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Reduced polyoxo anion with the bicapped quasi-Keggin structure [Ni(1,10′-phen)$_3$] [Ni(en)$_3$] [Ni(en)$_2$(H$_2$O)$_2$] {[Ni(en)$_2$]$_{0.5}$} [PMo$^{V}_2$Mo$^{VI}_6$V$^{IV}_4$V$^{V}_2$O$_{42}$]·6H$_2$O

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The title compound has been synthesised by a hydrothermal method and characterised by X-ray crystallography.

Polyoxometalates (POMs) represent an expanding class of compounds with wide applications in catalysis, electric conductivity, magnetism, sorption clathration and photochemistry.[1–6] Recently, various capped Keggin or capped pseudo-Keggin structural polyoxo anions such as bicapped [V$_{15}$O$_{42}$]$^{9-}$ were studied.[7] It is important to design and synthesise novel POMs with different structures in order to explore their properties. Here, we report the hydrothermal synthesis and characterization of the highly reduced polyanion [PMo$^{V}_2$Mo$^{VI}_6$V$^{IV}_4$V$^{V}_2$O$_{42}$]$^{7-}$ with the bicapped quasi-Keggin structure.

Compound [Ni(1,10′-phen)$_3$][Ni(en)$_3$][Ni(en)$_2$(H$_2$O)$_2$] {[Ni(en)$_2$]$_{0.5}$} [PMo$^{V}_2$Mo$^{VI}_6$V$^{IV}_4$V$^{V}_2$O$_{42}$]·6H$_2$O **1** was synthesised as black blocks by a hydrothermal method. A mixture of NiCl$_2$·6H$_2$O (0.8 g), Na$_2$MoO$_4$ (1.4 g), NaVO$_3$ (0.6 g), 1,10′-phenanthroline (phen) (0.2 g), ethylenediamine (en) (0.8 ml), H$_3$PO$_4$ (0.6 ml, 50%) and water (10 ml) was added to a Teflon-lined reactor, which was heated to 160 °C for four days. After cooling to room temperature, black block crystals were isolated. The IR spectrum of **1** exhibited an intense band at 727 cm^{-1}, which was attributed to ν(Mo–O, V–O); features at 1625, 1584, 1518, 1493, 1426, 1324 and 1276 cm^{-1} are characteristic of 1,10′-phenanthroline and en; bands at 1104 and 1034 cm^{-1} can be attributed to ν(P–O). Found (%): C, 19.12; H, 2.86; N, 8.39; P, 1.13; Mo, 25.48; V, 10.02; Ni, 6.88. Calc. for C$_{48}$H$_{88}$N$_{18}$PMo$_8$V$_6$O$_{50}$Ni$_{3.5}$ **1** (%): C, 19.04; H, 2.93; N, 8.33; P, 1.02; Mo, 25.36; V, 10.10; Ni, 6.79.

Crystals of **1** contain novel [PMo$^{V}_2$Mo$^{VI}_6$V$^{IV}_4$V$^{V}_2$O$_{42}$]$^{7-}$ heteropoly anions and four cations (Figure 1): [Ni(phen)$_3$]$^{2+}$, [Ni(en)$_3$]$^{2+}$, [Ni(en)$_2$(H$_2$O)$_2$]$^{2+}$ and {[Ni(en)$_2$]$_{0.5}$}$^{1+}$.[†] As shown in Figure 2, the reduced polyanion is formed from nine MO$_6$ (eight MoO$_6$ and one VO$_6$) octahedra, five VO$_5$ tetragonal pyramids and a PO$_4$ tetrahedron, which is in the centre of the molybdovanadate anion. In the [V$_{15}$O$_{42}$]$^{9-}$ (ref. 7) polyanion possessing the bicapped Keggin structure, the central VO$_4$ tetrahedron shares its oxygen atoms with four V$_3$O$_{13}$ groups (formed from twelve VO$_6$ octahedra) each of which is composed of three edge-sharing VO$_6$ octahedra whereas the polyanion in compound **1** adopts a structure which is a bicapped quasi-Keggin structure because its compositon corresponds to that of the bicapped Keggin anion.[8–10] For the PO$_4^{3-}$ tetrahedron, the P–O distances are 1.532(5)–1.547(5) Å, and the O–P–O angles vary from 108.9(3) to 110.4(3)°. The Mo–O and V–O distances can be grouped into three sets: Mo–O$_t$, 1.693(6)–1.719(5); V–O$_t$, 1.599(5)–1.629(6); Mo–O$_b$, 1.782(5)–2.083(5); V–O$_b$, 1.885(5)–1.989(5); and Mo–O$_c$, 2.432(5)–2.475(5); V–O$_c$, 2.457(5) Å. Compound **1** contains four kinds of cations: three six-coordinated Ni^{2+}, by three phen with an average Ni–N distance of 2.093 Å, by three en with an average distance of 2.147 Å, and by two en and two H$_2$O with an average distance of 2.095 Å and a Ni–O distance of 2.169 Å, and a four-coordinated Ni^{2+} by two en with an average Ni–N distance of 1.925 Å.

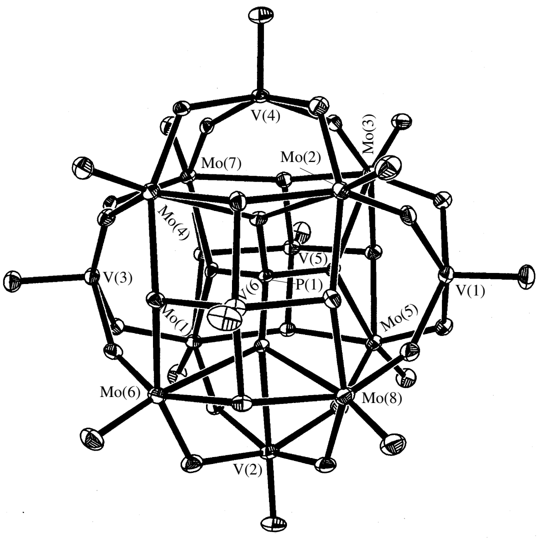

Figure 2 The structure of the new unit transition complex anion [PMo$^{V}_2$Mo$^{VI}_6$V$^{IV}_4$V$^{V}_2$O$_{42}$]$^{7-}$ in compound **1**.

The assignment of the oxidation states of Mo and V atoms is consistent with the electric charge balance. It was confirmed by bond valence sum calculations[11] using $S = \exp[-(R - 1.890)/0.314]$, which gives values of 5.688 for Mo(1), 5.834 for Mo(2), 5.741 for Mo(3), 5.838 for Mo(4), 5.740 for Mo(5), 5.774 for Mo(6), 5.734 for Mo(7) and 5.652 for Mo(8), the average value calculated for the oxidation state of Mo is 5.750, which is equal to an expected

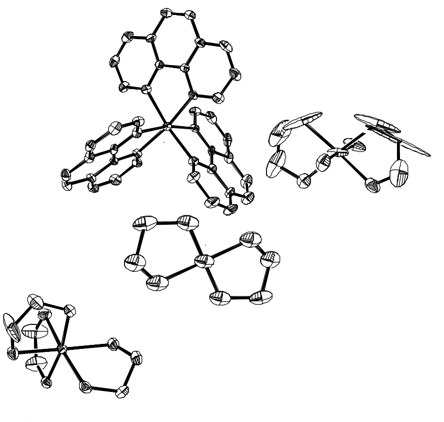

Figure 1 Four kinds of cations in compound **1**.

[†] The structure of compound **1** was determined by single crystal X-ray diffraction. A black block single crystal was mounted inside a glass fiber capillary. Data were collected on a Simens P4 four-circle diffractometer with MoKα radiation ($\lambda = 0.71073$ Å) at 293 K in the range $1.69 \le \theta \le 25.00$ using the ω-scan technique. An empirical absorption correction (Ψ-scan) was applied. Crystal data: space group $P2_1/n$ with $a = 24.117(5)$, $b = 13.213(4)$, $c = 28.566(9)$ Å, $\beta = 94.26(2)°$, $V = 9078(4)$ Å^3, $Z = 4$, $d_{calc} = 2.215$ g cm^{-3}. Of 19464 reflections collected ($1.69 \le \theta \le 25.00$), 15988 were independent ($R_{int} = 0.0243$), $R_1 = 0.0497$, $wR_2 = 0.1122$ for 1213 parameters. The structure was solved by the direct method and refined by the full-matrix least-squares on F^2 using the SHELXL-97 software. All non-hydrogen atoms were refined anisotropically. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2002. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/120.

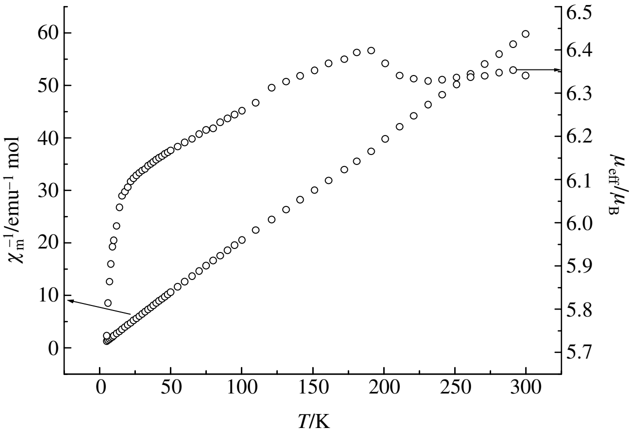

Figure 3 The temperature dependence of the effective magnetic moment u_{eff} and the inverse molar susceptibility for compound **1**.

value of 5.750 for $Mo^V_2Mo^{VI}_6$. The EPR spectrum (g = 2.05) of compound **1** at room temperature shows the existence of V^{IV}. Based on the above results and the elemental analysis of **1**, compound **1** is formulated as $[Ni(1,10'\text{-phen})_3]$ $[Ni(en)_3]$ $[Ni(en)_2(H_2O)_2]\{[Ni(en)_2]_{0.5}\}[PMo^V_2Mo^{VI}_6V^{IV}_4V^V_2O_{42}]\cdot 6H_2O$.

The variable temperature magnetic susceptibility of **1** was measured between 5 and 300 K. The compound obeys the Curie–Weiss law with a Curie constant C of 5.25 emu K mol^{-1} and a Weiss constant θ of –7.33 K (Figure 3) for **1**, and with a C of 1.56 emu K mol^{-1}. The effective magnetic moments μ_{eff} for **1** increase as increasing temperature except temperature range 191–231 K, which is in agreement with $\theta < 0$, indicating weak antiferromagnetic interaction. Because no suitable theoretical model is available in the literature[12] for such a complex system, detailed magnetic analyses were not performed for the compounds.

The EPR spectrum (Figure 4) at room temperature shows only a V^{4+} signal with g = 2.05 in accordance with the valence sum calculations. The lack of the Mo^{5+} signal suggests that the two electrons of Mo^{5+} centers are delocalised. This was also proved by the XPS measurements of compound **1** in the energy regions of $Mo^{3/2}_{3d}$ and $Mo^{5/2}_{3d}$. The XPS spectra (Figure 5) exhibit overlapped peaks at 232.7 and 230.8 eV, which are attributable to Mo^{6+} and Mo^{5+}, respectively. These results further confirm the valences of V and Mo atoms.

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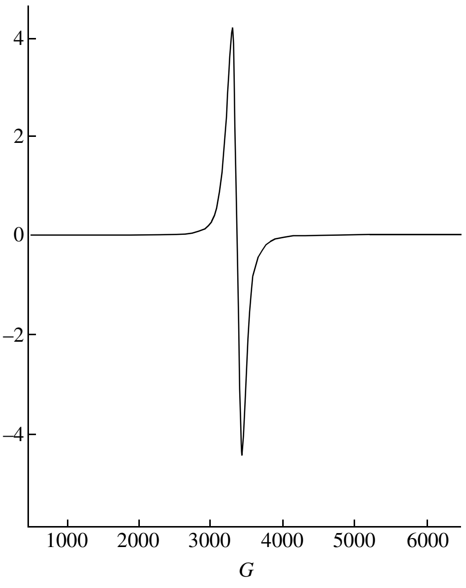

Figure 4 The EPR spectrum of compound **1**, g = 2.05.

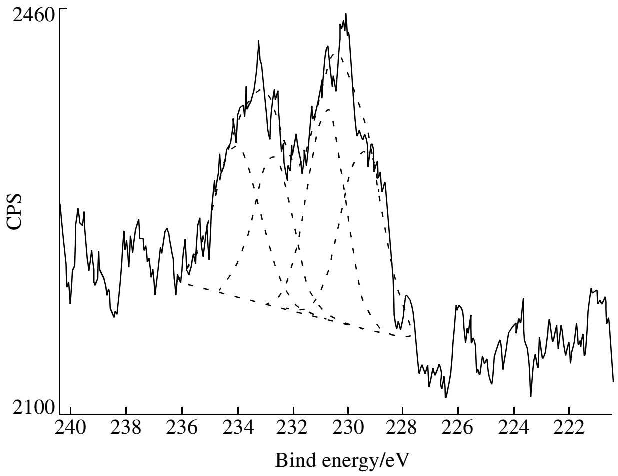

Figure 5 The XPS spectra with overlapped peaks at 232.7 and 230.8 eV, which are attributable to Mo^{6+} and Mo^{5+}, respectively.

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