Observation of an octameric water cluster containing a book-shaped hexamer in a 4f–3d complex

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An octameric water cluster consisting of a book-shaped water hexamer and two dangling water molecules has been observed in a 4f–3d ionic pair complex [Y(dpdo)$_2$(H$_2$O)$_4$][Co(CN)$_6$]·4H$_2$O.

The driving force behind the intensive experimental and theoretical investigations on water clusters lies in understanding the anomalous behavior of bulk water.[1] The structural elucidation of water clusters in diverse environments is key to gain insight into the nature of water–water interactions. The water hexamer is particularly interesting as it is a dominant form in ice and bulk water.[2] Theoretical calculation predicts that the hexamer represents the transition from 2D cyclic to 3D cage structure with a cage isomer as a stable configuration followed in order by the book, prism, ring and bag configurations.[3] A number of hexamers with different conformations have been observed in the solid state.[4] Larger water clusters including the octamer, decamer, dodecamer and hexadecamer have also been reported.[5] Theoretical prediction shows that the octameric water cluster exhibits two nearly isoenergetic isomers with S_4 and D_{2d} symmetries,[6] which gain experimental support in the observation of gas-phase C$_6$H$_6$(H$_2$O)$_8$ clusters and in molecular beams.[7] Octameric clusters observed in organic or organo-inorganic host matrixes exhibit conformations of cubane,[5e] opened cube[5f] and cyclic ring[5g] due to different environments imposed by the hosts. In this context, we report a new octameric water cluster in the crystalline solid [Y(dpdo)$_2$(H$_2$O)$_4$][Co(CN)$_6$]·4H$_2$O **1** (dpdo = 2,2′-dipyridine dioxide). The new cluster consists of a book-shaped cyclic water hexamer and two dangling water molecules.

Compound **1** was prepared by diffusion of an aqueous solution of Y(NO$_3$)$_3$ into an aqueous solution containing dpdo and K$_3$Co(CN)$_6$ at room temperature.† X-Ray diffraction analysis revealed that **1** is an ionic pair compound consisting of a [Y(dpdo)$_2$(H$_2$O)$_4$]$^{3+}$ cation, a discrete [Co(CN)$_6$]$^{3-}$ anion and four solvent water molecules (Fig. 1).‡ In **1** Y(III) lies on a two-fold axis and is eight coordinated to four O atoms originating from two dpdo molecules [Y–O1 2.291(3); Y–O2 2.323(3) Å], and four O atoms from water molecules [Y1–O3 2.389(3); Y1–O4 2.373(3) Å], forming a distorted square antiprism. The dihedral angle between the two pyridine rings of the dpdo ligand is 56.3° which is pronouncedly smaller than those in free dpdo (71°)[8] and in the corresponding binuclear complex [Y(dpdo)$_2$(H$_2$O)$_3$Fe(CN)$_6$]·4H$_2$O (*ca.* 63°).[9] The Co(CN)$_6^{3-}$ anion is octahedral with Co lying on an inversion center and N–C–Co bond angles are close to linearity.

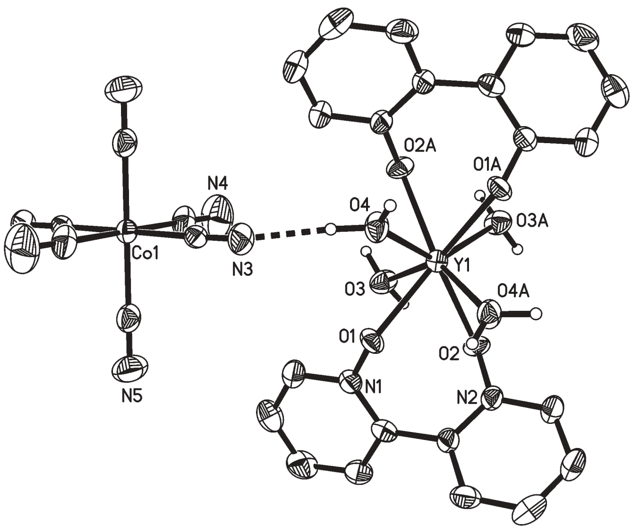

Fig. 1 Molecular structure of ionic pair complex **1**.

Interestingly, two coordinated (O3 and O3A) and four lattice water molecules (O5, O5A, O6B and O6C) related by a two-fold axis form a cyclic water hexamer through hydrogen bonds (Table 1). The cyclic hexamer assumes a book conformation with a dihedral angle of 82.4° (Fig. 2), in which the two coordinated water molecules are located on the 'spine' of the book. The average O···O distance within the hexamer is 2.84 Å, which is comparable to the corresponding value of 2.85 Å in liquid water.[10] The O···O···O angles range from 79.4 to 105.7°, considerably deviating from the preferred ideal tetrahedral geometry of water. Although the less stable cyclic conformers including boat, chair and quasi-planar (Scheme 1), have been experimentally observed in host matrixes, the book-shaped cyclic hexamer, to our knowledge, has not been previously described.[11] As calculated, the energy of the

Table 1 Hydrogen bond lengths (Å) and angles (°) associated with water molecules

D–H···A	D–H	H···A	D–H···A	D···A
O3–H1···O5	0.95(2)	1.75(2)	166(5)	2.677(5)
O3–H2···O6^a	0.94(2)	2.05(3)	164(5)	2.964(5)
O4–H3···O6	0.94(2)	1.96(2)	167(5)	2.886(5)
O4–H4···N3	0.95(2)	1.85(2)	175(6)	2.798(5)
O5–H5···N4	0.95(5)	1.82(2)	162(5)	2.737(6)
O5–H6···N3^b	0.93(2)	1.96(2)	168(4)	2.882(5)
O6–H7···N5^c	0.94(2)	1.92(4)	177(4)	2.855(6)
O6–H8···O5^d	0.94(2)	1.97(2)	163(5)	2.891(5)

^{a} $-x + 1, y - 1, -z + 1/2$. ^{b} $x, y - 1, z$. ^{c} $x - 1/2, y + 1/2, z$. ^{d} $x, y + 1, z$.

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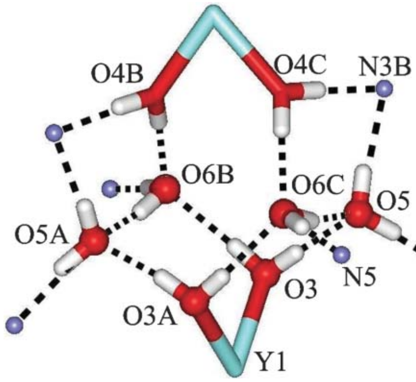
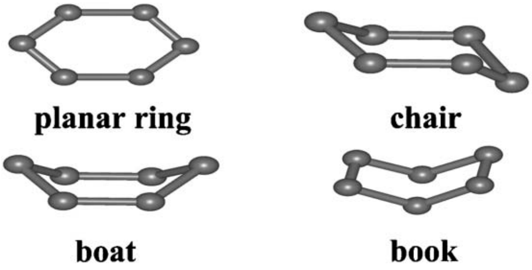


Fig. 2 An octameric water cluster formed by a book-shaped water hexamer (the oxygens of the water molecules of the hexamer are highlighted as spheres) and two dangling water molecules, and the surrounding environment: oxygen: red; nitrogen: purple; hydrogen: white; Y: light blue; hydrogen bonds: dashed lines.



Scheme 1

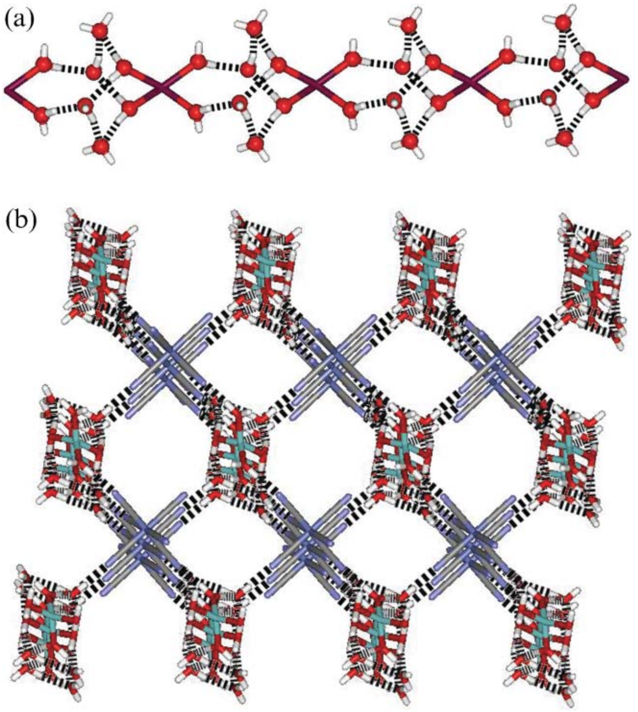


Fig. 3 (a) A polymeric water chain formed by metal coordination along the *b* direction; (b) 3D hydrogen-bonded network formed through metal ions and $Co(CN)_6^{3-}$ fragments down the *b* direction; dpdo molecules are omitted for clarity.

book conformer is only 0.1 kcal mol^{-1} higher than the lowest energy cage conformer and the book form would be more populated than the cage structure above 55 K.[1e] This implies that the book structure should be detectable and experimentally its presence would strongly depend on the physical and chemical environment. Though the currently described book hexamer has a different hydrogen bond orientation from the theoretically calculated one, it provides a crystallographic example of the book configuration for the water hexamer. The formation of this new conformation should be attributed to the influence of the specific surrounding host environments and nearby water molecules. Notably, the two recently reported water hexamers also involving two coordinated and four solvent water molecules in $[M(H_2biim)_2(H_2O)_2](ina)_2{\cdot}4H_2O$ (M = Zn, Co; H_2biim = 2,2′-biimidazole; ina = isoniconate)[4d] and $[Pr(pdc)(pdcH)_2(H_2O)]{\cdot}4H_2O$ ($pdcH_2$ = pyridine-2,6-dicarboxylic acid)[4i] adopt a chair conformation. The difference is that the two coordinated water molecules bind to two different metals in the above-mentioned cases, whereas they are ligated to the same metal ion in **1**. This should be responsible for the generation of this novel book conformation.

Furthermore, another two water molecules (O4B and O4C) from an adjacent $[Y(dpdo)_2(H_2O)_4]^{3+}$ moiety are bonded to two diagonal water corners of the hexamer, giving rise to an octamer (Fig. 2). The hydrogen bond length (2.886(5) Å) between the hexamer and the dangling waters is slightly longer than the average intra-hexameric length. Apparently, the octameric cluster described here is different from previously identified octameric cubane,[5e] opened cube[5f] and cyclic ring structures[5g] and represents a novel conformation of octameric water cluster not yet predicted. These results illustrate the structural diversity of water clusters and the sensitive dependence of their structures upon their environment.

The two water molecules from the 'spine' of the book-shaped hexamer and the two dangling waters bind to Y, producing a polymeric chain along the [010] direction (Fig. 3(a)). These chains are connected by the $[Co(CN)_6]^{3-}$ fragments through hydrogen bonds with peripheral water of the cluster, giving rise to a three-dimensional network (Fig. 3(b)). Six cyanide groups all participate in the hydrogen bonding networks with the clusters and one of them bridges the dangling water and hexamer, further stabilizing the octameric cluster. All the coordinated water molecules serve as double hydrogen bond donors, while all the crystal lattice water molecules are involved as double hydrogen bond donors and acceptors with a tetrahedral geometry.

In conclusion, we have observed a well-resolved octameric water cluster consisting of a novel book-shaped cyclic hexamer and two dangling water molecules in a 4f–3d complex. This demonstrates that the formation of water clusters is highly associated with their coordination to metal ions and surrounding environments.

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Notes and references

† *Preparation* of **1**: A mixture of dpdo (0.5 mmol) and $K_3Co(CN)_6$ (0.25 mmol) was dissolved in 15 mL distilled water, followed by slow addition of a 10 mL aqueous solution of $Y(NO_3)_3 \cdot 6H_2O$ (0.25 mmol). The resulting solution was allowed to stand at room temperature in the dark. Branch-shaped crystals appear after three days. A small single crystal was cut off and analysed by X-ray diffraction. Elemental analysis: calc. for $YCoC_{26}H_{32}N_{10}O_{12}$: C, 37.84; H, 3.88; N, 16.98; found: C, 37.71; H, 3.86; N, 16.97%. FT-IR (KBr, cm^{-1}): ν_{CN}: 2026 (m), 2062 (m), 2113 (s), 2131 (m); ν_{OH}: 3418 (m).

‡ *Crystal data*: $C_{26}H_{32}CoN_{10}O_{12}Y$ **1**, $M = 824.46$, monoclinic, $C2/c$, $a = 19.384(4)$, $b = 8.2478(16)$, $c = 22.090(4)$ Å, $\beta = 100.02(3)^\circ$, $U = 3477.9(12)$ Å^3, $Z = 4$, $D_c = 1.575$ Mg m^{-3}, $\mu = 2.210$ mm^{-1}, $F(000) = 1680$, GoF = 0.988, crystal size 0.26 × 0.10 × 0.08 mm. $R1$ and $wR2$ are 0.0542 and 0.0763, respectively, for 260 parameters and 1862 reflections [$I > 2\sigma(I)$]. The data were collected on a Nonius Kappa CCD with Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The structure was solved by direct methods and refined by a full-matrix least squares technique based on F^2 using the SHELXL 97 program. The hydrogen atoms on organic ligands were placed according to their calculated positions, while the water hydrogen atoms were located from difference Fourier maps and refined isotropically. CCDC 261999. See http://www.rsc.org/suppdata/cc/b5/b501161b/ for crystallographic data in CIF or other electronic format.

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