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A novel two-dimensional mixed molybdenum–vanadium polyoxometalate with two types of cobalt(II) complex fragments as bridges†

Cai-Ming Liu,[a] De-Qing Zhang,*[a] Ming Xiong[b] and Dao-Ben Zhu*[a]

[a] *Organic Solids Laboratory, Center for Molecular Science, Chinese Academy of Sciences, Beijing 100080, P. R. China. E-mail: dqzhang@infoc3.icas.ac.cn*

[b] *Geoscience Laboratory, China University of Geoscience, Beijing 100083, P. R. China*

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A heterometallic polyoxometalate $[Co(en)_2][Co(bpy)_2]_2[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]\cdot 4.5H_2O$ (en = ethylenediamine, bpy = 2,2′-bipyridine) 1, has been hydrothermally synthesized, which is the first example of a two-dimensional framework where polyoxometalate anions are linked by two types of complex fragments.

Over the past decades, polyoxometalates have become a focus of contemporary chemical research due to their structural diversity and potential applications in many areas such as catalysis, analytical chemistry, nanotechnology, chemical sensing, biochemical and geochemical processes, medicine and materials science.[1] The rational design of high-dimensional polyoxometalate based materials, which contain well characterizable motifs with desired features, therefore, is of considerable appealing since their properties can be possibly modified in terms of their constitents at the molecular level.[2] One promising synthesis approach to the synthesis of extended solids composed of polyoxometalates is to connect polyoxovanadate ions with metal cations *via* covalent bonds,[3] and a series of mixed-metal framework materials based on $[V_{18}O_{42}]$ clusters are recent examples.[2,4] Another advance is to introduce organic ligands to form organic–inorganic hybrid materials. This method has been utilized to prepare several organodiamine–molybdenum oxide composite materials, organoammonium–molybdenum oxide phases, and molybdenum oxide phases containing organodiamine-ligated heterometals.[5]

The aim of our work is to study extended solids based on mixed molybdenum–vanadium polyoxometalates. In this paper, we report the hydrothermal synthesis, crystal structure and properties of a novel two-dimensional layered complex, $[Co(en)_2][Co(bpy)_2]_2[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]\cdot 4.5H_2O$ **1** (en = ethylenediamine, bpy = 2,2′-bipyridine). The most remarkable structural feature of **1** is that the mixed molybdenum–vanadium hexadecametal polyoxoanion clusters $[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]^{6-}$ are linked to each other through both $Co(en)_2$ and $Co(bpy)_2$ fragments as the warp and weft, respectively. To our knowledge, this is the first example of two-dimensional organic–inorganic hybrid oxide materials with two types of transition metal complex fragments as bridges, though covalently linked transition metal complex fragments have also been observed in many high-dimensional organic–inorganic hybrid oxide materials.[5–7]

Complex **1** was synthesized by the hydrothermal reaction of NH_4VO_3, $H_3[P(Mo_3O_{10})_4]\cdot xH_2O$, $Co(en)_3Cl_3$, 2,2′-bipyridine and H_2O in a molar ratio 4 : 0.5 : 1 : 1 : 1000 at 170 °C for six days.‡ It is noteworthy that complex **1** is difficult to prepare by the conventional hydrothermal procedure, so a metal amine complex $Co(en)_3Cl_3$ was used as starting material. This route had also been used to synthesize open-framework cobalt phosphates by Rao's group.[8] The bands at 1056, 951 and 769 cm^{-1} in the IR spectrum could be ascribed to ν(P–O), ν(M=O), ν(M–O–M) (M = V or Mo), respectively. The presence of a Co $2p_{3/2}$ satellite peak in the X-ray photoelectron spectrum indicates the valence of cobalt is +2 in complex **1**. Thermogravimetric analysis (TGA) of **1** revealed distinct weight losses of 2.7 (up to 125 °C), 4.1 (190–340 °C) and 21.5% (340–470 °C), corresponding to the loss of uncoordinated water, coordinated en and 2,2′-bpy.

Single-crystal structure analysis of **1** revealed a two-dimensional extended layer framework composed of $[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]^{6-}$ polyoxoanion clusters, $Co(en)_2$ and $Co(bpy)_2$ fragments as bridges and uncoordinated water molecules.§ To our knowledge, the only reported example of $[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]^{6-}$ polyoxoanion clusters is $[Ni(tea)_2]_3[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]\cdot tea\cdot H_2O$ (tea = triethylenediamine),[9] where the $[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]^{6-}$ cluster is a discrete anion and the transition metal complex $Ni(tea)_2$ simply acts as a counter ion. Another complex $\{Co(tea)_2\}_2Na[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}]\cdot 8H_2O$[6] also possesses a similar polyoxoanion cluster $[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}]$, but its net valence is −5 rather than −6.

The $[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]$ cluster in **1** (Fig. 1) is very similar to that in $[Ni(tea)_2]_3[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]\cdot tea\cdot H_2O$ and $[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}]$ in $\{Co(tea)_2\}_2Na[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}]\cdot 8H_2O$.[9] It shows a novel tetra-capping Keggin structural feature, which is based on α-Keggin structure with four additional five-coordinated terminal VO^{2+} units to form hexadecametal host shell, $[Mo^{VI}_5Mo^{V}_3V^{IV}_8O_{40}]^{3-}$, and there is a disordered PO_4^{3-} anion inside this host shell as a guest. This host cage $[Mo^{VI}_5Mo^{V}_3V^{IV}_8O_{40}]^{6-}$ is constructed from eight VO_5 square pyramids by sharing square edges to form a central belt and two Mo_4 rings bonded above and below this V_8 belt. Each MoO_5 also exhibits square pyramidal configuration. In each Mo_4 ring, four MoO_5 square pyramids share four oxygen atoms with each other, while their other non-terminal oxygen atoms are shared with neighboring VO_5 square pyramids in the V_8 central belt. The Mo–O and V–O bond lengths [$Mo–O_t$ 1.663(3)–1.689(3) Å, $Mo–O_b$ 1.853(3)–1.981(3) Å, $V–O_t$ 1.597(3)–1.650(3) Å and $V–O_b$ 1.918(3)–1.993(3) Å] are comparable with those in $[Ni(tea)_2]_3[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]\cdot tea\cdot H_2O$ [$Mo–O_t$ 1.664(6)–1.706(5) Å, $Mo–O_b$ 1.853(10)–2.037(10) Å, $V–O_t$ 1.562(14)–1.713(10) Å and V–

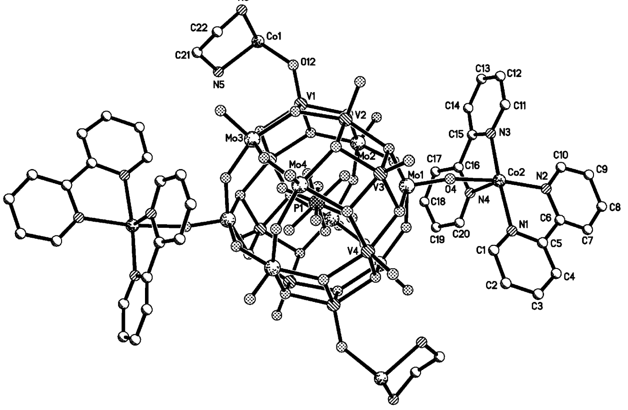

Fig. 1 ORTEP view of the building block unit in crystalline **1**. Only parts of atoms are labeled, and all H atoms and crystalline water molecules are omitted for clarity.

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† Electronic supplementary information (ESI) available: synthesis and characterization of **1**. Fig. S1: view of layers down the *a* axis of **1**. Fig. S2: plots of χT and χ^{-1} *vs.* T for **1**. See http://www.rsc.org/suppdata/cc/b2/b202540j/

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$\mathrm{O_b}$ 1.890(11)–2.105(9) Å] and $\{\mathrm{Co(tea)_2}\}_2\mathrm{Na[PMo^{VI}_6Mo^{V}_2}$-$\mathrm{V^{IV}_8O_{44}]\cdot 8H_2O}$ [Mo–$\mathrm{O_t}$ 1.652(10)–1.678(7) Å, Mo–$\mathrm{O_b}$ 1.834(11)–1.991(9) Å, V–$\mathrm{O_t}$ 1.600(8)–1.643(13) Å and V–$\mathrm{O_b}$ 1.918(7)–1.983(9) Å].[7] The disordered $\mathrm{PO_4}$ tetrahedron is in the center of host cage $\mathrm{[Mo^{VI}_5Mo^{V}_3V^{IV}_8O_{40}]^{6-}}$.

In comparison with tetra-capping Keggin polyanions in $\mathrm{[Ni(tea)_2]_3[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]\cdot tea\cdot H_2O}$ and $\{\mathrm{Co(tea)_2}\}_2$-$\mathrm{Na[PMo^{VI}_6Mo^{V}_2V^{IV}_8O_{44}]\cdot 8H_2O}$,[9] the unusual characteristic of $\mathrm{[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]}$ in **1** is that it acts as a ligand towards $\mathrm{Co^{2+}}$, to give a novel 2D layered transition metal oxide cluster complex (Fig. 2). There are two types of cobalt(II) fragments between $\mathrm{[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]}$ polyanions: the Co atom is coordinated by two ethylenediamine or two 2,2′-bipyridine ligands, respectively, while adjacent $\mathrm{[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]}$ polyanions provide oxygen atoms (O4, O8, O12 and their symmetry equivalents) to finish the other two coordinated positions at each Co atom. Therefore, each Co atom is located at a slightly distorted octahedral center, being coordinated by two oxygen atoms [*trans*-orientated for $\mathrm{Co(en)_2}$ but *cis*- for $\mathrm{Co(bpy)_2}$] connected to two neighboring $\mathrm{[PMo^{VI}_5Mo^{V}_3}$-$\mathrm{V^{IV}_8O_{44}]}$ polyanions and four nitrogen atoms from two ethylenediamine (for Co1) or two 2,2′-bipyridine ligands (for Co2). Each $\mathrm{Co(en)_2}$ fragment links two terminal V–O groups while each $\mathrm{Co(bpy)_2}$ fragment connects one terminal V–O group and one terminal Mo–O group.

Another interesting feature of **1** is that $\mathrm{Co(bpy)_2}$ fragments always occur in pairs and function as double bridges. These double bridges connect $\mathrm{[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]}$ polyanions along the *a*-axis (they are denoted as the warp), while the $\mathrm{Co(en)_2}$ fragments link $\mathrm{[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]}$ polyanions along the short diagonal line of the *ab* plane (they are denoted as the weft), so a 2D layered neutral network is generated along the plane formed by the *a*-axis and the short diagonal line of the *bc* plane (Fig. 2). All such networks are arranged in parallel with an interlayer distance of about 12.5 Å (Fig. S1, ESI†).

Preliminary magnetic studies have been performed on a powdered sample of **1** in the range 5–300 K (Fig. S2, ESI†) using a SQUID magnetometer. The product χT, where χ is the molar magnetic susceptibility in terms of the unit formula, continuously decreased as the temperature is lowered, indicating the presence of antiferromagnetic exchange interaction. The room temperature value (8.81 emu K $\mathrm{mol^{-1}}$, $\mu_{\mathrm{eff}} = 8.40\ \mu_{\mathrm{B}}$) is smaller than that expected for the total value of 8 uncoupled $S = 1/2$ spins of $\mathrm{V^{4+}}$ atoms, 3 uncoupled $S = 1/2$ spins of $\mathrm{Mo^{5+}}$ atoms and 3 uncoupled $S = 3/2$ spins of $\mathrm{Co^{2+}}$ atoms (≈ 14.25 emu K $\mathrm{mol^{-1}}$ assuming $g = 2.0$ for $\mathrm{V^{5+}}$ and $\mathrm{Mo^{5+}}$, and $g = 2.68$ and room temperature $\mu_{\mathrm{eff}} = 5.2\ \mu_{\mathrm{B}}$ for $\mathrm{Co^{2+}}$), indicative of antiferromagnetic coupling. Similar trends have also been observed in other high-nuclearity spin oxovanadium clusters.[10] These antiferromagnetic coupling interactions are related to electron delocalization of mixed-valence systems. Some electronic charges in $\mathrm{[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]^{6-}}$ polyoxoanion clusters of complex **1** are delocalized as denoted in $\mathrm{[Ni(tea)_2]_3}$-$\mathrm{[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]\cdot tea\cdot H_2O}$.[9] Previous studies indicated that electron delocalization can favor spin pairing,[10c] suggesting $\mathrm{[PMo^{VI}_5Mo^{V}_3V^{IV}_8O_{44}]^{6-}}$ polyoxoanion clusters of complex **1** may be antiferromagnetic coupled. Unfortunately, it is too difficult to fit the experimental magnetic data of this two-dimensional heterometallic high nuclearity spin system using a suitable theoretical model. However, the magnetic data of sample **1** obeys the Curie–Weiss law in the high-temperature region, and fitting in the range 50–300 K gives values of $C = 9.83\ \mathrm{cm^3\ mol^{-1}\ K}$ and $\theta = -35.3$ K, characteristic of an overall antiferromagnetic interaction.

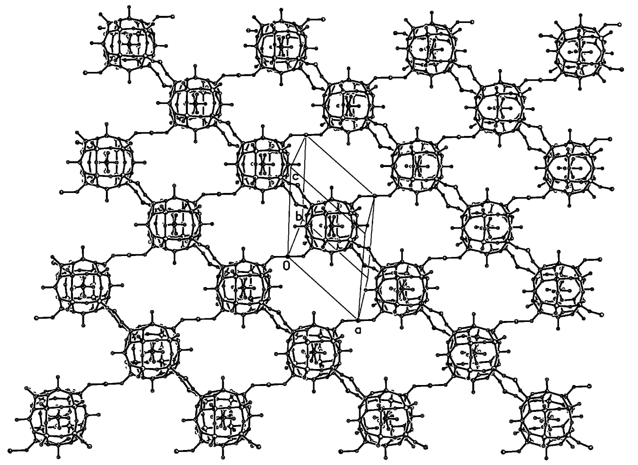

Fig. 2 Projection of the 2D network down the *b* axis in **1**. All C, H, N atoms and water guests are omitted for clarity.

This study demonstrates the utility of a pre-synthesized metal ligand as a precursor and the application of two types of transition metal complex fragments as bridges at the same time for constructing organic–inorganic hybrid oxide materials. This approach is expected to be effective for the preparation of further novel organic–inorganic hybrid transition metal oxide high dimensional polymers, and more investigations are underway.

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Notes and references

‡ Elemental analysis. Calc. for $\mathrm{C_{44}H_{49}N_{12}O_{28.50}PV_8Co_3Mo_8}$: C 18.14, H 1.97, N 5.77. Found: C 18.02, H 2.05, N 5.69%.

§ *Crystal data* for **1**: $\mathrm{C_{44}H_{57}N_{12}O_{48.50}PV_8Co_3Mo_8}$, $M_{\mathrm{r}} = 2912.82$, triclinic, space group $P1$, $a = 12.837(3)$, $b = 14.193(3)$, $c = 14.590(3)$ Å, $\alpha = 105.17(3)$, $\beta = 114.45(3)$, $\gamma = 105.95(3)°$, $V = 2101.8(8)$ Å^3, $Z = 1$, $D_{\mathrm{c}} = 2.301\ \mathrm{g\ cm^{-3}}$, $\mu = 2.683\ \mathrm{mm^{-1}}$, $F(000) = 1409$. A total of 20147 reflections were collected and 14695 are unique ($R_{\mathrm{int}} = 0.019$). The final $wR_1 = 0.0440$, $wR_2 = 0.1258$, GoF = 1.026 for 607 parameters and 11452 reflections ($I > 2\sigma(I)$). CCDC reference number 175863. See http://www.rsc.org/suppdata/cc/b2/b202540j/ for crystallographic data in CIF or other electronic format.

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