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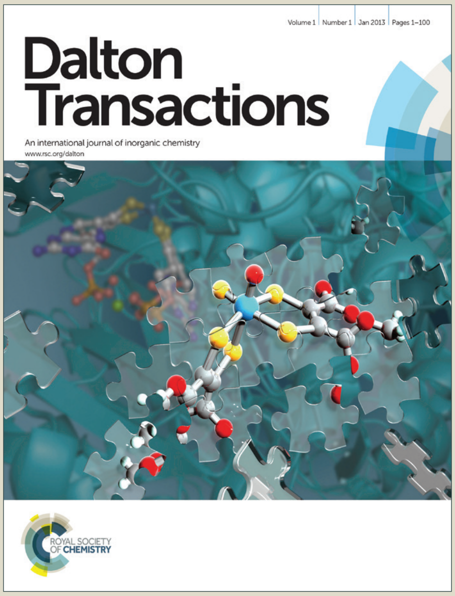

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Copper-organic frameworks assembled from *in-situ* generated 5-(4-pyridyl)tetrazole building blocks: synthesis, structural features, topological analysis and catalytic oxidation of alcohols

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Abstract

Two new metal-organic compounds $\{[Cu_3(\mu_3\text{-4-ptz})_4(\mu_2\text{-}N_3)_2(DMF)_2](DMF)_2\}_n$ **(1)** and $\{[Cu(4\text{-ptz})_2(H_2O)_2]\}_n$ **(2)** {4-ptz = 5-(4-pyridyl)tetrazolate} with 3D and 2D coordination networks, respectively, have been synthesized while studying the effect of reaction conditions on the coordination modes of 4-pytz by employing the [2+3] cycloaddition as a tool in generating *in-situ* the 5-substituted tetrazole ligands from 4-pyridinecarbonitrile and NaN_3 in the presence of a copper(II) salt. The obtained compounds have been structurally characterized and the topological analysis of **1** discloses a topologically unique trinodal 3,5,6-connected 3D network which, upon further simplification, results in a uninodal 8-connected underlying net with the **bcu** (body centred cubic) topology driven by the $[Cu_3(\mu_2\text{-}N_3)_2]$ cluster nodes and μ_3-4-ptz linkers. In contrast, the 2D metal-organic network in **2** has been classified as a uninodal 4-connected underlying net with the **sql** [Shubnikov tetragonal plane net] topology assembled from the Cu nodes and μ_2-4-ptz linkers. The catalytic investigations disclosed that **1** and **2** act as active catalyst precursors towards the microwave-assisted homogeneous oxidation of secondary alcohols (1-phenyletanol, cyclohexanol, 2-hexanol, 3-hexanol, 2-octanol and 3-octanol) with *tert*-butylhydroperoxide, leading to the yields of the corresponding ketones up to 86% (TOF = 430 h^{-1}) and 58% (TOF = 290 h^{-1}) in the oxidation of 1-phenylethanol and cyclohexanol,

respectively, after 1 h under a low power (10 W) microwave irradiation, and in the absence of any added solvent or additive.

Introduction

Tetrazole ligands have been extensively used to generate metal-organic and H-bonded frameworks of different topologies in last few years.[1] The versatility of the tetrazole building blocks provides the required template to create a hoard of new materials with interesting properties and diverse applications.[1g,1h] Among the various tetrazole ligands, 5-(4-pyridyl)tetrazole (4-ptz) has been one of the widely employed building blocks towards the design of metal-organic networks.[2] In particular, a combination of 4-ptz with copper ion has produced a handful of MOFs obtained either in the presence or absence of co-ligands.[3] However, in most of the reported cases, 4-ptz has been generated under solvothermal conditions by cycloaddition of 4-cyanopyridine and azide ion in the presence of different transition metals. In contrast, the synthesis of MOFs driven by the 4-ptz blocks in a more controlled manner (*i.e.*, at lower temperatures and pressures *via* a similar cycloaddition path) has not been reported so far though there are reports of formation of tetrazoles by milder conditions in presence of metal ion or other catalysts.[4]

From the other side, the synthesis of new MOFs and their application in oxidative catalysis represent an interesting research direction.[5,6] In the present study, we have selected the oxidation of secondary alcohols as a model reaction,[7] aiming at probing a catalytic potential of the compounds **1** and **2**. Classical methods for the liquid-phase oxidation of alcohols to ketones are unfeasible on an industrial-scale and undesirable from the environmental viewpoint due to the common use of chlorinated solvents, toxic[8a–c] or moisture-sensitive oxidants,[8d] high catalysts loadings, presence of bases and phase-transferring agents.[8e–h] Hence, aerobic[8h–l] and peroxidative[8m–p] oxidations of secondary alcohols are regarded as the simplest and most useful synthetic methods for the preparation of ketones, in view of the versatility of the metal catalysts, oxidants and alcohol substrates used. The improvement of these synthetic methodologies, according to green chemistry principles,[8q-r] is a challenge to be tackled, focusing on the use of alternative green solvent systems for more efficient and clean syntheses.[8s]

Herein we report the synthesis and structural features of two copper metal-organic frameworks which have been generated by the cycloaddition reaction between sodium azide and 4-cyanopyridine in the presence of a copper(II) salt. Furthermore, the present work discloses the catalytic properties of these two compounds toward the oxidation of secondary alcohols under rather mild and green conditions.

Experimental section

Materials and Instrumentation

Reagents were purchased from commercial sources and used without further purification. Microwave irradiation experiments for the synthesis of **2** and for the catalytic tests under MW irradiation were performed in a focused microwave CEM discover reactor (300 W for the synthesis or 10 W for the catalysis), using a 10 mL capacity reaction tube with a 13 mm internal diameter, fitted with a rotational system and an IR temperature detector. Infrared spectra (4000–500 cm^{-1}) were recorded with a Bio-Rad FTS 3000MX instrument in KBr pellets. Elemental analyses were carried out with a ThermoFlash 2000 elemental analyser. Powder X-ray diffraction patterns for complexes **1** and **2** were recorded on a Rigaku Smart Lab X-ray diffractometer. The X-rays were produced using a sealed tube and the wavelength of the X-ray was 0.154 nm (CuK-alpha). The X-rays were detected using a linear counting detector (Scintillator NaI photomultiplier detector). Spectrophotometric measurements were performed on a Varian UV-Vis spectrophotometer (Model: Cary 100) using a quartz cuvette with path length of 1 cm. 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 120 ºC for 1 min, then raised 10 ºC/min to 200 ºC and held at this temperature for 1 min. Helium was used as the carrier gas.

Caution! *Azide and tetrazolate compounds are potentially explosive. Only a small amount of material should be prepared and handled with care.*

Synthesis of $\{[Cu_3(\mu_3\text{-4-ptz})_4(\mu_2\text{-}N_3)_2(DMF)_2](DMF)_2\}_n$ (1): An excess of solid 4-cyanopyridine (249 mg, 2.4 mmol) was added to the brown coloured mixture of $CuCl_2{\cdot}2H_2O$

(102 mg, 0.6 mmol) and NaN_3 (78 mg, 1.2 mmol) in water (1 mL) and DMF (6 mL). The obtained brown solution was stirred at 85 °C for 3 h, and a green coloured compound started to precipitate. The stirring was continued for another hour. The mixture was then filtered and the resultant filtrate was left to slowly evaporate in air. Green coloured rod shaped X-ray diffraction quality crystals started to form after 1 d. They were filtered and washed with DMF and diethyl ether. Yield = 112 mg, (16.2%), anal calc for C_{42} H_{58} Cu_3 N_{16} O_6, C, 46.98, H, 5.45, N, 20.87, found: C, 47.01, H, 5.47, N, 20.90 IR (KBr): 2081(s) 1670(s), 1624(s), 1434(m), 1383(w), 1296(w), 1219(w), 1093(m), 1015(m). Purity of bulk sample of **1** was confirmed by the PXRD patterns of the sample (Fig. S1).

Synthesis of {[Cu(4-ptz)$_2$(H$_2$O)$_2$]}$_n$ (2): Greenish brown mixture of $CuCl_2{\cdot}2H_2O$ (51 mg, 0.3 mmol), NaN_3 (39 mg, 0.6 mmol) and 4-cyanopyridine (125 mg, 1.2 mmol) in H_2O and DMF (1mL:6mL) mixture was placed into a reaction tube that was irradiated with microwave radiation for 30 min at 85 °C. The resultant green coloured precipitate was filtered off from brown solution and discarded. The filtrate was left to slowly evaporate in air resulting in the formation of blue cubic shaped crystals in 3 d. These were isolated and washed with DMF and diethyl ether. Yield = 55mg, (19.1%), anal calc for $C_{12}H_{12}CuN_{10}O_2$: C, 36.78, H, 3.09, N, 35.75, found: C, 37.00, H, 3.11, N, 35.78. IR (KBr): 3486(m), 1659(s), 1494(w), 1438(m), 1389(m), 1253(m), 1102(m). Purity of bulk sample of **2** was confirmed by the PXRD patterns of the sample (Fig. S2).

X-ray crystallography. Single crystal X-ray structural studies of compounds **1** and **2** were performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data were collected at 150(2) K using graphite-monochromoated Mo Kα radiation (λ_α = 0.71073 Å). The strategy for the data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard phi-omega scan techniques and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on F^2.[9]

The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2U_{eq} of their parent atoms. The crystal and refinement data are summarized in Table 1.

It is worthy to note that randomly dispersed solvent molecules (DMF/H_2O used for crystallization) were found in the framework of **2** and attempts made to refine the structure using conventional discrete-atom models remained unsuccessful. This issue was solved by deducting the contribution of the solvent electron density using SQUEEZE routine in PLATON.[10]

Typical procedures for the catalytic oxidation of alcohols and product analysis: Oxidation reactions were carried out in sealed cylindrical Pyrex tubes under focused microwave irradiation as follows: the alcohol substrate (5 mmol), catalyst precursor **1** or **2** (10 μmol, 0.2 mol% *vs*. substrate) and a 70 % aqueous solution of TBHP (10 mmol) were introduced into the tube. This was then placed in the microwave reactor and the system was stirred and irradiated (10 W) for 0.25-3 h at 80 ºC. After the reaction, the mixture was allowed to cool down to room temperature. 300 μL of benzaldehyde (internal standard) and 5 mL of NCMe (to extract the substrate and the organic products from the reaction mixture) were added. The obtained mixture was stirred during 10 min and then a sample (1 μL) was taken from the organic phase and analysed by GC using the internal standard method.

Results and Discussion

Compound **1** has been prepared by reacting a solution of copper(II) chloride with two equivalents of sodium azide along with an excess of 4-cyanopyridine (4 equivalents) in a 1:6 (v:v) mixture of water and DMF at 85 °C for 4 h (Scheme 1). A green coloured solid **1** was precipitated and its further crop was obtained upon filtration and subsequent evaporation of the mother liquor, producing green crystals suitable for single-crystal X-ray diffraction.

A different procedure involved a microwave irradiation, at 85 °C for 30 min, of a mixture containing copper(II) chloride, sodium azide and 4-cyanopyridine in a 1:2:4 molar ratios using a water-DMF mixture (1:6, v:v). The obtained mixture was filtered and the filtrate was left in air for 3 d, resulting in blue coloured cubic crystals of **2**, suitable for single-crystal X-ray diffraction analysis.

The obtained compounds were characterized by IR spectroscopy, elemental analysis and single-crystal X-ray crystallography. The IR spectrum of **1** shows a strong band at 2081 cm^{-1} typical for μ-azide ions in a 1,1-bridging mode.[11] Additional band due to the presence of tetrazole ions is observed in the 1655–1670 cm^{-1} range.[12] In **2**, the stretching band at 1659 cm^{-1} indicates the presence of tetrazolate ion,[12] while the characteristic broad band of water molecule at 3486 cm^{-1} arises from the O-H stretching.[11] Powder X-ray diffraction (PXRD) patterns were recorded for samples **1** and **2** showing a very good matching with the respective simulated patterns acquired from the single crystal X-ray data, thus demonstrating the phase purity of the bulk samples.

Crystal structure of $\{[Cu_3(\mu_3\text{-4-ptz})_4(\mu_2\text{-}N_3)_2(DMF)_2]\cdot(DMF)_2\}_n$ (1): The 3D polymeric structure of compound **1** bearing a trinuclear Cu(II) core was revealed by single crystal X-ray diffraction data. There are two types copper centres observed in the trinuclear secondary building unit (SBU) (Fig 1a). The “central” six-coordinate Cu1 atom possesses a distorted octahedral geometry filled by four bridging 4-ptz ligands in the equatorial sites, whereas the axial positions are taken by the azide moieties that bridge in a $\mu_{1,1}$-mode linking the copper centres into a Cu_3 SBU. The copper azide bond distances are relatively large (2.326 Å) because of Jahn-Teller effect. The bond length and bond angle data are summarized in Table 2. Apart from azide linkers, the “outer” six-coordinate Cu2 atoms are connected with the “central” Cu1 ion by means of two tetrazolate moieties which are bridging in a N2/N3 mode. The other coordination positions of the Cu2 atoms are occupied by two pyridyl groups of the bridging 4-ptz ligands and one terminal DMF molecule. Each of these trinuclear SBUs is interlinked with eight adjacent Cu_3 units via the 4-ptz moieties, resulting in an intricate 3D metal-organic framework with the box type open-end voids having the 1.3 × 1.5 nm dimensions (Fig 1b). The solvent of crystallization (DMF molecules) occupy the voids and further stabilize the obtained framework via H-bonding interactions (Table 3).

To better understand an intricate structure of the 3D metal-organic framework **1**, we have carried out its topological analysis[13] using the concept of the simplified underlying net.[14,15]

Hence, after omitting the terminal DMF ligands and reducing the μ$_2$-N$_3$ and μ$_3$-4-ptz moieties to their centroids, the resulting network (Fig. 2a) can be described as an underlying net constructed from the 6-connected Cu1 and 5-connected Cu2 nodes, 3-connected μ$_3$-4-ptz nodes and 2-connected μ$_2$-N$_3$ linkers. The topological analysis of this net reveals a complex trinodal 3,5,6-connected network with a unique topology depicted by the point symbol of $(3.8^2)_4(3^2.4.8^3.9^3.10)_2(3^4.4^2.9^6.10^3)$, wherein the (3.8^2), $(3^2.4.8^3.9^3.10)$ and $(3^4.4^2.9^6.10^3)$ indices correspond to the μ$_3$-4-ptz, Cu2 and Cu1 nodes, respectively. The obtained network can be simplified further, namely by treating the tricopper [Cu$_3$(μ$_2$-N$_3$)$_2$] units as the 8-connected cluster nodes and the μ$_3$-4-ptz blocks as the 2-connected linkers, resulting in a uninodal 8-connected net (Fig. 2b) with the **bcu** (body centred cubic) topology and the point symbol of $(4^{24}.6^4)$.[14,16,17]

Crystal structure of {[Cu(μ$_2$-4-ptz)$_2$(H$_2$O)$_2$]}$_n$ (2): Single crystal X-ray diffraction data revealed that the structure of **2** features a 2D coordination framework assembled from the Cu(II) centres and μ$_2$-4-ptz linkers. The geometry around the six-coordinate Cu1 atom is also distorted octahedral, being filled by a pair of N atoms from pyridyl group and another pair of tetrazolato N atoms from the 4-ptz moieties in the mutually *trans*-fashion to complete the square base, whereas the remaining axial positions are occupied by oxygen atoms of two terminal water ligands (Fig 3a). The coordinated water molecules are arranged comparatively far from the basal plane moieties (Table 2). Hence, each 4-ptz acts as a μ$_2$-linker sewing the Cu centres into a grid-like 2D network. The adjacent 2D layers are stacked and zipped through hydrogen bonding interactions [C(5)-H(5)...O(1), to generate a 3D supramolecular network (Table 3). The inter-layer distance between two adjacent layers is 13.072 Å (Fig. 3b). A 3D supramolecular network features porosity due to the presence of open-ended rhombic shaped voids along the *c* axis, with the dimensions of 1.6 × 1.1 nm (Fig. 3c). In addition, the above voids were loaded with disordered solvent molecules (probably water and DMF used during crystallization), which could not be refined by discrete-atom models and thus were subtracted from the diffraction pattern by the "SQUEEZE" method.

The 2D metal-organic network of **2** has also been simplified for the sake of topological analysis, namely by omitting the terminal H$_2$O moieties and contracting the μ$_2$-4-ptz ligands to their centroids. The obtained underlying layer is thus assembled from the 4-connected Cu1 nodes and 2-connected μ$_2$-4-ptz linkers (Fig. 4). From the topological viewpoint, this 2D network can be classified as a uninodal 4-connected net with the **sql** [Shubnikov tetragonal plane net] topology described by the point symbol of ($4^4.6^2$).[14,16] A number of 4-ptz derivatives with the **sql** topology have been reported.[3g,18]

Added Solvent-Free Microwave-Assisted Oxidation of Secondary Alcohols

Complexes **1** and **2** have been tested as catalyst precursors for the homogeneous oxidation of secondary alcohols (1-phenyletanol, cyclohexanol, 2-hexanol, 3-hexanol, 2-octanol and 3-octanol) to the corresponding ketones using *tert*-butylhydroperoxide (TBHP) or hydrogen peroxide as oxidizing agent, under typical conditions of 80 ºC, and low power (10 W) microwave irradiation (MW), 1 h reaction time and in the absence of any added solvent or additive (Scheme 2). Selected results are summarized in Table 4, whereas the complete set of results is presented in Table S1.

Under typical conditions the ketone yields up to 86% (TOF = 430 h^{-1}) are obtained for the oxidation of 1-phenylethanol (entry 18, Table 4) by **2**. As expected, the aliphatic alcohols are less reactive than the benzylic derivative, 1-phenylethanol, leading under the same reaction conditions to moderate yields in the 38-67 % range (Table 4), as reported in other cases.[7] Higher yields of cyclohexanone were previously obtained with a related TBHP/MW system in the presence of the tetranuclear Cu(II) complex derived from 2-(2-(dicyanomethylene)hydrazinyl)benzoic acid[19a], although requiring a 4 times longer reaction time. An almost quantitative formation of acetophenone after 4 or 2 h reaction was achieved by oxidation of 1-phenylethanol with TBHP catalysed by $[(PhSiO_{1.5})_{10}(CuO)_2(NaO_{0.5})_2\cdot 4EtOH]$ [19b] or $[(PhSiO_{1.5})_{12}(CuO)_4(NaO_{0.5})_4]$,[19c] respectively. However, the oxidation of 1-phenylethanol by the **1** or **2**/TBHP/MW systems affords acetophenone in much higher yields (86% (**2**) or 79% (**1**), Table 4) than in the presence of various mononuclear Cu(II) complexes bearing N_2S_2 macrocycles[20] or dinuclear Mn(II) compounds.[7h,i]

Moreover, it appears that the efficiency of oxidation of linear aliphatic alcohols (C_6 or C_8) is not affected by the position of the OH group in the aliphatic chain of the substrate, as attested by similar yields of 2- and 3-hexanones or 2- and 3-octanones (compare *e.g.*, entries 27 and 29 or 31 and 33, Table 4). However, alcohols with a shorter aliphatic chain typically lead to higher product yields (Table 4, entries 10, 12 *vs.* 14, 16).

The relevance of the 4-ptz ligands on the catalytic activity of the obtained compounds is shown by the catalytic performances of $CuCl_2$ in the oxidation of the used substrates (yields in the 2–7 % range, entries 69 and 72-76, Table S1) compared with those of **1** and **2** under the same reaction conditions.

Addition of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) radical, an efficient mediator for the aerobic oxidation of alcohols[7d,j,21] although scarcely used for the peroxidative oxidation [7h,i,m,22] of those substrates, provided the quantitative formation of acetophenone (entry 22, Table 4) and a significant increase in all other ketone yields (see *e.g.*, entries 1, 4, 10, 12, 14 or 16 *vs.* 2, 8, 11, 13, 15 or 17, Table 4).

It should be noted that in contrast to TBHP, hydrogen peroxide (30% aqueous solution) is a less efficient reagent for the oxidation of the tested alcohols, as attested by the marked ketone yield lowering (see Fig. 5 and Table S1), in accord with the known decomposition of H_2O_2 under the used reaction conditions (80 ºC). Moreover, the use of a higher amount of oxidant (see entries 5, 19 or 2, 45 of Tables 4 and S1, respectively) or longer reaction time (see *e.g.*, entries 3, 9, 23 26, Table 4) does not lead to a better conversion.

Attempts to perform the oxidation of secondary alcohols in the presence of **1** or **2** at room temperature failed, whereas the reaction conducted at 50 °C resulted in a marked ketone yield drop relative to that at 80 °C (*e.g.*, for **1**, from 79, 58, 63, or 38 % at 80 °C to 22, 15, 23 or 17 % at 50 °C, respectively, Table S1 and Fig. 6). Moreover, the ketone yield does not increase significantly above 80 °C (see Fig. 6 and entries 1, 10, 19, 24, 27, 35, 44, 56, or 64 *vs.* 9, 18, 23, 26, 31, 43, 52, 60 or 68, Table S1).

Microwave irradiation (MW) can provide a more efficient synthetic method than conventional heating, thus allowing the attainment of similar yields in shorter times or improved yields and/or selectivities.[7c,h-m, 22] A favourable effect of MW is also observed in this study, even with the low power of 10 W. Hence, for example, 86% yield of acetophenone was obtained after 1 h reaction under the microwave irradiation, while similar reaction under conventional heating (oil bath) gives only 7% yield. A noteworthy feature of our MW-assisted oxidations is the application of a very weak MW irradiation (10 W). This contrasts with most of the MW-assisted organic reactions reported,[23] which require a much higher power of MW irradiation (typically above 200 or even 500 W).

Furthermore, important features of **1** and **2** concern their relatively low loading (0.2 mol% *vs*. substrate) necessary to reach high yields of ketone (*e.g*., up to 99% of acetophenone when in the presence of TEMPO), also undergoing under solvent- and additive-free conditions. This is advantageous in comparison with the common use of organic solvents or costly ionic liquids in various state-of-the-art methods for the oxidation of alcohols.[23b, 24]

The peroxidative oxidation of the tested secondary alcohols is believed to proceed mainly via a radical mechanism which involves both carbon- and oxygen-centred radicals. In fact, the addition to the reaction mixture of Ph_2NH or $CBrCl_3$, well known oxygen- and carbon-radical traps, respectively,[25] led to a large yield drop of over 90% (Table S1, entries 4, 38 *vs*. 5, 39 for 1-phenylethanol or 13, 47 *vs*. 14, 48 for cyclohexanol, respectively), compared to the reaction carried out under the same conditions but in the absence of a radical trap (Table S1, entries 1, 10, 35 or 44, respectively). This result suggests the generation of oxygen and carbon radicals in the reaction, which are trapped by those radical scavengers.

A possible mechanism [21i,21k,26] for this system may involve coordination of the alcohol *e.g*., PhCH(OH)Me (with deprotonation to form an alkoxide ligand) and TEMPO radical, followed by H transfer from the former to the latter with formation of the *O*-ligated radical $PhC^{\bullet}(O)Me^{-}$ and TEMPOH. Intramolecular electron-transfer from the $PhC^{\bullet}(O)Me^{-}$ coordinated to Cu^{II} leads to the formation of the ketone PhC(O)Me and Cu^{I} which is reoxidised to Cu^{II} by O_2/TBHP. The TEMPO radical is also regenerated upon oxidation of TEMPOH.

In order to get further insight into the catalytic cycle, the model reaction with 5 mmol of cyclohexanol, 10 mmol of aqueous solution of TBHP and 5 mol% TEMPO was monitored, under dinitrogen atmosphere in the presence of catalyst precursors **1** and **2**, by spectrophotometry. Upon addition of the catalyst precursor into the reaction mixture [cyclohexanol and TBHP (70 wt % in water)] a strong MLCT band was instantaneously observed at 442 nm (Fig. S3), being characteristic for a copper(I) species.[27] After addition of TEMPO the solution color changes from colorless to orange and this color upon exposure to dioxygen gradually changed to brown with time, indicating the initial reduction of copper(II) (green) to copper(I) (orange) in the presence of alcohol and TEMPO. These results also confirm the radical mechanism where reduction of copper(II) leads to the oxidation of alcohol, followed by the subsequent oxidation of copper(I) by O_2/TBHP.

The solids obtained after the oxidation reactions with the catalyst precursors **1** and **2** have been analyzed by IR spectroscopy, PXRD and elemental analyses. From the IR spectrum of a solid derived from **1** after the catalytic reaction, it has been found that the band at 2081 cm^{-1} has vanished, clearly indicating the absence of azide in the system, whereas the observed hump at 1656 cm^{-1} might suggest the presence of tetrazole in the residue. The elemental analysis result with a high percentage of nitrogen also indicates the probable presence of tetrazole in the residual compound derived from **1**. The PXRD pattern confirms that **1** lost its crystalline nature and has a structure well distinct from that of the parent compound **1** (Fig. S4). In the case of **2**, although the IR spectrum of the corresponding residual compound after the catalytic reaction is almost similar to that of **2** and elemental analysis data suggest the presence of tetrazole moieties, the PXRD pattern also indicates the deformation of the framework (Fig. S5). These observations indicate that both compounds **1** and **2** are not intact during the course of catalytic tests and thus behave as precursors of homogeneous catalytically active species. We believe further research aiming at the incorporation of the present types of tetrazole based copper-organic frameworks on solid matrices or supports would allow the generation of more stable and potentially recyclable catalytic systems. This research direction as well as the detailed investigation of the mechanism will be explored in our future studies.

Conclusions

Two different metal-organic frameworks **1** and **2** have been synthesized by means of 1,3-dipolar cycloaddition between 4-cyanopyridine and azide in the presence of copper(II) chloride by varying the reaction conditions only. A notable feature of an underlying 3,5,6-connected 3D net of **1** concerns its novel topology described by the point symbol of $(3.8^2)_4(3^2.4.8^3.9^3.10)_2(3^4.4^2.9^6.10^3)$, which can be further simplified to a body centred cubic (**bcu**) network bearing a trinuclear Cu_3-secondary building unit. In contrast, the 2D network of **2** reveals an underlying Shubnikov tetragonal plane net (**sql**). Thus, the present work also contributes to the identification of novel topological types observed within the metal-organic framework materials. Furthermore, both compounds show a high activity as catalyst precursors towards the microwave-assisted homogeneous oxidation of secondary alcohols leading to the ketone yields up to 99% (**2**) under added solvent-free conditions. Hence, this study also widens the scope of MW-assisted transformations applied to the oxidative functionalization of organic substrates and extends the range of efficient catalytic systems applicable to such reactions.

Supplementary Materials

CCDC 940211 and 940212 (squeezed refined structures) contain the supplementary crystallographic data for **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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References:

[1] (a) M-X. Yang, L-J. Chen, S. Lin, X-H. Chen and H. Huang, *Dalton Trans.* 2011, **40**, 1866-1872.

(b) W. Ouellette, K. Darling, A. Prosvirin, K. Whitenack, K.R. Dunbar and J. Zubieta, *Dalton Trans.* 2011, **40**, 12288-12300.

(c) S. Jeong, X. Song, S. Jeong, M. Oh, X. Liu, D. Kim, D. Moon and M.S. Lah, *Inorg.Chem.* 2011, **50**, 12133-12140.

(d) J.-Z. Liao, H. Ke, J.-J. Liu, Z.-Y. Li, M.-J. Lin, J.-D. Wang and C.-C. Huang, *Cryst. Eng. Comm.* 2013, **15**, 4830-4837.

(e) H. Deng, Y-C. Qiu, Y-H. Li, Z-H. Liu, R-H. Zeng, M.Zeller and S.R.Batten, *Chem.Commun.* 2008, 2239-2241.

(f) B. Liu, Y-C. Qiu, G. Peng and H. Deng, *Cryst.Eng.Comm.* 2010, **12**, 270-276.

(g) W-T. Liu, J-Y. Li, Z-P. Ni, X. Bao, Y-C. Ou, J-D. Leng, J-L. Liu and M-L. Tong, *Cryst. Growth Des.* 2012, **12**, 1482−1488

(h) P. Cui, Z. Chen, D. Gao, B. Zhao, W. Shi and P. Cheng, *Cryst. Growth Des*. 2010, **10**, 4370-4378

(i) R. Nasani, M. Saha, S.M. Mobin and S. Mukhopadhyay, *Polyhedron*, 2013, **55,** 24–36.

(j) M. Saha, R. Nasani, S.M. Mobin, B. Pathak and S. Mukhopadhyay, *Inorg. Chem. Commun.,* 2013, **34**, 62–67.

[2] (a) W. Ouellette and J. Zubieta, *Chem.Commun.* 2009, 4533-4535.

(b) C-C. Chang, Y-C. Huang, S-M. Huang, J-Y. Wu, Y-H. Liu and K-L. Lu, *Cryst.Growth Des.,* 2012, **12**, 3825-3828.

(c) X. Wang, J. Peng, M-G Liu, D-D. Wang, C-L. Meng and Y. Li, Z-Y Shi, *Cryst. Eng. Comm.,* 2012, **14**, 3220-3226.

(d) Y-T. Yang, F-H. Zhao, Y-X. Che and J-M. Zheng, *Inorg. Chem. Commun.,* 2011, **14**, 1855-1859.

(e) K.Darling, W.Ouellette, S.Pellizzeri, T.Smith, J.Vargas, S.Tomaszfski, C.J.O'Connor and J.Zubieta, *Inorg. Chim. Acta.* 2012, **392**, 417-427.

(f) F. Yang, B. Li, W. Xu, G. Li, Q. Zhou, J. Hua, Z. Shi and S. Feng, *Inorg. Chem.*, 2012, **51**, 6813-6820.

(g) S.Mukhopadhyay, B.G.Mukhopadhyay, A.F.C.G.da Silva, J.Lasri, M.A.J.Charmier and A.J.L.Pombeiro, *Inorg.Chem.*, 2008, **47**, 11334-11341.

[3] (a) K.Darling, W.Ouellette and J.Zubieta, *Inorg.Chim.Acta.*, 2012, **392**, 52-60.

(b) C. Jiang, Z. Yu, S. Wang, C. Jiao, J. Li, Z. Wang, Y. Cui, *Eur. J. Inorg. Chem.*, 2004, 3662-3667.

(c) J-Q. Sha, J-W. Sun, M-T. Li, C. Wang, G-M. Li, P-F. Yan and L-J. Sun, *Dalton Trans.*, 2013, **42**, 1667-1677.

(d) S.Jones, H. Liu, C.C.O'Connor and J.Zubieta, *Inorg. Chem. Commun.*, 2010, **13**, 412-416.

(e) F. Wang, J. Zhang, S-M. Chen, Y-M. Xie, X-Y. Wu, S-C. Chen, R-M. Yu and C-Z. Lu, *Cryst.Eng.Comm.*, 2009, **11**, 1526-1528.

(f) F. Wang, R-M. Yu, X-Y. Wu and C-Z. Lu, *Inorg.Chem.Commun.*, 2012, **19**, 70-72.

(g) F. Wang, R. Yu, Q-S. Zhang, Z-G. Zhao, X-Y. Wu, Y-M. Xie, L. Qin, S-C. Chen and C-Z. Lu, *J. Solid State Chem.* 2009, **182**, 2555-2559.

(h) F. Wang, J. Zhang, R. Yu, S-M. Chen, X-Y. Wu, S-C. Chen, Y-M. Xie, W-W. Zhou and C-Z. Lu, *Cryst.Eng.Comm.*, 2010, **12**, 671-673.

[4] (a) L.V. Myznikov, J. Roh, T.V. Artamonova, A. Hrabalek and G. I. Koldobskii, *Russ. J. Org. Chem.*, 2007, **43**, 765-767.

(b) F. Himo, Z. P. Demko,L. Noodleman, and K. B. Sharpless, *J. Am. Chem. Soc*., 2003, **125**, 9983-9987.

(c) Y. Zhou, C. Yao, R. Ni and G. Yang, *Synth. Comm.*, 2010, **40**, 2624-2632.

(d) V. Aureggi and G. Sedelme, *Angew. Chem. Int. Ed*., 2007, **46**, 8440-8444.

[5] (a) *Functional Metal-Organic Frameworks: Gas Storage, Separation and Catalysis*; Ed.: M. Schroder, Springer, 2010.

(b) *Metal-Organic Frameworks: Applications from Catalysis to Gas Storage*; Ed.: D. Farrusseng, Wiley, 2011.

[6] (a) A.M. Kirillov, M.V. Kirillova and A.J.L. Pombeiro, *Coord. Chem. Rev.*, 2012, **256**, 2741-2759.

(b) M.V. Kirillova, A.M. Kirillov, A.N.C. Martins, C. Graiff, A. Tiripicchio and A.J.L. Pombeiro, *Inorg. Chem*., 2012, **51**, 5224-5234.

(c) Y.Y. Karabach, M.F.C.G. da Silva, M.N. Kopylovich, B. Gil-Hernandez, J. Sanchiz, A.M. Kirillov and A.J.L. Pombeiro, *Inorg. Chem*., 2010, **49**, 11096-11105

(d) A. M. Kirillov, J. A. S. Coelho, M. V. Kirillova, M. F. C. Guedes da Silva, D. S. Nesterov, K. R. Gruenwald, M. Haukka and A. J. L. Pombeiro. *Inorg. Chem*., 2010, **49**, 6390-6392.

[7] (a) M.N. Kopylovich, J. Lasri, M.F.C. Guedes da Silva, J.J.R. Fraústo da Silva and A.J.L. Pombeiro, *Chem. Commun*., 2010, **46**, 2766-2768.
(b) R.R. Fernandes, J. Lasri, M.F.C. Guedes da Silva, J.A.L. da Silva, J.J.R. Fraústo da Silva and A.J.L. Pombeiro, *Appl. Catal. A: Gen.*, 2011, **402**, 110-120.
(c) M.N. Kopylovich, Y.Y. Karabach, M.F.C. Guedes da Silva, P.J. Figiel, J. Lasri and A.J.L. Pombeiro, *Chem. Eur. J.*, 2012, **18**, 899-914.
(d) P.J. Figiel, A. M. Kirillov, Y. Y. Karabach, M. N. Kopylovich and A. J. L. Pombeiro *J. Mol. Catal. A: Chem*., 2009, **305**, 178-182.
(e) P. J. Figiel, A. M. Kirillov, M. F. C. Guedes da Silva, J. Lasri and A. J. L. Pombeiro. *Dalton Trans*., 2010, **39**, 9879-9888.
(f) A. M. Kirillov, M. V. Kirillova, L. S. Shul'pina, P. J. Figiel, K. R. Gruenwald, M. F. C. Guedes da Silva, M. Haukka, A. J. L. Pombeiro and G. B. Shul'pin. *J. Mol. Catal. A: Chem*., 2011, **350**, 26-34.
(g) M. V Kirillova, A. M. Kirillov, D. Mandelli, W. A. Carvalho, A. J. L. Pombeiro and G. B. Shul'pin, *J. Catal*., 2010, **272**, 9-17.

(h) 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 and V.B. Arion, *Eur. J. Inorg. Chem.*, 2014, 120-131.

(i) M. Sutradhar, L.M.D.R.S. Martins, M.F.C. Guedes da Silva, E.C.B.A. Alegria, C.-M. Liu and A.J.L. Pombeiro, *Dalton Trans*., 2014, **43**, 3966-3977.

(j) Z. Ma, L. Wei, E.C.B.A. Alegria, L.M.D.R.S. Martins, M.F.C. Guedes da Silva and A.J.L. Pombeiro, *Dalton Trans*., 2014, **43**, 4048-4058.

(k) R.R. Fernandes, J. Lasri, M.F.C. Guedes da Silva, J.A.L. Silva, J.J.R. Fraústo da Silva and A.J.L. Pombeiro, *J. Mol. Catal. A*, 2011, **351**, 100–111.

(l) J. Lasri, M.J.F. Rodriguez, M.F.C. Guedes da Silva, P. Smolenski, M.N. Kopylovich, J.J.R. Fraústo da Silva and A. L. Pombeiro, *J. Organomet. Chem*., 2011, **696**, 3513–1520.

(m) A. Sabbatini, L.M.D.R.S. Martins, K.T. Mahmudov, M.N. Kopylovich, M.G.B. Drew, C. Pettinari, A.J.L. Pombeiro, *Cat. Com*., 2014, **48**, 69-72.

[8] (a) W.G. Dauben, M. Lorber and D.S. Fullerton, *J. Org. Chem*., 1969, **34**, 3587-3592.

(b) G. Rothenberg, H. Wiener and Y. Sasson, *J. Mol. Catal. A: Chem.* 1998, **136**, 253-262.

(c) J. Singh, M. Sharma, M. Chhibber, J. Kaur and G.L. Kad, *Synth. Commun*., 2000, **30**, 3941-3945.

(d) M. Hudlicky, *Oxidations in Organic Chemistry*, ACS Monograph 186, Washington, DC, 1990.

(e) I.E. Markó, P.R. Giles, M. Tsukazaki, S.M. Brown and C.J. Urch, *Science*, 1996, **274** 2044-2046.

(f) G. Rothenberg, L. Feldberg, H. Wiener and Y. Sasson, *J. Chem. Soc. Perkin Trans.* 1998, **2**, 2429-2434.

(g) R. Chakrabarty, P. Sarmah, B. Saha, S. Chakravorty and B.K. Das, *Inorg. Chem*., 2009, **48**, 6371-6379.

(h) I.E. Markó, A. Gautier, R. Dumeunier, K. Doda, F. Philippart, S.M. Brown and C.J. Urch, *Angew. Chem. Int. Ed.*, 2004, **43**, 1588-1591.

(i) S.S. Stahl, *Angew. Chem. Int. Ed.*, 2004, **43**, 3400-3420.

(j) G.-J. ten Brink, I.W.C.E. Arends and R.A. Sheldon, *Science* 2000, **287**, 1636-1639.

(k) Y. Uozumi and R. Nakao, *Angew. Chem. Int. Ed.*, 2003, **42**, 194-197.

(l) D.S. Bailie, G.M.A. Clendenning, L. McNamee and M.J. Muldoon, *Chem. Commun.*, 2010, **46**, 7238-7240.

(m) D. S.-Rozner, P.L. Alsters and R. Neumann, *J. Am. Chem. Soc*., 2003, **125**, 5280-5281.

(n) V.R. Choudary, D.K. Dumbre, B.S. Uphade and V.S. Narkhede, *J. Mol. Catal. A: Chem*. 2004, **215**, 129-135.

(o) J. Boudreau, M. Doucette and A.N. Ajjou, *Tetrahedron Lett*. 2006, **47**, 1695-1698.

(p) W. Zhao, Y. Zhang, B. Ma, Y. Ding and W. Qiu, *Catal. Commun.*, 2010, **11**, 527-531.

(q) R.A. Sheldon, I. Arends and U. Hanefeld, *Green Chemistry and Catalysis*, Wiley-VCH, 2007.

(r) P. Anastas and N. Eghbali, *Chem. Soc. Rev*., 2010, **39**, 301-312.

(s) S. Liu and J. Xiao, *J. Mol. Catal. A: Chem*., 2007, **270**, 1-43.

[9] (a) G.M. Sheldrick, *Acta Crystallogr., Sect. A,* 2008, **A64**, 112-122.

(b) Program for Crystal Structure Solution and Refinement; University of Goettingen: Goettingen, Germany, 1997.

[10] A. L. Spek, J. Appl. Crystallogr., 2003, **36**, 7–13

[11] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New Jersey, **2009**.

[12] (a) S. Mukhopadhyay, J. Lasri, M. A. J. Charmier, M. F. C. G. Silva and A. J. L. Pombeiro, *Dalton Trans*. 2007, 5297-5304.

(b) P. Smolenski, S. Mukhopadhyay, M. F. C. G. Silva, M. A. J. Charmier and A. J. L. Pombeiro, *Dalton Trans*., 2008, 6546-6555.

[13] V.A. Blatov, *IUCr Comp. Comm, Newsletter* 2006, **7**, 4.

[14] (a) V.A. Blatov and D.M. Proserpio, *In Modern Methods of Crystal Structure Prediction*; A. R. Oganov, Ed.; Wiley: 2010,1−28.

(b) V.A. Blatov, M. O'Keeffe and D.M. Proserpio, *Cryst.Eng.Comm.*, 2010, **12**, 44-48.

(c) E.V. Alexandrov, V.A. Blatov, A.V. Kochetkova and D.M. Proserpio, *Cryst.Eng.Comm.*, 2011, **13**, 3947-3958.

[15] M. O'Keeffe and O.M. Yaghi, *Chem. Rev*., 2012, **112**, 675-702.

[16] The Reticular Chemistry Structure Resource (RCSR) Database; M. O'Keeffe, M.A. Peskov, S.J. Ramsden and O.M. Yaghi, *Acc. Chem. Res*., 2008, **41**, 1782-1789.

[17] For examples of Cu networks with the **bcu** topology, see:

(a) T.-T. Lian and S.-M. Chen, *Inorg. Chem. Comm*., 2012, **18**, 8-10.

(b) H.-Q. Hao, J. Wang, W.-T. Liu and M.-L. Tong, *Cryst.Eng.Comm.*, 2008, **10**, 1454-1459.

(c) Z.-M. Hao, R.-Q. Fang, H.-S. Wu and X.-M. Zhang, *Inorg. Chem.*, 2008, **47**, 8197-8203.

[18] (a) J.M. Seco, M.A. Farias, N.M. Bachs, A.B. Caballero, A. S.-Castillo, A. R.-Dieguez, *Inorg. Chim. Acta.*, 2010, **363**, 3194-3199.

(b) X.-H. Wei, *Acta Crystallogr.*, 2010, **E66**, m551.

(c) W. Ouellette, H. Liu, C.J. O'Connor and J. Zubieta, *Inorg. Chem*., 2009, **48**, 4655-4657.

(d) X.-M. Zhang, Y.-F. Zhao, H.-S. Wu, S.R. Batten and S. W. Ng, *Dalton Trans.*, 2006, 3170-3178.

[19] (a) M.N. Kopylovich, A. Mizar, M.F.C. Guedes da Silva, T.C.O. MacLeod, K.T. Mahmudov and A.J.L. Pombeiro, *Chem. Eur. J.*, 2013, **19**, 588-600.

(b) M.S. Dronova, A.N. Bilyachenko, A.I. Yalymov, Y. N. Kozlov, L.S. Shul'pina, A.A. Korlyukov, D.E. Arkhipov, M.M. Levitsky, E.S. Shubina, G. B. Shul'pin, *Dalton Trans*. 2014, **43**, 872-882.

(c) A.N. Bilyachenko, M.S. Dronova, A.I. Yalymov, A.A. Korlyukov, L.S. Shul'pina, D.E. Arkhipov, E.S. Shubina, M.M. Levitsky, A.D. Kirilin, G.B. Shul'pin, *Eur. J. Inorg. Chem*., 2013, 5240-5246.

[20] R.R. Fernandes, J. Lasri, A.M. Kirillov, M.F.C. Guedes da Silva, J.A.L. Silva, J.J.R. Fraústo da Silva and A.J.L. Pombeiro, *Eur. J. Inorg. Chem*., 2011, 3781-3790.

[21] (a) M.V.N. de Souza, *Mini-Rev. Org. Chem*., 2006, **3**, 155.

(b) T. Vogler and A. Studer, *Synthesis*, 2008, 1979-1993.

(c) R. A. Sheldon and I. W. C. E. Arends *J. Mol. Cat. A: Chem*., 2006, **251**, 200-214.

(d) A. Dijksman, I. W. C. E. Arends and R. A. Sheldon, *Org. Biomol. Chem.*, 2003, **1**, 3232-3237.

(e) R. A. Sheldon and I. W. C. E. Arends, *Adv. Synth. Catal*., 2004, **346**, 1051-1071.

(f) R.A. Sheldon, *Chem. Commun*., 2008, **29**, 3352-3365.

(g) F. Minisci, F. Recupero, G.F. Pedulli and M. Lucarini, *J. Mol. Catal. A: Chem.*, 2003, **204-205**, 63-90.

(h) K.T. Mahmudov, M.N. Kopylovich, M.F.C. Guedes da Silva, P.J. Figiel, Y.Y. Karabach and A.J.L. Pombeiro, *J. Mol. Catal. A: Chem*., 2010, **318**, 44-50.

(i) P.J. Figiel, M. Leskelä and T. Repo *Adv. Synth. Catal*., 2007, **349**, 1173-1179.

(j) P. J. Figiel, A. Sibaouih, J. U. Ahmad, M. Nieger, M. T. Räisänen, M. Leskelä and T. Repo, *Adv. Synth. Catal.*, 2009, **351**, 2625-2632.

(k) J. U. Ahmad, P. J. Figiel, M. T. Räisänen, M. Leskelä and T. Repo, *Appl. Catal. A.*, 2009, **371**, 17-21.

[22] (a) J.A.L. Silva, J.J.R. Fraústo da Silva and A.J.L. Pombeiro, *Coord. Chem. Rev.*, 2011, **255**, 2232-2248.

(b) S.-S. Wang, Z. Popovic and H.-H. Wu, Y. Liu, *Chem. Cat. Chem.*, 2011, **3**, 1208–1213.

(c) M.N.M. Milunovic, L.M.D.R.S. Martins, E.C.B.A. Alegria, A.J.L. Pombeiro, R. Krachler, G. Trettenhahn, C. Turta, S. Shova and V.B. Arion, *Dalton Trans.*, 2013, **42**, 14388-14401.

[23] (a) O. C. Kappe, D. Dallinger, S. Murphree, *Practical Microwave Synthesis for Organic Chemists*, Wiley-VCH, Weinheim, Germany, 2008.

(b) V. Polshettiwar and R. S. Varma, *Acc. Chem. Res.*, 2008, **41**, 629-639.

(c) D. Dallinger and C. O. Kappe, *Chem. Rev.*, 2007, **107**, 2563-2591.

(d) *Microwave Assisted Organic Synthesis* (Eds.: J. P. Tierney, P. Lidström), Blackwell Publishing/CRC Press, Oxford, 2005.

(e) *Microwaves in Organic Synthesis* (Ed.: A. Loupy), Wiley-VCH, Weinheim, Germany, 2002.

(f) Y.Y. Karabach, M.N. Kopylovich, K.T. Mahmudov, A.J.L. Pombeiro, *Microwave-assisted Catalytic Oxidation of Alcohols to Carbonyl Compound* (Ch. 18), in *Advances in Organometallic Chemistry and Catalysis*: *The Silver/Gold Jubilee ICOMC Celebratory Book*, A.J.L. Pombeiro (ed.), Wiley, 2014, 233–245.

[24] (a) G. Tojo, M. Fernández, *Oxidation of Alcohols to Aldehyde and Ketones: A Guide to Current Common Practice*, Springer, New York, **2006**.

(b) I.W.C.E. Arends and R.A. Sheldon, in: *Modern Oxidation Methods* (Ed.: J.-E. Bäckvall), *Wiley-VCH, Weinheim, Germany*, 2004, 83–118.

(c) D. Betz, P. Altmann, M. Cokoja, W.A. Herrmann and F.E. Kühn, *Coord. Chem. Rev.*, 2011, **255**, 1518-1540.

(d) *Ionic Liquids in Synthesis* (Eds.: P. Wasserscheid, T. Welton), vol. 2, Wiley-VCH, Weinheim, Germany, **2008**.

(e) S.F. Liu and J. Xiao, *J. Mol. Catal. A*, 2007, **270**, 1-43.

(f) P.J. Dyson and T.J. Geldbach, *Metal Catalysed Reactions in Ionic Liquids*, Springer, **2005**.

[25] (a) I.N. Moiseeva, A.E. Gekham, V.V. Minin, G.M. Larin, M.E. Bashtanov, A.A. Krasnovskii and I.I. Moiseev, *Kinet. Catal*., 2000, **41**, 170–182.

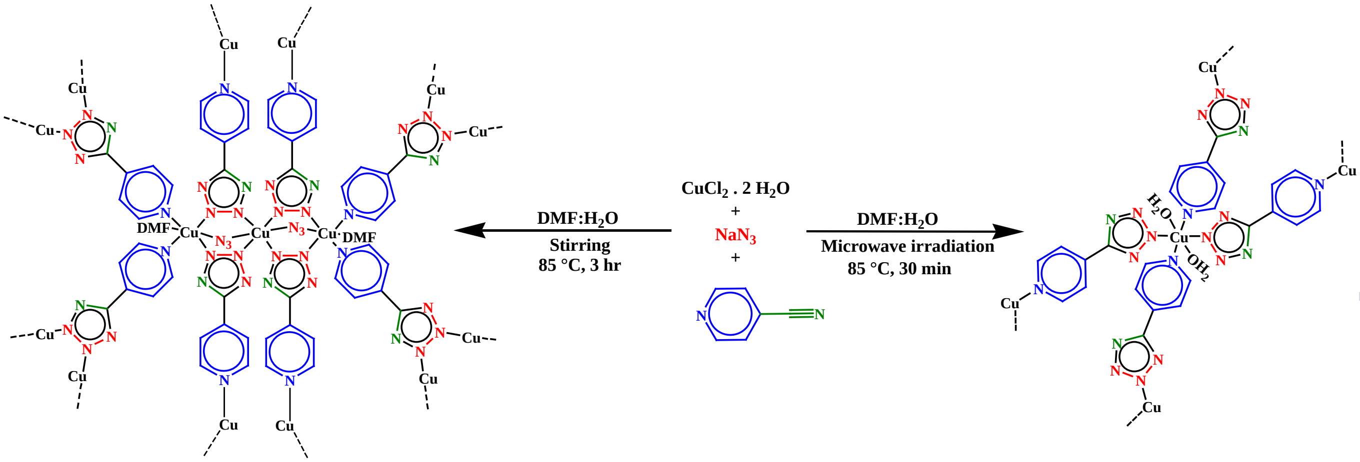
(b) J.M. Mattalia, B. Vacher, A. Samat and M. Chanon, *J. Am. Chem. Soc*., 1992, **114**, 4111–4119.

[26] (a) C. Michel, P. Belanzoni, P. Gamez, J. Reedijk and E. J. Baerends, *Inorg. Chem.*, 2009, **48**, 11909–11920.

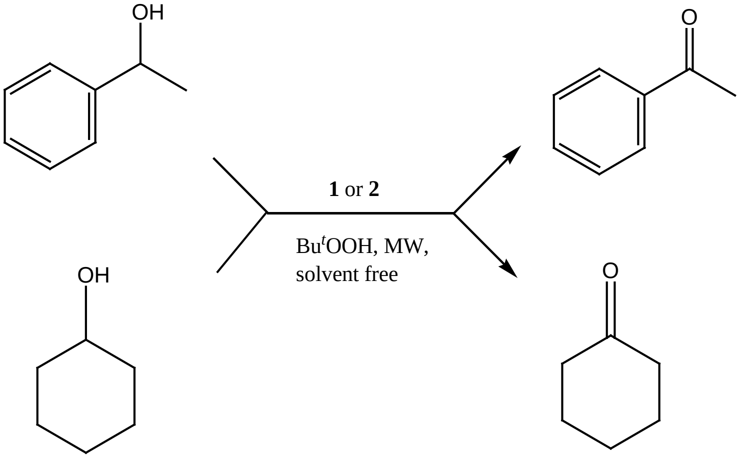
(b) P. Gamez, I. W. C. E. Arends, R. A. Sheldon and J. Reedijk, *Adv. Synth. Catal*., 2004, **346**, 805–811.

[27] (a) S. Samanta, S. Das, P. K. Samanta, S. Dutta and P. Biswas, *RSC Adv*., 2013, **3**, 19455-1946.

(b) G. B. Shaw, C. D. Grant, H. Shirota, E. W. Castner Jr., G. J. Meyer and L. X. Chen, *J. Am. Chem. Soc.*, 2007, **129**, 2147-2160.



Scheme 1: Synthesis and structural formulae of compounds **1** and **2**.



Scheme 2. Added solvent-free oxidation of 1-phenylethanol and cyclohexanol to acetophenoneand cyclohexanone, respectively, by the **1** or **2**/TBHP/MW system.

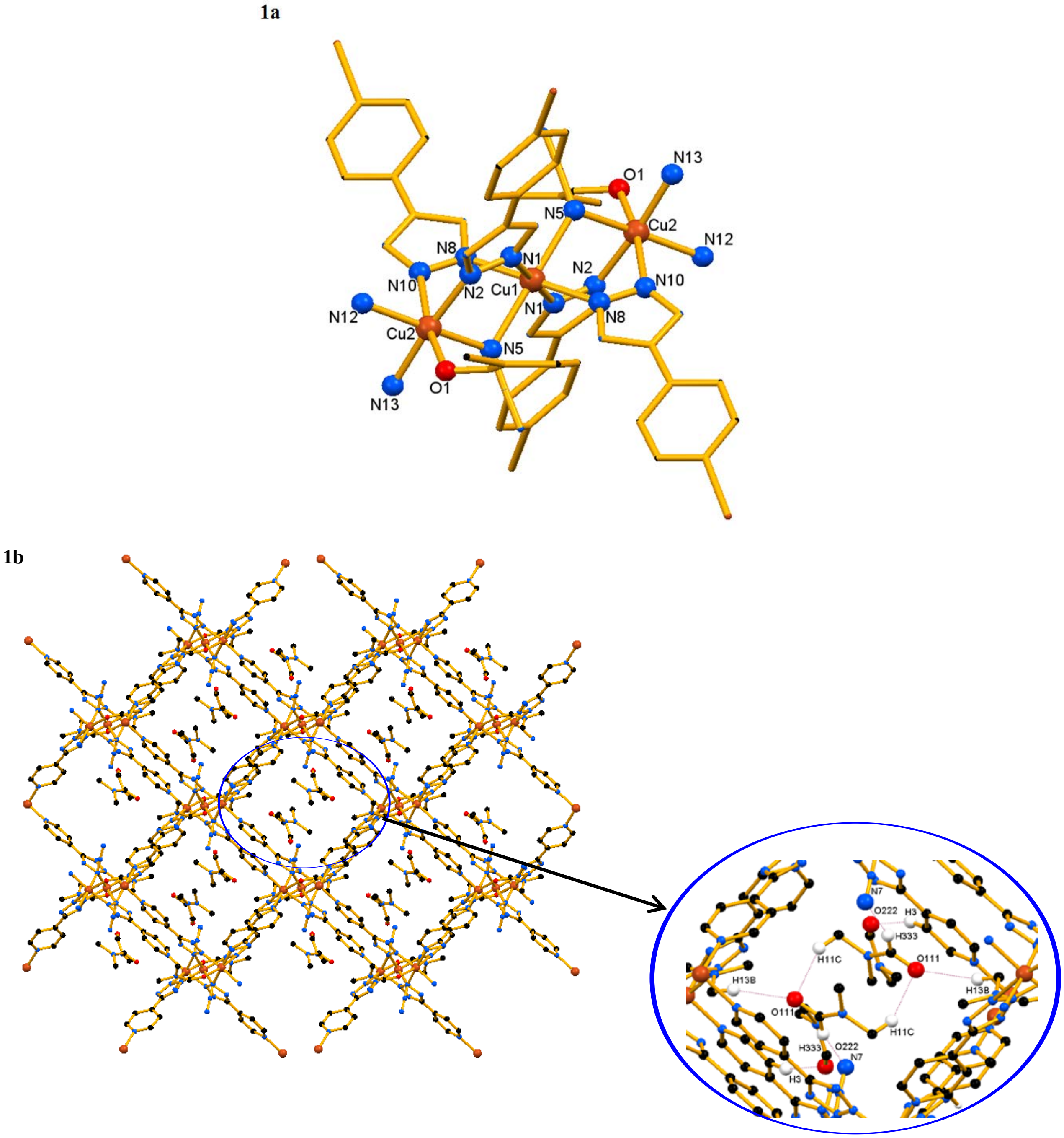
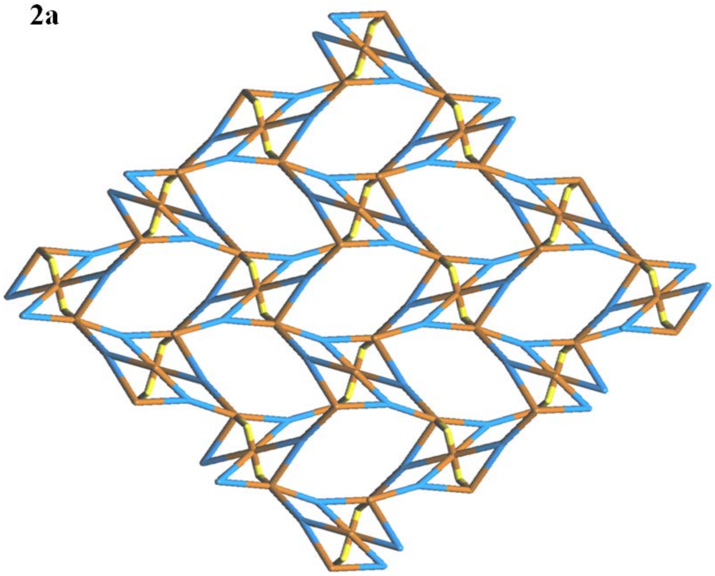


Fig 1. Structural fragments of **1**. (a) Tricopper(II) secondary building unit. (b) 3D metal-organic framework with open-end voids containing DMF molecules as solvent of crystallization (enlarged). Color codes: Cu brown, C black, H white, N blue and O red.

2a



2b

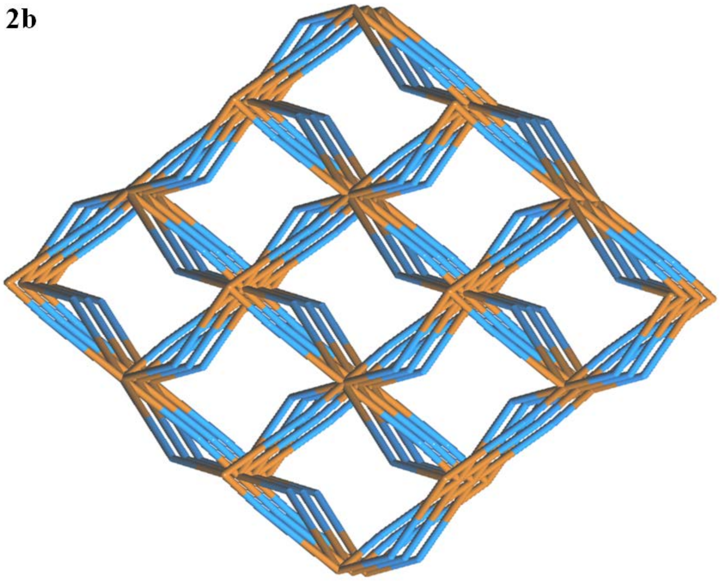


Fig. 2. Topological representations (views along the *a* axis) of the underlying 3D networks in **1** showing: (a) topologically unique trinodal 3,5,6-connected net with the point symbol of $(3.8^2)_4(3^2.4.8^3.9^3.10)_2(3^4.4^2.9^6.10^3)$, and (b) further simplified uninodal 8-connected net with the point symbol of $(4^{24}.6^4)$ and **bcu** (body centered cubic) topology obtained after considering the $[Cu_3(\mu_2\text{-}N_3)_2]$ units as cluster nodes. Further details: (a) 5- and 6-connected Cu2 and Cu1 nodes (brown), centroids of 3-connected μ_3-4-ptz nodes (blue), centroids of 2-connected μ_2-N_3 linkers (yellow); (b) centroids of 8-connected $[Cu_3(\mu_2\text{-}N_3)_2]$ cluster nodes (brown) and centroids of 2-connected μ_3-4-ptz linkers (blue).

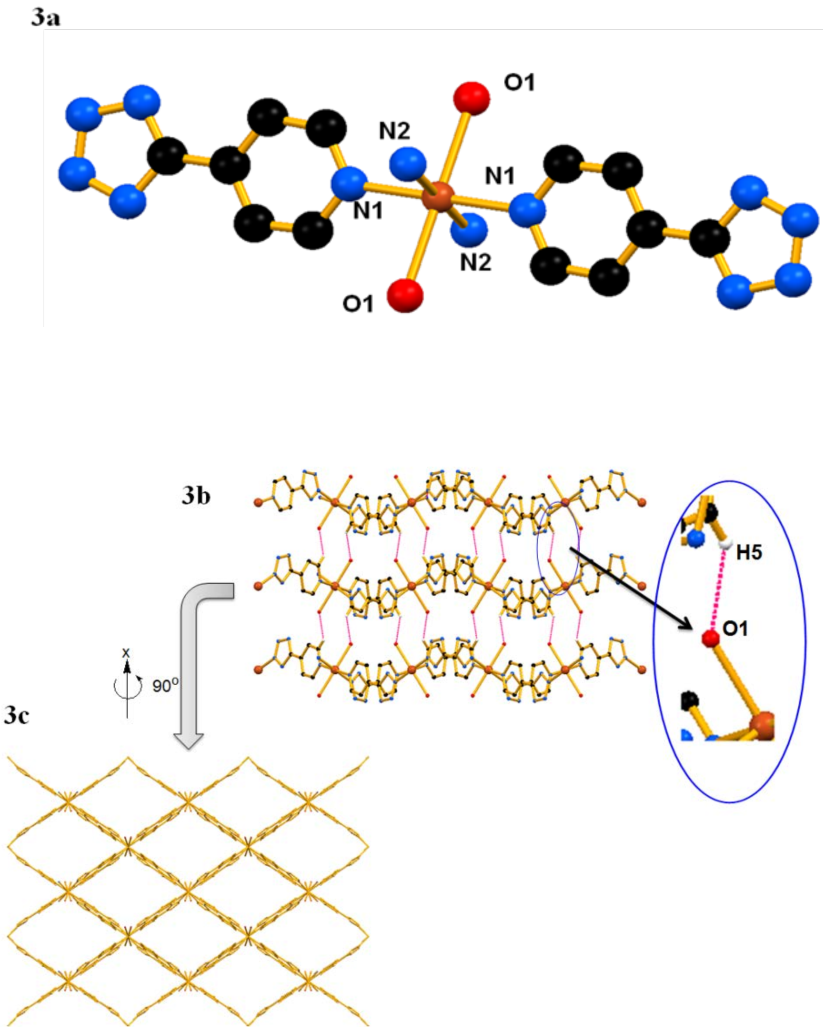


Fig 3. Structural fragments of **2** representing (a) basic unit, (b) stacking of three 2D metal-organic layers (side view of each layer) and hydrogen bonding interactions holding the layers together, (c) view of rhomboid voids along the *c* axis. Color codes: Cu brown, C black, H white, N blue and O red.

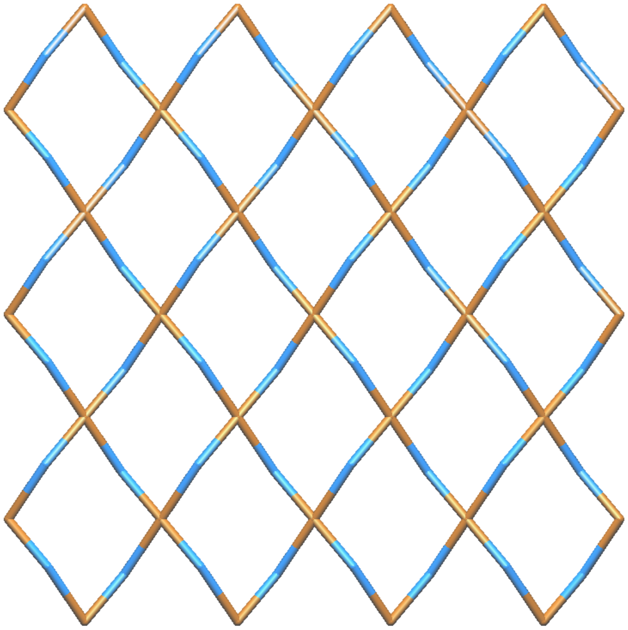


Fig. 4. Topological representation (view along the *c* axis) of the underlying 2D network in **2** showing a uninodal 4-connected net with the point symbol of ($4^4.6^2$) and **sql** [Shubnikov tetragonal plane net] topology. Further details: 4-connected Cu1 nodes (brown) and centroids of 2-connected μ_2-4-ptz linkers (blue).

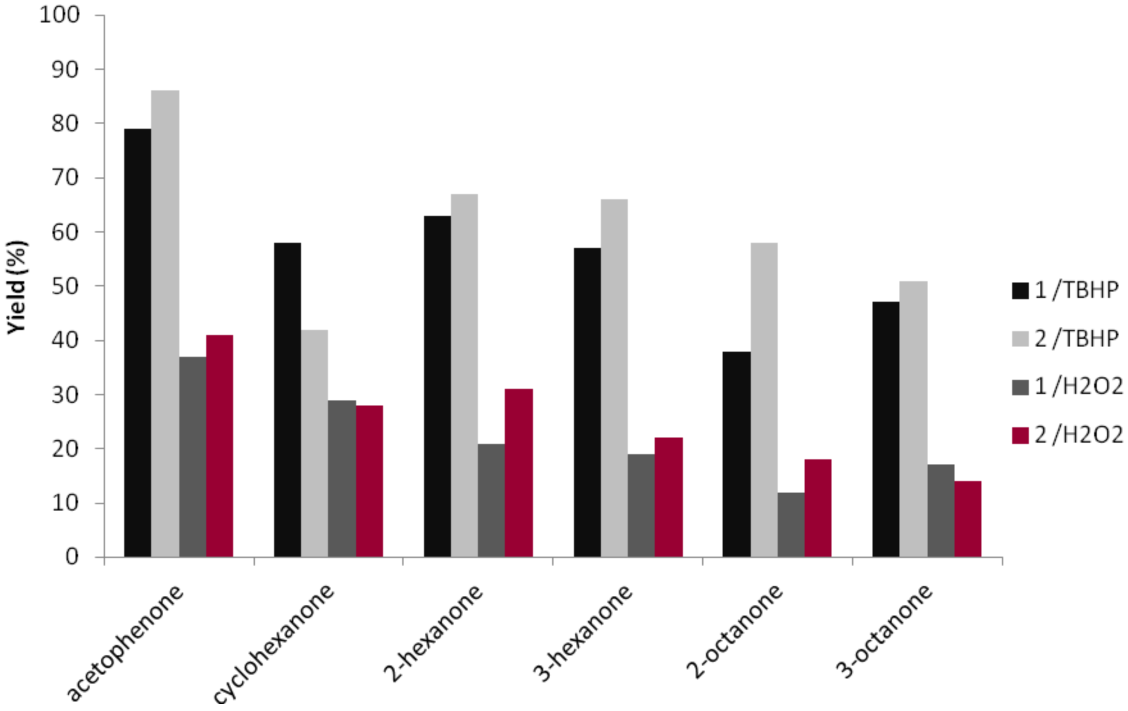


Fig. 5. Influence of the type of oxidant on the yield of ketone in the MW-assisted oxidation of secondary alcohols catalysed by **1** or **2**.

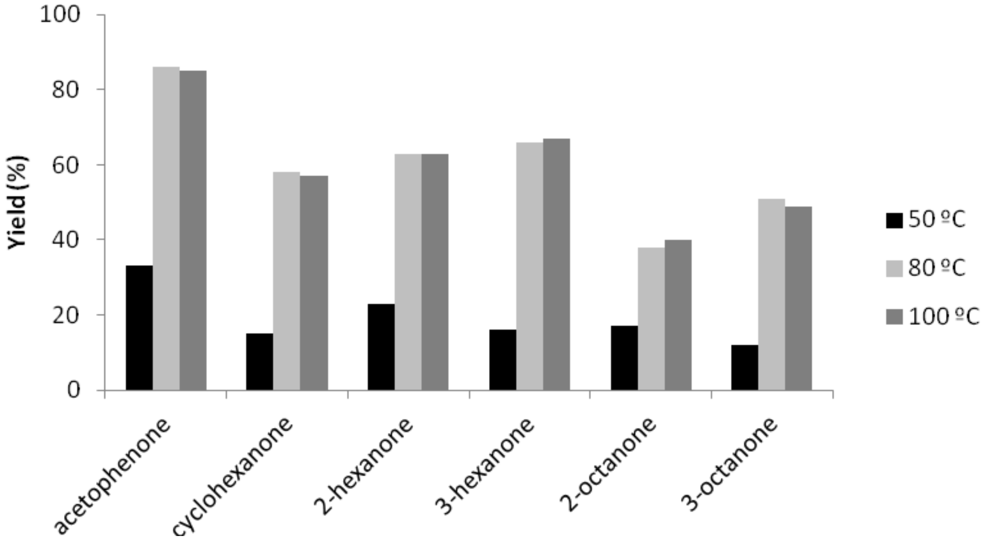


Fig. 6. Influence of temperature on the yield of ketone in the MW-assisted oxidation of secondary alcohols catalysed by **1** (cyclohexanol, 2-hexanol and 2-octanol) or **2** (1-phenylethanol, 3-hexanol and 3-octanol).

Table 1. Crystallographic data and refinement details for **1** and **2**.

	(1)	[a]**(2)**
Empirical formula	$C_{21}H_{29}Cu_{1.50}N_{16}O_3$	$C_{12}H_{12}CuN_{10}O_7$
Mr [g mol^{-1}]	648.91	471.86
Crystal system	Monoclinic	Orthorhombic
Space group	$P\ 2_1/n$	Pbcn
a [Å]	13.0662(3)	11.9883(7)
b [Å]	14.7659(3)	16.0417(6)
c [Å]	15.3925(3)	13.0715(7)
α [°]	90.00	90.00
β [°]	90.29	90.00
γ [°]	90.00	90.00
V [Å^3]	2969.70(11)	2513.8(2)
Z	4	4
D_{calcd}[mgm^{-3}]	1.451	1.247
F(000)	1338	956
GOF	1.095	1.107
Reflections collected / unique	25450 / 5226	19402 / 2218
Final *R* indices	R1 = 0.0463, wR2 = 0.1293	R1 = 0.0803, wR2 = 0.2307
R indices (all data)	R1 = 0.0505, wR2 = 0.1329	R1 = 0.0987, wR2 = 0.2465

[a] Contribution of the disordered solvent was subtracted and solvent electron density was removed by SQUEEZE routine in PLATON, before Refinement from diffraction data of **2**.

Table 2: Bond lengths (Å) and bond angles (°) within and around the trinuclear copper core of **1** and mononuclear copper centre of **2**.

Complex 1

	Distance		Angle		Angle
Cu(1)-N(8)	2.022(3)	N(1)-Cu(1)-N(5)	82.27(10)	N(12)#3-Cu(2)-N(2)	94.18(11)
Cu(1)-N(1)	2.024(3)	N(8)-Cu(1)-N(1)	89.57(10)	N(5)-Cu(2)-N(13)#2	87.78(11)
Cu(1)-N(5)	2.326(3)	N(8)-Cu(1)-N(5)	92.56(10)	N(5)-Cu(2)-N(12)#3	172.90(11)
Cu(2)-N(2)	2.024(3)	N(8)-Cu(1)-N(8)#1	180.0	N(5)-Cu(2)-O(1)	95.42(10)
Cu(2)-N(5)	1.996(3)	N(1)-Cu(1)-N(1)#1	180.0	N(13)#2-Cu(2)-N(12)#3	90.44(11)
Cu(2)-N(13)#2	2.013(3)	N(5)-Cu(1)-N(5)#1	180.00(14)	N(13)#2-Cu(2)-O(1)	91.10(10)
Cu(2)-N(12)#3	2.018(3)	N(5)-Cu(2)-N(2)	87.96(10)	N(12)#3-Cu(2)-O(1)	91.48(10)
Cu(2)-O(1)	2.381(3)	N(2)-Cu(2)-O(1)	86.00(10)		
		N(2)-Cu(2)-N(13)	174.58		

Complex 2

Cu(1)-N(2)	2.012(5)	N(2)-Cu(1)-N(1)	92.4(2)	N(2)#1-Cu(1)-N(2)	180.0(2)
Cu(1)-N(1)	2.066(5)	N(2)-Cu(1)-O(101)	87.88(19)	N(1)-Cu(1)-N(1)#1	180.0(1)
Cu(1)-O(101)	2.387(5)	N(1)-Cu(1)-O(101)	90.6(2)	O(101)-Cu(1)-O(101)#1	180.0

symmetry codes: : #1 -x,-y,-z+1, #2 x-1/2,-y+1/2,z-1/2, #3 x+1/2,-y+1/2,z-1/2

Table 3: Important hydrogen bonding interactions

D-H...A	d(D-H) / Å	d(H...A) / Å	d(D...A) / Å	∠D-H...A / °
Complex 1				
C(13)-H(13B)...O(111)	0.970	2.478	3.371	151.46
C(111)-H(11C)...O(111)	0.981	2.515	3.404	150.64
O(333)-H(333)...N(7)	0.950	2.601	3.514	161.41
Complex 2				
C(5)-H(5)...O(1)	0.930	2.558	3.370	146.09

Table 4. Selected results for the MW-assisted oxidation of secondary alcohols by TBHP with **1** and **2** as catalyst precursors.[a]

Entry	Catalyst Precursor	Substrate	TOF[b] (h^{-1})	Yield[c] (%)
1	**1**	1-phenylethanol	397	79
2[d]			460	92
3[e]			130	78
4		cyclohexanol	290	58
5[f]			265	53
6[g]			10	2
7[h]			20	4
8[d]			335	67
9[e]			92	55
10		2-hexanol	315	63
11[d]			385	77
12		3-hexanol	285	57
13[d]			370	74
14		2-octanol	190	38
15[d]			270	54
16		3-octanol	235	47
17[d]			315	63
18	**2**	1-phenylethanol	430	86
19[f]			405	81
20[g]			25	5
21[h]			15	3
22[d]			495	99
23[e]			142	85
24		cyclohexanol	210	42
25[d]			320	64
26[e]			67	40
27		2-hexanol	335	67
28[d]			405	81
29		3-hexanol	330	66
30[d]			420	84
31		2-octanol	290	58
32[d]			395	79
33		3-octanol	255	51
34[d]			335	67

[a] Reaction conditions unless stated otherwise: 5 mmol of substrate, 10 μmol (0.2 mol% *vs.* substrate) of catalyst precursor, 10 mmol of TBHP (70% aq.), 80 ºC, 1 h reaction time, microwave irradiation (10 W). [b] Turnover frequency = number of moles of product per mol of catalyst per hour (turnover number per hour). [c] Moles of ketone product per mol of alcohol. [d] In

the presence of TEMPO (5 mol% *vs*. substrate). [e] 3 h reaction time. [f] 20 mmol of TBHP (4 eq.). [g] In the presence of Ph_2NH (5 mmol). [h] In the presence of $CBrCl_3$ (5 mmol).

Copper-organic frameworks assembled from *in-situ* generated 5-(4-pyridyl)tetrazole building blocks: synthesis, structural features, topological analysis and catalytic oxidation of alcohols

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Two different metal-organic frameworks **1** and **2** have been synthesized by means of 1,3-dipolar cycloaddition between 4-cyanopyridine and azide in the presence of copper(II) salt. Both compounds show a high activity as catalyst precursors towards the microwave-assisted oxidation of secondary alcohols leading to the ketone.