

Novel organic–inorganic hybrid monomeric Keggin-type phosphotungstate containing heterometallic $\{\text{Ni}_6\text{W}\text{Ni}\}$ clusters

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ARTICLE INFO

Article history:

Received 21 November 2014

Received in revised form 25 December 2014

Accepted 2 January 2015

Available online 6 January 2015

Keywords:

Polyoxometalates

Hydrothermal synthesis

Heterometallic

Organic–inorganic hybrid

Nickel

ABSTRACT

A novel octanuclear heterometallic $\{\text{Ni}_6\text{W}\text{Ni}\}$ -substituted Keggin-type phosphotungstate $[\text{Ni}(\text{H}_2\text{O})(\text{en})_2][\text{WO}_4]\{\text{Ni}_6(\text{OH})_3(\text{H}_2\text{O})_2(\text{en})_3(\text{Im})_2\}(\text{B}-\alpha\text{-PW}_9\text{O}_{34})\cdot 2\text{H}_2\text{O}$ (**1**) with mixed organic ligands of en and Im (en = ethylenediamine, Im = Imidazole) has been hydrothermally synthesized and structurally characterized by IR spectra, powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA) and single-crystal X-ray diffraction. Notably, **1** is an interesting spoon-shaped monomeric polyoxometalate consisting of mixed organic ligands and unprecedented octanuclear heterometallic $\{\text{Ni}_6\text{W}\text{Ni}\}$ cores where the WO_4 tetrahedron is linked to the triangular $\{\text{Ni}_6(\text{OH})_3(\text{H}_2\text{O})_2(\text{en})_3(\text{Im})_2\}(\text{B}-\alpha\text{-PW}_9\text{O}_{34})$ clusters and $[\text{Ni}(\text{H}_2\text{O})(\text{en})_2]^{2+}$ cations through Ni–O_t–W linkages. Magnetic susceptibility measurements indicate ferromagnetic coupling within **1**.

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Polyoxometalates (POMs) have attracted considerable interest owing to their intriguing structures and wide potential applications in catalysis, photochemistry, ion exchange, electrochromism, and magnetism [1–4]. With the profound research of POM chemistry and the urgent requirement of science development, in recent years, great attractions are concentrated on the incorporation of transition metal (TM) ions in lacunary Keggin or Dawson polyoxotungstate (POT) fragments forming high-nuclear transition-metal-substituted POMs (TMSPs) with unique magnetic properties [5–7]. Hitherto, compared with the numbers of TM atoms in the diverse TMSPs [6–12], it can be found that the chemistry of Ni-substituted TMSPs has been extensively studied which is owing to that high-nuclear Ni clusters which may possess a large spin ground state and a negative axial anisotropy and may exhibit single-molecule magnetism [6]. Therefore, many groups have devoted great efforts to explore synthetic strategies for making TMSPs with novel high-nuclear Ni clusters [13–16]. Since our group isolated the first triangular inorganic–organic hybrid $\{\text{Ni}_6\}$ cluster core under hydrothermal conditions in 2007 [17,18], then, a series of novel organically covalently functionalized Ni-substituted TMSPs have been exploited continuously by changing various organic ligands [19–21]. Besides, the combinations among various Ni-substituted fragments by kinds of junctions (such as PO_4 , W_4O_{16} , BO_3 unit, and so on) can generate more novel high-nuclear Ni-substituted POMs: such as 7, 8, 9, 11, 12, 18, 20–22, 24 and 40 nickel centers [13–15,22–25]. However, it can be concluded that there are only two examples of W–Ni heterometallic TMSPs incorporating WO_4 tetrahedra: $\{\text{Ni}_{12}(\text{OH})_9\text{WO}_4(\text{W}_7\text{O}_{26}(\text{OH}))(\text{PW}_9\text{O}_{34})_3\}$ made by

Wang et al. in 2009 [14] as well as $\{\text{H}_4\text{Ni}_{40}\text{P}_8\text{W}_{72}(\text{OH})_{18}\text{O}_{272}(\text{en})_{18}(\text{OAc})_2-(\text{WO}_4)_2(\text{H}_2\text{O})_{18}\}$ reported by our group in 2012 [15], which provides us an excellent opportunity and great impetus to explore this domain. Furthermore, it is well-known that some adapted organic ligands play important roles in construction of novel polynuclear Ni-substituted inorganic–organic hybrid TMSPs that bear both features of inorganic and organic components [26,27]. Therefore, following this strategy, we took into consideration that whether novel Ni-substituted TMSPs with unexpected structural models and interesting properties could be isolated under hydrothermal conditions by changing various precursors as well as organic components. Herein, as our continuous work, a novel organic–inorganic hybrid hetero-metallic $\{[\text{Ni}(\text{H}_2\text{O})(\text{en})_2](\text{WO}_4)[\text{Ni}_6(\text{OH})_3(\text{H}_2\text{O})_2(\text{en})_3(\text{Im})_2]\}-\{\text{Ni}_6\text{W}\text{Ni}\}$ substituted POT with mixed organic ligands has been hydrothermally made, i.e. $\{[\text{Ni}(\text{H}_2\text{O})(\text{en})_2](\text{WO}_4)[\text{Ni}_6(\text{OH})_3(\text{H}_2\text{O})_2(\text{en})_3(\text{Im})_2](\text{B}-\alpha\text{-PW}_9\text{O}_{34})\}\cdot 2\text{H}_2\text{O}$ (**1**). As far as we know, **1** is the first example of octanuclear heterometallic cluster $\{\text{Ni}_6\text{W}\text{Ni}\}$ -containing POT and its most interesting feature is the $\{\text{Ni}_6\text{W}\text{Ni}\}$ core incorporating a WO_4 group, in which the triangular $[\text{Ni}_6(\text{OH})_3(\text{H}_2\text{O})_2(\text{en})_3]$ cluster and $[\text{Ni}(\text{H}_2\text{O})(\text{en})_2]^{2+}$ cations are joined by Ni–O–W linkage.

1 was synthesized in a good yield by a mixture of $\text{Na}_9[\text{A}-\alpha\text{-PW}_9\text{O}_{34}]\cdot 7\text{H}_2\text{O}$ (0.284 g, 0.170 mmol), $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (0.204 g, 0.858 mmol), imidazole (0.124 g, 1.821 mmol), en (0.05 mL, 0.740 mmol) and H_2O (5 mL) was stirred for 1 h, sealed in a 25 mL Teflon-lined steel autoclave, kept at 160 °C for 3 days and then cooled to room temperature. Green crystals were collected by filtration, washed with distilled water and dried in air at ambient temperature. Yield: ca. 55.8% (based on $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$). Anal. calcd for $\text{C}_{16}\text{H}_{61}\text{N}_{14}\text{Ni}_7\text{O}_{46}\text{PW}_{10}$ (**1**): C 5.54, H 1.77, N 5.65; Found: C 5.31, H 2.13, N 5.44. In addition,

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compound **1** can also be obtained by a mixture of $K_{12}[H_2P_2W_{12}O_{48}] \cdot 24H_2O$, $Ni(CH_3COO)_2 \cdot 4H_2O$, Im, en and H_2O kept at $120^\circ C$ for 6 days. Notably, although the $[A-\alpha-PW_9O_{34}]^{9-}$ or $[\alpha-H_2P_2W_{12}O_{48}]^{12-}$ polyoxoanions were used as starting materials, the product contains the $[B-\alpha-PW_9O_{34}]^{9-}$ fragments, indicating that the transformation of $[A-\alpha-PW_9O_{34}]^{9-}/[\alpha-H_2P_2W_{12}O_{48}]^{12-} \rightarrow [B-\alpha-PW_9O_{34}]^{9-}$ must have taken place during the course of the reactions. Such transformation phenomena have already been observed in previous studies [19,28]. When we replaced the $Na_9[A-\alpha-PW_9O_{34}] \cdot nH_2O$ by $Na_{10}[A-\alpha-SiW_9O_{34}] \cdot 25H_2O$ or $K_8Na_2[A-\alpha-GeW_9O_{34}] \cdot 25H_2O$, no analogous was harvested but only several hexa-nickel-substituted TMSPs ($[Ni_6(\mu_3-OH)_3(en)_3(H_2O)_6](B-\alpha-SiW_9O_{34})[Ni_{0.5}(en)] \cdot 3.5H_2O$ [18] and $[Ni(en)_2]_{0.5}[Ni_6(OH)_3(en)_3(H_2O)_6](B-\alpha-GeW_9O_{34}) \cdot 3H_2O$ [29]) were isolated. Bond–valence sum calculations [30] indicate that the oxidation states of W, Ni and P elements in **1** are +6, +2 and +5, respectively. The good phase purity of **1** has been characterized by the agreement between experimental PXRD pattern of the bulk product and simulated PXRD pattern from single-crystal X-ray diffraction (Fig. S1). The intensity difference between experimental and simulated XRD patterns is due to the variation in preferred orientation of the powder sample during collection of the experimental PXRD.

Single-crystal X-ray diffraction analysis [31] indicates that **1** crystallizes in the orthorhombic space group $P2_12_12_1$. The molecular structure of compound **1** can be described as a hybrid octanuclear heterometallic $\{Ni_6WNi\}$ cluster modified by en and Im, a trivalent $B-\alpha-PW_9O_{34}(PW_9)$ unit and two lattice water molecules (Fig. 1a). The PW_9 unit derived from the $[A-\alpha-PW_9O_{34}]^{9-}$ anion during the course of reaction is the well-known trivalent Keggin fragment obtained by removing three edge-sharing WO_6 octahedra from the saturated $[\alpha-PW_{12}O_{40}]^{3-}$ polyoxoanion, whereas, the hybrid octanuclear heterometallic $\{Ni_6WNi\}$ cluster capped on the trivalent $[B-\alpha-PW_9]^{9-}$ Keggin anion, which can be considered as a $\{Ni_6\}$ cluster and a $[NiO(H_2O)(en)_2]$ octahedron linked into octanuclear cluster by sharing corners with WO_4 tetrahedron. The $\{Ni_6\}$ cluster is similar to that reported by our group [17], that is, the six Ni^{II} cations located in octahedral geometry are arranged in an equilateral triangle with three ($Ni1/Ni3/Ni5$) on the vertex of the triangle and the remaining ($Ni2/Ni4/Ni6$) in the middle of the edge (Fig. 1b). In **1**, Ni_6 core is comprising of six coplanar Ni^{2+} ions with a triangle motif linked together by three hydroxyls (O36, O39 and O40) and further stabilized by six μ_3-O (O16, O19, O22, O25, O28 and O30) bridges from the lacunae of the $B-\alpha-PW_9$ moiety and one μ_4-O (O37) bridge from the central PO_4 unit (Fig. S2). It is also understood that the Ni_6 core can be viewed as a combination of three truncated cubanes of $\{Ni_3O_3(OH)\}$ via sharing one edge with each other with the aid of a vertex-sharing μ_4-O37 atom from PO_4 group, forming a flat triangle configuration with three μ_3-OH groups on one side. However, there are differences between **1** and the reported clusters [17]. Each vertical Ni^{II} cation remains three active coordination sites in three directions, which can be occupied by organic en ligands or water molecules or WO_4 groups; while the remaining Ni^{II} cations only have one active

coordination site, which can be occupied by organic Im ligands or WO_4 groups. This implies that the flexible ligand en bonds to $Ni(II)$ more easily than the rigid ligand Im, and en as a primary ligand may decrease the activity of Im to further substitute the terminal water in this system. To our best knowledge, such a $\{Ni_6WNi\}$ cluster core containing mixed ligands of en and Im has not been reported so far in TMSPs field. Furthermore, it is well-known that three μ_3-OH groups on the flat arrangement of the $\{Ni_6WNi\}$ core can be substituted by organic ligands, hence, the compound provides new potential binding sites and may derive a series of fascinating organic–inorganic hybrid POMs.

It can be found that the most striking structural feature of the heterometallic $\{Ni_6WNi\}$ cluster is incorporating a WO_4 tetrahedron. It is well known that the most common coordination for W^{6+} is octahedral as realized in POMs field, W^{6+} rarely occurs in tetrahedral coordination, whereas in compound **1**, the W–O bond lengths in the WO_4 tetrahedron range from 1.748(10) to 1.789(8) Å and are in agreement with the other WO_4 -containing POMs [14,15]. Analogous Ni-substituted Keggin-type POT derivatives $[Ni_{12}(OH)_9WO_4(W_7O_{26}(OH))(PW_9O_{34})_3]^{25-}$ (A) [14] and $[H_4Ni_{40}P_8W_{72}(OH)_{18}O_{272}(en)_{18}(OAc)_2(WO_4)_2(H_2O)_{18}]^{12-}$ (B) [15] have been isolated by Wang and us, respectively. By comparing **1** with them, it can be found that the role of the WO_4 groups is different (Fig. S3), which can be concluded as: 1) In A, four O atoms of the WO_4 group link to the Ni_{12} unit via three $\mu-O$ of three Ni_4 cores and a μ_4-O atom shared by one W and three Ni_4 cores, resulting in a unique three-petal flower-shaped Ni_{12} -based trimer; 2) In B, four O atoms of the WO_4 unit connect two adjacent Ni_6 clusters via four $\mu-O$ atoms lead to dimer $\{WNi_{12}\}$ then further to centric rod-shaped Ni_{40} -based octamer with the aid of $\{Ni_4(H_2O)_2(PW_9)_2\}$ and $\{Ni_6PW_9-(OAc)(H_2O)\}$ SBUs; 3) In compound **1**, three O atoms of the WO_4 unit connect the triangular Ni_6 clusters and $[Ni(H_2O)(en)_2]^{2+}$ cations via three $\mu-O$ atoms, so an interesting spoon-shaped Ni_7 -based monomer is formed. Here, the W atom acts as an inorganic bridge and plays a crucial role in the formation of **1**, and such a linking mode is first observed in TM-substituted poly(POM) chemistry.

The ability of lacunary polyoxoanions to incorporate magnetic TM clusters between nonmagnetic POM fragments makes them especially valuable for the quantification of magnetic interactions [32]. The magnetic behavior of **1** is studied in the range of 2 to 300 K and the plots of $\chi_m T$, χ_m^{-1} versus T are shown in Figs. 2 and 3. At 300 K, the $\chi_m T$ value is equal to $8.42 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ for **1**, which is in good agreement with the normal range ($6.79\text{--}9.10 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$) for seven high-spin Ni^{2+} ions in the absence of exchange coupling. Upon cooling, the $\chi_m T$ value gradually increases to a maximum of $23.10 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ at 10 K. This magnetic behavior typifies the ferromagnetic coupling interactions between adjacent Ni^{II} centers. A sudden decrease of $\chi_m T$ value below 10 K suggests the presence of the significant zero-field splitting (ZFS) effects in the ground state [33]. At the outset, when we neglect the small differences in the $Ni \dots Ni$ distances and $Ni-O-Ni$ angles of the Ni_6 core as well as the additional Im and en ligands with a slightly

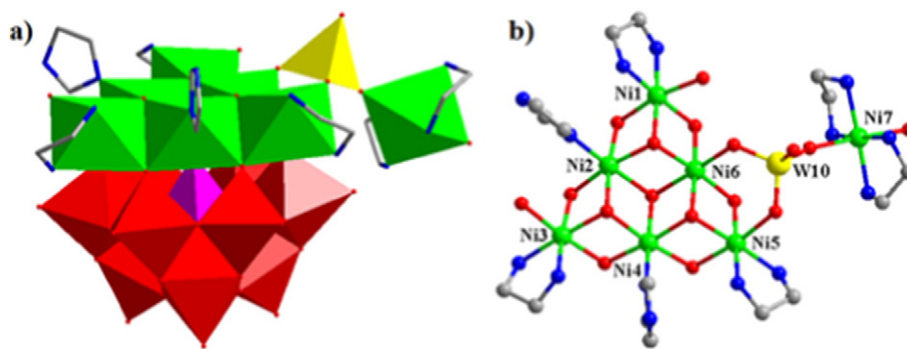


Fig. 1. (a) Combined polyhedral wires-or-sticks representation of **1**; (b) The atom-labeling scheme of $\{Ni_6WNi\}$ cluster in **1**. H atoms and lattice water molecules are omitted for clarity. Color codes: $\{WO_6\}$ octahedra, red; $\{PO_4\}$ tetrahedra, purple; $\{WO_4\}$ tetrahedra, yellow. $\{NiO_6\}$, $\{NiO_4N_2\}$, $\{NiO_2N_4\}$ octahedra, and nickel, green; oxygen, red; nitrogen, blue and carbon, gray.

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