$[\{Zn(enMe)_2\}_2(enMe)_2\{Zn_2As_8V_{12}O_{40}(H_2O)\}]\cdot 4H_2O$: A Hybrid Molecular Material Based on Covalently Linked Inorganic Zn−As−V Clusters and Transition Metal Complexes via enMe Ligands

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Keywords: Polyoxometalate / Vanadium / Arsenic / Zinc / Inorganic−organic hybrids

A novel zinc-substituted polyoxovanadate, $[\{Zn(enMe)_2\}_2(enMe)_2\{Zn_2As_8V_{12}O_{40}(H_2O)\}]\cdot 4H_2O$ **1** (enMe = 1,2-diaminopropane), which is built up from $Zn_2As_8V_{12}O_{40}(H_2O)$ clusters and $Zn(enMe)_2$ complexes, and further connected together by *trans*-enMe ligands, has been hydrothermally prepared and characterized by X-ray crystallography. The study of the magnetic susceptibility of **1** demonstrates the presence of antiferromagnetic interaction between V^{IV} cations in **1**.

Introduction

The design and synthesis of inorganic−organic hybrid materials have been of great interest for their unusual topological properties and potential applications in the fields of catalysis, biochemistry, magnetism and material science.[1−4] In recent years, the design of inorganic−organic hybrid polyoxometalates (POMs) made possible architectures that contribute to the increasing understanding of the methods that control the synergistic interaction between organic and inorganic chemical compositions.[1] A number of transition metal (TM) coordination complex-linked POMs with one-, two- and three-dimensional inorganic−organic hybrid frameworks, as well as some POMs-supported TM complexes have been reported.[5−15] In general, the early transition metals (TMs), especially V, Mo, and W, are flexible and are able to form POMs by using various coordination geometries (from regular and distorted octahedra and square pyramids to tetrahedra) in their highest or mixed oxidation states;[16] however, in contrast, the post TMs, such as Cu^{2+}, Zn^{2+}, and Cd^{2+}, tend to form various TM coordination complexes in which they act as the countercations, the decorated fragments or bridging units in inorganic−organic hybrid POMs. Since the post TMs exhibit extensive coordination chemistry involving a variety of organic ligands, the post TM-substituted POMs may, in principle, incorporate appropriate organic ligands. This offers opportunity for making new inorganic−organic hybrid complexes containing an inorganic cluster backbone decorated with organic functionalities. Such compounds are much less developed. We are currently exploring the potential of this approach in order to obtain some POMs with unusual structures and properties. This report describes the hydrothermal synthesis and characterization by IR and EPR spectroscopy, TGA, elemental analysis, magnetic properties and single-crystal X-ray structure analysis of the first zinc-substituted polyoxovanadate: $[\{Zn(enMe)_2\}_2(enMe)_2\{Zn_2As_8V_{12}O_{40}(H_2O)\}]\cdot 4H_2O$ **1**, in which *trans*-enMe molecules serve as bridges between the inorganic Zn−As−V clusters and $Zn(enMe)_2$ complexes.

Results and Discussion

Single-crystal X-ray analysis reveals that compound **1** is a neutral zinc-substituted polyoxovanadate: $[\{Zn(enMe)_2\}_2(enMe)_2\{Zn_2As_8V_{12}O_{40}(H_2O)\}]\cdot 4H_2O$. As shown in Figure 1, an unusual feature of **1** is that two Zn^{2+} take the place of two VO^{2+} groups located between the As_2O_5 units of the well-known $[As_8V_{14}O_{42}(X^{n-})]^{(8-n)-}$ ($X = SO_4^{2-}$, SO_3^{2-}, 0.5 H_2O) anion[17,18] and form a new metal cluster anion $[Zn_2As_8V_{12}(H_2O)]^{4-}$. Each $[Zn_2As_8V_{12}O_{40}(H_2O)]^{4-}$ anion is then decorated by two novel TM complexes $[(enMe)Zn(enMe)_2]^{2+}$ to generate an unprecedented inorganic−organic cluster **1**. In the structure of **1**, four crystallographically distinct zinc sites display two different coordination environments: $NZn(1,2)O_4$ square pyramids and distorted $N_2Zn(3,4)N_3$ trigonal bipyramids. The equatorial positions of the $NZnO_4$ square pyramids are occupied by four μ_3-O atoms linked to neighboring OVO_4 square pyramids and four As atoms [Zn−O = 2.007(8)−2.076(7) Å],

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and the axial position is occupied by one N atom from a enMe ligand [Zn−N = 2.030(10) Å]. Two distorted N_2ZnN_3 trigonal bipyramids are defined by five N donors of three enMe ligands, respectively, with the Zn−N bond lengths of 2.071(10)−2.203(10) Å. All V centers have a distorted OVO_4 square pyramidal environment with V−O bond lengths in the usual range, 1.596(8)−1.622(7) Å for the terminal oxygen atoms and 1.919(7)−2.007(7) Å for μ_3-O atoms. In the As_2O_5 fragments, the As−O distances vary from 1.741(8) to 1.805(8) Å.

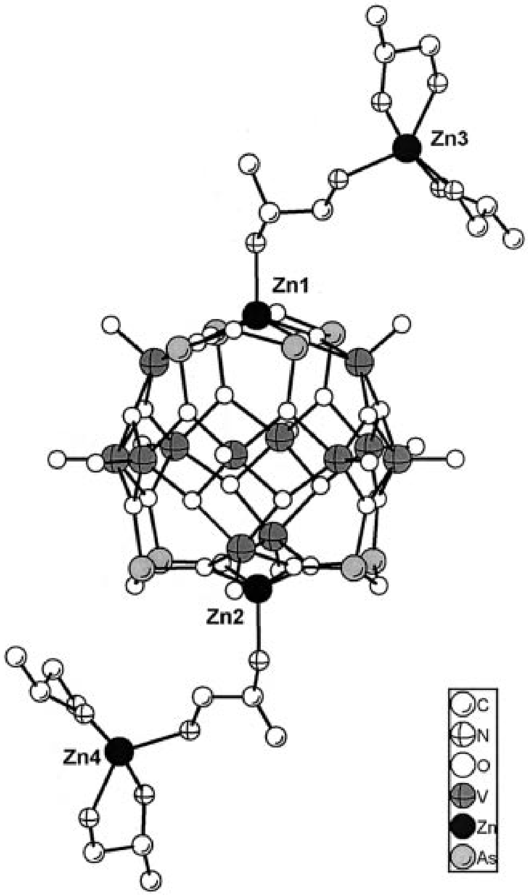

Figure 1. Molecular drawing of **1** (all H atoms are omitted for clarity)

Another unusual feature of **1** is the coordination modes of enMe. There are two types of configuration modes for *cis*- and *trans*-enMe. The *cis*-enMe molecules act as a bidentate chelating ligand and coordinate to the Zn(3) and Zn(4) atoms to form $Zn(enMe)_2$ fragments, while the *trans*-enMe molecules bridge the Zn center of the Zn−As−V cluster and $Zn(enMe)_2$ fragment in an end-to-end fashion, acting as a pillar between the polyoxoanion and the TM coordination fragment. To the best of our knowledge, this linking mode between polyoxoanion and TM coordination fragment in **1** has not been described in other polyoxometalates to date, although the topology of the $\{Zn(enMe)_2\}(enMe)$ group has already been described by Khan et al. in the free complex $[Zn_2(en)_5]^{2+}$.[15]

In compound **1**, each zinc-substituted polyoxovanadium cluster joins eight other adjacent clusters through strong hydrogen bonds between the amine nitrogen atoms and the oxygen atoms, thus resulting in an interesting three-dimensional supramolecular array (Figure 2).

On the basis of valence sum (Σ_s) calculations[19] in **1**, the oxidation states of all V atoms are +4 (Σ_s = 3.972-4.146), the eight As atoms are +3 (Σ_s = 3.043-3.176), and the four Zn atoms are +2 (Σ_s = 1.944−2.096). The EPR spectrum of **1** at liquid nitrogen temperatures shows that the g value is 1.9476, corresponding to the signal of V^{4+}. This is consistent with the results from the valence sum calculations.

The thermogravimetric study of compound **1**, which was carried out under a flow of nitrogen and at a heating rate of 10 °C min^{-1}, indicates that the weight loss of **1** cannot be completely divided into distinct stages. The whole stage, which occurs from 45 to 795 °C, is attributed to the loss of H_2O, enMe and the sublimation of As_2O_3. Assuming that the residue corresponds to VO_2 and ZnO, the observed weight loss (50.41%) is in good agreement with the calculated value (50.13%).[20,21]

The variable temperature magnetic susceptibility of **1** was measured between 5 and 300 K. The magnetism may be attributed solely to the presence of V^{4+} ions ($3d^1$, $S = 1/2$). Figure 3 shows the magnetic behavior of **1** in the form of a reciprocal molar susceptibility (χ_M^{-1}) and $\chi_M T$ vs. temperature. The $\chi_M T$ at room temperature, 1.23 emu K mol^{-1} (3.10 μ_B), is much lower than that expected for 12 uncoupled $S = 1/2$ spins with $g = 2$ (4.5 emu K mol^{-1}, 6.0 μ_B). This lower value is similar to that reported for $[V^{IV}_8V^{V}_4As_8O_{40}(HCOO-)]^{2-}$ or $[H_3KV^{V}_8V^{IV}_4As_3O_{39}(AsO_4)]^{6-}$ polyoxovanadate (1.2−1.26 emu K mol^{-1}),[22,23] corresponding to four uncoupled electrons (1.5 emu K mol^{-1} for $g = 2$, 3.46 μ_B). The fact that compound **1** has a much lower χT value at high temperature suggests that there is a possibility that at least eight electrons are already completely paired at room temperature, while the remaining four are unpaired, an observation which is similar to those seen in polyoxovanadates containing V^{IV} centers.[24,25] In compound **1**, all the equatorial vanadium atoms are bridged by one μ-oxo and a μ-arsenato group with a mean distance of 3.014 Å. The capped V atoms are connected to equatorial vanadium atoms through two different exchange pathways. One pathway is formed by a single μ-oxo bridge with a large V−V distance with a mean of 3.733 Å, while the other is formed by two μ-oxo groups with short V−V distance (2.903 Å). It is well-known[26] that μ-oxo bridges are more effective in transmitting antiferromagnetic exchange interactions between several transition metal elements, generally the extent of the coupling in dioxo-bridges is expected to be stronger than for single bridges, and the short metal-metal distance associated to these bridges gives the possibility of direct V−V overlap. The short distances of neighboring V···V pairs with dioxo-bridges, V1···V6 [2.900 Å], V3···V7 [2.895 Å], V8···V11 [2.903 Å] and V9···V10 [2.917 Å], lie in the range expected

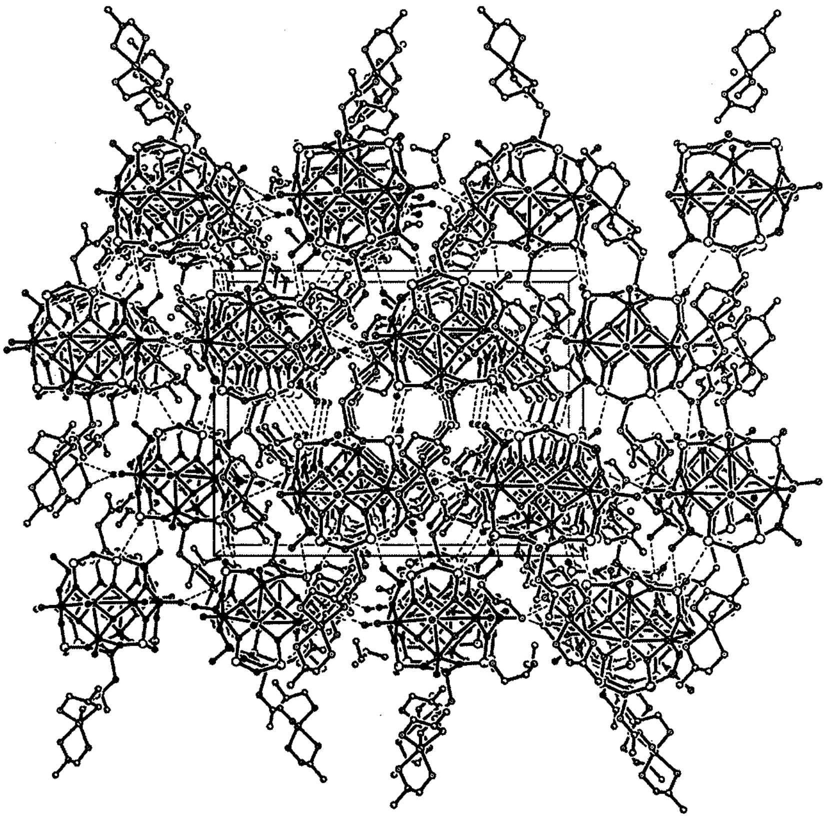

Figure 2. Packing of compound **1** down *a*-axis showing the intercluster hydrogen bonds (water molecules and all H atoms are omitted for clarity)

for strong antiferromagnetic coupling,[27] thus, it is reasonable to assume that these four pairs of vanadium centers between equatorial and capped sites are in the ground $S = 0$ state at relatively high temperature due to the very strong antiferromagnetic coupling provided by the di-μ-oxo bridge, leaving four uncoupled vanadium centers at the equator of the cluster in an approximate square arrangement. On cooling from room temperature, the $\chi_M T$ value decreases slowly until 50 K and then sharply falls to a minimum value of 0.4 $cm^3\,K\,mol^{-1}$ (1.79 μ_B) at 5 K, indicative of antiferromagnetic coupling between the remaining vanadium centers. This dominant antiferromagnetic character is in agreement with a negative Weiss constant ($\theta = -10$ K) obtained from a linear fitting of χ_M^{-1} vs. T using the Curie–Weiss equation. The susceptibility data at low temperature were analyzed using expressions[28,29] for an $S = 1/2$ tetramer based on the Heisenberg Hamiltonian $H = -J(\boldsymbol{S}_1\cdot\boldsymbol{S}_2 + \boldsymbol{S}_2\cdot\boldsymbol{S}_3 + \boldsymbol{S}_3\cdot\boldsymbol{S}_4 + \boldsymbol{S}_4\cdot\boldsymbol{S}_1)$, the intercluster interactions were included in the model in the molecular field approximation $\chi = \chi_{cluster}/[1 - (2zJ'/Ng^2\beta^2)\,\chi_{cluster}]$.[30] The best fit was obtained with $J = -3.59\ cm^{-1}$, $zJ' = -1.85\ cm^{-1}$, $g = 1.79$ and $R = 8.13 \times 10^{-4}$ for 36 observations at $T \leq 100$ K. R is the agreement factor defined as $\Sigma i[(\chi_M T)_{obs}(i) - (\chi_M T)_{cal}(i)]^2/\Sigma i\,[(\chi_M T)_{obs}(i)]^2$.

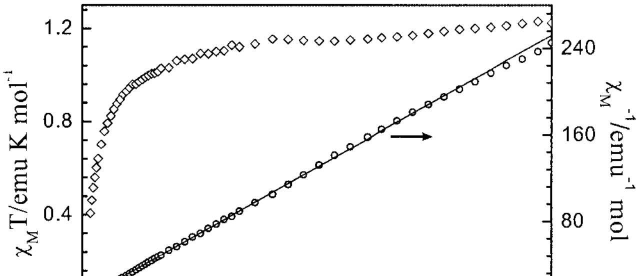

Figure 3. The temperature dependence of reciprocal magnetic susceptibility χ_M^{-1} (circle) and the product $\chi_M T$ (diamond) for complex **1**

Conclusion

In this communication we show the first zinc-substituted inorganic–organic hybrid polyoxovanadium cluster. This is a rare complex in which the organonitrogen ligand serves as a bridge between the metal oxide cluster and the TM coordination fragment. The results demonstrate the potential of post TM-substituted POMs as molecular building blocks for the construction of novel inorganic–organic materials. The substituted Zn centers can also be replaced with other TM ions.[31] Further investigation in this area is in progress.

Experimental Section

Synthesis and Initial Characterization: In a typical synthesis, a mixture of V_2O_5 (0.3 g, 1.66 mmol), As_2O_3 (0.36 g, 1.82 mmol), $ZnAc_2{\cdot}4H_2O$ (1.0 g, 3.98 mmol), enMe (1.1 mL, 14.86 mmol) and H_2O (10 mL, 555.56 mmol), in a molar ratio of 4:4.5:10:37:1389 was stirred under ambient conditions. The resulting gel was sealed in a Teflon-lined steel autoclave and heated at 180 °C for 7 days, and then cooled to room temperature. The resulting product, consisting of single crystals in the form of brown blocks, was recovered by filtration, washed with distilled water and dried in air. Yield 0.553 g (76.1% based on V). Elemental analysis showed that the sample contains 8.02, 2.58, and 6.42 wt% of C, H, and N, respectively, in good agreement with the expected values of 8.09, 2.67, and 6.38 wt%, respectively, on the basis of the empirical formula given by the single-crystal structure analysis. IR (KBr pellet ν/cm^{-1}): 3318 (s), 3262 (s), 2964 (m), 1587 (s), 1458 (w), 1390 (w), 1016 (s), 983 (vs), 718 (vs), 637(s), 460 (s).

X-ray Crystallography

$[\{Zn(enMe)_2\}_2(enMe)_2\{Zn_2As_8V_{12}O_{40}(H_2O)\}]{\cdot}4H_2O$ (1): Monoclinic, space group $P2_1/n$ (no.14), $a = 14.9617(6)$, $b = 19.1992(8)$, $c = 24.9403(11)$ Å, $\beta = 90.050(1)°$, $V = 7164.2(5)$ Å^3, $Z = 4$, $D_c = 2.454$ g cm^{-3}, $F(000) = 5128$, $M = 2646.98$, $S = 1.116$, $T = 293$ K. λ(Mo-K_α) = 0.71073 E, θ range 1.34–25.03°. Bruker Smart CCD diffractometer. ω and scan. 12308 reflections are unique, 8482 reflections with $I > 2\sigma(I)$ were used in the refinement and the calculation of R_1 and wR_2. The last successful full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms converged to $R_1 = 0.0631$, $wR_2 = 0.1209$. The positions of hydrogen atoms were calculated in ideal positions and not refined. The structure was solved by direct methods.

CCDC-221503 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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[31] During preparation of this Communication, another new POM cluster $[Cd(en)_2]_2[\{Cd(en)\}_2As^{III}{}_8V^{IV}{}_{12}O_{40}]$ which incorporates a pair of $Cd(en)^{2+}$ groups was successfully obtained as crystals. The single-crystal X-ray diffraction reveals that this compound possesses a 1-D chain structure constructed from Cd-substituted POMs and $Cd(en)_2$ coordination complex fragments.

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