Tapes of Cyclic Water Tetramers in the Double-Helical Complex $[Cd_2(bpa)_2Cl_4]\cdot 6H_2O$

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The new complex $[Cd_2(bpa)_2Cl_4]\cdot 6H_2O$ [bpa = *N*,*N′*-bis(picolinamide)azine] has been synthesized in which each bpa ligand is twisted into a spiral-like conformation and the two Cd^{II} ions are ligated by two bpa ligands to form a double-stranded binuclear helicate. Unprecedented water chains featuring cyclic water tetramers composed of three independent water molecules are trapped by $[Cd_2(bpa)_2Cl_4]$ double helicates by hydrogen bonds. The binuclear chiral helicates are interlinked into homochiral layers by hydrogen bonds with the water tapes. The layers are alternately stacked in a heterochiral fashion to yield the final racemic structure. The complex shows an endotherm at 65.7 °C in the DSC due to loss of water molecules, giving an enthalpy value of 47 $kJ\,mol^{-1}$ per water molecule.

Introduction

Considerable attention has been paid in the past decades to theoretical and experimental studies of small water clusters.[1,2] These studies facilitate an understanding of the structures and functions of liquid water and ice.[3] Among the water clusters, the cyclic $(H_2O)_4$ is very interesting as it is a simple two-structure model for liquid water.[4] Moreover, water chains are of great interest since many fundamental biological processes[5] and material properties[6] appear to depend on the unique properties of water chains. Structural studies have shown that water chains exist in gramicidin A membrane channels,[7] bacteriorhodopsin,[8] and α-amylase[9] for rapid transport of protons and act as "proton wires". The observation of water chains in porous materials[10] and organic hosts[11] exhibiting supramolecular interactions has significantly advanced the understanding of the structures and functions of water chains in biological systems. Furthermore, the homochiral units could assemble into higher dimensionalities and yield a conglomerate with coordination bonds[12] and/or hydrogen bonds.[13] Herein, we report the crystal structure of the double-helical complex $[Cd_2(bpa)_2Cl_4]\cdot 6H_2O$ (**1**) [bpa = *N*,*N′*-bis(picolinamide)azine], in which the lattice water molecules form an unprecedented water tape involving cyclic $(H_2O)_4$ units. Such a tape is relatively rare[14] and is further stabilized by hydrogen bonds to the host molecules. The chiral binuclear helicates are assembled into homochiral layers by the water tapes.

Results and Discussion

Complex **1** was obtained by the reaction of $CdCl_2$ and bpa in the molar ratio of 1:1 in a methanol/water solution. The crystal structure reveals that complex **1** consists of a neutral $[Cd_2(bpa)_2Cl_4]$ molecule and six lattice water molecules. As shown in Figure 1, each bpa ligand is twisted into a spiral-like conformation and the two Cd^{II} ions are ligated by two bpa ligands to form a double-stranded binuclear helicate. Two chloride anions complete a distorted octahedral coordination in a *cis* arrangement for each Cd^{II}, featuring potential chirality.

The two octahedra are bridged by two N–N single bonds in a twisted arrangement (Cd–N–N–Cd = 86.0° and Cd···Cd = 4.817 Å) with the diazine nitrogen atoms [Cd(1)–N(3) = 2.409(1) Å] in the metal equatorial plane and the pyridine nitrogen atoms [Cd(1)–N(1) = 2.421(1) Å] in the axial positions, resulting in a double helicate with each metal coordination environment having the same helicity (delta-delta or lambda-lambda), although both optical isomers coexist in the lattice. Notably, these binuclear chiral units are interlinked into homochiral units through hydrogen bonds [Cl···O(3w) = 3.23 Å] between the water chains, as shown in Figure 2.

The layers are alternately stacked in a heterochiral fashion to yield the final racemic structure. Although the bpa ligand bearing two bidentate sites have been used to construct binuclear triple helicates,[15] only three examples of double helicates have been prepared with competing counteranions and/or solvent molecules such as NO_3^-, N_3^- and H_2O.[16] The chloride ions arranged in the *cis* fashion in **1** not only serve as ligands, but also form hydrogen bonds with the water tapes. The homochiral helicates are interlinked into homochiral layers through the water tapes. This

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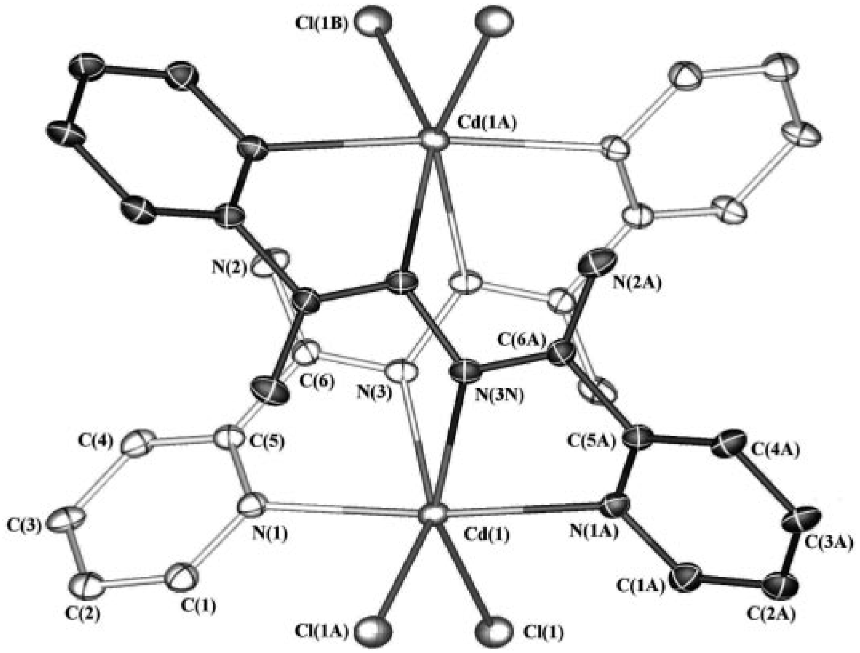

Figure 1. ORTEP view of the Cd^{II} coordination environments. Selected bond lengths [Å] and angles [°]: Cd(1)–N(1) 2.416(2), Cd(1)–N(3) 2.397(2), Cd(1)–Cl(1) 2.553(1); Cl(1)–Cd(1)–Cl(1a) 107.24(2), Cl(1)–Cd(1)–N(1) 97.29(6), Cl(1)–Cd(1)–N(3) 92.33(6), N(1)–Cd(1)–N(3) 68.59(7), C(6)–N(3)–N(3b)–C(6b) 147.4(2), Cd(1)–N(3)–N(3b)–Cd(1a) 86.0. Symmetry codes: a: 1/2 – *x*, 1/2 – *y*, *z*; b: 1/2 – *x*, *y*, 3/2 – *z*; c: *x*, 1/2 – *y*, 3/2 – *z*.

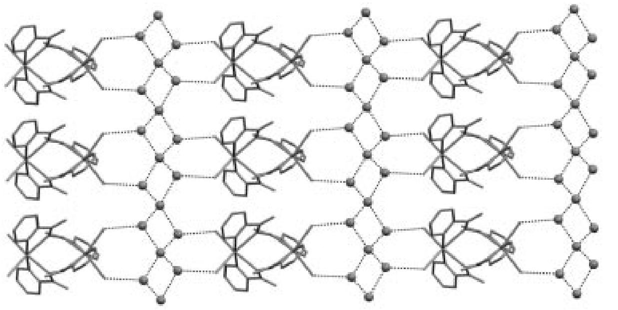

Figure 2. View of the hydrogen-bonded homochiral layer in the *ac* plane. The grey spheres represent the water oxygen atoms; all hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths and angles associated with the water tape and the host structure (D: donor atom; A: acceptor atom).

D–H···A	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]
293 K				
O(3w)–H···Cl	0.850	2.380	3.231	178
O(2w)–H···O(3w)	0.850	2.030	2.854	164
O(1w)–H···O(3w)	0.850	2.150	2.968	161
O(3w)–H···O(2w)	0.850	2.100	2.854	148
O(3w)–H···O(1w)	0.850	2.200	2.968	150
173 K				
O(3w)–H···Cl	0.850	2.380	3.228	172
O(2w)–H···O(3w)	0.850	2.000	2.829	163
O(1w)–H···O(3w)	0.850	2.080	2.919	168
O(3w)–H···O(2w)	0.850	2.110	2.829	141
O(3w)–H···O(1w)	0.850	2.260	2.919	136

is markedly different from the related complex $[Cd_2(bpa)_2(NO_3)_2(H_2O)_2](NO_3)_2\cdot 4H_2O$, in which no water chain was found due to the involvement of the NO_3^- anion in hydrogen bonds with water molecules.[16b]

Interestingly, infinite water tapes involving cyclic $(H_2O)_4$ units consisting of three types of water molecules extended along the *a* axis (Table 1, Figure 3) are observed in the solid state.

To the best of our knowledge, such an arrangementhas not been experimentally observed so far, althoughcyclic $(H_2O)_4$ units consisting of two[4c,4e,4g–4i,14] andfour[4a,4b,4d,4f] independent water molecules have been reported. However, cyclic water pentamers and hexamers containing three independent water molecules have been observed.[17,18] Both the O(1w) and O(2w) atoms are located on the axis of the water chain and are hydrogen bonded to four neighboring O(3w) water molecules [O(1w)···O(3w) = 2.969 or 2.919 Å, and O(2w)···O(3w) = 2.854 or 2.829 Å at 293 or 173 K] in a tetrahedral arrangement [∠O(3w)–O(1w)–O(3wc) = 91.3° and ∠O(3w)–O(2w)–O(3wc) = 96.1°, symmetry code c: *x*, 3/2 – *y*, 1/2 + *z*] to form a cyclic water tetramer. In contrast, the O(3w) molecule is trigonally distorted, in which hydrogen atom H(1wa) has a full occupancy and is hydrogen bonded to Cl(1d) [Cl(1d)···O(3w) = 3.23 Å, symmetry code d: –*x*, 1 – *y*, 1 – *z*]. The other hydrogen atoms H(1wb) and H(1wc) are positionally disordered and were treated as half occupancy atoms during the refinement. The average hydrogen bond length [2.912 (293 K) or 2.874 (173 K) Å] within the water tetramer in **1** is shorter than that (2.950 Å) observed in tac·$3H_2O$ (tac = 1,4,7,10-tetraazacyclododecane),[14] but significantly longer than those in other known cases (2.768–2.834 Å).[4f,4g,4i,4j] The four oxygen atoms in the tetramer are coplanar, with nonbonding dis-

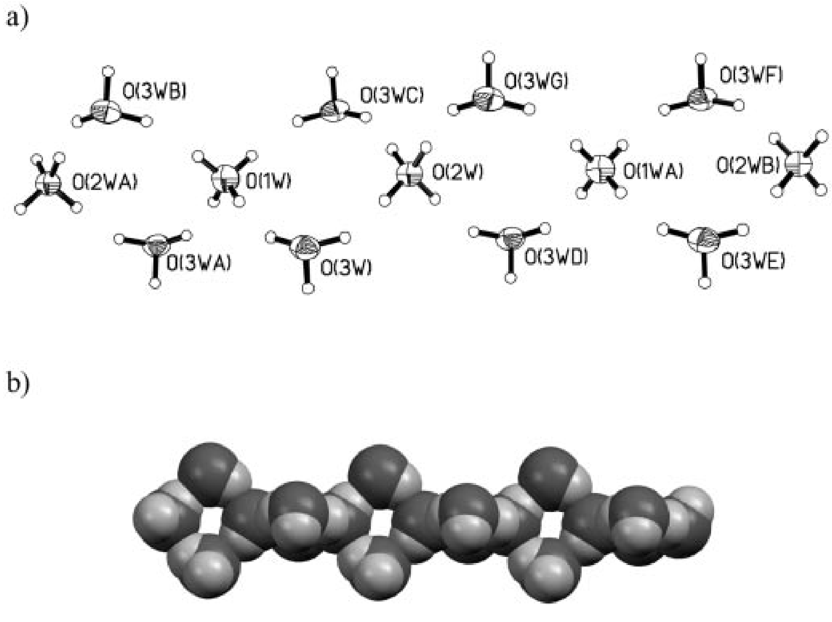

Figure 3. ORTEP (top) and CKP (bottom) plots showing a water chain involving the cyclic water tetramers running along the *a* axis. Symmetry codes: A: 1/2 – *x*, 3/2 – *y*, *z*; B: 1/2 – *x*, *y*, 3/2 – *z*; C: *x*, 3/2 – *y*, 1/2 – *z*; D: –1/2 – *x*, *y*, 3/2 – *z*; E: –1 + *x*, *y*, *z*; F: –1 + *x*, 3/2 – *y*, 3/2 – *z*; G: –1/2 – *x*, 3/2 – *y*, *z*.

tances O(1w)···O(2w) = 3.984 (293 K) or 3.947 (173 K) and O(3w)···O(3wc) = 4.254 (293 K) or 4.177 (173 K) Å, and an O(1w)–O(3w)–O(2w) angle of 92.3° (293 K) or 86.7° (173 K). Adjacent tetramers lie in a perpendicular fashion and are further assembled into a water tape by sharing corners. In fact, the water tape in **1** is very different from the only other example of a water tape involving cyclic water tetramers, which consists of two independent water molecules (O···O = 2.896 Å) that are further bridged by the third type of water molecule by hydrogen bonds (O···O = 3.004 Å) into a water chain with each water molecule tetracoordinate.[14] The nonbonding distances in the cyclic tetramer (O···O = 3.968 Å) and the successive tetramer (O···O = 4.923 Å) are markedly longer than those observed here. These differences may arise from the different hosts and the organization of the water molecules. This observation can help us understand the structure and formation of water clusters and tapes. Another significant phenomenon in **1** is that the water chains arranged in this unique fashion link the homochiral helicates into homochiral layers.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Figure 4) were also performed to observe the thermal stability of the water chain in **1**.

The TGA curve shows a weight loss of 11.0% in the temperature range 25–130 °C, which is consistent with the theoretical value of 11.3% for the loss of six water molecules. The DSC measurement done at 0–150 °C heating at a rate of 5 °C min^{-1} shows a single, sharp endotherm centered at 65.5 °C. The enthalpy is 47 kJ per water molecule, which is larger than that observed in infinite water chains (16 and 36 kJ mol^{-1}),[11e,11g] but similar to those in 4,4′-methylenebis(2,5-dimethylimidazole) dihydrate (44 kJ),[11e] tripeptides hydrates (53 kJ),[19] and theophylline monohydrate (47.3 kJ).[20] Obviously, these data can be correlated to the number and strength of hydrogen bonds per water molecule. In comparison with the IR spectrum of the free ligand (around 3464 and 3275 cm^{-1}), the peaks at 3234 and 3182 cm^{-1} of the complex can be assigned to the O–H stretching vibration of the water molecules of the tapes. These bands are close to the value reported for ice (3220 cm^{-1}),[21] but lower than those observed for the helical water chain in [Ni(Hsglu)(H$_2$O)$_2$]·3 H$_2$O [3368 and 3429 cm^{-1}, H$_2$sglu = *N*-(2-hydroxybenzyl)-L-glutamic acid][11h]

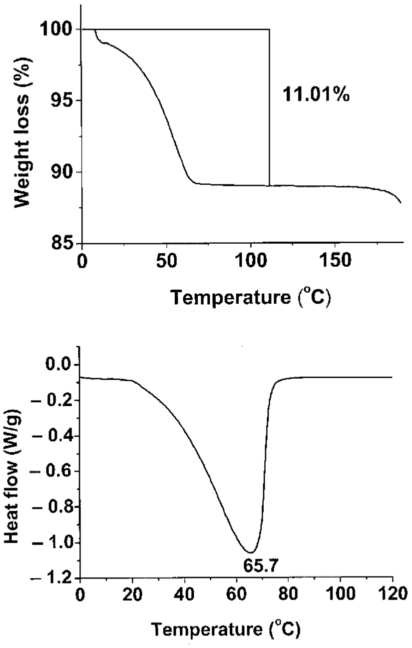

Figure 4. TG plot showing the weight loss of the sample on increasing the temperature (top) and a DSC plot displaying an endotherm for the loss of water molecules (bottom).

and the cyclic tetramer water in $[Fe_3(\mu_3\text{-}O)(\mu_2\text{-}CH_3COO)_6\text{-}(2\text{-pyridone})_2(H_2O)]ClO_4\cdot 4H_2O$ (3500 cm^{-1}).[4f]

Conclusions

In conclusion, we have described a new water tape featuring cyclic $(H_2O)_4$ units consisting of three independent water molecules, which is trapped by double-helical hosts through hydrogen bonds that link homochiral helicates into homochiral layers. This observation may provide an insight into the formation of water clusters and chains in nature and biological systems, and help our understanding of the mechanism of proton transport in living systems.

Experimental Section

General Remarks: The reagents and solvents employed were commercially available and used as received without further purification. The C, H and N microanalyses were carried out with a Vario EL elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Bruker Equinox 55 FT-IR spectrometer. ^{1}H NMR spectra were recorded on a Varian 300 MHz spectrometer at 25 °C. ESI-MS was carried out with a LCQ DECA XP. TGA analysis was performed on a NETZSCH TG 209 thermal analyzer under nitrogen atmosphere at a scan rate of 10 °C min^{-1}. The DSC curve was obtained with a NETZSCH DSC 204 Differential Scanning Calorimeter at a scan rate of 5 °C min^{-1}.

Synthesis of bpa: The bpa ligand was synthesized in accordance with a published procedure.[22] $C_{12}H_{12}N_6$ (240.11): calcd. C 59.99, H 5.03, N 34.98; found C 59.94, H 5.14, N 34.94. FT-IR (KBr): $\tilde{\nu}$ = 3464 cm^{-1} (vs), 1610 (vs), 1559 (vs), 1465 (s), 376 (s), 799 (s), 746 (vs), 672 (s). ^{1}H NMR (300 MHz, CD_3OD): δ = 8.58 (d, J = 3.0 Hz, 2 H), 8.34 (d, J = 5.1 Hz, 2 H), 7.84 (t, 2 H), 7.41 (t, 2 H) ppm. ^{13}C NMR (300 MHz, CD_3OD): δ = 1532, 150.8, 148.2, 136.0, 124.3, 120.7 ppm.

Synthesis of 1: $CdCl_2\cdot 2.5H_2O$ (0.3 mmol) and bpa were added in a 1:1 molar ration to a methanol/water solution (8:2 v/v) and the solution was stirred for 30 min. Crystals of **1** were obtained after one week (48% yield). $C_{24}H_{36}Cl_4Cd_2N_{12}O_6$ (955.27): calcd. C 30.18, H 3.80, N 17.60; found C 29.79, H 3.59, N 17.21. FT-IR (KBr): $\tilde{\nu}$ = 3396 cm^{-1} (m), 3303 (m), 3224 (m), 3182 (m), 1625 (vs), 1604 (s), 1582 (s), 1563 (s), 1483 (m), 1412 (vs), 1301 (m), 1011 (m), 796 (m),749 (m), 678 (m). ESI-MS: m/z = 810.67 $[Cd_2(bpa)_2Cl_3]^+$.

X-ray Crystallographic Study: Diffraction intensities of **1** were collected on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 293 and 173 K. Absorption corrections were applied using SADABS.[23] The structures were solved by direct methods and refined with a full-matrix least-squares technique based on F^2 using the SHELXTL program package.[24] Crystal data at 293 K: orthorhombic, space group *Pnnn*, a = 7.9680(4), b = 13.4830(7), c = 16.9690(8) Å, V = 1823.02(16) Å^3, Z = 2, D_c = 1.740 g cm^{-3}, F_{000} = 952, μ(Mo-K_α) = 1.514 mm^{-1}. Of the 2188 independent reflections (1.9° ≤ θ ≤ 28.3°), 2022 reflections were observed [$I \geq 2\sigma(I)$]. On the basis of all reflections and 111 refined parameters, $R1$ = 0.0207, $wR2$ = 0.0521, and GOOF on F^2 of 1.06 were obtained. At 173 K: orthorhombic, space group *Pnnn*, a = 7.8940(12), b = 13.418(2), c = 16.911(3) Å, V = 1791.2(5) Å^3, Z = 2, D_c = 1.771 g cm^{-3}, F_{000} = 952, μ(Mo-K_α) = 1.541 mm^{-1}. Of the 2097 independent reflections (1.9° ≤ θ ≤ 28.3°), 1815 reflections were observed [$I \geq 2\sigma(I)$]. On the basis of all reflections and 140 refined parameters, $R1$ = 0.0309, $wR2$ = 0.0761, and GOOF on F^2 of 1.04 were obtained. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C–H = 0.96 Å) and refined with isotropic temperature factors. The hydrogen atoms of the water molecule are disordered. One full-occupancy hydrogen atom H(3wa) and two half-occupancy hydrogen atoms H(3wb) and H(3wc) were located by difference maps and refined isotropically in a trigonal arrangement about O(3w). Water molecules O(1w) (1/4, 3/4, 3/4) and O(2w) (–1/4, 3/4, 3/4) are located on special positions with 0.25 occupancy; only two hydrogens [H(1w) and H(2w)] were located by difference map and refined isotropically as half-occupancy atoms and restrained using the DFIX command.

CCDC-253594 (at 293 K) and -253595 (at 173 K) 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.

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