Dalton Transactions

PAPER

Cite this: Dalton Trans., 2014, 43, 9944

Received 20th February 2014, Accepted 30th April 2014 DOI: 10.1039/c4dt00531g

www.rsc.org/dalton

Introduction

Tetrazole ligands have been extensively used to generate metal–organic and H-bonded frameworks of different topologies in the 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,h} Among the various tetrazole ligands, 5-(4-pyridyl)tetrazole (4-ptz) has been one of the widely employed building

E-mail: suman@iiti.ac.in; Fax: +91 731 2361 482; Tel: +91 731 2438 705

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

Rajendar Nasani,^a Manideepa Saha,^a Shaikh M. Mobin,^a Luísa M. D. R. S. Martins,*^{b,c} Armando J. L. Pombeiro,*^c Alexander M. Kirillov^c and Suman Mukhopadhyay*^a

Two new metal-organic compounds $\{[Cu_3(\mu_3-4-ptz)_4(\mu_2-N_3)_2(DMF)_2]_n$ (1) and $\{[Cu(4-1)_3(DMF)_2]_n$ $ptz_{2}(H_{2}O)_{2}]_{a}$ (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 for generating in situ the 5-substituted tetrazole ligands from 4-pyridinecarbonitrile and NaN₃ in the presence of a copper(μ) 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 $[Cu_3(\mu_2-N_3)_2]$ 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-phenylethanol, 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 low power (10 W) microwave irradiation, and in the absence of any added solvent or additive.

> blocks towards the design of metal–organic networks.² In particular, a combination of 4-ptz with a 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 an 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 under milder conditions in the presence of metal ions 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 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^{8*a*-*c*} or moisture-sensitive oxidants,^{8*d*}

^aDepartment of Chemistry, School of Basic Sciences, Indian Institute of Technology Indore, IET-DAVV Campus, Khandwa Road, Indore 452017, India.

^bChemical Engineering Department, ISEL, R. Conselheiro Emídio Navarro, 1959-007 Lisboa, Portugal. E-mail: lmartins@deq.isel.ipl.pt

^cCentro de Química Estrutural, Complexo I, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.

E-mail: pombeiro@tecnico.ulisboa.pt

[†]Electronic supplementary information (ESI) available. CCDC 940211 and 940212 (squeezed refined structures) for **1** and **2**, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c4dt00531g

high catalyst 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,^{8g,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 Thermo-Flash 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 a path length of 1 cm. Gas chromatographic (GC) measurements were carried out using a FISONS Instruments GC 8000 series gas chromatograph with an 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 °C. The initial temperature was maintained at 120 °C for 1 min, then raised at 10 °C min⁻¹ to 200 °C 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 { $[Cu_3(\mu_3-4-ptz)_4(\mu_2-N_3)_2(DMF)_2](DMF)_2_n$ (1). An excess of solid 4-cyanopyridine (249 mg, 2.4 mmol) was added to the brown coloured mixture of CuCl₂·2H₂O (102 mg, 0.6 mmol) and NaN₃ (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 then a green coloured compound started to precipitate. The stirring was continued for another hour. The mixture was then filtered and the resulting 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 $C_{42}H_{58}Cu_3N_{16}O_6$, 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). The purity of the bulk sample of 1 was confirmed by the PXRD patterns of the sample (Fig. S1†).

Synthesis of {[Cu(4-ptz)₂(H₂O)₂]}_n (2). A greenish brown mixture of CuCl₂·2H₂O (51 mg, 0.3 mmol), NaN₃ (39 mg, 0.6 mmol) and 4-cyanopyridine (125 mg, 1.2 mmol) in a H₂O and DMF (1 mL : 6 mL) mixture was placed into a reaction tube and that was irradiated with microwave radiation for 30 min at 85 °C. The resulting 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 = 55 mg (19.1%), anal. calc. for C₁₂H₁₂CuN₁₀O₂: 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). The purity of the bulk sample of **2** was confirmed using 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-monochromated Mo K α radiation ($\lambda_{\alpha} = 0.71073$ Å). The strategy for the data collection was evaluated using the CrysAlisPro CCD software. The data were collected by the standard phi–omega scan techniques and were scaled and reduced using the 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 worth notingthat randomly dispersed solvent molecules (DMF-H₂O used for crystallization) were found in the framework of 2 and attempts were 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 the 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), the catalyst precursor **1** or **2** (10 μ mol, 0.2 mol% *vs.* substrate) and a 70% aqueous solution

Table 1 Crystallographic data and refinement details for 1 and 2

C ₂₁ H ₂₉ Cu _{1.50} N ₁₆ O ₃	C12H12CuN1007
648.91	471.86
Monoclinic	Orthorhombic
$P2_1/n$	Pbcn
13.0662(3)	11.9883(7)
14.7659(3)	16.0417(6)
15.3925(3)	13.0715(7)
90.00	90.00
90.29	90.00
90.00	90.00
2969.70(11)	2513.8(2)
4	4
1.451	1.247
1338	956
1.095	1.107
25 450/5226	19 402/2218
$R_1 = 0.0463$,	$R_1 = 0.0803$,
$wR_2 = 0.1293$	$wR_2 = 0.2307$
$R_1 = 0.0505$,	$R_1 = 0.0987$
$wR_2 = 0.1329$	$wR_2 = 0.2465$
	$\begin{array}{l} C_{21}H_{29}Cu_{1.50}N_{16}O_{3}\\ 648.91\\ Monoclinic\\ P2_{1}/n\\ 13.0662(3)\\ 14.7659(3)\\ 15.3925(3)\\ 90.00\\ 90.29\\ 90.00\\ 2969.70(11)\\ 4\\ 1.451\\ 1338\\ 1.095\\ 25450/5226\\ R_{1}=0.0463,\\ wR_{2}=0.1293\\ R_{1}=0.0505,\\ wR_{2}=0.1329\\ \end{array}$

^{*a*} Contribution of the disordered solvent was subtracted and solvent electron density was removed by the SQUEEZE routine in PLATON, before refinement from diffraction data of **2**.

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 °C. After the reaction, the mixture was allowed to cool down to room temperature. 300 μ L 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 for 10 min and then a sample (1 μ L) 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(n) 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 ratio 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 An 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 ions,¹² while the characteristic broad band of water molecules 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 match 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 ${[Cu_3(\mu_3-4-ptz)_4(\mu_2-N_3)_2(DMF)_2]_n(1)}$

The 3D polymeric structure of compound 1 bearing a trinuclear Cu(I) core was revealed by single crystal X-ray diffraction data. There are two types of 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 Cu₃ SBU. The copper azide bond distances are relatively large (2.326 Å) because of the Jahn–Teller effect. The bond length and bond angle data are summarized in Table 2.



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



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 the solvent of crystallization (enlarged) (hydrogen atoms other than those involving in interactions have been omitted for clarity). Color codes: Cu brown, C black, H white, N blue and O red.

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 Cu₃ 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) occupies the voids and further stabilizes the obtained framework *via* H-bonding interactions (Table 3).

To better understand the intricate structure of the 3D metal–organic framework **1**, we have carried out its topological analysis¹³ using the concept of the simplified underlying

net.^{14,15} Hence, after omitting the terminal DMF ligands and reducing the μ_2 -N₃ 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 -N₃ 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 $(3\cdot8^2)_4(3^2\cdot4\cdot8^3\cdot9^3\cdot10)_2(3^4\cdot4^2\cdot9^6\cdot10^3)$, wherein the $(3\cdot8^2)$, $(3^2\cdot4\cdot8^3\cdot9^3\cdot10)$ and $(3^4\cdot4^2\cdot9^6\cdot10^3)$ 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 [Cu₃(μ_2 -N₃)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 $(4^{24}\cdot6^4)$.^{14,16,17}

Table 2	Bond lenaths (A	and bond angles (°)	within and around the trinuclear coppe	r core of 1 and the mononuclear copper centre of 2 ^a
		, J		

	Distance		Angle		Angle
Complex 1					
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

Table 3 Important hydrogen bonding interactions

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

Crystal structure of $\{[Cu(\mu_2-4-ptz)_2(H_2O)_2]\}_n$ (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 the 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 $[C(5)-H(5)\cdots O(1)]$, 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 $1.6 \times$ 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 discreteatom 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 H₂O 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 (4⁴·6²).^{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-phenylethanol, cyclohexanol, 2-hexanol, 3-hexanol, 2-octanol and 3-octanol) to the corresponding ketones using *tert*-butylhydroperoxide (TBHP) or hydrogen peroxide as an oxidizing agent, under typical conditions of 80 °C, 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 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 N2S2 macrocycles²⁰ or dinuclear Mn(II) compounds.^{7h,i}

Paper





Fig. 3 Structural fragments of **2** representing (a) 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 (hydrogen atoms other than those involving in interactions have been omitted for clarity). Color codes: Cu brown, C black, H white, N blue and O red.

Fig. 2 Topological representations (views along the *a* axis) of the underlying 3D networks in **1** showing: (a) a topologically unique trinodal 3,5,6-connected net with the point symbol of $(3\cdot8^2)_4(3^2\cdot4\cdot8^3\cdot9^3\cdot10)_2(3^4\cdot4^2\cdot9^6\cdot10^3)$, and (b) a further simplified uninodal 8-connected net with the point symbol of $(4^{24}\cdot6^4)$ and **bcu** (body centered cubic) topology obtained after considering the $[Cu_3(\mu_2-N_3)_2]$ 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 -N₃ linkers (yellow); (b) centroids of 8-connected $[Cu_3(\mu_2-N_3)_2]$ cluster nodes (brown) and centroids of 2-connected μ_3 -4-ptz linkers (blue).

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 to 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.



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 (4⁴·6²) 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).



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



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.

Addition of a 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 °C). 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 and 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,



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 4Selected results for the MW-assisted oxidation of secondary
alcohols by TBHP with 1 and 2 as catalyst precursorsEntryCatalyst precursorSubstrate $TOF^b(h^{-1})$ Yield^c (%)

Entry	Catalyst precursor	Substrate	$\operatorname{TOF}^{b}\left(\mathbf{h}^{-1}\right)$	Yield ^c (%)
1			397	79
2^d		1-Phenylethanol	460	92
3 ^e			130	78
4			290	58
5^f			265	53
6^g		Cyclohexanol	10	2
7^h	1		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			430	86
19^{f}			405	81
20^g		1-Phenylethanol	25	5
21^h		2	15	3
22^d			495	99
23^e			142	85
24			210	42
25^d	2	Cyclohexanol	320	64
26^e		J	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 °C, 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 TEHP (5 mmol). ^{*b*} In the presence of CBrCl₃ (5 mmol).

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 microwave irradiation, while a 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^{21*i*,*k*,26} for this system may involve coordination of the alcohol *e.g.*, PhCH(OH)Me (with deprotonation to form an alkoxide ligand) and a TEMPO radical, followed by H transfer from the former to the latter with formation of the O-ligated radical PhC[•](O)Me⁻ and TEMPOH. Intramolecular electron-transfer from the PhC[•](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 O₂/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 a 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 of a copper(1) 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(I) (green) to copper(I) (orange) in the presence of alcohol and TEMPO. These results also confirm the radical mechanism where reduction of copper(I) 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 that further research aimed 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 $(3\cdot8^2)_4(3^2\cdot4\cdot8^3\cdot9^3\cdot10)_2(3^4\cdot4^2\cdot9^6\cdot10^3)$, which can be further simplified to a body centred cubic (bcu) network bearing a trinuclear Cu₃-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 microwaveassisted homogeneous oxidation of secondary alcohols leading to ketone yields up to 99% (2) under added solvent-free conditions. Hence, this study also widens the scope of MWassisted transformations applied to the oxidative functionalization of organic substrates and extends the range of efficient catalytic systems applicable to such reactions.

Acknowledgements

We are grateful for the financial support received from the Council of Scientific and Industrial Research, New Delhi and from the Fundação para a Ciência e a Tecnologia (FCT), Portugal, and its projects PTDC/EQU-EQU/122025/2010, PTDC/QUI-QUI/121526/2010 and PEst-OE/QUI/UI0100/2013. One of us (M. S.) thanks CSIR for the award of JRF in a CSIR sponsored project. We are also thankful to the Sophisticated Instrument Centre, IIT Indore for the structure elucidation.

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, CrystEngComm, 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, CrystEngComm, 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, Y. Li and Z.-Y. Shi, CrystEngComm, 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 and 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, *CrystEngComm*, 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, *CrystEngComm*, 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. Commun.*, 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, 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; M. V. Kirillova, A. M. Kirillov, D. Mandelli, (g)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: Chem.*, 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 and A. J. L. Pombeiro, *Catal. Commun.*, 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. 2, 1998, 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: Fundam. Crystallogr., 2008, 64, 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. Newslett., 2006, 7, 4.

- 14 (a) V. A. Blatov and D. M. Proserpio, in Modern Methods of Crystal Structure Prediction, ed. A. R. Oganov, Wiley, 2010, 1–28; (b) V. A. Blatov, M. O'Keeffe and D. M. Proserpio, CrystEngComm, 2010, 12, 44–48; (c) E. V. Alexandrov, V. A. Blatov, A. V. Kochetkova and D. M. Proserpio, Cryst-EngComm, 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. Commun.*, 2012,
 18, 8–10; (b) H.-Q. Hao, J. Wang, W.-T. Liu and M.-L. Tong, *CrystEngComm*, 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 and A. R. Dieguez, *Inorg. Chim. Acta*, 2010, 363, 3194–3199; (b) X.-H. Wei, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2010, 66, 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 and G. B. Shul'pin, Dalton 2014, 43, 872-882; (c) A. N. Bilyachenko, Trans.. S. Dronova, A. I. Yalymov, A. A. Korlyukov, M. Shul'pina, D. E. Arkhipov, E. S. Shubina, L. S. M. M. Levitsky, A. D. Kirilin and 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. Catal. 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, 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, H.-H. Wu and Y. Liu, *Chem-CatChem*, 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 and 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 O. Kappe, Chem. Rev., 2007, 107, 2563-2591; C. (d) Microwave Assisted Organic Synthesis, ed. J. P. Tierney and 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 and A. J. L. Pombeiro, Microwave-assisted Catalytic Oxidation of Alcohols to Carbonyl Compound, in Advances in Organometallic Chemistry and Catalysis: The Silver/Gold Jubilee ICOMC Celebratory Book, ed. A. J. L. Pombeiro, Wiley, 2014, ch. 18, pp. 233-245.
- 24 (a) G. Tojo and 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, pp. 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, ed. P. Wasserscheid and T. Welton, Wiley-VCH, Weinheim, Germany, 2008, vol. 2; (e) S. F. Liu and J. Xiao, J. Mol. Catal. A: Chem., 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, 19455–11946; (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.