Inorg. Chem. **2002**, *41*, 6953–6955

Inorganic Chemistry

Communication

Identification of a Near-Linear Supramolecular Water Dimer, $(H_2O)_2$, in the Channel of an Inorganic Framework Material

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Received June 18, 2002

Supramolecular water dimer, $(H_2O)_2$, is fundamentally important. During the course of our work on polyoxometalates, we have been able to identify the existence of hydrogen-bonded, near-linear water dimers in the “sinuous” channels of an inorganic framework material, $Na_{3n}(H_2O)_{6n}[Al(OH)_6Mo_6O_{18}]_n \cdot 2nH_2O$, **1**. The three-dimensional network structure of **1** in the solid state is assembled by the Anderson type of heteropolyanions as building blocks sharing sodium cations. Vibrational spectroscopy, X-ray powder diffraction technique, TG-DSC analyses, and single-crystal X-ray structure analysis have characterized this host–guest system, **1**. Crystal data for **1**: triclinic space group $P\bar{1}$, $a = 12.0618$ (3) Å, $b = 13.1570$ (4) Å, $c = 14.1563$ (4) Å, $\alpha = 80.7850$ (10)°, $\beta = 75.2660$ (10)°, $\gamma = 68.9210$ (10)°, and $Z = 3$.

Small water clusters, $[(H_2O)_n, n = 2-10]$, have been a subject of both theoretical and experimental research, as they can provide insight into structure and characteristics of bulk water or ice.[1-3] Most of these clusters have been characterized spectroscopically[4] using liquid water (or D_2O), and clusters with $n = 2$, 4, 6, 8, and 10 have been observed crystallographically in crystalline hydrates.[5-9] Of particular interest is water dimer. Supramolecular water dimer has been previously identified by molecular beam electric resonance and maser spectroscopy[10] and also by infrared photodissociation spectra.[11] Recently, Saykally and co-workers have described the determination of water pair potential (which is an essential component for modeling the condensed phases of water) from microwave, terahertz, and infrared vibration−rotation−tunneling (VRT) spectroscopy of the water dimer $(D_2O)_2$.[12] Thus, the simplest water cluster $(H_2O)_2$ has always been characterized in the vapor phase,[3,10-12] and in a crystalline organic molecular host.[5] We describe here the crystallographic observation of water dimers in the channels of an inorganic framework material $Na_{3n}(H_2O)_{6n}[Al(OH)_6Mo_6O_{18}]_n \cdot 2nH_2O$, **1**, derived from the Anderson type[13] of heteropolyanion cluster $[Al(OH)_6Mo_6O_{18}]^{3-}$.

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(14) To a solution of $AlCl_3 \cdot 6H_2O$ (1.5 g, 6.21 mmol) in 25 mL of water which was acidified with 10 mL of acetic acid (100%) was added $Na_2MoO_4 \cdot 2H_2O$ (3.5 g, 14.46 mmol), and this solid was dissolved by stirring; the pH of the resulting clear solution was adjusted to 1.8 by the dropwise addition of 35% hydrochloric acid. The reaction mixture was kept at 20−22 °C in an open 100 mL conical flask. After one week, the precipitated white crystals were filtered, washed with water, and dried at room temperature in air. Yield: 2.0 g (68% based on Mo).

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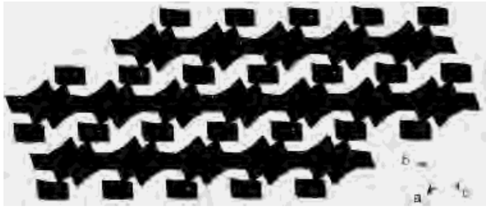

Figure 1. Illustration of the "S"-shaped channels in the polymer framework (polyhedral representation) of **1**. Guest water molecules in the channels are omitted for clarity.

Compound **1** was prepared[14] by treating an acidified aqueous solution of $AlCl_3$ with Na_2MoO_4. White crystals of **1**, which grew over a period of 7 days, were characterized by single-crystal X-ray structure analysis,[15] elemental analysis, vibrational spectroscopy,[16] and thermogravimetry.

The crystal structure of **1** shows a three-dimensional framework having "sinuous" channels (Figure 1), which is constructed by the Anderson type of anions as building blocks sharing sodium cations (Figure 2). The Anderson heteropoly anion consists of seven edge-shared octahedra, six of which are Mo octahedra arranged hexagonally around the central octahedron containing a heterometal ion (for example, Al^{3+} in the present case) at the center (Figure 2). In the crystal structure of **1**, the Anderson anion $[Al(OH)_6Mo_6O_{18}]^{3-}$ coordinates sodium cations via Mo═O terminal oxygen atoms (Figure 2). Similar sodium coordination for other Anderson anions is known in the literature.[17] The guest water molecules,[18] which do not show any covalent interactions, fill the "S"-shaped voids (Figure 1). The hydrogen-bonding situation involving guest and host-coordinated water molecules is separately presented in Figure 3. O(49) and O(50) water molecules arrange themselves to form a near-linear hydrogen-bonded water dimer. This supramolecular water dimer (as guest) is associated with the host by hydrogen-bonds in the channel of **1** (Figure 3). The geometrical parameters of the water dimer and its association with host are provided in Table 1. The O···O distance in the $(H_2O)_2$ dimer (present study) is 2.84 Å. For comparison, the corresponding values in regular ice, in liquid water, and in the vapor phase are 2.74, 2.85, and 2.98 Å, respectively.[3a] The water dimer was described in the vapor phase for the first time by Dyke and co-workers.[10] The molecular beam

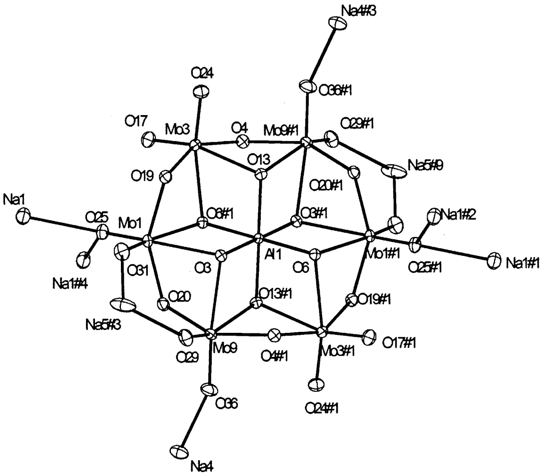

Figure 2. Sodium coordination of an Anderson anion, $[Al(OH)_6Mo_6O_{18}]^{3-}$ via terminal oxygen atoms on molybdenum in **1**. Thermal ellipsoids at 50% probability. Atoms with additional labels #1−#4 and #9 are related to each other by symmetry operations: #1 $-x + 2, -y + 1, -z$; #2 $x + 1, y, z$; #3 $x, y + 1, z$; #4 $-x + 1, -y + 1, -z$; #5 $-x + 1, -y - 1, -z + 1$; #6 $x - 1, y, z$; #7 $x, y - 1, z$; #8 $-x, -y, -z + 1$; #9 $-x + 2, -y, -z$; #10 $x - 1, y - 1, z + 1$.

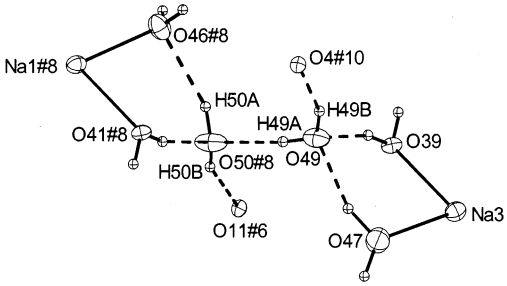

Figure 3. Representation of the supramolecular water dimer (guest) consisting of O(49) and O(50) water molecules and its immediate environment (host) as found in **1** (50% thermal ellipsoids). Covalent chemical bonds are shown as solid lines (−) and H-bonds as dashed lines (---). O(4) is a bridging oxygen atom between two molybdenum atoms in an Anderson anion (see Figure 2), and O(11) is a bridging oxygen atom of another Anderson anion (see the asymmetric unit, submitted as Supporting Information). O(39), O(41), O(46), and O(47) are sodium-coordinated water ligands (part of the host), which show additional hydrogen-bonding interactions with the guest water dimer. Atoms with additional labels #6, #8, and #10 are related to each other by symmetry operations specified in the caption of Figure 2.

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(15) Crystal data of **1**: $AlH_{22}O_{32}Mo_6Na_3$, $M = 1205.77$ g mol^{-1}, triclinic, space group $P\bar{1}$, $a = 12.0618$ (3) Å, $b = 13.1570$ (4) Å, $c = 14.1563$ (4) Å, $\alpha = 80.7850$ (10)°, $\beta = 75.2660$ (10)°, $\gamma = 68.9210$ (10)°, $U = 2021.43$ (10) Å^3, $T = 183$ (2) K, $Z = 3$, $D_c = 2.971$ g cm^{-3}, $\mu = 2.913$ mm^{-1}, $F(000) = 1728$, crystal size $= 0.20 \times 0.18 \times 0.08$ mm^3. A total of 28895 reflections (1.66° < θ < 29.99°) were collected of which 11686 unique reflections ($R_{int} = 0.0187$) were used. The structure was solved using SHELXS-97 and refined using SHELXL-97 to R1 = 0.0215, wR2 =0.0536, for 9885 reflections with $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from difference Fourier maps and refined isotropically. However, the hydrogen atoms on O(46), O(47), and O(48) became unstable during refinement, and therefore, the corresponding O−H distances were constrained at 0.96 Å. This original cell was transformed to a smaller cell ($a = 6.4776$ (2) Å, b =10.8548 (3) Å, c =10.8549 (3) Å; $\alpha = 109.3800$ (10)°, $\beta = 95.43$°, $\gamma = 106.79$°; $V = 673.80$ (3) Å^3) based on the unit cell dimension of the known similar compound $Na_3[Cr(OH)_6Mo_6O_{18}]\cdot 8H_2O$ (ref 17: $a = 10.9080$ (4) Å, $b = 10.9807$ (4) Å, $c = 6.4679$ (2) Å; $\alpha = 107.594$ (2)°, $\beta = 84.438$ (2)°, $\gamma = 112.465$ (3)°), but the structure, obtained using a smaller cell, manifested disorder of sodium atoms and one oxygen atoms. The sodium atoms are situated a bit apart from the "ideal" positions, and that is why the larger cell, which describes the situation more precisely, was chosen.

(16) Selected data for **1**, IR (KBr pellet) (ν/cm^{-1}): 1620m {$\delta(H_2O)$}, 947s/920s {ν(Mo═O)}, 845w, 650s, 574m, 530w, 447w, 390w. Raman (KBr matrix) (ν/cm^{-1}): 958s, 890m, 568w, 362m, 224s. Anal. Calcd for $AlH_{22}Mo_6Na_3O_{32}$ (1205.77): Na, 5.72; H, 1.84. Found: Na, 5.69; H, 1.79. The number of Al and Na sites revealed by X-ray analysis is consistent with the result of EDAX analysis, which gave an average value of Mo/Al of ≈6.0 and Mo/Na of ≈2.0.

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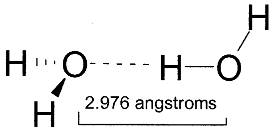
(18) There are a total of eight water molecules per formula unit of **1** (12 water molecules in the asymmetric unit consisting of 1.5 molecules). Among them, two water molecules (as guests) do not show any covalent interactions, but they are hydrogen-bonded to host channels (they are O(49), O(50), and O(51) waters in the asymmetric unit of 1.5 molecules). Whereas O(49) and O(50) water molecules arrange themselves to form a water dimer (Figure 3), the O(51) water molecule is hydrogen-bonded to one of the sodium-coordinated waters. The rest of the six water molecules of **1** are coordinated to sodium cations, two of which (they are O(43), O(44) and O(45) waters in the asymmetric unit) are coordinated in a μ_2-type bidentate fashion (forming chain) and the remaining four (namely O(39), O(41), O(42), O(46), O(47) and O(48) waters in the asymmetric unit) are coordinated to sodium cations in the chain as monodentate ligands.

Table 1. Geometrical Parameters of Hydrogen-Bonds (Å, deg) for the near-linear Water Dimer and Its Association with Host (Figure 3) in **1**

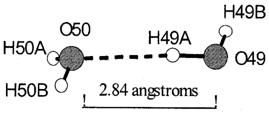
D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	∠(DHA)
O(49)−H(49A)O···(50)#8	0.87(4)	1.99(4)	2.843(3)	170(3)
O(49)−H(49B)···O(4)#10	0.74(4)	2.15(4)	2.815(2)	149(4)
O(39)−H(39B)···O(49)	0.86(3)	1.82(3)	2.650(2)	163(3)
O(47)−H(47A)···O(49)	1.00[a]	1.87	2.817(3)	157.2
O(50)−H(50A)···O(46)	0.91(4)	2.18(4)	2.938(3)	141(3)
O(50)−H(50B)···O(11)#6	0.74(4)	2.08(4)	2.754(2)	150(4)
O(41)−H(41B)···O(50)	0.81(3)	1.87(3)	2.664(2)	165(3)

[a] Restrained; D = donor; A = acceptor. Atoms with additional labels #6, #8, and #10 are related by symmetry operations specified in the caption of Figure 2.

Scheme 1



(a) Structural drawing of the water dimer (in vapor phase) as measured from molecular beam resonance studies (ref. 3 and 10).



(b) Water dimer in the solid state, present work.

resonance experiments carried out by this group clearly showed that the lowest energy arrangement has a plane of symmetry containing the hydrogen donor molecule to the right and the symmetry axis of the molecule to the left (Scheme 1a). Experiments using advanced techniques including VRT spectroscopy[12] of $(D_2O)_2$ as well as extensive theoretical works[3b,c] have converged on this translinear structure. The plane containing the hydrogen donor water molecule to the right bisects the water molecule to the left through the oxygen atom of the hydrogen acceptor molecule (Scheme 1a). On the other hand, the water dimer, found in the channel of **1** (Figure 3 and Scheme 1b), is near-linear, but it is not isosymmetrical with the water dimer theoretically predicted and/or the water dimer of the vapor phase (Scheme 1a).[3,10] They differ by the position of one hydrogen atom (H49B in Scheme 1b), which is out of plane bisecting the water molecule (O50 water) to the left. This is because the present water dimer, which exists in the solid state, is hydrogen-bonded to all of its possible sites (Figure 3), and the resulting steric constraints decide the present conformation. Interestingly, both oxygen atoms of the water dimer (Figure 3) have a "formal" coordination number of four (two hydrogen atoms of each oxygen of the dimer act as acceptors and the two lone pairs as donors) with (approximately) tetrahedral arrangements. It is thus possible to envision that the free water dimer (in the channel) is connected to the coordinated water molecules of the host framework through O−H···O hydrogen-bonding. However, it is logical to identify the pair of water molecules in the channel as a supramolecular water dimer, because this pair is not at all involved in covalent interaction and is solely hydrogen-bonded to its periphery. At this point, it is worth mentioning that, even though we have described this pair of water molecules as a water dimer, contributions from the peripheral hydrogen-bonding sites are inevitably significant for the existence of this smallest water cluster. In fact, for the most part, the H-bond contacts to the periphery are shorter than the intradimer distance (Table 1). Thus, the formation of supramolecular $(H_2O)_2$ in the channel appears to be facilitated by the peripheral hydrogen-bonding interactions. The importance of the surrounding host of the water dimer is also reflected by the fact that, once guest waters are released (thermally), the host becomes unstable with the loss of host-coordinated water molecules which are hydrogen-bonded to the guest water molecules.[19]

In conclusion, we have synthesized and characterized an inorganic material, $Na_{3n}(H_2O)_{6n}[Al(OH)_6Mo_6O_{18}]_n\cdot 2nH_2O$, **1**, which has three-dimensional framework structure with well-defined "S"-shaped channels. These channels encapsulate supramolecular water dimers as guests furnishing a novel example of a near-linear $(H_2O)_2$ cluster in the solid state.

Supporting Information Available: Text depicting TGA-DSC and XRD studies, a figure of the asymmetric unit as 1.5 molecules, a figure of the sodium coordination of an Anderson anion, a figure of illustration of the channels occupied by guest water molecules, and a complete X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) TGA performed on **1** showed a sharp weight loss (8.5%) at ~50 °C, and this corresponded to the loss of 5.7 water molecules per formula unit. Then, the lower hydrate remained stable up to 180 °C. When the sample of **1** was heated for 2 h at 125 °C, it removes quantitatively six water molecules. This supports the formulation of the desolvated compound as $Na_3(H_2O)_2[Al(OH)_6Mo_6O_{18}]$. This is in agreement with the elemental analyses. Anal. Found (calcd): Na, 6.35 (6.28); H, 1.05 (0.92). This result is consistent with the first weight loss in the TGA curve corresponding to two solvent and four coordinated water molecules.