



Structural influences of arsenic–vanadium clusters and transition metal complexes on final structures of arsenic–vanadium-based hybrids



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ABSTRACT

Three new compounds based on arsenic–vanadium clusters $\{[\text{Cu}(\text{im})_2]_4[\text{H}_2\text{As}_8\text{V}_{14}\text{O}_{42}(\text{SO}_4)]\} \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Cu}(\text{phen})(\text{im})]_3[\text{Cu}(\text{phen})_2][\text{As}_8\text{V}_{14}\text{O}_{42}(\text{H}_2\text{O})]$ (**2**, **3**) (im = imidazole, phen = phenanthroline) have been synthesized and characterized by IR, UV–Vis, XRD, TG analysis, elemental analysis, single-crystal X-ray diffraction analysis and catalytic properties. Crystal analysis reveals that compound **1** shows an unprecedented 3-D twofold interpenetrating network structure with each of the two interpenetrating frameworks exhibiting a novel diamondoid framework structure based on POMs and transition metal complexes. Compounds **2** and **3** are based on identical polyanions and identical transition metal complexes. However, the two compounds are not isomorphous and isostructural with each other. That is to say, the two compounds have an identical chemical formula with different structures: the two are polymorphs of each other. In addition, catalytic properties of compounds **1–3** have been studied.

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1. Introduction

The design and synthesis of organic–inorganic hybrid materials based on polyoxometalates (POMs) continue 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 [1–4]. Recently one of the most challenging tasks in POM chemistry is to find transition metal complexes (TMCs) and then use them to interact with POM building blocks into extended frameworks or supramolecular structures, which is of great interest not only because of their fascinating structural diversities but also because of their potential applications in broad areas such as catalysis, electrical conductivity, and biological chemistry [5]. On-going extensive research has demonstrated that transition metal (e.g. Fe, Co, Ni, Cu, Zn and Mn) complexes can be successfully introduced into POM hybrids [6–12]. On the other hand, another crucial requirement for the synthesis of this kind of POM-based hybrids is to find suitable metal–oxo clusters that could be readily assembled, and almost all POM species can be involved in this kind of materials.

An important subclass of POMs is the family of arsenic–vanadium clusters derived from the well-known $\{\text{V}_{18}\text{O}_{42}\}$ cluster

shell, which displays interesting electronic and magnetic properties [13–17]. Since the first vanadoarsenate cluster $[\text{As}_6\text{V}_{15}\text{O}_{42}(\text{H}_2\text{O})]^{6-}$ (As_6V_{15}) was obtained in 1988 [14], a large number of vanadoarsenates and vanadoarsenate derivatives have been obtained [18–25]. This kind of clusters and their derivatives provide an exciting opportunity to explore the potential of hybrids based on POMs and TMCs. Our group has focused on the synthesis of vanadoarsenate for several years [26–35], and we found that $\{\text{As}_8\text{V}_{14}\text{O}_{42}(\text{X})\}$ (As_8V_{14}) ($\text{X} = \text{H}_2\text{O}, \text{SO}_4^{2-}$, etc.) contains four tetrahedrally arranged As_2O_5 moieties, and has the possibility to act as a T_d -symmetric inorganic ligand. That is to say, As_8V_{14} has a higher symmetry. However, the influence of As_8V_{14} on its hybrids based on transition metal complexes is not thoroughly studied. In this paper, we report the syntheses and characterizations of three new compounds $\{[\text{Cu}(\text{im})_2]_4[\text{H}_2\text{As}_8\text{V}_{14}\text{O}_{42}(\text{SO}_4)]\} \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Cu}(\text{phen})(\text{im})]_3[\text{Cu}(\text{phen})_2][\text{As}_8\text{V}_{14}\text{O}_{42}(\text{H}_2\text{O})]$ (**2**, **3**). Compound **1** exhibits a novel 3-D twofold interpenetrating diamondoid framework structure, and compounds **2** and **3** are polymorphs of each other. Polymorphism, defined as the phenomenon of a chemical species having more than one crystal forms [36–41], is attracting much attention because different forms may result in significantly different in terms of both their structures and physical and chemical properties of compounds. To this date, several polymorphs based on different POMs have been reported in literatures [42–51]. However, to our knowledge, polymorphs based on As–V POMs have not been reported before. Compounds **2** and **3** are the

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first polymorphs based on As–V POMs. In addition, the high symmetry of the As_8V_{14} cluster greatly influences the final structures of compounds **1–3**. The epoxidation of styrene to styrene oxide with aqueous tertbutyl hydroperoxide (TBHP) using compounds **1**, **2** or **3** as a catalyst has been carried out.

2. Experimental

2.1. Chemicals and reagents

All chemicals used were of reagent grade and used as received from commercial sources without further purification. IR spectra were obtained on a Perkin-Elmer spectrophotometer from 200 to 4000 cm^{-1} with pressed KBr pellets. XPS measurements were performed on single crystals with an ESCALAB MARK II apparatus using a Mg $K\alpha$ X-ray radiation as the excitation source (1253.6 eV). Elemental analyses of As, V, S and Cu were determined by inductively coupled plasma (ICP) analyses on a Perkin-Elmer Optima 3300DV ICP spectrometer. UV–Vis spectra were recorded on a Shimadzu UV-3100 spectrophotometer using saturated solutions of compounds **1–3** in N,N-dimethylformamide. Small-angle X-ray diffraction (XRD) patterns were obtained on a Siemens D5005 diffractometer using the Cu $K\alpha$ radiation.

2.2. Synthesis procedures

2.2.1. Synthesis of $[Cu(im)_2]_4[As_8V_{14}O_{42}(SO_4)] \cdot H_2O$ (**1**)

Compound **1** was synthesized hydrothermally by reacting of V_2O_5 (0.458 g, 2.5 mmol), $H_2C_2O_4 \cdot H_2O$ (0.444 g, 3.5 mmol), $NaAsO_2$ (0.295 g, 2.3 mmol), $CuSO_4 \cdot 5H_2O$ (0.436 g, 1.75 mmol), im (0.068 g, 1 mmol) and H_2O (20 ml) was stirred for 0.5 h, and then was sealed in a Teflon-lined stainless bomb and heated at 160 °C for 5 days. The pH of the mixture was adjusted to 6 with $NH_3 \cdot H_2O$ solution. The resulting black block crystals of **1** were filtered off, washed with water, and air-dried at room temperature (ca. 38.0% yield based on V). Compound **1** can also be prepared using this procedure except that the pH is adjusted to 4. Attempt to synthesized compound **1** by only replacing $CuSO_4 \cdot 5H_2O$ (0.436 g, 1.75 mmol) with $Cu(NO_3)_2 \cdot 3H_2O$ (0.423 g, 1.75 mmol) and $Cu(CH_3COO)_2 \cdot H_2O$ (0.35 g, 1.75 mmol) are not successful.

Compound **1** can also be synthesized hydrothermally by reacting of NH_4VO_3 (0.117 g, 1 mmol), $H_2C_2O_4 \cdot H_2O$ (0.113 g, 1 mmol), $NaAsO_2$ (0.13 g, 1 mmol), $CuSO_4 \cdot 5H_2O$ (0.25 g, 1 mmol), im (0.068 g, 1 mmol), isonicotinic acid (0.089 g, 0.72 mmol) and H_2O (20 ml) was stirred for 0.5 h, and then was sealed in a Teflon-lined stainless bomb and heated at 160 °C for 5 days. The pH of the mixture was adjusted to 5 with $NH_3 \cdot H_2O$ solution. The resulting black columnar crystals of **1** were filtered off, washed with water, and air-dried at room temperature (ca. 24.0% yield based on V). Calc. for $C_{24}H_{36}As_8Cu_4N_{16}O_{47}S_1V_{14}$: As, 20.67; Cu, 8.77; V, 24.60; C, 9.94; H, 1.25; N, 7.73. Found: As, 20.87; Cu, 8.39; V, 24.34; C, 9.41; H, 1.10; N, 7.46%. IR (cm^{-1}): 3410, 3224, 3139, 3065, 2950, 2847, 2562, 1625, 1540, 1493, 1431, 1324, 1257, 1140, 1099, 1071, 995, 971, 822, 697, 658, 557, 448. Compound **1** can also be prepared using this procedure except that the pH is adjusted to 7.

2.2.2. Synthesis of $[Cu(phen)(im)]_3[Cu(phen)_2][As_8V_{14}O_{42}(H_2O)]$ (**2**)

Compound **2** was synthesized hydrothermally by reacting of V_2O_5 (0.15 g, 0.8 mmol), $H_2C_2O_4 \cdot H_2O$ (0.26 g, 2.0 mmol), $NaAsO_2$ (0.16 g, 1.3 mmol), $CuSO_4 \cdot 5H_2O$ (0.321 g, 1.3 mmol), phen (0.7 g, 0.4 mmol), im (0.07 g, 1 mmol) and H_2O (10 ml) was stirred for 0.5 h, and then was sealed in a Teflon-lined stainless bomb and heated at 170 °C for 5 days. The pH of the mixture was adjusted to 5 with $NH_3 \cdot H_2O$ solution. The resulting black columnar crystals of **2** were filtered off, washed with water, and air-dried at room

temperature (ca. 24.0% yield based on V). Compound **2** can also be obtained by the same procedure except that the pH is adjusted to 4. Calc. for $C_{69}H_{54}As_8Cu_4N_{16}O_{43}V_{14}$: As, 17.83; Cu, 7.56; V, 21.21; C, 24.65; H, 1.62; N, 6.67. Found: As, 17.43; Cu, 7.35; V, 21.30; C, 24.41; H, 1.10; N, 6.42%. IR (cm^{-1}): 3840, 3737, 3424, 3222, 3136, 3066, 2378, 1618, 1538, 1506, 1421, 1324, 1257, 1143, 1099, 1070, 997, 849, 823, 766, 713, 631, 556, 472.

2.2.3. Synthesis of $[Cu(phen)(im)]_3[Cu(phen)_2][As_8V_{14}O_{42}(H_2O)]$ (**3**)

Compound **3** can be prepared by NH_4VO_3 (0.16 g, 1.4 mmol), $H_2C_2O_4 \cdot H_2O$ (0.23 g, 1.8 mmol), $NaAsO_2$ (0.31 g, 2.4 mmol), $CuSO_4 \cdot 5H_2O$ (0.34 g, 1.3 mmol), phen (0.05 g, 0.25 mmol), im (0.15 g, 2.1 mmol) and H_2O (10 ml) was stirred for 0.5 h, and then was sealed in a Teflon-lined stainless bomb and heated at 170 °C for 5 days. The pH of the mixture was adjusted to 4 with HCl solution. The resulting black columnar crystals of **3** were filtered off, washed with water, and air-dried at room temperature (ca. 16.0% yield based on V). Calc. for $C_{69}H_{54}As_8Cu_4N_{16}O_{43}V_{14}$: As, 17.83; Cu, 7.56; V, 21.21; C, 24.65; H, 1.62; N, 6.67. Found: As, 17.87; Cu, 7.39; V, 21.10; C, 24.22; H, 1.22; N, 6.55%. IR (cm^{-1}): 3432, 3145, 3059, 2942, 1621, 1509, 1423, 1255, 1139, 1078, 1002, 849, 825, 770, 710, 659, 629, 554, 461.

2.2.4. X-ray crystallography

Crystal structures of compounds **1–3** were determined by single-crystal X-ray diffraction. Intensity data of compounds **1** and **3** were measured on a Rigaku R-AXIS RAPID IP diffractometer with a graphite monochromated Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation source and compound **2** was collected on a Bruker Smart-CCD diffractometer equipped with a Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) source at 293(2) K. No crystal showed evidence of crystal decay during data collections. The three structures were solved by direct methods and refined using full-matrix least squares on F^2 with the Wingx-2014.1 crystallographic software package. In final refinements, all non-hydrogen atoms were refined anisotropically. The hydrogen atoms of 1,10-phen and im ligands were placed in calculated positions and included in the structure factor calculations but not refined, while hydrogen atoms of water molecules were not added. The crystal structure of compound **1** contains lattice water molecules which appear to be highly disordered and it was not possible to model their positions and distributions reliably. Therefore, the SQUEEZE procedure of PLATON was employed to remove the contribution of the electron density associated with the disordered solvents from the intensity data [52]. The solvent free model and intensity data were used for the final results reported here. Both space groups of compounds **2** and **3** have been confirmed by PLATON software [52]. Attempts to solve the structure of compound **2** in the space group $P2(1)/c$ and to solve the structure of compound **3** in the space group $C2/c$ have already been made, neither of which were successful at all. The structure of compound **2** contains a $[Cu(phen)(im)]^+$ TMC, each atom of which is disorderly distributed over two positions with occupancy factor of 0.5 (Fig. S1). There is a A-alert in the check cif file of compound **2**, which is generated because of the disorder above mentioned in the structure. A summary of the crystallographic data and structure refinements for compounds **1–3** is given in Table 1.

3. Results and discussion

3.1. Discussion

The synthesis of compounds **1–3** are all under weakly acidic conditions. Our previous works has demonstrated that As_8V_{14} is easily to be obtained under weakly acidic condition and As_6V_{15} is

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