Synthesis and Crystallographic Characterization of an Octameric Water Complex, (H$_2$O)$_8$

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Small water clusters are the subject of considerable theoretical[1–5] and experimental[6–9] scrutiny and include a recently isolated water decamer.[9h] A detailed understanding of the numerous possible structures and stabilities is important for obtaining insight into the nature of water–water interactions in diverse environments. Of particular interest are octameric water clusters, (H$_2$O)$_8$. A cube-like structure of D_{2d} symmetry was originally predicted to be the most energetically favored.[4] However, more recent studies have led to predictions that (H$_2$O)$_8$ possesses an energetically low-lying structure of S_4 symmetry that is nearly isoenergetic with the D_{2d} octamer, as well as several higher lying cube-like structures.[1] Within the past year the O–H stretch vibrational spectra of the D_{2d} and S_4 forms of (H$_2$O)$_8$, attached to a benzene molecule, have been obtained under supersonic jet conditions.[8] However, until the present work, crystallographic observation and analysis of a water octamer has not been possible.

A two-to-one combination in acetonitrile of κ^4-[1,2-bis(2-oxy-2-methylpropanamido)-4,5-dimethoxybenzene]cobaltate(III), [**A**]$^-$, with bis-κ^3-(2,6-diacetamidopyridine)cobalt(II), [**B**]$^{2+}$, yields the crystalline solvate, [**A$_2$B**]·(CH$_3$CN)$_4$. On treatment with humid air for 10 to 12 days, [**A$_2$B**]·(CH$_3$CN)$_4$ forms the [**A$_2$B**](H$_2$O)$_8$ complex without crystal decay; both species have been crystallographically characterized.[10] Each species crystallizes in the monoclinic space group $C2/c$[11] with a common framework of

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linked Co complexes. Clearly defined channels extend throughout the crystal lattice, and these are readily accessible to acetonitrile and water molecules (see Figure 1). Diagrams of the water block and the surrounding host atoms are shown in Figure 2. Metal coordination serves to align the hydrogen-bonding donors and acceptors of the [**A**]$^-$ and [**B**]$^{2+}$ units into a favorable geometry to form the **A$_2$B** lattice and the associated **A$_4$B$_2$** cavities. The water molecules form octamers that are anchored in the cavity by four hydrogen bonds. These are formed between hydrogens located at vertices of the cluster with two methoxy O atoms and two alkoxide O atoms all derived from separate [**A**]$^-$ complexes. There are no other H bonds between the block and the inorganic framework. Comparatively narrow channels in the structure interconnect the large cavities (Figure 1) and allow for the diffusion of small molecules in a manner reminiscent of zeolitic compounds.

The relative arrangement of the oxygen atoms within a single water octamer and the associated hydrogen bond acceptors are highlighted in Figure 3, while Table 1 gives selected bond lengths and angles for the cluster. The oxygen atoms of the water cluster binding site and the oxygen atoms of the trapped water cluster both have C_i symmetry. This is noteworthy, since the C_i form of (H$_2$O)$_8$ is predicted[1] to be about 2 kcal/mol less stable than the D_{2d} or S_4 forms which have been observed previously.[8] Apparently, the C_i symmetry cluster is favored in the [**A$_2$B**](H$_2$O)$_8$ crystal because its free OH groups are more suitably arranged for bonding to the inorganic framework. It is noteworthy that the water molecules of the crystallized cluster are in dynamic equilibrium with atmospheric water since interchange of D$_2$O and H$_2$O can be observed by infrared analysis. Part or all of the broadening may be the result of the coexistence of different arrangements of hydrogen atoms within the (H$_2$O)$_8$ unit relative to the host binding sites. The hydrogen atoms were not resolved in the X-ray experiment, and there are two ways of arranging them in the C_i form. Table 1 reports the O–O distances for the theoretical C_i form of the water cluster. The calculated O–O distances differ by as much as 0.2 Å from those measured for [**A$_2$B**](H$_2$O)$_8$. This suggests that the interactions with the host induce structural perturbations within the water cluster.

The FTIR spectrum of [**A$_2$B**]·(CH$_3$CN)$_4$ (Figure 4) displays a band due to the characteristic C–N stretch of CH$_3$CN at 2250 cm^{-1}. The FTIR spectrum of [**A$_2$B**](H$_2$O)$_8$ is not well resolved. The O–H stretch transitions expected for the cluster fall in the same range as transitions due to the N–H and C–H groups of the host lattice making the separate bands difficult to resolve. Additionally, the spectrum for the [**A$_2$B**](H$_2$O)$_8$ unit is anticipated to be broader than that for its [**A$_2$B**](D$_2$O)$_8$ analogue due to differences in the thermal populations of the rotational levels. This effect is observed experimentally for IR spectra of bulk H$_2$O and bulk D$_2$O.[12] The FTIR spectrum of [**A$_2$B**](D$_2$O)$_8$ is more revealing, exhibiting two well-resolved transitions near 2370 and 2500 cm^{-1}, together with several weak shoulders. These transi-

(10) The dark green complexes [**A$_2$B**](H$_2$O)$_8$ (a = 22.2936(3) Å, b = 14.7240(3) Å, c = 21.9352(4) Å, β = 118.1400(10)°; V = 6349.2(2) Å^3; R = 0.0454, wR_2 = 0.1256) and [**A$_2$B**]·(CH$_3$CN)$_4$ (a = 22.5173(2) Å, b = 15.0882(2) Å, c = 22.1825(2) Å, β = 119.1750(10)°; V = 6580.3(1) Å^3; R = 0.0319, wR_2 = 0.0769) were both found to be monoclinic (space group $C2/c$ with Z = 4) and were analyzed in the same manner. The intensity data sets were collected on Siemens SMART CCD diffractometers with Mo Kα radiation at 120 and 203 K, respectively. The structures were solved by direct methods with use of the SHELXS program. F^2 refinements employed SHELXL to minimize the function $\sum w||F_o|^2 - |F_c|^2|^2$.

(11) The first crystal studied crystallographically had been exposed to a relatively humid atmosphere for about a week. The crystal was found to contain a mixture of approximately 90% water block and 10% acetonitrile solvate. A new crystal was taken directly from the dry acetonitrile mother liquor, and this showed the presence of acetonitrile only. New crystals were then exposed to moist air and independent structure determinations were carried out at Auckland (12 days exposure, T = 203 K) and Argonne (10 days, 120 K, data presented herein). Both structures gave essentially identical results, showing intact coherent water blocks with no trace residual acetonitrile.
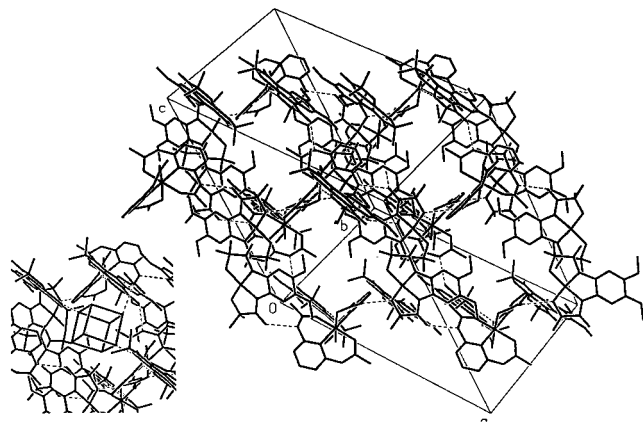
Figure 1. Packing diagram showing the channels running through the array common to both complexes with the solvent molecules removed. The inset left shows how the $(H_2O)_8$ block is positioned in one of the channel cavities of the array. Eight such blocks could be found in the partial array shown.
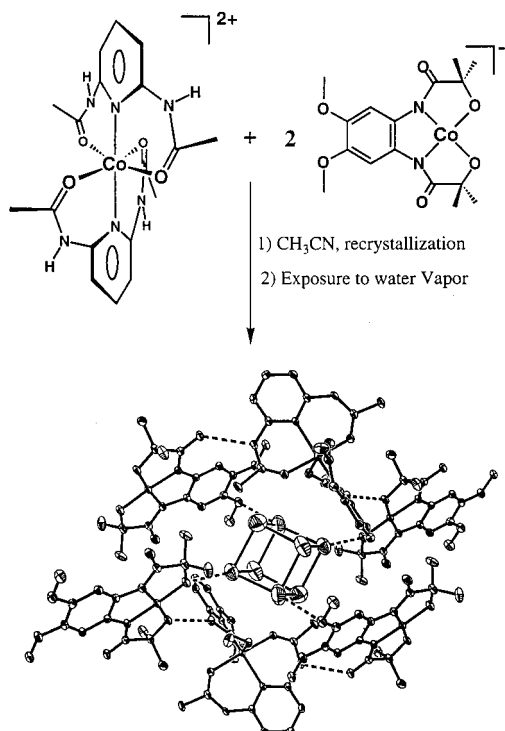

Figure 2. Basic synthetic scheme and diagram showing the octameric block of $[A_2B](H_2O)_8$. Atoms are shown at 50% displacement ellipsoids. Dashed lines represent hydrogen bonds.
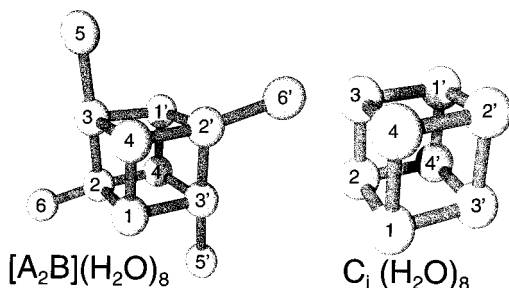

Figure 3. Ball and stick diagram of the **A₂B** water block with the hydrogen-bonded oxygens of $[A]^-$ also shown (left) and the theoretically calculated water block of C_i symmetry (right). The numbers correspond to the data in Table 1.

tions are assigned to octamer O—D stretch modes, although some intensity may also be arising from randomly distributed D_2O molecules and/or from N—D bonds in the exchanged compound. Anhydrous or acetonitrile-containing samples do not display

Table 1. Bond Lengths and Angles for $(H_2O)_8$ Complexes[a]

Oi−Oj−Ok	$[A_2B](H_2O)_8$ angle (deg)	C_i $(H_2O)_8$ angle (deg)	Oi−Oj	$[A_2B](H_2O)_8$ length (Å)	C_i $(H_2O)_8$ length (Å)
1−2−3	86.9(2)	87.68	1−2	2.871(6)	2.897
1−4−3	90.4(2)	92.74	1−4	2.784(7)	2.767
1−2−4′	79.9(1)	84.47	2−3	2.838(5)	2.753
2−3−4	92.1(2)	92.58	2−4′	2.903(5)	2.877
2−3−1′	90.5(2)	83.84	3−4	2.750(6)	2.641
2−1−4	90.7(2)	86.70	3−1′	2.929(7)	2.883
3−2−4′	88.4(2)	90.19	3−5	2.897(5)	
4−3−1′	81.5(2)	89.23	2−6	2.788(3)	
1−2−6	120.6(2)				
2−3−5	169.3(2)				
3−2−6	114.2(2)				

[a] Selected bond lengths and angles for $[A_2B](H_2O)_8$ and the theoretical C_i water cube. Oxygen numbers are shown in Figure 3.
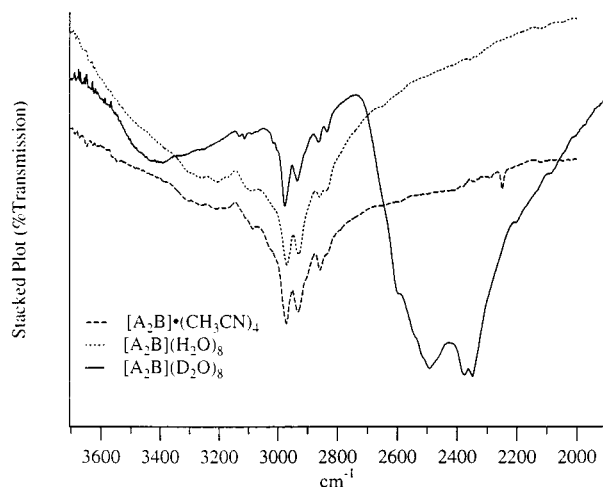

Figure 4. FTIR spectra for $[A_2B](H_2O)_8$, $[A_2B](D_2O)_8$, and $[A_2B]\cdot(CH_3CN)_4$.

multiple transitions in this region (Figure 4). Calculated O—D stretch vibrations of the D_2O monomer fall at 2757 and 2885 cm^{-1}, with bulk D_2O exhibiting experimentally a single broad peak centered at about 2600 cm^{-1}. We have used density functional theory[13] to calculate the vibrational spectrum of the C_i form of the unperturbed $(D_2O)_8$ cluster. The calculated frequencies range from near 2300 to 2800 cm^{-1}, with the two most intense transitions being predicted to occur at 2300 and 2610 cm^{-1}. Although the observed spectrum of $[A_2B](D_2O)_8$ is consistent with that calculated for the C_i form of $(D_2O)_8$ with regard to the large red shifts of the single-donor and double-donor O—D stretch transitions, the observed spectrum differs appreciably from that calculated for the unperturbed cluster. This is not surprising in light of the structural changes induced by the interactions with the host. Further calculations are in progress to model the interactions with the host lattice. Since we are able to obtain suitably large crystals, we are endeavoring to determine the hydrogen atom positions via low-temperature neutron diffraction.

Supporting Information Available: The synthesis and characterization of $[PPh_4][A]$, $[B][BF_4]_2$, $[A_2B]\cdot(CH_3CN)_4$, $[A_2B](H_2O)_8$, and $[A_2B]$-$(D_2O)_8$, the protocols employed to obtain the infrared spectra, and X-ray structural information on $[A_2B]\cdot(CH_3CN)_4$ and $[A_2B](H_2O)_8$ (PDF). An X-ray crystallographic file, in CIF format, is also available through the Internet. This material is available free of charge via the Internet at http://pubs.acs.org.

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