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A Novel Chainlike As–V–O Polymer Based on a Transition Metal Complex and a Dimeric Polyoxoanion

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The novel polyoxometalate $\{[As_8V_{13}NiClO_{41}][Ni(en)_2(H_2O)][Ni(en)_2]\}\{[Ni(en)_2(H_2O)_2]_{0.5}\}\cdot 4H_2O$ (**1**), which is the first example of a chainlike inorganic–organic hybrid polymer based on dimeric polyoxoanions linked by nickel complex fragments, has been synthesized in the system of As_2O_3–V_2O_5–$H_2C_2O_4$–en–$NiCl_2\cdot 6H_2O$–H_2O under hydrothermal conditions and characterized by IR, TGA, elemental analysis, single crystal X-ray diffraction, XPS, and magnetic susceptibility studies, respectively. This compound crystallized in the triclinic space group $P\bar{1}$ with $a = 13.358(3)$ Å, $b = 14.198(3)$ Å, $c = 19.723(4)$ Å, $\alpha = 83.88(3)°$, $\beta = 86.04(3)°$, $\gamma = 64.66(3)°$, $V = 3360.2(2)$ Å^3, and $Z = 2$. Interestingly, the dimeric polyoxoanion contains two $\{[Ni(en)_2(H_2O)][As_8V_{13}NiClO_{41}]\}$ cluster units linked by Ni–O–As bonds and is a Ni-substituted $[As_8V_{13}NiClO_{41}]$ cluster supported by $[Ni(en)_2(H_2O)]$ coordination fragment. The chainlike structure consists of $\{[Ni(en)_2(H_2O)][As_8V_{13}NiClO_{41}]\}_2$ dimeric polyoxoanions and $[Ni(en)_2]$ groups which are linked together through vertexes forming a unique one-dimensional polymer. The study of the magnetic susceptibility of **1** demonstrates the presence of antiferromagnetic interaction in **1**.

Introduction

Polyoxometalate (POM) chemistry continues to be a subject of great interest, since the wide and fascinating variety of structures and properties of these objects gives rise to numerous applications to fields as diverse as catalysis, ion exchange, sorption, and molecular electronics.[1]

Although various preparation methods have been proposed to obtain such metal−oxide clusters, the preparation of these complexes still remains elusive and often is described as self-assembly. One of the abilities of the polyoxoanions is that of acting as ligands accommodating transition metal (TM) ions between moieties of these metal−oxo clusters. This characteristic is exhibited particularly by POM structures that are deficient in one or more MO_6 octahedra; these lacunary metal−oxo clusters are represented by heteropolytungstates.[2] In the reactions of these lacunary metal−oxo cluster, metastable heteropoly complexes of W with TM or rare-earth ions have led to mono-, di-, and trisubstituted products.[2] These compounds constitute an important subclass of inorganic chemistry with significance in disciplines of magnetic research and catalysis.[3] Therefore, finding new lacunary POM ions is one of the great challenges facing chemists.

A fascinating aspect in POM chemistry is to find some novel units as building blocks and then to connect them up into one-, two-, and even three-dimensional extended solid frameworks in appropriate ways. It is quite attractive and appears to play a key role to the development of rational

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synthesis for tailor-making materials with desirable features. The crucial requirement for the success of this approach is to find some suitable metal−oxo clusters that could be readily assembled. These clusters and their derivatives provide an exciting opportunity to explore the potential of this approach. The hydrothermal synthesis techniques, in combination with the organic templates, have been demonstrated to be a powerful tool in the isolation of metal oxides.[4] A number of extended solid framework materials based on POMs as assembling groups have been hydrothermally synthesized.[5]

The arsenic−vanadium POMs have been extensively studied; typical examples include $[As_8V_{14}O_{42}(X)]^{6-}$ ($X = SO_3^{2-}$ or SO_4^{2-}), $[N(Me)_4]_4[As_8V_{14}O_{42}(H_2O)_{0.5}]$, and $K_6[As_6V_{15}O_{42}(H_2O)]\cdot 8H_2O$.[6] During our systematic experiments with the As−V−O clusters, we synthesized and characterized a novel compound $\{[As_8V_{13}NiO_{41}(Cl)][Ni(en)_2(H_2O)][Ni(en)_2]\}\{[Ni(en)_2(H_2O)_2]_{0.5}\}\cdot 4H_2O$ (**1**), which is the first TM-substituted As−V−O dimeric polyoxoanion linked by Ni−O−As bonds, and another interesting feature of **1** is that it is the first example of a chain of POM polymer where dimers of POMs acting as building blocks are connected by coordination complex fragments.

Experimental Section

Materials and Methods. All reagents were of analytical grade and were used as received from commercial sources without further purification. The content of vanadium, nickel, and arsenic elements (the inductively coupled plasma analysis) was determined by 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 a Perkin-Elmer spectrophotometer in the 400−4000 cm^{-1} region with a pressed KBr pellet. XPS measurements were performed on single crystals with an ESCALAB.MARKII apparatus, using the Mg Kα X-ray radiation as the excitation source ($E_{MgK\alpha} = 1253.6$ eV).

Synthesis. Compound **1** was synthesized by the hydrothermal method under autogenous pressure. In a typical synthesis, 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), $NiCl_2\cdot 6H_2O$ (0.48 g), and distilled water (21.6 mL) in a molar ratio of 1:1:1:2:1:600 was stirred for ca. 20 min and then transferred to a Teflon-lined reactor and heated at 160 °C for 3 days, and then cooled to room temperature. The resulting product, consisting of black block crystals, was recovered by filtration, washed with distilled water, and dried at ambient temperature (68% yield based on vanadium). Here, $H_2C_2O_4\cdot 2H_2O$ was used as reducing agent and was necessary to maintain the pH value of the reaction system. Compound **1** is stable to air, in water, and in acetone. Elemental analysis (%) for $C_{10}H_{52}As_8ClNi_{3.5}N_{10}O_{47}V_{13}$ calcd: As 23.35, V 25.79, Ni 8.00, C 4.66, H 2.03, N 5.44, Cl 1.38. Found: As 22.68, V 24.94, Ni 7.38, C 4.63, H 2.00, N 5.41, Cl 1.14. IR (KBr pellet): $\nu = 1595.05$ (m), 1457.49 (m), 1029.64(s), 986.84(s), 827.57(s), 718.58(s) cm^{-1}.

Table 1. Crystal and Structure Refinement Data for Compound **1**

empirical formula	$C_{10}H_{52}As_8ClN_{10}Ni_{3.5}O_{47}V_{13}$
fw	2567.13
space group	$P\bar{1}$ (No. 2)
a, Å	13.358(3)
b, Å	14.198(3)
c, Å	19.723(4)
α, deg	83.88(3)
β, deg	86.04(3)
γ, deg	64.66(3)
V, Å^3	3360.2(12)
Z	2
ρ_{calc}, g·cm^{-3}	2.537
μ(Mo Kα), mm^{-1}	6.720
R1^a [$I > 2\sigma(I)$]	0.0536
wR2^b [$I > 2\sigma(I)$]	0.1435

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]^2/\sum[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (0.1019P)^2 + 5.4001P]$, where $P = [|F_o|^2 + 2|F_c|^2]/3$.

Table 2. Ranges of Some Important Bond Lengths [Å] for Compound **1**

VO$_5$ Pyramids^a		AsO$_3$ Group^b	
V═O$_t$	1.589(5)−1.620(4)	As−O$_V$	1.732(4)−1.801(5)
V−O$_b$	1.901(5)−2007(5)	As−O$_{As}$	1.772(4)−1.810(4)
$[Ni(1)(en)_2O(H_2O)]$, $[Ni(2)(en)_2O_2]$, $[Ni(3)(en)_2(H_2O)_2]$, and $[Ni(4)O_5Cl]$ Octahedra^c			
Ni−N	2.019(8)−2.139(9)	Ni−O$_B$	2.062(4)−2.127(4)
Ni−O$_e$	2.005(4)−2.018(4)	Ni−O$_T$	2.340(4)
Ni−Cl	2.435(2)	Ni−OW	2.119(9)−2.128(5)

^{a} O$_t$, terminal oxygen atoms; O$_b$, oxygen atoms in basal plane of VO$_5$ pyramids. ^{b} O$_V$, oxygen atoms bridging arsenic and vanadium atoms in As−O−V linkages; O$_{As}$, oxygen atoms in As−O−As linkages. ^{c} O$_B$, oxygen atoms in V═O−Ni linkages; O$_e$, equatorial oxygen atoms in NiO$_5$Cl octahedra in cluster cage; O$_T$, oxygen atoms in Ni−O−As linkages.

Determination of Crystal Structures. A suitable single crystal of as-synthesized compound with the dimensions 0.32 × 0.22 × 0.20 mm^3 was carefully selected under a microscope and glued to a thin glass fiber with epoxy resin. Crystal structure determination by X-ray diffraction was performed on a Siemens SMART CCD diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation in the ω and φ scanning mode at room temperature (293 K). An empirical absorption correction was applied using the SADABS program. The structure was solved by direct methods. The vanadium, arsenic, and nickel atoms were first located, and the chlorine, oxygen, nitrogen, and carbon atoms were found in the final difference Fourier map. All the hydrogen atoms are positioned with idealized geometry and refined with fixed isotropic displacement parameters using a riding mode. The structure was refined on F^2 by full-matrix least-squares methods using the SHELXTL crystallographic software package.[7] All non-hydrogen atoms were refined anisotropically. The Ni(1) atom is disordered over two positions with occupancies given in parentheses: Ni(1)-(87%), Ni(5)(13%). The crystallographic data for **1** are presented in Table 1. The coordinates of all non-H atoms and selected bond distances and angles are listed in Tables S1 and S2, respectively. Ranges of bond lengths are in Table 2.

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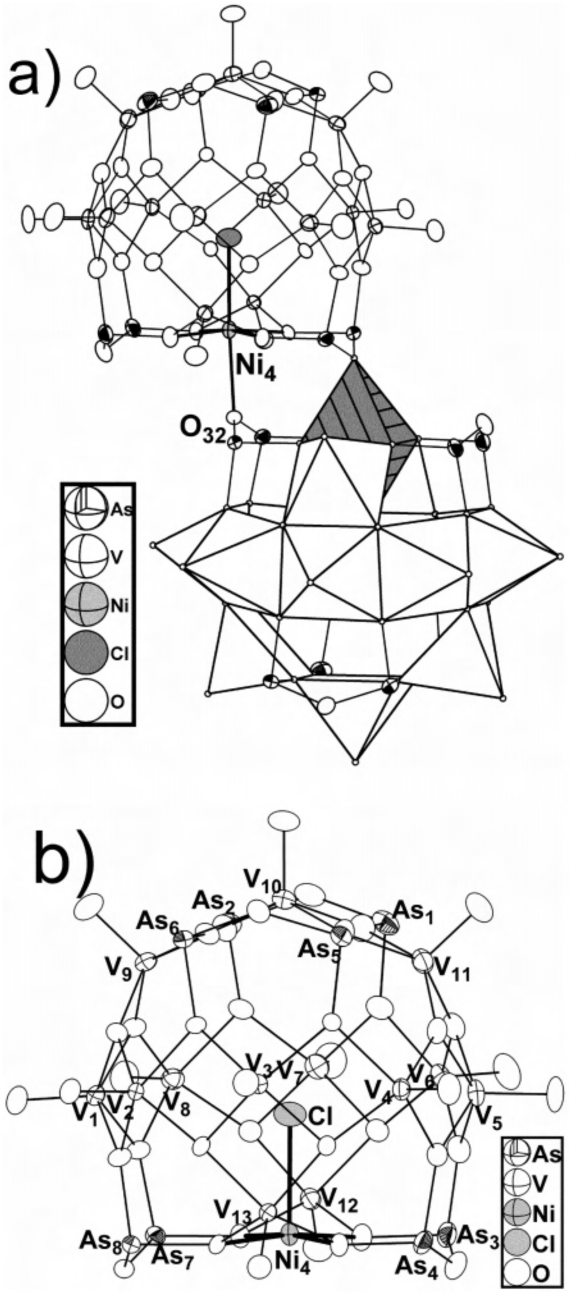

Figure 1. (a) Ball-and-stick and polyhedron representation of the dimer of compound **1**. (b) Ball-and-stick representation of a half-unit showing 50% probability ellipsoids and the labeling scheme.

Results and Discussion

The building block unit of **1**, as shown in Figure 1, can be described as a dimer containing a novel Ni-substituted arsenic−vanadium polyoxoanion linked together with four Ni−O−As bonds. The anion is derived from As_8V_{14} cluster by replacing a VO^{2+} with Ni^{2+} cation (Figure 1b). It is constructed from 13 VO_5 square pyramids, 8 AsO_3 groups, and 1 $ClNiO_4$ square pyramid, with a chloride ion at its center. Two AsO_3 groups are joined together by an oxygen bridge, forming a handlelike As_2O_5 moiety. In the half-unit, eight vanadium (V(1)−V(8)) oxygen square pyramids are linked with one another into a octagonal ring. In addition, three vanadium (V(9)−V(11)) oxygen square pyramids form one trimer, which is connected across the ring to V(1) and V(5) containing square pyramids. The Ni(4)O_4Cl group and vanadium (V(12) and V(13)) oxygen square pyramids form the other trimer, and it is similarly connected on the opposite side of the ring to V(3) and V(7) containing square pyramids. Two trimers are rotated by 90° with respect to each other. Thus, the 13 vanadium oxygen square pyramids and the Ni(4)O_4Cl group are joined together into a spherelike structure with four "windows" left, which are completed by four As_2O_5 moieties. All the vanadium oxygen square pyramids are linked with one another, with the Ni(4)O_4Cl group and with the As_2O_5 moieties by sharing edges. The Ni^{2+} center in the octahedral coordination environment receives contributions from a chloride ion, four oxygen donors belonging to one-half-unit and one oxygen donor belonging to the other half-unit, so the dimerization of two half-units is accomplished through sharing of two O(32) atoms. The same oxygen atom also bridges two arsenic atoms in the half-unit. These two triply bridging O(32) atoms are symmetry-related by the inversion center of **1** and are bound to two arsenic atoms of one-half-unit and, at the same time, to one nickel atom of the other half-unit (distances are Ni(4)−O(32), 2.338(4) Å).

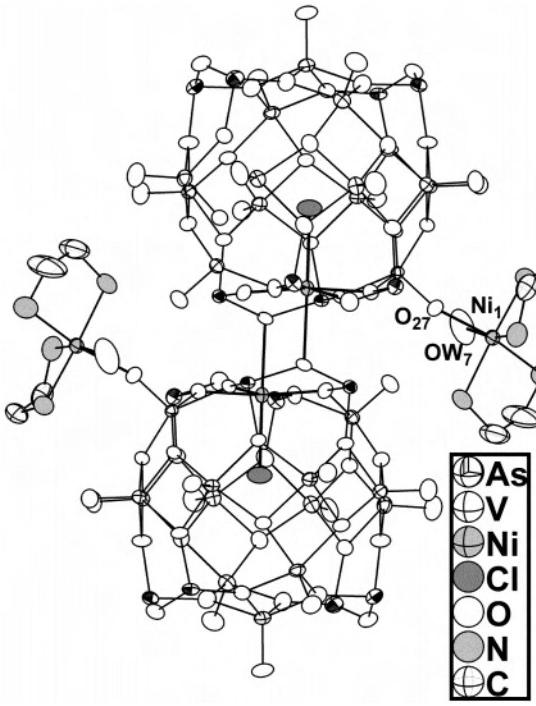

Figure 2. Ball-and-stick representation of the dimer supported transition metal complex.

The two half-units of **1** deserve special attention because each one contains a lacunary As_8V_{13} ion. These ions accommodate one Ni atom each, leading to the complete $As_8V_{13}Ni$ (As_8V_{14}-like) cluster structure. Compared to the As_8V_{14} clusters, the polyanion in **1** shows some subtle structure differences that are caused by the substituted nickel atom. For example, a chloride ion that coordinates to the nickel atom is located at the center of the cluster. Relevant examples where similar encapsulation of halide ions in POM clusters have been reported by Müller[8a−c] and Huang;[8d] the halide ions in those compounds show no interactions with those cluster shells. However, the chloride ion in **1** axially

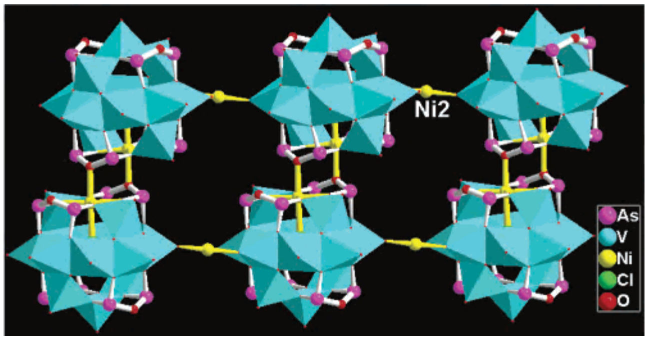

Figure 3. Ball-and-stick representation of the one-dimensional chain structure constructed from dimers of polyoxometalates and coordination complex fragments; the C and N atoms were omitted for clarity.

coordinates to the nickel atom of the cluster shell with Ni−Cl bond length 2.435(2) Å, and it is comparable with that in the compound $[Ni(H_2L)Cl_2]Cl_2{\cdot}2H_2O$ (L = 1,3,10,12,15,-18-hexaazatetracyclo[16,2,1,$1^{12.15}$,$0^{4.9}$]docosane),[9] where the nickel center exhibits similar six-coordinated geometry with Ni−Cl bond length 2.490(1) Å. To our knowledge, compound **1** is the first example of a POM with the guest molecule showing a strong covalent interaction with the cluster shell. Bond valence summations[10] (BVSs) have been applied to all the vanadium and arsenic atoms. These calculations suggest that the oxidation states of the vanadium and arsenic atoms are +4 and +3 in the structure, respectively. It is to say that 13 vanadium sites have been reduced to V(IV) by $H_2C_2O_4{\cdot}2H_2O$. Potentiometric titrations are also consistent with 13 V(IV) sites per cluster anion of $[As_8V_{13}NiO_{41}(Cl)]^{5-}$. Given such an oxidation assignment, the overall cluster charge for the anion $[As_8V_{13}NiO_{41}(Cl)]^{5-}$ is −5, balanced by one $[Ni(en)_2(H_2O)]^{2+}$, one $[Ni(en)_2]^{2+}$, and half of a $[Ni(en)_2(H_2O)_2]^{2+}$ complex fragment. The XPS spectrum[14] in the $V2p_{3/2}$ region for **1** shows a peak at 515.8 eV, ascribed to V^{4+}. The XPS estimation obtained on the valence state values is in reasonable agreement with those calculated from the bond valence sum calculations. These results accord with the result of valence sum calculations of **1** and further confirm that the valences of all the vanadium atoms in the structure are +4. In addition to these, the cluster $[As_8V_{13}NiO_{41}]^{4-}$ in **1** is electronically identical with the $[As_8V_{14}O_{42}]^{4-}$ cluster but the substituted transition metal atom, so we call it a lacunary cluster derived from As_8V_{14} clusters.

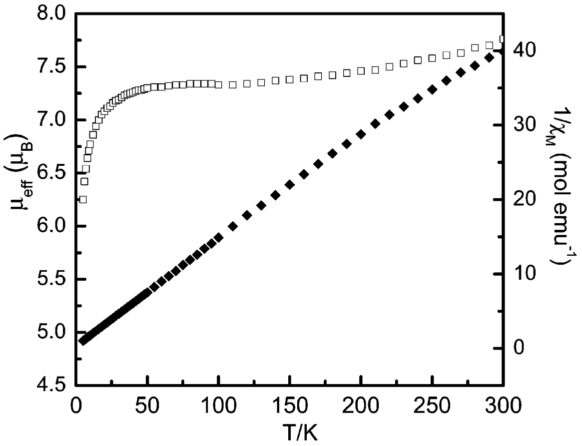

Figure 4. Temperature dependences of the reciprocal magnetic susceptibility χ_M^{-1} (□) and the product $\chi_M T$ (■) for the complex.

Another unusual feature of compound **1** is that it is the first example of a dimer of POMs supporting a TM complex; as shown in Figure 2, the dimer that acts as a ligand coordinates to two Ni(1) atoms related by an inversion center. Two O(27) atoms link the dimer and two Ni(1) atoms with Ni(1)−O(27) 2.128(4) Å. In addition, an O(27) atom, four nitrogen donors from two en ligands, and one oxygen donor from a water molecule complete the octahedral coordination of each Ni(1) atom, with Ni−OW 2.125(9) Å and Ni−N 2.082(7)−2.122(8) Å, respectively.

Compared with the discrete POM dimer of $[Mo_{16}V_{14}O_{84}]^{14-}$ containing two $\{Mo_8V_7O_{42}\}$ units linked together via two V−O bonds[11] and a chainlike polyanion constructed from a building block of $[Mo^{VI}{}_8V^{IV}{}_4O_{36}(V^VO_4)(V^{IV}O)_2]^{7-}$ linked together via edge-sharing,[12] the most unusual feature of the dimer in **1** consists of two $\{As_8V_{13}NiO_{41}(Cl)\}$ units supporting TM complexes and linked together via two As−O−Ni linkages. Furthermore, the dimers are connected with one another by two $Ni(2)(en)_2$ coordination complex fragments into an infinite one-dimensional chain structure. To our knowledge, it is the first example of a one-dimensional chain structure constructed from dimers of POMs and coordination complex fragments. As shown in Figure 3, two adjacent dimers are connected through two $[Ni(en)_2]$ units via corner-sharing interactions of the type V═O−Ni with Ni−O 2.062(4)−2.063(4) Å; the nickel site is defined by four nitrogen donors from two en molecules, and two *trans*-oxo donors from two adjacent dimers. The equatorial Ni−N bonds range from 2.022(8) to 2.098(9) Å. The chains are aligned in parallel with each other.

The $[Ni(3)(en)_2(H_2O)_2]^{2+}$ cations serve as charge compensation components. These cations occupy the regions between the adjacent chains. The nickel atom is located at an inversion center with occupancy factor 0.5 and coordinated by two *trans*-oxo donors (Ni(3)−O, 2.128(5) Å) from two water molecules and four nitrogen donors (Ni(3)−N, 2.099(7)−2.100(7) Å) from two en ligands, respectively.

Preliminary magnetic studies have been performed on a powered sample of **1** in the range 5−300 K. Figure 4 shows the magnetic behavior of **1** in the form of μ_{eff} versus T and $\chi_m{}^{-1}$ versus T plots. The product μ_{eff} continuously decreases

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as the temperature is lowered, indicating the presence of the antiferromagnetic exchange interactions. The room temperature value ($\mu_{\mathrm{eff}} = 7.57\ \mu_{\mathrm{B}}$) is smaller than the expected value ($\mu_{\mathrm{eff}} = 8.54\ \mu_{\mathrm{B}}$) of the 13 uncoupled $S = {}^1/_2$ spins of V^{4+} atoms and 3.5 uncoupled $S = 1$ spins of Ni^{2+} atoms (assuming $g = 2.0$ for V^{4+} and $g = 2.20$ for Ni^{2+}), indicative of antiferromagnetic coupling. Unfortunately, it is not easy to fit the experimental magnetic data of this one-dimensional hetero-polymetallic spin system using a suitable theoretical model.[13] However, the magnetic data of sample **1** obeys the Curie−Weiss law in the high temperature regions, and the fitting in the range 80−300 K gives values $C = 7.70$ emu·mol^{-1}·K and $\theta = -16.95$ K, characteristic of an overall antiferromagnetic interactions.

Conclusions

In conclusion, a novel transition metal substituted arsenic−vanadium POM has been synthesized by a hydrothermal method. It is the first example of a TM substituted arsenic−vanadium POM with one-dimensional chain structure constructed from polyoxoanion dimers and coordination complex fragments. The successful synthesis of **1** suggests that the synthesis of di- and tri-TM substituted arsenic−vanadium POMs will be feasible. The lacunary arsenic−vanadium POMs will form a new interesting field of POMs and will represent a new family of inorganic materials.

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Supporting Information Available: X-ray crystallographic file, in CIF format. Additional tables. Additional figures including IR, polyhedral representation for the cluster anion, TG, and XPS in PDF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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