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Research paper

Catalytic oxidation of a model volatile organic compound (toluene) with tetranuclear Cu(II) complexes



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Dedicated to Prof. M. Peruzzini on occasion of his 65th birthday as a recognition of his contribution to science.

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1. Introduction

The hydrocarbons with a high vapour pressure at ordinary room temperature, commonly entitled as volatile organic compounds (VOCs), are major contributors for air pollution, either directly through their toxicity or pungent smelling, or indirectly by generating other pollutants [1]. Benzene, toluene and xylene (BTX) are among the VOCs that are mainly used as common solvents as well as raw materials in the production of other chemicals [2–4]. All these three substances are known to be toxic for human health [5-8]. There are several technologies of VOC elimination such as flame combustion, catalytic combustion, catalytic destruction using ozone and plasma, photocatalytic decomposition, adsorption processes and biological treatments. [9,10,11-16]. Catalytic oxidation is acknowledged as one of the Best Available Techniques (BAT) normally applied in the Large Volume Organic Chemical Industry (LVOC) for the abatement of VOCs owing to its easy application with high efficiency and economically feasibility [17–23]. Apart from the elimination of VOCs, an important motive of catalytic oxidation of aromatic hydrocarbons (BTX) concerns their selective functionalization. The activation of bonds considered practically inert, such as the C-H

ABSTRACT

A tetranuclear Cu(II) cubane $[Cu_2(\mu-1\kappa ONO':2\kappa OO':3\kappa O-HL)(\mu-1\kappa ONO':2\kappa OO'-HL)]_2$ ·4dmf (1) derived form (2,3-dihydroxybenzylidene)-2-hydroxybenzohydrazide (H₃L) was synthesized at room temperature and characterized by elemental analysis, IR spectroscopy, ESI-MS and single crystal X-ray diffraction. The known tetranuclear Cu(II) open-cubane $[Cu(HL)]_4$ ·4EtOH (2) was synthesized from the same pro-ligand following a similar method or the reported one. The different tautomeric forms (*keto* and *enol*) of the organic ligands in 1 and 2 explain their different structural features. Both complexes were screened as catalysts for the peroxidative oxidation of toluene with *tert*-butyl hydroperoxide, achieving benzaldehyde and *o*-cresol as the main products. Complex 1 exhibits the highest activity (maximum product yield of 11%).

bond in alkanes, remains a huge challenge for the scientific community. At the industrial level, activation involving the C—H cleavage usually requires drastic conditions such as high temperatures [24–30]. There has been a considerable effort focusing on the establishment of clean synthetic routes, involving the design and development of new and efficient catalysts for the selective oxidation of hydrocarbons, from environmental and economic points of view [27,31,32]. Possible oxygenated products, such as benzyl alcohol, benzaldehyde, tolualdehyde, cresols, benzoic acid, toluic acid etc., can be useful intermediates for chemicals, agrochemicals, fragrances, pharmaceuticals and polymers manufacture [33–36].

Our group has been involved in developing and exploring the catalytic activity of a variety of transition metal complexes towards catalytic oxidation processes of industrial interest [37–43]. In particular Cu(II) complexes have been chosen for oxidation reactions due to their abundant resources, low cost, non-toxic properties and high catalytic efficiency [44,45]. In fact, Cu(II) species can act as attractive catalysts in the oxidation of aromatic hydrocarbons (BTX) [19–21]. In the present investigation, we have synthesized and characterized a new tetranuclear cubane complex [Cu₂(μ -1 κ ONO':2 κ OO':3 κ O-HL)(μ -1 κ ONO':2 κ OO':

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Scheme 1. Synthetic routes for 1 and 2.

HL]₂·4dmf (1) and the known [Cu(HL)]₄·4EtOH (2) [46]. Both cubanes were tested as catalysts for the peroxidative oxidation of VOCs and their activities were compared. We have chosen toluene as a model substrate for the study and *tert*-butyl hydroperoxide as oxidant achieving benz-aldehyde and *o*-cresol as the main products.

2. Experimental

2.1. Materials and methods

The synthetic part of this study was performed in air. Commercially available reagents and solvents were used as received, without further purification or drying. $Cu(NO_3)_2 \cdot 2.5H_2O$ was used as Cu(II) metal source.

C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Infrared spectra (4000–400 cm⁻¹) were recorded on a Bruker Vertex 70 instrument in KBr pellets; wavenumbers are in cm⁻¹. The ¹H NMR spectra were recorded at room temperature on a Bruker Avance II + 400.13 MHz (UltraShieldTM Magnet) spectrometer. Tetramethylsilane was used as the internal reference and the chemical shifts are reported in ppm. Mass spectra were run in a Varian 500-MS LC Ion Trap Mass Spectrometer equipped with an electrospray (ESI) ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35p.s.i. nebulizer pressure. Scanning was performed from m/z 100 to 1200 in methanol solution. The compounds were observed in the positive mode (capillary voltage = 80-105 V). Gas chromatographic (GC) measurements were carried in a FISONS Instruments GC 8000 series gas chromatograph with a capillary DB-WAX column (30 m \times 0.32 mm) and a FID detector under the following conditions: program 120 °C for 1 min, 10 °C/min, 200 °C for 1 min, injector at 240 °C and helium as the carrier gas. Gas Chromatography-



Scheme 2. Conversion of hazardous toluene in added-value products.

Mass Spectrometry (GC–MS) analyses were performed using a Perkin Elmer Clarus 600C (Shelton, CT, USA) 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 \times 0.25 mm \times 0.25 m).

2.2. Syntheses of the pro-ligand H_{3L}

The aroylhydrazone Schiff base pro-ligand (2,3-dihydroxybenzylidene)-2-hydroxybenzohydrazide (H₃L) (Scheme 1) was prepared following a literature method [46] upon condensation of the 2-hydroxy benzohydrazide with 2,3-dihydroxybenzaldehyde.Scheme 2.

2.3. Synthesis of [Cu₂(μ-1κΟΝΟ':2κΟΟ':3κΟ-HL)(μ-1κΟΝΟ':2κΟΟ'-HL)]₂·4dmf (1)

To a 10 mL DMF solution of H_{3L} (0.272 g, 1.00 mmol), 0.280 g (1.20 mmol) of $Cu(NO_3)_2 \cdot 2.5H_2O$ in 20 mL methanol was added and the reaction mixture was stirred for 30 min at room temperature. The resulting dark green solution was then filtered, and the filtrate was kept in a 100 mL beaker in open air at room temperature for slow evaporation. After 3 days, green crystals suitable for X-ray diffraction analysis were isolated, washed 2 times with cold methanol and dried in open air. The batch sent for microanalysis fits well for two crystallization water molecules per tetramer.

Yield: 72%. Anal. Calcd for (1·4dmf) $C_{68}H_{72}Cu_4N_{12}O_{22}$: C, 49.10; H, 4.36; N, 10.10. Found: C, 49.04; H, 4.31; N, 10.02. IR (KBr; cm⁻¹): 3446 ν (OH), 1609 ν (C=N), 1252 ν (C-O)_{enolic} and 1158 ν (N-N). ESI-MS(+): m/z 1336 [1+H]⁺ (100%).

2.4. Synthesis of [Cu(HL)]₄·4EtOH (2)

Compound **2** was synthesized as reported earlier at 50 $^{\circ}$ C [46], but it can be obtained by following the method described for **1** at room temperature using ethanol instead of methanol as solvent and an excess of pyridine. In this case, ethanol as solvent yielded good quality crystals. The presence of excess of pyridine (base) helps enolization and deprotonation of all coordinated ligands during the complex formation.

To a 30 mL ethanol solution of H_{3L} (0.272 g, 1.00 mmol), 0.280 g (1.20 mmol) of $Cu(NO_3)_2 \cdot 2.5H_2O$ in 10 mL ethanol was added and the reaction mixture was stirred for 20 min at room temperature. To this reaction mixture, 0.10 g (1.2 mmol) of pyridine was added dropwise and the stirring was continued for 10 min. The resulting dark green solution was then filtered, and the filtrate was kept in a 100 mL beaker in open air at room temperature for slow evaporation. Green crystals suitable for X-ray diffraction analysis were isolated in *ca*.3 days, washed 2 times with cold ethanol and dried in open air.

Anal. Calcd for C₅₆H₄₀N₈O₁₆Cu₄ (**2**): C, 50.38; H, 3.02; N, 8.39. Found: C, 50.30; H, 3.05; N, 8.31. IR (KBr; cm⁻¹): 3426 ν (OH). 1606 ν (C=N), 1252 ν (C=O)_{enolic} and 1071 ν (N=N). ESI-MS(+): *m*/*z* 1336 [**1**+H]⁺ (100%).

2.5. X-ray measurements

A poor-quality single crystal of 1 suitable for X-ray diffraction was immersed in cryo-oil, mounted in a Nylon loop and measured at room temperature. Intensity data were collected using a Bruker AXS PHOTON 100 diffractometer with graphite monochromated Mo-K α (λ 0.71073) radiation. Cell parameters were retrieved using Bruker SMART [47] software and refined using Bruker SAINT [47] on all the observed reflections. Absorption corrections were applied using SADABS [48]. The structure was solved by direct methods by using SHELXT2014/5 [49] and refined with SHELXL-2018/3 [50]. Calculations were performed using WinGX version 2018/3 [51]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included at geometrically calculated positions and refined using a riding model. A void of 742 ${\rm \AA}^3$ with 220 electrons was found in the structure by using the SQUEEZE routine of PLATON [52] but the identification of the disordered molecules could not be achieved; such electrons were removed from the model. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms were employed.

2.6. Catalytic studies

Under typical conditions, the peroxidative oxidation reactions were carried out in a glass tube under atmospheric pressure as follows: to 3 mL of acetonitrile (NCMe), 5 mmol of toluene, 10 μ mol of catalyst 1 or 2 and 10 mmol of H₂O₂ (30% aq.) or TBHP (70% aq.) were added and the

Table 1

Crystal data and structure refinement details for complex 1.

	1.4dmf
Empirical formula	C68H68Cu4N12O20
Formula Weight	1627.50
Crystal system	Monoclinic
Space group	C2/c
Temperature/K	296(2)
a/Å	26.58(4)
b/Å	21.76(3)
c/Å	14.060(19)
$\beta /^{\circ}$	102.89(3)
V (Å ³)	7926(18)
Ζ	4
D_{calc} (g cm ⁻³)	1.364
F000	3344
μ (Mo K α) (mm ⁻¹)	1.132
Rfls. collected/unique/observed	66144/ 7618/ 4323
R _{int}	0.1611
Final $R1^{a}$, $wR2^{b}$ $(I \ge 2\sigma)$	0.0741, 0.1716
Goodness-of-fit on F^2	1.022

^a $\mathbf{R} = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|.$

^b wR(F²) = $[\Sigma w(|F_o|^2 - |F_c|^2)^2 / \Sigma w |F_o|^4]^{\frac{1}{2}}$.

reaction mixture was maintained under stirring for 3 h at 80 °C. When HNO₃ was used as an additive, the additive/catalyst molar ratio of 25 or 50 was used. Finally, 90 μ L of cycloheptanone (internal standard) and 10 mL of diethyl ether (for substrate and organic products extraction) were added. The obtained mixture was stirred for 10 min and then an aliquot (1 μ L) from the organic phase was analyzed by GC using the internal standard method. For longer reaction periods, the reaction mixtures were also analyzed by GC–MS to detect possible formation of benzyl benzoate and benzoic acid, among other oxidation products.

3. Results and discussion

The aroylhydrazone Schiff base 2,3-dihydroxybenzylidene-2-hydroxybenzohydrazide (H₃L) [46] was used to synthesize two different tetranuclear Cu(II) compounds, the cubane $[Cu_2(\mu-1\kappa ONO':2\kappa OO':3\kappa O-HL)(\mu-1\kappa ONO':2\kappa OO'-HL)]_2\cdot4dmf$ (1) and the known [46] open-cubane $[Cu(HL)]_4\cdot4EtOH$ (2). The aroylhydrazone exhibits *keto-enol* tautomerism in solution (Scheme 1). Complex formation via deprotonation of the *enol* form in solution is more common and that can be accelerated by increasing the reaction temperature or by addition of a base [43,46,53]. However, in the absence of such a type of accelerating effect, the Cu(II) salt of a base of a strong acid can form an aroylhydrazone-Cu(II) complex in the *keto* form at room temperature [38,54]. In this study, we have synthesized a tetranuclear Cu(II) cubane where the aroylhydrazone is in both *keto* and *enol* forms.

Reaction of H_3L with $Cu(NO_3)_2 \cdot 2.5H_2O$ in the methanol-dmf medium and at room temperature results the formation of cubane **1** (Scheme 1) in

Tabl	e 2	
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Selected bond distances (Å) and angles (°) in complex 1.

	6	•	
N1-N2	1.419(7)	N3-N4	1.423(8)
N1–Cu1	1.953(6)	N3–Cu2	1.909(7)
O1–Cu1	1.987(5)	O2–Cu2	2.056(5)
O2–Cu1	2.007(4)	O4–Cu2	2.301(6)
O6–Cu1	2.023(5)	O5–Cu2	1.994(5)
O7–Cu1	2.340(5)	O6–Cu2 ⁱ	1.998(4)
N1-Cu1-O1	81.8(2)	N3-Cu2-O6 ⁱ	90.6(2)90.6(2)
N1-Cu1-O2	92.16(19)	N3-Cu2-O5	82.5(2)
O1-Cu1-O2	167.52(17)	O5-Cu2-O6 ⁱ	170.5(2)
N1-Cu1-O6	178.01(18)	N3-Cu2-O2	172.5(2)
O1-Cu1-O6	96.64(19)	O6–Cu2–O2 ⁱ	88.87(17)
O2-Cu1-O6	89.64(17)	O5-Cu2-O2	97.16(19)
N1-Cu1-O7	101.72(19)	N3-Cu2-O4	110.8(2)
01-Cu1-07	91.97(18)	O6–Cu2–O4 ⁱ	97.59(19)
O2-Cu1-O7	99.96(18)	O2-Cu2-O4	76.71(17)
O6-Cu1-O7	77.13(16)		



Fig. 1. (a) Thermal ellipsoid plot (drawn at 20% probability level) of the asymmetric unit of complex 1 with partial atom labelling scheme (dmf molecules are omitted for clarity, but their O101 and O201 oxygen atom are indicated). (b) The central cubane structure of 1 showing only the O- and *N*-coordinating atoms. Symmetry code: (*i*) 1-x,y,1/2-z. Hydrogen bonds, represented in dashed cyan colour, d(D - A) and $\angle(D - H - A)$: N2–H2N···O3: 2.639(8) Å, 133°; O4–H4A···O201: 2.728(15) Å, 144°; N4–H4N···O8: 2.610(10) Å, 134°; O4–H/A···O101: 2.669(10) Å, 130°.

good yield. The open-cubane complex **2** can be synthesized at 50 °C according to the literature method [46] or alternatively by following a similar procedure to that of **1** at room temperature but using ethanol and adding an excess of pyridine (Scheme 1). Complex **1** was characterized by elemental analysis, IR spectroscopy, ESI-Mass spectrometry, and single crystal X-ray crystallography. The m/z value at 1336 corresponds to $[1+H^+]^+$ and reveals the tetranuclear core in **1**.

3.1. X-ray structures

Crystals of the compound **1** were obtained from methanol upon slow evaporation, at room temperature. The molecular structure of **1**, crystallographic data and processing parameters are summarized in Table 1 and selected dimensions in Table 2.

Complex **1** crystallizes in the monoclinic system with space group C2/c and the asymmetric unit contains two copper cations, two HL^{2-} organic ligands, and two dmf molecules. Both the Schiff base anions coordinate in the *keto* tautomeric form (Scheme 1) using the O1 and O5 keto atoms, the deprotonated phenoxo atoms O2 and O6 (Fig. 1a), and the phenolic groups O4 and O7. Symmetry expansion revealed the

cubane Cu_4O_4 moiety built from the four phenoxo atoms (Fig. 1b). The Cu1 cations can be considered to be in a $N_{imine}(O_{keto})_1(\mu-O_{phenox})_1$ _o)₃O_{phenol} environment defining a highly distorted octahedron, despite the long Cu1-O2 bond distance (2.768(5) Å³). The Cu2-O6 dimension is even longer (2.849(5) Å³), though shorter than the sum of the van der Waals radii of copper and oxygen (1.40 and 1.52 Å, respectively), and the geometry around this metal cation is perhaps better described as a square pyramid drawn by a Nimine(Oenol)1(µ-Ophenoxo)2Ophenol setting. The remaining Cu–O bond distances (Table 1) range from 1.987(5) to 2.340(5) Å, and the Cu-N distances (1.953(6) and 1.969(6) Å) are slightly shorter than those found in related compounds [46]. The intramolecular Cu-Cu distances range from 3.359(5) to 3.505(5) Å, while the shortest intermolecular one assumes the value of 9.926(1) Å. The structure is stabilized by intramolecular bond interactions involving the NH group and the deprotonated and uncoordinated phenolate O3 and O8 atoms; the most relevant intermolecular H-contacts include the bridging phenolic groups as donors and the Odmf-atoms as acceptors (Fig. 1a).



Fig. 2. Effect of catalyst amount on the yield of the major products of oxidation of toluene (benzaldehyde + benzyl alcohol + *o*-cresol), catalyzed by 1 (a) and 2 (b). Reaction conditions: toluene (5.0 mmol), catalyst precursors 1 or 2 (2.5–20 μ mol), H₂O₂ (30% aq), NCMe (3 mL), 80 °C, n_{acid}/n_{cat} = 25, 3 h reaction time.

Table 3

Yields (benzaldehvde.	benzvl alcohol and	ortho-cresol) for the	e oxidation of toluene	by TBHP or H ₂ O ₂ with	1 or 2 as catalyst precursors.
				1 2 2 2	· · · · · · · · · · · · · · · · · · ·

Entry	Cat.	Ox.	$(n_{acid}/n_{cat})^{b}$	Benzyl alcohol (%) ^c	Benzaldehyde (%) ^c	o-cresol (%) ^c	Total Yield ^d	TON ^e
1	1	H ₂ O ₂	_	0.3	1.7	1.7	3.9	19
2^{f}		H ₂ O ₂	_	0.4	1.9	2.7	4.9	24
3 ^g		H_2O_2	_	-	2.2	3.0	5.2	26
4		H_2O_2	25	_	4.3	3.0	7.3	36
5		H_2O_2	50	_	2.8	3.6	7.3	37
6 ^h		H_2O_2	25	0.4	6.1	_	6.5	130
7 ⁱ		H_2O_2	25	0.7	5.2	_	5.9	59
8 ^j		H_2O_2	25	_	3.3	7.4	10.7	27
9 ^{h, k}		H_2O_2	25	-	0.3	0.3	0.6	3
10 ^{h,1}		H_2O_2	25	_	2.1	3.2	5.3	26
11 ^{h,m}		H_2O_2	25	0.5	3.6	_	4.1	82
12 ^{h,n}		H_2O_2	25	0.5	3.8	_	4.3	87
13		TBHP	-	_	3.1	3.1	6.2	31
14		TBHP	25	1.6	2.8	2.2	6.6	33
15		TBHP	50	0.9	3.0	1.5	5.4	27
16	2	H ₂ O ₂	_	_	2.7	2.9	5.6	28
17 ^f		H_2O_2	_	0.4	2.8	5.7	8.9	48
18 ^g		H_2O_2	_	0.4	2.8	6.5	9.7	44
19		H_2O_2	25	_	5.0	3.0	8.0	40
20		H_2O_2	50	_	4.9	5.2	10.1	51
21^{h}		H_2O_2	25	_	5.5	1.8	7.3	146
22^{i}		H_2O_2	25	_	4.8	4.3	9.1	91
23 ^j		H_2O_2	25	_	3.6	5.2	8.8	22
24 ^{h,k}		H_2O_2	25	_	0.13	-	0.13	0.7
25 ^{h,1}		H_2O_2	25	-	0.9	0.4	1.4	7
26 ^{h,m}		H_2O_2	25	_	3.4	0.04	3.5	70
27 ^{h, n}		H_2O_2	25	_	3.8	0.4	4.3	85
28		TBHP	-	_	1.8	-	1.8	9
29		TBHP	25	-	3.1	1.0	4.1	21
30		TBHP	50	-	3.2	0.9	4.1	21
31	-	H_2O_2	-	-	-	-	-	-

^a Reaction conditions: toluene (5.0 mmol), 10 µmol of catalyst precursor **1** or **2**, H₂O₂ (10 mmol, 30% aq.) or TBHP (10 mmol, 70% aq.), NCMe (3 mL), 80 °C, 3 h reaction time.

^b HNO₃/catalyst molar ratio.

^c Molar yield (%) based on the substrate *i.e.* moles of product (benzaldehyde, benzyl alcohol or *ortho*-cresol) per mole of substrate, determined by GC.

^d Total Yield (%) = (moles of benzaldehyde + benzyl alcohol + ortho-cresol)/100 mol of substrate.

^e Turnover number = (moles of benzaldehyde + benzyl alcohol + *ortho*-cresol)/mol of Cu catalyst.

^f 6 hours reaction.

g 24 hours reaction.

h 2.5 μmol of catalyst.

ⁱ 5 µmol of catalyst.

^j 20 µmol of catalyst.

^k 50 °C.

¹ Room temperature.

^m 5 mmol of oxidant.

ⁿ 20 mmol of oxidant.

3.2. Catalytic studies

The catalytic performance of complexes **1** and **2** was evaluated for the homogeneous oxidation of toluene using H_2O_2 (aq. 30%) or *t*-BuOOH (aq. 70%) as oxidants, in acetonitrile, under typical conditions of 80 °C and 3 h reaction. The Cu(II) complexes **1** and **2** show comparable catalytic performances, achieving an overall yield up to *ca*. 11%.

Under the abovementioned reaction conditions, toluene is oxidized to yield predominantly benzaldehyde and *o*-cresol (the *m* and *p*-cresol isomers were not observed), along with some amount of benzyl alcohol (Scheme 1), indicating the occurrence of both side-chain and ring oxidation. No traces of benzyl benzoate (PhCOOCH₂Ph) were observed, even for longer reaction periods (24 h) thus indicating that hemiacetal formation (PhCH(OH)OCH₂Ph) is not a preferred pathway under the applied conditions [55]. The oxidation of toluene was also investigated in the absence of the Cu(II) metal complexes and under the typical reaction conditions no products were detected significantly.

Fig. 2 shows the effect of the amount of catalyst on the oxidation of toluene. In general, the total yield increases with the catalyst amount. The results also indicate a relationship between the selectivity and the amount of catalyst used. Whereas 1 was found to be selective for

benzaldehyde for lower amounts of catalyst $(2.5-10 \mu mol)$ (entries 1, 6 and 7, Table 3) and *o*-cresol appears as the main product when an increased amount of catalyst (20 µmol) (entry 8, Table 3) is used, for 2 a considerable amount of *o*-cresol is already detected even for low Cu concentrations (entries 21 and 22, Table 3). Benzoic acid, a more oxidized product, is not observed even for the applied highest amount of 1 or 2 (20 µmol) (entries 8 and 23, Table 3, for 1 and 2, respectively) excluding the possibility of oxidation of the aldehyde to acid under these reaction conditions [56].

The effect of the amount and type of oxidant on the oxidation reaction was also investigated considering the reaction conditions of entries 6 and 21 from Table 3 (2.5 µmol and $n_{acid}/n_{cat} = 25$) for 1 and 2, respectively, for comparison. In both cases, the molar ratio 1:2 toluene/ H_2O_2 seems to be the most favourable to produce *o*-cresol (entries 1 and 16, Table 3, for 1 and 2, respectively). For both cases it appears that the production of *o*-cresol relates to the amount of catalyst, since for the lower amount of catalyst (2.5 µmol), the amount of oxidant does not seem to affect its production. For the same amount of catalyst (2.5 µmol) the 1:1 toluene/ H_2O_2 molar ratio favours mostly the formation of ring oxidation products such as benzyl alcohol and benzaldehyde (entries 11 and 26, Table 3, for 1 and 2, respectively) and for a 1:2 M ratio the



Fig. 3. Effect of reaction time on the yield of the major products of oxidation of toluene (benzaldehyde + benzyl alcohol + o-cresol), catalysed by 1 (a) and 2 (b). Reaction conditions: toluene (5.0 mmol), catalyst precursors 1 or 2 (10 μ mol), H₂O₂ (30% aq), NCMe (3 mL), 80 °C, n_{acid}/n_{cat} = 25, reaction time = 3, 6 or 24 h.

amount of benzaldehyde almost doubles (entries 6 and 21, Table 3, for 1 and 2, respectively), whereas a high excess of oxidant (1:4 toluene/ H_2O_2 molar ratio) (entries 12 and 27, Table 3, for 1 and 2, respectively) reduced the formation of the less oxidized products (benzyl alcohol and benzaldehyde) with the formation of benzoic acid (detected by GC–MS), probably due to the overoxidation of the benzaldehyde formed from benzyl alcohol oxidation [55,57].

Fig. 3 shows the influence of reaction time on the product yields and selectivities for the periods of 3, 6 and 24 h (10 μ mol of 1 or 2). When the reaction time is extended from 3 to 24 h, the yield of benzaldehyde increases slightly in the presence of 1 and keeps almost unchanged in the presence of 2, whereas the amount of *ortho*-cresol increases continuously in both cases (*e.g.*, in the presence of 2 it increases *ca*. 97% (from 2.9 to 5.7%) from 3 to 6 h reaction. In the case of 2 and for longer reaction periods, residual amounts of benzoic acid were detected probably due to the overoxidation of benzaldehyde since by using benzaldehyde as starting material and under the same reaction conditions just benzoic acid was formed [56].

Considering the previously recognized promoting effect of an acidic medium on the peroxidative oxidation of toluene [58], the presence of an acid additive was explored. Among the tested acids, such as pyridine-4-carboxylic acid (HPCA), trifluoroacetic acid (TFA) and nitric acid (HNO₃), the last two were equivalent and their effect was more expressive. The presence of the acid additive resulted in an improvement in the total yield and amount of produced *o*-cresol (entries 1, 4 and 5 for 1, and 16, 19 and 20 for **2**, Table 3).

The mechanism of this reaction is believed [59–62] to start with the formation of oxygen-based radicals HOO' and HO' (upon oxidation or reduction of the oxidant H_2O_2 involving the Cu^{2+}/Cu^+ redox pair), which can abstract an H atom from toluene (PhCH₃) to form the benzyl radical PhCH₂ that by reaction with O_2 leads to the PhCH₂OO' peroxyl radical. The peroxyl radical may abstract hydrogen from PhCH₃ and give rise to PhCH₂OOH, whereas PhCHO and PhCH₂OH can be produced by metal-assisted reduction of PhCH₂OO' (for PhCHO) or through PhCH₂OO' dismutation leading to PhCHO and PhCH₂OH (plus O_2). On the other hand, the H atom abstraction may occur at the aromatic ring to form an aromatic radical which may react with oxygen-based radicals producing cresoxy radicals. The resonance stabilized cresoxy radicals upon combination with H-atoms give cresols [63,64].

Our catalytic system can be compared to other Cu-based catalytic systems reported previously, and we can essentially highlight its selectivity for the toluene oxidation products, benzaldehyde and *ortho*-cresol isomer. Wang *et al.* conducted the liquid phase oxidation of toluene with molecular oxygen (1.0 MPa) and in the presence of pyridine (to avoid the overoxidation of benzaldehyde to benzoic acid) over heterogeneous catalysts of copper-based binary metal oxides achieving 7% conversion of toluene (86% selectivity for benzaldehyde) at 463 K after 2 h [65]. More recently, Acharyya et al. reported a toluene conversion of 57.5%

with high selectivity towards benzaldehyde after 10 h over a CuCr₂O₄ spinel nanoparticles catalyst (0.1 g) and using H₂O₂ (50% aq. solution) as oxidant [66]. Djinović et al. reported the production of CO₂ and water from the oxidation of toluene at high temperature (270–480 °C) in the presence of Cu-Fe functionalized disordered mesoporous silica catalysts. Under the applied reaction conditions, products of partial oxidation (benzaldehyde and benzoic acid) were not detected [67]. The predominance of ring-oxidation products (cresols) as well as the high selectivity for *o*-cresol isomer was also observed in the toluene oxidation with 30% aqueous H₂O₂ catalyzed by vanadium(V)-substituted polyoxometalates, at 80 °C for 3 h [68].

4. Conclusions

А novel tetranuclear Cu(II) cubane complex [Cu₂(u-1κONO':2κOO':3κO-HL)(μ-1κONO':2κOO'-HL)]2·4dmf (1) derived from (2,3-dihydroxybenzylidene)-2-hydroxybenzohydrazide (H₃L) is reported. Compound 1 is neutral as confirmed by X-ray crystallography, as the previously reported open-cubane [Cu(HL)]₄·4EtOH (2). Both copper (II) complexes were tested successfully as catalysts for the oxidation of toluene, used as a model substrate for the oxidative conversion of toxic VOCs to added value chemical products. Under the explored experimental conditions, both side-chain and ring oxidations occur, with formation of benzaldehyde and ortho-cresol as the main products. This study emphasizes the easy conversion of VOCs to valuable compounds by easy single-pot catalytic oxidations.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

CCDC 2053025 for **1**.4dmf contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.

ac.uk/data request/cif. Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2021.120314.

References

- [1] J.A. Horsley Catalytica Environmental Report No. E4, Catalytica Studies Division, Mountain View. 1993, CA, USA.
- [2] T. Cai, H. Huang, W. Deng, Q.G. Dai, W. Liu, X.Y. Wang, Appl. Catal. B. 166 (2015) 393-405.
- [3] S.A.C. Carabineiro, X. Chen, O. Martynyuk, N. Bogdanchikova, M. Avalos-Borja, A. Pestryakov, B. Tavares, J.J.M. Orfao, M.F.R. Pereira, J.L. Figueiredo, Catal. Today 244 (2015) 103-114.
- [4] J.L. Zeng, X. Liu, L.J. Wan, H.L. Lv, T.Y. Zhu, J. Mol. Catal. A: Chem. 408 (2015) 221-227
- [5] A. Jones, Atmos. Environ. 33 (1999) 4535-4564.
- [6] F.I. Khan, A.K. Ghoshal, J. Loss Prevent. Proc. 13 (2000) 527-545.
- [7] R. Balzer, V. Drago, W.H. Schreiner, L.F.D. Probst, J. Braz. Chem. Soc. 25 (2014) 2026-2031.
- [8] R. Balzer, L.F.D. Probst, V. Drago, W.H. Schreiner, H.V. Fajardo, Braz. J. Chem. Eng. 31 (2014) 757.
- [9] A.G.M. da Silva, H.V. Fajardo, R. Balzer, L.F.D. Probst, A.S.P. Lovon, J.J. Lovon-Quintana, G.P. Valenca, W.H. Schreine, P.A. Robles-Dutenhefner, J. Power Sources 285 (2015) 460.
- [10] A.G.M. da Silva, T.S. Rodrigues, T.J.A.: Slater, F.A. Lewis, R.S. Alves, H.V. Fajardo, R. Balzer, A.H.M. da Silva, I.C. de Freitas, D.C. Oliveira, J.M. Assaf, L.F.D. Probst, S. J. Haigh, P.H.C. Camargo, ACS Appl. Mater. Interfaces 7 (2015) 25624-25632.
- [11] W.X. Tang, G. Liu, D.Y. Li, H.D. Liu, X.F. Wu, N. Han, Y.F. Chen, Sci. China Chem. 58 (2015) 1359-1366.
- [12] Z. Jiang, M.X. Chen, J.W. Shi, J. Yuan, W.F. Shangguan, Catal. Surv. Asia 19 (2015) 1 - 16.
- [13] O.H. Trinh, S.B. Lee, Y.S. Mok, J. Hazard, Mater. 285 (2015) 525-534.
- [14] C. Zhang, H. Cao, C. Wang, M. He, W. Zhan, Y. Guo, J. Hazard. Mater. 402 (2021).
- [15] C. Zhang, Y. Wang, G. Li, L. Chen, Q. Zhang, D. Wang, X. Li, Z. Wang, Appl. Surf. Sci. 532 (2020).
- [16] K. Zeng, Z. Wang, D. Wang, C. Wang, J. Yu, G. Wu, Q. Zhang, X. Li, C. Zhang, X. S. Zhao, Catal. Today (2020), https://doi.org/10.1016/j.cattod.2020.05.043.
 [17] P. Gélin, M. Primet, Appl. Catal. B: Environ. 39 (2002) 1–37.
- [18] J.R.; González-Velasco, A. Aranzabal, J.I. Gutiérrez-Ortiz, R. López-Fonseca, M.A. Gutiérrez-Ortiz, Appl. Catal. B: Environ. 19 (1998) 189-197.
- [19] M. Sutradhar, E.C.B.A. Alegria, T. Roy Barmana, F. Scorcelletti, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Mol. Catal. 439 (2017) 224-232.
- [20] M. Sutradhar, T. Roy Barman, E.C.B.A. Alegria, M.F.C. Guedes da Silva, C-M. Liu, H-Z. Kou, A.J.L. Pombeiro, Dalton Trans. 48 (2019) 12839-12849.
- [21] M. Sutradhar, T. Roy Barman, E.C.B.A. Alegria, H.M. Lapa, M.F.C. Guedes da Silva, A.J.L. Pombeiro, New J. Chem. 44 (2020) 9163-9171.
- [22] M. Sutradhar, T. Roy Barman, A.J.L. Pombeiro, L.M.D.R.S. Martins, Molecules 24 (2019) 47 (1-12).
- [23] H. Falcke, S. Holbrook, I. Clenahan, A. L. Carretero, T. Sanalan, T. Brinkmann, J. Roth, B. Zerger, S. Roudier, L. D. Sancho, Best Available Techniques (BAT) Reference Document for the Production of Large Volume Organic Chemicals; EUR 28882 EN; Publications Office of the European Union, Luxembourg, 2017, ISBN 978-92-79-76589-6, doi:10.2760/77304, JRC109279.
- [24] S.-J. Li, Y.-G. Wang, Tetrahedron Lett. 46 (2005) 8013-8015.
- [25] A. Gunay, K.H. Theopold, Chem. Rev. 110 (2010) 1060-1081.
- [26] J.-B. Feng, X.-F. Wu, Appl. Organometal. Chem. 29 (2015) 63-86.
- A.J.L. Pombeiro, M.F.C. Guedes da Silva (Eds.), Alkane Functionalization, Wiley, [27] Hoboken, NJ, 2019. [28] A.J.L. Pombeiro, Alkane Functionalization: Introduction and Overview, in: Alkane
- Functionalization, A.J.L. Pombeiro, M.F.C Guedes da Silva, (Eds.), Wiley & Sons, Hoboken, NJ, 2019, Chapter 1, pp. 1-15.
- A.E. Shilov, G.B. Shul'pin, Chem. Rev. 97 (1997) 2879-2932. [29]
- [30] G.B. Shul'pin, Org. Biomol. Chem. 8 (2010) 4217-4228.
- [31] H.R. Mardani, H. Golchoubian, J. Mol. Catal. A Chem. 259 (2006) 197-200.
- [32] L.I. Matienko, L.A. Mosolova, G.E. Zaikov, Russ. Chem. Rev. 78 (2009) 211-230. [33] A. Bottino, G. Capannelli, A. Comite, R. Di Felice, Catal. Today 99 (2005) 171-177.

- [34] K. Gauli, R.N. Ram, H.P. Soni, J. Mol. Catal. A: Chem. 242 (2005) 161-167.
- [35] H. Gao, G.W. Chen, Q. Yuan, H.Q. Li, Catal. Today. 110 (2005) 171-178.
- [36] M.A. Gonzalez, S.G. Howell, S.K. Sikdar, J. Catal. 183 (1999) 159-162.
- [37] M. Sutradhar, L.M.D.R.S. Martins, M.F.C. Guedes, da, Silva, A.J.L. Pombeiro, Appl., Catal. A: Gen. 493 (2015) 50-57.
- [38] M. Sutradhar, L.M.D.R.S. Martins, M.F.C. Guedes da Silva, E.C.B.A. Alegria, C.-M. Liu, A.J.L. Pombeiro, Dalton Trans. 43 (2014) 3966-3977
- [39] M. Alexandru, M. Cazacu, A. Arvinte, S. Shova, C. Turta, B.C. Simionescu, A. Dobrov, E.C.B.A. Alegria, L.M.D.R.S. Martins, A.J.L. Pombeiro, V.B. Arion, Eur. J. Inorg. Chem. (2014) 120–131.
- [40] M.-F. Zaltariov, M. Alexandru, M. Cazacu, S. Shova, G. Novitchi, C. Train, A. Dobrov, M.V. Kirillova, E.C.B.A. Alegria, A.J.L. Pombeiro, V.B. Arion, Eur. J. Inorg. Chem. 29 (2014) 4946-4956.
- [41] M. Sutradhar, E.C.B.A. Alegria, K.T. Mahmudov, M.F.C. Guedes da Silva, A.J. . Pombeiro, RSC Adv. 6 (2016) 8079-8088.
- [42] M. Sutradhar, L.M.D.R.S. Martins, S.A.C. Carabineiro, M.F.C. Guedes da Silva, J.G. Buijnsters, J.L. Figueiredo, A.J.L. Pombeiro, ChemCatChem. 8 (2016) 2254-2266.
- [43] M. Sutradhar, E.C.B.A. Alegria, M.F.C. Guedes da Silva, L.M.D.R.S. Martins, A.J. L. Pombeiro, Molecules 21 (2016) 425.
- [44] S.E. Allen, R.R. Walvoord, R.P. Salinas, M.C. Kozlowski, Chem. Rev. 113 (2013) 6234-6458
- [45] M. Sutradhar, L.M.D.R.S. Martins, M.F.C. Guedes da Silva, A.J.L. Pombeiro in: A.J. L. Pombeiro, M.F.C Guedes da Silva, (Eds.), Alkane Functionalization, Wiley, Hoboken, NJ, 2019, ch 16, pp 319-336.
- [46] M. Sutradhar, M.V. Kirillova, M.F.C. Guedes da Silva, C.-M. Liu, A.J.L. Pombeiro, Dalton Trans. 42 (2013) 16578-16587.
- [47] Bruker, APEX2, Bruker AXS Inc., Madison, Wisconsin, USA, 2012.
- [48] G.M. Sheldrick, SADABS. Program for Empirical Absorption Correction. University of Gottingen, Germany, 2000.
- [49] M. George, Sheldrick, SHELXT Integrated space-group and crystal structure Determination, Acta Cryst. A71 (2015) 3-8.
- [50] G.M. Sheldrick (2015) Crystal structure refinement with SHELXL, Acta Cryst., C71, 3-8 (Open Access). https://doi.org/10.1107/S2053229614024218.
- [51] L.J. Farrugia, J. Appl. Crystallogr. 45 (2012) 849-854.
- [52] A.L. Spek, Acta Crystallogr., Sect. C 71 (2015) 9-18.
- [53] M. Sutradhar, L.M.D.R.S. Martins, M.F.C. Guedes da Silva, K.T. Mahmudov, C.-M. Liu, A.J.L. Pombeiro, Eur. J. Inorg. Chem. (2015) 3959-3969.
- [54] M. Sutradhar, E.C.B.A. Alegria, M.F.C. Guedes da Silva, C.-M. Liu, A.J.L. Pombeiro, Molecules 23 (2018) 2699.
- [55] M.I.B. Saiman, G.L. Brett, R. Tiruvalam, M.M. Forde, K. Sharples, A. Thetford, R. L. Jenkins, N. Dimitratos, J.A. Lopez-Sanchez, D.M. Murphy, D. Bethell, D. J. Willock, S.H. Taylor, D.W. Knight, C.J. Kiely, G.J. Hutchings, Angew. Chem. Int. Ed. 51 (2012) 1-6
- [56] X. Wang, J. Wu, M. Zhao, G. Yufen Lv, C.Hu Li, J. Phys. Chem. C 113 (2009) 14270-14278.
- [57] M. Nawab, S. Barot, R. Bandyopadhyay, New J. Chem. 43 (2019) 4406-4412. [58] H.M. Lapa, M.F.C. Guedes da Silva, A.J.L. Pombeiro, E.C.B.A. Alegria, L.M.D.R.
- S. Martins, Inorg. Chim. Acta 512 (2020). [59] M.V. Kirillova, M.L. Kuznetsov, Y.N. Kozlov, L.S. Shul'pina, A. Kitaygorodskiy, A.J.
- L. Pombeiro, G.B. Shul'pin, ACS Catal, 1 (2011) 1511-1520.
- [60] G.B., Shul'pin,, J. Mol. Catal. A: Chem. 189 (2002) 39-66.
- [61] G.B. Shul'pin, C. R. Chim. 6 (2003) 163-178.
- [62] Y.N. Kozlov, G.V. Nizova, G.B. Shul'pin, J. Phys. Org. Chem. 21 (2008) 119-126.
- [63] F. Battin-Leclerc, Prog. Energy Combust. Sci. 34 (2008) 440-498.
- [64] M.D. Boot, M. Tian, E.J.M. Hensen, S.M. Sarathy, Prog. Energy Combust. Sci. 60 (2017) 1-25.
- [65] F. Wang, J. Xu, X. Li, J. Gao, L. Zhou, R. Ohnishi, Adv. Synth. Catal. 347 (2005) 1987-1992
- [66] S.S. Acharyya, S. Ghosh, R. Tiwari, B. Sarkar, R.K. Singha, C. Pendem, T. Sasakib, R. Bal, Green Chem. 16 (2014) 2500-2508.
- [67] P. Djinovića, A. Ristića, T. Žumbara, V.D.B.C. Dasireddya, M. Rangusa, G. Dražića, M. Popovab, B. Likozara, N.Z. Logara, N.N. Tušar, Appl. Catal. B: Environ. 268 (2020)
- [68] K. Nomiya, K. Hashino, Y. Nemoto, M. Watanabe, J. Mol. Catal. A: Chem. 176 (2001) 79-86.