Hydrothermal Synthesis and Characterization of a Novel Sinusoidal Layer Structure Constructed From Polyoxometalates and Coordination Complex Fragments

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A novel polyoxometalate compound, $[As_8V_{14}O_{42}(SO_4)][Ni(en)_2]_3\cdot 4.5H_2O$ (**1**), has been synthesized by a hydrothermal method and characterized by X-ray crystallography, showing that the compound **1** is the first example of a sinusoidal layer structure constructed from polyoxometalates and coordination complex fragments.

Introduction

Polyoxometalates (POMs) are a fascinating class of metal-oxygen cluster compounds with a wide structural variety and interesting properties, which are of use in fields as diverse as catalysis, sorption, molecular electronics, and medicine, amongst others.[1−3] Despite the fundamental and practical importance of polyoxometalates, the preparation of these complexes still remains elusive and is often described as self-assembly. Recently, a novel approach to the synthesis of polyoxometalate chemistry has been to find some novel units as building blocks and then to connect them up into one-, two-, or even three-dimensional extended solid frameworks in appropriate ways. This method is quite attractive and appears to hold the key to the development of a rational synthesis for tailor-made materials based on polyoxometalates with desirable features. The crucial requirement for the success of this approach is to find suitable polyoxometalates that could be readily assembled. Polyoxometalates and their derivatives provide an exciting opportunity to explore the potential of this approach. Hydrothermal synthesis techniques, in combination with organic templates, have been demonstrated to be useful in the preparation of metal oxide materials.[4,5] A number of extended solid framework materials based on polyoxometalates as building blocks have been synthesized hydrothermally.[6−17]

Arsenic-vanadium clusters, one of the most important subclasses of polyoxometalates, have been thoroughly investigated, and typical examples include $[As_8V_{14}O_{42}(X)]^{6-}$ ($X = SO_3^{2-}$ or SO_4^{2-}),[18] $[N(Me)_4]_4[As_8V_{14}O_{42}(H_2O)_{0.5}$ [18] and $K_6[As_6V_{15}O_{42}(H_2O)]\cdot 8H_2O$.[18] Most of them exhibit discrete cluster structures and are able to function as building blocks. However, compared with the abundance of compounds based on the $[V_{18}O_{42}]$ cluster,[8−11,14] the linking of arsenic-vanadium clusters into one-, two-, and three-dimensional structures remains relatively unexplored.[12,13] We have therefore extended our search for solid framework complexes by exploiting arsenic-vanadium clusters as building blocks — the successful use of the $[As_8V_{14}O_{42}(SO_4)]^{6-}$ [18] cluster results in the formation of a two-dimensional structural compound $[As_8V_{14}O_{42}(SO_4)][Ni(en)_2]_3\cdot 4.5H_2O$ (**1**), which is the first example of a two-dimensional sinusoidal layer structure constructed from polyoxometalates and coordination complex fragments.

Results and Discussion

A novel metal-oxygen cluster polymer, $[As_8V_{14}O_{42}(SO_4)][Ni(en)_2]_3\cdot 4.5H_2O$, has been hydrothermally synthesized and structurally characterized. Selected bond lengths for **1** are given in Table 1. It crystallizes in the triclinic space group $P\bar{1}$ with a unit cell containing two units. There are four crystallographically independent nickel atoms in an asymmetric unit, Ni(2) and Ni(3) are located on inversion centers with occupancy factors of 0.5, and all other atoms are at general positions.

The X-ray crystal structural analysis suggests that compound **1** is a novel, sinusoidal layered compound containing $[As_8V_{14}O_{42}(SO_4)]^{6-}$ clusters, $[Ni(en)_2]^{2+}$ cations and waters of crystallization. The building block unit, shown in Figure 1, consists of fourteen distorted VO_5 square pyramids and eight AsO_3 triangular units, with a disordered SO_4^{2-} anion at its center. Every two AsO_3 groups are joined to-

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Table 1. Selected bond lengths (Å) for compound **1**

As(1)−O(31)	1.759(11)	V(5)−O(49)	2.009(9)
As(1)−O(47)	1.770(10)	V(5)−O(48)	2.024(10)
As(1)−O(32)	1.789(9)	V(6)−O(16)	1.600(11)
As(2)−O(23)	1.749(10)	V(6)−O(41)	1.934(10)
As(2)−O(11)	1.782(10)	V(6)−O(25)	1.956(10)
As(2)−O(42)	1.766(10)	V(6)−O(36)	2.016(10)
As(3)−O(44)	1.778(10)	V(6)−O(28)	2.032(10)
As(3)−O(26)	1.799(11)	V(7)−O(39)	1.571(11)
As(3)−O(32)	1.804(9)	V(7)−O(22)	1.943(10)
As(4)−O(49)	1.751(10)	V(7)−O(30)	1.968(10)
As(4)−O(38)	1.755(11)	V(7)−O(26)	2.003(10)
As(4)−O(11)	1.806(9)	V(7)−O(38)	2.035(11)
As(5)−O(33)	1.763(9)	V(8)−O(21)	1.639(10)
As(5)−O(8)	1.775(10)	V(8)−O(26)	1.945(10)
As(5)−O(40)	1.780(12)	V(8)−O(38)	1.978(10)
As(6)−O(48)	1.761(10)	V(8)−O(42)	2.014(10)
As(6)−O(9)	1.764(10)	V(8)−O(31)	2.009(10)
As(6)−O(19)	1.782(11)	V(9)−O(34)	1.601(10)
As(7)−O(28)	1.758(9)	V(9)−O(37)	1.937(10)
As(7)−O(45)	1.782(10)	V(9)−O(17)	1.947(10)
As(7)−O(40)	1.783(12)	V(9)−O(23)	2.008(10)
As(8)−O(29)	1.756(10)	V(9)−O(33)	2.012(9)
As(8)−O(36)	1.763(9)	V(10)−O(10)	1.630(9)
As(8)−O(19)	1.793(12)	V(10)−O(46)	1.910(10)
V(1)−O(24)	1.618(10)	V(10)−O(37)	1.932(10)
V(1)−O(46)	1.939(9)	V(10)−O(33)	2.006(10)
V(1)−O(25)	1.958(10)	V(10)−O(45)	2.008(10)
V(1)−O(45)	1.987(11)	V(11)−O(15)	1.599(12)
V(1)−O(47)	2.002(10)	V(11)−O(17)	1.955(10)
V(2)−O(35)	1.596(10)	V(11)−O(18)	1.952(10)
V(2)−O(22)	1.925(10)	V(11)−O(9)	2.014(11)
V(2)−O(41)	1.938(10)	V(11)−O(8)	2.042(10)
V(2)−O(44)	1.981(9)	V(12)−O(13)	1.607(11)
V(2)−O(29)	2.018(11)	V(12)−O(8)	1.956(11)
V(3)−O(14)	1.599(10)	V(12)−O(9)	1.961(11)
V(3)−O(46)	1.964(9)	V(12)−O(28)	1.971(11)
V(3)−O(37)	1.981(10)	V(12)−O(36)	1.981(11)
V(3)−O(42)	2.042(10)	V(13)−O(27)	1.634(11)
V(3)−O(31)	2.037(11)	V(13)−O(41)	1.934(9)
V(4)−O(20)	1.629(9)	V(13)−O(25)	1.934(10)
V(4)−O(22)	1.908(10)	V(13)−O(47)	1.981(9)
V(4)−O(30)	1.905(10)	V(13)−O(44)	1.978(10)
V(4)−O(29)	2.007(10)	V(14)−O(12)	1.604(11)
V(4)−O(48)	2.012(10)	V(14)−O(17)	1.936(10)
V(5)−O(43)	1.626(10)	V(14)−O(18)	1.963(10)
V(5)−O(30)	1.947(10)	V(14)−O(23)	1.998(9)
V(5)−O(18)	1.942(10)	V(14)−O(49)	2.023(9)

gether by an oxygen bridge, forming a handle-like As_2O_5 moiety. In the cluster, eight vanadium [V(1), V(2), V(4), V(5), V(9), V(10), V(13) and V(14)] oxygen square pyramids are linked to one another into a ring by sharing edges. In addition, three vanadium [V(6), V(11) and V(12)] oxygen square pyramids form a trimer by sharing edges. This trimer is connected across the ring by sharing edges with V(13)- and V(14)-containing square pyramids. Vanadium[V(3), V(7) and V(8)] oxygen square pyramids form another trimer by sharing edges, and this trimer is similarly connected on the opposite side of the ring to V(4)- and V(10)-containing square pyramids. Therefore, fourteen VO_5 square pyramids are arranged to form a cage, the overall chemical composition of which is $[(VO)_{14}O_{24}]$. Clearly there are twenty-four oxygen atoms occupying the vertices of the cage, which has a total of eighteen square faces. Fourteen of them are formed by the bases of the VO_5 square pyramids, and the remaining square faces are formed by the bases of the As_2O_5 units to give a total composition of $[As_8V_{14}O_{42}]^{4-}$. The V−O and the As−O distances are all similar to those in reported compounds.[18]

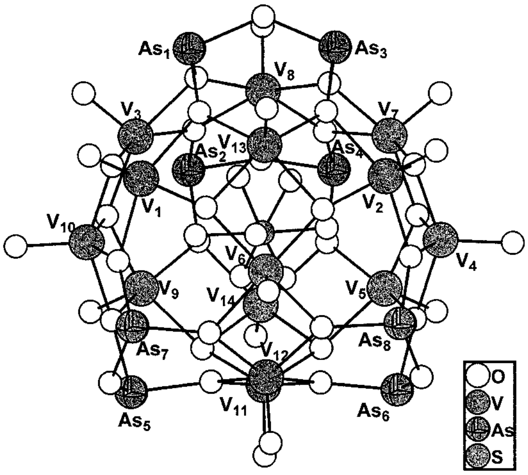

Figure 1. Ball-and-stick representation of the $[As_8V_{14}O_{42}(SO_4)]^{6-}$ cluster

There are two different types of $[Ni(en)_2]^{2+}$ cations in **1**. The first type contains $[Ni(2)(en)_2]^{2+}$, $[Ni(3)(en)_2]^{2+}$ and $[Ni(4)(en)_2]^{2+}$ cations, in which each octahedrally coordinated nickel atom bridges two clusters. The nickel site is defined by four nitrogen donors from two en ligands and *trans*-oxo atoms from two adjacent clusters, and these nickel atoms exhibit very strong covalent attachments to adjacent clusters, with Ni−O distances in the range 2.082(10)−2.110(10) Å. Four surface oxygen atoms of one cluster coordinate to four bridging nickel atoms [Ni(2), Ni(3) and two Ni(4)], so each cluster is connected to four neighboring ones into a two-dimensional network of $[\text{-}\{As_8V_{14}O_{42}(SO_4)\}\text{-}\{Ni(en)_2\}\text{-}\{As_8V_{14}O_{42}(SO_4)\}\text{-}]_n$ arrays, as shown in Figure 2 (a). This layer is arranged parallel to the crystallographic *ab* plane. In the layer, through the connection of each Ni(4) atom, the clusters are linked to one another along the $a - b$ axis into a novel straight chain, as shown in Figure 2 (b), while through the connections alternatively at Ni(2) and Ni(3), each chain is connected with the adjacent ones along the $a + b$ axis, forming a novel sinusoidal layer. Figure 2c clearly shows that the layer displays a beautiful sinusoidal ruffling look, with an amplitude of about 20.8 Å, which is larger than those in $[M(bpy)_2]_2V_6O_{17}$ (M = Zn, Ni, about 13 Å)[19,20] and $[Ni(Phen)_2]_2V_4O_{11}$ (about 18.5 Å),[21] whereas the period (about 25.9 Å) is also far larger than those in $[M(bpy)_2]_2V_6O_{17}$ (M = Zn, Ni, about 15 Å)[19,20] and $[Ni(Phen)_2]_2V_4O_{11}$ (about 9.7 Å).[21] These differences clearly originate from the fact that the layer of compound **1** is constructed from coordination complexes and bulky sphere-like $[As_8V_{14}O_{42}(SO_4)]^{6-}$ clusters, which makes the amplitude and period larger. The structure of compound **1** can be described as being built up from $[As_8V_{14}O_{42}(SO_4)]^{6-}$ clusters linked into a two-dimensional sinusoidal layer structure. It is the most unusual feature of compound **1**, and, to the best of our knowledge, such a feature has not been found in any other structures of polyoxometalates.

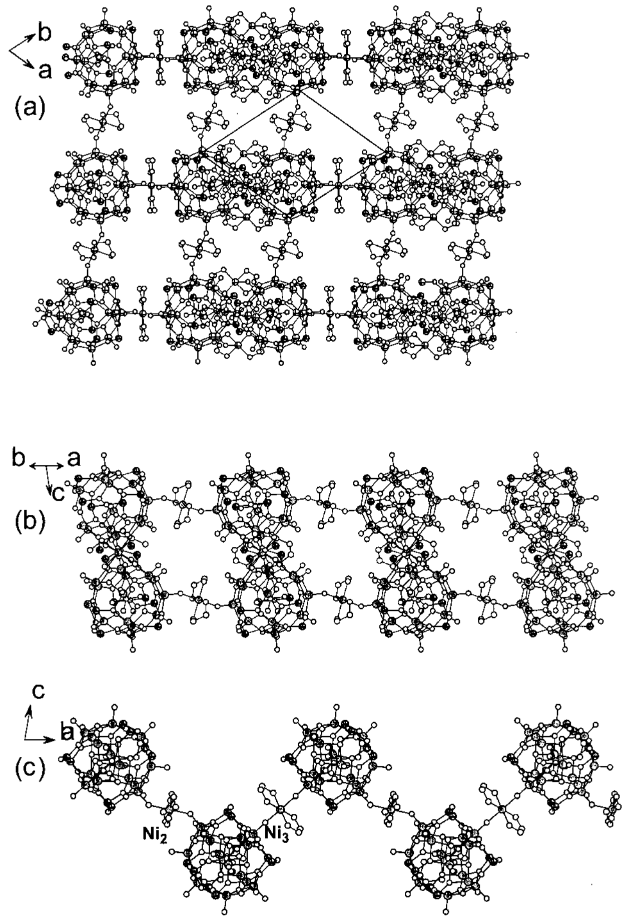

Figure 2. (a) A view of the sinusoidal layer of compound **1** down the *c* axis; (b) the sinusoidal layer of compound **1** extending along the *a* − *b* axis; (c) the sinusoidal layer of compound **1** extending along the *a* + *b* axis

The $[Ni(1)(en)_2]^{2+}$ cation is the second type of Ni atom, and it serves as a charge-compensating component. The $[Ni(en)_2]^{2+}$ cations of this type occupy the regions between the adjacent sinusoidal layers. In contrast to the bridging $[Ni(en)_2]^{2+}$ cations of the first group, the nickel atoms of the second group exhibit only weak interactions with the clusters, with Ni···O distances of 2.852(11)−3.145(11) Å.

The assignments of the oxidation states for the vanadium and arsenic atoms are consistent with the electric charge and confirmed by bond valence sum (BVS) calculations.[22] The BVS values for vanadium and arsenic atoms vary from 3.767 to 4.237 and from 2.997 to 3.240, respectively, indicating that the oxidation state for each vanadium atom and each arsenic atom is +4 and +3, respectively. The oxidation states of the vanadium atoms and the arsenic atoms are consistent with the formula of compound **1**.

Preliminary magnetic studies have been performed on a powered sample of **1** in the range 2−300 K. Plots of χ_m^{-1} and μ_{eff} vs. T for **1** are shown in Figure 3. The product μ_{eff} decreases continuously as the temperature is lowered, indicating the presence of an antiferromagnetic exchange interaction. The room-temperature value ($\mu_{eff} = 6.84\ \mu_B$) is smaller than the expected value ($\mu_{eff} = 7.83\ \mu_B$) for the 14 uncoupled $S = 1/2$ spins of the V^{4+} atoms and the two uncoupled $S = 1$ spins of the Ni^{2+} atoms (two nickel atoms of the first type are octahedrally coordinated, with $S = 1$, and the nickel atom of the second type displays a square-planar environment, with $S = 0$, assuming $g = 2.0$ for V^{4+} and $g = 2.20$ for Ni^{2+}), indicative of antiferromagnetic coupling. These antiferromagnetic coupling interactions are related to electron delocalization of high-nuclearity metal clusters.[23] Unfortunately, it is too difficult to fit the experimental magnetic data of this two-dimensional heteropolymetallic spin system using a suitable theoretical model.[24] However, the magnetic data of **1** obey the Curie−Weiss law in the high-temperature regions, and the fitting in the range 80−300 K gives values of $C = 5.26$ emu·mol^{-1}·K and $\theta = -1.11$ K, characteristic of an overall antiferromagnetic interaction.

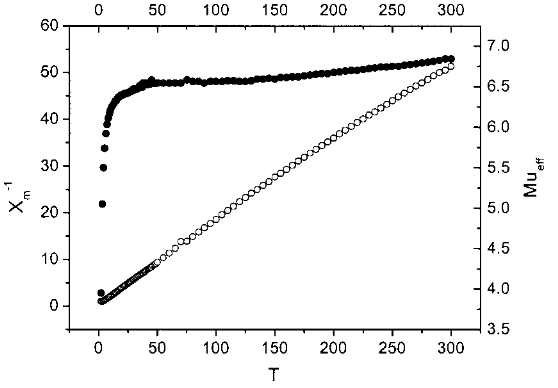

Figure 3. The effective magnetic moment μ_{eff} (filled circles) and inverse molar susceptibility (open circles) vs. temperature for **1**

The ESR spectrum of **1** at room temperature shows no signals for V^{4+}. This lack of signals indicates that the electrons of the cluster are spin-spin coupled. Figure 4 (a) shows the XPS[25] spectrum of **1** in the V 2p region, with the peak at 516.2 eV being ascribed to V^{4+}. Figure 4 (b) shows the spectrum of **1** in the As 3d region, with the peak at 45 eV being attributed to As^{3+}. The XPS estimation of the valence-state values seems to be in reasonable agreement with those calculated from the bond valence sum calculations. These results further confirm the valences of the arsenic and vanadium atoms.

Conclusion

Complex **1** is synthesized from V_2O_5 by exploiting the reducing ability of $H_2C_2O_4{\cdot}2H_2O$ and en. The presence of $H_2C_2O_4{\cdot}2H_2O$ and en is absolutely essential to the product formation. The successful synthesis of compound **1** provides another example of connecting arsenic-vanadium

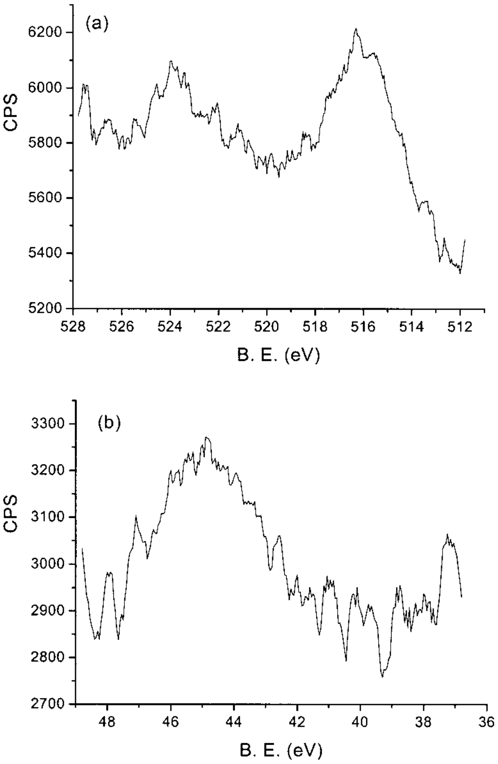

Figure 4. (a) XPS spectrum of V $2p_{3/2}$ for compound **1**; (b) XPS spectrum of As $3d_{5/2}$ for compound **1**

clusters by transition metal coordination complexes. It suggests that further condensation of clusters into higher dimensional solids through the linkage of the coordination complexes could be feasible. The bridging center may be replaced by other metal ions (Cu, Co, Mn etc.), and the building block clusters may be substituted by other arsenic-vanadium clusters, such as$[As_8V_{14}O_{42}(H_2O)_{0.5}]^{4-}$ [18] and $[As_6V_{15}O_{42}(H_2O)]^{6-}$.[18]

Experimental Section

General Remarks: All reagents were purchased commercially and used without further purification. The content of vanadium, nickel and arsenic was determined on a Perkin−Elmer Optima 3300DV spectrometer. Elemental analyses (C, H and N) were performed on a Perkin−Elmer 2400 Series II CHNS/O elemental analyzer. The infrared spectrum was obtained on an Perkin−Elmer spectrophotometer in the 200−4000 cm^{-1} region with pressed KBr pellet. Measurement of the electron-spin resonance (ESR) spectrum carried out on a Bruker ER 200D-SRC diffractometer. XPS measurements were performed on single crystals with an Escalab Mark II apparatus, using Mg-K_α X-ray radiation as the excitation source ($E_{\text{Mg-}K_\alpha} = 1253.6$ eV). Variable-temperature magnetic susceptibility measurements for **1** were performed on a MPMS-XL magnetometer over the range 2−300 K.

Synthesis of 1: Compound **1** was hydrothermally synthesized in 73% yield (based on V). A mixture of As_2O_3 (0.40 g), V_2O_5 (0.36 g), $H_2C_2O_4{\cdot}2H_2O$ (0.25 g), en (0.24 g), $NiSO_4{\cdot}6H_2O$ (0.53 g), and distilled water (21.6 mL) in a molar ratio of 1:1:1:2:1:600 was stirred for ca. 10 min and then transferred to a Teflon-lined reactor and heated at 160 °C for three days. $H_2C_2O_4{\cdot}2H_2O$ was used as reducing agent and it was necessary to maintain the pH value of the reaction system. After cooling to room temperature, black block crystals were isolated. The compound **1** is stable to air in water, and in acetone. Elemental analysis (%): calcd. As 22.21, V 26.43, S 1.19, Ni 6.53, C 5.34, H 2.13, N 6.23; found As 22.18, V 26.41, S 1.14, Ni 6.54, C 5.33, H 2.07, N 6.21. IR: 3451(w) cm^{-1}, 2925(w), 1587(m), 1139(m), 1016(m), 969(s), 704(s).

X-ray Crystallographic Study: $C_{12}H_{57}As_8N_{12}Ni_3O_{50}SV_{14}$ (**1**), $M_r = 2698.41$, triclinic space group $P\bar{1}$, $a = 12.9318(6)$ Å, $b = 13.4441(7)$ Å, $c = 21.2885(13)$ Å, $\alpha = 87.260(3)°$, $\beta = 77.637(2)°$, $\gamma = 68.699(3)°$, $V = 3366.5(3)$ Å^3, $Z = 2$, $\rho = 2.662$ mg·m^{-1}, μ(Mo-K_α) = 6.704 mm^{-1}, $F(000) = 2606$, $R\,[I \geq 2\sigma(I)] = 0.0707$, $wR2 = 0.2161$ for all reflections, goodness-of-fit = 0.883.
A black crystal (dimensions 0.447 × 0.367 × 0.273 mm^3) was carefully chosen from the batch sample and mounted on a glass fiber for data collection at 293 K on a Rigaku RAXIS-RAPID diffractometer equipped with Mo-K_α radiation. A total of 16168 reflections were measured, 9572 of which were unique. Structure solution was performed with SHELXS-97 by direct methods. All atoms except C(1) were refined anisotropically. The Ni(1) atom is disordered over two positions, with occupancy factors of 0.63 and 0.37, respectively. The hydrogen atoms were positioned with an idealized geometry and refined with fixed isotropic-displacement parameters using a riding model.
CCDC-210956 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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