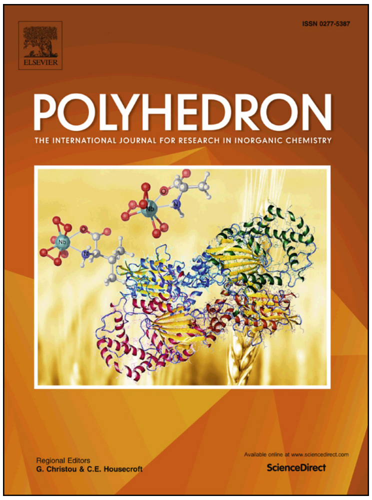

Copper(I) and copper(II) metallacycles as catalysts for microwave assisted selective oxidation of cyclohexane

Rossana Galassi, Oumarou Camille Simon, Alfredo Burini, Giorgio Tosi, Carla Conti, Claudia Graiff, Nuno M.R. Martins, M. Fátima C. Guedes da Silva, Armando J.L. Pombeiro, Luísa M.D.R.S. Martins

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COPPER(I) AND COPPER(II) METALLACYCLES AS CATALYSTS FOR MICROWAVE ASSISTED SELECTIVE OXIDATION OF CYCLOHEXANE

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Abstract: New copper(I) and copper(II) pyrazolate compounds have been prepared by similar synthesis procedures. For the 3,5-NO_2-pyrazole ligands, the dinuclear cyclic Cu(I) compound $[Cu_2(\mu\text{-}N,N\text{-}3,5\text{-}(NO_2)_2pz)_2(PPh_3)_2]$, **1**, was the only compound isolated in high yield, while in the case of the 3,5-bis(trifluoromethyl)-pyrazole ligand a spontaneous rearrangement to the hexanuclear cyclic $[trans\text{-}Cu_6(\mu\text{-}OH)_6(\mu\text{-}3,5\text{-}(CF_3)_2pz)_6]$, **2**, was observed. The formation of this latter compound ruled out an anion templating mechanism for the synthesis. X-ray diffraction analysis of **1** revealed that the copper cation is in a trigonal environment and involved in a six-membered Cu_2N_4 core; while the structural analysis of **2** showed that the metal adopts a square-planar geometry, forms five-membered Cu_2N_2O rings and ultimately gives rise to a large $Cu_6(N_2O)_6$ crown-type assembly. Compounds **1** and **2** act as very effective homogeneous catalysts towards the neat microwave (MW) assisted peroxidative (with aq. tert-butyl hydroperoxide, TBHP) oxidation of cyclohexane to cyclohexanol and cyclohexanone (total yield up to 58% in 30 min reaction time) via formation of cyclohexyl hydroperoxide (CyOOH) as the primary product.

Introduction

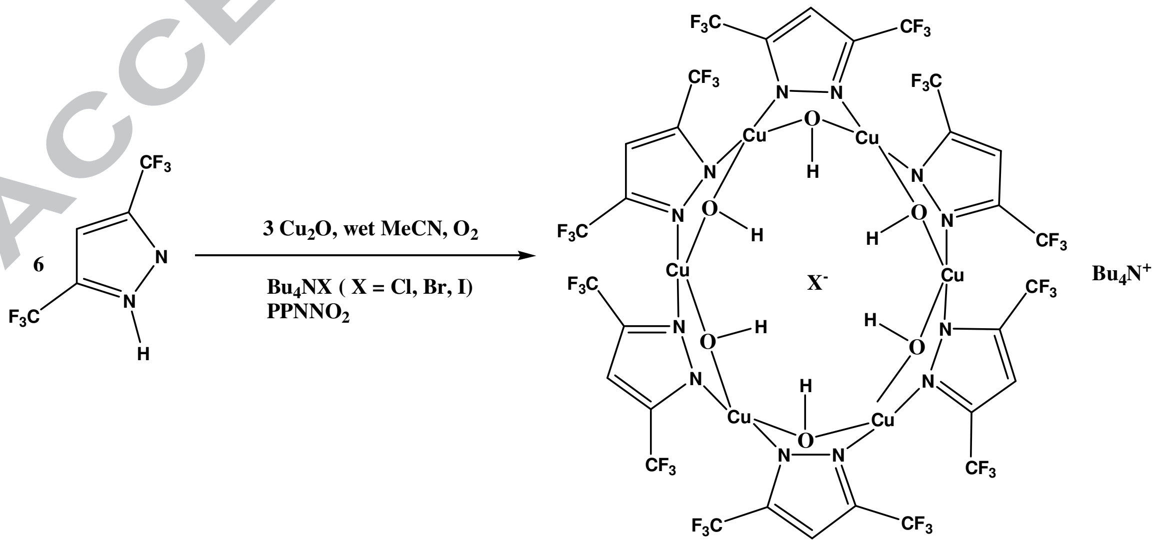
The coordination chemistry of polynuclear Cu(I) and Cu(II) compounds with N-donor ligands provides a wide number of complexes which are relevant in many areas such as catalysis [1], bioinorganic chemistry [2], materials chemistry [3] and molecular magnetism [4]. The above-mentioned areas are strictly related to each other. In fact, copper(II) ions are active catalysts in the oxidation of water to molecular oxygen [1] and copper(II) 1,10-phenanthroline complexes are involved in the aerobic oxidation of primary alcohols; moreover, dinuclear copper(II) proteins, such as hemocyanins, tyrosinase and catechol oxidase, activate molecular oxygen by a "side-on" bridging binding mode [2b], providing different biological functions: the (oxygen transport, ortho-hydroxylation of phenols with further oxidation of the cathecol product to o-quinone or the enantioselective oxidation of DOPA, DihydrOxyPhenylAlanine) [1e]. It is clear that the enzymatic catalysis of oxidations is largely based on cooperativity between the metal center and functional organic ligands located in its surroundings. As a consequence, a strategy on the design of copper based catalysts for oxidation reactions should consider a biomimetic approach [5]. The synthesis of bioinspired copper pyrazolate metallacycles may proceed by spontaneous self-assembly of deprotonated ligands and Cu(II) salts or Cu(I) oxide [6], by templating syntheses [7] or by rearrangements of polynuclear copper(I) compounds to copper(II) derivatives [3c,8]. In the last case, the reaction of a trinuclear Cu(I) metallacycle, depicted as $[\mu\text{-Cu-N,N-3,5-pz}(CF_3)_2]_3$, where $3,5\text{-}(CF_3)_2$-pz is 3,5-bis(trifluoromethyl)pyrazolate, with a halide source such as $[Bu_4N]X$ or $PPNNO_2$ ($[Bu_4N]$ = tetrabutyl ammonium, PPN = phosphoranylamide, X = Cl, Br or I) or Ph_3PAuCl, led to the formation of anion encapsulated adducts in a 1:1 mole ratio [3c,4c] The X-ray diffraction analyses revealed for all these compounds a core containing a hexanuclear copper(II) ring bridged by six hydroxyl groups and six pyrazolate ligands. The mechanism leading to the $Cu_6O_6N_6$ metal framework is not very clear and it was hypothesized that the anions could template the formation of the hexanuclear cycle.

The first aim of this work was to investigate the mechanism leading to the synthesis of such complexes. Moreover, to center this target, the synthesis has been extended to a similar pyrazolate ligand, having nitro groups in the 3,5 positions. Further, the catalytic activity of the obtained compounds towards the peroxidative oxidation of cyclohexane was tested. This reaction was selected as an alkane oxidation model due to its industrial and economical importance, in view of the significance of the oxidized products (cyclohexanol and cyclohexanone) for the manufacture of adipic acid and caprolactam (precursors to Nylon-6,6 and polyamides). Moreover, the current industrial process for cyclohexane oxidation requires 15 bar O_2, 160 ºC and leads to very low conversions (ca. 4%) to assure a reasonable selectivity (ca. 85%) [9]. Therefore, there is an urgent need to design selective and effective catalytic processes for cyclohexane oxidation under mild and solvent-free conditions, with environmentally benign oxidants [10] and, in this respect, a promising approach is presented herein.

Results and discussion

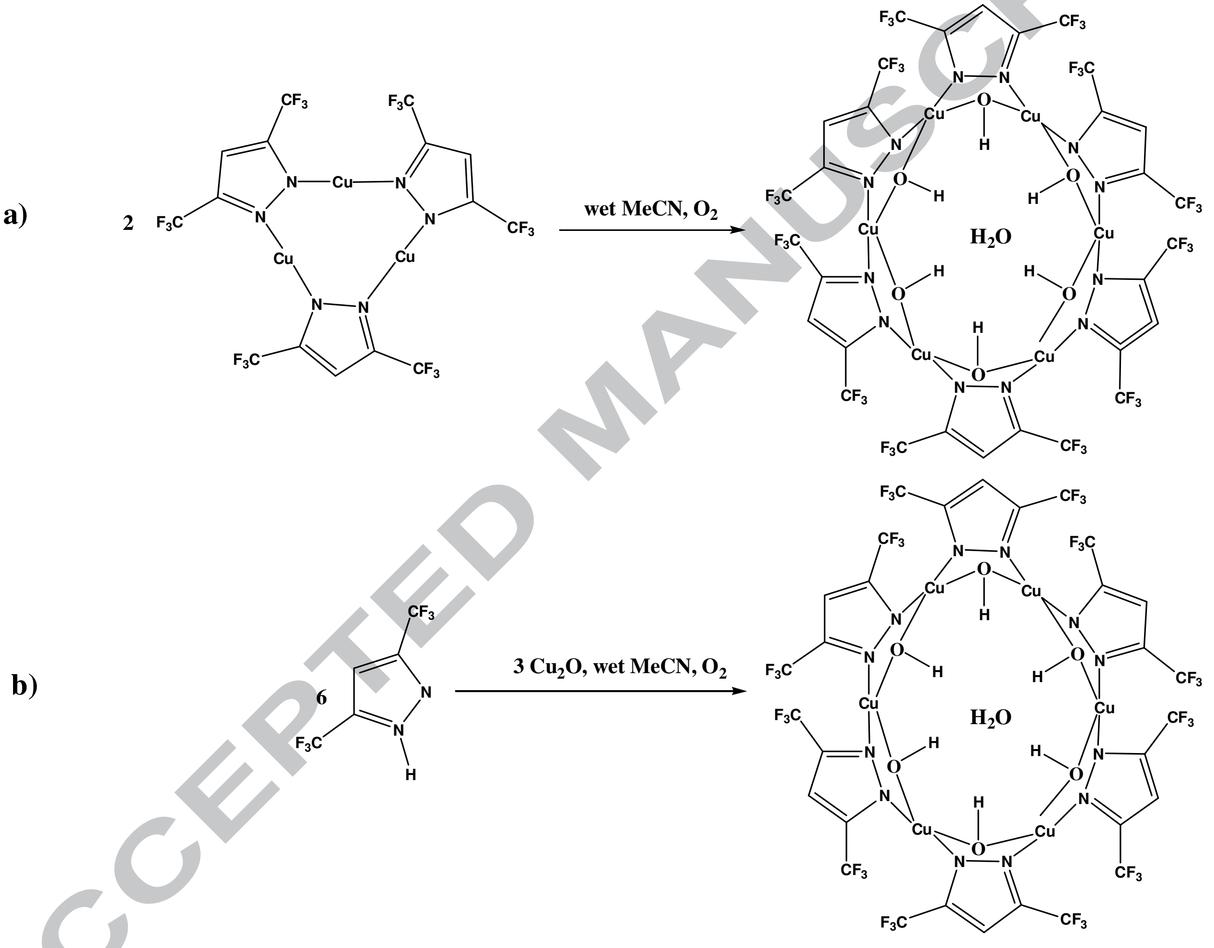
Syntheses. A general method for the formation of pyrazolate copper metallocycles proceeds by pyrazole deprotonation (by a base such as OH^-, O_2^-, H-, etc.) and the reaction with metal ion sources (i.e. Cu(I) halides, $[Cu(CH_3CN)_4]BF_4$, Cu_2O, etc.). In the case of 3,5-dinitro-pyrazole, the syntheses were attempted with the aim to obtain trinuclear and/or hexanuclear compounds according to the already reported reaction methods [3c,4c,6a,6b], though neither the trinuclear nor the hexanuclear complexes were obtained. This pyrazole holds withdrawing groups in the 3,5 positions, but the stronger withdrawing power of the nitro groups with respect to CF_3 groups seems not to allow the cyclization arrangement. On the other hand, the reaction of the 3,5-dinitropyrazole sodium salt with $Cu(BF_4)_2$ in the presence of PPh_3 affords the compound $[Cu_2(\mu\text{-N,N-3,5-}(NO_2)_2pz)_2(PPh_3)_2]$ **1**, an orange crystalline solid, the characterization of which showed two copper(I) centers bound to two pyrazole ligands and to PPh_3 co-ligands in a syn geometry, forming a cyclic dinuclear compound. The phosphane had the function to reduce the Cu(II) ions to Cu(I) ions and to satisfy the coordination requirements of the metal center, affording to a cycle where two pyrazole ligands bridge the metal centers. ESI MS, VT ^{1}H NMR, ^{31}P NMR and X-ray diffraction analyses of **1** underline a pretty stable boat shaped hexa-membered $N_2Cu_2N_2$ cycle with the phosphane ligand bound to the metal centers, given the + 7 ppm shift from the that of free PPh_3.

In the case of 3,5-(trifluoromethyl)pyrazole, the synthesis of the metallocyclic copper(II) derivatives has already been reported and, as it concerns a hexanuclear compound, it consists of a two step procedure [3c,4c]. The first step is the preparation of the trinuclear cyclic Cu(I) derivative by starting from the neutral pyrazole, $(CF_3)_2PzH$, and Cu_2O in an oxygen free environment, followed by conversion of the Cu(I) trinuclear derivative to the hexanuclear complex upon treatment with $[Bu_4N]X$ (X = Cl, Br or I) or $PPNNO_2$ in wet acetonitrile and in the presence of air. A synthetic mechanism through the template action of anions was proposed for these metallocycles [4c]. In this regard, the direct reaction of 3,5-bis(trifluoromethyl)pyrazole, Cu_2O and anion sources in a 6:3:1 molar ratio yielded compounds **2a**-**d** according to reaction Scheme 1.



Scheme 1. Reaction scheme for the direct synthesis of compounds **2a**-**d** with different anions starting from the neutral 3,5-$(CF_3)_2$-pyrazole ligand.

Compounds **2a**-**d** were characterized by elemental analysis, ^{1}H and ^{19}F NMR, IR, UV-visible spectroscopy and ESI MS spectrometry, and the data obtained were compared to those previously reported [3c]. This direct reaction was then repeated in the absence of any anion source, both starting from $[Cu\text{-}\mu\text{-}3,5(CF_3)_2pz)]_3$ and from the bare $3,5(CF_3)_2pz\text{-}1H$ and Cu_2O (Scheme 2). In both reactions, the hydrated hexanuclear metallacycle **2** was obtained.



Scheme 2. Reaction schemes for the formation of compound **2**: a) starting from the trimer (yield 82%), b) starting from the bare neutral pyrazole (yield 45%).

Compound **2** is poorly soluble in acetonitrile. The elemental analysis confirms the presence of the metallocycle, two molecules of CH_3CN and one of water. It readily encapsulates halides and NO_2-

anions when the corresponding anion source is added in a 1:1 molar ratio in acetonitrile or acetone solutions. The ^{1}H NMR characterization of **2** showed the C_4-H signal of the pyrazole group at δ 25 ppm in acetone-d^6 and δ 35 ppm in CD_3CN, as already observed for the other anion centered metallacycles **2a**-**d**. The line width at half height of the δ 25 ppm signal is 36 Hz, while the water of acetone falls at δ 3.93 ppm instead of the usual δ 2.8 ppm; these shifts suggest a likely water exchange process between the "encapsulated" water molecules and the free water molecules of the deuterated solvent. A VT NMR experiment (see Supporting Information) allowed the determination of the exchange rate constant as 7.1 x 10^7 s^{-1} (-20 °C), typical of a fast exchange regime [11]. A detailed solid state IR characterization of compounds **2** and **2a**-**d** was also performed. The MIR spectrum of **2** shows typical bands for the bridging hydroxyl groups, already observed in the other halide adducts, at 3650 and 1600 cm^{-1}, while the band at 1660 cm^{-1} is attributed to the H_2O bending vibrational mode. This value is blue-shifted respect liquid water, which is expected to show a band at 1610 cm^{-1} [12]. For the water molecule, the vibration mode is reported at 1595 cm^{-1}, while the symmetric and asymmetric stretches appear at 3657 and 3756 cm^{-1}, respectively. In the MIR spectrum, the asymmetric stretching of water appears as a broad band at 3667 cm^{-1}, overlapping with the bridging OH stretching. At 3167 cm^{-1} we can observe the C_4pz-H stretching, and the C=C and C=N stretchings can be attributed to the peaks at 1542 and 1504 cm^{-1}, respectively. C-F stretching modes are observed as intense bands at 1254 and 1113 cm^{-1}.

In the FIR spectrum of **2**, the absorption of the Cu-O bond is shown at 489 cm^{-1} (slightly blue shifted if compared to the Cl- or Br- adducts, **2a** and **2b**). The Cu-N bond absorption appears at 295 cm^{-1}, again blue shifted when compared to the similar halide structures (291 cm^{-1} for the Cl^- adduct, **2a** and 287 cm^{-1} for the Br^- adduct **2b**). The very weak band at 522 cm^{-1}, present only in the water encapsulated adduct **2**, might be attributed to the νL (hindered rotation, at 600 cm^{-1} for hydrogen networked water).

The NIR spectra of compounds **2** (Figure 1) and **2a-d** shows weak bands due to the O-H combination bands of the fundamental vibration modes of water and hydroxyl groups. The bands at 1398 (first vibrational overtone), 1614, 2187 and 2404 nm are attributable to overtones of OH and water, present in all the previously investigated adducts. In compound **2**, on the contrary to those observed for other adducts, the presence of additional bands, likely due to hydrogen bonding networks, such as 2153 and 2353 nm were observed. These bands were reported in the NIR spectra of ice [13]. Around 1896 nm, a medium sharp band is present, likely due to a combination of O-H stretch and H-O-H bending modes (1900 nm for liquid water). A broad large band going from 1870 to 2050 nm might be due to physically adsorbed water [14].

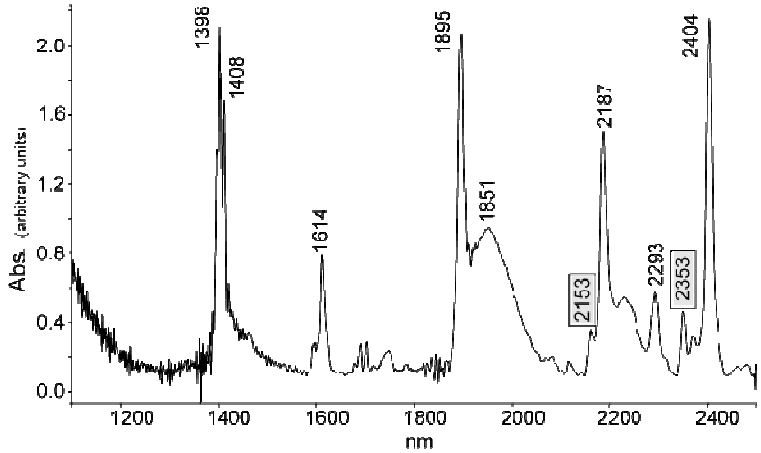


Figure 1. NIR spectrum of compound **2** in the region 1000-2500 nm.

X-ray crystal structure analyses. The dinuclear nature of the compound [Cu-(3,5-$(NO_2)_2$pz)(PPh_3)]$_2$, **1**, (pz = 3,5-bis(dinitro)-1H-pyrazolate anion), has been evidenced by single crystal X-ray diffraction analysis. The ORTEP view of the molecule is reported in Figure 2, together with the atom labelling scheme. The most important bond distances and angles are reported in the caption. Each copper atom is trigonally coordinated considering the two nitrogen atoms of the bridging ligands and the phosphorous atom of the phosphane molecule. The coordination around the copper atoms deviates significantly from the planarity, atoms Cu1 and Cu2 being out of the pertinent coordination plane by 0.1924(4) and 0.2674(4) Å respectively. The six-member Cu-[N-N]$_2$-Cu ring presents a boat conformation, but considering that the copper atoms lie out of the pyrazolate average planes, with deviations spanning from a minimum of 0.0231(4) Å for Cu1 with respect to the N5N6C4C5C6 ring up to 0.3376(4) Å for Cu2 with respect to the N1N2C1C2C3 ring, the resulting boat conformation is slightly twisted. The crystal packing of the compound is built up by a strong network of Van der Waals interactions between the nitro groups and between the nitro groups and the nitrogen atoms of the pyrazolate ring of adjacent molecules.

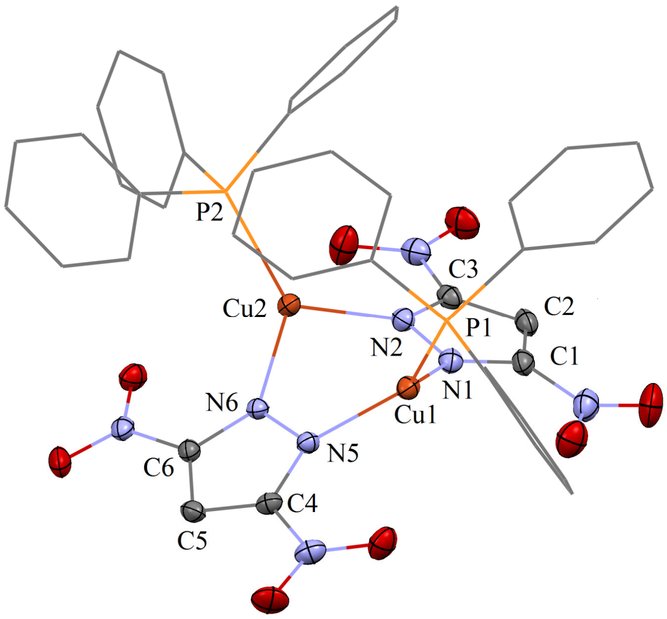


Figure 2. Ortep view of [Cu-(3,5-$(NO_2)_2$pz)(PPh_3)]$_2$, **1**. The phosphane ligands have been drawn sa a wireframe model. Ellipsoids, when shown, are at the 30% level. Selected bond distances (Å) and angles (°): N1-Cu1 2.0217(19), N5-Cu1 1.998(2), P1-Cu1 2.1981(7), N2-Cu2 1.974(2), N6-Cu2 2.004(2), P2-Cu2 2.1812(8); N5-Cu1-N1 104.09(8), N5-Cu1-P1 126.42(6), N1-Cu1-P1 126.87(6), N2-Cu2-N6 102.17(8), N2-Cu2-P2 132.41(6), N6-Cu2-P2 120.20(6).

The asymmetric unit of compound **2** is depicted in Figure 3. It contains one sixth of the neutral copper(II) hexanuclear metal core [Cu(μ-OH)(η^2,μ-$(CF_3)_2$pz')]$_6$ [pz' = 3,5-bis(trifluoromethyl)-1H-pyrazolate anion], an inversion centre is sited in the middle of the core and a 3-fold axis passes through that location. Selected bond distances and angles are given in the legend of Figure 3. The copper atoms present distorted square-planar geometries, as expressed by the Houser (τ4) 39 parameter of 0.29, join five-membered Cu_2N_2O rings and ultimately give rise to a large $Cu_6(N_2O)_6$ crown-type assembly. The structure can also be envisaged as a circular zig-zag Cu_6O_6 cluster, where the metal cations stand in the least-square plane defined by those atoms; the bridging η2-pyrazolate moieties are alternatively positioned above and below this plane, the minimum intramolecular Cu···Cu distance is 3.1425(17) Å and the Cu–O and Cu–N bond lengths are 1.917(2) and 1.970(3) (average values) Å, respectively. The structure is stabilized by intermolecular hydrogen bond interactions (Figure 3) involving the pyrazolate CH groups (as donors) and the F1 atoms (as acceptors) of vicinal complexes.

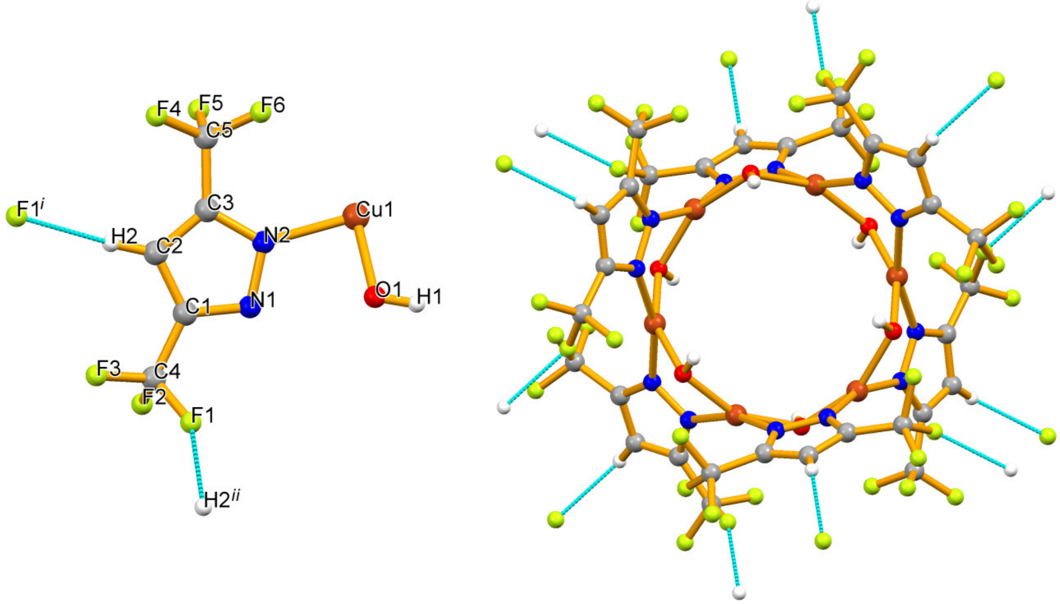
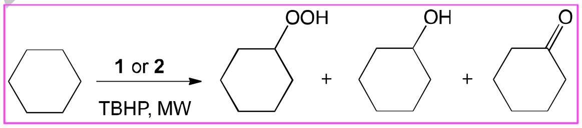


Figure 3. The asymmetric unit with the atom labelling scheme (left) and the structure (right) of compound **2**, also showing the donor (carbon)···acceptor (fluorine) contact interactions (in dashed light blue lines). Symmetry operations to generate equivalent atoms: i) 1.67-x+y,1.3(3)-x,1/3+z; ii) 1.3(3)-y,-1/3+x-y,-1/3+z. Selected bond distances (Å) and angles (º): N1–Cu1 1.972(3), N2–Cu1 1.965(3), O1–Cu1 1.918(2), N1–N2 1.346(4), C1–N1 1.340(4), C3–N2 1.342(4), C4–F3 1.328(4), C5–F5 1.340(4); O1–Cu1–N2 86.04(11), O1–Cu1–N1 97.84(11), N2– Cu1–N1 163.86(11), O1–Cu1–O1 155.30(14). Hydrogen bond interaction C2–H2···F1i: D···A 3.279(7) Å, D–H···A 153º.

Catalytic studies. Compounds **1** and **2** act as very effective homogeneous catalysts towards the neat microwave (MW) assisted peroxidative (with aq. tert-butyl hydroperoxide, TBHP) oxidation of cyclohexane to cyclohexanol, cyclohexanone and cyclohexyl hydroperoxide (Scheme 3).



Scheme 3 – Microwave-assisted neat oxidation of cyclohexane to cyclohexyl hydroperoxide, cyclohexanol and cyclohexanone with tert-butyl hydroperoxide catalysed by the Cu complexes **1** or **2**.

The formation of the hydroperoxide was proved by Shul’pin’s method [15] and allowed us to estimate the real concentrations of alkyl hydroperoxide, alcohol and ketone: the addition of PPh_3 prior to the GC analysis of the products resulted in a marked increase of the amount of cyclohexanol (due to the reduction of CyOOH by PPh_3, with the formation of phosphane oxide) and a corresponding decrease in the amount of cyclohexanone. The formation of cyclohexyl hydroperoxide (a typical intermediate product in radical-type reactions), along with the complete suppression of the catalytic activity upon the introduction of a radical trap (Ph_2NH, Figure 4) to the reaction mixture, supports the hypothesis of a free-radical mechanism for the cyclohexane oxidation carried out in this study. The radicals tert-BuOO• and tert-BuO•[16] could be produced in the catalyst promoted decomposition of TBHP with the formation of a reduced form of the catalyst and an hydroxo-Cu species (precursor of a tert-butylperoxide copper species). Those radicals could then react with cyclohexane (CyH) giving rise to the cyclohexyl radical Cy• upon hydrogen abstraction. Cy• reacts with oxygen, leading to CyOO•. CyOOH can be formed, e.g., upon hydrogen abstraction from tert-BuOOH by CyOO•. Metal-assisted decomposition of CyOOH to CyO• would then lead to CyOH and CyO products.

A very high yield, up to 58% (**2**) or 51% (**1**) of oxygenated products, is obtained under optimized conditions: 0.5 h (**2**) or 1.5 h (**1**) of MW irradiation at 100 ºC (see Figure 5 and Table S1, Electronic Supporting Information), using a 0.2 % molar ratio of the copper catalyst relative to the substrate, in the presence of the 2,2,6,6-tetramethyl-piperidinyloxyl radical (TEMPO, 2.5 % molar ratio vs. substrate).

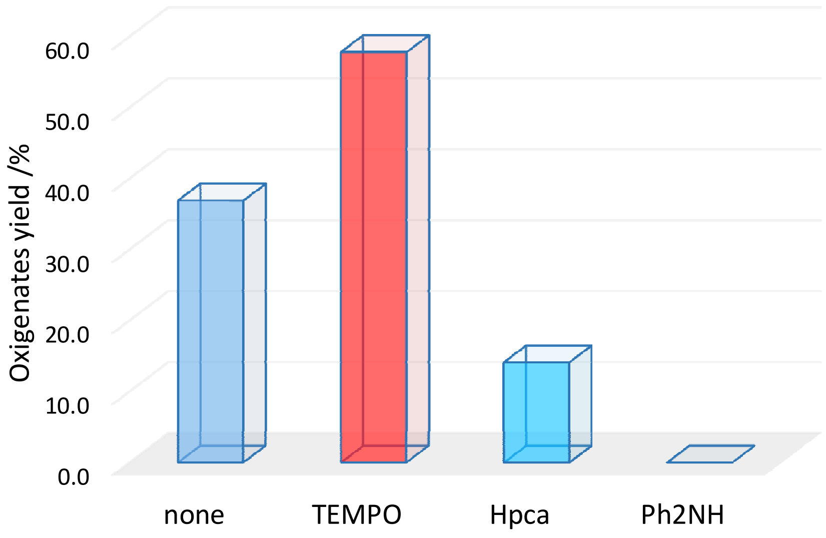


Figure 4 - Effect of different additives on the yield of cyclohexanol and cyclohexanone obtained by microwave-assisted neat oxidation of cyclohexane with THBP, catalysed by **2** (0.1% molar vs. substrate).

Complexes **1** and **2** were shown to be much more active than Cu(I) or Cu(II) salts (Table S1), suggesting the favourable involvement of the ligands in the metal-assisted steps of this catalytic oxidation reaction.

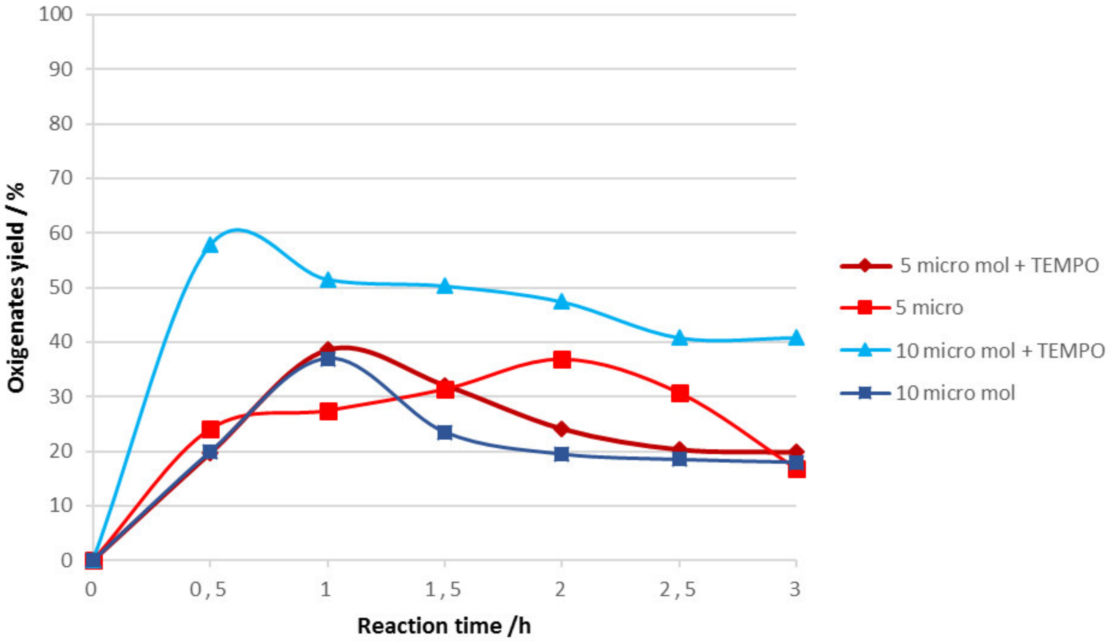


Figure 5 - Effect of the reaction time, catalyst **2** amount and TEMPO additive on the yield of cyclohexanol and cyclohexanone obtained by microwave-assisted neat oxidation of cyclohexane with THBP.

For the Cu(II) catalytic system, the amount of catalyst plays a significant role, as depicted in Figures 6 and 7. The increase from 1 to 5 µmol of **2** in the reaction medium leads to a yield increment from 22 to 37%, whereas 10 µmol of **2** allows the maximum yield to be reached faster (in 1 hour, instead of the 2 hours of MW irradiation needed for 5 µmol of **2**). The effect of the quantity of the catalyst on the yield of products is not so evident for the Cu(I) system, compound **1**. Moreover, addition of small amounts (2.5 mol% vs. substrate) of TEMPO to the reaction mixture allows the maximum yield of cyclohexanol and cyclohexanone to be achieved after a very short MW irradiation time of 0.5 or 1 h, for 10 or 5 µmol of **2**, respectively (Figure 6). The same behaviour is observed for the Cu(I) catalytic system, compound **1**. The promoting effect of TEMPO may be rationalized as follows: under the used oxidizing conditions TEMPO conceivably could be oxidized to the oxoammonium species [17] and thus also operate as an oxidant to transform cyclohexane into the corresponding oxygenated product, as well as acting as a hydrogen-atom abstractor from TBHP, reinforcing the formation of tert-BuOO•. However, when added in higher amounts, TEMPO can exhibit its well known inhibiting effect [10,18]: for **1**, addition of 2.5, 5, 50 and 100 mol % vs. cyclohexane led to total (cyclohexanol and cyclohexanone) yields of 21.6, 21.4, 3.8 and 0.0 %, respectively. The alcohol to ketone ratio (A/K) is known as an indicator for catalyst selectivity, reflecting the combined conversion of cyclohexane either directly to cyclohexanol or to cyclohexyl hydroperoxide, which subsequently is reduced to the alcohol as a result of reduction with triphenylphosphine [15]. In the present study, cyclohexanol is obtained in a larger amount than cyclohexanone, the alcohol/ketone molar ratio is ca. 3 for **1** in additive-free media (Table S1). As expected, the presence of TEMPO (a well-known promotor of alcohol oxidation) [19] promotes the formation of ketone (the molar ratio decreases to ca. 1.7). For **2**, the effect is only detectable for the highest catalyst amount used (0.2 % vs. substrate).

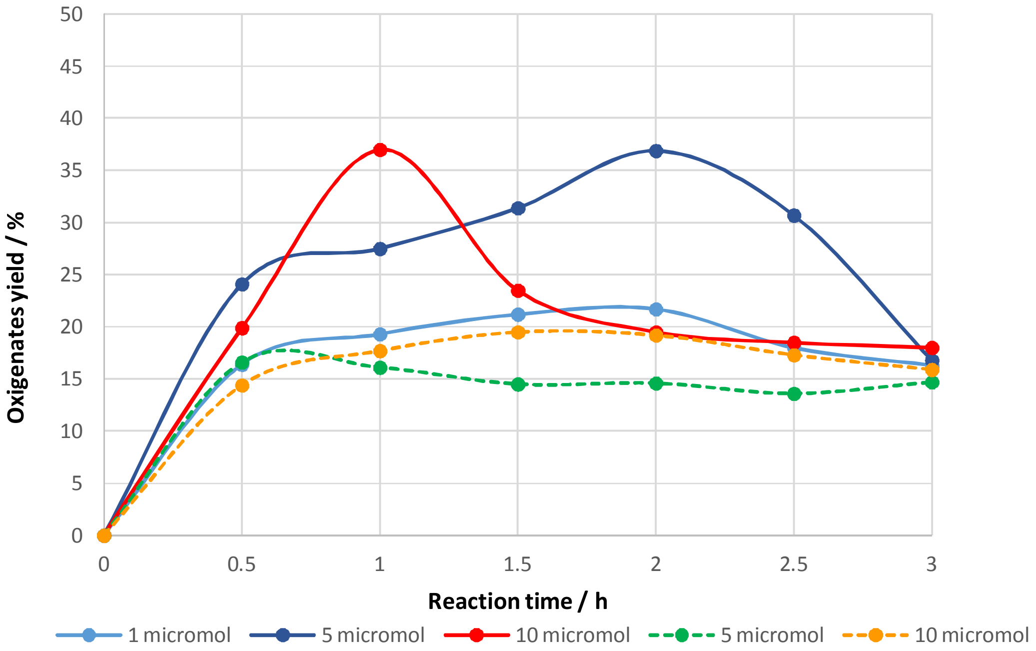


Figure 6 - Effect of the reaction time and catalyst (— **2** or ---- **1**) amount on the yield of cyclohexanol and cyclohexanone obtained by additive-free microwave-assisted neat oxidation of cyclohexane with THBP.

The catalytic activity of **1** and **2** is also sensitive to temperature, as depicted in Figure 7 for the catalyst **2**.

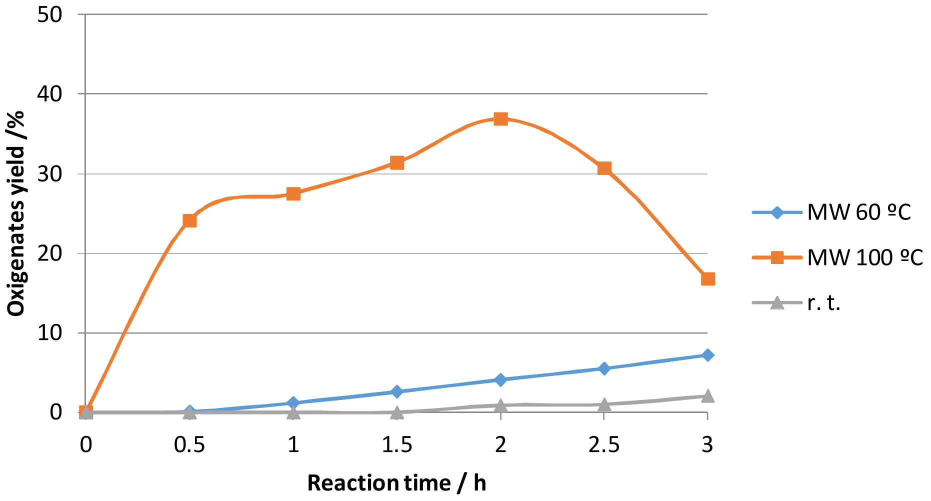


Figure 7. Effect of reaction temperature on the yield of cyclohexanol and cyclohexanone obtained by the additive-free neat oxidation of cyclohexane with THBP, catalysed by **2** (0.1% molar vs. substrate).

The promoting role of certain acids, in particular pyrazine carboxylic acid (Hpca), on the catalytic oxidation of various cycloalkanes catalysed by metal complexes is well known [20]. In our catalytic systems, the presence of Hpca has a strong inhibiting effect on the catalytic activity of both **1** and **2** (Figure 4). A similar behaviour was previously found [21].

Conclusions

A new route for the synthesis of $[Bu_4N][Cu_6(3,5\text{-}pzCF_3)_6(OH)_6 \supset X]$ (X = Cl, Br, I and NO_2) was found, starting from neutral $3,5\text{-}pzH(CF_3)_2$ and Cu_2O as the source both of the metal and the base (oxide) in aerated and wet acetonitrile. The reactions show lower yields when compared to that previously reported [3c,4c], but it was proven that anions do not template these reactions and a water encapsulated metallacycle, $[Cu_6(3,5\text{-}pzCF_3)_6(OH)_6 \supset H_2O]$, **2**, was synthesized. In complex **2** the presence of the water molecules inside the cavity was analyzed by NIR spectroscopy and by determining the rate constant of the water fast exchange reaction in acetone solution. Moreover, by considering that the internal diameter of the cavity is 6.2 Å and the height of the channel is 7.6 Å on average; these sizes can be compared to those of γ cyclodextrins formed by seven glucose molecules connected by γ-1,4 glycosidic bonds. In the hexanuclear copper(II) host, the upper and lower rim CF_3 groups merge, making the entrance very polar, while in the cavity, the OH groups are in a symmetric trans configuration, forming hydrophilic environments above and below the rim with pseudo spherical hydrogen bonding symmetry; this environment makes the host able to encapsulate spherical ions, but at the same time the circular disposition of electrophilic Cu(II) ions makes the host able to recognize neutral polar nucleophilic molecules with the appropriate size. The formation of tri or hexanuclear complexes is not a result that is easily repeated for similar pyrazoles: when 3,5-dinitropyrazole is used neither the trinuclear Cu(I) nor the hexanuclear Cu(II) complexes were obtained and the only product was that containing pyrazole, Cu(I) ions and the additional co-ligand PPh_3. The two complexes, $[Cu_2(\mu\text{-}N,N\text{-}3,5\text{-}(NO_2)_2pz)_2(PPh_3)_2]$, **1**, and $[Cu_6(3,5\text{-}pzCF_3)_6(OH)_6 \supset H_2O]$, **2**, despite their structural differences, were successfully tested as catalysts for the microwave-assisted neat oxidation of cyclohexane to a cyclohexanol and cyclohexanone mixture, likely through a radical mechanism, affording considerably high yields (up to 58%) in rather short reaction times (30 min for **2**). The presented catalytic procedure leads to significantly higher yields of cyclohexanol and cyclohexanone than those reported (although for considerably different conditions) for copper complexes with related ligands, such as the C-scorpionate Cu(II) complex [$CuCl_2(TpmOH)_2$] (TpmOH = 2,2,2-tris(pyrazol-1-yl)ethanol), 7% [22], copper coordination polymers with pyrazolato-based tectons, 11% [21a] or based on trinuclear triangular [$Cu_3(\mu^3$-OH)(μ-pz)$_3]^{2+}$ units, 36% [23]. Moreover, our catalytic protocol (TBHP/MW) is very fast, solvent-free and uses a green energy source.

Experimental Section

Elemental analyses (C, H, N, S) were performed in-house with a Fisons Instruments 1108 CHNS-O Elemental Analyser. Melting points were taken on an SMP3 Stuart Scientific Instrument. MIR spectra were recorded from 4000 to 600 cm^{-1} with a Perkin-Elmer SPECTRUM ONE System FT-FIR instrument. NIR spectra were recorded from 4000 to 600 cm^{-1} with a Perkin-Elmer SPECTRUM ONE System FT-IR instrument. IR annotations used: br = broad, m = medium, s = strong, sh = shoulder, vs = very strong, w = weak and vw = very weak. ^{1}H and ^{31}P NMR spectra were recorded on an Oxford-400 Varian spectrometer (400.4 MHz for ^{1}H and 162.1 MHz for ^{31}P). Chemical shifts, in ppm, for ^{1}H NMR spectra are relative to internal Me_4Si. ^{31}P NMR chemical shifts were referenced to an 85% H_3PO_4 standard. The ^{31}P NMR spectroscopic data were accumulated with ^{1}H decoupling. NMR annotations used: br = broad, d = doublet, dd = double doublet, t = triplet, m = multiplet, s = singlet. Electrospray mass spectra (ESI-MS) were obtained in the positive- or negative-ion mode on a Series 1100 MSD detector HP spectrometer, using an acetonitrile or methanol mobile phase. The compounds were added to reagent grade acetonitrile to give solutions of an approximate concentration of 0.1 mM. These solutions were injected (1 μL) into the spectrometer via an HPLC HP 1090 Series II fitted with an auto-sampler. The pump delivered the solutions to the mass spectrometer source at a flow rate of 300 μl min^{-1}, and nitrogen was employed both as a drying and nebulising gas. Capillary voltages were typically 4000 and 3500 V for the positive- and negative-ion modes, respectively. Confirmation of all major species in this ESI-MS study was aided by comparison of the observed and predicted isotope distribution patterns, the latter calculated using the IsoPro 3.1 computer program. The used solvents were HPLC grade and they were used as purchased, unless the reactions were water and oxygen sensitive, in which case, anhydrous and radical free THF was obtained by treating the solvent with Na/acetophenone under a N_2 atmosphere. 3,5-Bis(trifluoromethyl)-1H-pyrazole and other chemicals were purchased by Sigma Aldrich and used without further purification. The 3,5- dinitropyrazole [24] and the complex [Cu(3,5-$(CF_3)_2$pz)]$_3$ were prepared as previously described [3c,25].

Synthesis of [Cu_2(μ-N,N-3,5-$(NO_2)_2$pz)$_2$(PPh_3)$_2$], **1**.

To a mixture of Ph_3P (0.174 g, 0.66 mmol) and $Cu(BF_4)_2$ (0.104 g, 0.44 mmol) in dry THF, the sodium pyrazole salt (0.08 g, 0.44 mmol) was added and the suspension was stirred overnight at room temperature. The orange suspension was evaporated under vacuum to give an orange solid. The solid was dissolved in dichloromethane and extracted 3 times with 10 ml water. The organic phase was dried with Na_2SO_4, filtered over a paper filter and concentrated. The solution was layered with hexane and orange crystals of **1** were recovered.

Characterization of **1**: Yield 78 %. M.p: 121-123 °C. IR (cm^{-1}): 3154 (w), 3051.5 (w), 1586 (w), 1539.7 (s), 1492 (s), 1479 (s,sh), 1455 (m), 1436 (m), 1368 (s), 1329 (s), 1296 (m), 1222 (w), 1182 (s), 1161 (m), 1097 (s), 1076 (m), 1047 (m), 1025 (m), 1010 (w), 997 (w), 967 (m), 925 (w), 915 (w), 833 (s), 812 (s), 741 (s), 706 (vs), 691.05 (vs). ^1H NMR (acetone-d6, δ, ppm): 7.58 (s, 1H), 7.39 (m, 3H), 7.32 (m, 12H). ^{31}P NMR (acetone-d6, δ, ppm): 3.76 (s). ESI (-) MS (CH_3CN; m/z) : 377 (100) [(3,5$(NO_2)_2$pz)2 + Cu]-, 157 (63) [3,5$(NO_2)_2$pz]-. ESI (+) MS (CH_3CN; m/z): 603 (m/z), 587 (100) [PPh3)2 + Cu]+; 366 (61). Elemental analysis for $C_{42}H_{42}Cu_2N_8O_8P_2$ Calc.: C, 52.33; H, 3.34; N, 11.60; Found: C, 52.29; H , 3.38; N, 11.58 %.

Synthesis of [{trans-$Cu_6(\mu\text{-}OH)_6(\mu\text{-}3,5\text{-}(CF_3)_2pz\}_6\ H_2O$], **2**.

Method A: {[3,5-$(CF_3)_2$Pz]Cu}$_3$ (0.040 g, 0.050 mmol) was dissolved in 5 ml of MeCN (HPLC grade). The reaction mixture was stirred for 10 min and then left in air. Slowly the solution became blue and after few days blue crystals of compound **2** were formed.

Method B: Solid 3,5 trifluoromethyl pyrazole (0.100 g, 0.49 mmol) was dissolved in 5 ml of MeCN (HPLC grade) in air; to this solution solid Cu_2O (0.035 g, 0.245 mmol) was added. The resulting reaction mixture was left stirring for three days at 60 °C. After filtering on a celite bed, the solution was left to evaporate at room temperature. A blue microcrystalline solid was collected after a few days from a dark green solution.

Characterization of compound **2**. Yields: Method A 82%, Method B 45%. M.p. 242 °C with decomposition. IR (cm^{-1}): 3660, 3563, 3168, 1660, 1561, 1541, 1503, 1336, 1254, 1150, 1113, 1023, 935, 829, 758, 734, 729. ^1H NMR (acetone-d^6, r. t., δ, ppm): 25.97 (s, pzC_4-H). ESI(-) MS (CH_3CN, m/z): 203.1 m/z (100) [$CF_3)_2$pz], 469.1 (18), 648.7 (20), 1737.2 (100) [$Cu_6((CF_3)_2pz)_6(OH)_6Cl)$]. ESI (+) MS ($CH_3CN$, m/z): 242.4 m/z (100) [Bu_4N]. Elemental analysis for $C_{30}H_{14}Cu_6F_{36}N_{12}O_7$ + $2CH_3CN$: Calc.: C, 22.86; H, 1.12; N, 10.88; Found: C, 23.04; H, 1.12; N, 10.49%.

Synthesis of **2a-d** by method B.

3,5-Trifluoromethyl-1H-pyrazole (0.050 g, 0.245 mmol) and Cu_2O were dissolved in 10 ml of MeCN. Then $[Bu_4N]Cl$ (**2a**, 0.011 g, 0.040 mmol), $[Bu_4N]Br$ (**2b**, 0.013 g, 0.040 mmol), $[Bu_4N]I$ (**2c**, 0.0147 g, 0.040 mmol) or $[PPNNO_2]$ (**2d**, 0.014, 0.0375 mmol) was added to the solution.The reaction mixture was left to stir for 2 h. The precipitate formed was filtered on Celite, washed with acetone and finally dried under an air flow. Slowly the solution became blue or green, was dried under an air flow and the solid **2a** (Cl), **2b** (Br), **2c** (I) or **2d** (NO_2) product was isolated as a microcrystalline powder by slow evaporation. The yields are of **2a** (40%;), **2b** (35%;), **2c** (37%;), **2d** (30%). The spectroscopic and analytical characterizations were compared to those already reported [3c,4c].

X-ray crystal structure determination

Crystal data for **1** and **2** were collected at 203 (**1**) or 150 K (**2**) on a Bruker APEX II single-crystal diffractometer, working with Mo-Kα graphite monochromatic radiation (λ = 0.71073 Å) and equipped with an area detector. The raw frame data [20 (**1**) or 0.5 (**2**) s per frame scan time] for a sphere of diffraction data were processed using the SAINT software [26], with a correction for absorption being made using SADABS [27]. The structures were solved by direct methods with SHELXS-97 (**1**) or SIR97 (**2**) [28] and refined against F2 with SHELXL-2014/7 [27] using anisotropic thermal parameters. The hydrogen atoms attached to carbon atoms were inserted in calculated positions, their Uiso (H) were defined as 1.2Ueq of the parent carbon atoms. The pyrazolyl hydrogen atom in **2** was inserted in a calculated position and refined using a riding model. The hydroxyl hydrogen atom in **2** was located in the difference Fourier synthesis and refined with the help of distance restraint. During the refinement of this structure (**2**), electron density peaks were located and believed to be of highly disordered water molecules. All the attempts made to model the solvent molecules were not successful and they were removed using the SQUEEZE routine from Platon [29]. This procedure was applied to recover 123 electrons per unit cell (total volume 602 $Å^3$). Lattice solvent water molecules are thus present as ca. 12 water molecules per unit cell. These water molecules were not included in the cif. Details for the X-ray data collection are reported in Table 1.

Table 1. Details for the X-ray data collection for **1** and **2**

Complex	**1**	**2**
Formula	$C_{42}H_{32}Cu_2N_8O_8P_2$	$C_{30}H_{12}Cu_6F_{36}N_{12}O_6$
Molecular weight	965.77	1701.76
Crystal system	Triclinic	Trigonal

Space group	*P*-1	*R*-3
a/Å	10.093(2)	21.863(5)
b/Å	12.325(2)	21.863(5)
c/Å	19.251(3)	10.076(5)
α/°	72.496(3)	90
β/°	87.743(3)	90
γ/°	66.218(3)	120
Volume, $Å^3$	2080.9(6)	4171(3)
Z	2	3
D_{calc}/g cm^{-3}	1.541	2.032
F(000)	984	2466
μ(Mo-Kα)/mm^{-1}	1.163	2.425
Reflections collected	28774	20374
Unique reflections	10015	1707
Observed reflections [$I>2\sigma(I)$]	7113 [R_{int} = 0.0486]	1282 [R_{int} = 0.0793]
R, wR [$I > 2\sigma(I)$]	*R* = 0.0400; *wR* = 0.0860	*R* = 0.0319; *wR* = 0.0635
R, wR [all data]	*R* = 0.0673; *wR* = 0.0969	*R* = 0.0601; *wR* = 0.0692
CCDC ref code	1478672	1495587

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/ \Sigma[w(F_o^2)^2]]^{1/2}$

Catalytic studies. The catalytic tests under microwave irradiation (MW) were performed in a focused Anton Paar Monowave 300 microwave reactor using a 5 mL capacity reaction tube with a 10 mm internal diameter, fitted with a rotational system and an IR temperature detector. Gas chromatographic (GC) measurements were carried out using a FISONS Instruments GC 8000 series gas chromatograph with a FID detector and a capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm) and the Jasco-Borwin v.1.50 software. The temperature of injection was 240 ºC. The initial temperature was maintained at 100 ºC for 1 min, then raised at 10 ºC/min to 180 ºC and held at this temperature for 1 min. Helium was used as the carrier gas. GC-MS analyses were performed using a Perkin Elmer Clarus 600 C instrument (He as the carrier gas). The ionization voltage was 70 eV. The 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 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.

Appendix A. Supplementary data

CCDC reference codes 1478672 and 1495587 contain the supplementary crystallographic data for compounds **1** and **2**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, 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.

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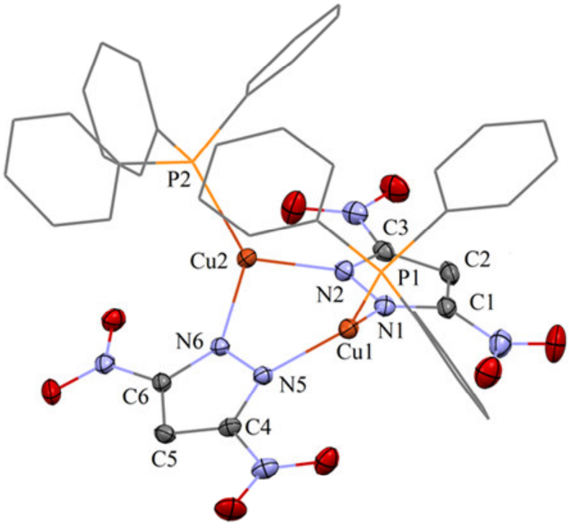
P2
Cu2
C3
C2
P1
N2
C1
N1
N6
Cu1
N5
C6
C4
C5

COPPER(I) AND COPPER(II) METALLACYCLES AS CATALYSTS FOR MICROWAVE ASSISTED SELECTIVE OXIDATION OF CYCLOHEXANE

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Cu(I) and Cu(II) metallocycles were prepared with pyrazolates having CF_3 or NO_2 groups in the 3 and 5 positions. According to similar reaction routes, they yielded a hydrated hexanuclear metallocycle [(μ-pz)Cu(μ-OH]$_6$ and a dinuclear compound with an N_2-$Cu_2(PPh_3)_2$-N_2 boat shaped core, respectively. Both compounds are active as homogenous catalysts for MW assisted neat peroxidation of cycloalkanes by a radical mechanism.