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Novel Self-Assembled Chain of Water Molecules in a Metal-Organic Framework Structure of Co(II) with Tartrate Acid

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1-D water chains constructed by dimer water clusters and edge-sharing cyclic pentamer have been observed in the compound $[Co(C_4H_4O_6)(2,2'\text{-bipy})\cdot 5H_2O]$ (**1**), in which the water chains join the 1-D coordination polymeric chains to a 3-D network through hydrogen-bond interactions.

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[1] and in designing new materials.[2] Hydrogen-bonding interactions and their fluctuations determine the properties of water in bulk, as well as in molecular confinements, although they still remain as ill-understood phenomena.[3] The key to understanding the behavior of water is the precise structural data of various hydrogen-bonded water networks in diverse environments. It is this realization that has prompted extensive investigations of water structures in recent years. Some discrete water clusters $(H_2O)_n$,[3a,4−16] where $n = 2-10$, 12, and 16, in various crystal hosts at room temperature have been reported. While the study on these clusters link themselves to form a larger network is very little,[17−20] we report here the structure of a highly ordered infinite chain of water molecules found in the host of a supramolecularly built metal−organic framework (MOF). These one-dimensional water chains assemble coordination polymeric chains to form the overall three-dimensional MOF structure.

The compound $[Co(C_4H_4O_6)(2,2'\text{-bipy})\cdot 5H_2O]$ (**1**) was prepared[21] by hydrothermal reaction of $Co(OAc)_2\cdot 4H_2O$ (0.46 g, 1.85 mmol), tartaric acid (0.56 g, 0.37 mmol), 2.2′-bipydine (0.30 g, 1.9 mmol), and water (15 mL) at 170 °C for 56 h. The X-ray crystallographic study[22] reveals that each Co^{2+} ion is coordinated by two halves of tartrate dianions

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(21) Synthesis of **1**: The hydrothermal reaction of the mixture of $Co(OAc)_2\cdot 4H_2O$ (0.46 g, 1.85 mmol), tartric acid (0.56 g, 0.37 mmol), 2.2′-bipidine (0.30 g, 1.9 mmol), and water (15 mL) was carried out at 170 °C for 56 h, when the pH value was adjusted to ca. 7. After the reactant was cooled to room temperature, the red block crystals were collected. Yield: 56%. Anal. Calcd for $CoC_{14}H_{22}N_2O_{11}$ **1**, (Mr = 453.27): C, 37.06; H, 4.85; N, 6.18. Found; C, 36.87; H, 4.92; N, 6.23%. FT-IR (KBr, cm^{-1}): 3421(br, m), 1637(s), 1605(s), 1472(m), 1447(m), 1363(s), 1314(m), 1129(m), 1058(m), 826(m), 776(m), 734(m).

(22) Crystal diffraction intensities for **1** were collected at 293 K with a Siemens SMART system equipped with a CCD detector with Mo Kα radiation at 0.71073 Å. Absorption corrections were applied using SADABS. The structure were solved with direct methods and refined with the full-matrix least-squares technique based on F^2 using the SHELXTL program package. Anisotropic thermal parameters were applied to all nonhydrogen atoms. The hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Crystal data for **1**: crystal dimensions $0.5 \times 0.2 \times 0.2$ mm^3, orthorhombic, space group $P2_12_12_1$, $a = 6.6289(13)$ Å, $b = 14.266(3)$ Å, $c = 19.151$ Å, $V = 1181.1(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.662$ g cm^{-3}, $M = 453.27$. μ(Mo Kα) = 1.012 mm^{-1}, 10 794 reflections were measured, and 4048 ($I \geq 2\sigma(I)$) unique reflections were used in all calculations. The final R1 = 0.0531, wR2 = 0.1255, GOF = 1.088.

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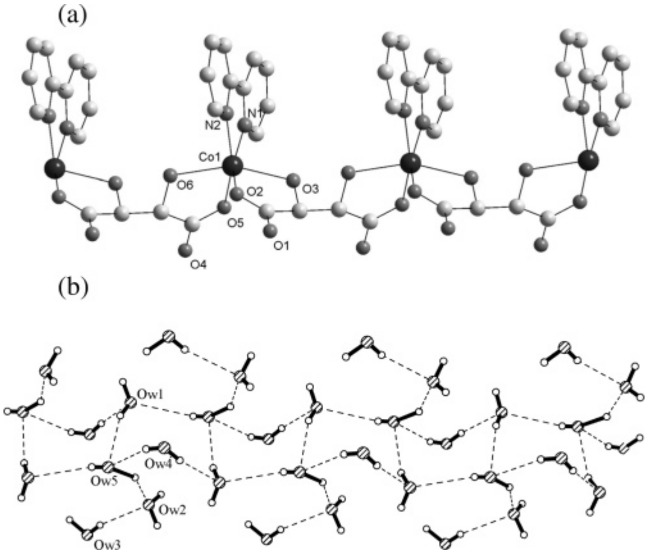

Figure 1. (a) View of the coordination polymeric chain along the crystallographic *a* axis and (b) hydrogen-bonding motif of the self-assembled chain of water molecules.

via chelation through the alcohol and the carboxylate groups. The octahedral geometry around each cobalt atom is completed by a chelating 2,2′-bipy molecule. Thus, the tartrates are tetradentate and link the metal ions to a one-dimensional supramolecular chain along an axis (shown in Figure 1a). It must be mentioned that the five crystallographically unique lattice water molecules and their symmetry-related molecules link to each other to form a 1-D water chain through hydrogen bonds. The IR spectrum shows the broad band centered around 3400 cm^{-1}, which is comparable to the O−H stretching vibrations of water clusters in other MOFs (3400−3500 cm^{-1} range).

Figure 1b displays the coordination environment of the water chain, which consists of a cyclic water pentamer and a dimer water cluster. The individual pentamer is formed by three types of water molecules, Ow1, Ow4, and Ow5. Ow1 hydrogen-bonds to three other water molecules as both hydrogen acceptor and as donor; Ow4 only acts as a hydrogen-bond donor to link Ow1 and Ow5, while the coordinated Ow5 is in a tetrahedral geometry, which is constructed by three hydrogen bonds in the cyclic pentamer and one hydrogen bond with the water dimer. So, the cyclic water pentamers are involved into a 1-D water chain through the sharing-edge Ow1−Ow5. The other two types of water molecules, Ow2 and Ow3, form the water dimer as acceptor and donor, respectively. The dimers attach to the sides of the 1-D water chain, alternatively, by hydrogen bonds between Ow5 and Ow2. Thus, the edge-sharing cyclic pentamer and the dimer water clusters constructed the 1-D infinite water chain along *a* direction. The hydrogen-bonding parameters are reported in Table 1. The average O···O distances in the water chain is 2.829 Å, which is slightly shorter than those observed in liquid water (2.854 Å)[23] and comparable to those in the ice II phase (2.77−2.84 Å).[24] This distance is comparable to the ones of other water chain examples in MOFs or organic hosts.

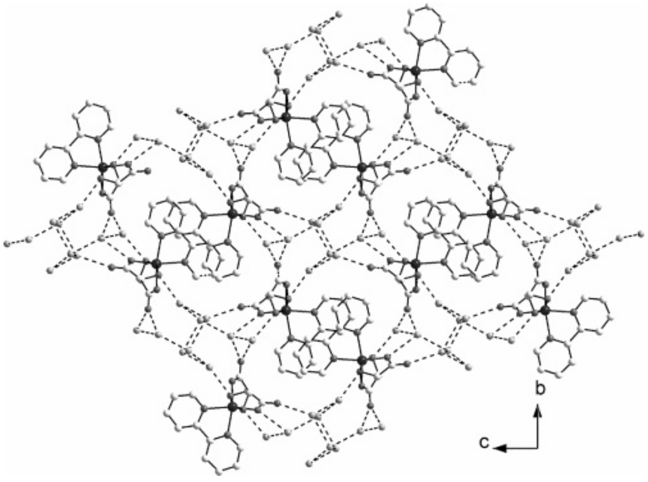

Figure 2. Packing diagram of the supramolecular system viewed along the crystallographic *a* axis. Carbon, white; nitrogen, medium gray; oxygen, medium gray; cobalt, dark gray; water molecule, light gray.

Table 1. Geometrical Parameters of Hydrogen Bonds (Å, deg) for the Water Chain and Its Association with the Host in **1**

D−H···A	d(D···A)	<DHA
OW1−H1B···O4	2.747	158.86
OW1−H1A···OW5[$-x, y + 1/2, -z + 1/2$]	2.757	149.99
OW2−H2B···O5	2.877	161.71
OW2−H2A···O1 [$-x, y + 1/2, -z + 1/2$]	2.924	145.64
OW3−H3B···OW2	2.859	165.13
OW3−H3A···O1 [$-x - 1, y + 1/2, -z + 1/2$]	2.806	167.47
OW4−H4A···OW5	2.880	155.19
OW4−H4B···OW1 [$-x - 1/2, -y + 1, z - 1/2$]	2.860	166.34
OW5−H5B···OW1 [$-x + 1/2, -y + 1, z - 1/2$]	2.816	166.73
OW5−H5A···OW2 [$-x - 1/2, -y + 1, z - 1/2$]	2.801	149.30
O3−H3C···OW3	2.679	171.09
O6−H6···OW4 [$x + 1, y, z$]	2.627	174.09

Figure 2 displays the packing structure parallel *bc* plane of compound **1**. The water chains act as a “glue” to reinforce the coordination polymeric chains forming an overall 3-D structure. Each water chain links four polymeric chains, and each polymeric chain attaches two water chains through hydrogen bonds between the water molecules and the carboxyl, as well as the hydroxyl, groups of tartrate. As listed in Table 1, the hydroxyl groups (O3 and O6) act as the hydrogen donors to bond with Ow3 and Ow4, respectively, while the carboxyl oxygen atoms (O1, O4, and O5) hydrogen-bonded as acceptors to Ow2 and Ow3, Ow1, and Ow2, respectively. Here, both water−MOF and water−water interactions are important for the stability of the overall structure. It is interesting that four water chains and four polymeric chains interact to form a 1-D channel with 2,2′-bipy molecules filled in. It can be supposed that the 2,2′-bipy molecule acts as a template for the formation of the overall 3-D network. That is to say, the MOF host sufficiently affects the structure of water clusters and the water clusters maybe also influence the arrange of the MOF host. This phenomenon is being verified by further study through changing the *N*-heterocyclic or polycarboxylate ligands.

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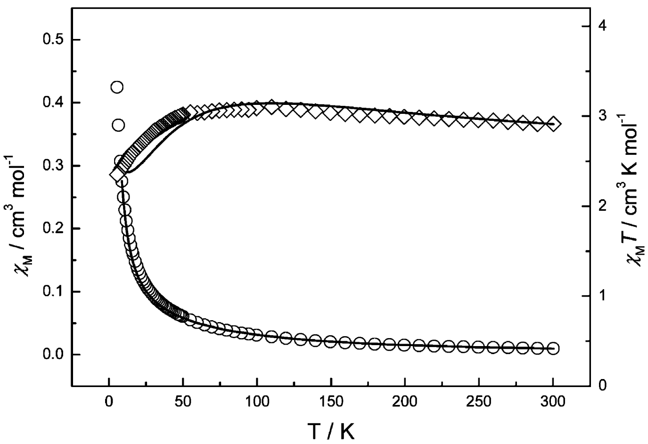

Figure 3. Temperature dependence of $\chi_M{}^{-1}$ and $\chi_M T$ for **1** (solid lines represent the theoretical fits).

The interactions among the water molecules themselves and the MOF are moderately strong, as thermal gravimetric analysis in air shows that weight loss occurs in stages beginning at 60 °C and the loss of 19.18% corresponding to all of the water (calculated 19.87%) takes place above 150 °C. Complete decomposition is achieved at 350 °C. Powder X-ray diffraction patterns of **1** show the changes in peak position and intensities before and after water expulsion, although sharp peaks remain, suggesting breakdown of the host lattice due to the exclusion of water.

Temperature-dependent magnetic susceptibility measurement for **1** was performed on the polycrystalline sample in the temperature range of 2−300 K. The temperature dependence of χ_M and $\chi_M T$ is shown in Figure 3. The $\chi_M T$ value is 2.91 cm^3 K mol^{-1} at room temperature, which is much larger than the spin-only value of 1.87 cm^3 K mol^{-1} for high-spin Co(II) ($S = 3/2$). The magnetic behavior should be due to a larger orbital contribution arising from the $^4T_{1g}$ ground state of Co(II). Upon cooling, the $\chi_M T$ value increases steadily to 3.10 cm^3 K mol^{-1} at 110 K, and then decreases to 2.12 cm^3 K mol^{-1} at 2 K, which implies the presence of ferromagnetic interactions between Co(II) ions in the 1-D supramolecular chain of **1**, which is further confirmed by a positive Weiss constant, $\theta = +\,11.4$ K, derived from the Curie−Weiss law.

A detailed quantitative analysis of the susceptibility data for cobalt(II) complexes is complicated by the fact that single-ion effects, such as the orbital moment, spin−orbit coupling, distortions from regular stereochemistry, electron delocalization, and crystal field mixing of excited states into the ground state, affect the magnetic properties (in addition to a possible magnetic interaction).[25] In a first approach, we have attempted to fit the experimental susceptibility using the classical spin Heisenberg model for a one-dimensional chain of $S = 3/2$.[26] A reasonable agreement was obtained with the parameters $J = 3.2$ cm^{-1} and $g = 2.2$ at $T > 70$ K, but the results are not very satisfactory in the low-temperature region. This may originate from the fact that the model does not take into account the effects of the zero-field splitting and/or spin−orbit coupling which are significant for Co(II).

Then we try to fit the data with the mononuclear Co(II) complex with the equation for spin−orbital coupling, calculating the λ value and A parameter, which gives the measurement of the crystal field strength to the interelectronic repulsions ($x = \lambda/k_BT$, k represents the electron delocalization).[27] A magnetic susceptibility equation was obtained as follows

$$\chi_{Co} = \frac{N\beta^2}{3kT}\,\frac{\left[\frac{7(3-A)^2x}{5} + \frac{12(A+2)^2}{25A} + \left\{\frac{2(11-2A)^2x}{45} + \frac{176(A+2)^2}{675A}\right\}\exp\left(-\frac{5Ax}{2}\right) + \left\{\frac{(A+5)^2x}{9} - \frac{20(A+2)^2}{27A}\right\}\exp(-4Ax)\right]}{\frac{x}{3}\left[3 + 2\exp\left(-\frac{5Ax}{2}\right) + \exp(-4Ax)\right]} \tag{1}$$

$$\chi_M = \chi_{Co}/[1 - \chi_{Co}(2zJ'/Ng^2\beta^2)] \tag{2}$$

λ is the spin−orbit coupling constant ($\lambda = -176.0$ cm^{-1} is the free-ion value). A is a crystal field parameter ($A = 1.5$ is the weak-field limit and $A = 1.0$ is the strong-field limit).

Second, because of the very weak magnetic interactions between ions, the expression (eq 1) must also be corrected for the magnetic exchange. The molecular field approximation may be used for this purpose and is illustrated in eq 2, where χ_M is the exchange coupled magnetic susceptibility actually measured, χ_{Co} is also the magnetic susceptibility in the absence of the exchange field, zJ' is the exchange parameter and the rest of the parameters have their usual meanings.

The best fit is obtained with values of $g = 2.11$, $\lambda = -130$ cm^{-1}, $A = 1.0$, $zJ' = 0.12$ cm^{-1}, and the agreement factor R is 6.7×10^{-3} ($R = \Sigma[(\chi_M)^{obs} - (\chi_M)^{calc}]^2/[(\chi_M)^{obs}]^2$). The calculated g value is comparable to that obtained from EPR results (2.063). The fitting results indicate that the surrounding of Co(II) is the comparatively strong-field state and a slightly distorted octahedral arrangement which is consistent with the crystal structure.

In conclusion, we have experimentally presented a well-resolved water chain, which acts as a glue to stabilize the host chains. The precise structural data and the cooperative association of the water cluster and crystal host in **1** may be helpful in improving our understanding of the contribution of water clusters to the stability and function of the biological assemblies, as well as anomalous properties of water.

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Supporting Information Available: X-ray crystallographic files in CIF format, TGA curve, and X-ray powder diffraction patterns for **1** before and after the exclusion of water. This material is available free of charge via the Internet at http://pubs.acs.org.

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