An organic–inorganic hybrid material constructed from a three-dimensional coordination complex cationic framework and entrapped hexadecavanadate clusters†

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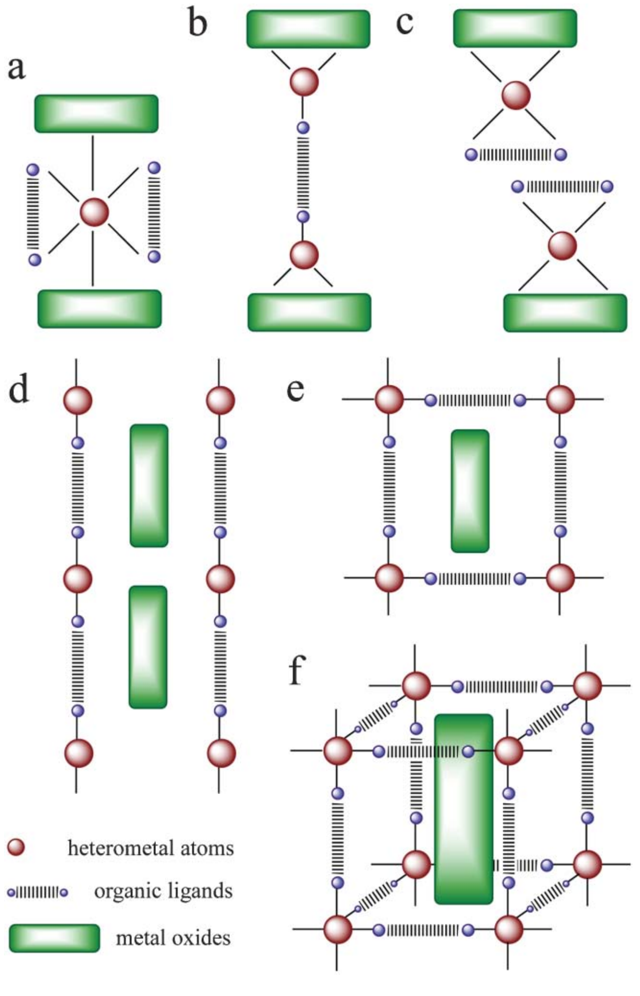
Received (in Cambridge, UK) 24th June 2005, Accepted 15th August 2005
First published as an Advance Article on the web 8th September 2005
DOI: 10.1039/b508930a

A unique organic–inorganic hybrid compound has been separated under hydrothermal condition, which is constructed from a three-dimensional second metal–organic subunit and entrapped hexadecavanadate clusters.

In recent years the synthesis and design of novel hybrid materials through the modification of metal oxides by organic molecules have been extensively investigated for the significance of discovering new materials.[1] A subclass of these materials is obtained by introducing a heterometal together with organic ligands to modify the microstructures of the metal oxides. The second metal–organic subunits generally serve two roles: 1) bridging linkers that link metal oxides to higher dimensional structures through either direct bonding[2,3] (Scheme 1a and b) or π–π interaction of the organic ligands (Scheme 1c);[4] 2) cation scaffolding whose void spaces are occupied by metal oxide anionic units (Scheme 1d, e and f).[5,6] The latter type hybrid material is of special interest because its second metal–organic subunit provides not only charge compensation for the anion oxide substructure but also a rigid framework for entraining and, to a degree, for controlling the surface of the growing oxide microstructure.[1] However, reports about hybrid bimetallic oxide materials with a three-dimensional (3-D) second metal–organic subunit are rare. To our knowledge, only Zubieta and co-workers have described two hybrid molybdate materials obtained by employment of multi-topic organoamine ligands,[6a,b] and Keller and co-worker have reported a 3-D Cu^I coordination polymer obtained from the spherical phosphotungstate ion template.[6c]

Polyoxovanadates show a structural variety (VO_x polyhedra, x = 4, 5, 6) and represent an important class of magnetic polyoxometalates.[7] However, no organic–inorganic hybrid vanadate material that belongs to the type 2f (Scheme 1f) has been reported hitherto. We have succeeded in isolating an organic–inorganic hybrid compound $[Ni(4,4'\text{-bpy})_2]_2[V^{IV}{}_7V^{V}{}_9O_{38}Cl]\cdot(4,4'\text{-bpy})\cdot6H_2O$ **1** (bpy = bipyridyl) constructed from a 3-D coordination complex cationic framework and entrapped hexadecavanadate (V_{16}) clusters in our attempts to prepare transition metal vanadium tellurites. Here we report the synthesis, structure and magnetic properties of the hybrid material.

A hydrothermal reaction of $NaVO_3$, Na_2TeO_3, $Ni(CH_3COO)_2$, 4,4′-bpy and HCl gives black octahedral crystals, the formula of which was established as $[Ni(4,4'\text{-bpy})_2]_2[V^{IV}{}_7V^{V}{}_9O_{38}Cl]\cdot(4,4'\text{-bpy})\cdot6H_2O$ through single-crystal X-ray study,‡ elemental analyses, thermogravimetric analysis (TGA) and manganometric titration. It is noteworthy that **1** cannot be obtained without the presence of Na_2TeO_3. When repeating the reaction without Na_2TeO_3 we only obtained some yellow precipitates likely corresponding to complexes of V^V. Consequently, we presume that the Na_2TeO_3 exerts a role as reducer for the V^V. We tried to obtain **1** by using Na_2SO_3 or some other common reducers such as oxalic acid, ethylenediamine and hydrazinium sulfate instead of



Scheme 1 Schematic representation of the roles of the second metal–organic units.

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† Electronic supplementary information (ESI) available: IR spectra, TGA curves and additional figures related to compound **1**. See http://dx.doi.org/10.1039/b508930a

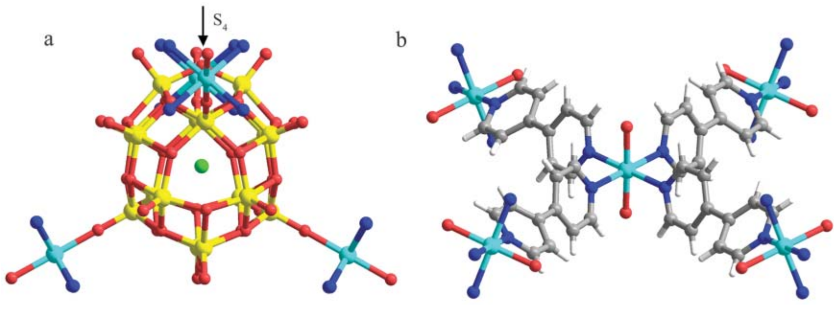

Fig. 1 a) Perspective view of the connection between the V_{16} cluster and the Ni atoms and b) a segment of the second metal–organic unit in **1**. V—yellow; Ni—turquoise; Cl—green; O—red; N—blue; C—gray.

Na_2TeO_3, but failed. However, when Na_2SeO_3 was used crystals of **1** were obtained, as determined by the measurement of unit cell parameters. These results justify our conjecture and indicate that the weak reducers are favoured for the formation of **1**. The exhibition of reductive ability for Na_2TeO_3 (or Na_2SeO_3) may be relative to the hydrothermal condition. Analogously it has been proved that tellurites absorb oxygen and form tellurates when heated in air to 400–500 °C.[8] We attempted to investigate the oxidation states of Te in the solution or amorphous by-product of the reaction but many difficulties were encountered owing to their complex components.

Single-crystal X-ray study revealed that the hybrid framework of **1** is composed of a 3-D coordination complex scaffolding $\{[Ni(4,4'\text{-bpy})_2]^{2+}\}_n$ and entrapped V_{16} clusters $[V^{IV}_7V^{V}_9O_{38}Cl]^{4-}$. Each cagelike V_{16} cluster with an encapsulated Cl^- ion is connected to four Ni atoms by four symmetrically equivalent (related by $\bar{4}$ axis) terminal oxygen atoms (O1) (Fig. 1a). Each crystallographic independent Ni atom is coordinated to four nitrogen atoms from four 4,4′-bpy molecules and two terminal oxygen atoms from two V_{16} clusters with a "4 + 2" distorted octahedral coordination geometry (Fig. 1b). Each 4,4′-bpy ligand in **1** connects with two Ni atoms. The connection of alternate Ni atoms and 4,4′-bpy ligands forms a unique 3-D porous cationic framework. There are two types of channels along the [001] direction with the bigger one occupied by V_{16} clusters and the smaller one occupied by severely disordered guest 4,4′-bpy molecules (Fig. 2). The existence of approximately one guest 4,4′-bpy molecule together with six H_2O molecules per formula in the void of the cationic framework found from the difference Fourier map is further confirmed by elemental analyses and TGA (see ESI†).

The V_{16} cluster, with S_4 symmetry, is composed of a $[V_{16}O_{38}]$ shell with an encapsulated Cl^- ion at its center. It is a feature of the polyoxovanadates to form cages built up from $\{O{=}VO_4\}$ pyramids with an encapsulated guest such as $[V_{15}O_{36}Cl]$,[9] $[V_{22}O_{54}(X)]$ ($X = ClO_4^-$, SCN^-, CH_3COO^-)[10] or $[V_{18}O_{42}(X)]$ ($X = H_2O$; Cl^-; Br^-; SO_4; VO_4) clusters.[11,12] Here the $[V_{16}O_{38}]$ shell consists of 16 VO_5 square pyramids through sharing edges and corners with 20 μ_3-oxygen atoms ((O2, O3, O4, O5, O6) × 4) and 2 μ_2-oxygen atoms (O10). The other 16 oxygen atoms ((O1, O7, O8, O9) × 4) are terminal in the polar positions of the 16 VO_5 square pyramids. The $[V_{16}O_{38}]$ shell can also be regarded as two $[V_8O_{19}]$ units twisted by 90° with respect to each other. The four terminal oxygen atoms (O1) bonded to the Ni atoms are related to the S_4 axis that drills through the two μ_2-oxygen atoms (O10) and the center Cl^- ion. The high symmetry of the V_{16} cluster and its special connection mode to the Ni atoms result in the crystallization of **1** in a high symmetry space group ($P\bar{4}n2$, no. 118). Similar V_{16} cluster have been reported in several compounds.[13,14] However, it is worth noting that the oxidation states for the V atoms of the V_{16} cluster in **1** are distinct from that observed in other reported compounds. Bond valence sum calculations[15] reveal that the valence sums for the four crystallographically independent V atoms are 4.154 (4 × V1), 4.672 (4 × V2), 4.812 (4 × V3) and 4.642 (4 × V4), respectively. The average value is 4.570, very close to the value of 4.562 for $V^{IV}_7V^{V}_9$. The result is unexpectedly consistent with the charge balance for the hybrid framework of **1** and is further confirmed by the manganometric titration of the V^{IV} sites. The difference in the oxidation state for the V atoms in **1** and those reported compounds ($V^{IV}_{11}V^{V}_5$) recalls the utilization of the special reducer Na_2TeO_3 in the synthesis of **1**. We also presume that there are some correlations between the arrangement of the oxidation states for the V atoms of the V_{16} clusters in **1** and the formation of the unique second metal–organic framework cation $\{[Ni(4,4'\text{-bpy})_2]^{2+}\}_n$. However, it is imprudent to say that the V_{16} cluster is the template for the formation of the coordination

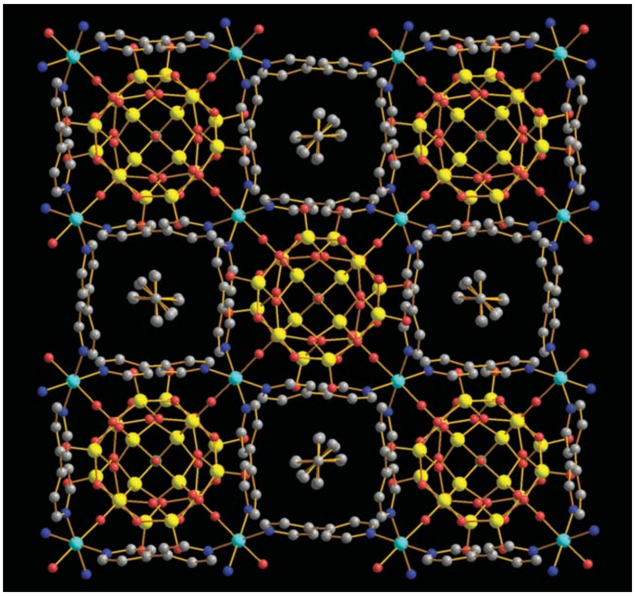

Fig. 2 Perspective view of the 3-D cationic framework along the [001] direction with the bigger channels occupied by V_{16} clusters and the smaller occupied by 4,4′-bpy. Hydrogen atoms are omitted for clarity. V—yellow; Ni—turquoise; Cl—green; O—red; N—blue; C—gray.

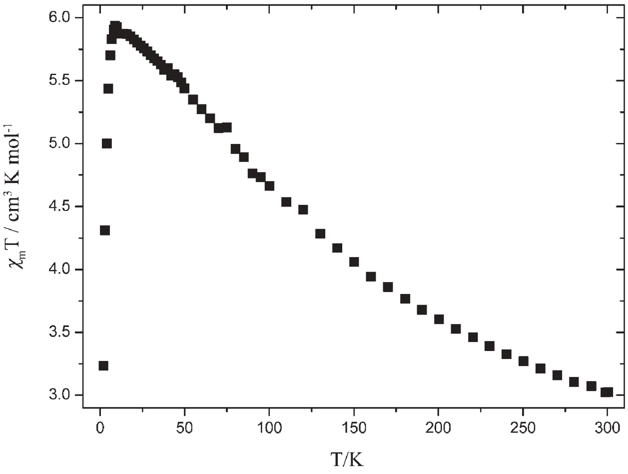

Fig. 3 Temperature dependence of magnetic susceptibility given by measurement of $\chi_m T$ over a temperature range of 2–300 K.

cationic framework, as there may be a synergistic interaction between them during the formation of **1**. In other words, the coordination cationic framework may also contribute to the formation of the V_{16} clusters with their special shape and oxidation state.

Primary magnetic studies have been performed on a powdered sample of **1** in the range 2–300 K. The product $\chi_m T$, where χ_m is the molar magnetic susceptibility in terms of the unit formula, increases as the temperature decreases from 300 to 9 K, indicating the presence of a ferromagnetic exchange interaction in **1** (Fig. 3). In the range 9–2 K, the $\chi_m T$ value decreases as the temperature decreases, showing that there is an antiferromagnetic coupled interaction in this temperature range. The room temperature value (3.03 cm^3 K mol^{-1}, $\mu_{eff} = 4.92\ \mu_B$) is smaller than the expected value (4.62 cm^3 K mol^{-1}, $\mu_{eff} = 6.08\ \mu_B$ assuming $g = 2.0$ for V^{4+} and Ni^{2+}) for the total value of 7 uncoupled $S = 1/2$ spins of V^{4+} and 2 uncoupled $S = 2/2$ spins of Ni^{2+}. In general, the antiferromagnetic behaviour is the most common feature for mixed valence clusters having electron delocalization.[2b,10] We presume that the existence of ferromagnetic interactions in **1** may be related to the special arrangement of the V atoms and Ni atoms, such that the V1–Ni1–V1 angle is approximately 180°. The magnetic data for sample **1** obeys the Curie–Weiss law in the high-temperature region, and fitting in the range 150–300 K gives values of $C = 2.3866$ cm^3 mol^{-1} K and $\theta = 65.847$ K. Further study on the magnetic properties of **1** is underway.

Compound **1** represents a dramatic incorporation of the spherical polyoxovanadate and the porous metal–organic framework. Its formation may be achieved by the synergistic interaction between the oxides and the second metal–organic subunit. Our work also reveals that the oxidation state of the mixed-valence cluster is a crucial factor for the formation of **1** that can be realized by the utilization of a special reducing agent. In fact, we have obtained several similar compounds based on this strategy recently, which will be reported later systemically with their magnetic properties.

This work was supported by the National Science Foundation of China (Grant No. 20071008) and the Scientific Research Foundation for Returned Overseas Chinese Scholars, the Ministry of Education.

Notes and references

‡ A mixture of $NaVO_3$ (244 mg, 2mmol), Na_2TeO_3 (110 mg, 0.5 mmol), $Ni(CH_3COO)_2 \cdot 4H_2O$ (124 mg, 0.5 mmol), 4,4′-bpy (156 mg, 1 mmol), HCl (3 mol L^{-1}, 0.2 ml) and H_2O (10 ml) adjusted with CH_3COOH (36%) to pH 4.5 was place in a 23 ml Telflon reactor and kept under autogenous pressure at 170 °C for 4 d. Then the mixture was cooled to room temperature at a rate of 10 °C h^{-1}, and black crystals of **1** were obtained (yield: 234mg, 76% based on V). Anal. Calc. (%) for **1**: C 24.34, H 2.11, N 5.68, Ni 4.76, V 33.10; found (%): C 24.78, H 2.56, N 5.78, Ni 4.68, V 32.89. X-Ray data for **1**: $Ni_2C_{50}H_{52}N_{10}V_{16}O_{44}Cl$, $M = 2464.93$, tetragonal, $P\bar{4}n2$ (no. 118), $a = 17.074(2)$ Å, $c = 14.606(3)$ Å, $V = 4257.8(12)$ Å^3, $Z = 2$, $T = 293$ K, $\mu = 2.220$ mm^{-1}, $\rho_{calcd} = 1.923$ g cm^{-3}, 36280 reflections measured, 4871 unique (R(int) = 0.0777), $R_1 = 0.0664$ for $I > 2\sigma(I)$, $wR_2 = 0.1567$ for all data, GOF = 1.227, 280 parameters and 8 restraints. CCDC 276944. See http://dx.doi.org/10.1039/b508930a for crystallographic data in CIF or other electronic format.

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