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Unusual T4(1) Water Chain Stabilized in the One-Dimensional Chains of a Copper(II) Coordination Polymer

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A novel T4(1) water chain in a new Cu^{II} coordination polymer, $\{[Cu(C_4H_6N_2)_2(C_4H_2O_4)]\ (H_2O)_3\}_n$ (**1**, where $C_4H_6N_2$ = 2-methylimidazole, $C_4H_2O_4$ = maleate), has been synthesized and structurally characterized by single-crystal X-ray diffraction. Thermogravimetry, infrared spectroscopy, elemental analysis, and magnetic analysis have also been used to characterize **1**. Complex **1** crystallizes in the trigonal space group $P3_221$, and the 1-D chains composed of cyclic water tetramers play an important role in stabilizing the overall polymeric structure. Furthermore, this 1-D water chain presents an unusual association mode of water molecules.

Introduction

Water in all its forms exhibits a mesmerizing collection of properties and functions. Because of its crucial role for life, its abundance in nature, and its importance in so many technological processes, many chemists, biochemists, and biologists study water in an attempt to achieve a comprehensive understanding of its properties.[1] The present upsurge in studying water clusters is aimed not only at understanding the "anomalous" behavior of bulk water but also in probing its possible roles in the stabilization and functioning of biomolecules[2] and in designing new materials.[3] Although considerable attention has been devoted to the theoretical and experimental investigation of water clusters, including a variety of oligomers and polymers consisting of the basis cyclic water subunits, they are still not fully understood. It is this realization that has prompted extensive investigations of water structures in recent years. Some discrete water clusters $(H_2O)_n$,[4–23] where n = 2–10, 12, 16 and 18, in various crystal hosts at room temperature have been reported. Further attention has also been paid to the infinite one- and two-dimensional water morphologies, which structurally lie between small water clusters and bulk water/ice, while investigations of these clusters that are interlinked to form a larger network is much less[24–35] and infinite water chains consisting of cyclic water tetramers are rare.[26]

On the other hand, the investigations of novel metal–organic hybrid compounds have attracted considerable interest in recent years, not only because of their intriguing structural motifs and promising photochemical, electrochemical, and magnetic properties, but also their because of their potential applications in catalysis, medicine and host–guest chemistry.[36–42] It is noteworthy that the dicarboxylates such as malonate, fumarate, and 1,4-benzenedicarboxylate have been widely used in constructing novel different dimensional metal–organic hybrid compounds.[43] In contrast to the ligands mentioned above, maleate is rarely used. Of further interest is that few cases of such coordination polymers, especially those mixed with the other chelating N-donor imidazole ligands, have been document so far.

In this work we report the preparation, structural characterization, and properties of an unusual 1D water chain consisting of cyclic water tetramers in a new 1D dicarboxylate-bridged Cu(II) polymer, $\{[Cu(C_4H_2O_4)(C_4H_6N_2)_2](H_2O)_3\}_n$ (**1**, where $C_4H_6N_2$ = 2-methylimidazole, $C_4H_2O_4$ = maleate); the water chains are linked with the 1-D polymer through hydrogen-bonding interactions to form a 3D network structure. We believe that the water structure demonstrated herein brings to light yet another novel mode of the cooperative association of water molecules, and this discovery is helpful in improving the modeling of some of unexplained properties of water and in understanding better the structure and behavior of water molecules in biological systems.[25]

Results and Discussion

Crystal Structures

Single-crystal structure analysis reveals that compound **1** consists of a polymer $\{[Cu(C_4H_6N_2)_2(C_4H_2O_4)](H_2O)_3\}_n$, which crystallizes in the chiral space group $P3_221$. The asymmetric unit contains one Cu^{II} ion, two 2-methylimid-

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azole ligands, one maleate, and three independent water molecules (Figure 1). Each copper(II) ion lies on a twofold axis and exhibits a Jahn–Teller distorted CuN_2O_4 octahedral geometry. Two nitrogen atoms [N(2) and N(2A)] from two monodentate 2-methylimidazole groups and two carboxylate oxygen atoms [O(1) and O(1A)] from the maleate ligand occupy the equatorial sites, and the Cu–N bonds [1.9579(15) Å] are somewhat shorter than the Cu–O bonds [2.0283(12) Å]. The axial sites are occupied by the second carboxylate oxygen atom of each maleate [Cu(1)–O(2) = 2.4833(14) Å]; the chelating bite of the carboxylate group leads to a significant distortion from true octahedral geometry [O(2)–Cu(1)–Cu(2A) = 143.59(7)°]. The neighboring Cu^{II} ions are connected through the dicarboxylate bridges to form a regular infinite 1D chain with a Cu···Cu distance of 6.977 Å (Figure 2). Simultaneously, the chains are interconnected though two types of hydrogen bonds to form a three-dimensional network, which involve the equatorial carboxyl oxygen atom O(1) of maleate and the O(3) atom of a water molecule [O(3)···O(1) = 2.879 Å] and the uncoordinated nitrogen atom N(1) from the 2-methylimidazole group and the carboxyl oxygen atom O(2) of maleate; the N(1)··· O(2) distance of 2.771 Å [$-x + y + 1$, $-x + 1$, $z + 1/3$] is shorter than those reported previously [N···O = 2.851(19) and 3.088(18) Å].[10a]

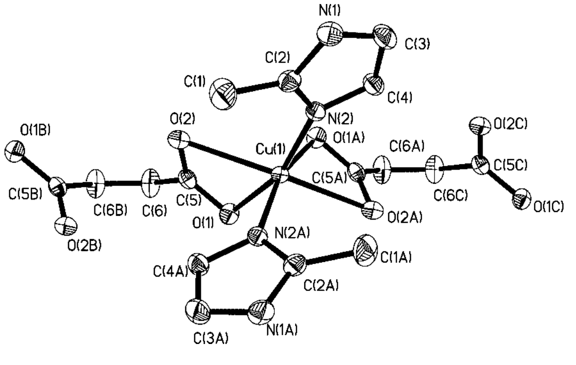

Figure 1. An ORTEP view of complex **1**, with selected atom numbering. The hydrogen atoms and uncoordinated water molecules are omitted for clarity.

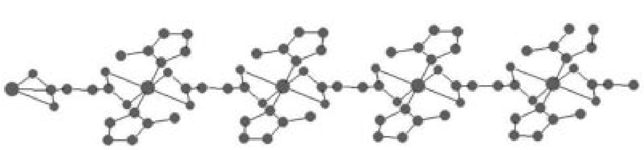

Figure 2. Infinite 1D network of **1**. The hydrogen atoms and dissociated water molecules are omitted for clarity.

The most striking feature is that the structure contains extensive hydrogen bonding between the uncoordinated water molecules [O(3), O(4)] to form infinite 1D water chains containing cyclic water tetramers (Figure 3). The average O···O distance in the water chain is 2.790 Å, which is shorter than those observed in liquid water (2.854 Å) and comparable to those in the ice phase (2.77–2.84 Å).[32] However, this distance is a little longer than 2.768 Å[10a] and shorter than 2.95 Å[26] relative to the reported plane tetramer O···O distances.[26] The individual tetrameric clusters differ from the corner-sharing tetrameric and discrete tetrameric water clusters reported previously.[10,26] Two O(4) molecules form one side of the tetramer, and two O(3) molecules form the opposite side. The chains lie about the 3_2 screw axes, and the tetramers are connected through the shared O(4) corners to give chains with a T4(1) symmetry[44] (Figure 4). The O(3) molecules lie on the periphery of the chain, and form hydrogen bonds with the coordinated O(1) carboxylate atoms of the coordination polymer chains (O···O = 2.879 Å); the 3_2 screw axis means that each water chain is hydrogen bonded in this way to three adjoining coordination polymer chains. On a more local level, the two O(3) molecules within each tetramer bond to different coordination chains, whereas the two coordinated O(1) atoms in each Cu coordination environment form hydrogen bonds with the O(3) molecules belonging to two different (but adjoining) tetramers. Figure 5 displays the packing structure parallel to the *ab* plane of complex **1**. The water chains act as a "glue" to link the coordination polymer chains, forming an overall 3D structure.[32] Each water tetramer unit links two polymer chains, and each water chain links three 1D polymer chains through hydrogen bonds between the water molecules and the carboxyl groups. The T4(1) water chain is located in six polymer chains, and this plays a complementary role in stabilizing the network structure.

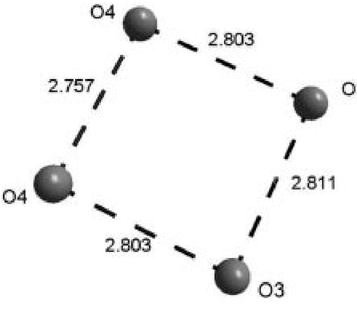

Figure 3. Tetrameric water cluster [O3···O3 = 2.811 Å, O4···O4 = 2.757 Å, O3···O4 = 2.803 Å].

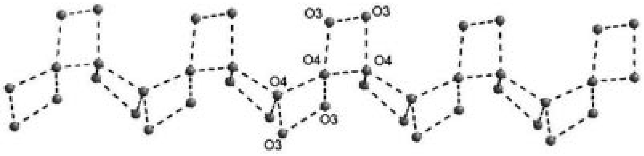

Figure 4. Hydrogen-bonding motif of the self-assembled infinite chain of water molecules.

The thermal stability of the water cluster was determined by thermogravimetric analysis (TGA) (see Figure S1 in the Supporting Information). TGA was performed at a heating rate of 10 °C/min with the single-crystal samples of **1**. Thermal analysis of the complex shows that the onset of water loss begins at 24 °C, and complete loss of water occurs within 200 °C. A 12.13-% weight loss was observed, which is almost equivalent to a loss of 2.7 water molecules – this value is lower than the calculated weight content of three water molecules (13.64%). In the infrared spectrum of **1**,

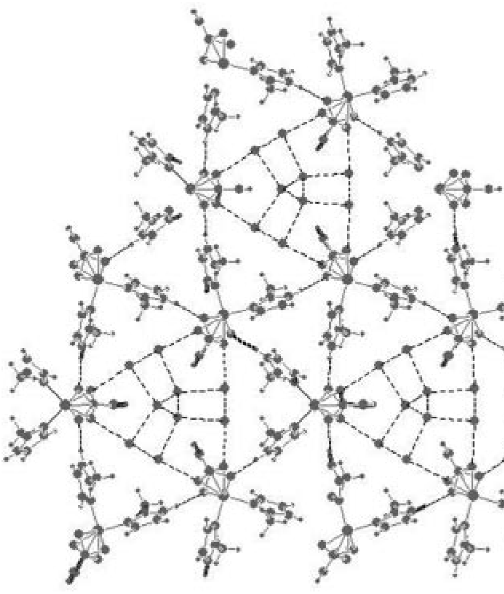

Figure 5. Packing diagram along the *c* axis of the supramolecular system for **1**.

the stretching frequency of the O–H bonds of the water cluster is observed as a band at about 3200 and 1631 cm^{-1}. The IR spectrum of ice shows the O–H stretching at 3220 cm^{-1}, while this stretching vibration in liquid water appears at 3490 and 3280 cm^{-1}.[16–18,29] This suggests that the water cluster in **1** shows an O–H stretching vibration similar to that of ice. It effectively proves that the O···O distance in the water chain is comparable to those in the ice phase (2.77–2.84 Å). In addition, there are several absorption bands observed at higher frequencies, 3133 cm^{-1} and 3051.3 cm^{-1}, which are characteristic of the 2-MeIm groups. One strong peak corresponding to the $\nu(COO^-)$ vibration is observed at 1549 cm^{-1} (see Figure S2 in the Supporting Information). The structural consistency and phase purity of compound **1** was confirmed by X-ray powder diffraction patterns (see Figure S3).

Magnetic Properties

Magnetic measurement of **1** was carried out with a magnetic field of 500 Oe in the temperature range 2–300 K, and the results were presented in the form of a $\chi_M T$ vs. T plot and χ_M^{-1} vs. T plot (Figure 6), where χ_M is the corrected magnetic susceptibility per asymmetric $[Cu(C_4H_2O_4)(C_4H_6N_2)_2]$ unit.

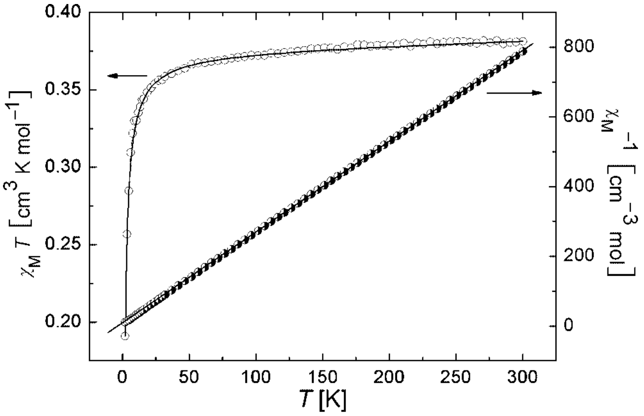

Figure 6. Plot of $\chi_M T$ vs. T and χ_M^{-1} vs. T for **1**.

Magnetic susceptibility data per Cu unit for **1** can be fitted by the Curie–Weiss law: $\chi_M = C/(T - \theta)$ above 2 K, and this gives a Curie constant C of 0.38 $cm^3 mol^{-1} K$ and a Weiss constant θ of –4.7 K. The C value is slightly larger than that expected (0.375 $cm^3 mol^{-1} K$) for one Cu^{II} (S = 1/2) ion. The negative Weiss constant indicates that there are weak antiferromagnetic interactions between the Cu^{II} ions through the maleate carboxyl bridge. The $\chi_M T$ value at room temperature is 0.38 $cm^3 mol^{-1} K$ and decreases gradually with decreasing temperature to a value of 0.35 $cm^3 mol^{-1} K$ at 25 K. The value then decreases sharply down to a minimum of 0.19 $cm^3 mol^{-1} K$ at 2 K, as shown Figure 6; this behavior is characteristic of an antiferromagnet.

The magnetic properties have been analyzed through the Bonner–Fisher result as shown in Equation (1), with $\chi = J/kT$ (J is the intrachain magnetic coupling parameter). We take into account a proportion ρ of a monomeric impurity, of which the susceptibility is assumed to follow the Curie law $Ng^2\beta^2S(S + 1)\rho/3kT$. The best fit obtained using a nonlinear regression analysis leads to $J = -1.54\ cm^{-1}$, $g = 2.05$, $R = 7.105395 \times 10^{-5}$, and $\rho = 0.048$; R is the agreement factor defined as $\sum i[(\chi_M T)_{obs}(i) - (\chi_M T)_{calcd.}(i)]^2/\sum[(\chi_M T)_{obs}(i)]^2$, TIP is temperature-independent paramagnetism.

Conclusions

An unusual 1D water chain with cyclic tetramers in a new 1D copper(II) coordination polymer chain has been successfully synthesized and structurally characterized. It is to be noted that the 1D water chain extends in an unusual association mode and is hydrogen bonded to surrounding 1D polymer chains to give a 3D network, thus highlighting

$$\chi = \frac{Ng^2\beta^2}{kT} \times \frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3} \times (1-\rho) + Ng^2\beta^2 S(S+1)\rho/3kT + TIP \quad (1)$$

the indispensable contribution to the stability of the coordination polymer frameworks. The unusual T4(1) water chain will enrich the water cluster family, and brings to light a novel mode for the cooperative association of water molecules and enhances the understanding of the 1D structural aspects of bulk water.

Experimental Section

Materials: All reagents for syntheses were purchased from commercial sources and used as received.

Physical Measurements: Elemental analyses (C, H, N) were performed with an Elementar Vario EL instrument. Infrared spectra (KBr pellets) were measured on a MAGNA-IR 560 FTIR spectrometer in the 400–4000 cm^{-1} region. Thermogravimetric analysis (TGA) was investigated with a standard TG-DTA analyzer under a flow of nitrogen at a heating rate of 10 $°Cmin^{-1}$ for all measurements. Magnetic studies were performed with MPMS SQUID and Maglab 2000 magnetometers in the temperature range 2–300 K. Powder diffraction data were collected with a Rigaku D/max-RC Diffractometer by using a Cu target (λ = 1.54060 Å) operated at 45 KV and 180 mA.

Synthesis of $\{[Cu(C_4H_2O_4)(C_4H_6N_2)_2](H_2O)_3\}_n$ (1): $Cu(OAc)_2\cdot H_2O$(0.20 g, 1 mmol), maleic acid (0.12 g, 1 mmol) and 2-methylimidazole (0.16 g, 2 mmol) in the molar ratio of 1:1:2 were dissolved in distilled water (25 mL). The pH value was then adjusted to about 7 with 2 M NaOH. The resulting solution was heated at 60 °C for 1 hr while stirring. The solvent was allowed to evaporate slowly at room temperature; small light blue single crystals appeared at the bottom of the cup. $C_{12}H_{20}CuN_4O_7$: C 36.41, H 5.09, N 14.15; found C 37.26, H 4.95, N 14.48%.

X-ray Crystallography: Single-crystal X-ray diffraction data for complex **1** was collected with a R-AXIS RAPID IP diffractometer, by using the ω-scan technique with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined on F^2 by full-matrix least-squares with SHELXTL-97.[45] Non-hydrogen atoms were refined with anisotropic temperature parameters and the hydrogen atoms of the ligands were refined as rigid groups; the hydrogen atoms of water were not found or assigned. Crystal data of **1**: M = 395.86 $g mol^{-1}$, trigonal, space group $P3_221$, a = 14.868(3), b = 14.868(3), c = 6.9774(14) Å, γ = 120°, V = 1335.8(5) Å^3, Z = 3, R_1 = 0.0223, wR_2 = 0.0592, $d_{calcd.}$ = 1.476 $g cm^{-3}$, μ = 1.266 mm^{-1}, $F(000)$ = 615. A total of 12859 reflections were collected, of which 2049 unique reflections were used. The selected bond lengths and angles of **1** are presented in Table 1.

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

C(1)–C(2)	1.486(3)	C(2)–N(2)	1.330(2)
C(2)–N(1)	1.333(3)	C(3)–C(4)	1.350(3)
C(3)–N(1)	1.375(3)	C(5)–O(2)	1.248(2)
C(5)–O(1)	1.267(2)	C(5)–C(6)	1.489(3)
C(6)–C(6)#1	1.316(4)	Cu(1)–N(2)	1.9579(15)
Cu(1)–N(2)#2	1.9579(15)	Cu(1)–O(1)	2.0283(12)
Cu(1)–O(1)#2	2.0283(12)	Cu(1)–O(2)	2.4833(14)
N(2)–C(2)–N(1)	109.63(16)	N(2)–C(2)–C(1)	126.79(18)
N(1)–C(2)–C(1)	123.58(19)	C(4)–C(3)–N(1)	106.21(18)
C(3)–C(4)–N(2)	108.63(17)	O(2)–C(5)–O(1)	121.77(16)
O(2)–C(5)–C(6)	120.05(18)	O(1)–C(5)–C(6)	118.14(17)
C(6)#1–C(6)–C(5)	124.31(10)	N(2)–Cu(1)–N(2)#2	97.37(9)
N(2)–Cu(1)–O(1)	161.91(6)	N(2)#2–Cu(1)–O(1)	91.74(6)
O(1)–Cu(1)–O(1)#2	84.03(8)	O(2)–Cu(1)–O2)#2	143.59(7)

[a] Symmetry codes for **1**: $^{\#1}$ $y, x, -z$; $^{\#2}$ $y, x, -z + 1$.

CCDC-615376 (for **1**) contains 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.

Supporting Information (see footnote on the first page of this article): The TG curve, IR spectra, and XRD powder diffraction of **1** (Figure S1, Figure S2 and Figure S3).

Acknowledgments

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