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First hexadecavanadate compound: hydrothermal synthesis and characterization of a three-dimensional framework $[\{Cu(1,2\text{-}pn)_2\}_7\{V_{16}O_{38}(H_2O)\}_2]\cdot 4H_2O$

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The hydrothermal reaction of V_2O_5, $Cu(CH_3COO)_2\cdot H_2O$, 1,2-diaminopropane and $[N(CH_3)_4]OH$ yields the novel three-dimensional open-framework solid $[\{Cu(1,2\text{-}pn)_2\}_7\{V_{16}O_{38}(H_2O)\}_2]\cdot 4H_2O$ constructed from the new mixed-valence $[V_{16}O_{38}(H_2O)]^{7-}$ clusters interconnected through μ_2-$[Cu(1,2\text{-}pn)_2]^{2+}$ groups.

There contemporary interest in polyoxometalate clusters reflects their applications in areas such as catalysis, nanotechnology, analytical chemistry and photochemistry.[1,2] Due to the remarkable features of metal oxide surfaces[3] and the diversities in the geometric topology and the oxidation state of clusters,[1,4] these has recently been increasing interest in assembly of polyoxometalate clusters with inorganic or organometallic bridging complexes into extended structures.[5–15] Typical examples include one-dimensional $[Ni(2,2'\text{-}bpy)_2Mo_4O_{13}]$[8] and $Cs_{10.5}[\{V_{16}O_{40}\}(Si_{4.5}V_{1.5}O_{10})]\cdot 3.5H_2O$,[9] two-dimensional $[\{Cu(en)_2\}_2Mo_8O_{26}]$[10] and $[\{Cu_3\{4,7\text{-}phen\}_3\}_2Mo_{14}O_{45}]$,[11] three-dimensional $(N_2H_5)_2[Zn_3(H_2O)_{12}V_{18}O_{42}(SO_4)]\cdot 24H_2O$,[12] $[Fe_3(H_2O)_{12}V_{18}O_{42}(VO_4)]\cdot 24H_2O$[13] and $[\{Gd(H_2O_3)\}_3\{GdMo_{12}O_{42}\}]\cdot 3H_2O$.[14] We report herein the hydrothermal synthesis and characterization of a novel three-dimensional framework $[\{Cu(1,2\text{-}pn)_2\}_7\{V_{16}O_{38}(H_2O)\}_2]\cdot 4H_2O$ **1**. Unlike most of these known materials with extended structures composed of well-characterized metal oxo cluster types, compound **1** is built up of a new type of mixed-valance vanadium oxo clusters $[V_{16}O_{38}(H_2O)]^{7-}$ as structural motifs.

Compound **1** was prepared as black rhombs in 60% yield (based on vanadium) from the hydrothermal reaction of V_2O_5, $Cu(CH_3COO)_2\cdot H_2O$, 1,2-diaminopropane (= 1,2-pn), $[N(CH_3)_4]OH$ and water in the molar ratio of 3 : 1 : 6.7 : 6 : 667 at 150 °C for 70 h in a 17 mL Teflon-lined autoclave. The crystalline product was characterized by element analysis, IR spectroscopy,† redox titration, magnetic measurement, and single-crystal X-ray diffraction.‡

The structure of **1** is made up of the $[V_{16}O_{38}(H_2O)]^{7-}$ clusters linked by the $[Cu(1,2\text{-}pn)_2]^{2+}$ complex coordination groups into a three-dimensional open-framework, as shown in Fig. 1(a), where the lattice water molecules occupy the channels in the framework. This structure can also be described as a series of two-dimensional layers, each layer is constructed from the $[V_{16}O_{38}(H_2O)]^{7-}$ clusters cross-bridged by some *trans*-$\{Cu(1,2\text{-}pn)_2O_2\}$ motifs (Fig. 1(b)). The neighbouring layers are held together by the other *trans*-$\{Cu(1,2\text{-}pn)_2O_2\}$ motifs, forming a three-dimensional framework structure (Fig. 1(*a*)). As depicted in Fig. 2, each cagelike $[V_{16}O_{38}(H_2O)]^{7-}$ cluster, with approximate S_4 symmetry, is composed of the $\{V_{16}O_{38}\}$ shell encapsulating a neutral H_2O molecule. The shell is built up from sixteen VO_5 distorted square pyramids that share edges and corners through two μ_2- and twenty μ_3-oxygen atoms, respectively. The sixteen V atoms are arranged at the surface of a sphere with radius of 3.55 ± 0.34 Å from the central H_2O. In the structure of **1**, the $[V_{16}O_{38}(H_2O)]^{7-}$ cluster acts as a heptadentate ligand coordinating to seven Cu(II) ions through the terminal oxygen atoms with Cu–O distances ranging from 2.382(7) to 2.739(8) Å, such that each $[V_{16}O_{38}(H_2O)]^{7-}$ cluster is connected with seven others through $[Cu(1,2\text{-}pn)_2]^{2+}$ groups in a staggered manner to generate a three-dimensional framework. The octahedral geometry around Cu(II) is completed by four equatorial nitrogen atoms from two 1,2-diaminopropane ligands and two *trans*-oxo groups from two neighboring clusters.

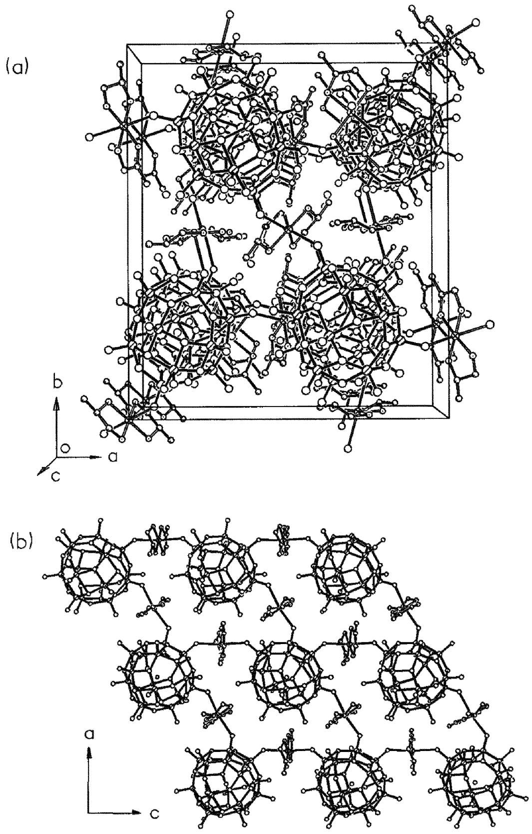

Fig. 1 (a) The structure of **1** projected along the *c* axis showing arrays of $\{V_{16}O_{38}(H_2O)\}$ clusters interconnected through $\{Cu(1,2\text{-}pn)_2\}$ bridging groups and channels occupied by the water molecules of crystallization. Cu and V atoms are represented by cross-hatched and striped circles, respectively, while O, N and C are represented by open, dotted and shaded circles, respectively. Hydrogen atoms are omitted for clarify. (b) A view of **1** at $y \approx 1/4$.

As determined by the redox titration of the acidic solution against standardized $KMnO_4$ solution, there are eleven reduced V^{IV} centers in the $[V_{16}O_{38}(H_2O)]^{7-}$ unit of **1**. The assignment of the oxidation state for the V atoms is consistent with the electric charge and confirmed by bond valence sum calculations.[16] The valence sums for sixteen V atoms are 4.58, 4.27, 4.59, 4.67, 3.97, 4.48, 4.65, 4.01, 4.57, 4.13, 4.40, 4.56, 3.97, 4.48, 4.57 and 4.29, respectively. The average value is 4.38, very close to the expected value 4.31 for $V^{IV}{}_{11}V^{V}{}_5$. The molar effective magnetic moment (μ_{eff}) of **1** at 260 K was 7.42 μ_B,

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slightly less than the sum value expected for a nineteen isolated paramagnetic system with $S = 0.5$ ($\mu_{eff} = 7.55\ \mu_B$). After deducing the seven Cu(II) centers' contribution, the origin from each $[V_{16}O_{38}(H_2O)]^{7-}$ unit is equivalent to that from six unpaired electrons. This fact indicates that the eleven unpaired d^1 electrons within each polyanion unit in **1** are partially delocalized, as observed in most observed polyoxometalate clusters.[1,17] Examination of the magnetic behavior with temperature is in progress.

To the best of our knowledge, the $[V_{16}O_{38}(H_2O)]^{7-}$ cluster in **1** represents the first observation of a hexadecamatalate structure in polyoxovanadate chemistry. Since the 'naked' cluster has not been observed up to date, the Cu–O covalent interactions between the cluster units and the bridging complexes may play an important role in the stabilization of the hexadecavanadate clusters in the structure of **1**. This M–O interaction effect has also been observed in the formation of the hexavanadate $V_6O_{19}{}^{8-}$ core in $[(C_5Me_5)Rh]_4[V_6O_{19}]$.[18] Additionally, it is noteworthy that the linkage between polyoxometalate clusters in the structure of **1** is different from those in the known analogous frameworks.[12–15] While each polyoxometalate cluster is connected to six others in $(N_2H_5)_2[Zn_3(H_2O)_{12}V_{18}O_{42}(SO_4)]\cdot 24H_2O$,[12] $[Fe(H_2O)_{12}V_{18}O_{42}(VO_4)]\cdot 24H_2O$[13] and $[\{Gd(H_2O_3)\}_3\{GdMo_{12}O_{42}\}]\cdot 3H_2O$,[14] each $[V_{16}O_{38}(H_2O)]^{7-}$ cluster in **1** is linked to seven other neighboring units through the bridging groups. In summary, the success in preparing compound **1** demonstrates that the combination of hydrothermal techniques and incorporation of appropriate templates affords a well-suited method for the isolation of framework solids containing chemically robust polyoxometalate clusters as building units.

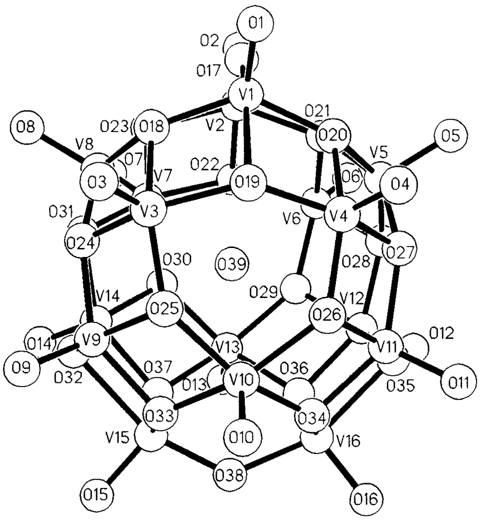

Fig. 2 The $\{V_{16}O_{38}(H_2O)\}$ cluster unit in the structure of **1**. Bond length ranges (Å): V–O_{term} 1.561(8)–1.628(9), V–(μ_2-O) 1.749(7)–1.902(7), V–(μ_3-O) 1.834(8)–2.290(9). Bond angle ranges (°): O_{term}–V–(μ-O) 95.6(4)–112.3(4), (μ-O)–V–(μ-O) 75.6(3)–109.6(4) and 135.2(4)–159.6(3) V–(μ_2-O)–V 128.3(4)–129.4(7), V–(μ_3-O)–V 91.1(3)–106.1(4) and 126.8(4)–145.2(4).

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Notes and references

† The synthesis was carried out in a 17mL Teflon-lined stainless steel vessel filled to 45% at room temperature. A mixture of V_2O_5, $Cu(CH_3COO)_2\cdot H_2O$, 1,2-pn, $[N(CH_3)_4]OH$ and water in a molar ratio of 3 : 1 : 6.7 : 6 : 667 at 150 °C for 70 h gave black rhombs of **1** in 60% yield (based on V). Anal. Calc. for $C_{42}H_{152}Cu_7N_{28}O_{82}V_{32}$ **1**: C, 11.37; H, 3.45; N, 8.84; Cu, 10.03; V, 36.74. Found: C, 11.29; H, 3.40; N, 8.91; Cu, 10.11; V, 36.66%. IR (KBr pellet): 3227(m), 2963(w), 1585(s), 1454(m), 1380(w), 1192(w), 1056(s), 1023(w), 975(vs) and 678(s) cm^{-1}.

‡ *Crystal data*: diffraction data for **1** were collected on a crystal with dimensions 0.32 × 0.20 × 0.08 mm using a Rigaku R-AXIS-Parid IP diffractometer and Mo-Kα radiation (λ = 0.71069 Å) at 293(2) K. Monoclinic, space group $P2_1/n$, a = 21.510(2), b = 25.580(3), c = 12.632(1) Å, β = 91.17(1)°, Z = 2, D_c = 2.120 g cm^{-3}, μ = 3.179 mm^{-1}. Of 25395 data collected ($2\theta_{max}$ = 55°), 15162 were independent (R_{int} = 0.0731) and 5546 were observed ($I > 2\sigma(I)$). An empirical absorption correction from φ-scans was applied. All non-hydrogen atoms were refined anisotropically, except that the O atoms of the encapsulating water in the cluster and the lattice water molecules were done isotropically. While the hydrogen atoms riding on C and N atoms were located in calculated positions, those on O atoms were in the positions from difference Fourier map. At convergence, R_1 = 0.0655, wR_2 = 0.1610 for 847 parameters.

CCDC reference number 190056. See http://www.rsc.org/suppdata/cc/b2/b206880j/ for crystallographic data in CIF or other electronic format.

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