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New solids from old cluster: Syntheses and structural characterization of $[Zn(2,2'\text{-bpy})_3]_2[As_8V_{14}O_{42}(H_2O)]\cdot 4H_2O$ and $[Zn(2,2'\text{-bpy})(\text{dien})]_2[As_8V_{14}O_{42}(H_2O)]\cdot 2H_2O$

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Abstract

Two new arsenic–vanadium clusters, $[Zn(2,2'\text{-bpy})_3]_2[As_8V_{14}O_{42}(H_2O)]\cdot 4H_2O$ (**1**, 2,2′-bpy = 2,2′-bipyridine) and $[Zn(2,2'\text{-bpy})(\text{dien})]_2[As_8V_{14}O_{42}(H_2O)]\cdot 2H_2O$ (**2**, dien = diethylenetriamine), have been hydrothermally synthesized and characterized by IR, elemental analysis, EPR, XRD, TGA, magnetic measurements, and single-crystal X-ray diffraction analysis. Crystal data: **1**, triclinic, $P\bar{1}$, $a = 14.3793(2)$ Å, $b = 16.7706(2)$ Å, $c = 24.7077(1)$ Å, $\alpha = 93.740(1)°$, $\beta = 93.182(1)°$, $\gamma = 113.363(1)°$, $Z = 2$; **2** orthorhombic, $P4(3)2(1)2$, $a = 21.3442(7)$ Å, $b = 21.3442(7)$ Å, $c = 15.8837(7)$ Å, $Z = 4$. X-ray crystallographic study showed that compound **1** is composed of the discrete $[As_8V_{14}O_{42}(H_2O)]^{4-}$ polyoxoanions and chiral $[Zn(2,2'\text{-bpy})_3]^{2+}$ cations, while compound **2** is constructed from $[As_8V_{14}O_{42}(H_2O)]^{4-}$ cluster anions and novel $[Zn(2,2'\text{-bpy})(\text{dien})]^{2+}$ complex fragments linked through hydrogen bonds into a network. Variable temperature susceptibility measurements demonstrate the presence of antiferromagnetic interaction between V^{IV} cations in **1** and **2**.

Keywords: Polyoxometalate; Arsenic; Vanadium; Hydrothermal synthesis; Crystal structure

1. Introduction

Polyoxometalates present an expanding class of molecular systems with intriguing structural diversity and wide ranging applications in several areas such as catalysis, material science, medicine, nanotechnology and magnetochemistry [1–4]. During the past decade, Zubieta et al. [4–6] have developed a hydrothermal synthetic strategy which employ an organic component as a ligand to a secondary metal cation, which provides charge-compensation and serves space-filling, passivating and structure-directing roles. This general approach has been already extensively exploited in the development of the TMCs/V/O isopolyoxovanadates (TMCs = transition metal complexes) [7–13], such as $[(2,2'\text{-}Py_2NH)_2Co]_3V_8O_{23}$ [7], $[M_2(H_2N(CH_2)_2NH_2)_5][\{M(H_2N(CH_2)_2NH_2)_2\}_2V_{18}O_{42}(X)]\cdot 9H_2O$ ($M =$ Zn, Cd; $X = H_2O$, Cl^-, Br^-) [8], $[\{Cu(1,2\text{-pn})_2\}_7\{V_{16}O_{38}(H_2O)\}_2]\cdot 4H_2O$ [9], $[Cu(enMe)_2]_3[V_{15}O_{36}Cl]\cdot 2.5H_2O$, $Cs_{0.5}[Ni(en)_2]_3[V_{18}O_{42}Cl]\cdot 2en\cdot 6H_2O$ [10]. In contrast, the use of TMCs has remained relatively undeveloped in the preparation of hetero-polyoxovanadates. Arsenic–vanadium clusters, one of the most important subclasses of hetero-polyoxovanadates, have been extensively studied, with a large number of structurally characterized examples now known [14–20], such as $[NHEt_3]_2[NH_2Me_2][As_8V_{12}O_{40}(HCO_2)]\cdot 2H_2O$ [14], $[N(Me)_4]_4[As_8V_{14}O_{42}\ (0.5H_2O)]$ [15], $[NBu^n{}_4]_4[As_8V_6O_{26}]$ [16], and $K_6[As_6V_{15}O_{42}(H_2O)]\cdot 8H_2O$ [17]. But arsenic–vanadium clusters combining with TMCs have not been systematically explored. We therefore seek to explore the assembly of arsenic–vanadium clusters in the presence of TMCs, and we have synthesized several interesting compounds [21–23]. As a continuation of our work in this system, we report here the hydrothermal syntheses and

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crystal structures of two new arsenic–vanadium clusters: $[Zn(2,2'\text{-bpy})_3]_2[As_8V_{14}O_{42}(H_2O)]\cdot 4H_2O$ (**1**) and $[Zn(2,2'\text{-bpy})(dien)]_2[As_8V_{14}O_{42}(H_2O)]\cdot 2H_2O$ (**2**), which both contain spherical arsenic–vanadium clusters cocrystallized with zinc coordination complexes.

2. Experimental

2.1. Syntheses of compounds

Synthesis of $[Zn(2,2'\text{-bpy})_3]_2[As_8V_{14}O_{42}(H_2O)]\cdot 4H_2O$ ***1***. A mixture of V_2O_5 (0.30 g, 1.65 mmol), As_2O_3 (0.35 g, 1.77 mmol), $Zn(CH_3COO)_2\cdot 2H_2O$ (1.00 g, 4.57 mmol), 2,2′-bipyridine (0.25 g, 1.60 mmol), piperazine (1.00 g, 11.63 mmol) and H_2O (10 ml) was sealed in a 40 ml Teflon-lined autoclave and heated under autogenous pressure at 180 °C for 6 days. 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 (72.6% yield based on V). The pH value was about 7.0 before and after the reaction. Anal. calcd for $(C_{60}H_{58}N_{12}O_{47}As_8V_{14}Zn_2)$: C, 22.91; H, 1.86; N, 5.35%. Found: C, 22.82; H, 1.93; N, 5.22%. IR (KBr pellet ν, cm^{-1}) : 3444(s), 1601(s), 1479(m), 1433(s), 1311(m), 1250(w), 1167(w), 991(s), 832(m), 764(s), 710(s), 634(m), 558(m), 466(m).

Synthesis of $[Zn(2,2'\text{-bpy})(dien)]_2[As_8V_{14}O_{42}(H_2O)]\cdot 2H_2O$ ***2***. A mixture of V_2O_5 (0.20 g, 1.10 mmol), As_2O_3 (0.24 g, 1.21 mmol), $Zn(CH_3COO)_2\cdot 2H_2O$ (0.54 g, 2.47 mmol), 2,2′-bipyridine (0.166 g, 1.06 mmol), dien (0.4 g, 3.88 mmol) and H_2O (10 ml) was sealed in a 40 ml Teflon-lined autoclave and heated under autogenous pressure at 180 °C for 6 days. 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 (67.5% yield based on V). The pH value was about 7.0 before and after the reaction. Anal. calcd for $(C_{28}H_{48}As_8N_{10}O_{45}V_{14}Zn_2)$: C, 12.50; H, 1.80; N, 5.21%. Found: C, 12.45; H, 1.88; N, 5.19%. IR (KBr pellet ν, cm^{-1}) : 3414(s), 3308(s), 1617(s), 1471(m), 1441(s), 1319(w), 1251(w), 1167(w), 999(s), 839(s), 763(s), 718(s), 664(m), 634(m), 558(m), 466(m).

2.2. Physical measurements

All chemicals used during the course of this work were of reagent grade and used as received from commercial sources without further purification. IR spectrum was recorded on an ABB Bomem MB102 spectrometer in KBr pellet. Thermal analysis was performed in a dynamic nitrogen atmosphere with a heating rate of 10 °C min^{-1}, using a METTLER TGA/SDTA851^e thermal analyzer. The elemental analyses (C, H, and N) were determined on a Elementar Vario EL III analyzer. EPR spectrum was carried out on powder samples at X-band frequency with a Bruker ER-420 spectrometer at room temperature. XRD spectrum was obtained using a Philips X'Pert-MPD diffractometer with Cu Kα radiation ($\lambda = 1.54056$ Å). Powder X-ray diffraction patterns of the bulk product are in good agreement with the calculated patterns based on the results from single-crystal X-ray diffraction (Fig. 1). Variable temperature susceptibility measurements were carried out in the temperature range 5–300 K at a magnetic field of 1 T on polycrystalline samples with a SQUID MPMS-7 magnetometer manufactured by Quantum Design. Background corrections for the sample holder assembly and diamagnetic components of the compound were applied.

2.3. X-ray crystal structure determination

Crystal structure determinations by X-ray diffraction were performed on a Siemens SMART-CCD

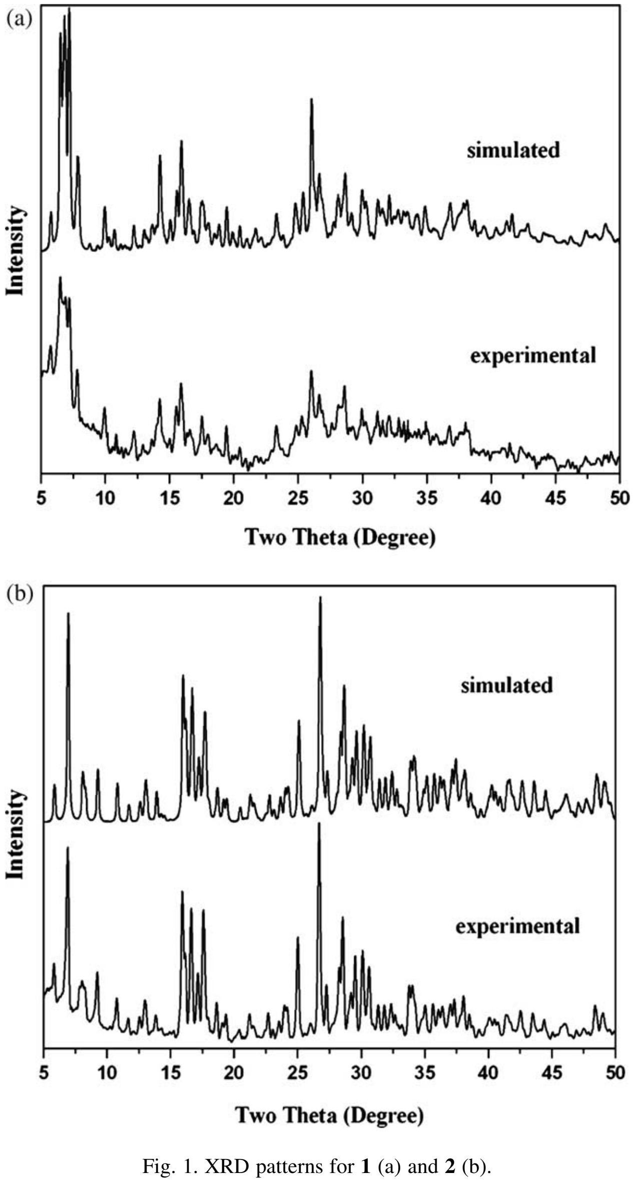

Fig. 1. XRD patterns for **1** (a) and **2** (b).