

# Keggin unit supported transition metal complexes: hydrothermal synthesis and characterization of $[\text{Ni}(2,2'\text{-bipy})_3]_{1.5}[\text{PW}_{12}\text{O}_{40}\text{Ni}(2,2'\text{-bipy})_2(\text{H}_2\text{O})]\cdot 0.5\text{H}_2\text{O}$ and $[\text{Co}(1,10'\text{-phen})_3]_{1.5}[\text{PMo}_{12}\text{O}_{40}\text{Co}(1,10'\text{-phen})_2(\text{H}_2\text{O})]\cdot 0.5\text{H}_2\text{O}$

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Two new Keggin unit supported transition metal complexes,  $[\text{Ni}(2,2'\text{-bipy})_3]_{1.5}[\text{PW}_{12}\text{O}_{40}\text{Ni}(2,2'\text{-bipy})_2(\text{H}_2\text{O})]\cdot 0.5\text{H}_2\text{O}$  **1** and  $[\text{Co}(1,10'\text{-phen})_3]_{1.5}[\text{PMo}_{12}\text{O}_{40}\text{Co}(1,10'\text{-phen})_2(\text{H}_2\text{O})]\cdot 0.5\text{H}_2\text{O}$  **2**, are synthesized by a hydrothermal method; complex **1** is characterized by X-ray crystallography, showing that the  $[\text{Ni}(2,2'\text{-bipy})_2(\text{H}_2\text{O})]^{2+}$  units are covalently bonded to the  $\alpha$ -Keggin cluster  $[\text{PW}^{\text{VI}}_{10}\text{W}^{\text{V}}_2\text{O}_{40}]^{5-}$ .

There is considerable current interest in metal-oxo cluster compounds reflecting their diverse properties, with applications to sorption clathration, catalysis, electrical conductivity, magnetism and photochemistry.<sup>1–11</sup> Recently an important advance in transition metal oxide cluster chemistry has been study of polyanions substituted by transition-metal and polyoxoanion-supported inorganic or organometallic complexes.<sup>12–20</sup> Structures determined included  $[\{\text{Cu}(4,4'\text{-bipy})_4(\text{Mo}_8\text{O}_{26})\}]^{16}$  and  $[\{\text{Cu}(\text{en})_2(\text{Mo}_8\text{O}_{26})\}]^{17}$  which possess infinite extended structures,  $[\text{La}(\text{Mo}_8\text{O}_{26})_2]^{5-}$ ,<sup>18</sup> a molecular cluster and the organometallic compounds  $[(\text{CO})_3\text{Mn}(\text{cis-Nb}_2\text{W}_4\text{O}_{19})]^{19}$  and  $[\{\text{C}_5\text{Me}_5\text{Rh}\}_2(\text{Mo}_{13}\text{O}_{40})]^{2+,20}$  which have discrete cluster structures.

Here, we reported the hydrothermal synthesis and characterization of a  $\alpha$ -Keggin heteropoly anion-supported nickel-bipyridyl and cobalt-phenanthroline complexes,  $[\text{Ni}(2,2'\text{-phen})_3]_{1.5}[\text{PW}_{12}\text{O}_{40}\text{Ni}(2,2'\text{-bipy})_2(\text{H}_2\text{O})]\cdot 0.5\text{H}_2\text{O}$  **1** and  $[\text{Co}(1,10'\text{-phen})_3]_{1.5}[\text{PMo}_{12}\text{O}_{40}\text{Co}(1,10'\text{-phen})_2(\text{H}_2\text{O})]\cdot 0.5\text{H}_2\text{O}$  **2**. No previous structural examples of transition metal complexes coordinated to Keggin anions have been reported. The structure determination of  $[\text{PW}_{12}\text{O}_{40}\text{Ni}(2,2'\text{-bipy})_2(\text{H}_2\text{O})]^{3-}$  in **1** indicates a novel  $\alpha$ -Keggin heteropolyanion coordinated to a transition metal complex.

Compound **1** was synthesized as black blocks in 34% yield based on W (0.37 g) by a hydrothermal method. A mixture of  $\text{Ni}(\text{OAc})_2$  (0.4 g),  $\text{Na}_2\text{WO}_4$  (1.0 g), 2,2'-bipyridine (0.4 g), and water (10 ml) was neutralized to pH = 4.0 with 50%  $\text{H}_3\text{PO}_3$  and sealed in a 15 cm<sup>3</sup> Teflon-lined reactor, which was heated to 160 °C for seven days. After cooling to room temperature, black block crystals were isolated. The IR spectrum of **1** exhibited an intense band at 950 cm<sup>-1</sup>, attributed to  $\nu(\text{W}=\text{O})$ , and features at 1595, 1475, 1432 and 1309 cm<sup>-1</sup> characteristic of 2,2'-bipyridine, bands at 1060 and 1090 cm<sup>-1</sup>, can be attributed  $\nu(\text{P}-\text{O})$ . Black prism crystals of **2** (0.30 g, yield 30% based on Mo) were obtained under the same reaction conditions using  $\text{CoCl}_2$  (0.4 g),  $\text{Na}_2\text{MoO}_4$  (0.8 g) and 1,10'-phenanthroline (0.4 g). Compound **2** was characterized by elemental analyses<sup>†</sup> and IR spectroscopy, while compound **1** was characterized by elemental analyses IR spectroscopy and single-crystal analyses.<sup>‡</sup> Compounds **1** and **2** were soluble in DMF but not in water.

Crystals of **1** contain  $[\text{PW}^{\text{VI}}_{10}\text{W}^{\text{V}}_2\text{O}_{40}\text{Ni}(2,2'\text{-bipy})_2(\text{H}_2\text{O})]^{3-}$  heteropoly anions and  $[\text{Ni}(2,2'\text{-bipy})_3]^{2+}$  cations. As shown in Fig. 1, the novel anion  $[\text{PW}_{12}\text{O}_{40}\text{Ni}(2,2'\text{-bipy})_2(\text{H}_2\text{O})]^{3-}$  consists of a reduced Keggin heteropolyanion  $[\text{PW}^{\text{VI}}_{10}\text{W}^{\text{V}}_2\text{O}_{40}]^{5-}$  and the cation  $[\text{Ni}(2,2'\text{-bipy})_2(\text{H}_2\text{O})]^{2+}$ . As in other Keggin structures,<sup>1</sup> the reduced polyanion is formed

from twelve  $\text{WO}_6$  octohedra and one  $\text{PO}_4$  tetrahedron. For  $\text{PO}_4$ , the P–O distances are 1.509(5)–1.565(5) Å while the O–P–O angles vary from 108.8(3) to 111.1(3)°. The W–O distances can be grouped into three sets:  $\text{W}-\text{O}_t$  1.677(5)–1.727(5),  $\text{W}-\text{O}_b$  1.780(4)–1.957(5),  $\text{W}-\text{O}_a$ , 2.378(5)–2.467(5), while bond angles at the W atoms range from 70.8(2) to 103.2(3)°. In comparison with other Keggin polyanions,<sup>1</sup> the unusual feature here is that the Keggin structural unit  $[\text{PW}^{\text{VI}}_{10}\text{W}^{\text{V}}_2\text{O}_{40}]^{5-}$  acts as a ligand towards  $\text{Ni}^{2+}$ , to give a novel transition metal anion. A  $\mu$ -oxygen, O(29) links the Keggin unit and Ni(3), the  $[\text{W}(12)-\text{O}(29)$  1.780(4) Å,  $\text{O}(29)-\text{Ni}(3)$  2.010(4) Å,  $\text{Ni}(3)-\text{O}(29)-\text{W}(12)$  160.6(3), the  $\text{W}(12)-\text{O}(29)$  distance is longer than the other  $\text{W}-\text{O}_t$  bond lengths but shorter than  $\text{W}-\text{O}_b$ . In the polyanion, the Ni atom is coordinated by two 2,2'-bipy, one water molecule and one Keggin unit, with  $\text{Ni}-\text{O}(\text{W}(1))$  2.140(6) Å and  $\text{Ni}-\text{N}$  2.072(7)–2.106(6) Å. The coordinated water

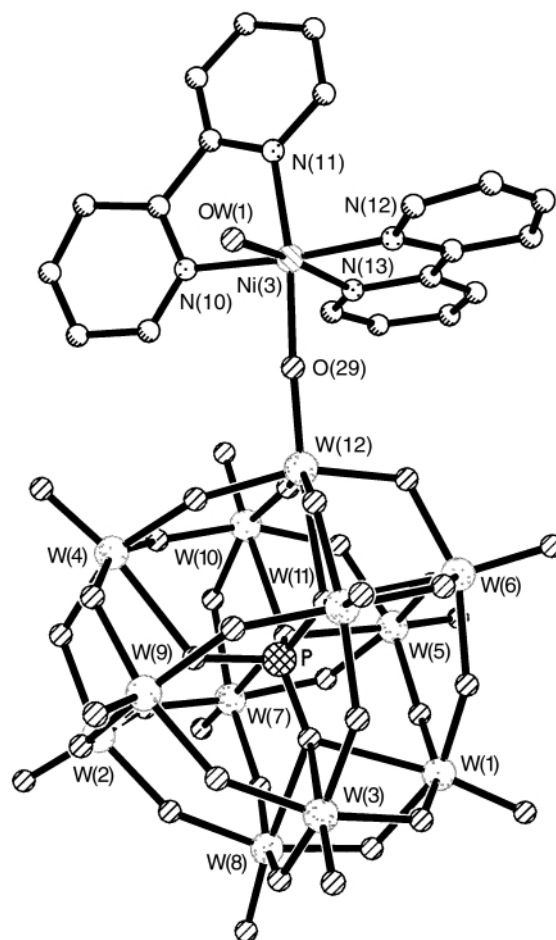


Fig. 1 The structure of the Keggin unit supported transition complex anion  $[\text{PW}^{\text{VI}}_{10}\text{W}^{\text{V}}_2\text{O}_{40}\text{Ni}(2,2'\text{-bipy})_2(\text{H}_2\text{O})]^{3-}$  in **1**.

molecule [OW(2) and its symmetry-related partner] link different polyanions by hydrogen bonding, to form a supramolecular assembly [OW(2)⋯O(17a)(-x,1-y,1-z) 2.768(12) Å]. In each unit of **1**, the water molecules and heteropolyanion are involved in hydrogen bonding interactions, with OW(2)⋯OW(1) and OW(1)⋯O(29) 2.810(11) and 2.934(12) Å, respectively. In the cation [Ni(2,2'-bipy)<sub>3</sub>]<sup>2+</sup> of **1**, Ni is coordinated by three 2,2'-bipy molecules, with Ni–N 1.966(7)–2.102(6) Å. There are two W<sup>V</sup> centres in the Keggin unit of **1**, and the assignment of the oxidation state for the W atoms is consistent with the electric charge and confirmed by bond valence sum calculations. Using an empirical bond valence calculation,<sup>21</sup>  $S = \exp[-(R - 1.898)/0.315]$  ( $S$  = bond valence,  $R$  = bond length), leads to  $S$  values for W(1), W(2), W(3), W(4), W(5), W(6), W(7), W(8), W(9), W(10), W(11) and W(12) of 5.788, 5.950, 5.750, 6.081, 6.04, 5.786, 5.751, 6.060, 5.590, 5.946, 6.070 and 5.577, respectively. The average value for the calculated oxidation state of W is 5.866 (expected value 5.833 for W<sup>VI</sup><sub>10</sub>W<sup>V</sup><sub>2</sub>), consistent with the formula of **1**. Absorption of 600–2000 nm in the reflectance UV–VIS spectrum can be ascribed to d–d transitions and electron transitions between W<sup>V</sup> and W<sup>VI</sup> centres. Only a Ni<sup>2+</sup> signal was observed ( $g = 2.013$ ) in the room temperature EPR spectrum of **1**, the lack of signals for W<sup>V</sup> indicate that the two unpaired electrons of the Keggin unit are delocalised.<sup>1</sup>

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## Notes and references

† Anal. Calc. for W<sub>12</sub>Ni<sub>2.5</sub>PO<sub>41.5</sub>N<sub>13</sub>C<sub>65</sub>H<sub>55</sub> **1**: W, 54.01; Ni, 3.61; P, 0.76; C, 19.18; N, 4.48; H, 1.35. Found: W, 53.74; Ni, 3.42; P, 0.84; C, 19.39; N, 4.52; H, 1.31%. Calc. for Mo<sub>12</sub>Co<sub>2.5</sub>PO<sub>41.5</sub>N<sub>13</sub>C<sub>78</sub>H<sub>55</sub> **2**: Mo, 36.36; Co, 4.65; P, 0.98; C, 29.55; N, 5.75; H, 1.74. Found: Mo, 36.06; Co, 4.56; P, 1.03; C, 29.50; N, 5.69; H, 1.79%.

‡ *Crystal data*: diffraction data for **1** were collected on a crystal with dimensions 0.38 × 0.21 × 0.21 mm using a Siemens P4 diffractometer and Mo-K $\alpha$  radiation, at 193 K. Monoclinic, space group  $C2/c$ ,  $a = 46.768(9)$ ,  $b = 14.340(3)$ ,  $c = 25.945(5)$  Å,  $\beta = 90.21(3)^\circ$ ,  $Z = 8$ ,  $D_c = 3.114$  g cm<sup>-3</sup>. Of 14314 data collected ( $2\theta_{\max} = 23.02^\circ$ ). 12113 were independent ( $R_{\text{int}} =$

3.11%) and 7841 were observed [ $2\sigma(I)$ ]. An empirical absorption correction from  $\psi$ -scans was applied ( $\mu = 16.434$  mm<sup>-1</sup>). All metal, P, O and N atoms were refined anisotropically, while all C atoms were refined isotropically,  $R_1 = 0.0732$ ,  $R_w = 0.1827$  for 891 parameters. CCDC 182/1504. See <http://www.rsc.org/suppdata/cc/a9/a908527k/> for crystallographic files in .cif format.

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