

Short communication

Structure and magnetic property of a cubane-type Ni-substituted polyoxotungstate based on trivalent Dawson-type unit



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ABSTRACT

A novel cubane-type Ni-substituted polyoxotungstate based on trivalent Dawson-type $[P_2W_{15}O_{56}]^{12-}$ unit with the formula of $Na_4H_4[P_2W_{15}O_{56}(W_{0.5}Ni_{3.5})(OH)_6(H_2O)_3] \cdot 18.5H_2O$ (**1**) has been synthesized in aqueous medium and characterized by IR spectroscopy, EDX spectrum, thermogravimetric analysis and magnetic measurements. Structural analysis indicates that **1** consists of a trivalent Dawson-type unit $[P_2W_{15}O_{56}]^{12-}$ incorporated in a cubane-type $\{Ni_{3.5}W_{0.5}O_7(OH)_6(H_2O)_3\}$ group. Magnetic studies show that the ferromagnetic Ni–Ni exchange interactions exist in the cubane-type cluster.

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Since the pioneering work of sandwich-type polyoxometalate (POM) $[Co_4(H_2O)_2(B-\alpha-PW_9O_{34})_2]^{10-}$ was discovered in 1973 [1], the explosion in the number of publications concerning transition metal substituted polyoxometalates (TMSPs) over the last decades has largely arisen thanks to their potential applications in catalysis, magnetism, photochemistry and medicine [2–5]. To date, many groups have devoted themselves to encapsulating d-electron transition metals into lacunary POMs (such as $[\gamma-XW_{10}O_{36}]^{8-}$, $[A-\alpha-XW_9O_{34}]^{9/10-}$ ($XP^V/Si^{IV}/Ge^{IV}$)) for making novel TMSPs. Therefore, a large quantity of TMSPs containing polynuclear TM clusters have been frequently synthesized with unique structures and interesting magnetic properties [6–9]. In this field, Ni-substituted polyoxotungstates (POTs) are well-known and extensively investigated. In 1994, Coronado reported the first sandwich-type Ni-substituted POT $[Ni_4(H_2O)_2-(P_2W_{15}O_{56})_2]^{16-}$ [10]. In 1999, Coronado obtained three different nickel clusters encapsulated in trivalent Keggin fragments, $[Ni_3(H_2O)_3(PW_{10}O_{39})H_2O]^{7-}$, $[Ni_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$ [11]. The same year, Kortz also reported a cubane-type Ni-substituted POT $[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]^{2-}$ based on trivalent Keggin polyanion $B-\alpha-[PW_9O_{34}]^{9-}$ [12]. Since then, lots of sandwiched Ni-substituted POTs containing di-, tri-, hexa-, hepta-, octa- and nonanuclear nickel ions were ceaselessly reported [13–21], such as $[Ni_3Na(H_2O)_2(PW_9O_{34})_2]^{11-}$ [14], $[\{Ni_6(H_2O)_4(\mu_2-H_2O)_4(\mu_3-OH)_2\}(x-SiW_9O_{34})_2]^{10-}$ [19]. Additionally, many other Ni-substituted POTs that are not proverbial sandwich type have been also continuously addressed [22–28], in which some impressive examples like the $[Ni_6(OH)_3(H_2O)_6(L)_3(B-\alpha-XW_9O_{34})]$ ($X = P, Si, Ge; L = en \text{ or } dap$) [22,23]; $[Ni(H_2O)(en)_2][WO_4]$ $[\{Ni_6(OH)_3(H_2O)_2(en)_3(Im)_2(B-\alpha-PW_9O_{34})\}]$ [24]; $[Ni_{12}(OH)_9WO_4(W_7O_{26}(OH))(PW_9O_{34})_3]^{25-}$ [25];

$[H_4Ni_{40}P_8W_{72}(OH)_{18}O_{272}(en)_{18}(OAc)_2(WO_4)_2(H_2O)_{18}]^{12-}$ [28] display unique structures and interesting magnetic behaviors. However, it is worthy to point out that these above-mentioned compounds with different structures are almost based on lacunary Keggin-type precursors, especially trivalent Keggin-type polyanions. In contrast, the investigations on Ni-containing trivalent Dawson-based POTs can only be enumerated sporadically apart from those classical sandwich structures [29–32] mainly because of the following reasons: 1) For one thing, when extending the reaction systems from trivalent Keggin to trivalent Dawson POTs, only two precursors $[X_2W_{15}O_{56}]^{12-}$ ($X = P, As$) can be invoked, which is far fewer than the number of trivalent Keggin precursors, namely $[XW_9O_{33/34}]^{9-}$ ($X = P, As, Si, Ge, Sb, Bi, Se, \text{ etc.}$); 2) On the other hand, trivalent Dawson-type precursor was proven to be metastable in the solution and easily can be transformed (usually undergoing $[a-P_2W_{15}O_{56}]^{12-} \rightarrow [a_2-P_2W_{17}O_{61}]^{10-}/[\alpha-PW_9O_{34}]^{9-}/[a-PW_{11}O_{39}]^{7-}$) during the various reaction conditions [33–35]. Therefore, it is a challenging topic that provokes our keen interest to keep the skeleton of trivalent Dawson precursor when constructing novel TMSPs. Herein, we report on the subtle synthesis of a novel Ni-containing POT based on trivalent Dawson unit $Na_4H_4[P_2W_{15}O_{56}(W_{0.5}Ni_{3.5})(OH)_6(H_2O)_3] \cdot 18.5H_2O$ (**1**), as well as its magnetic property. In this compound, the cubane-type unit $\{Ni_{3.5}W_{0.5}O_7(OH)_6(H_2O)_3\}$ (denoted $\{Ni_{3.5}W_{0.5}\}$) caps on the top of $[P_2W_{15}]$ to generate a new Ni-substituted TMSPs. To the best of our knowledge, this is a rare pure inorganic example of a cubane-type fragment, which is bound on an isolated trivalent Dawson-type polyanion.

Compound **1** has been synthesized directly by reaction of Ni^{2+} ions with the trivalent precursor $Na_{12}[P_2W_{15}O_{56}] \cdot 24H_2O$ in the routine conditions (see the Supporting Information). Single crystal X-ray diffraction indicates [36] that the polyanion $[P_2W_{15}O_{56}(W_{0.5}Ni_{3.5})(OH)_6(H_2O)_3]^{8-}$ (**1a**) consists of a trivalent Dawson-type unit $[P_2W_{15}O_{56}]^{12-}$ incorporated in a distorted cubane-type $\{Ni_{3.5}W_{0.5}\}$ group (Fig. 1a), which

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resembles those of previously reported cubane-type Keggin-type fragments $[\text{Ni}_3(\text{H}_2\text{O})_3(\text{PW}_{10}\text{O}_{39})\text{H}_2\text{O}]^{7-}$ and $[\text{H}_2\text{PW}_9\text{Ni}_4\text{O}_{34}(\text{OH})_3(\text{H}_2\text{O})_6]^{2-}$ where $\{\text{Ni}_3\text{W}\}$ or $\{\text{Ni}_4\}$ unit caps the trivacant Keggin-type precursor [11,12] (Fig. S1). As illustrated in Fig. 1, it is interesting to notice that the $\{\text{Ni}_3\text{W}_{0.5}\}$ unit exhibits a unique structure only found for nickel ions. A $\{\text{Ni}_3\text{O}_{13}\}$ core is constructed by three edge-sharing NiO_6 octahedra, on which a $\text{Ni}/\text{W}(\text{OH})_6$ octahedron capped via three protonated μ_3 -bridging oxygen atoms (O4, O5, O6) (Fig. 1b). In the structure of the $\{\text{Ni}_3\text{O}_{13}\}$ cluster, three crystallographically unique Ni^{2+} cations all display distorted octahedral geometries. Each Ni atom is defined by three oxygen atoms from $[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ fragment, two protonated bridging oxygen atoms and one terminal water ligand. The above mentioned protonation is well-inferred from bond valence sum (BVS) calculations (Table S2). More interestingly, the $\{\text{Ni}_3\text{O}_{13}\}$ group is perfectly inserted into the lacuna of the trivacant Dawson-type unit $[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$. Such a reconstitution structure is completely like the monomeric species $[\text{Fe}^{\text{III}}_3(\text{H}_2\text{O})_3\text{P}_2\text{W}_{15}\text{O}_{62}]^{9-}$ [37] except that the **1a** contains an additional cap of nickel/tungsten to stabilize the Dawson-type $\{\text{Ni}_3\text{P}_2\text{W}_{15}\text{O}_{62}\}$ unit. Hence, the structure of **1a** can also be described as a reconstituted Dawson-type $\{\text{Ni}_3\text{P}_2\text{W}_{15}\}$ fragment capped by a disordered $\text{W}/\text{Ni}(\text{OH})_6$ octahedron. Finally, all the polyanions are well charge-balanced by the Na^+ cations and H^+ , meanwhile, these polyanions can further form a 2D layer-like framework with the help of Na^+ ions along the ac plane (Fig. S2).

In the IR spectrum of **1** (Fig. 2), there are four characteristic vibration bands in the range of $1100\text{--}700\text{ cm}^{-1}$ resulting from the trivacant Dawson-type skeleton, namely, $\nu_{\text{as}}(\text{P--O}_a)$, $\nu_{\text{as}}(\text{WO}_t)$, $\nu_{\text{as}}(\text{W--O}_b)$ and $\nu_{\text{as}}(\text{W--O}_c)$. In comparison with the spectrum of trivacant $[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$ precursor [38], the most remarkable difference is that one peak of the $\nu_{\text{as}}(\text{P--O}_a)$ about at 1130 cm^{-1} disappeared, the possible reason is that the symmetry of **1** increases due to the insertion of the $\{\text{Ni}_3\text{O}_{13}\}$ group resulting in the plenary Dawson skeleton. At the same time, it can also be observed that the vibration bands of $\text{W--O}_{b/c}$ have different red-shifts, the possible major reasons for which may be that the $\{\text{Ni}_3\text{O}_{13}\}$ cluster has stronger interactions to oxygen atoms of trivacant precursor, reducing the $\text{W--O}_{b/c}$ bond force constant, and leading to decreasing of their vibration frequency.

The thermal stability of compound **1** was determined under the nitrogen atmosphere by thermogravimetric analysis (TGA) between 25 and $700\text{ }^\circ\text{C}$ (Fig. 3). TGA shows a total weight loss of 11.71%, corresponding to the removal of 18.5 lattice water molecules and 3 coordinated water molecules, together with the dehydration of 4 protons and 6 hydroxyl groups (calcd 11.55%).

Magnetic susceptibility of **1** was measured at 1000 Oe and from 2.0 to 300 K on a polycrystalline sample. As shown in Fig. 4, the χ_{MT} value at room temperature is $3.60\text{ emu}\cdot\text{mol}^{-1}\cdot\text{K}$, which is very close to the expected value for 3.5 uncoupled $\text{Ni}(\text{II})$ centers ($C = 1.00\text{ emu}\cdot\text{mol}^{-1}\cdot\text{K}$,

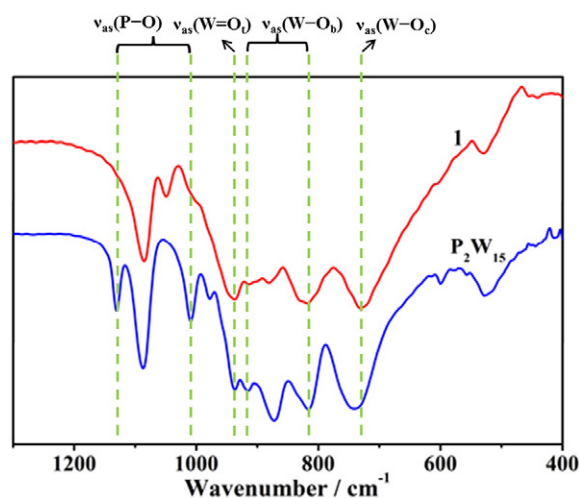


Fig. 2. IR spectra of **1** and the trivacant precursor $[\alpha\text{-P}_2\text{W}_{15}\text{O}_{56}]^{12-}$.

$S = 1$, $g = 2.0$ for each Ni^{2+} ion), thus, to some degree, provides structural evidence supporting the exact quantity of the Ni centers obtained from X-ray diffraction analysis. Subsequently, χ_{MT} shows an increase as the temperature is decreased and reaches a maximum of $5.55\text{ emu}\cdot\text{mol}^{-1}\cdot\text{K}$ at 13.8 K. Finally, χ_{MT} quickly drops to the $4.70\text{ emu}\cdot\text{mol}^{-1}\cdot\text{K}$ at 1.8 K probably attributed to the presence of zero-field splitting and intercluster magnetic interactions. Such behavior indicates that intramolecular ferromagnetic interactions are predominant between Ni(II) centers in this compound. Moreover, the experimental data have been well fitted by the Curie-Weiss law above 25 K with the following Curie and Weiss constants: $C = 3.44\text{ emu}\cdot\text{mol}^{-1}\cdot\text{K}$ and $\theta = 7.14\text{ K}$. The positive Weiss constant validates again the presence of dominating ferromagnetic interactions between Ni cores. In fact, such ferromagnetic couplings are prevalent for the Ni-containing TMSPs. Moreover, it is well known that Ni–Ni ferromagnetic exchange pathways are dominant when the scale of Ni–O–Ni angles are in the range of $(90 \pm 14)^\circ$ [10–12,29,39]. Examining the reported structures, the monomeric polyanions, $[\text{Ni}_3(\text{H}_2\text{O})_3\text{PW}_{10}\text{O}_{39}\text{H}_2\text{O}]^{7-}$ [11] and $[\text{H}_2\text{PW}_9\text{Ni}_4\text{O}_{34}(\text{OH})_3(\text{H}_2\text{O})_6]^{2-}$ [12] are structurally the ones most similar to **1**, it is not hard to find the occurrence of the ferromagnetic exchange interactions since the Ni–O–Ni angles are approximately between 90° and 100° in both cases, which are all located in the defined range as is mentioned above. Likewise, the case that the angles of Ni–O–Ni ranging from 92.6° to 103.2° in **1** (Table S3) also shows that the ferromagnetic coupling is “to be expected”. As for the investigation of the magnetization

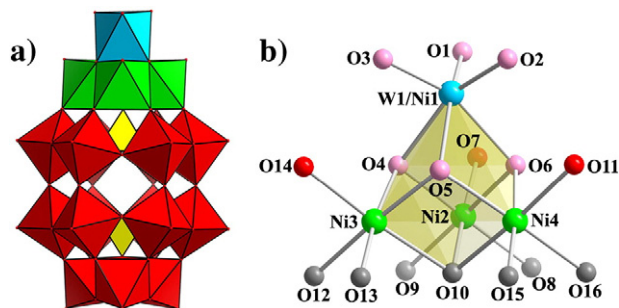


Fig. 1. a) The structure of **1a** (color code: red octahedra, WO_6 ; green octahedra, NiO_6 ; blue octahedron, disordered W/NiO_6 ; yellow tetrahedra, PO_4); b) Ball-and-stick representation of the cubane-type $\{\text{Ni}_3\text{W}_{0.5}\}$ unit in **1a** with BVS assignments (color code: red balls, water molecules; pink balls, monoprotonated O atoms; grey balls, non-protonated O atoms).

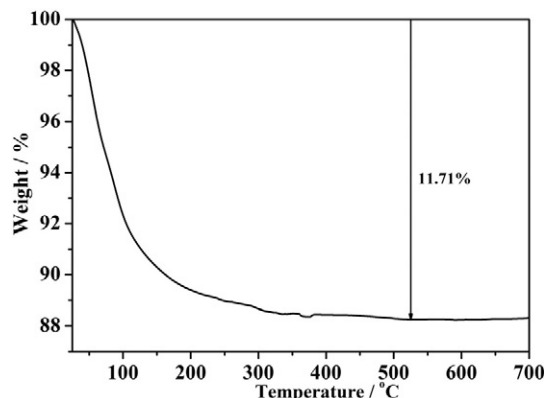


Fig. 3. TGA curve of compound **1**.

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