

# [Mo<sup>V</sup><sub>2</sub>Mo<sup>VI</sup><sub>6</sub>V<sup>IV</sup><sub>8</sub>O<sub>40</sub>(PO<sub>4</sub>)<sup>5-</sup>: the first polyanion with a tetra-capped Keggin structure

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The new mixed Mo/V heteropoly compound [Ni(C<sub>2</sub>N<sub>2</sub>H<sub>8</sub>)<sub>3</sub>]<sub>2</sub>Na[Mo<sup>V</sup><sub>2</sub>Mo<sup>VI</sup><sub>6</sub>V<sup>IV</sup><sub>8</sub>O<sub>40</sub>(PO<sub>4</sub>)<sub>4</sub>·H<sub>2</sub>O with a tetra-capping Keggin structure has been synthesized hydrothermally and its structure determined by X-ray diffraction

There is considerable current interest in polyoxometalates containing Keggin moieties from both fundamental and practical points of view.<sup>1,2</sup> They are capable of being fine-tuned at the molecular level to promote a variety of applications ranging from catalysis to medicinal use.<sup>3–7</sup> To our knowledge, in contrast to an extensive literature on Keggin and transition metal substituted Keggin species, structural information relating to capped Keggin structures is very limited due to the lack of good quality single crystals, and only bi- and mono-capped Keggin derivatives are structurally known.<sup>8–18</sup> It has been recently demonstrated that the hydrothermal technique is well suited for the preparation and crystal growth of mixed Mo/V heteropoly compounds.<sup>16–18</sup> Here, we report the application of this technique to an Mo/V system which has resulted in the formation of [Ni(C<sub>2</sub>N<sub>2</sub>H<sub>8</sub>)<sub>3</sub>]<sub>2</sub>Na[Mo<sup>V</sup><sub>2</sub>Mo<sup>VI</sup><sub>6</sub>V<sup>IV</sup><sub>8</sub>O<sub>40</sub>(PO<sub>4</sub>)<sub>4</sub>·H<sub>2</sub>O **1**, the first mixed Mo/V tetra-capped Keggin structure heteropoly compound to be structurally characterised.

Compound **1** was prepared hydrothermally from a mixture of NH<sub>4</sub>VO<sub>3</sub>, Ni(OAc)<sub>2</sub>, Na<sub>2</sub>MoO<sub>4</sub>, en, H<sub>3</sub>PO<sub>3</sub> and H<sub>2</sub>O heated to 160 °C for six days.<sup>†</sup> The IR spectrum of **1** exhibited a complex pattern of bands at 1060, 940, 920, 720 and 650 cm<sup>-1</sup>, ascribed to ν(P–O), ν(M=O), ν(M–O–M) (M = V or Mo), respectively. A novel discrete polyanion [Mo<sup>V</sup><sub>2</sub>Mo<sup>VI</sup><sub>6</sub>V<sup>IV</sup><sub>8</sub>O<sub>40</sub>(PO<sub>4</sub>)<sub>4</sub>]<sup>5-</sup>, counter ions Na<sup>+</sup>, [Ni(C<sub>2</sub>N<sub>2</sub>H<sub>8</sub>)<sub>3</sub>]<sup>2+</sup> and lattice water molecules were revealed by X-ray analysis.<sup>‡</sup> The polyanion [Mo<sup>V</sup><sub>2</sub>Mo<sup>VI</sup><sub>6</sub>V<sup>IV</sup><sub>8</sub>O<sub>40</sub>(PO<sub>4</sub>)<sub>4</sub>]<sup>5-</sup> (Fig. 1) is based on the well known Keggin structure of [XM<sub>12</sub>O<sub>40</sub>]<sup>n-</sup> with four additional five-coordinated terminal VO<sup>2+</sup> units, which include V(3) and

its symmetry-related partner V(4) and V(5). The polyanion lies on a crystallographic twofold axis at x, 0, 0.25 which passes through P, V(4) and V(5), and it is disordered. The cluster anion contains a central P<sup>5+</sup> in an almost regular tetrahedral environment of PO<sub>4</sub> with P–O distances in the range 1.514(7)–1.518(6) Å, and bond angles of 108.5(4)–110.3(4)°.

The number of Mo sites revealed by X-ray analysis is consistent with the result of elemental analysis§ which gave an average ratio Mo/V of 1.0. While all the Mo atoms have a distorted octahedral environment, vanadium displays two different coordination environments square pyramidal and distorted octahedral. The Mo–O and V–O bond lengths are in the range 1.661(9)–2.543(5) and 1.589(8)–2.562(7) Å, respectively, comparable to those found in capping-Keggin structures. As shown in Fig. 1, the unusual feature of compound **1** is that the V=O units cap four of the six available four coordinate sites on the surface of the [Mo<sup>V</sup><sub>2</sub>Mo<sup>VI</sup><sub>6</sub>V<sup>IV</sup><sub>8</sub>O<sub>40</sub>(PO<sub>4</sub>)<sub>4</sub>]<sup>13-</sup> Keggin anion so as to produce a structure in which the vanadium atoms form a central belt, and each trimetallic group of [Mo<sup>V</sup><sub>2</sub>Mo<sup>VI</sup><sub>6</sub>V<sup>IV</sup><sub>4</sub>O<sub>40</sub>(PO<sub>4</sub>)<sub>4</sub>]<sup>13-</sup> (Keggin part) contains one V and two Mo atoms. The Mo<sub>4</sub> rings (each one-electron-reduced) are bonded above and below this V<sub>8</sub> belt. To the best of our knowledge, such a tetra-capped Keggin structural polyanion has not been previously observed in other heteropoly compounds. Only a Ni<sup>2+</sup> signal was evident (g = 2.07) in the room temperature EPR spectra, the lack of signals for Mo<sup>5+</sup> and V<sup>4+</sup> indicating that the 10 electrons of the polyanion are delocalised. The assignment of oxidation states for the vanadium and molybdenum atoms are consistent with their coordination geometries and are confirmed by valence sum calculations<sup>19</sup> which gives the values for Mo(1), Mo(2), Mo(3) and Mo(4) of 5.45, 6.007, 5.656 and 5.870, while the calculated valence sum for V(1), V(2), V(3), V(4) and V(5) are 3.901, 4.180, 4.103, 4.501 and 3.685, respectively. The average value for calculated oxidation state of Mo and V are 5.746 and 4.074, consistent with the formula of **1**. The Ni<sup>2+</sup> cations are coordinated by three ethylene diamine ligands with Ni–N distances in the range 1.999(4)–2.208(7) Å.

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## Notes and references

<sup>†</sup> A mixture of NH<sub>4</sub>VO<sub>3</sub> (0.40 g), Ni(OAc)<sub>2</sub> (0.40 g), Na<sub>2</sub>MoO<sub>4</sub> (0.8 g), en (2 ml) and H<sub>2</sub>O (10 ml) ratio was neutralized to pH = 6.0 with 50% phosphorous acid. It was then sealed in a 15 cm<sup>-3</sup> Teflon-lined reactor, which was heated to 160 °C for six days. After cooling to room temperature, black needle crystals were isolated (0.4 g, 48% based on Mo).

<sup>‡</sup> Crystal data for **1**: tetragonal, space group P4<sub>3</sub>22, a = b = 15.829(2) c = 28.712(6) Å, v = 7194(2) Å<sup>3</sup>, Z = 4. A black needle crystal with dimension of 0.22 × 0.16 × 0.14 mm was mounted on a glass fiber. Data were collected on Siemens P4 four-circle diffractometer at 20 °C in the range 3.64 < 2θ < 23.05° using the ω scan technique. A total of 12486 reflections was collected of which 8353 with I > 2σ(I<sub>0</sub>) were used. An empirical absorption correction was applied. The structure was solved by direct methods and refined using SHELX86 and SHELXL93 programs. The occupancy factor of major conformation [Mo(1)–Mo(4), V(1)–V(3),

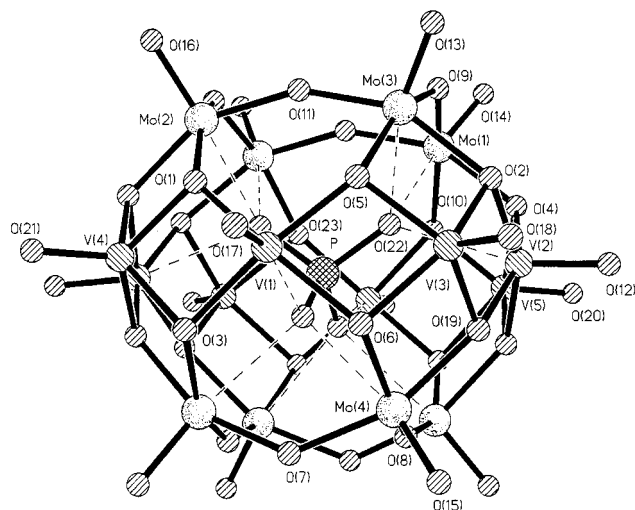


Fig. 1 Ball-and-stick representation of the structure of the polyanion [Mo<sup>V</sup><sub>2</sub>Mo<sup>VI</sup><sub>6</sub>V<sup>IV</sup><sub>8</sub>O<sub>40</sub>(PO<sub>4</sub>)<sub>4</sub>]<sup>5-</sup> in **1**

O(91)–O(19)] is 0.8564(6). The metal atoms and P atom were refined anisotropically, and the remaining non-metal atoms were refined isotropically. Structure solution and refinement based on 5046 reflections with  $I > 2\sigma(I_0)$  and 382 parameters gave  $R(R_w) = 0.0765$  (0.1987). CCDC 182/1204. See <http://www.rsc.org/suppdata/cc/1999/787/> for crystallographic files in .cif format.

§ Anal. Calc. for  $\text{Mo}_8\text{Ni}_2\text{V}_8\text{NaPO}_{45}\text{C}_{12}\text{N}_{12}\text{H}_{50}$ : Mo, 31.28; V, 16.80; Ni, 4.83; P, 1.28; Na, 0.95; C, 5.93; N, 6.91; H, 2.02. Found: Mo, 29.60; V, 16.24; Ni, 4.98; P, 1.36; Na, 1.10; C, 5.79; N, 6.71; H, 2.16%.

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