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Formation of One-Dimensional Metal–Water Chain Containing Cyclic Water Hexamers

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Cyclic water hexamers containing 1-D metal–water chains have been observed in the complexes of $[M(H_2biim)_2(OH_2)_2](ina)_2\cdot 4H_2O$ [M = Zn (**1**) and Co (**2**), H_2biim = 2,2′-biimidazole, ina = isoniconate]. The water clusters are trapped by the cooperative association of coordination interactions as well as hydrogen bonds.

The study of water clusters is important to an understanding of the structures and characteristics of liquid water and ice.[1,2] In the past several decades, considerable attention has been paid to theoretical[3,4] and experimental[5−7] studies of small water clusters. Among the clusters, the water hexamer is markedly interesting as it is the building block of ice I_h[8] and appears to be relevant to liquid water as well.[9] Theoretical calculations have found that several different isomers for the water hexamer, such as ring, book, bag, cage, and prism topologies, are almost isoenergetic.[4] The less-stable ring hexamers have been isolated and characterized by IR spectroscopy[10] and X-ray crystallographic analysis.[11−13] To date, chair,[11] boat,[12] and planar[13] cyclic hexamers trapped by hydrogen bonding in host lattices have been reported. Herein, we report two metal−water chain complexes of $[M(H_2biim)_2(OH_2)_2](ina)_2\cdot 4H_2O$ [M = Zn (**1**) and Co (**2**), H_2biim = 2,2′-biimidazole, ina = isoniconate] containing the cyclic water hexamer, in which the water cluster is trapped not only by hydrogen bonds but also by coordination interactions.

Complexes **1** and **2** were obtained by the reaction of metal salt, H_2biim, and ina in the molar ratio of 1:2:2 at pH = 4.8 in methanol solution,[14] and they were revealed by X-ray diffraction to be isostructural.[15] They consist of one $[M(H_2biim)_2(OH_2)_2]^{2+}$ cation, two ina anions, and four lattice water molecules. The M^{II} ion locates on a symmetry center and is

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Table 1. Hydrogen-Bonding Parameters in **1** and **2**

D-H···A	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (deg)
Complex **1**				
O(1w)−H(1wa)···(1)	0.82	1.97	2.789	178
O(1w)−H(1wb)···O(3w)	0.85	2.01	2.813	157
N(3)−H(3)···O(2)	0.86	1.86	2.715	171
N(4)−H(4)···O(1)	0.86	1.88	2.739	172
O(2w)−H(2wa)···O(1w)	0.85	2.00	2.839	170
O(2w)−H(2wb)···N(5)	0.84	2.02	2.847	169
O(3w)−H(3wb)···O(2)	0.85	2.02	2.865	174
O(3w)−H(3wb)···O(2w)	0.85	1.97	2.806	167
Complex **2**				
O(1w)−H(1wa)···O(1)	0.82	1.95	2.766	180
O(1w)−H(1wb)···O(3w)	0.87	1.88	2.751	170
N(3)−H(3)···O(2)	0.86	1.86	2.711	172
N(4)−H(4)···O(1)	0.86	1.89	2.747	173
O(2w)−H(2wb)···O(2)	0.85	2.01	2.853	174
O(2w)−H(2wa)···O(1w)	0.83	2.09	2.892	162
O(3w)−H(3wa)···O(2w)	0.71	2.16	2.840	178
O(3w)−H(3wb)···N(5)	0.91	1.96	2.849	166

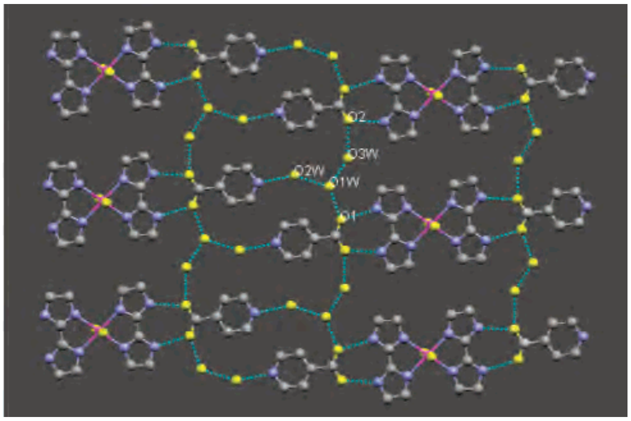

Figure 1. View of the coordination environment of metal ion and the 2-D hydrogen-bonded net concerned on *ab* plane. All hydrogen atoms are omitted for clarity.

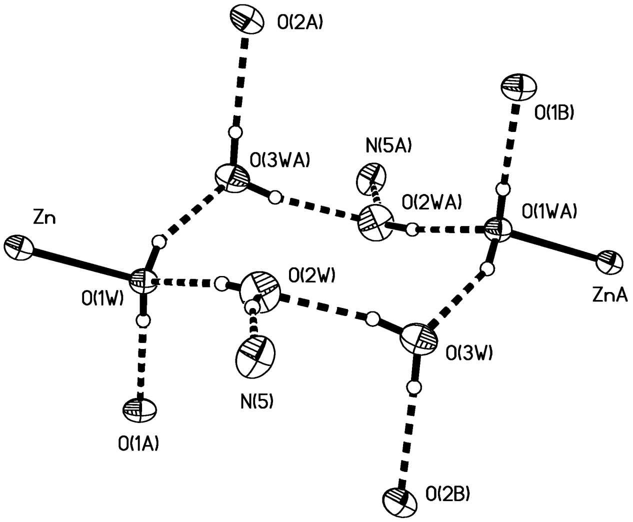

Figure 2. ORTEP plot showing the cyclic water hexamer and its coordination environment.

coordinated by four nitrogen atoms from two H$_2$biim ligands [Zn−N(1) = 2.132(2) Å and Zn−N(2) = 2.160(3) Å for **1**; Co−N(1) = 2.133(2) Å and Co−N(2) = 2.151(2) Å for **2**] arranged trans to each other on the equatorial plane and two aqua ligands [Zn−O(1W) = 2.218(2) Å and Co−O(1W) = 2.157(2) Å] occupying the apical coordination sites to furnish an octahedral geometry. The two rings of H$_2$biim are almost coplanar, with dihedral angels of 1.8° for **1** and 1.9° for **2**, and the metal ion locates on the plane. These angles are comparable to previously reported values.[16,17] Each [M(H$_2$-biim)$_2$(H$_2$O)$_2$]$^{2+}$ cation is attached to two ina anions via hydrogen bonds with distances of N(3)···O(2) = 2.715(4) and 2.711(3) Å and N(4)···O(1) = 2.739(4) and 2.747(3) Å for **1** and **2**, respectively. The N−H···O hydrogen bonds are basically linear (Table 1), and the four atoms N(4), O(1), N(3), and O(2) are almost coplanar, with a mean deviation of 0.028 Å for **1** and 0.03 Å for **2**. The [M(H$_2$biim)$_2$(OH$_2$)$_2$]-(ina)$_2$ moieties are further connected to each other via hydrogen bonds with the water molecules as bridges [O(2w)···O(1w) = 2.839 and 2.892 Å, O(1w)···O(1) = 2.789 and 2.766 Å, O(2w)···N(5) = 2.847 and 2.849 Å, O(3w)···O(2) = 2.865 and 2.853 Å, and O(1w)···O(3w) = 2.813 and 2.751 Å for **1** and **2**, respectively], resulting in 2-D layers in the *ab* plane, as shown in Figure 1.

Interestingly, a cyclic centrosymmetric water hexamer that adopts a chair conformation (Figure 2) is observed in the solid state. The hydrogen-bonding parameters are reported

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(14) The detailed syntheses for **1** and **2** are as follows: M(NO$_3$)$_2$·6H$_2$O (0.5 mmol) dissolved in methanol (10 mL) was added to a methanol solution (10 mL) containing H$_2$biim (0.134 g, 1 mmol) dropwise, and the mixture was refluxed until the ligand had dissolved. To the resulting solution was added isonicotinic acid (0.121 g, 1 mmol). The resulting mixture was adjusted to pH ≈ 4.8 with dilute sodium hydroxide and further stirred at 60 °C for 2 h. The insoluble components were removed by filtration, and the filtrate was allowed to stand at room temperature. The colorless and orange products, respectively, were collected after slow evaporation at room temperature for about 2 weeks. Yields: 45% for **1** and 50% for **2**. Anal. Calcd for $C_{24}H_{32}N_{10}O_{10}Zn$, **1** ($M_r$ = 685.99): C, 42.13; H, 4.62; N, 20.49. Found: C, 41.99; H, 4.66; N, 20.41%. FT-IR (KBr, cm^{-1}): 3517−2556 (br, m), 1587 (s), 1552 (m), 1533 (m), 1444 (m), 1390 (vs), 1133 (m), 993 (m), 769 (s), 690 (s). Calcd for $C_{24}H_{32}N_{10}O_{10}Co$, **2** ($M_r$ = 679.53): C, 42.55; H, 4.66; N, 20.47. Found: C, 42.38; H, 4.71; N, 20.60%. FT-IR (KBr, cm^{-1}): 3387−2556 (br, m), 1587 (s), 1551 (m), 1533 (m), 1443 (m), 1390 (vs), 1132 (m), 992 (m), 769 (s), 688 (s).

(15) Crystal diffraction intensities for **1** and **2** were collected at 293 K on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were applied using SADABS. The structures 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 non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C−H = 0.96 Å); the water hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Crystal data for **1**: _crystal dimensions 0.29 × 0.12 × 0.08 mm, triclinic, space group $P\bar{1}$, a = 8.757(4) Å, b = 9.427(4) Å, c = 10.313(5) Å, α =104.909(8)°, β = 101.030(7)°, γ = 107.872(7)°, V = 748.4(6) Å^3, Z = 1, ρ_{calcd} = 1.522 g cm^{-3}, M = 685.96, μ(Mo Kα) = 0.892 mm^{-1}. Of the 2627 symmetry-independent reflections (2.143° < θ < 24.99°), 2428 reflections are observed [$I > 2\sigma(I)$]. On the basis of all of these data and 242 refined parameters, R1= 0.0333, wR2 = 0.0865, and GOF on F^2 of 1.050 were obtained. Crystal data for **2**:_crystal dimensions 0.30 × 0.08 × 0.06 mm, triclinic, space group $P\bar{1}$, a = 8.7494(8) Å, b = 9.4132(8) Å, c = 10.2955(9) Å, α = 105.300(1)°, β = 101.326(2)°, γ = 107.627-(1)°, V = 743.4(1) Å^3, Z = 1, ρ_{calcd} = 1.518 g cm^{-3}, M = 679.51, μ(Mo Kα) = 0.649 mm^{-1}. Of the 2612 symmetry-independent reflections (2.143° < θ < 24.99°), 2461 reflections are observed [$I > 2\sigma(I)$]. On the basis of all of these data and 242 refined parameters, R1= 0.0306, wR2 = 0.0871, and GOF on F^2 of 1.001 were obtained.

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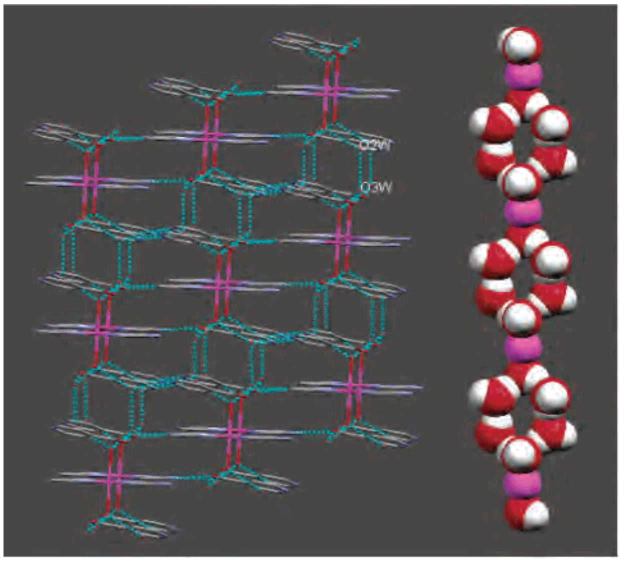

Figure 3. 3-D hydrogen-bonded network of the complexes (left). View of a cyclic water hexamer containing a metal−water chain containing running along the *c* axis, with H_2biim ligands are omitted for clarity (right).

in Table 1. The average O···O distances are 2.82 and 2.83 Å for **1** and **2**, respectively. These distances are slightly longer than the corresponding values in ice I_h (2.759 Å)[8] and in water trapped in organic compound of DMNY·2.5H_2O (2.776 Å, DMNY = 2,4-bimethyl-5-aminobenzo[*b*]-1,8-naphthyridine)[11c] and metal−organic framework of [Pr(pdc)(Hpdc)(H_2O)$_2$]·4H_2O (2.783 Å, pdc = pyridine-2,6-dicarboxylic acid),[11g] as well as the calculated value of 2.718 Å for cyclic water hexamer.[5] However, they are shorter than those observed in liquid water (2.854 Å)[9] and the ring water hexamer with a planar geometry (2.905 Å)[13a] and comparable to those in the ice II phase (2.77−2.84 Å).[1a] The average O···O···O angles are 109.7° for **1** and 110.0° for **2**, which are comparable to the value of 109.3° in the hexagonal ice, but smaller than that observed in DMNY·2.5H_2O (116.5°)[11c] and larger than that in [Pr(pdc)(Hpdc)(H_2O)$_2$]·4H_2O (98.36°).[11g] The coordinated water molecule is in a tetrahedral geometry with two water−water hydrogen bonds, one from the water−carboxylate hydrogen bond and one from the water−metal coordination bond. Meanwhile, each of the other water molecules involves three hydrogen bonds with two water−water interactions and one water−carboxylate oxygen or water−pyridyl nitrogen atom of the ina ligand. Therefore, each water molecule acts as both donor and a hydrogen acceptor to form a cyclic water hexamer. This is very different from the unique example of a metal-coordinated hexameric cluster in which the coordinate water molecules behave only as hydrogen donors, resulting in a tricoordination, and the other water molecules show tetracoordination.[11g] Finally, the average O···O distances (2.82 Å for **1** and 2.83 Å for **2**) and O···O···O angles (109.7° for **1** and 110.0° for **2**) of the hexamer are larger than those observed in [Pr(pdc)(Hpdc)(H_2O)$_2$]·4H_2O (2.783 Å, 98.36°).[11g] Two of the water molecules in the cyclic hexamers of **1** and **2** bind to the metal ions, resulting in an infinite metal−water chain (Figure 3). To the best of our knowledge, such cyclic water clusters containing metal−water chains are very rare.[11g,17,18] This observation indicates that the water hexamer is stabilized not only by hydrogen bonding but also by coordination interactions. Another remarkable feature is that the 2-D layers are assembled into a 3-D structure uniquely by the water hexamers through hydrogen bonding between symmetry-related O(2w) and O(3w) [O(2w)···O(3w) = 2.806 Å for **1** and 2.840 Å for **2**], indicating that the cyclic water hexamer plays a crucial role in the formation of the 3-D structure. Indeed, when the lattice water molecules were removed under reduced pressure, the crystals broke down. However, a single crystal of [Zn(H_2biim)$_2$(H_2O)$_2$](MeCO_2)$_2$ suitable for X-ray crystallographic analysis was obtained by the similar reaction in an ethylene glycol solution,[16a] in which the geometries of the coordinate cation [Zn(H_2biim)$_2$(H_2O)$_2$]$^{2+}$ are almost the same as those of **1** except that the distance of Zn−O(w) = 2.150(3) Å is significantly shorter than that in **1** [2.218(2) Å]. These observations strongly indicate that the water cluster elongates the metal−water bond via formation of hydrogen bonds.

In summary, we have observed two cyclic water hexamers containing metal−water chains in which the water clusters are trapped not only by an organic molecule via hydrogen bonds but also by the metal ion via coordination interactions. The cooperative association among the metal ion, the water molecule, and the organic molecule plays a crucial role in the formation of the water cluster and its multidimensional architecture. Moreover, the formation of the water cluster has a significant influence on the water molecule binding to the metal ion. This observation can help us understand the formation of water clusters in nature and biological system.

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Supporting Information Available: X-ray crystallographic file in CIF format for the structure determination of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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