$[Cu(H_2btec)(bipy)]_\infty$: a novel metal organic framework (MOF) as heterogeneous catalyst for the oxidation of olefins†

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A new extended metal-organic framework $[Cu(H_2btec)(bipy)]_\infty$ (**1**) (H_4btec= 1,2,4,5-benzenetetracarboxylic acid; bipy= 2,2′-bipyridine) has been hydrothermally synthesized. Violet crystals are formed in a monoclinic system with a space group $C2/c$; $a = 10.1810(18)$ Å, $b = 14.4360(18)$ Å, $c = 12.894(3)$ Å, $\beta = 112.94(3)°$. In the title compound **1** each Cu(II) centre has a distorted square planar environment, completed by two N atoms from one bipy ligand and two O atoms belonging to two dihydrogen benzene-1,2,4,5-tetracarboxylate anions (H_2btec^{2-}). The $\{Cu(bipy)\}^{2+}$ moieties are bridged by H_2btec^{2-} anions to form an infinite one-dimensional coordination polymer with a zig-zag chain structure along the c axis. A double-chain structure is formed by hydrogen bonds between adjacent zig-zag chains. There are also π–π stacking interactions between the bipy ligands, with an average distance of 3.62 Å resulting in a two-dimensional network structure. Compound **1** was tested as a catalyst for the oxidation of cyclohexene and styrene, with *tert*-butyl hydroperoxide (TBHP) as oxidant. The catalytic activity (24 h and 75 °C) found for $[Cu(H_2btec)(bipy)]_\infty$ shows a high value for the conversion of cyclohexene (64.5%), and a lower one for styrene (23.7%). High turnover frequency (TOF) values for the epoxide products were observed, indicating that the catalyst synthesized in this work, not only has a high activity and selectivity for epoxidation reactions but is also very efficient.

Introduction

The design and synthesis of supramolecular coordination polymeric networks, especially those constructed by hydrogen bonding and π–π stacking interactions, have been a field of rapid growth due to their special physical properties and potential application in functional materials, for molecular adsorption, ion exchange, and heterogeneous catalysis.[1–4]

The aromatic polycarboxylate transition metal complexes are interesting due to the variety of bridging abilities of the polycarboxylate ligand in the formation of extended porous frameworks. 1,2,4,5-Benzenetetracarboxylic acid (H_4btec) presents interesting characteristics such as four carboxylate groups, which may be completely or only partially deprotonated. This fact allows interesting structures with high dimensionalities. Depending upon the number of deprotonated carboxylate groups, this ligand can act not only as hydrogen-bond acceptor, but also as hydrogen-bond donor. Hence, H_4btec may be a good choice for the construction of polymeric structures. Numerous complexes with the H_4btec ligand have been reported.[5–14] although the construction of complexes from H_4btec, 2,2′-bipyridine or 1,10-phenantroline, and Cu(II) building blocks is still limited.

In the catalysis area, the epoxidation of olefins using metal catalysts plays a central role in the selective and partial oxidation of both saturated and unsaturated hydrocarbons.[15–22] Selective oxygen transfer to olefins remains an important research area in industrial and synthetic chemistry, because epoxides are widely used as epoxy resins, paints, surfactants, and intermediates in various organic syntheses.[23]

The activation of hydroperoxides by transition metals has received much attention, since Group IV–VII metals have been employed for industrial olefin epoxidation with organic hydroperoxides (the Halcon–Arco process).[24] Besides, heterogenized homogeneous catalysts, mixed metal exchanged zeolites and resins,[25] polymerized chiral ligand[26] complexes have been used in liquid phase epoxidation of olefins.[27]

However, epoxidations with copper are still rare. Examples, such as iodosylbenzene with copper(II) nitrate and

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† Electronic supplementary information (ESI) available: Fig. S1: simulated (black) and experimental (red) X-ray powder diffraction patterns of $[Cu(H_2btec)(bipy)]_\infty$, at room temperature. Fig. S2: TGA and calculated DTA curves of $[Cu(H_2btec)(bipy)]_\infty$. Fig. S3: the field dependence of magnetization at two different temperatures. Fig. S4: catalytic activity of $[Cu(H_2btec)(bipy)]_\infty$ for the cyclohexene oxidation. (a) Substrate conversion (%). (b) Chemoselectivity for cyclohexene epoxide (%) (white bars = 30 °C; gray bars = 50 °C; black bars = 75 °C). Fig. S5: catalytic activity of $[Cu(H_2btec)(bipy)]_\infty$ for the styrene oxidation. (a) Substrate conversion (%). (b) Chemoselectivity for styrene epoxide (%) (white bars = 30 °C; gray bars = 50 °C; black bars = 75 °C)]. CCDC reference number 682181 for complex **1**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b810414j

triflate with stilbenes,[28] silylalkyl peroxybenzoate with Cu(II) trifluoroacetate,[29] and binuclear trisamino Cu(II) complexes have been reported.[30] Recently the heterogeneous copper(II) complex with the MCM-41 polymer has shown a good activity in epoxidation reactions, with a variety of olefinic compounds, using *tert*-BuOOH (TBHP) as oxidant.[31]

Herein we report the hydrothermal synthesis, structural and magnetic characterization, and catalytic behavior of a new metal-organic framework [Cu(H$_2$btec)(bipy)]$_\infty$ (**1**), in the epoxidation of cyclohexene and styrene using TBHP as an oxidant.

Results and discussion

Crystal structure of [Cu(H$_2$btec)(bipy)]$_\infty$ (1)

X-Ray crystallographic analysis shows that compound **1** exhibits an infinite 1D chain-like structure. Fig. 1 presents a diagram of the structure showing the labelling scheme used.

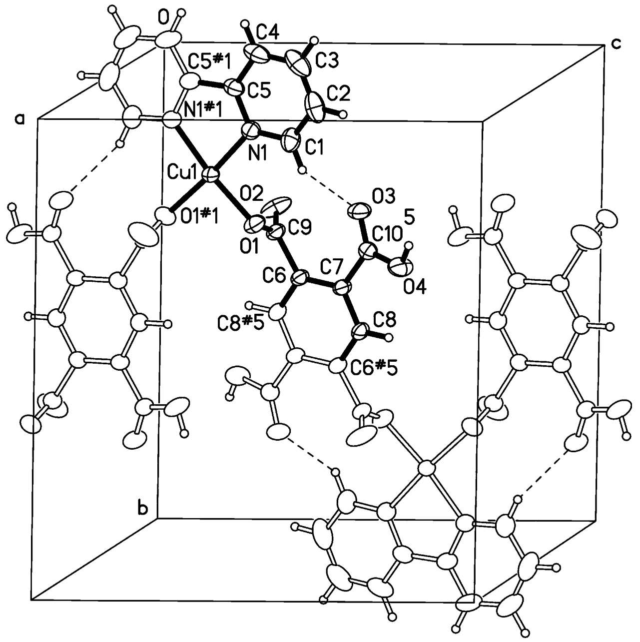


Fig. 1 Molecular diagram of **1** extended to see the way in which strips build up. The intra-chain C1–H1 · · · O3 H-bond is shown in broken lines. Displacement ellipsoids drawn at a 50% level [symmetry codes: #1: 1 – *x*, *y*, 0.5 – *z*; #5: 1 – *x*, 1 – *y*, 1 – *z*].

The Cu(II) center is coordinated into an almost square planar arrangement by two nitrogen atoms from one chelating 2,2′-bipyridine ligand, and two O atoms from two carboxylate groups from two bridging H$_2$btec groups. The copper coordination polyhedron presents crystallographic symmetry, being bisected by a two-fold axis which goes through the metal and the central C–C bond of the bipy unit, while the H$_2$btec ligand evolves around a symmetry center. As a result only half of a formula unit is independent ($z' = 0.5$). Table 1 shows selected bond angles and distances. The single (but doubled by symmetry) Cu–O and Cu–N bond lengths are 1.934(19) and 1.973(2) Å respectively; *cis* angles in the coordination plane have values of 81.86(13)° 89.69(12) and 94.62(9)°, while *trans* ones have values of 172.24(8)°, confirming the distorted square-planar coordination environment of the copper(II) centre. The symmetric H$_2$btec ligand presents two independent carboxylate groups, one of which is unprotonated, and thus accounts for charge balance of the copper cation, which lies at a special position. The ligand acts as a bridge between neighboring copper centres, by way of atom O1 in two symmetry related carboxylate groups binding in a monodentate fashion. The remaining three carboxylate oxygens (O1, O2, O3) enter in stabilizing H-bonding interactions, to be discussed below. This bridging action of the H$_2$btec ligand results in the formation of zig-zag chains running along *c*, with acute turning points which make them to look like broad strips, some 20 Å wide, along the *b* direction. The planar elements in the strip (bipy and H$_2$btec) are almost coplanar to each other and parallel to (100). Thus interdigitation of lateral strips promotes π–π interactions between adjacent aromatic rings, and the result is the interconnection of strips into layers parallel to (100) (Fig. 2). The C4–H4 · · · O3#3 H-bond further contributes to the interplanar cohesion. These layers, in turn, are linked to each other through the strong O4–H4A · · · O2#2 H-bond. A summary of the most relevant non-bonding interactions is presented in Table 2 (H-bonds and π–π contacts).

Table 1 Selected bond distances (Å) and angles (°) for (**1**)

Bond distances			
Cu1-N1	1.973(2)	Cu1-O1	1.934(19)
Bond angles			
O1-Cu1-O1	89.69(12)	N1-Cu1-N1 #	81.86(13)
O1-Cu1-N1	94.62(9)	O1-Cu1-N1#	172.24(8)

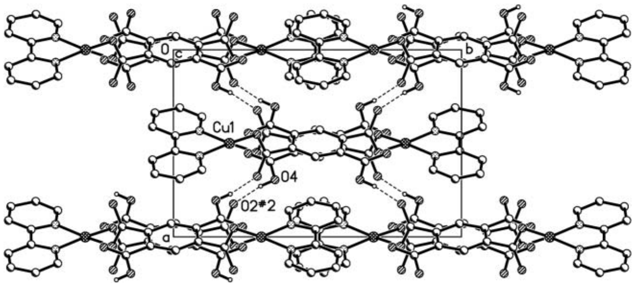


Fig. 2 Packing scheme of **1** shown down the *c* axis [symmetry code: #2: 0.5 + *x*, 0.5 – *y*, 0.5 + *z*].

With respect to the previous description, the title metal-organic hybrid compound **1** is the first polymeric complex that contains the mixed ligands (bipy and H$_2$btec^{2-}), where the {Cu(bipy)}$^{2+}$ moieties are bonded by H$_2$btec^{2-}, displaying one μ$_2$-bridging mode and a monodentate coordination mode.

Additionally, other similar MOF containing 1,2,4,5-benzene tetracarboxylic acid and diimine ligands have been previously reported.[5–8] Structural parameters of (**1**) and the above related compounds are summarized in Table 3.

XRPD and TG-DTA analyses of the polycrystalline material

The simulated diffraction pattern of the reflections of the single crystal diffraction agrees with the experimental XRPD pattern of the violet microcrystalline powder as shown in Fig. S1.†

Table 2 Hydrogen bonds and π–π contacts for **1**

D-H···A	d(D–H)/ Å	d(H···A)/ Å	d(D···A)/ Å	<(DHA)/°
O(4)–H(4a)···O(2)#2	0.82(3)	1.78(4)	2.585(3)	167(4)
C(1)–H(1)···O(3)	0.93	2.48	3.214(4)	136
C(4)–H(4)···O(3)#3	0.93	2.52	3.142(4)	125

Symmetry codes: #2 $x + 1/2, -y + 1/2, z + 1/2$; #3 $-x + 1, -y, -z + 1$.

Group1-Group2	ccd[a]/Å	ipd[a]/Å	sa[a]/°
[Cg1···Cg1]#4	3.629(2)	3.36(1)	22.3(1)
[Cg1···Cg2]#5	3.656(2)	3.37(2)	22.9(7)

Cg1: N(1), C(1), C(2), C(3), C(4), C(5); Cg2: C(6), C(7), C(8), C(6), C(7), C(8).
Symmetry codes: #4 = $1 - x, -y, 1 - z$; #5 = $1/2 + x, -1/2 + y, z$.

[a] ipd, interplanar distance (distance from one plane to the neighbouring centroid); ccd, center-to-center distance (distance between ring centroids); sa, slippage angle (angle subtended by the intercentroid vector to the plane normal). For details, see C. Janiak, *J. Chem. Soc., Dalton Trans.* 2000, 3885.

Thermogravimetric analysis (TGA) is shown in Fig. S2.† This shows that compound **1** possesses good thermal stability up to 250 °C. The TGA curve exhibits three continuous weight loss stages in the temperature range 250–445 °C. The total weight loss (85.1%) is in good agreement with the calculated value (Δm% 86.9), corresponding to the concomitant release of bipy and H_2btec ligands. The DTA curve also confirms that the network of compound **1** is stable below 250 °C, and shows that the weight loss corresponds to an exothermic process.

Magnetic susceptibility

Variable-temperature magnetic susceptibility measurements were performed at 0.1 T on powdered crystals of $[Cu(H_2btec)(bipy)]_\infty$ in a temperature range 2.5–292 K. The data for **1** are plotted in Fig. 3 as χ_M *versus* T and $\chi_M T$ *versus* T, together with the fit of the experimental data. For **1**, the $\chi_M T$ value at 292 K is 0.38 cm^3 mol^{-1} K, which is very close to that of the spin only value of 0.375 cm^3 mol^{-1} K, calculated for non interacting Cu(II) centers with a g value equal 2.0. The value of $\chi_M T$ decreases smoothly from 292 to 30 K; below this temperature the value of $\chi_M T$ shows a sharper decrease reaching a value of 0.25 cm^3 mol^{-1} K at 2.5 K, suggesting a very weak antiferromagnetic interaction at low temperatures between the copper(II) ions. This antiferromagnetic interaction can also be observed in the plots of M *versus* H at different temperatures (see Fig. S3†).

The plot of χ_M^{-1} *versus* T obeys the Curie-Weiss law, in the range of 40–292 K with $\chi_M = C/(T - \theta)$, giving a Curie constant of 0.378 cm^3 K mol^{-1} with a negative Weiss constant θ of –0.8 K.

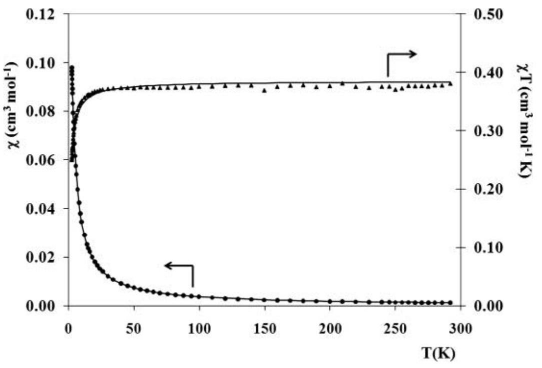


Fig. 3 Temperature dependence of molar magnetic susceptibility for $[Cu(H_2btec)(bipy)]_\infty$.

In order to determine the magnitude of the exchange interaction, the magnetic susceptibility data were fitted using the magnetic chain model.[32]

$$\chi_M = \frac{N\beta^2 g^2}{kT}\left\{\frac{0.25 + 0.074975x + 0.75235x^2}{1 + 0.9931x + 0.172135x^2 + 0.757825x^3}\right\} \qquad (1)$$

$$x = |J|/kT$$

The best fit to eqn (1) gave $g = 2.05$, $J = -1.4$ cm^{-1}. The very small value of J is in the order of those found for other copper (II) complexes with carboxylate bridging ligands, in which there is no coplanarity between the CuNO moiety and tetracarboxylate ligand. A similar small J value was reported by Kopel *et al.*, who found a $J = -0.56$ cm^{-1} for $[Cu_3(mdpta)_3(btc)](ClO_4)_3{\cdot}4H_2O$, where mdpta corresponds to N,N-bis-(3-aminopropyl)methylamine and H_3btc to 1,3,5-benzenetricarboxylic acid.[33] Copper complexes with the 1,2,4,5-tetracarboxylic acid (H_4btec) having different degrees of deprotonation, $[\{Cu(btec)(4\text{-}apy)_2\}{\cdot}(4\text{-}Hapy)_2{\cdot}(H_2O)_4]_n$, and $[\{Cu(H_3btec)_2(pyz){\cdot}(H_2O)_2\}{\cdot}H_2O]_n$, were reported by Majunder *et al.*, with an isotropic interaction parameter of $J = -0.50$ and -0.79 cm^{-1} respectively.[34]

Catalytic results

The catalytic activity of $[Cu(H_2btec)(bipy)]_\infty$ (**1**) was investigated using cyclohexene and styrene as substrates, and TBHP as the oxidant. The catalytic oxidation results were analyzed in terms of conversion and chemoselectivity. The reaction of epoxidation of olefins using **1** as an heterogeneous catalyst were monitored under nitrogen, and the conversion and chemoselectivity were estimated at different time-intervals and temperatures. The informed TOF (moles of epoxide per mole of copper center per hour) values are informed for 30 °C, 50 °C, 75 °C and 24 h of reaction

Table 3 Structural parameters of metal-organic hybrid compounds

Hybrid compound	Crystal system, space group	Geometry	Synthesis	Cavity size/Å	Dimensionality	Ipd/Å	Ref.
(**1**) $[Cu(H_2btec)(2,2'\text{-}bipy)]_\infty$	Monoclinic, *C*2/*c*	Dist. square planar	Hydrothermal	—	2D	3.63	This work
(**2**) $[Cu(H_2btec)(1,10\text{-}phen)]_\infty$	Monoclinic, *C*2/*c*	Dist. square planar	Hydrothermal	—	2D	3.64	5
(**3**) $[Cu(btec)(2,2'\text{-}bipy)_2]_\infty$	Monoclinic, $P2_1/n$	Dist. square planar	Conventional	4.5 × 6.1	3D	3.56	6
(**4**) $[Cu(btec)(2,2'\text{-}bipy)_2]_\infty$	Monoclinic, $P2_1/n$	Dist. tetrahedral	Hydrothermal	8.0 × 4.5	3D	3.41	7
(**5**) $[Cu(btec)(1,10\text{-}phen)_2]_\infty{\cdot}(H_2O)_\infty$	Monoclinic, $P2_1/c$	Dist. tetrahedral	Solvothermal	6.5 × 6.6	3D	3.26	8

Table 4 Effect of the catalytic activity of **1** on the epoxidation of cyclohexene[a] at different temperatures and 24 h of reaction time

				Chemoselectivity (%)		
$T/°C$	TON	TOF/h^{-1}	Conversion (%)	Epoxide	Cyclohexanone	2-Cyclohexenone
30	738	31	27.4	67.3	16.8	15.8
50	1550	65	54.5	71.1	8.9	18.3
75	1886	79	64.5	73.1	7.7	19.2

[a] Reaction conditions: catalyst $[Cu(2,2\text{-bipy})(H_2btec)]_\infty$ 0.01 mmol; cyclohexene, 40 mmol; TBHP 40 mmol; cyclohexene/TBHP/catalyst 400:400:1, 1,2-dichloroethane 10 mL.

Table 5 Effect of the catalytic activity of **1** on the epoxidation of styrene[a] at different temperatures and 24 h of reaction time

				Chemoselectivity (%)	
$T/°C$	TON	TOF/h^{-1}	Conversion (%)	Epoxide	Benzaldehyde
30	65	3	6.2	26.0	74.0
50	314	13	14.5	54.2	45.8
75	673	28	23.7	71.0	29.0

[a] Reaction conditions: catalyst $[Cu(2,2\text{-bipy})(H_2btec)]_\infty$ 0.01 mmol; styrene, 40 mmol; TBHP 40 mmol; styrene/TBHP/catalyst 400:400:1, 1,2-dichloroethane 10 mL.

in Tables 4 and 5. With these results it is possible to observe that the $[Cu(H_2btec)(bipy)]_\infty$ system presents a good efficiency as heterogeneous catalyst for the epoxidation of cyclohexene, and a moderate efficiency for the epoxidation of styrene.

Fig. S4† presents the conversion and chemoselectivity graphs obtained for the cyclohexene oxidation. The cyclohexene oxidation catalyzed by **1** yielded mainly the following products: cyclohexene epoxide, 2-cyclohexenone and cyclohexanone, where the epoxide corresponds to the principal product.

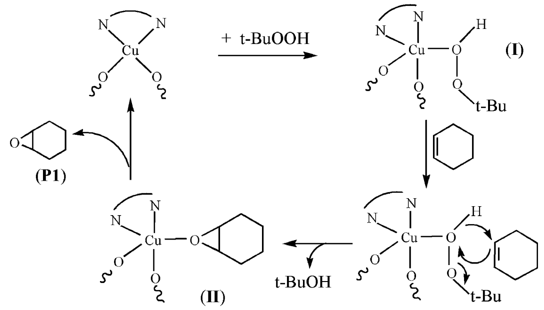
The conversion of cyclohexene at 75 °C and 24 h of reaction time is doubled when the catalyst is used as compared with the control reaction in the absence of **1**. These results show the great efficiency of the $[Cu(H_2btec)(bipy)]_\infty$ catalyst on the oxidation.

The catalyst also presents a high chemoselectivity toward the epoxide formation, reaching a value of 73.1% at 24 hours of reaction time and 75 °C. For the side products such as 2-cyclohexenone and cyclohexanone, the chemoselectivity is only 19.2% and 7.7%, respectively (Table 4). The values obtained in the absence of the catalyst for the same experimental conditions (control experiment: 24 h, 75 °C) were of 0.2%, 40.0% and 43.2% for cyclohexene epoxide, 2-cyclohexenone and cyclohexanone respectively. Therefore, it is important to remark that the $[Cu(H_2btec)(bipy)]_\infty$ catalyst presents a high chemoselectivity towards the epoxide formation.

The epoxidation of styrene was done in similar conditions as those used for cyclohexene. The results of conversion and chemoselectivity for the epoxidation reaction of styrene using **1** are summarized in Table 5 and Fig. S5.† The conversion of styrene is three times lower as compared to the conversion of cyclohexene. The oxidation reaction of styrene with TBHP yielded only benzaldehyde and styrene epoxide as products.

For short times of reaction (30 min) both in the presence and absence of the catalyst, only benzaldehyde was observed as product, indicating that the benzaldehyde production does not depend on the catalyst. However, with increasing reaction time the production of benzaldehyde decreases while the concentration of styrene epoxide increases.

Scheme 1 shows the proposed mechanism for the formation of the epoxide based on previous literature.[35–37] The mechanism begins with the generation of the oxygenated intermediary species **I**, which is produced by the coordination of the TBHP to the Cu(II) center, with an expansion of the coordination number. In the second step, a nucleophilic attack of the olefin substrate on species **I** occurs, followed by a concerted oxygen transfer, leading to the formation of species **II** and *t*-butanol. Finally, in the last step the rupture of the Cu–O bond is produced, giving epoxide (**P1**) and regenerating the catalyst.



Scheme 1

The difference in conversion observed for cyclohexene and styrene is related with the mechanism involved in the oxidation reactions. When a peroxide like as TBHP is used as oxidant, two mechanisms for oxygen activation have been reported. One of them involves the homolytic cleavage of the O–O bond, producing a low chemoselectivity in the obtained products, while the other mechanism involves the heterolytic cleavage of the O–O bond.[38] For the oxidation of cyclohexene the allylic hydrogen is as reactive as the olefinic double bond, in the presence of the following radical species: tert-butilperoxide $C(CH_3)_3OO^\bullet$ and alcoxide $C(CH_3)_3O^\bullet$ generating the secondary products, 2-cyclohexenone and cyclohexanone.[31b,c] However in the heterolytic mechanism proposed in Scheme 1, the main obtained product is cyclohexene epoxide beside a greater total conversion in products is obtained. In the case of styrene, only two products are generated. These also correspond to a competitive mechanism in which the *t*-butylperoxide radical attacks the double bond to give the benzaldehyde and the heterolytic mechanism similar to the one proposed for cyclohexene generates the cyclohexene epoxyde.

Experimental

Synthesis of [Cu(H_2btec)(bipy)]$_\infty$ (1)

The reaction mixture for the synthesis of 1 consists of V_2O_5 (0.091 g), $Cu(NO_3)_2 \cdot 3H_2O$ (0.2416 g), 2,2′-bipyridine (0.078 g), 1,2,4,5-benzenetetracarboxylic acid (0.127 g) and water (10 mL) in a molar ratio of 1:2:0.5:0.5:550. The mixture is loaded in a Teflon-lined stainless steel autoclave (23 mL) and heated at 160 °C for 48 h, and then the temperature is slowly lowered to 80 °C (10 °C/h). After, the reaction vessel is slowly cooled down to room temperature and the resulting product filtered, washed with distilled water and dried at 60 °C. The solid phase consisted of violet crystals and powder corresponding to 1. The violet product was collected in *ca.* 90% yield. Crystals, suitable for X-ray diffraction studies, were also collected by filtration several weeks later. Microcrystalline solid 1: Anal. found (calcd.) C: 50.75% (50.86%); N: 5.99% (5.93%); H: 2.56% (2.54%); Cu: 13.55% (13.47%). IR spectrum: uncoordinated protonated carboxylate group, 1718 cm^{-1}; monodentate mode of carboxylate group, $\nu_{as\,(COO)}$ 1573 cm^{-1}, $\nu_{s\,(COO)}$ 1380 cm^{-1} ($\Delta\nu = 193$ cm^{-1}). If V_2O_5 is not used a mixture of different products is obtained, with 1 in a lower yield.

Materials and measurements

All reagents were purchased commercially and used without further purification. Infrared spectra were recorded in KBr pellets using a Bruker Vector 22 FTIR instrument in the range 400–4000 cm^{-1}. The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a NETZSCH equipment. The TG/DTA curves were registered in the 293–773 K range, under nitrogen atmosphere (20 mL/min) using a 5 °C/min heating rate. The magnetic susceptibility measurements at variable temperature between 2.5–292 K were performed on a polycrystalline sample, using a Cryogenics S600 SQUID susceptometer-magnetometer at 0.1 T. The diamagnetic corrections were calculated using Pascal constants.[39]

X-Ray diffraction

A violet 0.60 × 0.25 × 0.10 crystal of compound 1 was taken directly from the synthesis vessel. Data collection was made on a Bruker SMART APEX diffractometer, using 0.3° of separation between frames and monochromated Mo Kα radiation ($\lambda = 0.71073$). Data integration was made using SAINT. Absorptions corrections have been made using SADABS. The structure was solved by means of direct methods using XS in SHELXTL and completed by Fourier Difference Synthesis. Refinement until convergence using XL SHELXTL. Table 6 presents the crystal and structure refinement data.[40–45] Phase identification was carried out with X-ray powder diffraction technique on a D5000 Siemens diffractometer, using Cu Kα1 radiation ($\lambda = 1.54056$ Å).

Table 6 Crystal and structure refinement data for **1**

Empirical formula	$C_{20}H_{12}CuN_2O_8$
Formula weight	471.86
Temperature (K)	294(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C*2/*c*
a (Å)	10.1810(18)
b (Å)	14.4360(18)
c (Å)	12.894(3)
β (°)	112.94(3)
Volume $(Å)^3$	1745.2(7)
Z	4
D_c (gcm^{-3})	1.796
F(000)	956
Crystal size (mm^3)	0.60 × 0.25 × 0.10
θ range for data collection (°)	2.59 to 27.89
Index ranges	$-13 \le h \le 12$, $-18 \le k \le 18$, $-16 \le l \le 16$
Reflections: collected, indep. (R_{int}), observed [$I > 2\sigma(I)$]	7220, 1972(0.0360), 1664
Absorption correction, μ (mm^{-1})	Semi-empirical from equivalents, 1.310
Max. and min. transmission	0.88 and 0.68
Goodness-of-fit on F^2	1.054
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0420$, $wR2 = 0.1121$
R indices (all data)	$R1 = 0.0515$, $wR2 = 0.1179$
Largest diff. peak and hole (e $Å^{-3}$)	0.541, −0.278

Catalytic studies

The epoxidation reactions were performed using a reactor (25 mL) provided with a mechanical stirrer and an oil bath. All the reactions were carried out under nitrogen atmosphere. Experiments were done at 30 °C, 50 °C and 75 °C, using the following reaction condition: the catalyst (0.01 mmol) was added in the autoclave reactor together with 1,2-dichloroethane (10 mL) as solvent; when the temperature reaction was reached the substrate (cyclohexene, 40 mmol) and the oxidant (TBHP 40 mmol) were added. Aliquots of the solution (10 µL) were removed at intervals of 0; 0.5; 1; 2; 4; 6 and 24 h and analyzed by gas chromatography (GC). The epoxidation reaction was also tested for styrene as substrate, using the same procedure and molar ratio. Gas chromatographic analyses were carried out with a Perkin Elmer 5890 GC, equipped with a flame ionization detector (FID). Styrene was analyzed with a capillary column Carbowax 20M (25 m × 0.2 mm × 0.2 µm), and cyclohexene with Equity™-1 (30 m × 0.25 mm × 1.0 µm) column and nitrogen as carrier gas. The oxidation products were identified by spiking, using standard compounds and the measurements of retention times were performed using the following conditions: temperature program 180 °C, initial time 5 min; 10 °C/min; final time 15 min, the retention times registered were: cyclohexene, $T_R = 10.3$ min; cyclohexene epoxide, $T_R = 15.2$ min; 2-cyclohexen-1-one, $T_R = 17.2$ min; cyclohexanone, $T_R = 16.0$ min, and the retention times for styrene, $T_R = 9.9$ min; styrene oxide, $T_R = 16.1$ min; benzaldehyde, $T_R = 15.6$ min.

Conclusions

The metal organic framework [Cu(H_2btec)(bipy)]$_\infty$ was prepared by hydrothermal synthesis and characterized by X-ray diffraction, thermal gravimetric analysis and magnetic susceptibility. This material was tested as catalyst for the oxidation of olefins, and to the best of our knowledge the first MOF copper(II) catalyst, with H_2btec and bipy as ligands, for the oxidation of olefins is being reported.

The use of **1** as catalyst for the conversion of cyclohexene and styrene to the corresponding epoxide products, at 75 °C and 24 h of reaction, doubles the percentage of the product with respect to the control experiment. It is important to remark that the activity of the catalyst with cyclohexene is almost three times higher than with styrene.

For cyclohexene similar chemoselectivity and TOF values were obtained at 50 and 75 °C, while for styrene the best chemoselectivity and TOF values were obtained at 75 °C. In this way it is possible to conclude that the reaction is more temperature dependent for styrene.

High turnover frequency (TOF) values for the epoxide products were observed, indicating that the catalyst synthesized in this work, not only has a high activity and selectivity for epoxidation reactions but is also very efficient.

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