1-D Open-Channeled 3-D Supramolecular Self-Assembled Frameworks Encapsulating Unprecedented Cyclic $(H_2O)_8$ Clusters or Solvent Molecules

Dong-sheng Li,[a,b] Yao-yu Wang,*[a] Xin-jun Luan,[a] Ping Liu,[a] Cai-hua Zhou,[a,b] Hai-rui Ma,[a] and Qiz-hen Shi[a]

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Two novel 1-D coordination polymers, $\{[Cu(Hhbd)(bpy)]\cdot 3H_2O\}_n$ (**1**) and $\{[Cu(Hhbd)(phen)]\cdot H_2O\cdot MeOH\}_n$ (**2**) [Hhbd = α-hydroxybutanedioicate dianion, bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline], were rationally designed and synthesized with an identical construction strategy, using Hhbd ligands as bridges and chelating aromatic ligands as terminal ligands. Interestingly, the chelating aromatic ligand and the –OH groups of the Hhbd ligand play an important role in the self-assembly of the polymeric coordination chain by providing potential supramolecular recognition sites for π–π aromatic stacking and hydrogen-bond interactions, resulting in the self-assembly of the molecular double chains to give a 3-D supramolecular framework with 1-D open channels. More significantly, in **1** the host framework encapsulates unprecedented centrosymmetric cyclic $(H_2O)_8$ clusters that have a chair conformation and are connected into 1-D arrays by supramolecular association along the 1-D open channels. In contrast, the channels of **2** contain lattice water and disordered methanol molecules. TGA and XRPD show that the host frameworks of **1** and **2** are stable when the guest solvent molecules are removed from the channels. Variable-temperature magnetic susceptibility measurements for both complexes indicate the presence of weak antiferromagnetic exchange interactions between adjacent copper(II) ions.

Introduction

Research into self-assembling processes has recently become a rapidly growing area in supramolecular chemistry, biochemistry, and materials science.[1–4] Indeed, self-assembling processes are utilized by nature in many interesting chemical and biomolecular systems, such as in the folding of proteins and nucleic acids.[5–7] Moreover, the principles of self-assembly provide a new strategy for the rational design and synthesis of new supramolecular architectures, especially for the preparation of extended channel-containing metal-organic frameworks. Such systems are of potential utility for molecular recognition, ion exchange, gas storage, heterogeneous catalysis, and for the development of new magnetic materials.[8–10] Therefore, chemists have made significant efforts to introduce the self-assembling process into artificial systems.[11–13] As a result of this work, the self-assembly of organic, organometallic, and/or inorganic building blocks through metal-ligand binding, hydrogen bonds, or π–π interactions has become a powerful tool for the generation of large cage-like molecules and porous substances with channels.[14–18] Although important progress has been made in the construction of such assemblies by the exploitation of any one of these individual intermolecular interactions, a lot of research dealing with the combination of two or all three of them can still be carried out, allowing for the construction of an almost infinite number of new supramolecular entities.[19]

During the past decades, for materials chemists and especially for inorganic chemists, polycarboxylates have become one of the most used spacers in the synthesis of compounds that have potential applications as molecular-based magnetic materials, and for the preparation of porous materials that show host–guest behavior.[20–25] However, hydroxypolycarboxylic acids, although important as polycarboxylate ligands, have been seldom used to date. The unique features of hydroxypolycarboxylic acids have drawn our attention. First of all, these acids possess terminal carboxylic acid and hydroxyl groups that may be completely or partially deprotonated. This leads to a versatile coordination behavior, and as such, distinct bonding modes towards metal cations, such as nonchelating, chelating, and bridging modes can be realized.[26,27] Secondly, hydroxypolycarboxylic acids can act not only as hydrogen-bond acceptors, but also as hydrogen-bond donors to form new extended structures by means of additional hydrogen-bond interactions. Thirdly, some hy-

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[a] Department of Chemistry & Shaanxi Key Laboratory of Physico-inorganic Chemistry, Northwest University,
Xi'an 710069, P. R. China
Fax: +86-29-8837-3398
E-mail: wyaoyu@nwu.edu.cn
[b] Department of Chemistry & Chemical Engineering, Yan′an University,
Yan'an 716000, P. R. China

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droxypolycarboxylic acids [α-hydroxybutanedioic acid (H_3hbd), 2,3-dihydroxybutanedioic acid (H_4dhbd), and 2-hydroxy-1,2,3-tricarballylic acid (H_4htb), etc.] are present in fruits and living cells, and they also play an important role in biological processes.[28–30]

Currently we are exploring the self-assembly of metal ions with ligands that are capable of forming hydrogen bonds and bringing about π–π interactions, and that behave as directional motifs capable of extending the dimensionality of the channel-containing product materials. In the present work, by using H_3hbd as the bridging ligand, and 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen) as terminal ligands, we have prepared two similar neutral 1-D coordination polymers, namely $\{[Cu(Hhbd)(bpy)]\cdot 3H_2O\}_n$ (**1**) and $\{[Cu(Hhbd)(phen)]\cdot H_2O\cdot MeOH\}_n$ (**2**) [Hhbd = α-hydroxybutanedioicate dianion]. Interestingly, under the direction of supramolecular recognition, and attraction through π–π aromatic stacking, and hydrogen-bond interactions provided by Hhbd and the aromatic chelating ligands, these 1-D chains may self-assemble to form molecular double chains that may also self-assemble to give a final 3-D framework that contains 1-D open channels. Unexpectedly, we found unprecedented cyclic $(H_2O)_8$ clusters encapsulated within the host framework of **1**. These clusters are connected into 1-D arrays along the 1-D open channels by supramolecular association.

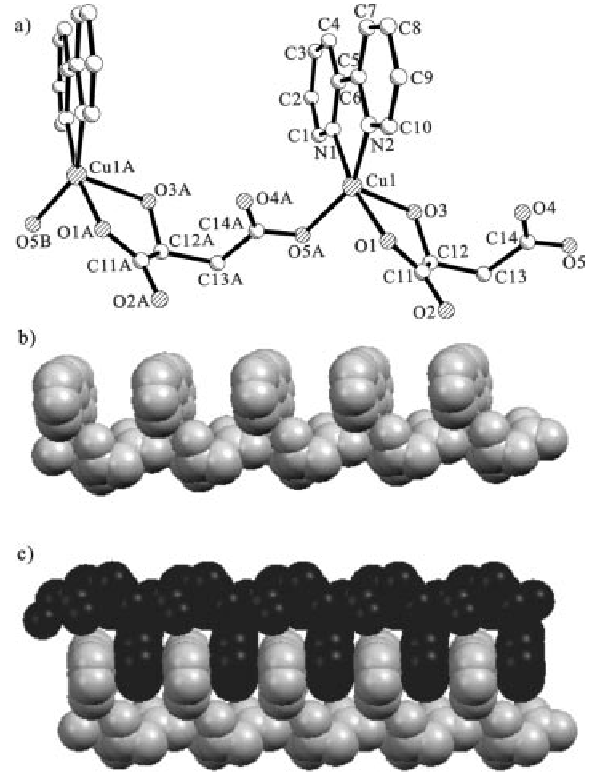

Figure 1. (**a**) View of the coordination environment of the copper atoms in **1**; (**b**) 1-D single-stranded polymeric chain; (**c**) ladder-like, double-stranded chains.

Results and Discussion

Description of the Structures

$\{[Cu(Hhbd)(bpy)]\cdot 3H_2O\}_n$ (1)

A single-crystal X-ray structural analysis showed that **1** crystallizes in the monoclinic space group $P2_1/c$, with one copper(II) atom, one tridentate Hhbd ligand, one bpy ligand, and three lattice water molecules in each crystallographic unit. Each copper(II) atom is coordinated to three oxygen atoms from two different Hhbd ligands, and two nitrogen atoms from a chelating bpy ligand to give 3+1+1 distorted trigonal-bipyramidal geometry at the metal centers with a trigonality index $\tau = 0.93$.[31] Copper(II) is approximately coplanar with the equatorial plane defined by atoms O3, O5, N2, and shows a deviation of 0.0375 Å toward O1, as seen in part a of Figure 1. Selected bond lengths and angles are listed in Table 1, and are in close agreement with bond parameters previously reported for carboxylate and bpy containing copper(II) complexes.[32,33] In addition, the fact that the $Cu–O_{carboxyl}$ bonds [av.1.967(2) Å] are significantly shorter than the $Cu–O_{hydroxyl}$ bond [2.209(3) Å] indicates that the hydroxyl group of **1** is protonated; this is also found in many other α-hydroxycarboxylate complexes.[27,34]

Table 1. Selected bond lengths [Å] and angles [°] for **1** and **2**.

1		**2**	
Cu–O(1)	1.943(2)	Cu–O(1)	1.943(2)
Cu–O(5A)	1.992(2)	Cu–O(4A)	1.984(3)
Cu–O(3)	2.209(3)	Cu–O(3)	2.183(3)
Cu–N(1)	1.984(3)	Cu–N(1)	2.008(4)
Cu–N(2)	2.001(3)	Cu–N(2)	2.016(4)
O(1)–Cu–N(1)	168.40(12)	O(1)–Cu–N(1)	170.53(15)
N(1)–Cu–O(5A) [a]	94.26(11)	N(1)–Cu–O(4A)	91.89(11)
N(1)–Cu–N(2)	80.82(12)	N(1)–Cu–N(2)	82.16(16)
O(1)–Cu–O(3)	78.33(10)	O(1)–Cu–O(4A)	95.54(11)
O(5A)–Cu–O(3)	92.31(10)	O(1)–Cu–N(2)	93.69(15)
O(1)–Cu–O(5A)	94.83(11)	O(4A)–Cu–N(2)	153.24(15)
O(1)–Cu–N(2)	94.73(11)	O(1)–Cu–O(3)	78.36(13)
O(5A)–Cu–N(2)	150.15(11)	O(4A)–Cu–O(3)	97.61(14)
N(1)–Cu–O(3)	94.12(11)	N(1)–Cu–O(3)	94.86(14)
N(2)–Cu–O(3)	117.31(11)	N(2)–Cu–O(3)	108.85(15)

[a] Symmetry codes: A: $x - 1, y, z$ for **1** and A: $x + 1, y, z$ for **2**.

It is worthwhile to note that the Hhbd dianion adopts an *R* conformation and bridges the copper centers to form 1-D polymeric chains running along the crystallographic *a* axis with an adjacent Cu···Cu distance of 7.013 Å (part b in Figure 1). The bpy ligands lie on one side of this chain in a parallel fashion. Interestingly, a pair of 1-D chains self-assemble to generate a molecular double chain under the direction of strong aromatic π–π interactions between the bpy units with a face-to-face distance of ca.3.375–3.422 Å (part c in Figure 1). There are significant C–H···O hydrogen bonds involving the bpy carbon atoms (C7) and the uncoordinated carboxyl oxygen atoms (O4) (C···O 3.357 Å, C–

H···O 164°), and these provide an additional attractive force between the strands.[35] To the best of our knowledge, the double chains represent the first example of perfect molecular double chains formed using hydroxypolycarboxylate ligands. Furthermore, neighboring pairs of double chains interact with each other through strong hydrogen bonds between the uncoordinated carboxyl oxygen atoms (O2) and the coordinated, protonated hydroxyl groups (O3) (O···O 2.676 Å, O–H···O 177°). These interactions form the final 3D framework that feature 1-D open channels when viewed along the crystallographic *a* axis (Figure 2). The approximate dimensions of these channels are 10.41 Å × 6.67 Å, which are large enough to encapsulate guest solvent molecules.

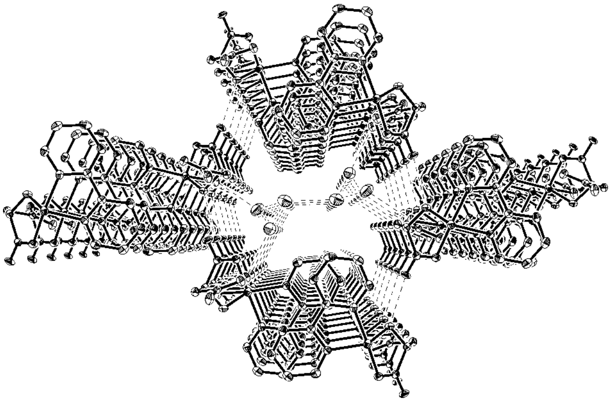

Figure 2. View of the 3-D supramolecular framework of **1** containing 1-D open channels encapsulating arrays of cyclic $(H_2O)_8$ clusters.

The most remarkable feature in **1** is that, in the 1-D open channels, the guest water molecules form a centrosymmetric cyclic $(H_2O)_8$ cluster that adopts a chair conformation (Figure 3). Two closely related isomers of nearly identical low-energy with S_4 and D_{2d} symmetries have been theoretically predicted for the $(H_2O)_8$ cluster.[36] Evidence for the existence of both of these isomers has been obtained from studies of gas-phase $C_6H_6(H_2O)_8$ and molecular beams.[37,38] However, only three kinds of $(H_2O)_8$ clusters, namely, the cubic cage-like $(H_2O)_8$ cluster with *Ci* symmetry, the ice-like cyclic $(H_2O)_8$ cluster with –4*m*2 symmetry, and the opened-cube $(H_2O)_8$ cluster with centrosymmetric symmetry, have been found within different crystal hosts,[39–41] but no centrosymmetric cyclic $(H_2O)_8$ clusters have ever been reported.

Within the centrosymmetric cyclic $(H_2O)_8$ cluster only three water molecules are crystallographically unique. The hydrogen bond O···O distances range from 2.772 to 2.850 Å (mean value 2.799 Å), and are slightly longer than the average hydrogen bond length observed in icelike cyclic $(H_2O)_8$ clusters with –4*m*2 symmetry.[40] There is a narrow variation in the O···O···O angles, with an average value of 120.72°. These structural parameters are similar to those of cyclic $(H_2O)_6$ clusters.[42] Each water molecule in the cluster is involved in the formation of two hydrogen bonds with an adjacent water molecule. The water octamers are self-assembled along the channels, and are held together by O7W···O6W and O7W···O8W hydrogen bonds to give extended 1-D arrays consisting of eight-membered rings of water,which share a common side formed by an O7W···O7W hydrogen bond (Figure 4). Additionally, atoms O6W and O8W both donate a hydrogen bond towards a carboxyl oxygen atom situated on the Hhbd ligand of the host framework (O4, O5) (av.2.850 Å). These additional interactions play an important role incontributing to the stability of the 1-D cyclic $(H_2O)_8$ cluster arrays. The supramolecular association of water molecules into arrays is presumably enforced by the shape and the condition of the interior of the host's channel. These results further illustrate the structural diversity possible for water clusters and the sensitive dependence of their structures on the nature of their environment.

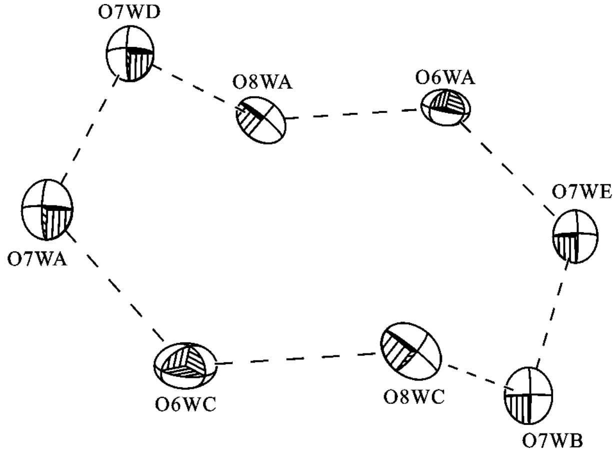

Figure 3. A centrosymmetric cyclic $(H_2O)_8$ cluster in **1** displaying a chair conformation. The view is along the crystallographic *b* axis; hydrogen bond O···O distances [Å] and O···O···O angles [°]: O7WA···O7WD 2.777(3), O7WA···O6WC 2.798(6), O6WC···O8WC 2.850(7), O8WC···O7WB 2.722(8), O6WC···O8WA 5.437(9); O7WD···O7WA···O6WC 118.65(11), O7WA···O6WC···O8WC 127.49(9), O6WC···O8WC···O7WB 125.85(10), O8WC···O7WB···O7WE 110.78(9).

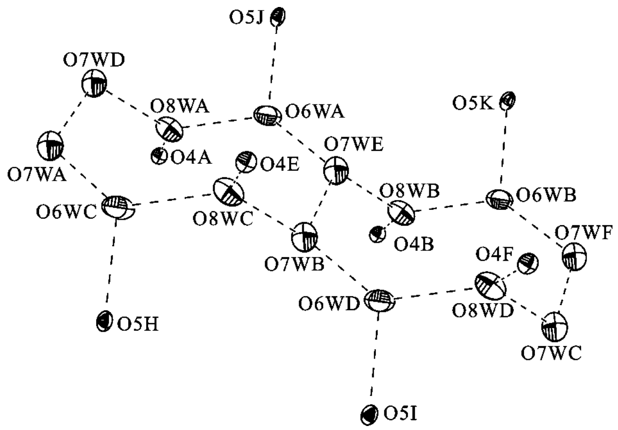

Figure 4. Extended 1-D array consisting of eight-membered rings of water molecules that shared an edge; these arrays are located in the 1-D open channels of **1**. The O···O···O angle for adjacent eight-membered water rings: O6WA···O7WE···O8WB 115.07(8)°.

$\{[Cu(Hhbd)(phen)]\cdot H_2O\cdot MeOH\}_n$ (2)

Complexes **1** and **2** have the same space group, $P2_1/c$, and similar crystal data. The central copper(II) atoms in both complexes have the same coordination geometry, and the bond lengths and angles, as shown in Figure 5, part a, Table 1, are also similar. In other dicarboxylate complexes, such as the manganese maleate/diimine systems, and the copper ipa/diimine systems, the replacement of bpy with phen, a chelating aromatic ligand of a larger size, led to a dramatic change in the framework topologies.[33,43] In the study reported in this paper, we used phen instead of bpy, and having used similar reaction conditions, only the analogous neutral polymeric chains were formed in **2** (part b in Figure 5). However, there are some subtle differences between the two complexes; the aromatic π–π stacking interactions between the phen entities are stronger in **2** (the distance between the phen rings is ca.3.27–3.30 Å). Additionally, the 1-D open channels in the final 3-D host framework of **2** (ca. 9.97 × 4.67 Å),which are also formed through molecular double chains held together by $O_{hydroxyl}$–$H\cdots O_{carboxyl}$ hydrogen bonds, are occupied by water and disordered methanol molecules (Figure 6). As shown above, the most critical factor to note for the two complexes is that their structural identity does not derive from their chemically very similar ancillary ligands, phen and bpy, but from the coordination geometry of their Hhbd ligands, in particular, of the hydroxyl groups bound to the central metal atom.

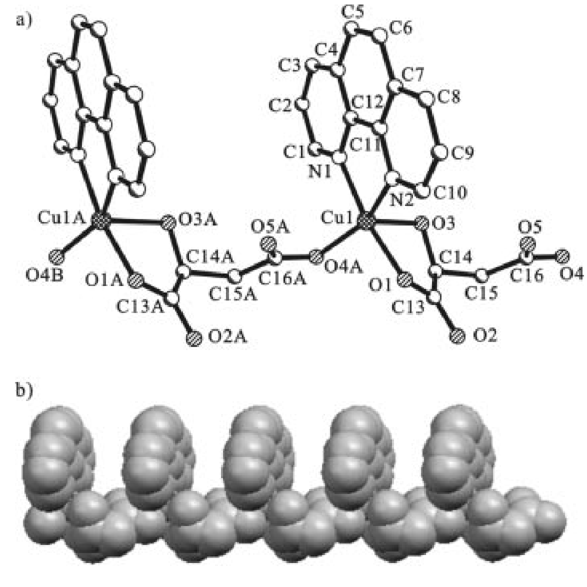

Figure 5. (a) Veiw of the coordination environment of the copper(II) atoms in **2**; (b) a neutral 1-D single-stranded polymeric chain.

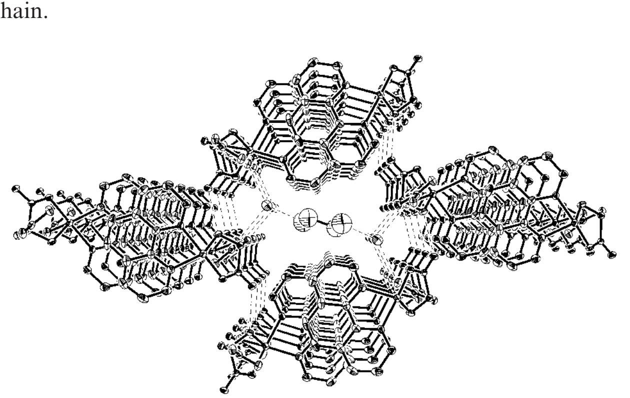

Figure 6. View of the 3-D supramolecular formwork of **2** with 1-D open channels containing the free water and disordered methanol molecules.

IR Spectra and TGA Analysis

The infrared spectra of the two complexes are quite similar, with a broad band centered at ca. 3420–3380 that is due to the –OH stretchingvibration of the water molecules involved in extensive hydrogen-bonding interactions.[44] Furthermore, the spectra exhibit the ν_{as}(OCO) and ν_s(OCO) vibrations of the carboxylate groups that occur at 1608 and 1393 cm^{-1} for **1** and at 1604 and 1403 cm^{-1} for **2**. $\Delta[\nu_{as(OCO)} - \nu_{s(OCO)}] > 200$ cm^{-1} for both complexes, a value that suggests that the carboxylate is coordinated in a monodentate fashion, This is in agreement with the crystal structure. Less significant absorption bands occur at 3050–2920 (stretching vibrations of the aromatic C–H groups), 860–720 (out-of-plane motion of the C–H groups of the pyridyl rings) and 570 cm^{-1} ($\nu_{(M-N)}$ vibration).

Thermogravimetric analysis (TGA) showed that the weight of **1** remains almost unchanged from 40 to 210 °C (first stage). The second stage occurs between 210 and 230 °C. A weight loss of 12.86% (calcd. 13.30%) over this range is attributed to the loss of three water molecules. When the temperature is above 235 °C, the product begins to lose the Hhbd and bpy ligands and then starts to decompose. In contrast to **1**, the lattice water and disordered methanol molecules of **2** are lost between 50 and 110 °C; the overall observed loss (11.67%) is in agreement with the calculated value (11.75%). When the temperature is above 240 °C, the complex begins to lose its ligands and then starts to decompose. These data analyses reveal that: (1) The free water and the disordered methanol molecules are removed from the channels of **2** in the range of 50–110 °C, whereas the coordinated phen and Hhbd ligands do not decompose over this temperature range. (2) The water molecules in **1** are involved in strong and extensive hydrogen-bond interactions, leading to the loss of water at higher temperatures. (3) The 1-D neutral polymeric chains of **1** and **2** are stable under 235 °C and 240 °C, respectively. In addition, after heating a sample of **1** at 230 °C, and a sample of **2** at 120 °C, for 2 h the guest solvent molecules are removed (the evacuated frameworks are defined as **1′** and **2′**, respectively). The X-ray power diffraction patterns of **1′** and **2′** are similar to those of **1** and **2**, although minor differences can be seen in the positions, intensities and widths of some peaks, indicating that the frameworks of **1** and **2** are retained after the removal of the guest species. On the other hand, it may also indicate that the 1-D open channels in **1** and **2** have the ability to absorb other hydrophilic small molecules. An investigation of these properties and the synthesis of other metal-Hhbd frameworks are underway.

Magnetic Properties

Variable-temperature magnetic susceptibility measurements over the 5–300 K range were carried out for **1** and **2**, and the plots of χ_M and $1/\chi_M$ vs. T are shown in Figure 7.Both $1/\chi_M$ vs. T plots are almost linear down to very low temperatures. Fitting the curves to the Curie–Weiss law [$1/\chi_M = (T - \theta)/C$] gives a Curie–Weiss constant of $C = 0.387\ \mathrm{cm^3\,K\,mol^{-1}}$ and a Weiss temperature, θ, of –0.431 K for **1** with an agreement factor of $R = 7.13 \times 10^{-4}$, and $C = 0.420\ \mathrm{cm^3\,K\,mol^{-1}}$ and $\theta = -0.456$ K for **2** with an agreement factor of $R = 4.07 \times 10^{-4}$, where $R = \Sigma[(1/\chi_M)_{obs} - (1/\chi_M)_{calc}]^2/\Sigma[(1/\chi_M)_{obs}]^2$. The θ values for the two complexes are indicative of weak antiferromagnetic interactions.[45,46] In order to evaluate the exchange interaction between neighboring copper(II) atoms, the experimental data were fitted using the expression (see below) obtained from the Bonner–Fisher calculation based on the effective spin Hamiltonian $H = -J\Sigma(S_iS_{i+1})$.[47]

$$\chi_M{}^J = \frac{N\beta^2 g^2 S(S+1)}{3kT}\,\frac{1+u}{1-u}$$

where

$$u = \coth\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{kT}{JS(S+1)}\right]$$

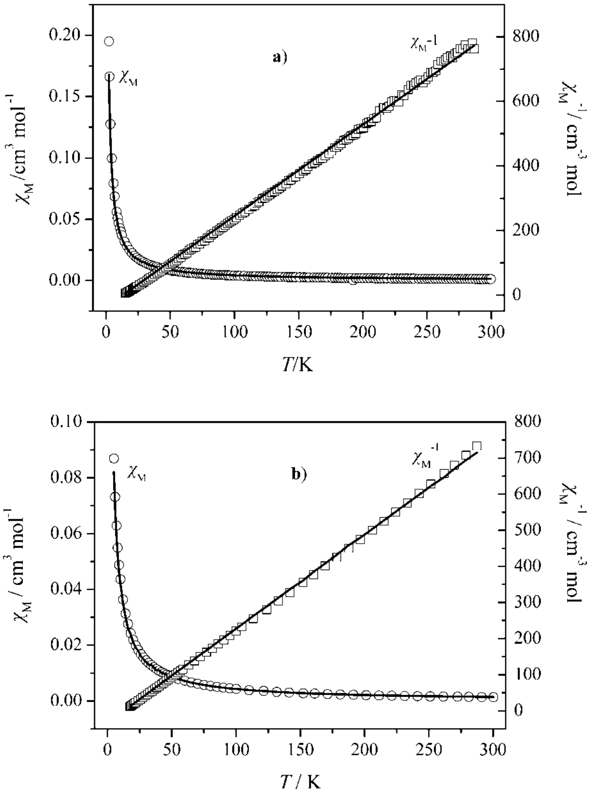

Figure 7. Experimental (○ and □) and fitted (–) curves showing the temperature dependence of χ_M and $\chi_M{}^{-1}$. (a) for **1**; (b) for **2**.

Finally, this expression fits very well with the experimental susceptibilities of **1** and **2**, giving $g = 2.09$ and $J = -0.487\ \mathrm{cm^{-1}}$ for **1** and $g = 2.15$ and $J = -0.517\ \mathrm{cm^{-1}}$ for **2**. These very low J values are in agreement with the values of θ reported above. The antiferromagnetic interactions are obviously due to a long-range superexchange pathway between adjacent magnetic centers.[48,49]

Conclusion

In summary, two 3-D supramolecular frameworks with 1-D channels, $\{[Cu(Hhbd)(bpy)]\cdot 3H_2O\}_n$ (**1**) and $\{[Cu(Hhbd)(phen)]\cdot H_2O\cdot MeOH\}_n$ (**2**), were constructed from Hhbd-bridged 1-D chains of copper(II) units and chelating aromatic ligands. The Hhbd ligand adopts a coordination geometry identical to that observed for very similar ancillary chelating ligands. This results in the same structure topologies, in which the aromatic chelating ligand and the –OH groups of the Hhbd ligand play an important role in the self-assembly of the polymeric coordination chains by providing potential supramolecular recognition sites for π–π aromatic stacking and hydrogen-bond interactions. More significantly, in **1** the host framework encapsulates unprecedented centrosymmetric cyclic $(H_2O)_8$ clusters that adopt a chair conformation and are connected into 1-D arrays by supramolecular association.

Experimental Section

Synthesis of $\{[Cu(Hhbd)(bpy)]\cdot 3H_2O\}_n$ (1) and $\{[Cu(Hhbd)(phen)]\cdot H_2O\cdot MeOH\}_n$ (2): Reagents and solvents were purchased from commercial sources (Aldrich) and used as received. The two complexes were prepared in a similar way. Firstly, a sample of copper acetate monohydrate (0.40 g, 2 mmol) was dissolved in deionized water (15 mL). Secondly, *dl*-α-hydroxybutanedioic acid (H_3hbd) (0.29 g, 2.2 mmol) with either 2,2′-bipyridine (bpy) (0.33 g, 2.1 mmol) or 1,10-phenanthroline (phen) (0.42 g, 2.1 mmol) was suspended in MeOH (20 mL) and stirred at ambient temperature for 20 min. Thirdly, the MeOH solution was added slowly drop by drop to the previously prepared copper acetate solution with continuous stirring. The resulting mixture was then stirred for a further 40 min and then filtered. Finally, the blue filtrate solution was transferred to a tube and placed inside a conical flask containing acetone under air. After 13 d, blue crystals of **1** and **2** were manually harvested under the microscope and analyzed using single-crystal X-ray diffraction. Yield: 71 % for **1** and 69 % for **2**. (**1**) $C_{14}H_{18}CuN_2O_8$ (405.85): calcd. C 41.43, H 4.47, Cu 15.66, N 6.90; found C 41.40, H 4.45, Cu 15.60, N 6.88. (**2**) $C_{17}H_{18}CuN_2O_7$ (425.89): calad. C 47.94, H 4.26, Cu 14.92, N 6.58; found C 47.91, H 4.23, Cu 14.84, N 6.55.

Physical Measurements: Elemental analyses (C,H,N) were determined with a PE 2400 Elemental analyzer, and the analyses of the copper contents were performed on a Perkin–Elmer Optima 3300 DV ICP analyzer. Infrared spectra of KBr pellets were recorded with a BRUKER EQUINOX-55 spectrometer in the range of 4000–400 cm^{-1}. Thermal analyses were performed with a NETZSCH STA 449C microanalyzer with a heating rate of 10 °C min^{-1} under air. The XRPD patterns were recorded with a Rigaku D/Max 3III diffractometer with a scanning rate of 4 deg min^{-1}. Magnetic measurements were carried out on a polycrystalline sample with a SQUID magnetometer operating in the 5–

300 K temperature range with an applied field of 5 kOe. Diamagnetic corrections were estimated from the Pascal constants.

Crystal Data Collection and Refinement: Diffraction experiments for **1** and **2** were carried out with Mo-K_α radiation using a BRUKER SMART APEX-CCD diffractometer at 293(2) K. A summary of the crystallographic data and structure refinement details are given in Table 2. Both structures were solved by direct methods and refined with the full-matrix least-squares technique on F^2 using SHELXS-97[50] and SHELXL-97.[51] All non-hydrogen atoms were refined anisotropically. CCDC-261630 (for **1**) and CCDC-261631 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystal data and structure refinement details for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{14}H_{18}CuN_2O_8$	$C_{17}H_{18}CuN_2O_7$
Formula mass	405.86	425.89
Temperature [K]	293(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	7.0132(10)	7.0968(7)
b [Å]	19.730(3)	11.2090(11)
c [Å]	11.8998(16)	20.829(2)
β [°]	94.551(3)	98.302(2)
V [Å^3]	1641.4(4)	1639.5(3)
Z	2	2
$D_{calcd.}$ [g·cm^{-3}]	1.642	1.725
μ [mm^{-1}]	1.377	1.397
F [000]	836	876
θ [°]	2.00–28.26	1.98–28.29
Reflections collected	9894	9802
Independent reflections (R_{int})	3757 (0.0829)	3795 (0.0788)
R_1, wR_2[a] [$I > 2\sigma(I)$]	0.0483, 0.0817	0.0651, 0.1364
Residuals [e·Å^{-3}]	0.632 / –0.477	0.880 / –0.679

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Supporting Information Available: XRPD patterns and the magnetic data for compounds **1** and **2**.

Acknowledgments

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