

One-Dimensional Arsenic-Vanadium Cluster Chain Bridged by Two Co(en)₂ Groups

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(Received January 24, 2000; CL-000078)

The hydrothermal reaction of As₂O₃, V₂O₅, Co(Ac)₂, H₃PO₄, en and H₂O produces [Co^{II}(en)₃][{Co^{II}(en)₂}₂-As^{III}₆V^{IV}₁₅O₄₂]₂·4H₂O, which consists of a one-dimensional arsenic-vanadium cluster chain bridged by two different geometries of Co(en)₂ groups. The interactions, which are established through hydrogen-bonding involving water molecules, the amine nitrogens, and terminal oxygen atoms, result in three-dimensional hydrogen-bonding network. Magnetic measurement indicates that the overall magnetic behavior is weakly antiferromagnetic.

Interest in polyoxometalates is expanding rapidly due to the enormous variety of structure topologies leading to interesting and unexpected properties in such diverse fields as catalysis, materials science and medicine.¹⁻⁴ Until now, the mechanism of the formation of polyoxometalates is still not fully understood and often is described as self-assembly. What appears to be evident in exploiting molecular building blocks is to employ polyoxoanions linked through some kinds of tethers to form extended structures.⁵⁻¹⁰ While the synthetic method leading to rational design remains a challenging topic, there seems to be an increasing use of a combination of hydrothermal synthesis method and structure-directing templates. On-going research has demonstrated that a number of transition metal oxides, typically reduced molybdenum oxides, mixed-valence vanadium oxides and tungsten oxides, are readily assembled to produce one-, two- and three-dimensional framework materials.⁵⁻⁸ For the heteropolyanions class of clusters, the V/As/O system has been extensively studied,¹¹⁻¹⁵ but the linking of arsenic-vanadium clusters into molecular and supramolecular structures is much less developed. As a continuation of our effort in the hydrothermal assembly of polyoxovanadium-based solid materials,¹⁶⁻¹⁹ we seek to explore the assembly of arsenic-vanadium clusters in the presence of transition metal ions and en. Here we report the hydrothermal synthesis and structural characterization of a novel one-dimensional hybrid solids, [Co^{II}(en)₃][{Co^{II}(en)₂}₂-As^{III}₆V^{IV}₁₅O₄₂]₂·4H₂O **1**.

Solid **1** was prepared from the hydrothermal reaction of V₂O₅, H₃PO₄, As₂O₃, Co(Ac)₂, en and H₂O (mole ratios: 3: 3: 4: 2: 2: 500). The mixture (20 mL) was sealed in a Teflon-lined stainless steel autoclave and heated at 160 °C for three days. The resulting black crystals were formed in the autoclave in 78% yield.²⁰ The infrared spectrum (KBr Pellet) of **1** exhibited a strong band at 965 cm⁻¹ ascribed to ν(V=O) and a series of bands in the 610-750 cm⁻¹ region characteristic of ν(M-O-M') (M, M'= As, V).

The X-ray structure analysis²¹ reveals that compound **1** consists of infinite chains of [As₆V₁₅O₄₂]⁶⁻ clusters covalently linked through two different geometries of [Co(en)₂]²⁺ groups, with water molecules and isolated [Co(en)₃]²⁺ cations as charge compensation occupying interchain regions. As shown in

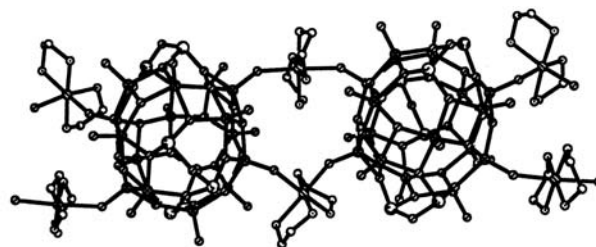


Figure 1: The view of one-dimensional chains of [Co(en)₂]₂As₆V₁₅O₄₂. Selected bond lengths (Å): V1-O1 (#1): 1.63(2); V2-O2: 1.62(2); V5-O5: 1.63(2); V6-O6 (#2): 1.62(2); Co2-O1: 2.19(2); Co2-O2: 2.27(2); Co1-O5: 2.15(2); Co1-O6: 2.13(2). (#1: x+0.5, 1.5-y, z+0.5; #2: x-0.5, 1.5-y, z-0.5).

Figure 1, each two [As₆V₁₅O₄₂]⁶⁻ clusters link each other by two μ₂-[Co(en)₂] bridges. It is of interest to examine the coordination of Co atoms. The Co1 has trans two en ligands whereas Co2 has cis two en ligands. To our knowledge, it is seldom seen in such extended structures. Each [As₆V₁₅O₄₂] unit is essentially identical with the isolated clusters in K₆[As₆V₁₅O₄₂(H₂O)]·8H₂O.¹¹ The assignment of oxidation states for the vanadium and arsenic atoms is consistent with their coordination geometries and confirmed by bond valence sums (BVS)²³ which give the average valence units (v.u.) for As and V of 3.103 and 4.062.

Each terminal oxygen of the four VO₅ pyramids (V(1) and V(2), V(3), V(4)) is linearly bonded to the cobalt(II) center (BVS=2.107) in contrast to the [(en)₂M][V₆O₁₄] (M=Cu, Zn) structures where the V=O oxygen atoms of the VO₄ tetrahedra are bonded to the metal cations.²² The octahedral geometry around each cobalt (II) is completed by two en groups. In **1**, the bridging Co²⁺ ions exhibit strong covalent attachments to the two adjacent clusters with Co-O distances of 2.135 Å, which is much stronger than that in the [(en)₂M][V₆O₁₄] (Cu-O: 2.53 Å; Zn-O: 2.54 Å).

Each [Co(en)₂]₂As₆V₁₅O₄₂ cluster joins two adjacent clusters through a pair of strong hydrogen bonds (N3-O10a(a: 0.5-x, 0.5+y, 0.5-z): 2.806 Å), thus resulting in two-dimensional layers. In fact, it is noteworthy that the structure **1** is the extensive three-dimensional network of hydrogen bonds which exhibit between the amine nitrogen atoms, water molecules and terminal oxygen atoms of the clusters. The isolated [Co(en)₃]²⁺ cations interact with the chains through hydrogen bonds: N9...O15b (b: 1-x, 2-y, -z): 3.115 Å, N10...O4c(c: 0.5+x, 1.5-y, 0.5+z): 3.087 Å, N11...O15b: 3.016 Å, N13...O8: 2.962 Å, N14...O4c: 3.276 Å. The water molecules interact with each other, also with the chains and the cations through hydrogen bonds of the type Ow...O (2.753-3.141 Å), Ow...N(3.023-3.198 Å), and Ow...Ow(2.856-3.000 Å). Such strong multi-point hydrogen bonding appears to be a structural determinant in the general class of inorganic/organic composite solids.

Hydrothermal techniques exploit the principle of "self assembly" of metastable solid phase from soluble precursors.²⁴

The complex **1** is synthesized from V_2O_5 and As_2O_3 by exploiting the reducing ability of H_3PO_3 . The presence of H_3PO_3 is absolutely essential to product formation. Under more reducing conditions the fully reduced V^{IV} clusters are isolated.^{11-13, 25} V^{IV} and V^{IV}/V^V clusters are cryptands and tend to form spherical structures. This feature is evident in the class of reduced and mixed valence polyoxovanadium described by Müller et al.²⁵ However, this result may originate from the natures of the transition metal ions employed. The cobalt (II) ion favors a six coordinated octahedral geometry. The Co-O-V linkages play a critical role in constructing the chain structure.

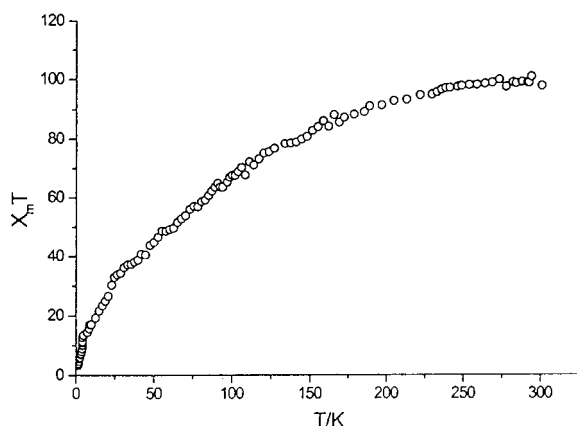


Figure 2: Plot of the products $\chi_m T$ vs T for **1**.

Magneto-structural data of complex and $Co(en)_2$ bridge allow us to foresee magnetic exchange coupling. The magnetic behavior of the compound is represented in Figure 2, in the form of $\chi_m T$ vs T . The value of $\chi_m T$ shows a gradual increase as the temperature is decreased. Because no suitable theoretical model is available in the literature²⁶ for such a complex system, detailed magnetic analyses were not done for the present compound, but Figure 2 clearly indicates the presence of an antiferromagnetic interaction within the molecule. Further studies on magnetic properties and similar systems are going on in our lab.

The title compound provides an example of different way of connecting arsenic-vanadium clusters and transition metal coordination complexes. It suggests that further condensation of clusters into higher dimensional solids through the linkage of $Co(en)_2$ groups could be feasible. The present study reveals the rich hydrothermal chemistry of arsenic-vanadium clusters.

We thank National Natural Science Foundation of China, and Key Lab of Supramolecular Structure and Spectroscopy for financial support.

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- 20 Anal. Calcd for $[Co(en)_3][\{Co(en)_2\}_2As_6V_{15}O_{42}] \cdot 4H_2O$: C, 6.58; H, 2.52; N, 7.68; As, 17.59; V, 29.90; Co, 6.92%. Found: C, 6.60; H, 2.50; N, 7.76; As, 17.56; V, 29.87; Co, 6.90%.
- 21 Crystallographic data: Formula: $[Co(en)_3][\{Co(en)_2\}_2As_6V_{15}O_{42}] \cdot 4H_2O$, Mr= 2555.20, Crystal system: Monoclinic, space group: $P2_1/n$, $\mu=1.67 \text{ mm}^{-1}$. $R1=0.0586$, $wR2=0.0712$. Unit cell dimensions: $a=18.913(5) \text{ \AA}$, $b=19.721(7) \text{ \AA}$, $c=20.097(7) \text{ \AA}$, $\beta=98.68(3)^\circ$, $V=7410(4) \text{ \AA}^3$, $Z=4$. Temperature of data collection: 293(2) K. Measured reflections: 10658, independent reflections: 10330, $R(\text{int})=0.0650$. Intensities were measured on a Siemens P4 diffractometer using Mo- $K\alpha$ radiation. The structure was solved by direct methods and refined using SHELXTL Version 5.01.
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