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Note

New Hydrogen Bond-Supported 3-D Molecular Assembly from Polyoxovanadate and Tetramethylbiimidazole

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Introduction

Synthesis and characterization of large assemblies of inorganic and/or organic molecules are actively investigated because, with the combination of approaches of organic, organometallic, and inorganic chemistry, it is possible to obtain materials that can perform many functions.[1−11] The aim of crystal engineering is to establish reliable connections between molecular and supramolecular structure on the basis of intermolecular interactions.[4,12,13] The predictable self-organization of molecules into one-, two-, or three-dimensional frameworks is of the utmost importance in crystal engineering. For such rational design, hydrogen bonding of conventional OH···N and NH···O motifs has been the most commonly used as supramolecular cement, yet weaker forces such as CH···O, CH···N, O···I, or even C···H and C···C have been used.[4,5,14]

Applications of polyoxovanadate compounds to optical, electronic, and magnetic materials represent an area of considerable general and topical interest.[1,7,8,15−23] Simple oxovanadates (V) present in aqueous solution include those which are mononuclear ($H_2VO_4^-$, HVO_4^{2-}, VO_4^{3-}), dinuclear ($H_2V_2O_7^{2-}$, $HV_2O_7^{3-}$, $V_2O_7^{4-}$), tetranuclear ($V_4O_{12}^{4-}$), pentanuclear ($V_5O_{15}^{5-}$), and decanuclear ($H_2V_{10}O_{28}^{4-}$, $HV_{10}O_{28}^{5-}$, $V_{10}O_{28}^{6-}$) with different protonation numbers.[24] However, none of these vanadate oxoanions have been characterized by X-ray crystallography.[24] In the solid state, protons in the polyoxometalate crystals are important in defining the crystal packing through hydrogen bonds.[25] In the polyoxometalate crystals, protons could prefer the most basic oxygen atoms, which also serve as binding sites for cationic groups on the polyoxometalate surface.[25] Biimidazole derivatives also possess multiple hydrogen bonding sites, and several hydrogen bonding assemblies of the mononuclear complexes are synthesized.[14] In particular, biimidazole and polyoxometalates can interact by hydrogen bonding. Therefore, we chose a biimidazole derivative as a supramolecular module

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Table 1. Crystallographic Data for **1**

empirical formula	$C_{20}H_{42}O_{32}N_8V_{10}$
fw	1416.0
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	12.151(4)
b, Å	13.127(8)
c, Å	13.93(1)
β, deg	94.90(5)
V Å^3	2213(2)
Z	1
D_c, g cm^{-3}	2.12
μ(Cu Kα), cm^{-1}	179.14
cryst size, mm^3	$0.15 \times 0.1 \times 0.1$
scan type	$\omega-2\theta$
$2\theta_{max}$	120.1°
no. of reflns measured	total: 3653 unique: 3471 ($R_{int} = 0.099$)
no. observations ($I > 2.00\sigma(I)$)	1425
R^a ($I > 2.00\sigma(I)$)	0.064
wR2 (for all data)	0.193

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

to assemble polyoxovanadates, which have both basic oxygen atoms and acidic proton atoms.

Our investigations have focused on the use of polyoxovanadate as a structural building block in the synthesis of a hydrogen bonded inorganic−organic three-dimensional structure. Although several organic−inorganic hybrid materials are synthesized, inorganic−organic hydrogen bonded three-dimensional assembly of decavanadate systems are still sparse. In this paper, we report the synthesis and single-crystal X-ray structural characterization of $[H_2V_{10}O_{28}](H_4bim)_2(H_2O)_4$ (**1**) (H_2bim = 2,2′-bis(4,5-dimethylimidazole)). The three-dimensional network is built up from inorganic decavanadate cluster anions and organic biimidazolium dications with hydrogen bond.

Experimental Section

All manipulations were carried out using standard Schlenk technique. Solvents were purified by standard methods before use. $VOSO_4 \cdot nH_2O$ and LiOH were purchased from Wako Chemical Co. 2,2′-Bis(4,5-dimethylimidazole) was purchased from Aldrich Chemical Co. and used without further purification. IR spectra of KBr disks were measured on a Hitachi I-5040-FT-IR spectrophotometer. X-band EPR spectra were recorded with a JEOL RE-3X spectrometer. ^{51}V NMR spectra were measured with a JEOL GSX270 FT-NMR spectrometer.

Preparation of $[H_2V_{10}O_{28}](H_4bim)_2(H_2O)_4$ (1). $VOSO_4 \cdot nH_2O$ (1.085 g, 6.657 mmol) was dissolved in 150 mL of water, and the pH value was adjusted to 6 with lithium hydroxide (~0.42 g, 17.53 mmol). H_2bim (0.950 g, 4.993 mmol) was dissolved in 350 mL of ethanol, and the solution was added slowly to the former solution. The mixed solution was stirred for 24 h, and gray precipitate was filtrated off. The resultant yellow solution was obtained and then sealed in a tube to form yellowish brown crystals within 1 month (yield 40%). IR (KBr disk, cm^{-1}): 976(s), 1645(m), 1441(m). Anal. Calcd for $V_{10}O_{32}C_{20}N_4H_{42}$: C, 17.01; H, 2.71; N, 7.94. Found: C, 17.45; H, 3.25; N, 7.94

X-ray Crystallography and Structure Solution. A yellowish brown crystal having approximate dimensions of $0.15 \times 0.1 \times 0.1$ mm^3 was mounted on a glass fiber. The crystal parameters and experimental conditions are summarized in Table 1. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Cu Kα (1.54178 Å) radiation at room temperature. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range 20.27° < 2θ < 48.50°, corresponded to a primitive monoclinic cell. The data were corrected for Lorentz and polarization effects. An empirical absorption correction based on azimuthal scan of several reflections was applied. The structure was solved by direct methods (Rigaku TEXSAN crystallographic software package of Molecular Structure Corporation), refined with full-matrix least-squares technique (SHELXL-93),[26] and expanded using Fourier techniques. The hydrogen atoms were located in the Fourier difference maps. The non-hydrogen atoms were refined anisotropically.

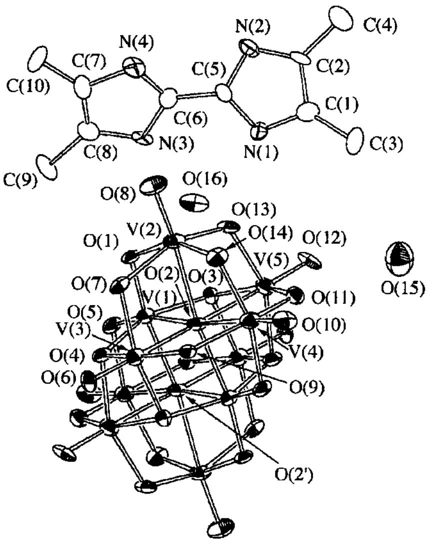

Figure 1. ORTEP representation of $[H_2V_{10}O_{28}](H_4bim)_2(H_2O)_4$ (**1**) depicted at the 30% probability level, showing the atom labeling scheme. Hydrogen atoms are omitted for clarity.

Results and Discussion

Crystal Structure. The decavanadate anion forms readily in acidic solution and has been well characterized both in solution and in the solid state.[24] The yellow solution gave no EPR spectrum at 77 K, indicating that the main species in solution are vanadium(V) ions. ^{51}V NMR spectrum of the reaction mixture of **1** affords resonances at −411, −511, and −524 ppm, attributable to the decavanadate.[24,27] This spectrum indicates no coordination of H_2bim to vanadium ions in the solution. Isolation of polyanions from the solution is generally achieved by addition of an appropriate countercation, such as an alkali metal, ammonium, or tetraalkylammonium cation.[28] We have used a biimidazole derivative as a dication source which could cocrystallize with the polyanions to form a hydrogen bonding network in the solid state.

The yellow solution containing the decavanadate unit yielded crystalline **1**. The X-ray crystal structure of **1** reveals the presence of water molecules, biimidazolium dications (H_4bim^{2+}), and a decavanadate anion ($[H_2V_{10}O_{28}]^{2-}$). Figure 1 shows the structure and labeling scheme of the water

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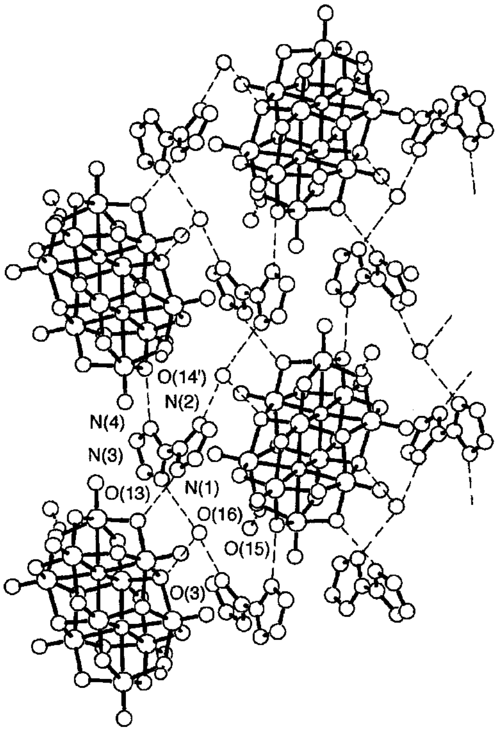


Figure 2. Drawing of hydrogen bonding structure of **1**. Hydrogen bonds between the polyoxovanadate anions, $(H_4bim)^{2+}$ dications, and water molecules are indicated by dashed lines.

Table 2. Selected Bond Distances (Å) of **1**

atom	atom	distance	atom	atom	distance
V(1)	O(1)	1.677(8)	V(3)	O(6)	1.582(9)
V(1)	O(2)	2.103(8)	V(3)	O(7)	1.916(9)
V(1)	O(2′)	2.121(8)	V(3)	O(9)	1.785(9)
V(1)	O(3)	1.965(9)	V(4)	O(2)	2.329(8)
V(1)	O(4)	1.900(9)	V(4)	O(5′)	1.988(9)
V(1)	O(5)	1.701(9)	V(4)	O(9)	1.904(9)
V(2)	O(1)	2.042(9)	V(4)	O(10)	1.589(9)
V(2)	O(2)	2.318(8)	V(4)	O(11)	1.868(9)
V(2)	O(7)	1.983(9)	V(4)	O(14)	1.853(9)
V(2)	O(8)	1.59(1)	V(5)	O(2)	2.270(9)
V(2)	O(13)	1.84(1)	V(5)	O(3)	2.031(9)
V(2)	O(14)	1.823(9)	V(5)	O(4′)	1.943(8)
V(3)	O(2)	2.254(9)	V(5)	O(11)	1.809(9)
V(3)	O(4)	2.039(8)	V(5)	O(12)	1.580(9)
V(3)	O(3′)	1.950(9)	V(5)	O(13)	1.882(9)

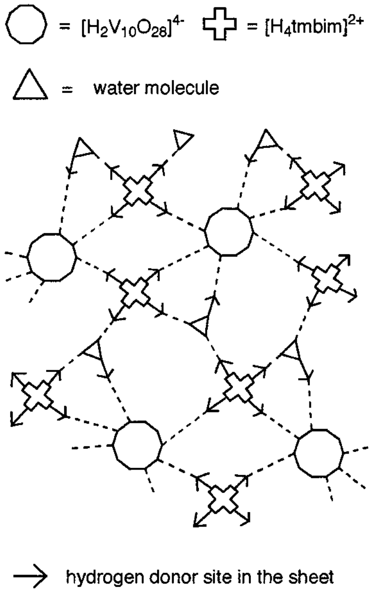
molecules, decavanadate anion, and biimidazolium dication, while Figure 2 shows the hydrogen-bonding network constructed by these three components. Selected bond distances are listed in Table 2.

The decavanadate anion has a crystallographic inversion center on the midpoint of the O(2) and O(2′) and has approximately D_{2h} symmetry. The $[H_2V_{10}O_{28}]^{4-}$ anion consists of an octahedrally packed aggregation of 10 VO_6 octahedra sharing edges. The bond angles and distances observed for the $V_{10}O_{28}{}^{6-}$ unit indicate that the geometry is quite similar to that found in previously reported structures of decavanadate salts.[24,29,30] The decavanadate anion core includes two hydrogen atoms at doubly bridged oxygen atoms (O(7) and O(7′)) to give a total charge of −4. The protonation sites are consistent with the location of the Fourier difference maps and consideration based on the standard bond valence summations.[31−33] The sums ($\Sigma s = \Sigma(d/1.791)^{-5.1}$, d = V−O distance in Å) of V−O bond valences for the bridging oxygen atoms are in the range 1.6−2.0 except 1.3 for O(7) and O(7′). Bond valence summations for **1** indicate that O(7) and O(7′) are protonation sites. Furthermore, the protonation sites agree well with those of structurally characterized decavanadate anion previously synthesized.[29]

Table 3. Interatomic Distances (Å) and Angles (deg) Involving Hydrogen Bonded Atoms in Crystal **1**

A	H	B	A−H distance/Å	H···B distance/Å	A−H···B angle/°	A···B distance/Å
N(1)	H(2)	O(13)	1.24	1.44	169.8	2.67(1)
N(2)	H(3)	O(16)	1.28	1.50	173.5	2.77(1)
N(3)	H(4)	O(16)	1.26	1.65	156.3	2.85(1)
N(4)	H(5)	O(14)	1.24	1.41	172.4	2.65(1)
O(7)	H(1)	O(15)	0.95	1.84	160.1	2.76(2)
O(16)	H(18)	O(3)	0.92	2.12	121.6	2.71(1)

Scheme 1



All three components are hydrogen-bonded to afford a layered structure. The interatomic distances and angles regarding hydrogen bonding are listed in Table 3. Each H_4bim^{2+} dication forms a hydrogen bond with a doubly bridging oxygen atom of a decavanadate anion as a hydrogen acceptor to provide a one-dimensional structure. Moreover, the residual hydrogen donor sites of H_4bim^{2+} dications are bound to the crystal water (O(16)) molecules to afford a two-dimensional layer structure (Scheme 1). Hydrogen bond linked systems have been previously synthesized, including $[V_6O_6F(OH)_3\{(OCH_2)_3CCH_3\}_3]^-$ (**2**),[34] $[V_{10}O_{14}(OH)_2\{(OCH_2)_3CCH_2OH\}_4]^{2-}$ (**3**),[35] and $[H_3V_{10}O_{28}]^{3-}$ (**4**).[30] The hydrogen atoms of the bridging OH groups in compounds **2**−**4**

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are used in hydrogen bonding to link polyoxovanadate anions directly; **2** and **3** afford 1-D chain structures with this linkage, while in **4** a dimeric structure forms. On the other hand, as far as organic molecules are considered as cement, literature including well-characterized crystal structures is still sparse; $(NH_4)_6(gly-gly)_2V_{10}O_{28}\cdot 4H_2O$ (**5**) and $(H_2dpds)_2[V_{10}O_{22}(OH)_2]\cdot 10H_2O$ (**6**) are examples.[24,36] However, **5** has no infinite structure,[25] and **6** exhibits 1-D structure.[36] From this point of view, **1** is the first hydrogen-bonded decavanadate-based compound having higher dimensional infinite structure with organic molecules as cement. The organic $(H_4bim)^{2+}$ unit has four proton donor sites so flexible that the direction is tunable by a rotation along the C(5)−C(6) axis, resulting in a staggered conformation with the N(2)−C(5)−C(6)−N(4) dihedral angle, 48.4° in **1**. This appears to be a reason that the stable linkage of $(H_4bim)^{2+}$ units with the decavanadates and the water molecules in **1** forms and the two-dimensional structure is constructed.

The water molecules in **1** act as not only a proton acceptor but also as a proton donor, classified into two types. First, the type 1 water molecules (O(16)) form hydrogen bonds with both $[H_2V_{10}O_{28}]^{4-}$ anions and H_4bim^{2+} dications to give the two-dimensional layer. Second, the type 2 molecules (O(15)) link the layers. The water molecules of type 1 form hydrogen bonds with triply bridging oxygen atoms of the $[H_2V_{10}O_{28}]^{4-}$ anion. The basicity of the bridging oxygen atoms has been examined by ^{17}O and ^{51}V NMR chemical shifts as well as by ab initio MO calculations, and the increasing order in the basicity is obtained as follows: triply > doubly > terminal oxygen atoms.[30,37,38] The X-ray crystallographic structure of **5**[24] shows that the hydrogen bonding occurs between the organic molecule and the triply bridging oxygen atoms, in good agreement with both experimental and theoretical predictions regarding the basicity of oxygen sites on the vanadate decamer. Thus, the triply bridging oxygen atoms prefer proton acceptors to the doubly and terminal oxygen atoms. This trend is not the exception in **1**.

Linkage of Layers. The motif of **1**, $[H_2V_{10}O_{28}]^{4-}$, has hydrogen atoms at O(7) and O(7′) sites, which have no interaction with the nearest neighbor $[H_2V_{10}O_{28}]^{4-}$ because of their direction to the neighboring layer. These sites are considered to be hydrogen donor ones for acceptor molecules in the interlayer space. Therefore, $\{[H_2V_{10}O_{28}](H_4bim)_2(H_2O)_2\}_n$ layers could be able to interact with molecules by hydrogen bonding. Inspection of the crystal structure of **1** reveals that there are water molecules (O(15)) between the layers. Figure 3 shows the hydrogen bonding interaction between vanadate decamers and water molecules in interlayer space. Although there are many inorganic component-based layers of polyoxovanadates,[6,17,39−42] which span the entire range from three-dimensional to zero-dimensional frameworks, literature on hydrogen-bonded decavanadate systems having inorganic−organic component-based 3-dimensional compounds is still sparse. On this basis, **1** is also the first example. This structure is depicted schematically in Scheme 2. The interlayer water molecules link the $\{[H_2V_{10}O_{28}](H_4bim)_2(H_2O)_2\}_n$ layers to extend the three-dimensional structure. This structural feature is considered to be a sort of layered system, in which various molecules having hydrogen acceptor sites could be intercalated.

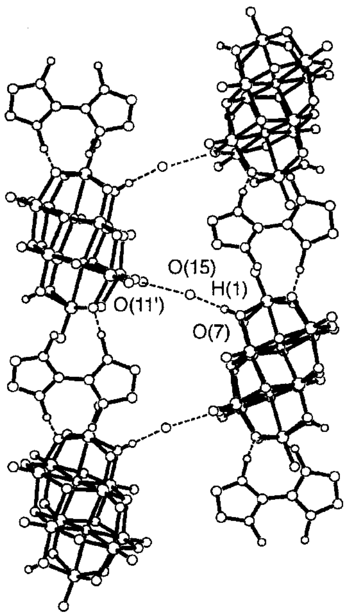
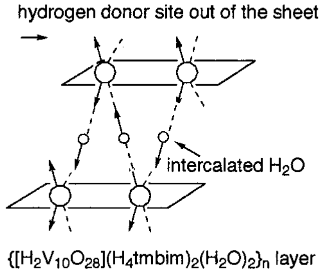


Figure 3. Linkage structure of **1** with the two-dimensional hydrogen bonding layers. Methyl groups are omitted for clarity. Spheres of the hydrogen atoms have been arbitrarily reduced.

Scheme 2



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Supporting Information Available: Four X-ray crystallographic files, in CIF format, and three additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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