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Synthesis and characterization of a new compound based on mixed Mo/V polyoxometalates connected and modified by [Ni(en)$_2$]$^{2+}$ groups

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The compound [Ni(en)$_2$]$_2${[Ni(en)$_2$][Mo$^{VI}_5$Mo$^V_3$V$^{IV}_8$O$_{40}$(V^{V}O$_4$)]}[(NH$_2$)$_2$(C$_2$H$_4$)$_2$NH]·2H$_2$O has been synthesised and characterised by X-ray crystallography, EPR, XPS, TG-DTA, IR spectroscopy and temperature-dependent magnetic susceptibility.

Solid-state polyoxometalates have received considerable attention due to their diverse structural flexibility and special properties.[1–3] The hydrothermal synthesis in combination with metal-organic complexes acting as bridging groups is a popular strategy in the assembly of extended networks.[4–7] Although several compounds based on tetra-capped Keggin clusters with different Mo/V ratios and metal centres (P, V or Mo)[8–11] have been reported, data on the thermal analysis and magnetic behaviours of these compounds are deficient.[9] Here, we report the synthesis and characterization of a new compound [Ni(en)$_2$]$_2${[Ni(en)$_2$]-[Mo$^{VI}_5$Mo$^V_3$V$^{IV}_8$O$_{40}$(V^{V}O$_4$)]}[(NH$_2$)$_2$(C$_2$H$_4$)$_2$NH]·2H$_2$O **1** (en = = ethylenediamine).

The above compound was hydrothermally synthesised from a mixture of (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (1.24 g, 1 mmol), NiCl$_2$·6H$_2$O (0.48 g, 2 mmol), V$_2$O$_5$ (0.36 g, 2 mmol), KOH (0.28 g, 5 mmol) and distilled water (18 ml, 1000 mmol), and pH 8 was adjusted using ethylenediamine. The mixture was heated for three days at 170 °C in a 30 ml Teflon-lined stainless steel autoclave; after cooling, the black block crystals of compound **1** were obtained.†

X-ray structural analysis revealed that compound **1**‡ consists of [Mo$_8$V$_8$O$_{40}$(VO$_4$)]$^{6–}$ clusters, [Ni(en)$_2$]$^{2+}$ groups, diethylene-triamine and water molecules. The tetra-capped Keggin cluster is based on the Keggin structure of [Mo$_8$V$_4$O$_{36}$(VO$_4$)]$^{14–}$ with four additional five-coordinated terminal VO^{2+} units. All Mo atoms in compound **1** have distorted octahedral environments with Mo–O(terminal) distances of 1.618(8)–1.651(7)Å, Mo–O(bridge) of 1.846(8)–2.017(7) and Mo–O(centre) of 2.365(12)–2.494(12) Å. As shown in Figure 1, all of the vanadium atoms display three different coordination environments, including a disordered VO$_4$ tetrahedron at the centre, distorted VO$_6$ octahedron as the sphere shell composition and VO$_5$ square pyramids at the capping positions. The central V(5) is surrounded by eight oxygen atoms with each oxygen site half-occupied and V(5)–O bond lengths from 1.635(12) to 1.735(11) Å, whereas in VO$_5$ square pyramid the V–O(terminal) distances V(2)–O(7) and V(5)–O(22) are 1.628(6) and 1.617(7) Å, respectively. It is just the capping terminal oxygen atoms linking the [Mo$_8$V$_8$O$_{40}$(VO$_4$)]$^{6–}$ cluster units together through the [Ni(en)$_2$]$^{2+}$ bridging groups with the Ni(1)–O(7) distance of 2.129(7) Å, which leads to the inter-
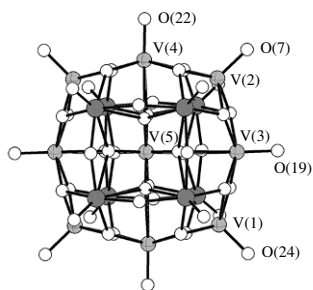
Figure 1 A view of the $[Mo_8V_8O_{40}(VO_4)]^{6-}$ anion.

secting chains running roughly along the $a + b$ and $a - b$ axes alternately (Figure 2). In addition, each infinite chain is modified by $[Ni(en)_2]^{2+}$ fragments at opposite positions along the b axis roughly, as shown in Figure 3, each cluster anion is connected with two $[Ni(en)_2]^{2+}$ groups through the terminal oxygen atoms of VO_6 octahedra *via* weak interactions with the Ni(2)–O(22) distance of 2.782(19) Å.

In compound **1**, some oxygen atoms of the cluster anions form hydrogen bonds with the nitrogen atoms of $[Ni(en)_2]^{2+}$ groups and the remaining lattice volume is occupied by lattice water along with diethylenetriamine molecules, which were obtained *via* deammoniation between ethylenediamine molecules under special conditions. Some types of self-reactions between ligands could happen under hydrothermal conditions.[12–14]

The thermal behaviour of compound **1** was studied at 30–800 °C in air. The observed weight loss of 5.6% from 50 to 240 °C is comparable with the calculated result of 5.3% for the removal of one diethylenetriamine and two lattice water molecules. A further weight loss about 14.6% between 240 and 520 °C corresponds to the loss of six ethylenediamine ligands (13.8%). The residue of 79.8% at 520 °C is consistent with the mixture of $3NiO$, $8VO_2$, $0.5V_2O_5$, $5MoO_3$ and $1.5Mo_2O_5$ (80.9%). The increased weight of about 2.3% from 520 to 650 °C is com-
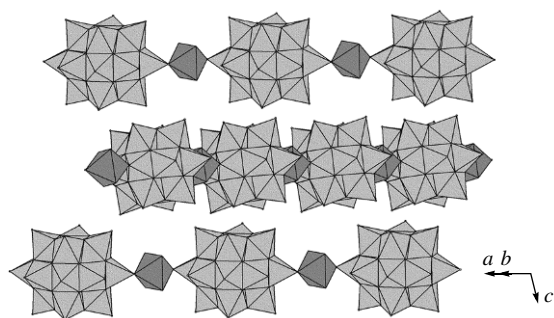
Figure 2 View of intersecting chains for compound **1** running roughly along the $a + b$ and $a - b$ axes alternately, the ethylenediamine molecules are omitted for clarity.

‡ *Crystal data for* **1**: monoclinic, space group $C2/c$, $a = 26.054(5)$, $b = 13.447(3)$ and $c = 19.637(4)$ Å, $\beta = 106.35(3)°$, $V = 6602(2)$ Å³, $Z = 4$, $d_{calc} = 2.622$ g cm⁻³, $\mu = 3.607$ mm⁻¹, MoKα radiation ($\lambda = 0.71073$ Å). Final R values ($R_1 = 0.0622$, $wR_2 = 0.1643$ and $S = 1.092$) were obtained for 4585 unique reflections with $I > 2\sigma(I)$ and a total of 459 parameters. Single-crystal X-ray data were collected on a Siemens Smart CCD diffractometer at 293 K in the range $2.16 < \theta < 23.40°$. Absorption corrections were performed using an empirical method. The structure was solved by direct methods using the SHELXS-97 program[16] and refined by full-matrix least-squares methods on F^2. All of the non-hydrogen atoms in the structure were refined using anisotropic thermal displacement parameters and all hydrogen atoms were treated as idealised contributions.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 228077. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2005.
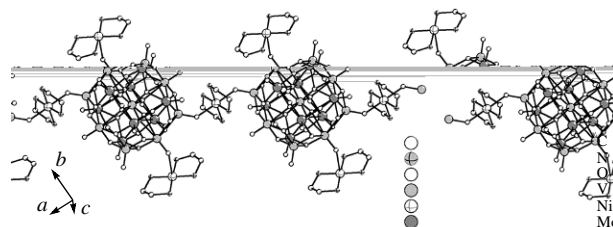
Figure 3 View of the chain structure modified with $[Ni(en)_2]^{2+}$ groups for compound **1**.

parable with the calculated value of 2.5% attributed to the oxidation of $8VO_2$.

The assignment of oxidation states for Mo and V atoms in compound **1** is confirmed by BVS calculation,[15] which gives the values of 4.10, 4.05, 4.11 and 4.01 for V(1) to V(4), respectively, and 5.02 for V(5). The valence sums for Mo atoms are 5.93, 5.92, 5.78 and 5.74 with an average value of 5.84. The XPS spectra give two peaks at 515.7 and 517.0 eV, attributed to V $2p_{3/2}$ of V^{IV} and V^{V}, respectively; two overlapped peaks at 231.3 and 232.7 eV, attributed to Mo $3d_{5/2}$ of Mo^{V} and Mo^{VI}, respectively, and the area ratio of Mo^{VI} and Mo^{V} peaks is about 1.4 (expected value is 1.67 for $5Mo^{VI}:3Mo^{V}$). The lack of Mo^{V} and V^{IV} signals in EPR spectra of compound **1** at room temperature suggests that eleven Mo^{V} and V^{IV} ions of the $[Mo_5^{VI} Mo_3^{V} V_8^{IV} O_{40}(V^{V}O_4)]^{6-}$ cluster are in spin–spin coupling.

The variable-temperature magnetic susceptibility of compound **1** was measured between 2 and 300 K, and the effective magnetic moment (μ_{eff}) showed a gradual decrease as the temperature was decreased. The value of $5.06\mu_B$ at 300 K is much smaller than that of expected $7.88\mu_B$ (uncoupled $8V^{4+}$, $3Mo^{5+}$ and $3Ni^{2+}$ atoms assuming $g = 2.0$ for V^{4+} and Mo^{5+}, $g = 2.2$ for Ni^{2+}) and close to the value of 5.38 for three uncoupled Ni^{2+} atoms, which indicates the existence of stronger antiferromagnetic coupling of eleven Mo^{V} and V^{IV} ions. Thus, the only magnetically active ions would be Ni^{II}, which is consistent with the EPR spectra.

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