

Hybrid materials based on metal–organic coordination complexes and cage-like polyoxovanadate clusters: Synthesis, characterization and magnetic properties

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Abstract

Under hydrothermal conditions, reactions of NaVO_3 , 4,4'-bipyridine and metal salts in the presence of Na_2TeO_3 and halide ions produce hybrid materials $[\text{M}(4,4'\text{-bpy})_2][\text{V}_7^{\text{IV}}\text{V}_9^{\text{V}}\text{O}_{38}\text{X}] \cdot (4,4'\text{-bpy})_m(\text{H}_2\text{O})_n$ (bpy = bipyridine; M = Ni (**1**), Co (**3**), Mn (**4**); X = F (**1**), Br (**2**), Cl (**3**, **4**); $m = 1.5$ (**1**, **2**, **3**), 1 (**4**); and $n = 3$ for **1**, 3.5 for **2**, 2 for **3**, 2.5 for **4**). The variation of organic ligands can modify the inorganic oxide microstructure, just as the synthesis of $[\text{Ni}(2,2'\text{-bpy})_3][\text{V}_8^{\text{IV}}\text{V}_7^{\text{V}}\text{O}_{38}\text{Cl}] \cdot (\text{H}_2\text{O})_3$ (**5**) by using 2,2'-bpy instead of 4,4'-bpy. Compounds **1–5** were characterized by elemental analyses, infrared spectroscopy, thermogravimetry, manganometric titration, temperature-dependent magnetic susceptibility measurement and single-crystal X-ray structure analysis. Compounds **1–4** are isostructural with cage-like $[\text{V}_{16}\text{O}_{38}(\text{X})]^{4-}$ clusters incorporated into the 3D scaffolding afforded by $[\text{M}(4,4'\text{-bpy})_2]_n$ subunits. There exist left and right-handed helical channels in the 3D cationic framework, filled with disordered 4,4'-bpy molecules. To the best of our knowledge, compounds **1** and **2** are the first examples of hybrid materials that contain V_{16} clusters with F^- and Br^- ions in the center, respectively. Compound **5** consists of $[\text{M}(2,2'\text{-bpy})_3]^{2+}$, $[\text{V}_8^{\text{IV}}\text{V}_7^{\text{V}}\text{O}_{36}\text{Cl}]^{6-}$ cluster and H_2O molecules. Magnetic studies prove that there exist ferrimagnetic interactions in **3** and **4**.

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1. Introduction

The contemporary interest in the chemistry of polyoxometallates (POMs) stems from not only their potential applications in fields as diverse as catalysis, medicine, molecular magnetism and material science [1–4] but also their intriguing variety of architectures and topologies. The incorporation of metal–organic moieties into inorganic oxide clusters provides a powerful method for structural modification and synthesis of novel metallorganic–inor-

ganic hybrid materials that combine different characteristics of the components to obtain unusual structures or properties. Oxovanadium compounds have provided a long-standing fascination for chemists due to their potential applications and their intriguing variety of topologies [5–8].

In recent years, the significant interest in mixed-valence cage-like polyoxovanadate clusters [9–14] represents mainly the following aspects: (1) Cage-like polyoxovanadate clusters are very attractive in view of their diverse topologies. These clusters, containing mixed-valence vanadium centers, can act as host systems for a variety of neutral or anionic guest species, such as $[\text{V}_{14}\text{O}_{36}\text{X}]$ (X = Cl^-) [10], $[\text{V}_{15}\text{O}_{36}\text{X}]$

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(X = Cl⁻, Br⁻ and CO₃) [11], [V₁₆O₃₈(X)] (X = Cl⁻, H₂O) [12,8d], [V₂₂O₅₄(X)] X = (ClO₄⁻, SCN⁻ and CH₃COO⁻) [13] and [V₁₈O₄₂(X)] (X = H₂O, Cl⁻, Br⁻, I⁻, SO₄ and VO₄) [14] clusters. The central guest species in the shell exert templating effects on the electronic and framework structures of the host metal-oxide shells [15]. (2) The important family of magnetic polyoxometallates involves the mixed valence V^{IV/V} oxometallates [16]. Magnetic studies performed on the mixed valence vanadium (IV/V) clusters arising from the full or partial delocalization of single 3d electrons of the V^{IV} ions over both V^{IV} and V^V have shown antiferromagnetic coupling and a few ferromagnetic coupling [17,14a]. (3) The mixed-valence vanadium oxide clusters have luminescence properties. This class of compounds could be active in photo-oxidation reactions and a potential photocatalyst, which is worth further investigating [9].

Owing to the synergistic interaction between the metal–organic and inorganic components, this class of compounds reveals some remarkable properties. We are currently exploring to design and develop organic–inorganic hybrid materials by the amalgamation of cage-like mixed-valence vanadium clusters with metal–organic complexes. The mixed-valence vanadium clusters that fuse paramagnetic transition metal complexes might be of interest in molecular magnetism [18,8d]. During this ongoing effort, different paramagnetic metal ions have been introduced into the reaction system, such as manganese (II), cobalt (II) and nickel (II). As a result, magnetic materials are obtained through combining paramagnetic metal ions and [V₇^{IV}V₉^VO₃₈X]⁴⁻ clusters. In addition, the significant role of organic components in controlling the inorganic oxide microstructure was investigated by using different organic ligands. In this paper, we describe the synthesis and characterization of hybrid materials **1**–**5**. The magnetic properties of compounds **3**, **4** and **5** are reported as well.

2. Experimental

2.1. General remarks

All reagents were readily available from commercial sources and were used as received without further purification. The IR spectra in KBr pellets were recorded in the range 400–4000 cm⁻¹ with an Alpha Centaur FT/IR Spectrophotometer. Elemental Analyses (C, H and N) were performed with a Perkin–Elmer 2400 CHN Elemental Analyzer. M and V were determined with a PLASMA-SPEC (I) ICP atomic emission spectrometer. X-ray photoelectron spectrometry (XPS) spectra were measured on an ESCALAB spectrometer. Thermogravimetric analyses were carried out using a Pyris Diamond TG/DTA instrument, with a heating rate of 10 °C/min, under a nitrogen atmosphere. Magnetic susceptibility and magnetization data were collected over the temperature range 1.8–300 K in an applied field up to 50 kOe on a Quantum Design MPMS-5 SQUID magnetometer.

2.2. Preparation

2.2.1. Synthesis of [Ni(4,4'-bpy)₂]₂[V₇^{IV}V₉^VO₃₈F]·(4,4'-bpy)_{1.5}(H₂O)₃ (**1**)

A mixture of NaVO₃ (122 mg, 1 mmol), Na₂TeO₃ (222 mg, 1 mmol), Ni(CH₃COO)₂ (177 mg, 1 mmol), 4,4'-bipyridine (50 mg, 0.38 mmol), HF (40%, 0.2 mL), CH₃CH₂OH (2 mL) and H₂O (5 mL) was stirred for ca. 1 h in air until it was homogeneous, and adjusted by CH₃COOH to pH 4.6, and then transferred and sealed in a 16 mL Teflon-lined stainless steel container. After heated to 170 °C under autogenously pressure for 4d, the bomb was cooled down to room temperature. Black octahedron block crystals of **1** along with an amorphous grey impurity were filtered from the colorless mother liquor, washed by distilled water and air-dried at room temperature. The crystals were mechanically separated from the powdery grey impurity to give a yield of 61% (based on V), and were stable in air and insoluble in water and common organic solvents. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3446 (m), 1601 (m), 1559 (m), 1530 (m), 1487 (m), 1408 (m), 1066 (m), 983 (m), 813 (m), 733 (m), 670 (m), 657 (m), 631 (m), 507 (m), 459 (m), 418 (m), 403 (m). Elemental Anal. Calc. for Ni₂C₅₅H₅₀N₁₁O₄₁V₁₆F: C, 26.72; H, 2.04; N, 6.23; Ni, 4.75; V, 32.97. Found: C, 27.01; H, 2.27; N, 6.54; Ni, 4.27; V, 32.79%.

2.2.2. Synthesis of [Ni(4,4'-bpy)₂]₂[V₇^{IV}V₉^VO₃₈Br]·(4,4'-bpy)_{1.5}(H₂O)_{3.5} (**2**)

The reaction was carried out in the same way as for **1** except that HBr (0.25 mL) was used instead of HCl. Yield: 62% based on V. IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3442 (m), 1600 (m), 1548 (m), 1516 (m), 1479 (m), 1412 (m), 990 (m), 946 (m), 731 (m), 669 (m), 656 (m), 631 (m), 472 (w), 417 (m). Elemental Anal. Calc. for Ni₂C₅₅H₅₁N₁₁O_{41.5}V₁₆Br: C, 25.98; H, 2.02; N, 6.06; Ni, 4.62; V, 32.06. Found: C, 26.21; H, 2.19; N, 6.35; Ni, 4.34; V, 29.87%.

2.2.3. Synthesis of [Co(4,4'-bpy)₂]₂[V₇^{IV}V₉^VO₃₈Cl]·(4,4'-bpy)_{1.5}(H₂O)₂ (**3**)

The preparation of **3** was similar to that of **1** except that Co(CH₃COO)₂ (177 mg, 1 mmol) was used in place of Ni(CH₃COO)₂. Yield: 59% based on V; IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3680 (w), 3446 (w), 2360 (m), 1743 (m), 1692 (m), 1646 (m), 1546 (m), 1531 (m), 1515 (m), 1482 (m), 1411 (m), 985 (m), 816 (w), 677 (m), 575 (w), 455 (w). Elemental Anal. Calc. for Co₂C₅₅H₄₈N₁₁O₄₀V₁₆Cl: C, 26.73; H, 1.96; N, 6.23; Co, 4.77; V, 32.98. Found: C, 27.03; H, 2.31; N, 6.44; Co, 4.59; V, 32.65%.

2.2.4. Synthesis of [Mn(4,4'-bpy)₂]₂[V₇^{IV}V₉^VO₃₈Cl]·(4,4'-bpy)(H₂O)_{2.5} (**4**)

The reaction was carried out in the same way as for **1** except that MnSO₄ (151 mg, 1 mmol) was used instead of Ni(CH₃COO)₂. Yield: 65% based on V; IR (KBr, cm⁻¹): $\tilde{\nu}$ = 3740 (m), 3681 (m), 3416 (w), 2358 (m), 1743 (m), 1688 (m), 1609 (m), 1525 (m), 1514 (m), 1462 (m), 1406

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