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Synthesis and structural characterization of six Cu(II)-based coordination polymers using the thermally tunable 1,2,3,4-cyclobutanetetracarboxylic acid

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The synthesis and structural characterization of new six Cu(II) coordination polymers of formulae $\{[Cu_2(ctc\text{-}cbut)(H_2O)_4]\cdot 2(H_2O)\}_n$ (**1**), $\{[Cu_5(ctc\text{-}cbut)_2(OH)_2(H_2O)_8]\cdot 7(H_2O)\}_n$ (**2**), $\{[Cu_2(ctc\text{-}Hcbut)(OH)(H_2O)_2]\cdot 4(H_2O)\}_n$ (**3**), $[Cu_2(ttt\text{-}cbut)(H_2O)_4]_n$ (**4**), $\{[Cu_2(ttt\text{-}cbut)(H_2O)_4]\cdot 4(H_2O)\}_n$ (**5**) and $\{[Cu_4(ttt\text{-}cbut)_2(H_2O)_2]\cdot 3(H_2O)\}_n$ (**6**) ($ctc\text{-}H_4cbut = cis,trans,cis$-1,2,3,4-cyclobutanetetracarboxylic acid and $ttt\text{-}H_4cbut = trans,trans,trans$-1,2,3,4-cyclobutanetetracarboxylic acid), have been carried out, together with a computational study of the electronic and thermal free energies of the four isomers of the given ligand. The compounds **1-3** exhibit the ligand in its commercial $cis,trans,cis$ conformation while **4-6** were synthesized with the $trans,trans,trans$ isomer, after thermal treatment of the ctc-isomer. The topology of the six complexes synthetized are of different dimensionality, compound **4** shows a one-dimensional topology, compound **3** presents a 2D-topology with a binodal $[4^{12}6^{12}8^4][4^6]$-**flu** net, while **1**, **2**, **5** and **6** exhibit a 3D-topology with a binodal network 3,6-c for **1** and $[4^{12}6^{12}8^4]$ $[4^6]$2-**flu** for **2**. Compound **5** presents a triply interpenetrated $[6^6]$-**dia** net while **6** exhibits a three-nodal net with $[4^3][4^46^2][4^76^{10}8^4]$ point symbol.

Introduction

The coordination polymers (CPs) are crystalline materials formed by the combination of metal ions or clusters and organic spacers.[1] The construction of CPs is currently of interest due to their potential applications as gas absorption, hydrogen storage, ferroelectric, thin films, or magnetic materials.[2] These properties entirely depend on the crystal structures of these materials, therefore some structural prediction for new metal-organic architectures and the control of their dimensionality are desirable. However, predictability is confronted with polymorphism or pseudo-polymorphism in the sense that sometimes different arrangements are found for the same ligands and metal ions, despite some minor variations in the solvent contents. These systems offer a unique opportunity to investigate the influence of the solvent in the crystallization process. The systematic exploration of the synthetic routes can modify the solvent contents and consequently can induce a different template role on the coordination polymers, giving rise to different final topologies.[3] The choice of carboxylate ligands as organic linkers in the CPs synthesis is common due to their sufficiently rigid carboxylate

groups, the ability of these groups to act as H-bond acceptor and/or donor and their abundant coordination modes to produce extended frameworks with high structural stability. The 1,2,3,4-cyclobutanetetracarboxylic acid (H_4cbut) is a good candidate to form open frameworks due to its semi-rigid morphology, with its flexibility limited to the rotation of the carboxylic groups and the puckering of the cyclobutane ring. Moreover, this ligand has been found into two isomeric forms, the centrosymmetric $cis,trans,cis$ and the non-centrosymmetric $trans,trans,trans$. Of particular interest is the $trans,trans,trans$ isomer, which can act as tetrahedral linker among the metal centers.

Recently, some new coordination polymers involving the cbut ligand and different metal ions such as Co(II),[4] Ba(I),[5] the whole Li(I)-Cs(I) series,[6] U(II),[7] Ni(II) or Cu(II),[8] K(I)/Mg(II),[9] Cd(II),[10] and La(III)[11] show the high versatility of this ligand to coordinate metal centers giving rise to networks with variable dimensionality. Although commercially, the cbut ligand is available only in the $cis,trans,cis$ isomer, some of the above mentioned works reported crystal structures with the $trans,trans,trans$ isomer. These works show that under solvothermal conditions at temperatures above 150ºC, either in acid or basic media, the ligand undergoes an isomerization

towards the *trans,trans,trans* isomer.[4,6,9] A recent work by Chanthapally *et al.* shows that the isomerization also occurs on the solid state.[5]

The utilization of reactions at mild conditions to prepare coordination polymers with the *trans,trans,trans* isomer remains unexplored, since the reported isomerizations are always part of the reaction of the synthesis of the coordination complex.

This work is focused in the synthesis of Cu(II) coordination compounds based on the commercial *cis,trans,cis* form of the 1,2,3,4-cyclobutanetetracarboxylic acid but also with the thermally induced *trans,trans,trans* isomer at ambient conditions and with hydrothermal growth methods. A systematic screening on the different crystallization techniques and conditions like the metal/ion molar ratios, the temperature and the pH of the reaction media were accomplished. Three compounds with the commercial *cis,trans,cis* isomer and three metal-organic complexes with the *trans,trans,trans* cbut[4-] ligand have been successfully synthesized.

Here we report the synthesis and crystallographic studies of six copper(II) compounds involving the 1,2,3,4-cyclobutanetetracarboxylic acid with the formulae $\{[Cu_2(ctc\text{-}cbut)(H_2O)_4]\cdot 2(H_2O)\}_n$ (**1**) $\{[Cu_5(ctc\text{-}cbut)_2(OH)_2(H_2O)_8]\cdot 7(H_2O)\}_n$ (**2**), $\{[Cu_2(ctc\text{-}Hcbut)(OH)(H_2O)_2]\cdot 4(H_2O)\}_n$ (**3**), $[Cu_2(ttt\text{-}cbut)(H_2O)_4]_n$ (**4**), $\{[Cu_2(ttt\text{-}cbut)(H_2O)_4]\cdot 4(H_2O)\}_n$ (**5**) and $\{[Cu_4(ttt\text{-}cbut)_2(H_2O)_2]\cdot 3(H_2O)\}_n$ (**6**) [see Scheme S1].

Experimental

Materials and methods.

Reagents and solvents used in the synthesis were purchased from commercial sources and used without further purification. The *trans,trans,trans* isomer of the 1,2,3,4-cyclobutanetetracarboxylic acid was obtained through a thermal treatment at 150ºC in basic medium. The synthetic procedure for **1** has been already reported,[8b] but a new preparative method has been found and it is described hereunder. Compounds **1** and **5** were prepared using the gel technique according to the methods described by Henisch.[12] Elemental analyses (C, H, N) were performed with an EA 1108 CHNS/0 automatic analyzer. IR spectra on powder samples of **1-6** were performed on a IR Affinity-1 FTIR spectrophotometer in the 4000–400 cm^{-1} range equipped with a Pike Technologies GladiATR. The thermogravimetric analysis were carried out on a Perkin-Elmer Pyris Diamond TGA/DTA, under a flux of dry nitrogen, with a flowing at 100.0 mL min^{-1}. The measurements were done with a heating rate of 5 K min^{-1} in the temperature range from RT to 750 K using aluminum crucibles.

Synthetic procedures.

Synthesis of $\{[Cu_2(ctc\text{-}cbut)(H_2O)_4]2(H_2O)\}_n$ (1). An aqueous ammonia solution (25% v/v) was poured into an aqueous solution (10 cm^3) of H_4cbut (0.058 g, 0.25 mmol) to adjust the pH to 5.0. Tetramethylorthosilicate (0.7 cm^3) was added to this solution under vigorous stirring, and the resulting mixture was introduced into a test tube, covered, and stored for one day at room temperature to allow the formation of the gel. Once it was set, an aqueous solution (4 cm^3) of $Cu(NO_3)_2\cdot 2.5(H_2O)$ (0.116 g, 0.5 mmol) was layered on the gel,

care being taken to avoid any damage of its surface, and the tube was stored at room temperature. Blue needles of **1**, which were suitable for single crystal X-ray diffraction, appeared after few days. They were mechanically separated and washed with a water/ethanol (1:1 v/v) solution [yield *ca*. 72%]. Anal. Calcd for $C_8H_{16}Cu_2O_{14}$ (**1**): C, 20.74; H, 3.48%. Found: C, 20.70; H, 3.39%. FT-IR (cm^{-1}): 3327(w), 3049(w), 1554(m), 1511(s), 1400(s), 1300(m), 1230(w), 1145(w), 1038(w), 1006(w), 816(w), 761(w), 700(w), 655(s), 556(m), 504(s).

Synthesis of $\{[Cu_5(ctc\text{-}cbut)_2(OH)_2(H_2O)_8]\cdot 7(H_2O)\}_n$ (2). An aqueous solution (50 cm^3) of H_4cbut (0.116 g, 0.5 mmol) was mixed with a water solution (5 cm^3) of sodium carbonate (0.10 g, 1 mmol). The copper(II) nitrate hemipentahydrate (0.116 g, 0.5 mmol) was dissolved in a minimum amount of water and added to the previous solution under continuous stirring. The resulting clear solution was allowed to evaporate at room temperature. X-ray quality dark blue prismatic crystals of **2** were obtained after a week. Once collected, they were washed with water and air dried. Yield *ca*. 47%. Anal. Calcd. for $C_{16}H_{40}Cu_5O_{33}$ (**2**): C, 17.83; H, 3.74% Found: C, 17.79; H, 3.92%. FT-IR (cm^{-1}): 3510(w), 3084(w), 1537(s), 1402(s), 1310(m), 1300(m), 1232(w), 1004(w), 835(w), 763(m), 659(s), 449(s).

Synthesis of $\{[Cu_2(ctc\text{-}Hcbut)(OH)(H_2O)_2]\cdot 4(H_2O)\}_n$ (3). An aqueous ammonia solution (25% v/v) was added dropwise into an aqueous solution (5 cm^3) of H_4cbut (0.058 g, 0.25 mmol) until a pH of 5.0 is obtained. The resulting solution was placed into one arm of an H-shaped tube, and a $Cu(NO_3)_2\cdot 2.5(H_2O)$ (0.116 g, 0.5 mmol) aqueous solution (4 cm^3) was put into the other arm. A 50/50 MeOH/water solution was added dropwise to fill the H-shape tube. The H-tube was sealed and stored at RT. Thin green needles of **3** appeared within a week. They were collected, washed with a mixture of MeOH/water 50/50 and kept in humid conditions, since they rapidly became amorphous upon dryness. Yield *ca*. 22%. Anal. Calcd. for $C_8H_{18}Cu_2O_{15}$ (**3**): C, 19.97; H, 3.77 % Found: C, 20.11; H, 3.43 %. FT-IR: 3342(w), 3097(w), 1547(s), 1412(s), 1312(m), 1302(w), 1256(w), 1163(w), 1055(w), 1011(m), 773(s), 669(s), 561(m), 500(m).

Synthesis of $[Cu_2(ttt\text{-}cbut)(H_2O)_4]_n$ (4). An aqueous solution of triethylamine (0.140 cm^3, 1 mmol) was added dropwise into an aqueous solution (10 cm^3) of H_4cbut (0.058 g, 0.25 mmol) until a pH value of 6 was attained. The resulting colorless solution was sealed in a 45 cm^3 stainless-steel reactor with a Teflon liner, and it was heated at 150 ºC during 24 h. After cooling down, a water solution (5 cm^3) of $Cu(NO_3)_2\cdot 2.5(H_2O)$ (0.116 g, 0.5 mmol) was then added dropwise under continuous stirring. The resulting mixture was allowed to evaporate at room temperature, giving prismatic light blue crystals of **4** within two days. They were collected, washed with water and air dried. [yield *ca*. 60%] Anal. Calcd. for $C_8H_{12}Cu_2O_{12}$ (**4**): C, 22.49; H, 2.83% Found: C, 22.21; H, 2.82%. FT-IR (cm^{-1}): 3379(w), 3038(w), 1571(m), 1473(m), 1379(s), 1311(s), 1273(s), 1165(w), 1074(w), 1037(m), 941(m), 827(m), 775(s), 694(w), 648(s), 519(s).

Synthesis of $\{[Cu_2(ttt\text{-}cbut)(H_2O)_4]\cdot 4(H_2O)\}_n$ (5). An aqueous solution of triethylamine (0.140 cm^3, 1 mmol) was added dropwise into an aqueous solution (10 cm^3) of H_4cbut (0.058 g, 0.25 mmol) until a pH value of 6 was attained. The resulting colorless solution

was sealed in a 45 cm³ stainless-steel reactor with a Teflon liner, and it was heated at 150 ºC during 24 h. Once cooled, this solution was used to prepare a gel using a similar procedure than that of **1**. Tetramethylorthosilicate (0.7 cm³) was added under vigorous stirring and the resulting mixture was introduced into a test tube, covered, and stored for one day at room temperature to allow the formation of the gel. Once the gel was set, an aqueous solution (3 cm³) of $Cu(NO_3)_2 \cdot 2.5(H_2O)$ (0.232 g, 1 mmol) was layered on the gel, care being taken to avoid any damage of its surface, and the tube was stored at room temperature. Dark blue needles of **5** which were suitable for single crystal X-ray diffraction appeared after two days. They were mechanically separated, washed with a water/ethanol (1:1 v/v) solution and kept in wet conditions, since they lose crystallinity upon dehydration [yield *ca*. 19%]. Anal. Calcd for $C_8H_{20}Cu_2O_{16}$ (**5**): C, 19.25; H, 4.04%. Found: C, 19.07; H, 4.23%. FT-IR (cm⁻¹): 3251(w), 3003(w), 1574(s), 1394(s), 1284(s), 1174(w), 1055(w), 869(w), 800(m), 655(s), 555(w), 438(m).

Synthesis of {[Cu₄(*ttt*-cbut)₂(H₂O)₂]·3(H₂O)}ₙ (6). An aqueous ammonia solution (25% v/v) was added dropwise into an aqueous solution (10 cm³) of H₄cbut (0.058 g, 0.25 mmol) until a pH value of 6 was reached. The resulting colorless solution was sealed in a 45

cm³ stainless-steel reactor with a Teflon liner, and it was heated at 150 ºC during 24 h. An aqueous solution (3 cm³) of $Cu(NO_3)_2 \cdot 2.5(H_2O)$ (0.116 g, 0.5 mmol) was added to this solution and sealed again in the stainless-steel reactor with a Teflon liner under 150ºC during 48 h. Once cooled, prismatic green crystals of **6**, suitable for single crystal X-ray diffraction, were collected from the solution. They were mechanically separated, washed with a water/ethanol (1:1 v/v) solution and air dried. Yield *ca*. 34%. Anal. Calcd for $C_{16}H_{18}Cu_4O_{21}$ (**6**): C, 24.01; H, 2.27. Found: C, 24.12; H, 2.20 %. FT-IR (cm⁻¹): 3124(w), 1556(m), 1387(s), 1271(m), 1164(w), 1072(w), 1044(w), 1015(w), 942(m), 779(m), 759(m), 700(m), 650(m), 418(s).

Computational Details

All structures were optimized using Gaussian09 Rev A.02 with Becke's three-parameter hybrid functional (B3LYP) and the 6–31G (d) basis set. The stable configurations of the compounds were confirmed by means of frequency analysis, whereby no imaginary frequency was found for any of the configurations at the energy minima. The sum of the electronic and thermal free energies was used to compare stability.

Table 1. Crystal Data and Details of the Structure Determination for Complex **2-6**.

Compound	1	2	3	4	5	6
Formula	$C_8H_{16}Cu_2O_{14}$	$C_{16}H_{40}Cu_5O_{33}$	$C_8H_{18}Cu_2O_{15}$	$C_8H_{12}Cu_2O_{12}$	$C_8H_{20}Cu_2O_{16}$	$C_{16}H_{18}Cu_4O_{21}$
FW	463.29	1078.18	481.30	427.26	499.32	800.46
Crystal System	Tetragonal	Triclinic	Triclinic	Orthorhombic	Tetragonal	Triclinic
Space Group	$I 4_1/a$	P-1	P-1	$Pccn$	$I4_1/a$	P-1
a / Å	24.770(4)	8.7022(3)	6.2340(12)	7.9815(5)	18.6107(5)	8.0007(8)
b / Å	24.770(4)	8.9520(3)	11.118(2)	14.4504(6)	18.6107(5)	11.0476(9)
c / Å	4.7880(10)	12.6698(6)	11.948(2)	10.2757(6)	4.8022(3)	14.0408(11)
α / °	-	106.807(4)	86.78(3)	-	-	110.768(8)
β / °	-	90.983(3)	79.95(3)	-	-	96.370(8)
γ / °	-	110.054(2)	83.01(3)	-	-	97.671(7)
V / Å	2937.7(10)	880.10(6)	808.8	1185.16(11)	1663.28(12)	1133.1(2)
Z	8	1	2	4	4	2
μ / cm⁻¹	2.973	3.088	2.708	5.169	3.977	5.245
T / K	100	293	100	293	150	293
ρ_{calc} / g cm⁻³	2.095	2.034	1.976	2.395	1.994	2.346
λ / Å	0.7383	0.71073	0.7383	1.54184	1.54184	1.54184
	$-31 \leq h \leq 31$	$-11 \leq h \leq 11$	$-7 \leq h \leq 7$	$-9 \leq h \leq 9$	$-21 \leq h \leq 23$	$-6 \leq h \leq 9$
Index ranges	$-31 \leq k \leq 31$	$-10 \leq k \leq 11$	$-14 \leq k \leq 14$	$-17 \leq k \leq 17$	$-22 \leq k \leq 14$	$-13 \leq k \leq 13$
	$-6 \leq l \leq 6$	$-16 \leq l \leq 11$	$-15 \leq l \leq 15$	$-4 \leq l \leq 12$	$-5 \leq l \leq 5$	$-17 \leq l \leq 17$
Total reflect.	24290	8527	14167	2658	2644	7596
Indep. reflect. (R_{int})	1620(0.0498)	3975(0.0197)	3509(0.0766)	1161(0.0501)	815(0.0300)	4405(0.0343)
Obs. reflec. [$I > 2\sigma(I)$]	1532	3323	2941	931	779	3608
Parameters	128	277	259	100	77	379
Goodness-of-fit	1.091	1.036	1.059	1.055	1.083	1.047
R [$I > 2\sigma(I)$]	0.0352	0.0343	0.0614	0.0570	0.0299	0.0498
R_w [$I > 2\sigma(I)$]	0.0994	0.0820	0.1762	0.1449	0.0788	0.1361
R [all data]	0.0368	0.0471	0.0718	0.0692	0.0314	0.0614
R_w [all data]	0.1012	0.0881	0.1907	0.1576	0.0805	0.1493

Crystallography

Single crystal X-ray diffraction data sets for compound **2** were collected at 293 K on a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-Kα radiation (0.71073 Å). Data were indexed, integrated and scaled using the EVALCCD program.[13] Single crystal X-ray diffraction data of **1** and **3** were collected at 100 K using synchrotron radiation (at the ESRF

Spanish beamline BM16) with λ = 0.7383 Å and a CCD ADSCq210rCCD detector. A phi scan strategy was followed in the data collection with an oscillation range ($\Delta\phi$) for each image of one degree. Two different orientations of the crystal were measured in order to increase the data completeness. Data were indexed, integrated and scaled using the HKL2000 program.[14] The X-ray single crystal data collection for compounds **4-6** was carried out in an Agilent Supernova diffractometer with Cu

radiation (λ = 1.5418 Å) at 293 K for compounds **4** and **6** and at 150 K for **5**. The data were indexed, integrated and scaled with the CrysAlisPRO program.[15]

The crystal structures of **1-6** were solved by direct methods and refined with the full-matrix least-squares technique on F^2 by using the SHELXS-97 and SHELXL-97 programs,[16] respectively; included in the WINGX software package.[17] Anisotropic thermal parameters were used to refine all non-hydrogen atoms. The hydrogen atoms of the cyclobutane ring were geometrically set and refined with a riding model. The hydrogen atoms of the water molecules were neither found nor set, except for the coordinated water molecules in compounds **2** and **3**, and for the coordinated and uncoordinated water molecules in **1** and **5,** which were found in the difference Fourier map and refined with soft-restraints (DFIX). The hydrogen atoms of the carboxylic and the hydroxo groups in **3** were found in difference Fourier maps and refined with DFIX soft-restraints. The protocol used for the discrimination of the OH groups in **2** and **3** was similar. From the Fourier difference maps, we found the electron density of the hydrogen atoms and a slightly shorter bond distance (Cu-O) allow us to unambiguously determine the OH group (see Fig. S8 in the supplementary material). The final geometrical calculations and the graphical manipulations were carried out with the PLATON[18] and DIAMOND[19] programs. A summary of the crystal data and refinement conditions is listed in Table 1, whereas selected bond lengths and angles are shown in Table S1. Crystallographic data for the structures of **2-6** have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference numbers 1032973-1032977 for **2-6**, respectively.

Results and Discussion

The 1,2,3,4-cyclobutanetetracarboxylic acid has been recently utilized in the formation of different metal-organic networks.[4-11] The conformations of the ligand on the reported structures are the *cis,trans,cis* and *trans,trans,trans* isomers. However, there are two more possible isomers, the *cis,cis,cis* and the *cis,cis,trans* conformations (see Table 2). A theoretical calculation was performed in order to estimate the stability of these four isomers. The electronic and the thermal free energies for the four structures were summed and compared, and they are listed in Table 2. The minimum energy was found for the *trans,trans,trans* configuration, and thus, upon overcome of the thermal barrier among isomers, the *trans,trans,trans* is the most probable result.

Table 2. Calculated energies for the different conformational isomers of the 1,2,3,4-cyclobutanetetracarboxylic acid.

	trans,trans,trans	*cis,trans,cis*	*cis,cis,trans*	*cis,cis,cis*
a.u.	-911.48177	-911.47661	-911.47587	-911.46915
a.u. (ΔG)	0.00000	0.00516	0.00590	0.01262
Kcal mol^{-1} (ΔG)	0.00000	3.23607	3.70482	7.91729
kJ mol^{-1} (ΔG)	0.00000	13.53971	15.50096	33.12596

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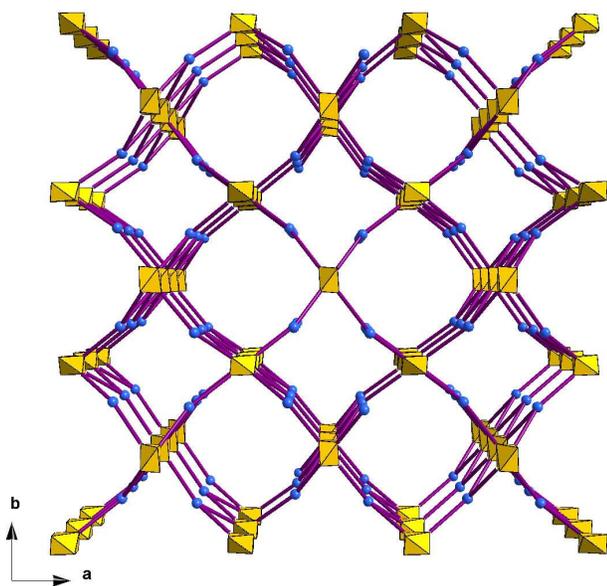
Figure 1. A view of the topological network of **1** along the *c* axis. Yellow polyhedra and blue spheres represent the six- and three-fold nodes, respectively, corresponding to cbut ligand and Cu(II) ions.
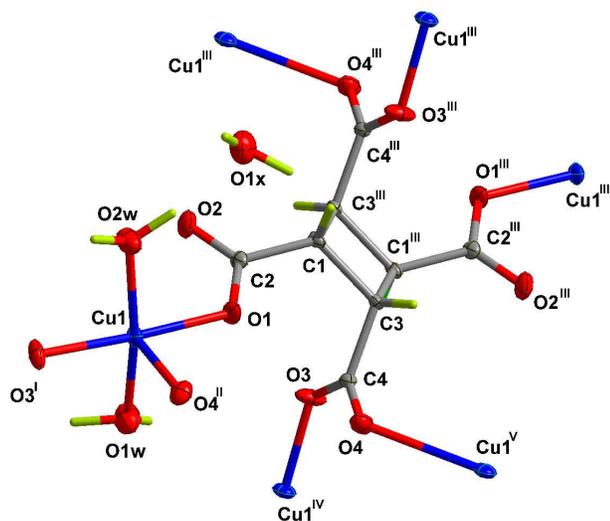
Figure 2. View of a fragment of the structure of **1** together with the atom numbering. Ellipsoids are depicted at 50% probability. Symmetry codes: (I) = -1/4+*y*, 5/4-*x*, 1/4-*z*; (II) = -1/4+*y*, 5/4-*x*, -3/4-*z*; (III) = 1/4+*y*, 5/4-*x*, -3/4-*z*; (IV) = 5/4-*y*, 1/4+*x*, 1/4-*z*; (V) = 5/4-*y*, 1/4+*x*, -3/4-*z*.

Structural Descriptions

$\{[Cu_2(ctc\text{-}cbut)(H_2O)_4]\cdot 2(H_2O)\}_n$ **(1).** Although the crystal structure of compound **1** has been recently reported,[8b] a detailed

structural description has been included hereafter in order to facilitate the comparisons. The compound $\{[Cu_2(ctc\text{-}cbut)(H_2O)_4]\cdot 2(H_2O)\}_n$ **(1)** crystallizes in the centrosymmetric $I4_1/a$ space group and its structure is three-dimensional with a new bi-nodal 3,6-c topological network (Fig. 1) composed of six-$[4^2 6^{10} 8^3]$ and three-fold $[4 \cdot 6^2]$ nodes (in Schläfli notation).[20] The 3D crystal structure consists of regular *anti-syn* carboxylate bridged diaqua-Cu(II) chains running along the *c* axis (Fig. S1a) which are connected to six adjacent chains through the skeleton of the *ctc*-cbut[4-] ligand. Two different one-dimensional pores of diameter 10.2879(12) and 7.5516(10) Å (A and B cavities, respectively, in Fig. S1b) run along the 4_1 symmetry element parallel to the *c* axis. The conformation of the carboxylate groups plays a key role on the formation of the cavities. The *trans*-carboxylate groups of all the *ctc*-cbut[4-] ligands in **1** build the largest channels whereas the *cis*-carboxylate groups form the B pores. Both channels are filled with coordination water molecules and the A pores also contain a unique crystallization water molecule [O(1x)]. The coordinated water molecules reduce the pore diameter to 7.1755(12) and 5.3643(10) Å for A and B cavities, respectively.

An extensive H-bond network occurs within the A and B pores. Interestingly, in the A pore the crystallization water molecule [O(1x)] establishes hydrogen bonds with its symmetry equivalents to form a helical water chain that runs along the channel (Fig. S1c). O(1x) is anchored to the pore wall through H-bonds towards the coordination water molecule O(2w) and the uncoordinated carboxylate oxygen atom O(2). The donor···acceptor lengths and the O-H···O angles range from 2.6742(3) to 2.8799(3) Å and from 157.8(6) to 169.1(7)º, respectively. The hydrogen bonding in the B cavity involves the coordinated O(1w) water molecule and the coordinated O(4) carboxylate oxygen atom (Fig. S1d). The close packing of **1** was analyzed by PLATON through the Kitaigorodskii index showing a KPI value of 0.73 [0.65 when the crystallization water molecule O(1x) is excluded].[18] The void volume once the crystallization water molecules have been removed is 472 Å³ per unit cell. This value represents the 16.1% of the total unit cell volume.[18]

The crystallographically independent Cu(1) atom is five coordinated exhibiting a distorted square pyramidal environment [τ value[21] being 0.16]. The basal positions are occupied by two carboxylate oxygen atoms [O(1) and O(3)I] from two different *ctc*-cbut[4-] ligands and two coordination water molecules [O(1w) and O(2w)] and the apical site is occupied by a carboxylate oxygen atom [O(4)II] [symmetry codes: (I) = -1/4+*y*, 5/4-*x*, 1/4-*z*; (II) = -1/4+*y*, 5/4-*x*, -3/4-*z*;] (Fig. 2). The apical and the average equatorial bond distances are 2.419(2) and 1.943(2) Å, respectively (see Table S1).

The *ctc*-cbut[4-] ring lays on a inversion centre located in the middle of the cyclobutane ring, which shows planar conformation (see Table S2), in agreement with the Margulis rule that establishes that centrosymmetric substituted rings can be puckered or not, whereas the non-centrosymmetric ones should be puckered.[22] The ligand adopts a *hexakis*-monodentate coordination mode, acting as a six-fold connector (see Fig. 2 and Scheme S2).

The metal-metal separation distance within the *anti-syn* carboxylate bridged chains is 4.7880(11) Å, whereas the separation between copper atoms from adjacent chains coordinated through the *cis*- and *trans*-carboxylate groups are 5.3642(7) and 7.9342(10) Å, respectively.

{[**Cu₅(*ctc*-cbut)₂(OH)₂(H₂O)₈]·7(H₂O)**}ₙ **(2).** The crystal structure of compound **2** is three-dimensional and consists of a sandwich system with inorganic layers pillared by the *ctc*-cbut ligand along the *b* axis in a regular *AAAA* conformation (Fig. S2a). The inorganic layers (Fig. S2b) are built up by copper(II) pentanuclear units linked through *anti-syn* carboxylate-bridges to form chains running along the *c* axis (Fig. 3) which are further connected with their adjacent ones through a OCCCCO pathway of the *ctc*-cbut ligand. From a topologically point of view, and considering the pentanuclear units a single eight-fold node, the complex **2** exhibits a binodal [4¹²6¹²8⁴][4⁶]-**flu** net (in Schläfli notation) (see Fig. 3).[20] This topological network has been observed previously in a Cobalt(II)-based metal-organic framework, but it is still unusual and only four reported structures present the same topology.[23] The KPI value calculated for **2** is 0.69 and the void volume without the crystallization water molecules is 880 Å³ per unit cell, and represents the 20.3% of the total unit cell volume.[21]

Each pentanuclear unit is centrosymmetric with Cu(1) laying on the inversion centre. Cu(1) is connected to Cu(2) through a double bridge (a *μ*-aqua and a OCCCCO bridge). Cu(2) is then linked to Cu(3) by a double bridge, a *μ*-hydroxo and a *syn-syn* carboxylate [the angle at the *μ*-hydroxo bridge is 107.40(13)°]. Cu(3) is located almost perpendicular to the Cu(2)···Cu(1)···Cu(2)ᴵ line [(I) = -*x*, -*y*, -*z*], and the separations between copper atoms are 4.1118(4) and 3.0988(6) Å for Cu(1)···Cu(2) and Cu(2)···Cu(3), respectively. Each pentanuclear
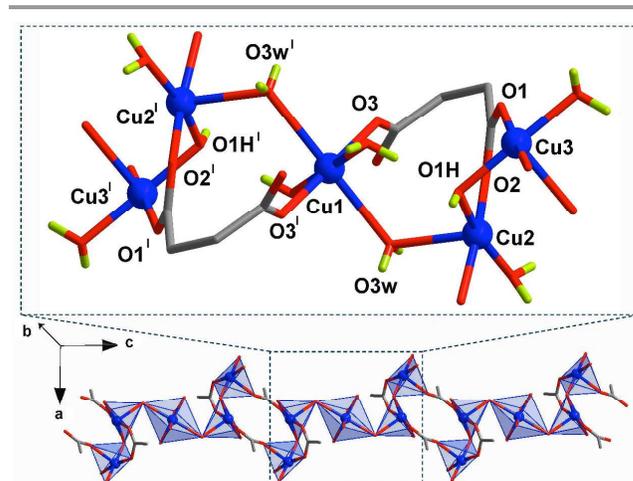
Figure 3. (Top) Topological representation of **2** along the *a* axis. Yellow and blue polyhedra represent the four-fold connectors (the cbut ligand) and the eight-fold nodes (the pentanuclear SBU), respectively. (Middle) Detailed view of the pentanuclear SBU with the atom numbering scheme. (Bottom) View of a fragment of the carboxylate bridged chain of Cu₅-SBUs running along the *c* axis. Symmetry code: (I) = -*x*, -*y*, -*z*
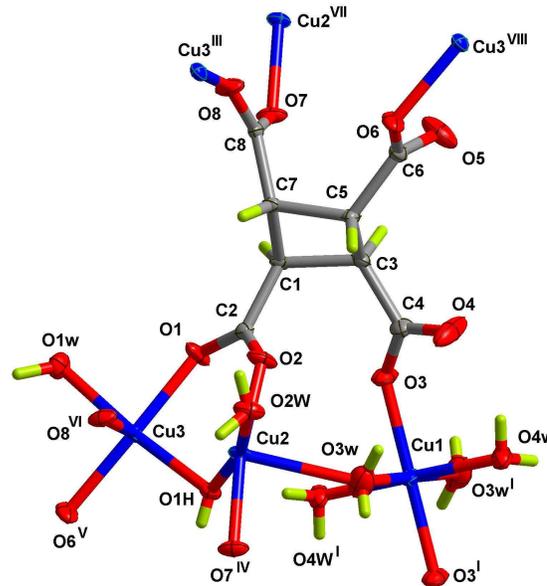
Figure 4. View of a fragment of the structure of **2** together with the atom numbering. Ellipsoids are depicted at 50% probability. Symmetry codes: (I) = -*x*, -*y*, -*z*; (III) = -*x*, 1-*y*, 1-*z*; (IV) = *x*, -1+*y*, *z*; (V) = -1+*x*, -1+*y*, *z*; (VI) = -*x*, 1-*y*, 1-*z*; (VII) = 1+*x*, 1+*y*, *z*; (VIII) = *x*, 1+*y*, *z*.
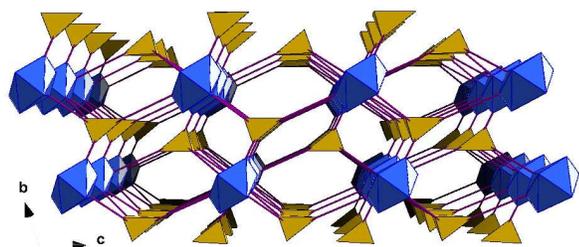
unit is linked to its two adjacent ones along the *c* direction through *anti-syn* carboxylate bridges involving the Cu(2)-Cu(3) pair [Cu(2)···Cu(3)ᴵᴵ separation is 5.4015(7) Å]; (II)= -*x*, -*y*, 1-*z*]. The chains are connected to the adjacent ones in the same layer and to the adjacent layers through pathways involving the skeleton of the *ctc*-cbut ligand, but it is noteworthy that all the *cis*-carboxylate groups are involved in the intralayer connections while *trans*-carboxylate groups link the layers along the *b* axis (see Fig. S2a). The shortest metal-metal inter-layer distance is 7.3988(7) Å [Cu(2)···Cu(3)ᴵᴵᴵ] [(III) = -*x*, 1-*y*, 1-*z*].

Compound **2** exhibits four crystallization water molecules [O(1x)-O(4x)] in the pores located in the interlayer space along the *c* axis. They are anchored to the host through hydrogen bonds involving the coordination water molecules and uncoordinated carboxylate oxygen atoms [O···O in the range 2.606(7) to 3.223(11) Å].

Three crystallographic independent sites are occupied by Cu(II) ions in **2** (see Fig. 4). The Cu(1) atom, which lies on a crystallographic inversion site, exhibits a distorted octahedral environment with two long apical positions [Cu(1)–O(3w) being 2.501(5)Å]. The basal plane is formed by two carboxylate oxygen atoms [O(3) and O(3)^I] from two different *ctc*-cbut^{4-} ligands and two coordination water molecules [O(4w) and O(4w)^I] with an average bond length of 1.9628 Å (selected interatomic distances and angles are listed in Table S1). The values of φ and s/h parameters are 54.36 and 1.44 (to be compared to 60º and 1.22 for an ideal octahedron).[24] Cu(2) and Cu(3) exhibit a square pyramidal environment [τ value[21] being 0.06 and 0.11, respectively]. Two carboxylate oxygen atoms [O(2) and O(7)^{IV}] from two different *ctc*-cbut^{4-} ligands, one hydroxo oxygen atom [O(1H)] and one coordination water molecule [O(2w)] build the basal plane of Cu(2) whereas other coordination water molecule [O(3w)] occupies the apical position [(IV) = *x*, -1+*y*, *z*;] [the equatorial bond lengths vary in the range 1.923(2)-1.961(3) Å and the apical bond distance is 2.367(3) Å]. In the case of Cu(3), two carboxylate oxygen atoms [O(1) and O(6)^V], one hydroxo oxygen atom [O(1H)] and a coordination water molecule [O(1w)] build the basal plane while a carboxylate oxygen atom [O(8)^{VI}] occupies the apical position [the equatorial bond distances range from 1.923(2) to 1.9808(4) Å and the apical bond length is 2.342(2) Å; (V) = -1+*x*, -1+*y*, *z*; (VI) = -*x*, 1-*y*, 1-*z*;].

The *ctc*-cbut^{4-} ligand exhibits a *hexakis*-monodentate coordination mode trough O(1), O(2), O(3), O(6), O(7) and O(8) oxygen atoms towards Cu(3), Cu(2), Cu(1), Cu(3)^{VII}, Cu(2)^{VIII} and Cu(3)^{III}, respectively [(VII) = 1+*x*, 1+*y*, *z*; (VIII) = *x*, 1+*y*, *z*;] (Fig. 4 and Scheme S2). The cyclobutane ring exhibits a puckered conformation with the dihedral angles between the C(1)C(3)C(5) and C(1)C(7)C(5), and C(3)C(5)C(7) and C(3)C(1)C(7) planes of 16.8(3) and 16.7(3)º, respectively. These values are within the range observed in a CSD search for cyclobutane ring-containing structures (version 5.35 May 2014) (see Fig. S3 and Table S2).[25]
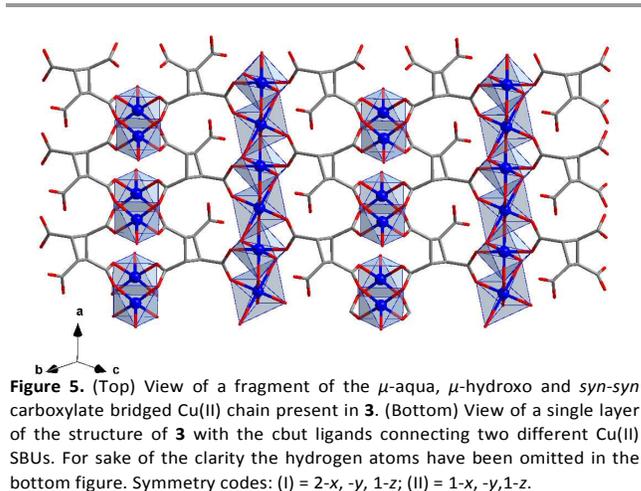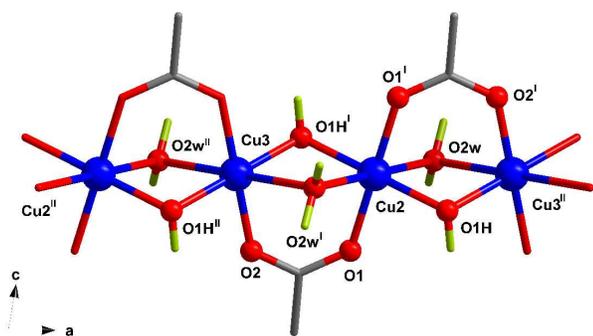
Figure 5. (Top) View of a fragment of the *µ*-aqua, *µ*-hydroxo and *syn-syn* carboxylate bridged Cu(II) chain present in **3**. (Bottom) View of a single layer of the structure of **3** with the cbut ligands connecting two different Cu(II) SBUs. For sake of the clarity the hydrogen atoms have been omitted in the bottom figure. Symmetry codes: (I) = 2-*x*, -*y*, 1-*z*; (II) = 1-*x*, -*y*,1-*z*.

{[Cu$_2$(*ctc*-Hcbut)(OH)(H$_2$O)$_2$]·4(H$_2$O)}$_n$ **(3).** The crystal structure of compound **3** is two-dimensional and it features two distinct copper(II) SBUs linked through the *ctc*-Hcbut to form almost planar layers. One of the SBUs is a copper(II) chain running along the *a* axis formed by the regular alternation of Cu(2) and Cu(3) (both sited on inversion centres) with a unique triple bridge, a *µ*-hydroxo, a *µ*-aqua and a *syn-syn* carboxylate (Fig. 5a). The Cu(2)···Cu(3) separation is 3.1170(6) Å and the values of the dihedral angles at the *µ*-hydroxo and *µ*-aqua bridges are 107.63(16) and 76.30(11)º, respectively.
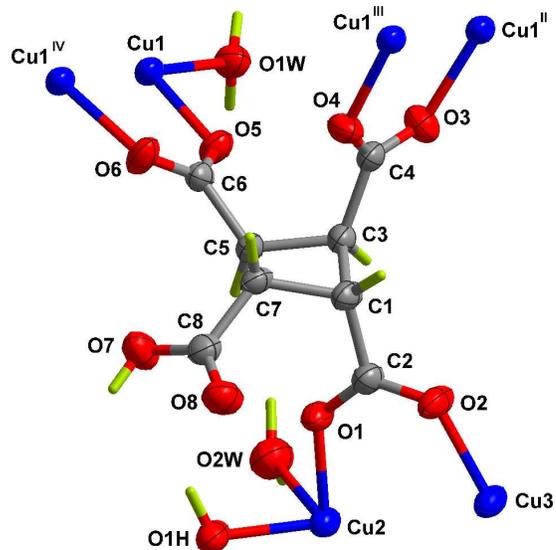
Figure 6. View of a fragment of the structure of **3** together with the atom numbering. Ellipsoids are depicted at 50% probability. Symmetry codes: (II) = 1-*x*, -*y*,1-*z*; (III) = 2-*x*, 1-*y*, -*z*; (IV) = 3-*x*, 1-*y*, -*z*.

The other SBU is a centrosymmetric paddle wheel formed by Cu(1) with the copper ions separated by 2.6204(11) Å (Fig. S4). The chains and the paddle wheel motifs are linked through the *ctc*-Hcbut ligand, and they regularly alternate along the [01-1] direction following an *ABABAB* sequence (Fig. 5b). These layers

are connected by hydrogen bonds involving the coordination and crystallization water molecules together with the protonated carboxylic group, they follow an *ABABAB* sequence along the [011] direction (Fig. S4). The 2D structure of compound **3** is a three nodal 4,4,4-c net with four- $[3·4·5^2·6^2]$, four- $[3^25^27^2]$ and four-fold $[4^25^27^2]$ nodes in Schläfli notation.[20] The void volume when the crystallization water molecules are removed is 209 Å[3], which represents the 25.8% of the total unit cell volume.[18] The high mobility that exhibits the guest molecules precludes the calculation of the KPI index, but when they are removed, the KPI is 0.51.

Three crystallographically independent sites are occupied by Cu(II) ions [Cu(1), Cu(2) and Cu(3)] on **3** (see Fig. 6). Cu(1) exhibits a square pyramidal environment [τ value[21] being 0.003] with four oxygen atoms [O(5), O(3)^V, O(4)^{III} and O(6)^{IV}; [(V) = 1+*x*, *y*, *z*; (III) = 2-*x*, 1-*y*, -*z*; (IV) = 3-*x*, 1-*y*, -*z*] from four different *ctc*-Hcbut[3-] ligands building the basal plane and a coordination water molecule [O(1w)] occupying the apical position. However, Cu(2) and Cu(3), which lay on crystallographic inversion centers, exhibit a elongated octahedral surroundings and they share an edge of the polyhedra. The basal plane of Cu(2) is formed by two oxygen atoms [O(1) and O(1)^I; (I) = 2-*x*, -*y*, 1-*z*] from two different *ctc*-Hcbut[3-] ligands and two hydroxo groups [O(1H) and O(1H)^I], whereas the two long apical positions are occupied by O(2w) and O(2w)^I [Cu(2)–O(2w) being 2.502(4) Å]. In the case of Cu(3), the basal plane is formed by carboxylate oxygen atoms O(2) and O(2)^{II} [(II) = 1-*x*, -*y*,1-*z*] from two distinct *ctc*-Hcbut[3-] ligands and two hydroxo groups O(1H)^I and O(1H)^{VI}[(VI) = -1+*x*, *y*, *z*], and as occurs with Cu(2), the two long apical bonds are Cu(3)–O(2w)^{VI} and Cu(3)–O(2w)^I [2.4643(8)Å]. The values of φ and *s/h* parameters are 54.05 and 1.47 for Cu(2) and 54.05° and 1.45 for Cu(3) atoms, respectively (to be compared to 60° and 1.22 for an ideal octahedron).[24]

There is one crystallographically independent *ctc*-Hcbut[3-] ligand in **3** and it adopts a *hexakis*-monodentate coordination mode trough O(1), O(2), O(3), O(4), O(5) and O(6) towards Cu(2), Cu(3), Cu(1)^{VI}, Cu(1)^{III}, Cu(1) and Cu(1)^{IV}, respectively (see Fig. 6 and Scheme S2). The cyclobutane ring has a puckered conformation, with dihedral angles between the C(1)C(3)C(5) and C(1)C(7)C(5) and C(3)C(5)C(7) and C(3)C(1)C(7) planes of 22.9(3) and 23.1(3)°, respectively. These values are within the range previously observed (see Fig. S3 and Table S2).

[Cu₂(*ttt*-cbut)(H₂O)₄]ₙ (4). The structure of **4** is one-dimensional and it is formed of μ-carboxylate bridged dinuclear copper(II) entities linked by the skeleton of the *ttt*-cbut[4-] ligand giving rise to corrugated chains (Fig. 7 and S5). Chains of adjacent layers grow in different directions, one along the [1-10] and other towards the [-1-10] direction forming an angle of 57.827° between them, and the stacking follows an *ABABAB* sequence along the *c* axis (see Fig. 8). An extensive hydrogen bonded network, involving the coordinated water molecules [O(1w) and O(2w)] and the uncoordinated carboxylate oxygen atoms [O(1) and O(3)], connects the different chains and generates a supramolecular 3D network. The O···O bond distances range from 2.680(5) to 2.908(6) Å. The dinuclear unit is generated by an inversion centre at the midpoint between the Cu(1) atoms, and

they are linked through the O(2) and O(2)^I carboxylate oxygen atoms [(I) = -*x*, 1-*y*, -*z*]. The copper-copper separation distance is 3.3240(9) Å and the dihedral angle through the μ-carboxylate bridge is 103.73(13)°. The shortest separation between Cu(II) ions of different dinuclear units within the chains is 7.9608(9) Å. The Cu(1)O(2)Cu(1) planes of adjacent dinuclear units within the chains are tilted, being almost perpendicular, with a dihedral angle of 82.25(7)°. The Kitaigorodskii packing index for **4** is 0.77 showing no accessible void to guest solvent molecules.[18]

One crystallographically independent Cu(II) ion is present in compound **4** which is five-coordinated forming a slightly distorted square pyramidal polyhedron [τ value[21] being 0.116]. The basal plane is formed by two *trans*-coordinated water molecules [O(1w) and O(2w)] and two carboxylate oxygen atoms [O(2) and O(4)^{II}; (II) = -1/2+*x*, 1/2+*y*, -*z*], whereas the axial position is filled by O(2)^{II}. The average value of the equatorial bond lengths is 1.954(4) Å and the apical bond distance is 2.267(3) Å (Table S1).

One crystallographically independent *ttt*-cbut[4-] ligand in *trans-trans-trans* conformation is present in **4** (Fig. 7). The fully deprotonated ligand is generated by a two-fold axis crossing at midpoint of the cyclobutane ring. The *ttt*-cbut[4-] adopts *bis*-bidentate [through O(2) and O(4)^{III} toward Cu(1)^I and their symmetry equivalents (s.e.)] and *bis*-monodentate [through O(2) towards Cu(1) and s.e.] coordination modes (Fig. 7) [(III) = 1/2-*x*, 1/2-*y*, *z*]. The cyclobutane ring exhibits a puckered conformation, in agreement with the Margulis rule,[22] with values of 11.2(3)° and 11.3(4)° for the dihedral angles between the C(1)C(3)C(1)^{III} and C(1)^{III}C(3)^{III}C(1), and C(3)C(1)C(3)^{III} and C(3)^{III}C(1)^{III}C(3) planes, respectively. These puckering values are within the range of previously reported compounds (Fig. S3).
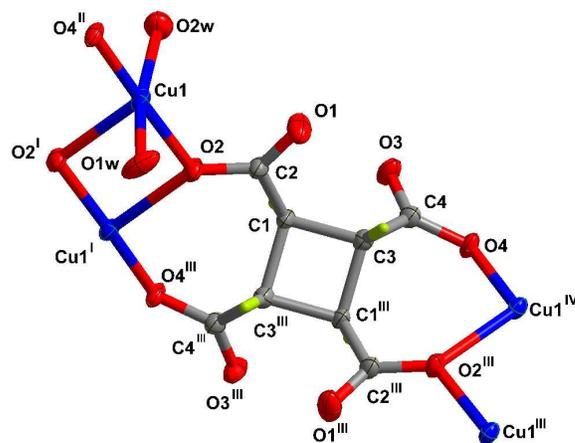
Figure 7. View of a fragment of the structure of **4** together with the atom numbering. Ellipsoids are depicted at 50% probability. Symmetry codes: (I) = -*x*, 1-*y*, -*z*; (II) = -1/2+*x*, 1/2+*y*, -*z*; (III) = 1/2-*x*, 1/2-*y*, *z*; (IV) = 1/2+*x*, -1/2+*y*,-*z*.
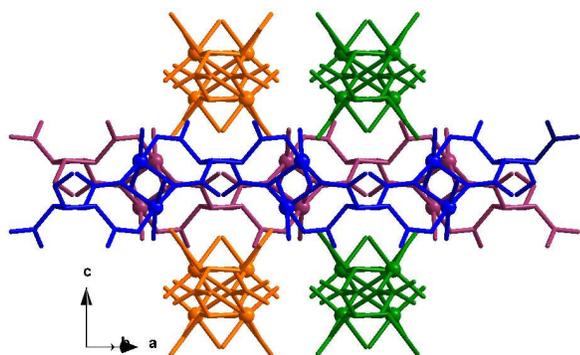
Figure 8. Crystal packing of **4** with the chains running along the [1-10] (the orange and green ones) and along the [-1-10] directions (blue and purple). For clarity each chain is depicted using different colors and the hydrogen atoms are omitted.

The shortest metal-metal separation between adjacent layers is 5.2676(9) Å, a value shortest than the shortest separation between copper atoms of consecutive dinuclear units within the chain.

$\{[Cu_2(ttt\text{-}cbut)(H_2O)_4]\cdot4(H_2O)\}_n$ **(5).** The compound **5** crystallizes in the centrosymmetric space group $I4_1/a$, as occurs in **1** (Table 1 and Fig. 9). The crystal structure is three-dimensional and it consists of a triple interpenetrated diamond $[6^6]$-**dia** network comprising the *ttt*-cbut ligands as four-fold nodes and *trans*-diaquacopper(II) ions as linear connectors (Fig. 10 top). The separation between consecutive four-fold nodes in the structure is 9.9780(2) Å producing cavities of approximately 1.6 nm of diameter, which are occupied by the other two interpenetrating diamond nets. Although the crystal structure is interpenetrated, there are enough void for crystallization water guest molecules. There are chiral channels running along the *c* axis of 9.6101(2) Å in diameter [measured from metal to metal separation], reduced to 6.7782(2) Å in diameter when the coordination water molecules are taken into account. The chiral channels share edges with four other pores of opposite handedness, leading to the global centrosymmetry of the structure (Fig. 10 bottom). The unique crystallization water molecule forms an helical chain via hydrogen bonds which is of opposite handedness to that of the channel where it is located (Fig. S6) [O(1x)–H⋯O(1x), D⋯A separation and angle are 2.927(3) Å and 169.6(2)º, respectively]. The water helix is anchored to the host through hydrogen bonds involving the coordination water molecule O(1w), which also serves as linker between the three interpenetrating networks. The KPI value calculated for **5** is 0.73 (0.59 with crystallization water molecules excluded).[18] The void volume of the cell when the crystallization water molecules are removed is 299 Å^3, which represents the 18% of the total unit cell volume.[18]
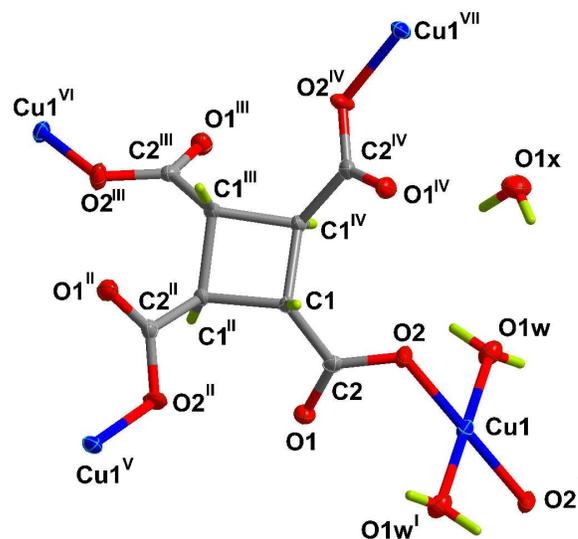
Figure 9. View of a fragment of the structure of **5** together with the atom numbering. Ellipsoids are depicted at 50% probability. Symmetry codes: (I) = -*x*, 1-*y*, -*z*; (II) = -3/4+*y*, 3/4-*x*, 3/4-*z*; (III) = -*x*, 3/2-*y*, *z*; (IV) = 3/4-*y*, 3/4+*x*, 3/4-*z*; (V) = 3/4-*y*, 3/4+*x*, 3/4+*z*; (VI) = -*x*, 3/2-*y*, *z*; (VII) = -1/4+*y*, 3/4-*x*, 3/4+*z*.

One crystallographically independent Cu(II) ion is present in **5** (see Fig. 9). Cu(1) lies on an inversion centre and it is four-coordinated with an almost perfect square planar environment. Two carboxylate oxygen atoms [O(2) and O(2)^I; (I) = -*x*, 1-*y*, -*z*] from two different *ttt*-cbut^{4-} ligands and two coordination water molecules [O(1w) and O(1w)^I] built the environment of Cu(1). The mean Cu–O bond distance is 1.929(2) Å and the O–Cu–O dihedral angles lay in the range from 88.44(8) to 91.56(8)º (see Table S1).

There is a crystallographically unique *ttt*-cbut^{4-} ligand in **5**, which is generated by a -4 symmetry axis crossing the midpoint of the cyclobutane ring. The ligand exhibits a *tetrakis*-monodentate conformation through O(2), O(2)^{II}, O(2)^{III} and O(2)^{IV} towards Cu(1), Cu(1)^V, Cu(1)^{VI} and Cu(1)^{VII} (Fig. 9 and Scheme S2) [(II) = -3/4+*y*, 3/4-*x*, 3/4-*z*; (III) = -*x*, 3/2-*y*, *z*; (IV) = 3/4-*y*, 3/4+*x*, 3/4-*z*; (V) = 3/4-*y*, 3/4+*x*, 3/4+*z*; (VI) = -*x*, 3/2-*y*, *z*; (VII) = -1/4+*y*, 3/4-*x*, 3/4+*z*.]. The cyclobutane ring shows a puckered conformation with a dihedral angle between C(1)C(1)^{VIII}C(1)^{IX} and C(1)C(1)^{X}C(1)^{IX} of 24.162º [symmetry code: (VIII) = 1/4-*y*, 1/4-*x*, -3/4-*z*; (IX) = -*x*, 1/2-*y*, *z*; (X) = -1/4+*y*, 1/4-*x*, -3/4-*z*]. The separation between Cu(II) ions of the same network is 7.5011(2) Å, a value which is longer than the 4.8022(3) Å observed for the separation distance from Cu(II) ions of different interpenetrated networks.
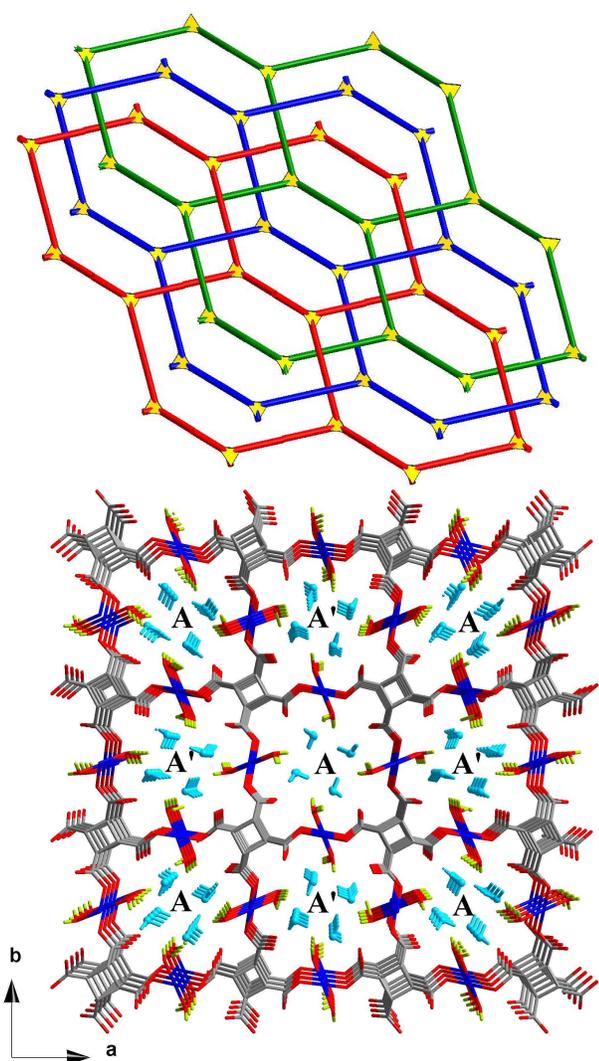
Figure 10. (Top) Topological representation of the triple interpenetrated diamond [6^6]-**dia** network of **5**. The nodes are represented as yellow tetrahedra and each one of the three interpenetrated networks is represented in a different color. (Bottom) Perspective view along the *c* axis of the crystal structure showing the left- and the right-handed helical water chains embedded within pores A and A', respectively.

$\{[Cu_4(ttt\text{-cbut})_2(H_2O)_2]\cdot 3(H_2O)\}_n$ **(6).** The crystal structure of **6** is three-dimensional and it consists of tetranuclear Cu(II) SBUs linked through carboxylate bridges to form inorganic layers in the *ab* plane which are pillared along the *c* axis by the *ttt*-cbut ligand. From a topological point of view, **6** exhibits a three-nodal net with three- [4^3], four- [4^{4}6^2] and seven-fold [4^{7}6^{10}8^4] nodes giving rise a new topology with a point symbol net [4^3][4^{4}6^2][4^{7}6^{10}8^4] in Schläfli notation (see Fig. 11).[20]
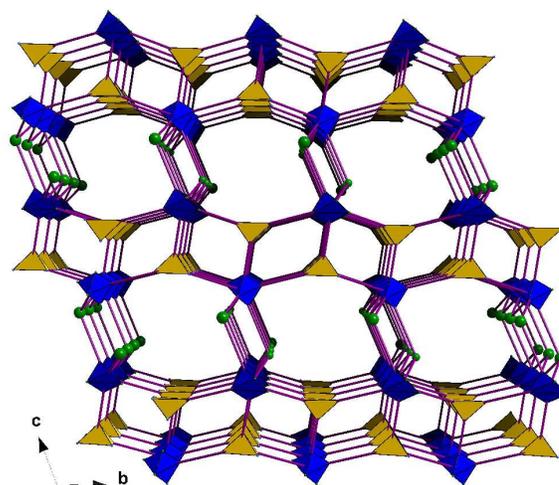
Figure 11. Central projection of the topology of **6** along the *a* axis. The four- (cbut A), three- (cbut B) and eight-fold [the tetranuclear Cu(II) SBU] nodes are represented as yellow tetrahedra, green spheres and blue polyhedra, respectively.

The crystal structure contains four crystallization water molecules [O(1x)-O(4x)] that occupy the void space between layers. They are hydrogen bonded to the coordination water molecules O(1w) and O(2w) and to the uncoordinated carboxylate oxygen atom O(1) [the O···O distances range from 2.629(8) to 2.7065(7) Å]. The packing of **6** was analyzed by PLATON through Kitaigorodskii index showing no accessible voids due by the high mobility of the guest molecules (a KPI value of 0.66 is obtained when the crystallization water molecules are excluded).[18] The solvent accessible volume when the crystallization water molecules are removed is 81 Å^3, which represents the 7.2% of the total unit cell volume.[18]

The secondary building unit comprises four crystallographically different Cu(II) ions linked through different bridges. Cu(1) is connected to Cu(2) through a double μ-carboxylate bridge [O(2) and O(10)], with Cu(1)···Cu(2) separation of 3.2834(10) Å and dihedral angles at the bridgeheads O(2) and O(10) of 104.9(2) and 103.2(2)°, respectively (Fig. S7a). Cu(2) is linked to Cu(3) through a double *syn-syn* carboxylate and a single μ-carboxylate [O(3)]; with a Cu···Cu separation of 3.1829(10) Å and a dihedral Cu(2)–O(3)–Cu(3) angle of 108.0(2)°. Cu(3) and Cu(4) are connected by a single *syn-syn* carboxylate and a double μ-carboxylate bridge [O(6) and O(12)] with a separation between metal ions of 3.1733(10) Å and bridgehead angles at O(6) and O(12) of 91.68(13) and 91.86(13)°, respectively. Cu(2) is also connected to Cu(4) through an *anti-syn* carboxylate bridge.

Each of these SBUs is linked to their six nearest neighbors through carboxylate bridges to form an inorganic layer in the *ab* plane (Fig. S7b). These layers are pillared along the *c* axis following an *ABABAB* sequence with each one of the crystallographically independent *ttt*-cbut ligands connecting different set of layers (Fig. S7c). It deserves to be noted that three of the four carboxylate groups of each *ttt*-cbut^{4-} ligand are involved in the building of the organic-inorganic *ab* layers while

the remaining carboxylate groups [O(7)-C(8)-O(8) and O(15)-C(16)-O(16)] connect the adjacent layers. The shortest interlayer metal-metal separation between layers [Cu(1)···Cu(1)^I; (I) = 1-x, 1-y, -z] is 6.0443(11) Å.
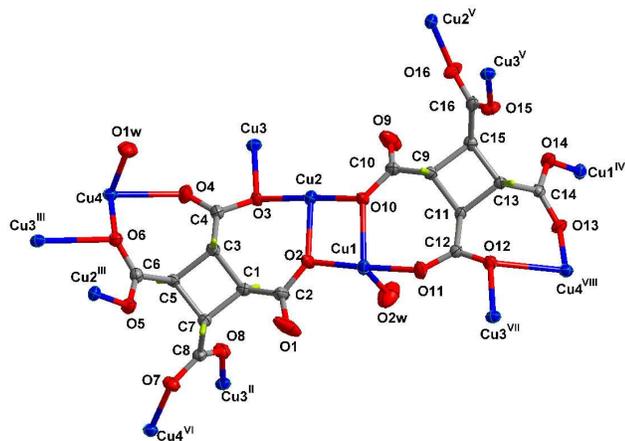
Figure 12. View of a fragment of the structure of **6** together with the atom numbering. Ellipsoids are depicted at 50% probability. Symmetry codes: (II) = 1-x, 2-y, -z; (III) = -1+x, y, z; (IV) = 1+x, y, z; (V) = 2-x, 2-y, 1-z; (VI) = -x, 2-y, -z; (VII) = x, -1-y, z; (VIII) = 1+x, -1+y, z.

Four crystallographically independent Cu(II) ions are present in **6** (Fig. 12). Three of them, Cu(1), Cu(2) and Cu(3) are five-coordinated, and while Cu(1) and Cu(3) exhibit a distorted square pyramidal environment with τ values[21] being 0.22 and 0.02, respectively; Cu(2) shows a polyhedron at midway between a trigonal bipyramid and a square pyramid with a τ parameter[21] of 0.61. The basal plane of Cu(1) is formed by three carboxylate oxygen atoms [O(2), O(11) and O(14)^{III}] from three different *ttt*-cbut^{4-} ligands and one coordination water molecule O(2w) [mean basal Cu–O distance is 1.960(6) Å], whereas the apical position is filled by the carboxylate oxygen atom O(10) [Cu(1)–O(10) bond distance is 2.239(3) Å] [(III) = -1+x, y, z;]. Considering Cu(2) with a trigonal bipyramidal surroundings, the triangular basal plane is formed by the carboxylate oxygen atoms O(2), O(5)^{IV} and O(16)^V with a mean basal bond distance of 2.040(4) Å [(IV) = 1+x, y, z; (V) = 2-x, 2-y, 1-z;]. The axial positions are filled by O(10) and O(3) [Cu–O axial average bond distance of 1.958(4) Å]. Cu(3) basal plane is formed by O(3), O(8)^{II}, O(12)^{IX} and O(15)^V from four *ttt*-cbut^{4-} ligands and with O(6)^{IV} occupying the apical position [Cu–O equatorial average bond distance is 1.950(4) Å and Cu(1)–O(6)^{IV} is 2.409(4) Å; (IX) = x, 1+y, z]. The fourth copper atom, Cu(4), is six-coordinated with one coordination water molecule [O1(w)] and five carboxylate oxygen atoms [O(4), O(6), O(7)^X, O(12)^{XI} and O(13)^{XI}] describing a elongated octahedron [(X) = -x, 2-y, z; (XI) = -1+x, 1+y, z]. The basal equatorial plane is formed by O(6) O(1w), O(7)^{IX}, O(13)^{XI} with a basal bond lengths ranging from 1.954(4) to 1.996(4)Å. The axial positions, occupied by O(4) and O(12)^{XI}, show an average bond length of 2.441(4) Å. The values of φ and s/h parameters are 54.6° and 1.40 (to be compared to 60° and 1.22 for an ideal octahedron).[24]

Two crystallographically independent *ttt*-cbut^{4-} ligands are present in **6** (Fig. 12). The *ttt*-cbut-*a* [defined by the C(1), C(3), C(5) and C(7) cyclobutane ring] acts simultaneously in a *hexakis*-monodentate [through O(2), O(3), O(5), O(6), O(7) and O(8) oxygen atoms towards Cu(3), Cu(1), Cu(2)^{III}, Cu(1)^{III}, Cu(4)^{VI} and Cu(1)^{II}, respectively] and *bis*-bidentate coordination modes [through O(2) and O(3) to Cu(2) and O(4) and O(6) towards Cu(4) atoms] [(VI) = -x, 2-y, -z]. The *ttt*-cbut-*b* [defined by the C(9), C(11), C(13) and C(15) cyclobutane ring] shows *penta*-monodentate [through O(10), O(12), O(14), O(15) and O(16) towards Cu(2), Cu(3)^{VII}, Cu(3)^{IV}, Cu(1)^V and Cu(2)^V, respectively] and *bis*-bidentate coordination modes [through O(10) and O(11) towards Cu(3) and O(12), and O(13) to Cu(4)^{VIII}; (VII) = x, -1+y, z; (VIII) = 1+x, -1+y, z]. The two cyclobutane rings exhibit puckered conformation with the dihedral angles values for *ttt*-cbut-*a* between the C(1)C(3)C(5) and C(1)C(7)C(5) and C(3)C(5)C(7), and C(3)C(1)C(7) planes are 19.1(3) and 19.1(3)°, respectively. For the *ttt*-cbut-*b*, the dihedral angles between the C(9)C(11)C(13) and C(9)C(15)C(13) and C(11)C(13)C(15) and C(11)C(9)C(15) are 24.0(3) and 24.0(3)°, respectively. These values are within the range previously observed (Fig. S3 and Table S2).

Discussion

The crystal structures of **1-6** are quite different, with different protonation of the cbut ligand, different metal/ligand ratios, different number of coordination and/or crystallization water molecules as well as two different conformation of the 1,2,3,4-cyclobutanetetracarboxylate ligand are present in six studied compounds. Among all the differences, this last one is the most remarkable. The ligands on **1-3** exhibit the commercial *cis,trans,cis* isomer while on **4-6** the ligands present the *trans,trans,trans* isomer. In order to obtain the isomerization between *ctc*- and *ttt*-, the *ctc*-isomer was treated under soft-thermal conditions, giving rise to the *ttt*-isomer, which is stable at ambient conditions after transformation.

The remarkable ability of the copper(II)-based cbut compounds to crystallize with different topologies is most likely due to two factors: *i*) the high coordination versatility of the ligand to connect the Cu(II) centers and linked to it *ii*) the variable SBUs observed in **1-6**.

Few correlations can be made between the crystal structures and the synthetic procedures. Hydrothermal synthesis usually produces compact networks with high dimensionality, in this sense, compound **6** exhibits a compact 3D network with the less water molecules per copper(II) ions ratio.

In order to attain a deep understanding about how the two cbut isomers form coordination networks with different metal centers, all previously reported cbut-containing compounds (without co-ligands) with at least one metal-ligand coordination bond, have been included in this section. The *ctc*- and *ttt*-cbut coordination modes and selected structural parameters from the seventeen reported structures are summarized in Table 3 and Scheme S2.

Concerning the cbut coordination modes, the *ctc*-isomer adopts six different linking modes connecting to 4, 6 or 8 metal ions. However, the *ttt*-isomer exhibits nine coordination modes linking

2, 4, 6, 7 or 8 metal ions indicating a greater versatility of this isomer respect to the *ctc-* form. It deserve to be noted that the cbut ligands can display all possible degrees of protonation from one to four. However, even in the partially protonated compound, there is a trend to form three-dimensional networks indistinctly of the isomer form and the metal used. Looking at the different topologies and the serendipitous arrangement of the SBUs observed for **1-6**, the prediction of the topology of a cbut-based coordination polymer seems unreasonable. The only trend we can observe from the whole set of coordination modes is that *ctc-*cbut conformations exhibit more symmetry than those formed with the *ttt-*isomer. In particular, from the eleven *ctc-*cbut conformations, nine exhibit at least a centre of inversion, one a unique reflection plane (*r* in Scheme S2) and one does not exhibit symmetry at all (*s* in Scheme S2).

The KPI index values for the **1-6** compounds are somewhat lower than those previously reported for cbut-based coordination compounds (Table 3), indicating that the coordination to the copper(II) ions promotes the formation of open frameworks.

Table 3. The known examples of CPs involving cbut ligand that contains at least a metal-ligand coordination bond.

Compound	nD	KPI	Isomer	Coordination mode of the cbut	Coord.ᵃ	Panelᵇ	Ref.
$[(UO_2)_2(cbut)(H_2O)_2] \cdot 2H_2O$	3D	0.66	*ctc-*	*Tetrakis*-monodentate and *bis*-bidentate	6	a	7b
$[(UO_2)_2(cbut)(H_2O)_2] \cdot H_2O$	3D	0.76	*ctc-*	*Tetrakis*-monodentate and *bis*-bidentate	6	a	7b
$[K_2(H_2cbut)(H_2O)_4]_n$	3D	0.89	*ctc-*	*hexakis*-monodentate	6	g	6
$[Rb(H_3cbut)]_n$	3D	0.81	*ctc-*	*tetrakis*-monodentate and *bis*-bidentate	6	j	6
$[Na_2(H_2cbut)(H_2O)_4]_n$	3D	-	*ctc-*	*tetrakis*-monodentate	4	k	5
$[Na_2(H_2cbut)(H_2O)_4]_n$	3D	-	*ctc-*	*hexakis*-monodentate	6	l	5
$[K_2(H_2cbut)(H_2O)_2]_n$	3D	-	*ctc-*	*hexakis*-monodentate and *bis*-bidentate	8	m	5
$[Ba_2(cbut)(H_2O)_6]_n$	3D	-	*ctc-*	*bis*-monodentate and *tetrakis*-bidentate	6	n	5
1	3D	0.65	*ctc-*	*hexakis*-monodentate	6	q	8b
2	3D	0.55	*ctc-*	*hexakis*-monodentate	6	r	This work
3	2D	0.51	*ctc-*	*hexakis*-monodentate	6	s	This work
$[Na_3(H_2cbut)(H_3cbut)(H_2O)_3]_n$	3D	-	*ttt-*	*bis*-monodentate and *bis*-bidentate	4	o	5
$[Co_2(cbut)(H_2O)_3]_n$	3D	0.71	*ttt-*	*tetrakis*-monodentate and *bis*-bidentate	6	p	4a
$[H_3O]_2[(UO_2)_5(cbut)_3(H_2O)_6]$	3D	0.30ᶜ	*ttt-*	*tetrakis*-bidentate	4	b	7b
$[K_2Mg(H_2O)_2(cbut)]_n$	3D	-	*ttt-*	*tetrakis*-monodentate and *tetrakis*-bidentate	8	c	9
$[La(H_2O)(Hcbut)]_n$	3D	-	*ttt-*	*tetrakis*-monodentate *and bis*-bidentate	6	d	11
$[Li_2(H_2cbut)(H_2O)_2]_n$	2D	0.80	*ttt-*	*bis*-bidentate	2	e	6
$[Na(H_3cbut)]_n$	3D	0.84	*ttt-*	*bis*-monodentate and *bis*-bidentate	4	f	6
$[K(H_3cbut)]_n$	3D	0.82	*ttt-*	*tetrakis*-monodentate and *bis*-bidentate	6	h	6
$[Cs(H_3cbut)]_n$	3D	0.86	*ttt-*	*tris*-monodentate and *pentakis*-bidentate	8	i	6
4	1D	0.77	*ttt-*	*bis*-monodentate and *bis*-bidentate	4	t	This work
5	3D	0.59	*ttt-*	*tetrakis*-monodentate	4	u	This work
6	3D	0.66	*ttt-*	*hexakis*-monodentate and *bis*-bidentate (cbut-a); *penta*-monodentate and *bis*-bidentate (cbut-b)	7	v, w	This work

ᵃ Number of coordinated metal ions to the cbut ligand. ᵇ Panel letters refer to structures depicted in Scheme S2. ᶜ This value is approximate.

Remarkably, compounds **1** and **5** exhibit helical water chains in the pores of the structures. Considering that in **1** the cbut ligand is on the *ctc-*isomer, whereas in **5** is on the *ttt-*isomer; that the coordination mode of the ligand and the number of coordinated ions also differ; that the structure of **1** resembles a pillared square-grid net, while that of **5** is a triple interpenetrated diamond framework, is noteworthy that the helical water arrangements of **1** and **5** are exactly the same (Fig. S1 and S5). In the case of **5**, the water helices are located in chiral pores of the **dia**-net, with inverse chirality to that of the water helix it hosts. To our knowledge, this situation is unprecedented, although symmetrical and unsymmetrical water helices have been found in a variety of hosts.[26, 27] These helical water chains have attracted great interest because of their crucial role in the biological transport of protons and ions.[28] The helical water chains in **5** are linked to the host by hydrogen bonds involving the coordinated water molecules in the wall of the hydrophilic channel, which in turn transfers its chirality to the water chain in opposite handedness.

Conclusions

Six metal-organic frameworks involving Cu(II) ions and the 1,2,3,4-cyclobutanetetracarboxylic acid have been synthesized (**1-6**) through different crystal growth techniques including the gel method (**1** and **5**), slow evaporation (**2** and **4**), liquid diffusion (**3**) and hydrothermal method (**6**) yielding 1D (**4**), 2D (**3**) and 3D (**1**, **2**, **5** and **6**) networks. These structures are built up from the *cis,trans,cis* cbut isomer (**1-3**) and the *trans,trans,trans* cbut isomer (**4-6**). The energy landscape of the four possible conformations of the cbut ligand has been studied via theoretical calculations showing that the *ttt-*cbut is the most stable isomer. Water helical chains have been found in **1** and **5**, being of opposite handedness to that of the host channel in the case of the **dia**-net of **5**.

This work reflects the complex structural speciation resulting from the interaction between the cbut ligand and divalent copper atoms. Although the ligand flexibility is limited, and the position carboxylate groups are fixed, we found an extreme variation of coordination modes. In particular, the *ttt-*cbut acting as a

tetrahedral four-fold node which can be predicted from the geometrical arrangement of the carboxylate groups has been encountered only once (**5**).

The systematic screening of the growing conditions together with the control exerted on the isomerization of the *ttt*-cbut ligand open new possibilities within the crystal engineering field for the study of new coordinated polymeric architectures.

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Notes and references

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Electronic supplementary information (ESI) available: Further supplementary material to this paper includes X-ray crystallographic data in CIF format, selected bond lengths and angles for **1-6** compounds, the relevant torsion angles for compounds**1-6** details of the crystal structure and views of the crystal packing diagrams and scheme of the formulae for **1-6** compounds, the distribution of the puckering angles reported in CSD for cyclobutane ring and for the cbut ligand containing structures, the TGA curves for compounds **1**, **2**, **4** and **6**, the IR measurements of compounds **1- 6**, the structural representation of formulae of **1-6** compounds in CCDC format, and a scheme with all the coordination modes of the cbut ligand.

1   H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.* 2012, **112**, 673.

2   (a) K. Sumida, L. D. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.* 2012, **112**(2), 724; (b) M. P. Suh, H. J. Park, T. K. Prasad and D.-W. Lim, *Chem. Rev.* 2012, **112**(2), 782; (c) W. Zhang and R.-G. Xiong, *Chem. Rev.* 2012, **112**(2), 1163; (d) A. Betard and R. A. Fisher, *Chem. Rev.* 2012, **112**(2), 1055; (e) M. Kurmoo, *Chem. Soc. Rev.* 2009, **38**, 1353.

3   (a) S. Biswas and N. Stock, *Chem. Rev.* 2012, **112**(2), 933; (b) K.E. Plass, K. Kim and A.J. Matzger *J. Am. Chem. Soc.*, 2004, **29**, 9042; (c) A. Nangia and G. R. Desiraju *Chem. Commun.*, 1999, 605; (d) G.R. Desiraju *Cryst. Growth Des.*, 2004, **4**, 1089.

4   (a) P. Diaz-Gallifa, O. Fabelo, J. Pasán, L. Cañadillas-Delgado, J. Rodríguez-Carvajal, F. Lloret, M. Julve and C. Ruiz-Pérez, *Inorg. Chem.* 2014, **53**, 5674; (b) D. Braga, O. Benedi, L. Maini and F. J. Grepioni,. *J. Chem. Soc.*, *Dalton Trans*. 1999, 2611.

5   A. Chanthapally, H. Quah and J.J. Vittal, *Cryst. Growth Des.* 2014, **14(5)**, 2605.

6   P. Thuéry, *CrystEngComm*, 2014, **16**, 1724.

7   (a) P. Thuéry, *CrystEngComm*, 2013, **15**, 6533; (c) P. Thuéry, *Eur. J. Inorg. Chem.*, 2013, 4563; (b) P. Thuéry and B. Masci, *Cryst. Growth Des.*, 2008, **8**, 3430.

8   (a) S. Mistri, E. Zangrando and S. C. Manna, *Polyhedron*, 2013, **49**, 252. (b) M. Menelaou, N. Lalioti, V. Psycharis, C. P. Raptopoulou, A. Terzis, C. Mateescu and A. Salifoglou, *Polyhedron*, 2012, **40**, 134; (c) K. Y. Choi and I. T. Lim, *J. Inorg. Organomet. Polym. Mater*. 2012, **22**, 1194.

9   Z. Hulvey and A. K. Cheetham, *Solid State Sci*. 2007, **9**, 137.

10 J. Luo, F. Jiang, R. Wang and M. Hong, *Inorg. Chem. Commun*. 2004, **7**, 638.

11 Y. J. Kim and D. Y. Jung, *Inorg. Chim. Acta*, 2002, **338**, 229.

12 H. K Henisch, *Crystal Growth in Gels*; The Pennsylvania State Univ. Press: Pittsburgh, 1970.

13 A. J. M. Duisenberg, L. M. J. Kroon-Batenburg and A. M. M Schreurs, (EVALCCD). *J. Appl. Crystallogr.* 2003, **36**, 220.

14 Z. Otwinowski and W. Minor, "*Processing of X-ray Diffraction Data Collected in Oscillation Mode",* Methods in Enzymology, Volume 276: Macromolecular Crystallography, part A, p.307-326, 1997, C.W. Carter, Jr. & R. M. Sweet, Eds., Academic Press (New York).

15 Agilent, CrysAlis PRO. Agilent Technologies UK Ltd, Yarnton, England, 2011.

16 G. M. Sheldrick, *Acta Crystallogr., Sect. A,* 2008, **64**, 112.

17 L. J. Farrugia, *J. Appl. Crystallogr.,* 1999, **32**, 837 (WINGX).

18 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.

19 DIAMOND 2.1d, Crystal Impact GbR, CRYSTAL IMPACT, K Brandeburg & H. Putz GbR, Postfach 1251, D-53002 Bonn, Germany, 2000.

20 The topological analysis has been done by using the TOPOS 4.0 program: V.A. Blatov, *IUCr CompComm*, Newsletter 2006, **7**, 4.

21 A. W. Addison, T. N. Rao, J. Reedijk, J. Van Rijn and G. C. Verschoor, *Dalton Trans.,* 1984, 1349.

22 T. N. Margulis, *J. Am. Chem. Soc.*, 1971, **93**, 2193.

23 (a) H. Chun, D. Kim, D. N. Dybtsev and K. Kim, *Angew. Chem., Int. Ed.,* 2004, **43**, 971; (b) S. Wu, L. Ma, L. S. Long, L. S. Zheng and W. B. Lin, *Inorg. Chem.*, 2009, **48**, 2436; (c) Y. E. Cheon and M. P. Suh, *Chem. Commun.*, 2009, 2296.

24 E. I. Stiefel and G. F. Brown, *Inorg. Chem.*, 1972, **11**, 189.

25 F. H. Allen, *Acta Cryst.,* 2002, **B58**, 380.

26 (a) B. Sreenivasulu and J.J. Vittal, *Angew. Chem., Int. Ed.,* 2004, **43**, 5769; (b) A. Mukherjee, M. K. Saha, M. Nethaji and A. R. Chakravarty, *Chem. Commun.*, 2004, 716; (c) B. Y. Lou, F. L.

Jiang, D. Q. Yuan, B. L. Wu and M. C. Hong, *Eur. J. Inorg. Chem.,* 2005, 3214; (d) P. S. Wang, C. N. Moorefield, M. Panzer and G. R. Newkome, *Chem. Commun.,* 2005, 4405; (e) S. Zang, Y. Su, C. Duan, Y. Li, H. Zhu and Q. Meng, *Chem. Commun.,* 2006, 4997; (f) S. C. Sahoo, T. Kundu and R. Banerjee, *J. Am. Chem. Soc*., 2011, **133**, 17950.

27 (a) S.-C. Chen. F. Tian, K.-L. Huang, C.-P. Li, J. Zhong, M.-Y. He, Z.-H. Zhang, H.-N. Wang, M. Du and Q. Chen, *CrystEngComm* 2014, **16**, 7673; (b) X.-Y. Duan, X. Cheng, J.-G. Lin, S.-Q. Zang, Y.-Z. Li, C.-J. Zhu and Q.-J. Meng, *CrystEngComm* 2008, **10**, 706; (c) K.-L. Zhang, C.-T. Hou, J.-J. Song Y. Deng, L. Li, S. W. Ng and G.-W. Diao, *CrystEngComm* 2012, **14**, 590.

28 (a) R. Pomes and B. Roux, *Biophys. J.* 1998, **75**, 33. (b) R. Pomes, and B. Roux, *Biophys. J.* 2002, **82**, 2304. (c) J.P. Cowin, A.A. Tsekouras, M.J. Iedema, K. Wu and G.B. Ellison, *Nature,* 1999, **398**, 405; (d) Z-F. Fei, D-B. Zhao, T.J. Geldbach, R. Scopelliti, P.J. Dyson, S. Antonijevic and G. Bodenhausen, *Angew. Chem., Int. Ed.,* 2005, **44**, 5720; (e) G. Hummer, J.C. Rasaiah and J.P. Noworyta, *Nature*, 2001 **414**, 188

Table of Content

Synthesis and structural characterization of six Cu(II)-based coordination polymers using the thermally tunable 1,2,3,4-cyclobutanetetracarboxylic acid

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Six Cu(II)-based coordination polymers have been synthetized, using the thermally tunable 1,2,3,4-cyclobutanetetracarboxylic acid, and characterized through single crystal X-ray diffraction.