function of metalloenzymes, using low molecular weight dinuclear coordination complexes as models [8–15]. Recent studies have demonstrated that certain enzyme model dinuclear complexes can promote catechol oxidation more efficiently than the mononuclear analogs [12], what encourages the search for other modalities of dinuclear complexes with a high catalytic oxidizing efficiency.

In addition, the development of atom efficient and environmentally benign methods for the catalytic oxidation of alcohols to the corresponding carbonyl compounds (aldehydes or ketones) constitutes an important area of research [16–30], since it leads to the production of added value chemicals and components for the pharmaceutical, agrochemical and perfumery industries. However, most of the protocols [16–19] for the oxidation of alcohols possess several inherent limitations, such as the need for stoichiometric metal containing oxidants, the use of expensive catalysts, additives and solvents, showing also poor substrate versatility and environmental effects [26]. Therefore, the search for alternative alcohol oxidation protocols that use cheap, readily available and efficient catalysts, and can proceed in aqueous or solvent-free medium under mild conditions, constitutes an important aim to be achieved.

In the context of the above objectives, in this paper we report the catalytic activity of the benzoyl hydrazone based dimeric dicopper(II) $[Cu_2(R)(CH_3O)(NO_3)]_2(CH_3O)_2$ (**R-Cu^{2+}**) complex (Scheme 1) derived from a Schiff base chemosensor **R**, which we have recently reported [31], in catechols [catechol (S1), 3,5-ditertiarybutylcatechol (S2) and 3-nitrocatechol (S3)] and alcohol (1-phenylethanol) oxidation reactions.

2. Results and discussion

2.1. Catecholase like activity

Catechol oxidases are type III copper proteins which act as catalysts in the oxidation of catechols to quinones in the presence of molecular oxygen [32]. Many of $Cu^{II}Cu^{II}$ based model complexes with catechol oxidase activity have been described [8–11,33–41]. In this work, the catecholase activity of **R-Cu^{2+}** has been studied with the help of electronic spectroscopy by monitoring the appearance of the wave with the absorbance maximum at ca. 410 nm of the corresponding quinones derived from three different substrates (catechol (S1), 3,5-ditertiarybutylcatechol (S2) and 3-nitrocatechol (S3)) at 25 °C in a methanol/HEPES buffer (pH 8.2) medium (Scheme 2), under air. The spontaneous oxidation of the

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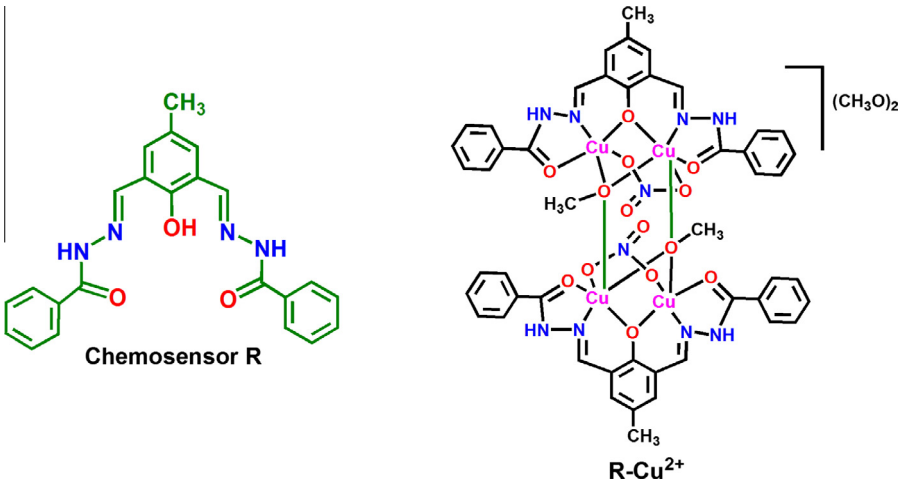
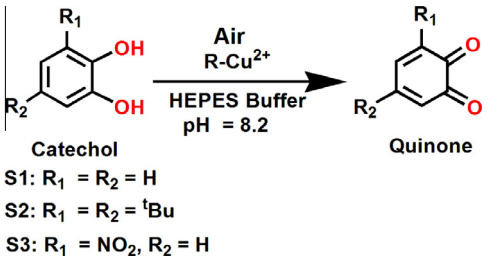


Scheme 1. Molecular structure representations of **R** and **R-Cu^{2+}**.



Scheme 2. Catalytic oxidation of catechols to quinones by **R-Cu^{2+}**.

substrate catechol (S1, S2 and S3), in the absence of the catalyst, does not occur significantly in comparison with that in the presence of **R-Cu^{2+}**.

Initially, pH-dependence studies were undertaken to determine the pH value at which catecholase activity is maximum (Fig. 1). The initial rate value (V_0) was obtained from the slope of the linear plot of the absorbance of the corresponding quinone at 410 nm versus time. The V_0 increased with the pH until 8.2 for all substrates (S1, S2 and S3), beyond which no appreciable change was observed. Therefore the studies were typically performed at this pH. The turnover frequency (k_{cat}) for the formation of quinones (Fig. 2) from these catechols (S1, S2 and S3) was found to be 1.06×10^3, 1.13×10^3 and 983 h^{-1}, respectively (see below).

The initial rates obtained for the range of used substrate [(catechol (S1), 3,5-dtbc (S2) and [3-nitrocatechol (S3)] concentrations were fitted to the Michaelis–Menten equation (Fig. 3) and linearized by means of the Lineweaver–Burk method (Fig. 3B, D and F), and the kinetic parameters are depicted in Table 1. The turnover frequency value for the oxidation of the catechol (S2) with the electron donor tertiary butyl groups (TOF = 1.13×10^3 h^{-1}) is higher than those for simple catechol (1.06×10^3 h^{-1}) and for the electron withdrawing group substituted 3-nitrocatechol (983 h^{-1}). These

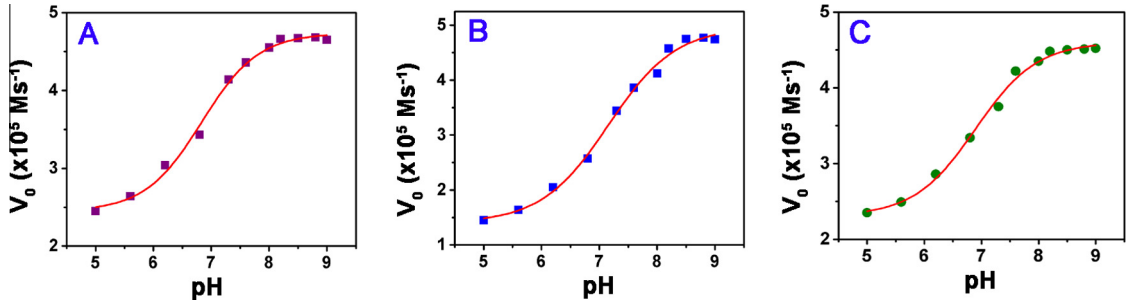


Fig. 1. Dependence of the initial rate on pH for the aerobic oxidation of catechol (A), 3,5-ditertiarybutylcatechol (B) and 3-nitrocatechol (C) catalyzed by **R-Cu^{2+}**.

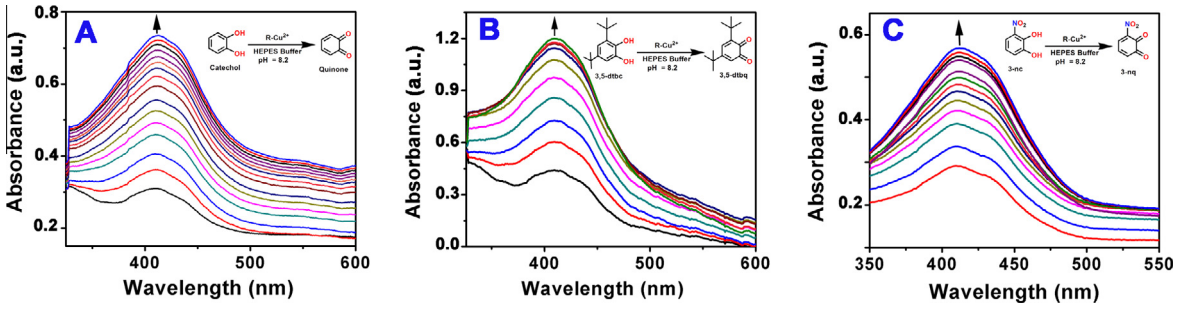


Fig. 2. Oxidation of catechol (A), 3,5-ditertiarybutyl catechol (B) and 3-nitrocatechol (C) catalyzed by **R-Cu^{2+}** in methanol/HEPES buffer (pH 8.2).

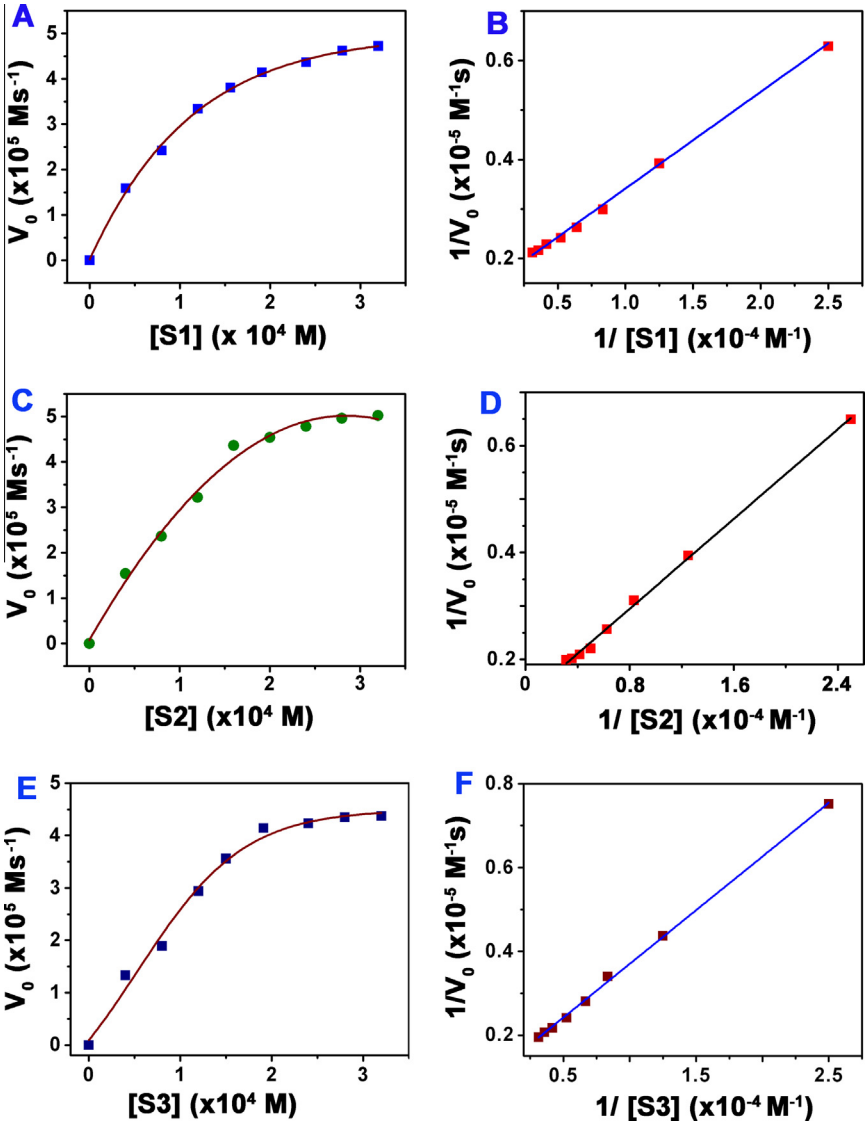


Fig. 3. Dependence of the reaction rate on concentration of the substrate (S1 (A), S2 (C) and S3 (E)) at pH 8.2, in a methanol/HEPES buffer (2:8, v/v) medium, and corresponding Lineweaver–Burk plots (B, D and F). Conditions: [**R-Cu^{2+}**] = 1.6×10^{-6} M; [substrate] = 0.4×10^{-4} – 3.2×10^{-4} M; at 25.0 °C.

Table 1
Michaleis-Menten parameters of oxidation catechol (S1), 3,5-ditertiarybutylcatechol (S2) and 3-nitrocatechol (S3) by **R-Cu^{2+}**.

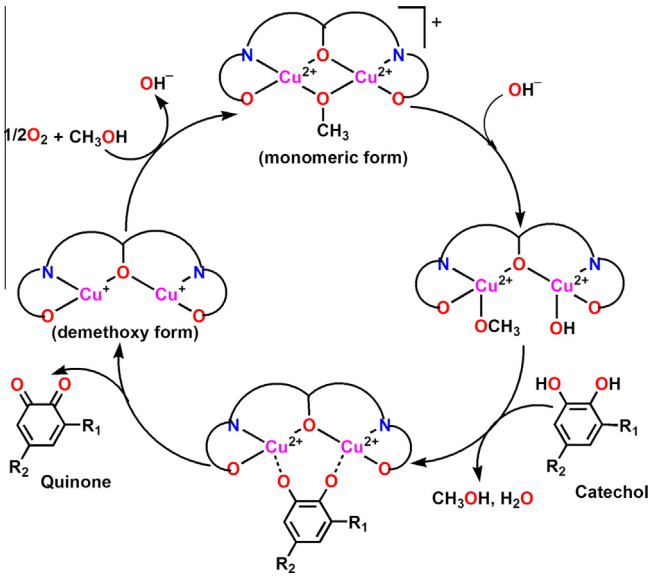
Substrate	K_M (M)	V_{max} (Ms^{-1})	k_{cat} (s^{-1})	TOF (h^{-1})	k_{cat}/K_M ($M^{-1}\,s^{-1}$)
S1	7.16×10^{-5}	4.72×10^{-5}	0.295	1.06×10^3	1.88×10^3
S2	8.14×10^{-5}	5.02×10^{-5}	0.313	1.13×10^3	1.76×10^3
S3	8.28×10^{-5}	4.37×10^{-5}	0.273	983	1.51×10^3

turnover frequency values are higher than those for other μ-OR/μ-RCOO (R = H, alkyl) bridged dicopper(II) complexes described in the literature [8,10,40,41–44]. However, our complex shows a moderate activity compared to the most efficient μ-OH bridged dicopper(II) model catalysts reported to date [45,46].

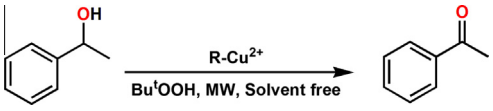
We have also used ^{1}H NMR spectroscopy to ascertain the 3,5-di-*tert*-butyl-1,2-benzoquinone formation. The dicopper(II) complex **R-Cu^{2+}** shows a good conversion of 3,5-dtbc into 3,5-dtbq (isolated yield of 46%) in methanol/HEPES buffer (pH 8.2) (see Section 4).

Thus, the dicopper(II) complex **R-Cu^{2+}** is particularly active in the oxidation of catechols and it can be considered as a functional model for the active site of catechol oxidases. The reason for the remarkable catecholase activity of **R-Cu^{2+}** may be related to the geometry and distance between the Cu centers, which play a preponderant role for the activity. As observed [31] in the X-ray structure of the μ-methoxy complex (**R-Cu^{2+}**) the metallic centers are easily accessible due to the short Cu–Cu distance (2.92 Å), which allows a bridging catechol coordination compatible with the distance between the two *o*-diphenol oxygen atoms. It is noteworthy that the Cu–Cu distance is 2.9 Å in the oxidized enzyme, which is characterized by a μ-hydroxo dicopper(II) active site [47].

On account of the proposed mechanistic steps of catechol oxidase activity of some μ-hydroxy dicopper(II) complexes [8,10,11], we suggest the plausible mechanistic pathway shown in Scheme 3 for catechol oxidation promoted by our complex **R-Cu^{2+}** as follows. We consider the monomeric form of the dicopper(II) complex, i.e. $[Cu_2(R)(OCH_3)(NO_3)]^+$, which is detected in solution by ESI-MS [31]. Upon hydrolysis at high pH, it is expected to form a methoxy and hydroxy complex with the $\{Cu_2(R)(OCH_3)(OH)\}$ site, which by reaction with the catechol leads to an intermediate catecholate complex with the $\{Cu_2(R)(catecholate)\}$ center upon release of methanol and water [11]. Oxidation of the catecholate by electron



Scheme 3. A plausible mechanism for catecholase like activity promoted by **R-Cu^{2+}** (the nitrate ligand is omitted for the sake of clarity).



Scheme 4. Solvent-free oxidation of 1-phenylethanol to acetophenone by **R-Cu^{2+}**.

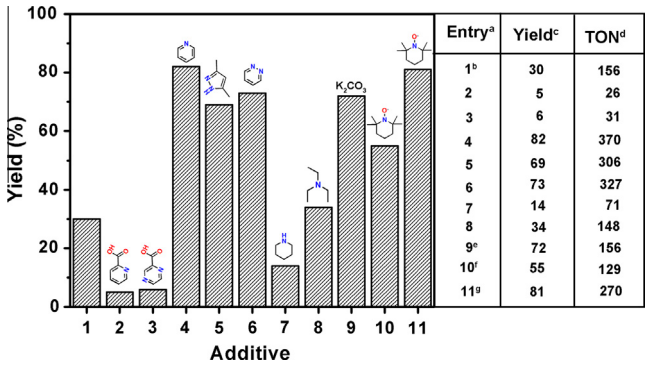
transfer to the two Cu^{2+} centers yields the corresponding orthoquinone which is released. Finally, oxidation of the Cu^{+} centers by O_2 completes the catalytic cycle [47].

2.2. Alcohol oxidation

The investigation of the catalytic properties of the **R-Cu^{2+}** complex was undertaken for the oxidation of 1-phenylethanol to acetophenone using Bu^tOOH (TBHP) (2 eq.) as oxidizing agent, under typical conditions of 80 °C, low power (10 W) microwave (MW) irradiation, 1 h reaction time and in the absence of any added solvent (Scheme 4). Selected results are summarized in Table 1 and Fig. 4. The complex **R-Cu^{2+}** catalyzes moderately the peroxidative oxidation of 1-phenylethanol under a low MW irradiation power (5–10 W), leading to 30% of acetophenone after 1 h at 80 °C of reaction (Table 2, entry 2, for a catalyst/substrate molar ratio of 0.2%). The reaction is very fast, since after 15 min (Table 2, entry 5) a yield of 26% is already reached. After 6 h reaction, acetophenone product yield slightly increases from 30 (for 1 h reaction time) to 37% (for 6 h reaction time) (Table 2, entries 2 and 6, respectively). The chemosensor **R** does not appear to be active under the same reaction conditions (1 h, 80 °C and 5–10 W) (Table 2, entry 11).

The influence of the catalyst amount on the yield and TON was investigated. Its increase results in a yield enhancement, e.g., from 4% to 54% upon changing the amount of catalyst from 0.02 to 1.4 mol% versus substrate (Table 2, entries 1 to 4). As expected, the catalyst amount increase results in a corresponding TON (moles of product/mol of catalyst) lowering from 238 to 66. Blank tests (in the absence of any catalyst) were performed under common reaction conditions and no significant conversion was observed.

The temperature is also an important factor and at 100 °C (after 15 min) a yield of 45% was obtained after 15 min (Table 2, entry 9).



Entry[a]	Yield[c]	TON[d]
1[b]	30	156
2	5	26
3	6	31
4	82	370
5	69	306
6	73	327
7	14	71
8	34	148
9[e]	72	156
10[f]	55	129
11[g]	81	270

Fig. 4. Effects of various additives in the MW-assisted solvent-free peroxidative oxidation of 1-phenylethanol catalyzed by **R-Cu^{2+}**. [a]*Reaction conditions*: 5 mmol of substrate, catalyst **R-Cu^{2+}** (10 μmol, 0.2 mol% vs. substrate), 10 mmol of Bu^tOOH (aq. 70%), 80 °C, 1 h reaction time, microwave irradiation (10 W). [b]Entry 1 corresponds to entry 2 of Table 2. [c]Molar yield (%) *i.e.* moles of acetophenone per 100 mol of 1-phenylethanol, determined by GC. [d]Turnover number = number of moles of product per mol of catalyst. [e]In K_2CO_3 aqueous solution (1 M). [f]In the presence of TEMPO (0.125 mmol). [g]In the presence of TEMPO (0.125 mmol) at 90 °C.

Table 2
Oxidation of 1-phenylethanol using **R-Cu^{2+}** as catalyst precursor.[a]

Entry	Catalyst	Catalyst amount[b] [%]	TON[c]	Yield[d] [%]
1	R-Cu^{2+}	0.02	238	4
2	R-Cu^{2+}	0.2	156	30
3	R-Cu^{2+}	1.0	78	47
4	R-Cu^{2+}	1.4	66	54
5[e]	R-Cu^{2+}	0.2	128	26
6[f]	R-Cu^{2+}	0.2	118	37
7[g]	R-Cu^{2+}	0.2	4	2
8[h]	R-Cu^{2+}	0.2	–	–
9[i]	R-Cu^{2+}	0.02	223	45
10[j]	R-Cu^{2+}	0.2	27	6
11	R	0.4	14	3

[a] *Reaction conditions:* 5 mmol of substrate, 1–70 μmol of catalyst (0.02–1.4 mol% vs. substrate), 10 mmol of TBHP (2 eq.), 80 °C, 1 h reaction time, microwave irradiation (5–10 W).
[b] Catalyst amount as mol% vs. substrate.
[c] Turnover number = number of moles of product per mol of catalyst.
[d] Moles of ketone product per 100 mol of alcohol.
[e] Reaction time of 15 min.
[f] Reaction time of 6 h.
[g] In the presence of Ph_2NH (10 mmol).
[h] In the presence of $CBrCl_3$(10 mmol).
[i] At 100 °C and 15 min reaction time.
[j] 50 °C and 1 h reaction time.

We failed the attempt of performing the oxidation of 1-phenylethanol in the presence of **R-Cu^{2+}** at room temperature, whereas the use of 50 °C resulted in an important ketone yield reduction relatively to that at 80 °C (from 30% at 80 °C to 6% at 50 °C, Table 2, entries 2 and 10, respectively).

The addition to the reaction mixture of Ph_2NH or $CBrCl_3$, well known oxygen- or carbon-radical traps, respectively [48,49], suppresses (or almost) the catalytic activity (Table 2, entries 7 and 8), suggesting the involvement of oxygen and carbon radicals in the reaction, which are trapped by those radical scavengers. The mechanism may involve the metal-assisted generation of $Bu^tOO^{\cdot}$ and $Bu^tO^{\cdot}$ radicals (upon oxidation and reduction of Bu^tOOH by a Cu^{II} or a Cu^{I} center, respectively) [26,50–53] the latter behaving as an H-atom abstractor from the alcohol [26,50,52].

In order to attempt to increase the activity of **R-Cu^{2+}** in the solvent-free MW-assisted peroxidative oxidation of 1-phenylethanol, we have investigated the influence of different additives (co-catalysts) on the acetophenone product yield (Fig. 4). For this purpose, heteroaromatic *N*-based acids, such as 2-pyridinecarboxylic acid

(Hpic) and 2-pyrazinecarboxylic acid (Hpca), or bases such as pyridine, 3,5-dimethyl-1H-pyrazole, pyridazine, piperidine and triethylamine were tested, since they have been reported [54–61] to act as promoters in peroxidative oxidations of cyclic, linear and branched saturated hydrocarbons and alcohols (primary and secondary ones). The heteroaromatic *N*-based acids, Hpic and Hpca, demonstrated an inhibitory effect on the reaction, and e.g. the presence of 200 μM of acid (Hpic and Hpca) ((n(acid)/(n(catalyst **R-Cu^{2+}**)) = 20) results in an important yield drop (5% and 6%, Fig. 4, entries 2 and 3, respectively) compared to the reaction carried out under the same conditions (10 μM of catalyst, 80 °C, MW, 1 h) but in the absence of any additive (30%, Fig. 4, entry 1). A similar inhibitory effect was observed for other Cu(II) systems [59,60].

In contrast, heteroaromatic *N*-based base additives have a beneficial effect on the acetophenone product yield. In fact, the use of 200 μM of a *N*-based base (*n*(base)/(*n*(catalyst **R-Cu^{2+}**)) = 20) results normally in a significant yield increase. The most efficient systems contain pyridine, 3,5-dimethyl-1H-pyrazole or pyridazine leading to the yields of 82%, 69% and 73%, respectively (Fig. 4, entries 4, 5 and 6, respectively). The systems containing triethylamine and piperidine are much less active. However, the use of K_2CO_3 (1 M solution), a *N*-free base, results in a high increase of the conversion of the alcohol to the ketone (72%, entry 9, Fig. 4), comparable to those obtained for pyridazine or 3,5-dimethyl-1H-pyrazole. The role of basic additives, which facilitate the deprotonation of the alcohol, was already observed in other cases [62–69].

The effect of the presence of 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO), a nitroxyl radical that is a known [62–68,70–72] promoter in oxidation catalysis of alcohols, was also evaluated. In accord, a significant yield increase was observed for the 1-phenylethanol oxidation catalyzed by **R-Cu^{2+}**, from 30% in the absence of TEMPO to 55% in its presence (Fig. 4, entries 1 and 10, respectively). The reaction performed at 90 °C and in the presence of TEMPO achieved 81% product yield (Fig. 4, entry 11). The TEMPO promoted reaction conceivably involves its coordination, as well as of the alcohol substrate, followed by Cu-centered oxidative dehydrogenation of the alcohol upon H-abstraction [26–29,71–75]. Our group reported some efficient systems involving alkoxy-1,3,5-triazapentadienate Cu(II) complexes [69], bis- and tris-pyridyl amino and imino thioether Cu complexes [52] for the MW-assisted oxidation of secondary alcohols to the corresponding ketones. The above catalytic systems lead to comparable yields and/or TONs to those of this work. A highly efficient system involving self-assembled dicopper(II) diethanolaminate cores toward (i) the aerobic aqueous medium oxidation of benzyl alcohols, mediated by TEMPO radical, and (ii) the solvent-free oxidation of secondary alcohols to ketones by Bu^{t}OOH under microwave (MW) irradiation was also reported [30]. Recently, a cage-like silsesquioxane based-dicopper(II) complex has been described with a high catalytic activity in the oxidation reactions of benzene and alcohols with peroxides in acetonitrile [76]. Quantitative amount of acetophenone was produced in the oxidation of 1-phenylethanol with Bu^{t}OOH, after 4 h at 50 °C, in the presence of the copper(II) silsesquioxane $[(PhSiO_{1.5})_{10}(CuO)_2(NaO_{0.5})_2(EtOH)_4]$ compound [76].

3. Conclusions

We have designed a new benzoyl hydrazone based dimeric copper(II) complex **R-Cu^{2+}** which displays an efficient catecholase like activity in slightly basic medium. This system also provides an experimental evidence that the proximity of the Cu^{II} centers plays an important role in the two electron aerobic oxidation of the model substrates catechol, 3,5-ditertiarybutyl catechol and 3-nitrocatechol. In addition, the Cu(II) complex shows a good catalytic activity in an important alcohol oxidation with an organoperoxide reaction under added solvent free conditions.

4. Experimental

4.1. Materials and measurements

4.1.1. Catechol oxidation

4.1.1.1. Absorption spectroscopy. The catecholase like activity of the complex described herein has been evaluated under air at 25 °C by reaction with three different substrates (catechol (S1), 3, 5-ditertiarybutylcatechol (S2) and 3-nitrocatechol (S3)). Initially, pH-dependent studies were carried out to determine the pH value at which catecholase-like activity reached a maximum. The influence of the pH on the reaction rate for oxidation of catechol (S1, S2 and S3) catalyzed by complex **R-Cu^{2+}** was determined over the pH range of 5.0–9.5 at 25 °C. To a quartz cell were added 5 μL of a methanolic complex solution ([**R-Cu^{2+}**] = 1.0×10^{-3} M), 195 μL of buffer [MES (pH 5.0–6.5) or HEPES (pH 7.0–9.5)], and 2500 μL of air-saturated methanol. The reaction was initiated with the addition of 300 μL of a methanolic substrate solution ([substrate] = 3.00×10^{-3} M) and monitored for 15 min. The absorption at λ_{max} = 410 nm (ε = 1900 M^{-1} cm^{-1}), characteristic of the formed corresponding quinone, was measured as a function of time on a Perkin-Elmer LAMBDA 750 UV–Vis spectrophotometer. To take into account the spontaneous oxidation of the substrate, correction was carried out using a reference cell under identical conditions but without the addition of the catalyst. The initial rate was obtained from the slope of the absorbance versus time plot over the first 15 min of the reaction. The Michaelis–Menten model was applied and the kinetic parameters were obtained from nonlinear square fits using the program Origin 8.0.

4.1.1.2. ^{1}H NMR spectroscopy. 3,5-Di-*tert*-butyl catechol (43 mg, 0.192 mmol) dissolved in methanol (2 mL) was added to methanol/HEPES buffer (pH 8.2) solution of **R-Cu^{2+}** (2.5 mg, 0.002 mmol) (3 mL) (100:1 ratio of substrate and catalyst). The mixture was stirred for 1 h, and the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (3 × 10 mL). The organic fractions were combined, filtered through Celite, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue (36 mg), as analyzed by ^{1}H NMR spectroscopy in $CDCl_3$ is a mixture of the product 3,5-dtbq (54%) and the substrate 3,5-dtbc (46%). Yield of 3,5-dtbq relative to the starting 3,5-dtbc = 46%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 3,5-dtbc: 6.92 (CH aromatic, s, 1H), 6.78(CH aromatic, s, 1H), 5.48 (OH, s, 1H), 4.90 (OH, s, 1H), 1.44 (CH aliphatic, s, 9H) and 1.29 (CH aliphatic, s, 9H); 3,5-dtbq: 6.91 (CH aromatic, s, 1H), 6.77 (CH aromatic, s, 1H), 1.27 (CH aliphatic, s, 9H) and 1.22 (CH aliphatic, s, 9H).

4.1.2. Alcohol oxidation

Oxidation reactions of the alcohols were carried out in sealed cylindric Pyrex tubes under focused microwave irradiation as follows: the alcohol (5 mmol), catalysts **R** and **R-Cu^{2+}** (1–100 μmol) and a 70% aqueous solution of Bu^{t}OOH (10 mmol) were introduced in the tube. This was then placed in the microwave reactor and the system was left under stirring and under irradiation (10 W) for 0.25–6 h at 80 °C. After cooling to room temperature, 300 μL of benzaldehyde (internal standard) and 5 mL of CH_3CN (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred during 10 min and then a sample (1 μL) was taken from the organic phase and analyzed by GC using the internal standard method.

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