Novel Extended Linear Structure of Decavanadate Anions Linked by Bis(4-Pyridinium) Disulfide (H_2dpds), {(H_2dpds)$_2$[$V_{10}O_{26}(OH)_2$]•10H_2O}$_n$

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New porous coordination polymer, {(H_2dpds)$_2$[$V_{10}O_{26}(OH)_2$]·10H_2O}$_n$ (H_2dpds = bis(4-pyridinium) disulfide), was synthesized and structurally characterized. X-ray analysis demonstrates that the decavanadate anions are doubly bridged by H_2dpds ligands to provide a one-dimensional structure. This network affords channeling cavities with dimension of about 2 x 4 Å along the *c*-axis.

Synthesis and structural characterization of coordination polymers with new channel properties are of current interest. This is not only because of their intriguing structural diversity, but also because of their potential functionalities, such as molecular adsorption, ion exchange, and heterogeneous catalysis.[1] Although a number of porous coordination networks have been synthesized to date, examples of the channel structures with new chemical environments are quite rare.[1b] It is well known that polyoxometalate compounds reveal unique functional properties, such as proton conductivity or several catalysis.[2] Construction of a porous network from the polyoxometalate compounds and organic moieties could provide a porous material with new functional properties.

We have succeeded in the synthesis and structural characterization of a new coordination polymer, {(H_2dpds)$_2$[$V_{10}O_{26}(OH)_2$]·10H_2O}$_n$ (H_2dpds = bis(4-pyridinium) disulfide); **1**·10H_2O). This compound was obtained as yellow needles from the H_2O/EtOH mixed solution containing $VOSO_4$ and dpds under air.[3]

Figure 1 shows ORTEP drawing of the circumstance of the decavanadate anion of **1**·10H_2O.[4] In general, this type of decavanadate is comprised of ten V(V) centers, twenty-six of O^{2-} anions, and two OH^- sites. The positions of OH^- sites are assigned on the basis of the Σs values, in which the s is defined by the power function $s = (R/1.791)^{-5.1}$ (R = V-O distances).[5] According to this procedure, the O(14) and O(14*) sites were ascribed to the OH^- sites, whose Σs value (1.48) is significantly smaller than the others (1.66-1.99) which are normal for the O^{2-} sites.[5]

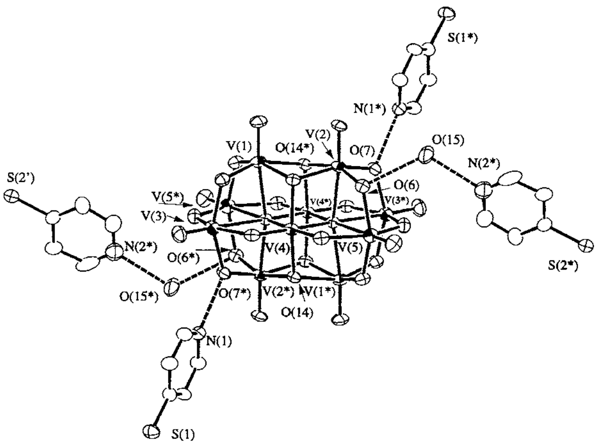

Figure 1. ORTEP drawing of circumstance of the [$V_{10}O_{26}(OH)_2$]$^{4-}$ anion of **1**·10H_2O with 30% probability level. Broken lines indicate hydrogen bonding. Hydrogen atoms are omitted for clarity.

Four pyridinium cations are associated with the decavanadate anion. Two of the four pyridinium cations directly bind to the decavanadate anion by the hydrogen bondings (N(1)-O(7) = 2.60(1) Å). The other two pyridinium cations are hydrogen bonded to the water molecules that connect with the decavanadate anion by hydrogen bondings (N(2)-O(15) = 2.57(1) Å, O(6)-

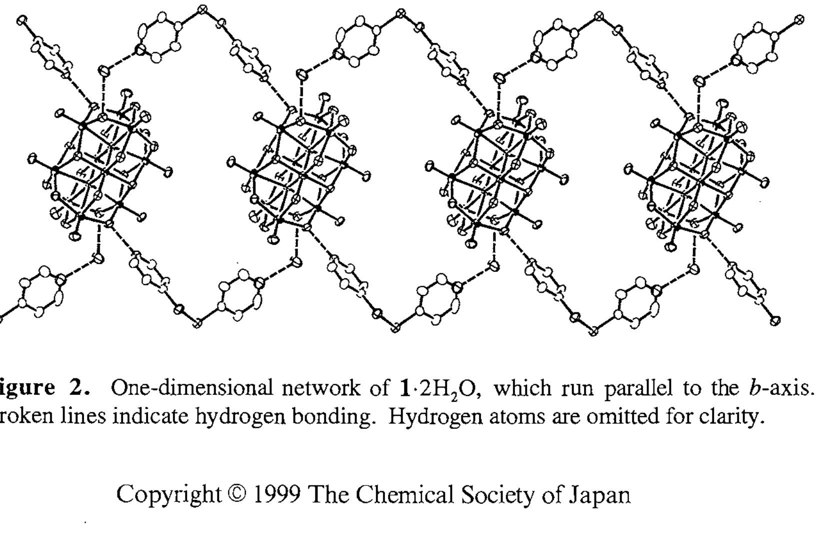

Figure 2. One-dimensional network of **1**·2H_2O, which run parallel to the *b*-axis. Broken lines indicate hydrogen bonding. Hydrogen atoms are omitted for clarity.

O(15) = 2.73(1) Å). Similar associations of pyridinium cations with decavanate anions via hydrogen bondings were reported in some decavanadate compounds.[5]

Each decavanadate anion is bridged by H_2dpds to form a one-dimensional network of $(\mathbf{1}\cdot 2H_2O)_n$ along the *b*-axis as shown in Figure 2. The torsion angle of the S-S bond of the H_2dpds ligand is 86.2(5)°. The regulated arrangement of these chains creates microchannels along the *c*-axis, whose dimension is about 2 x 4 Å. To the best of our knowledge, this is the first example of microporous network constructed from polyoxometalates and organic moieties. This size of channel structure is comparable to those of some zeolite compounds; analcime (2.2-2.4 Å), natrolite or thomsonite (2.6 x 3.9 Å). The channeling cavities of $\mathbf{1}\cdot 10H_2O$ are filled with crystal water molecules, O(16), O(17), O(18) and O(19), which are connected by hydrogen bondings each other. These crystal waters except for O(17) are linked to oxygen atoms of the decavanadate anion by hydrogen bondings (O(14)-O(16) = 2.69(1) Å, O(4)-O(18) = 3.14(2) Å, O(3)-O(19) = 2.99(2) Å).

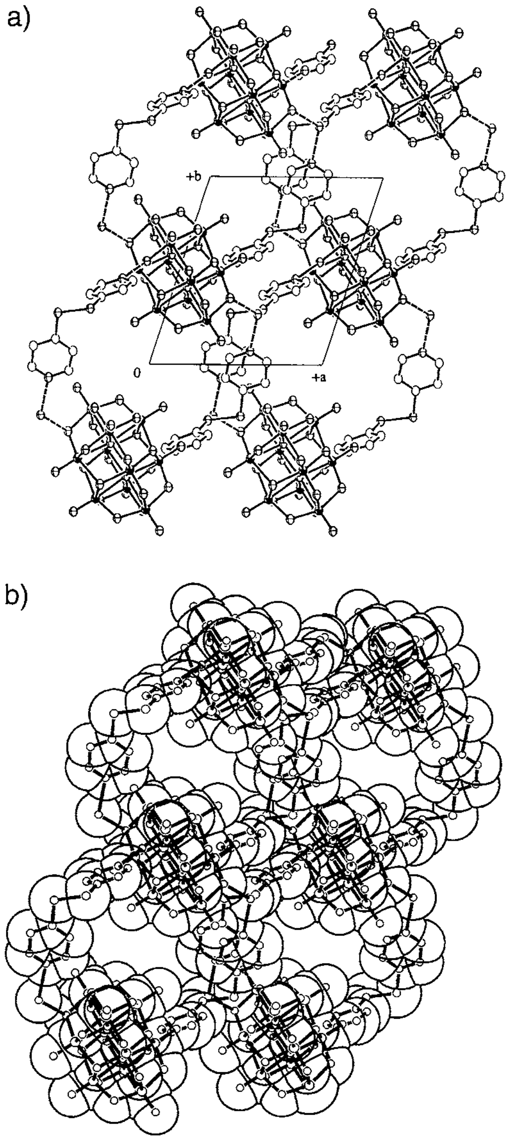

Figure 3. View of the channel structure of $\mathbf{1}\cdot 10H_2O$ along the *c*-axis (a) and the space-filling model (b). Broken lines indicate hydrogen bonding. Crystal water molecules (O(16), O(17), O(18), and O(19)) and hydrogen atoms are omitted for clarity.

The channel structure of $\mathbf{1}\cdot 10H_2O$ is novel in that the polyoxometalates afford new chemical environments which could be interacted with guest molecules in the channels. This synthetic approach could provide various functional porous materials by means of combination of several polyoxometalates and organic moieties, and the study is in progress.

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References and Notes

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3 Elemental analysis: $\mathbf{1}\cdot 4H_2O$; Anal. Calcd for $C_{20}H_{30}N_4O_{32}S_4V_{10}$: C, 16.27; H, 2.05; N, 3.80%. Found: C, 15.90; H, 1.85; N, 3.61%; Yield; 5%.

4 Crystal data for $\mathbf{1}\cdot 10H_2O$: $C_{20}H_{42}N_4O_{38}S_4V_{10}$, M = 1584.2, triclinic, space group $P\bar{1}$ (no. 2), a = 11.098(6), b = 12.176(5), c = 10.863(4) Å, α = 100.17(3), β = 109.23(4), γ = 70.11(3)°, V = 1299(1) Å^3, Z = 1, D_{calcd} = 2.024 g/cm^3, MoKα (λ = 0.71069 Å), μ = 19.76 cm^{-1}, T = 296 K , 6278 reflections measured, 5970 independent, 2258 [$I > 2.0\sigma(I)$] included in the refinement, anisotropic refinement for non-hydrogen atoms by full-matrix least-squares with a program package teXsan (MSC), 344 parameters R = 0.061, R_w = 0.063, $\Delta\rho_{max}$ = 0.73 eÅ^{-3}, $\Delta\rho_{min}$ = -0.72 eÅ^{-3}.

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