

Supporting Information

Hexa-substituted polyoxometalates made of trivacant Dawson {P₂W₁₅} fragments and {Ni₆} clusters under hydrothermal conditions

Yong-Chao Liu,^a Chun-Hua Fu,^a Shou-Tian Zheng,^a Jun-Wei Zhao,^{b,*} and Guo-Yu Yang^{a,*}

^a State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China; Fax: (+86)591-8371-0051, E-mail: ygy@fjirsm.ac.cn

^b Henan Key Laboratory of Polyoxometalate Chemistry, College of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475004, P. R. China; E-mail: zhaojunwei@henu.edu.cn

Experimental section:

All chemicals employed in this study were analytical reagent. Elemental analyses of C, H and N were carried out with a Vario EL III elemental analyzer. Inductively coupled plasma atomic emission spectrometry (ICP–AES) was performed on a Perkin–Elmer Optima 2000 ICP–AES spectrometer. IR spectra (KBr pellets) were recorded on an ABB Bomen MB 102 spectrometer. Thermal analyses were performed in a dynamic oxygen atmosphere with a heating rate of 10°C/min, using a METTLER TGA/SDTA851^e thermal analyzer. Variable temperature susceptibility measurements were carried out in the temperature range 2–300 K at a magnetic field of 0.5 T for **3** on polycrystalline samples with a Quantum Design PPMS-9T magnetometer. The experimental susceptibilities were corrected for the Pascal's constants.

Syntheses of compounds **1**, **2** and **3**:

Na₁₂[α -P₂W₁₅O₅₆]·24H₂O (P₂W₁₅) and K₁₂[α -H₂P₂W₁₂O₄₈]·24H₂O (P₂W₁₂) were prepared by a literature method.¹ NiCl₂·6H₂O (0.473 g), P₂W₁₅ (0.449 g) and NaCl (1.151 g) were stirred in H₂O (5 mL) for 4 h. Then, 2,2'-bpy (0.061 g) was added and stirred for 30 min. The resulting mixture was sealed in a 30-mL stainless steel autoclave with a teflon liner and heated at 120°C for 8 days, and then cooled to room temperature, upon which green prismatic crystals of **1** were obtained. Yield 15% (based on P₂W₁₅). P₂W₁₂ (0.788 g) and Ni(CH₃COO)₂·4H₂O (0.498 g) were stirred in H₂O (10 mL). Then, 0.10 mL dien for **2** (or 0.10 mL en for **3**) was added dropwise and stirred for 100 min. The resulting mixture was sealed in a 30-mL stainless steel autoclave with a teflon liner and heated at 150°C for 8 days, and then cooled to room temperature, upon which green prismatic crystals of **2** (or **3**) were obtained. Yield: 18% for **2** (or 25% for **3**) (based on P₂W₁₂). Elemental analysis calcd (%) for C₂₀H₁₂₈N₄Ni₁₄O₁₇₀P₄W₃₀ (**1**): C 2.50, H 1.34, N 0.58, P 1.29, Ni 8.55, W 57.41; found: C 2.91, H 1.28, N 0.63, P 1.37, Ni 8.38, W 57.59; For C₁₂H₆₀N₉Ni₆O_{66.5}P₂W₁₅ (**2**): C 3.16, H 1.32, N 2.76, P 1.36, Ni 7.71, W 60.39; found: C 2.97, H 1.64, N 2.97, P 1.28, Ni 7.87, W 60.52. For C₁₀H₆₇N₁₀Ni₇O_{70.5}P₂W₁₅ **3**: C 2.56, H 1.44, N 2.99, P 1.32, Ni 8.77, W 58.85; Found: C 2.66, H 1.44, N 2.49, P 1.46, Ni 8.54, W 58.88.

¹ A. P. Ginsberg, *Inorganic Syntheses*, **1990**, 27, 104–111. Wiley, New York.

Crystal data for **1:** $M_r = 9606.58$, triclinic, space group $P\bar{1}$, $a = 12.853(4)$ Å, $b = 14.550(5)$ Å, $c = 22.905(8)$ Å, $\alpha = 86.152(13)^\circ$, $\beta = 82.553(13)^\circ$, $\gamma = 64.101(8)^\circ$, $V = 3821(2)$ Å³, $Z = 1$, $\rho = 4.175$ g·cm⁻³, $\mu = 24.329$ mm⁻¹, $F(000) = 4308$, GOF = 1.031. A total of 23662 reflections were collected and 12976 of which were unique ($R_{\text{int}} = 0.0625$). $R_1/wR_2 = 0.0548/0.1321$ for 9496 reflections ($I > 2\sigma(I)$) and 1065 parameters. **Crystal data for **2**:** $M_r = 4566.64$, monoclinic, $P2_1/c$, $a = 14.850(5)$ Å, $b = 17.906(6)$ Å, $c = 28.881(10)$ Å, $\beta = 95.649(5)^\circ$, $V = 7642(5)$ Å³, $Z = 4$, $\rho = 3.969$ g·cm⁻³, $\mu = 24.064$ mm⁻¹, $F(000) = 8140$, GOF = 1.074. A total of 46664 reflections were collected and 13405 are unique ($R_{\text{int}} = 0.1095$). $R_1/wR_2 = 0.0844/0.2030$ for 9001 reflections ($I > 2\sigma(I)$) and 923 parameters. **Crystal data for **3**:** $M_r =$

4686.40, monoclinic, $P2_1/c$, $a = 14.221(7)$ Å, $b = 18.116(10)$ Å, $c = 28.841(15)$ Å, $\beta = 86.547(11)^\circ$, $V = 7417(7)$ Å³, $Z = 4$, $\rho = 4.197$ g·cm⁻³, $\mu = 25.049$ mm⁻¹, $F(000) = 8388$, GOF = 1.068. A total of 44381 reflections were collected and 12782 are unique ($R_{\text{int}} = 0.0708$). $R_1/wR_2 = 0.0669/0.1715$ for 10237 reflections ($I > 2\sigma(I)$) and 971 parameters.

The intensity data were collected on a Mercury CCD diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at room temperature. The program SADABS was used for the absorption correction. The structures **1-3** were solved by direct methods and refined by full-matrix least squares on F^2 with the SHELXTL-97 program package. All non-H atoms (except C3, OW10, OW11, OW12 and OW13 in **1**, C1–C3, C5–C12, OW1, OW2 in **2**, and C2, C7–C10, N7–N10, C2, O44, OW5, disordered O26/O26', O27/O27' and O28/O28' in **3**) were refined anisotropically. Due to the large structures of **1-3** and the existence of a large amount of weight atoms, their intensity data are not very good, leading to the ADP max/min ratio of some atoms, and it is very difficult to refine these large structures, therefore, some unit-occupancy atoms have been refined isotropically and restrainedly refined. For **1**: the ISOR instruction is used for O6, O42, O2, O24, O34, O4, O3, O57, C6, O7W, C2, C8, O38, O39, O56, O47, O16, O59, O58, O48, O21, N2, C4, O37, O40 and O46; the DFIX instruction is used for C2 and C3, C10 and N2; the DELU instruction is used for C2 and C3, C8 and C9, C7 and C8, C6 and C7, C5 and C6, P2 and O46; C3, OW10, OW11, OW12 and OW13 are refined isotropically. Now, 163 restraints are used in the refinement. For **2**: the ISOR instruction is used for O42, O49, N5, O15, O52, N1, C4, O32, O44, N2, O41, O21, O16 and O14; the DELU instruction is used for N3 and C4; the DFIX instruction is used for C7 and C8, C11 and C12, C1 and C2, C3 and C4, N9 and C12, C11 and N7, N7 and C10, C2 and N2, C7 and N6, C8 and N4, C9 and N8, C1 and N1; C1-C3, C5-C12, OW1 and OW2 are refined isotropically. Now, 97 restraints are used in the refinement. For **3**: the ISOR instruction is used for C1, C4, C6, C6', O42, O56, OW7, O48, OW4, O65, O12, O45, O51, O53 and O39; the DFIX instruction is used for Ni7 and N7, Ni7 and N8, Ni7 and N9, Ni7 and N10, Ni7 and C9, Ni7 and C10, C7 and N7, C2 and N2, C5 and N5, C6 and N6, C8 and N8, C9 and N9, C10 and N10, C7 and C8, C5 and C6, C9 and C10, Ni7 and C7, Ni7 and C8, C1 and C2, C3 and C4; the DELU instruction is used for C1 and C2, N2 and C2; C7-C10, N7-N10, OW5, O26, O27, O28, O44 and C2 are refined isotropically. C6, O26, O27 and O28 are disordered over two positions. Now, 110 restraints are used in the refinement. The main reasons of Solvent Accessible VOIDS in **2** and **3** are as follows: It is well known that the packing of the large molecules often result in the occurrence of a large number of pores or channels in the solid-state structures, which is related to the fact that it is rather difficult for large molecules to adopt the most close arrangement when they form the crystals. This phenomenon has been also observed in cobalt, manganese, nickel and vanadium derivatives of the cyclic 48-tungsto-8-phosphate [H₇P₈W₄₈O₁₈₄]³³⁻ (see U. Kortz, et al. *Inorg. Chem.*, 2010, **49**, 4949), [H₂bpy][Cu(4,4'-bpy)]₂[HPCuMo₁₁O₃₉] (see E. B. Wang, et al. *Cryst. Growth Des.*, 2005, **5**, 257) and [Mn(H₂O)₂{Mn₃(B-β-GeW₉O₃₃(OH))(B-β-GeW₈O₃₀(OH))}₂]²²⁻ (see U. Kortz, et al. *Inorg. Chem.*, 2009, **48**, 5884). CCDC-926539 (**1**), 926540 (**2**) and 926541 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Furthermore, for structure **2**, SQUEEZE method was used to show the structure contains voids located at $x = 0.500$, $y = 0.603$, $z = 0.250$ and $x = 0.500$, $y = 0.891$, $z = 0.750$ (~813.0 Å³). These voids might be suitable to take up solvent (crystals from dien/H₂O), but none was seen in difference Fourier syntheses and squeezing with program PLATON did not give significant improvement or change. Based on the count of void electrons obtained from SQUEEZE result, these voids can accommodate about four disordered dien molecules or 21 disordered water molecules.

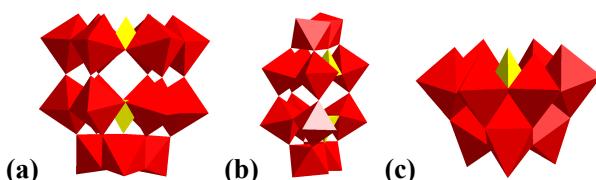


Fig. S1 The structural units of the α -P₂W₁₅ (a), α -P₂W₁₂ (b), and B- α -XW₉ (X = P, Si, Ge) (c) fragments.

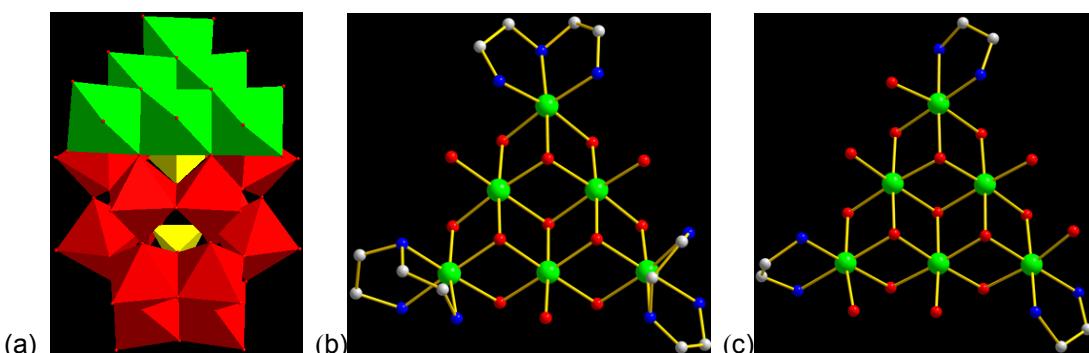


Fig. S2 (a) The polyhedral view of the $[Ni_6(\mu_3-OH)_3(H_2O)_{11}H_2(P_2W_{15}O_{56})]$ cluster unit in **1**. Color codes: NiO₆, green; WO₆, red; PO₄, yellow. (b) Ball-and-stick representation of the $[Ni_6(\mu_3-OH)_3O_7(dien)_3(H_2O)_3]$ cluster in **2**. (c) Ball- and-stick representation of the $[Ni_6(\mu_3-OH)_3O_7(en)_3(H_2O)_6]$ cluster in **3**. Color codes: Ni, green; O, red; Ni, blue and C, gray.

By examining the structure of the Ni₆ core, find that it is similar to those induced by B- α -XW₉, Keggin unit of Ni₆XW₉, reported in our group.¹ Why can the similar Ni₆ core be induced by different types of fragments? This is because that both Keggin B- α -XW₉ and Dawson P₂W₁₅ units have the same tri-vacant sites (Fig. S1a,c) with seven available O atoms, six from six W centers and one from the X/P center, which act as a heptadentate ligand to chelate to the in-situ formed Ni₆ core and further enhance the stability of the resulting products of Ni₆XW₉ and Ni₆P₂W₁₅. Generally, the α -XW₉ unit has relative high stability in diverse lacunary fragments. To two different types of A- and B- α -XW₉, the latter is more stable than the former, which has further been confirmed by the isomerization of A- α -XW₉ \rightarrow B- α -XW₉ during the course of the reactions, though the A- α -XW₉ precursor was used as starting materials.^{1,2} The rational reason is that the A- α -XW₉ has six exposed surface O atoms at its trivacant site, while the B- α -XW₉ has seven such O atoms at its tri-vacant site, which results in that the B- α -XW₉ as heptadentate ligand can more enhance the stability of the products than the A- α -XW₉ as hexadentate ligand when they chelated to the TM clusters formed in-situ. So far, the transformations from P₂W₁₂/P₂W₁₅ fragments to B- α -PW₉ by the rearrangement or degradation have been observed.³ Though the stability of the P₂W₁₅/P₂W₁₂ fragments is lower than that of the B- α -XW₉ unit in the reactions, the Ni₆-substituted **1-3** constructed from P₂W₁₅ fragments have still been obtained by carefully exploring hydrothermal reaction conditions.

1 (a) S.-T. Zheng, D.-Q. Yuan, H.-P. Jia, J. Zhang and G.-Y. Yang, *Chem. Commun.*, **2007**, 1858-1860; (b) S.-T. Zheng, D.-Q. Yuan, J. Zhang and G.-Y. Yang, *Inorg. Chem.*, **2007**, *46*, 4569-4574; (c) J.-W. Zhao, J. Zhang, S.-T. Zheng and G.-Y. Yang, *Chem. Eur. J.*, **2007**, *13*, 10030-10045; (d) J.-W. Zhao, J. Zhang, S.-T. Zheng and G.-Y. Yang, *Inorg. Chem.*, **2007**, *46*, 10944-10946; (e) J.-W. Zhao, J. Zhang, S.-T. Zheng and G.-Y. Yang, *Chem. Commun.*, **2008**, 570-572; (f) S.-T. Zheng, J. Zhang and G.-Y. Yang, *Angew. Chem. Int. Ed.*, **2008**, *47*, 3909-3913; (g) J.-W. Zhao, C.-M. Wang, J. Zhang, S.-T. Zheng and G.-Y. Yang, *Chem. Eur. J.*, **2008**, *14*, 9223-9239; (h) S.-T. Zheng, J. Zhang, J. M. Clemente-Juan, D.-Q. Yuan and G.-Y. Yang, *Angew. Chem. Int. Ed.*, **2009**, *48*, 7176-7179; (i) B. Li, J.-W. Zhao, S.-T. Zheng and G.-Y. Yang, *Inorg. Chem.*, **2009**, *48*, 8294-8303.

2 U. Kortz, L. M. Mbomekalle, B. Keita, L. Nadjo and P. Berthet, *Inorg. Chem.*, **2002**, *41*, 6412.

3 (a) Z. Zhang, J. Liu, E. Wang, C. Qin, Y. Li, Y. Qi and X. Wang, *Dalton Trans.*, **2008**, 463-467; (b) C.-H. Fu, S.-T. Zheng and G.-Y. Yang, *Chin. J. Struct. Chem.*, **2008**, *27*, 943-948.

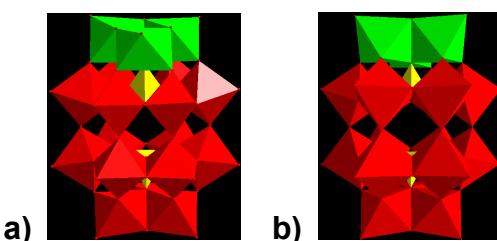


Fig. S3. a) The β - $\text{Ni}_3\text{P}_2\text{W}_{15}$ (b) and the α - $\text{M}_3\text{P}_2\text{W}_{15}$ cluster, corresponding to the β - and α - $\text{P}_2\text{W}_{18}\text{O}_{62}$ Dawson unit, respectively.

Notice that the structures **1-3** contain β - $\text{Ni}_3(\mu_3\text{-OH})_3(\text{H}_2\text{O})_3\text{P}_2\text{W}_{15}\text{O}_{56}$ (β - $\text{Ni}_3\text{P}_2\text{W}_{15}$, Fig. S3a) unit when three exterior Ni-complex groups were removed from the $\text{Ni}_6\text{P}_2\text{W}_{15}$ unit. So far, only several monomeric trisubstituted Dawson α - $\text{M}_3\text{P}_2\text{W}_{15}$ ($\text{M} = \text{V}/\text{Nb}/\text{Sn}/\text{Rh}/\text{Mn}$, Fig. S3b) units have been made in conventional solution syntheses,¹ no monomeric trisubstituted Dawson β - $\text{M}_3\text{P}_2\text{W}_{15}$ cluster are documented. Here, the monomeric Dawson cluster **2** and its derivatives **1** and **3** containing β - $\text{Ni}_3\text{P}_2\text{W}_{15}$ unit are first harvested under hydrothermal conditions.

1(a) S. P. Harmalker, M. A. Leparulo and M. T. Pope, *J. Am. Chem. Soc.*, **1983**, *105*, 4286-4292; (b) R. G. Finke, B. Rapko, R. J. Saxton and P. J. Domaille, *J. Am. Chem. Soc.*, **1986**, *108*, 2947-2960; (c) D. J. Edlund, R. J. Saxton, D. K. Lyon and R. G. Finke, *Organometallics*, **1988**, *7*, 1692-1704; (d) B. M. Rapko, M. Pohl and R. G. Finke, *Inorg. Chem.*, **1994**, *33*, 3625-3634; (e) F. Xin and M. T. Pope, *Organometallics*, **1994**, *13*, 4881-4886; (f) T. Nagata, M. Pohl, H. Weiner and R. G. Finke, *Inorg. Chem.*, **1997**, *36*, 1366-1377; (g) T. M. Anderson, X. Zhang, K. I. Hardcastle and C. L. Hill, *Inorg. Chem.*, **2002**, *41*, 2477-2488; (h) Y. Sakai, Y. Kitakoga, K. Hayashi, K. Yoza and K. Nomiya, *Eur. J. Inorg. Chem.*, **2004**, 4646-4652, and references therein; (i) C. P. Pradeep, M. F. Misrahi, F. Y. Li, J. Zhang, L. Xu, D. L. Long, T. B. Liu and L. Cronin, *Angew. Chem. Int. Ed.*, **2009**, *48*, 8309-8313, and references therein.

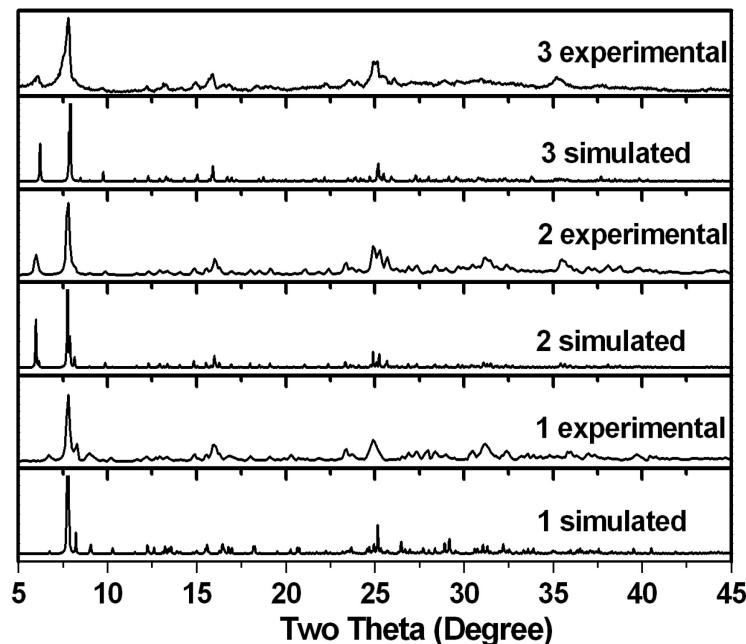


Fig. S4 The simulated and experimental Powder XRD patterns for compounds **1**, **2** and **3**.

The phase purity of compounds **1**, **2** and **3** was confirmed by the experimental powder X-ray diffraction patterns, which were consistent with the simulated patterns on the basis of the single-crystal structure, indicating the phase purity of the as-synthesized samples.

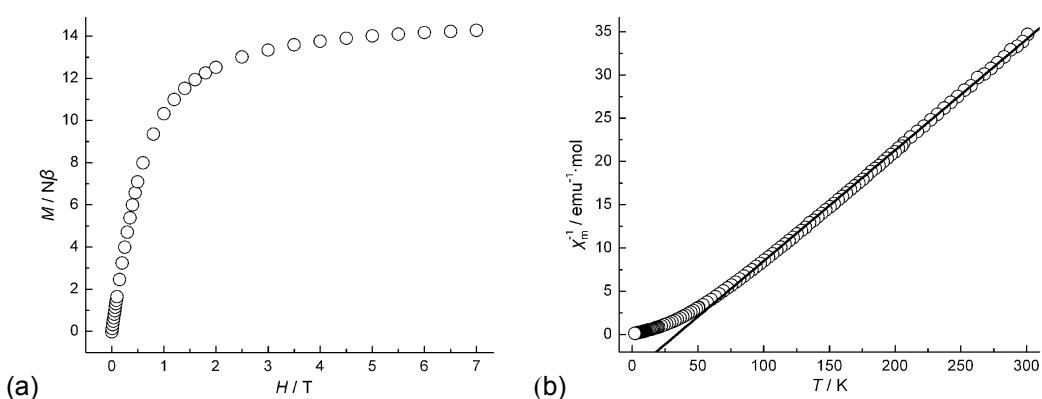


Fig. S5 (a) Field dependence of the magnetization of **3** in the field range of 0–7 T at 2 K. (b) Temperature dependence of χ_m^{-1} for **3**. The solid lines are the best-fit according to the Curve–Weiss law in the range of 75 and 300 K with the Curie constant $C = 7.80$ emu \cdot K \cdot mol $^{-1}$ and the Weiss constant $\theta = 33.84$ K, which indicate of the presence of overall ferromagnetic exchange interactions among the Ni(II) centers.

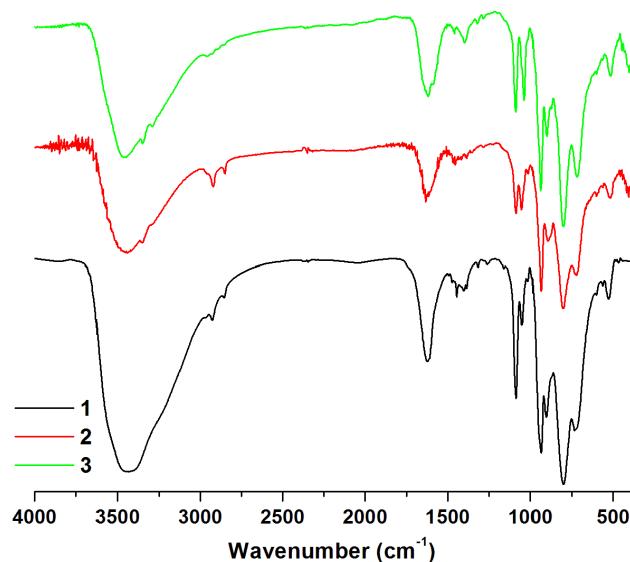


Fig. S6 IR spectra of compounds **1-3**.

The similarity of the IR spectra of **1-3**, show six characteristic vibration bands resulting from the Dawson-type structure: bands at around 1087 and 1037 cm $^{-1}$, attributed to the $\nu(P-O)$; at around 938 and 902 cm $^{-1}$, attributed to the $\nu(W=O)$, at around 802 and 719 cm $^{-1}$, attributed to the $\nu(W-O-W)$. The stretching bands of the NH $_2$ and CH $_2$ groups are observed at 3346–3286 cm $^{-1}$ and 2963–2850 cm $^{-1}$, respectively. In comparison with the spectrum of α -/ β -K $_6$ [P $_2$ W $_{18}$ O $_{62}$]·14H $_2$ O, the $\nu(P-O)$ and $\nu(W-O-W)$ stretching vibration peaks of **1-3** split because of their lower symmetry resulted from the substitution of W $_3$ units by Ni $_6$ clusters.

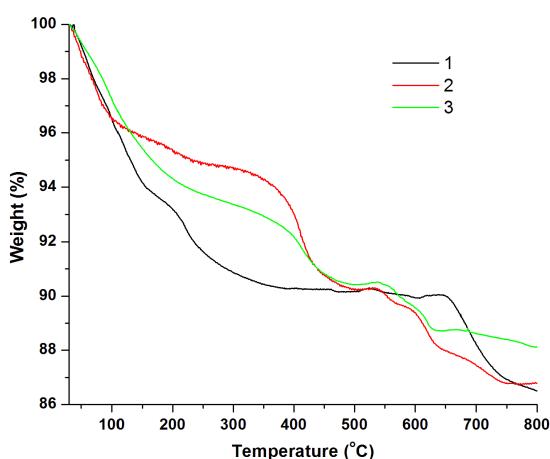


Fig. S7 TG curves of compound **1-3**.

All TG analyses were carried out in flowing N₂ with a heating rate of 10°C min⁻¹ in the temperature range of 30-800°C for **1-3**. Two distinct weight loss stages are observed on the TG curve of **1**. The first stage, which occurs from 30 to 350°C, is attributed to the loss of crystalline and coordination water molecules, the observed weight loss (9.92%) is in agreement with the calculated value (10.48%). The second stage occur between 650 to 800°C , which is due to the loss of organic ligand 2,2'-bipy, the observed weight loss (3.15%) is consistent with the calculated value (3.08%). The TGA curves of both **2** and **3** exhibit a series of continued weight losses, which are attributed to the loss of organic ligands and water molecules. The observed total weight losses (**2**, 13.12%; **3**, 12.11%) are in agreement with the calculated values (**2**, 11.00%, corresponding to the loss of 10.5 water molecules and 3 dien molecules; **3**, 11.90%, corresponding to the loss of 14.5 water molecules and 5 en molecules).