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Metal–Organic Frameworks from Copper Dimers with *cis*- and *trans*-1,4-Cyclohexanedicarboxylate and *cis,cis*-1,3,5-Cyclohexanetricarboxylate

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Single crystals of three coordination networks containing the $Cu_2(COO)_4$ core bridged by cyclohexane have been hydrothermally prepared by the reaction of 1,4-cyclohexanedicarboxylic (1,4-H_2*chdc*) or 1,3,5-cyclohexanetricarboxylic (1,3,5-H_3*chtc*) acid and $Cu(NO_3)_2 \cdot 6H_2O$. We report their characterizations by single-crystal X-ray structure determinations, IR spectroscopy, thermal analyses, and their magnetic properties. [Cu_2(*trans*-1,4-*chdc*)$_2$] (**1**) consists of 4 × 4 grids with the dimeric nodes connected by the *trans*-1,4-*chdc*, and these grids are then connected to each other by Cu–O bonds, resulting in a porous network (void volume of 130 Å^3 per cell or 25%) with no solvent in its cavities. [Cu_2(*cis*-1,4-*chdc*)$_2$(H_2O)$_2$] (**2**) consists of two-legged ladders where the dimer nodes are bridged by pairs of *cis*-1,4-*chdc* and the water molecules cap the ends of the Cu dimers. [Cu_2(1,3,5-H*chtc*)$_2$] (**3**) displays 4 × 4 grids, but each dimeric node is connected to its neighbors within the same grid by Cu–O bonds to form a layered network which further makes hydrogen-bond interactions with its neighbors. **2** and **3** have compact structures without any space for solvents. IR and DT-TGA confirm the absence of water in the empty channels of **1**, while IR shows the presence of both protonated and deprotonated carboxyl groups for **3**. The magnetic properties of all three compounds are dominated by the strong Cu–Cu antiferromagnetic interaction resulting in singlet–triplet gaps of 450–500 K.

Introduction

Copper acetate is a remarkable molecule in the field of coordination chemistry.[1] The report of the unusual temperature dependence of its EPR spectra by Bleaney et al.[2] which followed shortly by the first description of the propeller-shaped dimeric unit in its crystal structure by Schoening et al.,[3] created a surge of interests in this compound. In particular, many chemists were eager to understand the bonding within the dimer, while finding an explanation for the temperature dependence of the magnetic susceptibility kept physicists and magnetochemists very busy for a considerable time.[4,5] Once these were resolved, there was less interest in this molecule until the 70's when Mori et al. observed the absorption of various gases by copper

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terephthalate.[6−8] It took them several years to determine its crystal structure and to characterize the porosity.[9] Yaghi et al. have successfully developed porous materials with controllable shape and size of the cavities using dimeric metal carboxylates, and Zaworotko et al. have used them to generate Kagomé lattices which appeared to have unusual magnetic properties.[10] In a series of related materials using polycarboxylates with adjustable linear backbones, Yaghi et al. and Schröder et al. reported high efficiency for H_2 absorption exceeding the US-DOE recommendation of 6 wt %.[11,12] The most celebrated of these is the discovery of the cubic phase of Cu trimesate ($Cu_3(TMA)_2(H_2O)_3$; HKUST-1) displaying larger pores than those in Cu terephthalate.[13] The absorption and catalytic properties of this compound are currently being exploited.[14,15] Using neutron diffraction, Kepert et al. have recently identified the positions of the active absorption sites for molecular hydrogen and their hierarchy.[16] Replacing the benzene ring of the terephthalate by a cyclohexane in copper terephthlate was thought to potentially provide several advantages associated with the additional flexibility of cyclohexane to the framework, and this was one of the early extensions that Mori et al. performed.[17] However, this chemical modification proved to be more problematic than expected due to the different geometrical isomers possible. To circumvent the problem of isolating pure phases, the syntheses of copper-1,4-cyclohexanedicarboxylate was performed in methanol at moderate temperatures. The results were quite astonishing to them when they found that the complex with the trans isomer exhibits gas sorption but the one with the cis isomer does not. It led them to logically propose a structure similar to copper terephthalate for the one made of the trans isomer. The crystal structure of copper-*trans*-1,4-*chdc* was finally determined by Rietveld refinement of the X-ray powder diffraction patterns from a synchrotron source and from a laboratory source. Both structures agree with that proposed.[18,19] The cell parameters for the two independent determinations were quite different (Inoue et al.:[18] $a = 10.55$ Å, $b = 9.89$ Å, $c = 5.07$ Å, $\alpha = 86.26°$, $\beta = 93.19°$, $\gamma = 100.95°$, $V = 517.74$ Å^3; Mori et al.:[19] $a = 10.552$ Å, $b = 10.351$ Å, $c = 5.103$ Å, $\alpha = 72.317°$, $\beta = 90.844°$, $\gamma = 101.576°$, $V = 519.53$ Å^3). The absorption of gases and vapors of solvents, as well as the catalytic activities of copper-*trans*-1,4-*chdc*, were also documented. The structure of copper-*cis*-1,4-*chdc* remains unknown.

For our continuing interests in making porous magnets, we have made use of both rigid and flexible polycarboxylates and divalent transition metals.[20] In many cases, the compounds are rather compact, while in a handful, the structures support porosity and the magnetic exchanges via M−O−M and M−O−C−O−M favor long-range ordered magnetism. Quite interestingly, we have observed the transformation between magnetic ground states from antiferromagnet for the hydrated form of cobalt squarate to a ferromagnet for the dehydrated form.[21] For the nickel complexes with 1,4-*chdc*, ferrimagnetism for a hydrate to ferromagnetism for the dehydrate was demonstrated.[22] For the layered hydroxide of cobalt pillared by *trans*-1,4-*chdc*, the transition from the paramagnetic to the ferrimagnetic state at 60.5 K remains unaltered upon dehydration and rehydration.[23] We note that

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Table 1. Summary of X-ray Data

	[Cu_2(*trans*-1,4-*chdc*)$_2$][a]	[Cu_2(*trans*-1,4-*chdc*)$_2$][b]	[Cu_2(*cis*-1,4-*chdc*)$_2$(H_2O)$_2$][c]	[Cu_2(*cis*, *cis*-1,3,5-H*chtc*)$_2$][a]
empirical formula	$C_8 H_{10} Cu O_4$	$C_8 H_{10} Cu O_4$	$C_8 H_{12} Cu O_5$	$C_{36} H_{36} Cu_4 O_{24}$
fw	233.71	233.71	251.72	1106.85
T, K	288	293	294	288
wavelength, Å	0.7107	0.7107	0.71073	0.7107
cryst syst	triclinic	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	5.140(2)	5.084(15)	6.9016(4)	11.489(4)
b, Å	9.856(5)	9.82(3)	8.4508(7)	5.041(2)
c, Å	10.673(5)	10.56(3)	8.5767(6)	16.067(6)
α, °	77.310(9)	77.28(13)	72.792(5)	
β, °	80.697(6)	81.17(13)	84.770(5)	110.338(7)
γ, °	85.024(9)	84.98(14)	85.633(5)	
V, Å^3	519.8(4)	507(2)	475.21(6)	872.4(5)
Z	2	2	2	1
d (calcd), Mg/m^3	1.493	1.531	1.759	2.107
abs. coeff., mm^{-1}	2.081	2.134	2.290	2.514
F(000)	238	238	258	560
reflns collected	7533	3883	3184	5303
ind reflns	2289	2216	2158	2085
refinement method	F^2	F^2	F^2	F^2
data/restraints/params	2234/0/118	1276/0/128	1637/8/127	2027/0/145
GOF on F^2	1.309	1.010	1.024	1.432
final R indices	0.0630, 0.1422, $2\sigma(F^2)$	0.0657, 0.1505, $2\sigma(F^2)$	0.031, 0.050, $>3\sigma(I)$	0.0875, 0.1275, $2\sigma(F^2)$
largest diff. peak and hole, e Å^{-3}	2.27, −0.70	1.13, −1.11	0.457, −0.439	2.04, −3.03

[a] Data collected on a Bruker Apex. [b] Data collected on a Rigaku AFC. [c] Data collected on a Nonius Kappa CCD.

all the above transformations are reversible. To extend this study, we now present the syntheses of single crystals of [Cu_2(*trans*-1,4-*chdc*)$_2$] (**1**), 1,4-*chdc* = 1,4-cyclohexanedicarboxylate, [Cu_2(*cis*-1,4-*chdc*)$_2$(H_2O)$_2$] (**2**), and [Cu_2(1,3,5-H*chtc*)$_2$] (**3**), 1,3,5-H_3*chtc* = *cis*,*cis*-1,3,5-cyclohexanetricarboxylic acid, their single-crystal X-ray structure determinations, IR spectroscopy, thermal analyses, and temperature dependence of their magnetic susceptibilities. The structure determinations from the single crystals of copper-*trans*-1,4-*chdc* are more accurate than those determined from the powder data and suggests no water in the cavities. A comparison of the structures of **1** and **2** clearly demonstrates the reason for the different absorption properties of the two isomeric forms of copper-*chdc*.

Experimental Section

Materials. All chemicals were commercially available and used as received without further purification. 1,4-Cyclohexanedicarboxylic acid is available either as a mixture of 65 wt % of cis and 35 wt % of trans isomers or as the pure trans isomer.

Physical Techniques. The syntheses were carried out in homebuilt Teflon-lined cylindrical stainless steel pressure bombs with a maximum capacity of 120 mL. Thermogravimetric analyses (30−500 °C) were performed on a Seiko SSC5200 TG-DTA system. IR spectra were recorded on KBr pellets containing about 1 wt % of the compounds using a Perkin-Elmer (BX) FT-IR spectrometer. XRD data were collected on a Rigaku RINT-TTR equipped with Cu Kα (1.5406 Å) using the Bragg−Brentano geometry. XRD data were measured from 2° to 80° at 0.02° intervals and counting for 8 s per point. The temperature and field dependence of the magnetization of the complexes were measured on a Quantum Design MPMS-XL SQUID operating in the temperature range 2−300 K and fields up to 5 T.

Preparation of [Cu_2(*trans*-1,4-*chdc*)$_2$] (1). Copper(II) nitrate hexahydrate (2.47 g) and *trans*-1,4-cyclohexanedicarboxylic acid (1.76 g) were mixed in distilled water (30 mL). The mixture was placed in the Teflon liner of an autoclave, sealed, and heated to 120 °C for 2 days. The bomb was allowed to cool to room temperature in a water bath. Blue crystals were obtained, washed with water and acetone, and dried in air. (Yield 65%). Anal. Calcd for $CuC_8H_{10}O_4$: C, 41.11; H, 4.31 Found: C, 40.64; H, 4.30.

Preparation of [Cu_2(*cis*-1,4-*chdc*)$_2$(H_2O)$_2$] (2). Copper(II) nitrate hexahydrate (2.47 g) and a mixture of *cis*- and *trans*-1,4-cyclohexanedicarboxylic acid (1.76 g) were mixed in distilled water (30 mL). The mixture was then placed in the Teflon liner of an autoclave, sealed, and heated to 120 °C for 2 days. It was then cooled to room temperature in a water bath. Blue crystals were obtained, which were washed with water and acetone and dried in air. (Yield 60%). Anal. Calcd for $CuC_8H_{12}O_5$: C, 38.17; H, 4.80, Found: C, 37.64; H, 4.30.

Preparation of [Cu_2(*cis*,*cis*-1,3,5-H*chtc*)$_2$] (3). Copper(II) nitrate hexahydrate (2.47 g) and *cis*,*cis*-1,3,5-cyclohexanetricarboxylic acid (2.21 g) were mixed in distilled water (30 mL). The mixture was placed in the Teflon liner of an autoclave, sealed, and heated to 170 °C for 2 days. The bomb was allowed to cool to room temperature in a water bath. Green crystals were obtained. The crystals were washed with water and acetone and dried in air. (Yield 40%). Anal. Calcd for $Cu_2C_{18}H_{18}O_{12}$: C, 39.07; H, 3.28 Found: C, 39.48; H, 3.79.

X-ray Crystallography and Structure Solution. Selected single crystals were glued on the tip of glass fibers. Diffraction data for the complexes were collected on a Kappa-CCD Nonius diffractometer (for **2**) and Bruker SMART APEX CCD area detector (for **1** and **3**) at room temperature. For **1**, a second data collection was made on a different crystal using a Rigaku AFC7 Mercury CCD diffractometer equipped with a fine-focused 5.4 kW rotating anode source. The diffractometers are all equipped with graphite-monochromated Mo Kα1 (0.7107 Å) radiation. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and expanded using Fourier techniques.[24] The non-

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hydrogen atoms were refined anisotropically. They converged (large parameter shift was σ times its esd) with agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. No extinction corrections have been applied. Details of crystallographic data are collected in Table 1. The crystal data have been deposited at CCDC, Cambridge, UK and given the reference numbers CCDC 269992−269994.

Results and Discussion

The first observation is that the inorganic molecular bricks for nickel and cobalt in their complexes with the above carboxylates have some common features, for example, $\{M_3O_2\}_\infty$ chains are formed, which is not the case for copper.[22,23,25] For both nickel and cobalt, sodium hydroxide is needed to neutralize the acids, while different temperatures favor different phases with different geometrical isomers. It was therefore possible to isolate pure phases starting from mixture of the acids by performing the syntheses at different temperatures.[26] The higher temperatures favor the complex with the trans isomer. However, for copper, the two phases with *cis*- and *trans-chdc* are formed for all working temperatures but the proportion of trans isomer increases with increasing temperature. In the present work, we prepared the cis complex from a cis and trans mixture as starting material at low temperature and the trans complex from pure trans acid. It is known that in certain compounds both isomers are involved within the same structure. For copper, neutralization of the acids with NaOH results in copper oxides.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Cu_2(*trans*-1,4-*chdc*)$_2$]

Cu(1)−Cu(1)	2.576(2)	Cu(1)−Cu(1)’	3.240(2)
Cu(1)−O(1)	1.926(4)	Cu(1)−O(2)	1.927(4)
Cu(1)−O(3)	1.980(4)	Cu(1)−O(3)’	2.231(4)
Cu(1)−O(4)	1.947(4)		
O(1)−Cu(1)−O(2)	169.3(2)	O(3)−Cu(1)−O(4)	168.8(2)
O(1)−Cu(1)−O(3)	93.4(2)	O(1)−Cu(1)−O(3)	89.7(2)
O(1)−Cu(1)−O(4)	88.1(2)	O(2)−Cu(1)−O(3)	97.0(2)
O(2)−Cu(1)−O(3)	89.9(2)	O(2)−Cu(1)−O(4)	90.2(2)
O(3)−Cu(1)−O(3)	79.5(2)	O(3)−Cu(1)−O(4)	111.5(2)

Table 3. Selected Bond Distances (Å) and Angles (deg) for [Cu_2(*cis*-1,4-*chdc*)$_2$(H_2O)$_2$]

Cu(1)−Cu(1)	2.578(2)	Cu−O(1)	2.156(2)
Cu−O(2)	1.951(2)	Cu−O(3)	1.969(2)
Cu−O(4)	1.959(2)	Cu−O(5)	1.979(2)
O(2)−Cu−O(3)	169.56(7)	O(4)−Cu−O(5)	169.50(7)
O(1)−Cu−O(2)	93.81(8)	O(1)−Cu−O(3)	96.47(8)
O(1)−Cu−O(4)	94.90(8)	O(1)−Cu−O(5)	95.38(8)
O(2)−Cu−O(4)	92.36(9)	O(2)−Cu−O(5)	89.04(9)
O(3)−Cu−O(4)	88.54(9)	O(3)−Cu−O(5)	88.23(9)
O(3)−Cu(1)−O(3)	79.5(2)	O(3)−Cu(1)−O(4)	111.5(2)

Table 4. Selected Bond Distances (Å) and Angles (deg) for [Cu_2(*cis*,*cis*-1,3,5-H*chtc*)$_2$]

Cu(1)−Cu(1)	2.523(2)	Cu(1)−Cu(1)′	3.152(2)
Cu(1)−O(1)	1.909(5)	Cu(1)−O(3)	1.891(4)
Cu(1)−O(2)	1.898(5)	Cu(1)−O(4)′	2.152(4)
Cu(1)−O(4)	1.970(4)		
O(1)−Cu(1)−O(2)	170.4(2)	O(1)−Cu(1)−O(3)	91.2(2)
O(1)−Cu(1)−O(4)	88.5(2)	O(1)−Cu(1)−O(4)	94.5(2)
O(2)−Cu(1)−O(3)	87.0(2)	O(2)−Cu(1)−O(4)	91.6(2)
O(2)−Cu(1)−O(4)	95.0(2)	O(3)−Cu(1) O(4)	169.8(2)
O(3)−Cu(1)−O(4)	110.0(2)	O(4)−Cu(1)−O(4)	80.3(2)

The key feature of the three compounds is the dimeric four-blade paddle wheel unit of copper which is also known for several divalent metals such as Cr, Co, Ni, Zn, Mo, Ru, Rh, etc.[27] Copper provides a further complexity depending on the oxidation state; when it is in the +1 state, it usually forms a two-blade paddle wheel,[28] when it is in a mixed-valence +1/+2 state, it exhibits a three-blade paddle wheel,[29] and for the +2 state, it is almost exclusively a four-blade paddle wheel.[27a] These four-blade paddle wheel complexes have two available divergent sites for coordination and these positions are used for generating coordination polymers where the dimensionality depends on the number of coordinating atoms in the connector and their spatial arrangement.[30] These positions have recently been identified, by neutron diffraction analyses, to be the most active sites for the absorption of molecular hydrogen.[14] In the absence of an exogenous ligand, Cotton et al. have identified three modes of polymerization in one dimension by coordination of the copper of one dimer to the oxygen atom of the neighboring dimers.[28] The three modes are called (a) flat ribbon, (b) venetian blind, and (c) copper trifluoroacetate. The three modes have different Cu−Cu distances within and between dimers and Cu−O distances between dimers (Tables 2−4). For the three complexes of this work, we find two of the complexes (**1** and **3**) without exogenous ligands and adopting the flat ribbon mode and the other (**2**) has two exogenous water molecules coordinated in the axial positions. While complexes **1** and **2** have Cu−Cu distances (2.577(2) Å) lying within the range found for other dimers (2.57−2.63 Å), that of **3** is shorter (2.523(2) Å). The dimer is less distorted for **2** with the axial oxygen of the water molecule more centrally placed at the apex of the square-base pyramid and making $O_{ax}-Cu-O_{eq}$ angles in the range 93.8−96.5°.

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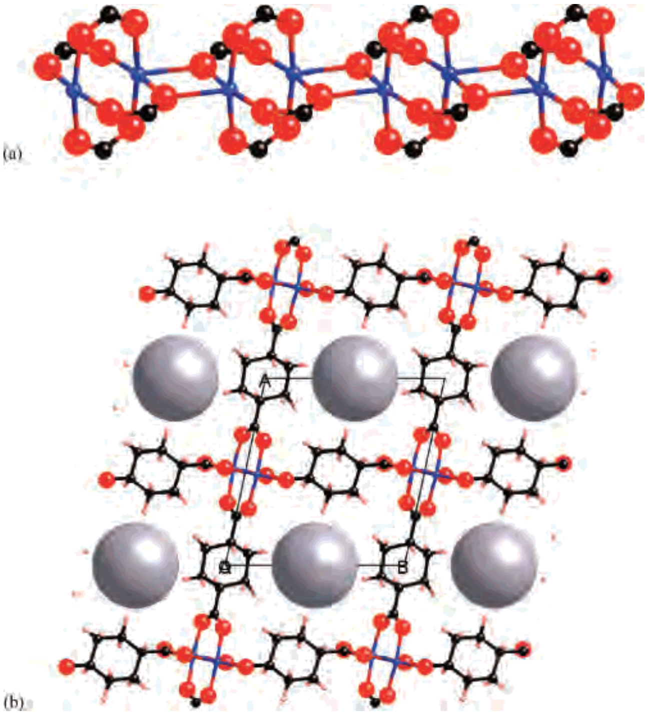

Figure 1. Structure of [Cu_2(*trans*-1,4-*chdc*)$_2$]; (a) a single inorganic chain of copper−oxygen network forming the rigid pillar of the structure and (b) the 3D packing showing the bridging of the inorganic chain by the cyclohexane moieties. The gray spheres highlight the empty space.

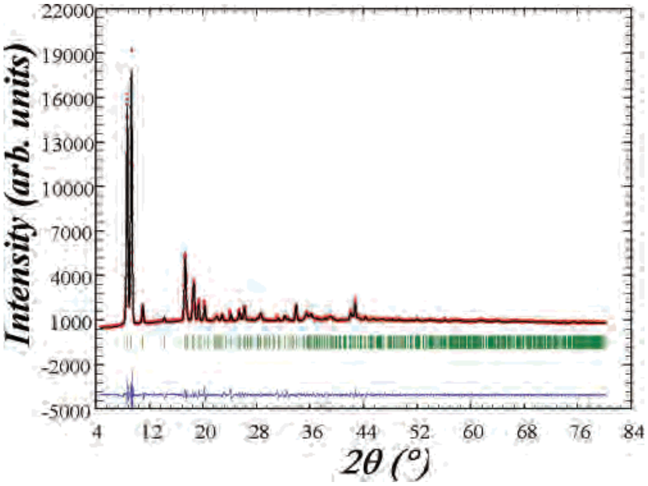

Figure 2. Powder XRD pattern (red circles) and the theoretical pattern matching (black line) of [Cu_2(*trans*-1,4-*chdc*)$_2$]. The blue trace is the residual, and the green ticks are the position of the Bragg reflections.

However, those of **1** and **3** are severely distorted due to the Cu−O−Cu′ connections, with the axial oxygen of the neighboring dimer offset from the top of the pyramid resulting in O_{ax}−Cu−O_{eq} angles in the range 79.6−111.5° and 80.3−109.5°, respectively. The interdimer Cu−O and Cu−Cu distances for **1** and **3** are, respectively, 2.230 and 2.150 Å and 3.240 and 3.152 Å.

An important part of the work with these carboxylic acids is to understand the way the molecular bricks are organized in the solid through the connections by the cyclohexane with the divergent carboxyl groups differently oriented in the different isomers. In all cases, the cyclohexane adopts the boat geometry. For all three compounds, the acids act as a dianion. Thus, *chtc* in **3** has one protonated carboxyl group which is not involved in coordination but instead form hydrogen bonds with the carboxyl group of neighboring layers.

For **1**, the carboxyl groups of the *trans-chdc* adopt the equatorial positions of the boat and the directional property is linear (Table 2). Therefore, as expected, the four-blade propeller of the dimer with linear connectors generates a 4 × 4 lattice (Figure 1). However, the angles are not 90°. This is due to the absence of exogenous ligands (water, in the present case, as the synthesis was performed in aqueous medium) which, as discussed earlier, resulted in the formation of Cu−O−C−O−Cu−O−Cu chain along the *a* axis. Consequently, a three-dimensional network is obtained. In the presence of 4,4′-bipyridine and its derivatives, the grids can be separated through the bridges.[26h] The combined rigidity of the dimer, especially with its involvement in the chain and the slight flexibility of the *trans-chdc* connectors, result in a striking stability of this compound which sustain sizable channels running along the *a* and *b* crystallographic axes. The residual electron densities observed from different crystals studied amount to less than 3e/Å^3 in each case, suggesting hardly any solvent in the cavities. This was confirmed by careful thermogravimetric analyses and IR spectroscopy (see below). Figure 1b shows the empty cavities along the *a* axis. Using PLATON,[31] we found very little electron density inside the pores and estimated the void volume to be 130 Å^3 per cell, or 25%, and the pore dimensions to be 3.6 × 3.4 Å^2. The absence of water in our crystals is different than the crystals obtained from methanol, which are reported to have one water molecule per dimer in the cavities. We also analyze the X-ray powder diffraction data using Rietveld method (Figure 2).[32] The cell parameters obtained from our powdered sample, $a = 5.1048(5)$ Å, $b = 9.870(1)$ Å, $c = 10.709(1)$ Å, $\alpha = 74.91(1)°$, $\beta = 80.44(1)°$, $\gamma = 85.49(1)°$, $V = 513.3(1)$ Å^3, are in agreement with those found by single crystals (Table 1), $a = 5.140(2)$ Å, $b = 9.856(5)$ Å, $c = 10.673(5)$ Å, $\alpha = 77.31(1)°$, $\beta = 80.70(1)°$, $\gamma = 85.02(1)°$, $V = 519.8(4)$ Å^3 and $a = 5.084(15)$ Å, $b = 9.82(3)$ Å, $c = 10.56(3)$ Å, $\alpha = 77.28(13)°$, $\beta = 81.17(13)°$, $\gamma = 84.98(14)°$, $V = 507(2)$ Å^3. The reason for the absence of water molecules in the cavities may be due to the lack of accessible hydrogen-bonding sites. The cyclohexane provides a hydrophobic character to the surface of the cavities and thus repels the water molecules.

For **2**, the geometry of the dianion is *cis-chdc*, which adopts the energetically most favorable equatorial-axial conformation and consequently, has an L shape. The adjacent copper dimers are then bridged by pairs of the *cis-chdc* to form one-dimensional chains parallel to the crystallographic *b* axis (Figure 3, Table 3). Such one-dimensional chain structure has been found in $Cu_2(DPhA)(H_2O)_2$ (DPhA =

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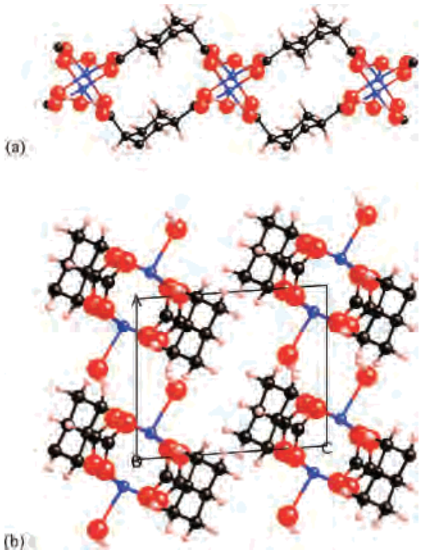

Figure 3. Structure of [Cu_2(*cis*-1,4-*chdc*)$_2$(H_2O)$_2$]; (a) a single organic−inorganic chain and (b) the 3D packing within the structure.

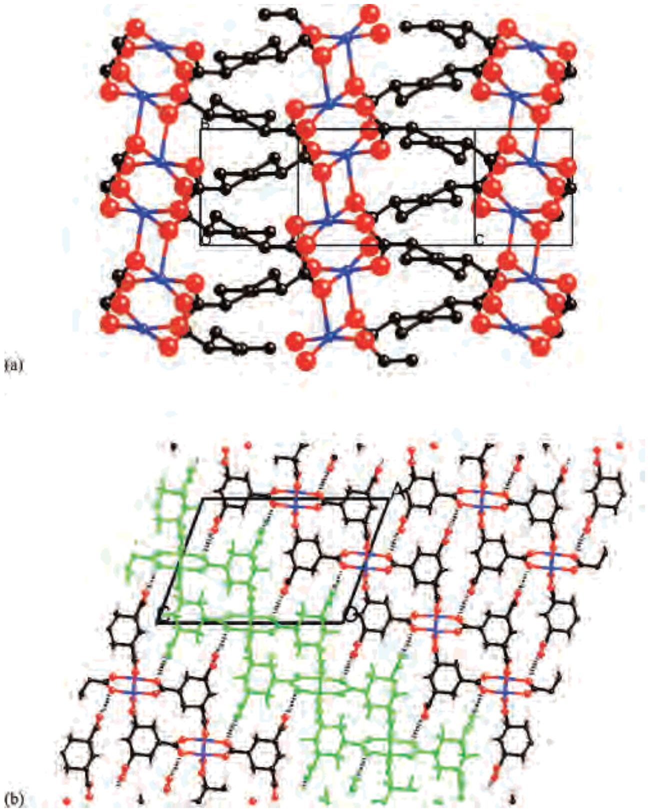

Figure 4. Structure of [Cu_2(*cis,cis*-1,3,5-H*chtc*)$_2$]; (a) a single organic−inorganic layer showing the copper−oxygen chain forming the rigid pillar of the structure and (b) the 3D packing with a single layer highlighted in green and the hydrogen bonds (dotted).

2,2′-biphenyldicarboxylate) where the orientations of the two carboxylate groups are similar to those of *cis-chdc*.[33] Due to the loose packing of these chains, there is enough space for two water molecules to coordinate the copper atoms of each dimer. The coordinated water molecules act as hydrogen donors to generate the two-dimensional layer structure in **2**. However, there is not enough space for the adsorption of gases or solvents. We note that the density is, consequently, higher than that of **1** (Table 1).

Similar to the unsaturated 1,3,5-benzenetricarboxylate acid (H_3*btc*, sometimes abbreviated as TMA for trimesic acid), the saturated 1,3,5-cyclohexanetricarboxylic acid (H_3*chtc*) is able to carry three different charges depending on the reaction conditions. In most cases for their binary complexes with divalent metals, these acids are trivalent, and consequently, the metal/ligand ratio is 3:2.[34] The present compound has a different stoichiometry, and the ratio is 1:1. It is interesting to note that the hydrothermal synthesis provide in the general cases crystals or powder of the less-soluble phases while metathesis of a dicarboxylic acid, for example, with a divalent transition metal ion in water usually form the soluble complexes, such as ionic $M(H_2O)_6^{2+}(acid)^{2-}$, $\{M(H_2O)_4\ acid\}_\infty$ chains, or $\{M(H_2O)_2\ acid\}_\infty$ layers.[35]

The most stable of the geometrical isomers of 1,3,5-H_3*chtc* is the *cis,cis* form and is the one commercially available.[25,36,37] Upon reaction of it with divalent copper, the geometry of the acid is retained. The structure is formed of two-dimensional layers (Figure 4a, Table 4) of propeller dicopper tetracarboxylate dimers, and the layers are connected to one another via the hydrogen-bonding interaction to form a three-dimensional framework (Figure 4b). Due to the 1,3 positions of the coordinating carboxylates, the directional properties are quite different than those of **1** and **2** as a consequence of the axial−axial conformations. One common factor of this structure and that of **1** is that the acids around one dimer connect four equivalent dimers. However, the positions of the near-neighbor dimers are different than those of **1**. In the present case, the dimers are twisted to position themselves next to one another within the same grid to form the Cu−O−C−O−Cu−O−Cu′ inorganic backbone like in **1**. One of the characteristic points of the structure is the role of the carboxylic acid group. Here, it is hydrogen bonded to neighboring coordinated carboxylate oxygen atoms with O−H···O distance of 2.769 Å. For *btc*, there is the possibility of having different coordination modes of the carboxylate groups of one acid. We have reported three different coordination modes of the three carboxylate groups in [M_3(*chtc*)$_2$(μ_2-H_2O)$_2$(H_2O)$_2$]·5(H_2O) (M = Co, Ni).[25] One is monodentate, the second acts as a bidentate bridge, and

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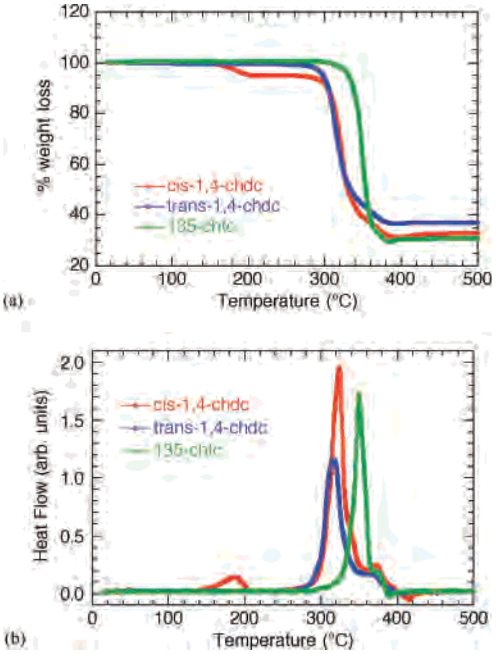

Figure 5. Thermogravimetry and differential thermal analysis for [Cu_2(*trans*-1,4-*chdc*)$_2$] (blue circles), [Cu_2(*cis*-1,4-*chdc*)$_2$(H_2O)$_2$] (red circles), and [Cu_2(*cis*,*cis*-1,3,5-H*chtc*)$_2$] (green circles).

the third carboxylate group coordinates to three independent metal ions. In the present, case there is only one type: syn−syn.

Thermal Properties. The thermal properties of the three compounds were examined by combined thermogravimetric and differential thermal analyses under nitrogen on powdered samples of 5, 6, and 8 mg for **1**, **2**, and **3**, respectively. The results are collected in Figure 5. The first observation is the two anomalies for **2** in contrast to only one anomaly for **1** and **3**. The first one centered at 180 °C for **2** corresponds to the loss of one molecule of water per Cu dimer. The loss of only one water suggests that the chains within the structure may reorganize to form Cu−O bond with neighboring carboxylate group like those observed for **1** and **3**, thereby forming fused double chains. The second anomaly for all three compounds corresponds to the exothermic pyrolysis of the organic parts, resulting in all cases in CuO. The respective expected (observed) residues are 34 (36.4)%, 31.5 (31.1)%, and 28.6 (29.2)%. There is a difference of 30 °C in the decomposition temperature between the complexes with *chdc* and the one with *chtc*. This slightly higher stability of the latter may be due to the more compact structure, higher density, and shorter Cu−Cu and Cu−O bond distances than the other two complexes or it could just be the difference in the acids. We prefer the first possibility to the second one, as we do not expect that there is a big difference in the bond energies for the pure acids.

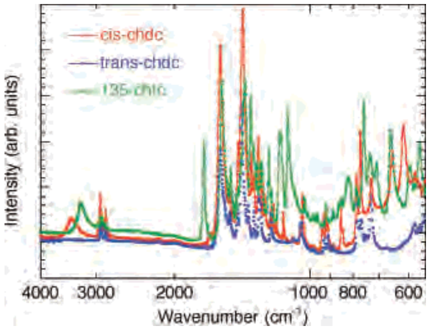

Figure 6. IR spectra for [Cu_2(*trans*-1,4-*chdc*)$_2$] (blue circles), [Cu_2(*cis*-1,4-*chdc*)$_2$(H_2O)$_2$] (red circles), and [Cu_2(*cis*,*cis*-1,3,5-H*chtc*)$_2$] (green circles).

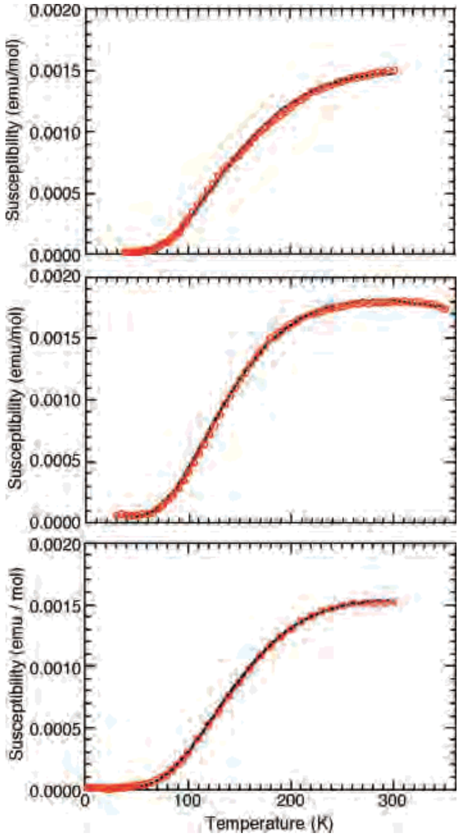

Figure 7. Magnetic susceptibility (red circles) after subtracting a Curie tail and fitting to the dimer model (black line) for [Cu_2(*trans*-1,4-*chdc*)$_2$] (top), [Cu_2(*cis*-1,4-*chdc*)$_2$(H_2O)$_2$] (middle), and [Cu_2(*cis*,*cis*-1,3,5-H*chtc*)$_2$] (bottom).

IR Spectroscopy. The IR spectra of the three complexes are quite detailed with many bands corresponding to the vibrations of the organic moieties (Figure 6). We should note that the number of bands is much more for the complexes with *cis-chdc* and *cis*,*cis*-H*chtc* than the one with *trans-chdc*. This may be related to the local geometry of the coordination polymers, that is, 2D for **1** and **3** and 1D for **2**. There are two regions in the spectra that provide clear answers concerning the structures. One is the region of the stretching modes of O−H around 3400 cm^{-1}. **2** shows an overlap of two broad bands at 3412 and 3320 cm^{-1}, which are assigned to the antisymmetric and the symmetric O−H modes, respectively. The corresponding bending mode is observed at 1676 cm^{-1}. These three bands are absent from the spectrum of **1**, as expected for an anhydrous compound, confirming the X-ray structure determination. We note that it is not the case for the crystal structure reported.[18,19] Whether the difference comes from the different methods of preparation is presently unclear. It is to be noted that hydrothermal reactions tend to produce higher condensation and therefore less water molecules in the solids, as has been shown for Co succinate.[34] For **3**, the band at 3266 cm^{-1} is assigned to the O−H of the free carboxylic acid. It is shifted to lower energy as expected. An additional strong sharp peak at 1726 cm^{-1} is assigned to the C−O stretching mode of the free carboxylic acid. Consequently, the intensity of the latter is nearly half those of the coordinated carboxylate mode at 1574 cm^{-1} in relation to the ratio of the free carboxylic acid to carboxylate. The antisymmetric carboxylate mode is close to one another for the three compounds (1584, 1585, and 1574 cm^{-1}, respectively), while the symmetric mode is at 1419, 1412, and 1394 cm^{-1}. The difference in energy between these two modes is usually correlated to the bond strength, and we note that the larger difference corresponds to the higher degree of torsion of the carboxylate group, that is, in the order **3** > **2** > **1**.

Magnetic Properties. The temperature dependence of the magnetic susceptibilities of the three compounds, after subtracting a Curie term in each case, are shown in Figure 7. In each case, the susceptibility exhibits a broad maximum at high temperature and a minimum around 50 K, while below 50 K a Curie tail dominates. After subtracting the Curie tail, the data for each compound were fitted to the sum of a dimer of $s = 1/2$ and a temperature-dependent paramagnetic component. The latter was found to be very small (maximum observed is 3.5×10^{-5} emu/mol). The two fitted parameters for the dimer were the Landé *g*-value and the singlet−triplet gap energy. The *g*-values were 2.259 for **1**, 2.188 for **2**, and 2.207 for **3**. The gap energy was 457 K for **1**, 493 K for **2**, and 485 K for **3**. Both the *g*-value and the gap are in good agreement for the ranges observed for similar compounds. For a rigorous treatment of the data for **1** and **3** considering their crystal structures, an alternate chain model with two exchange interactions would have been more appropriate. However, the large exchange interaction (>450 K) between Cu atoms within the dimeric core and available data only up to 350 K do not allow such analyses to be done with high accuracy.

Conclusion

In this study, we have synthesized and characterized three coordination networks having the dimeric $Cu_2(CO_2)_4$ node connected by different geometrical isomers of cyclohexane carboxylates. The resulting solids are stabilized with and without empty channels. Both self-organization with Cu−O bonding between dimers and the flexibility of the connector strengthened the structures. In the absence of Cu−O bonding between dimers, water is coordinated to complete the coordination sphere of the copper atoms. The results clearly demonstrate the reason why [Cu_2(*trans*-1,4-*chdc*)$_2$] can absorb gases and solvents but [Cu_2(*cis*-1,4-*chdc*)$_2$(H_2O)$_2$] does not. [Cu_2(*cis*,*cis*-1,3,5-H*chtc*)$_2$] displays both coordinated carboxylates and hydrogen-bonded carboxylic acid.

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Supporting Information Available: Crystallographic data in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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