Supporting Information

Three new high-nuclear transition-metal-substituted heteropolytungstates : syntheses, crystal structures, magnetic studies and NLO properties

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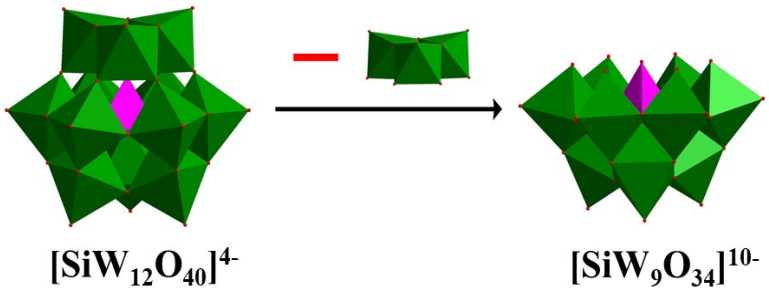
1. Structure



Scheme S1 The polyhedral representation of $[SiW_9O_{34}]^{10-}$ anion derived from $[SiW_{12}O_{40}]^{4-}$ anion schema.

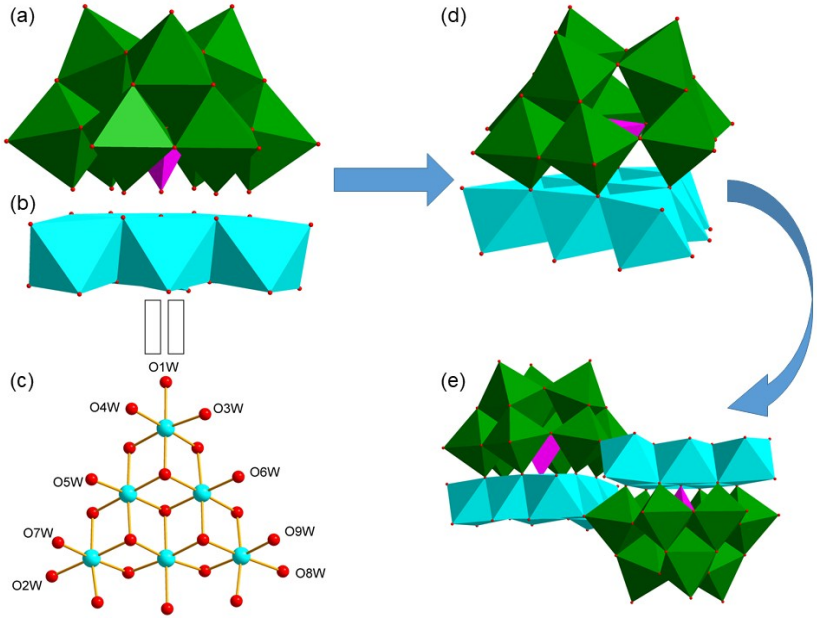


Fig. S1 The polyhedral representation of $[SiW_9O_{34}]^{10-}$ anion (a), {$\mathbf{Ni_6}$} cluster (b), {$\mathbf{Ni_6SiW_9}$} subunit (d), and compound **1** (e). The ball-and-stick representation of {$\mathbf{Ni_6}$} cluster (c). H atoms and water molecules are omitted for clarity. Color codes: W, green; Ni, sky blue; O, red; WO_6, green; NiO_6, sky blue; SiO_4, purple.

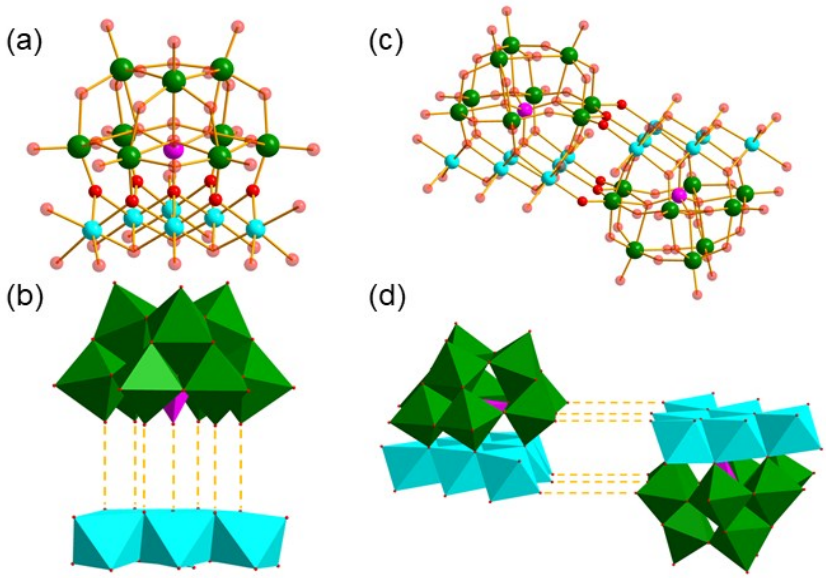


Fig. S2 The ball-and-stick (a) and polyhedral (b) of the connection between **SiW_9** anion and {**Ni_6**} cluster. The ball-and-stick (c) and polyhedral (d) of the connection between the {**Ni_6SiW_9**} subunits. H atoms and water molecules are omitted for clarity. Color codes: Si, purple; W, green; Ni, sky blue; O, red; WO_6, green; NiO_6, sky blue; SiO_4, purple.

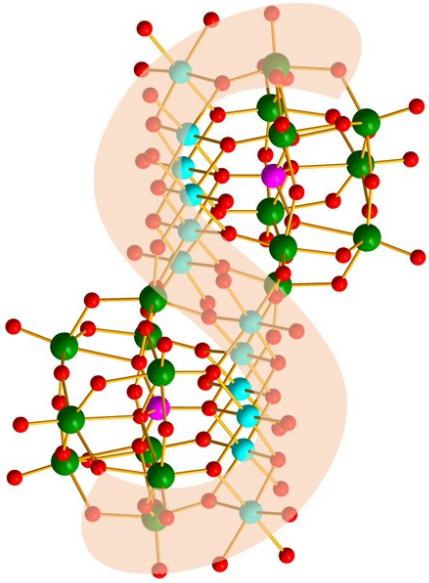


Fig. S3 The 'S-shape' dimer $\{(\mathbf{Ni_6SiW_9})_2\}^{4-}$ structure of compound **1**. Color codes: Si, purple; W, green; Ni, sky blue; O, red.

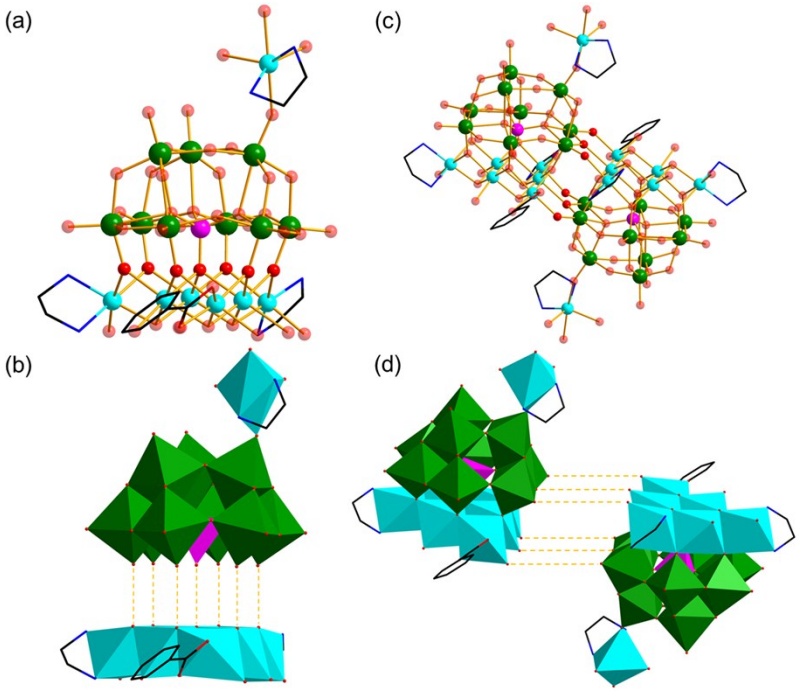


Fig. S4 The ball-and-stick (a) and polyhedral (b) of the connection between **SiW_9** anion and **$Ni_6L(en)_2$** cluster containing ligands. The ball-and-stick (c) and polyhedral (d) of the connection between the **$Ni_6L(en)_2SiW_9$** subunits. H atoms and water molecules are omitted for clarity. Color codes: Si, purple; W, green; Ni, sky blue; O, red; C, black; N, blue; WO_6, green; NiO_6, sky blue; SiO_4, purple.

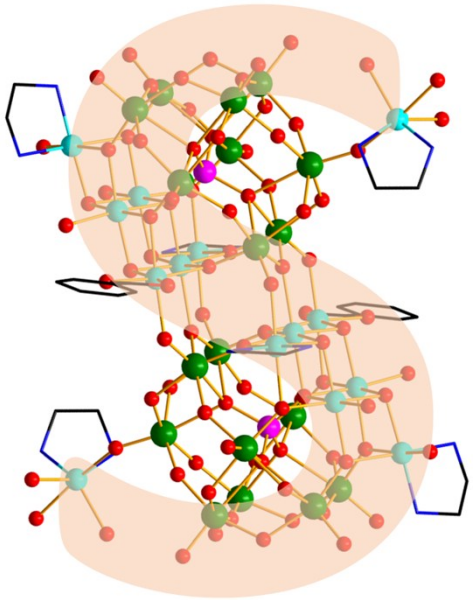


Fig. S5 The 'S-shape' structure of compound **2**. Color codes: Si, purple; W, green; Ni, sky blue; O, red; C, black; N, blue.

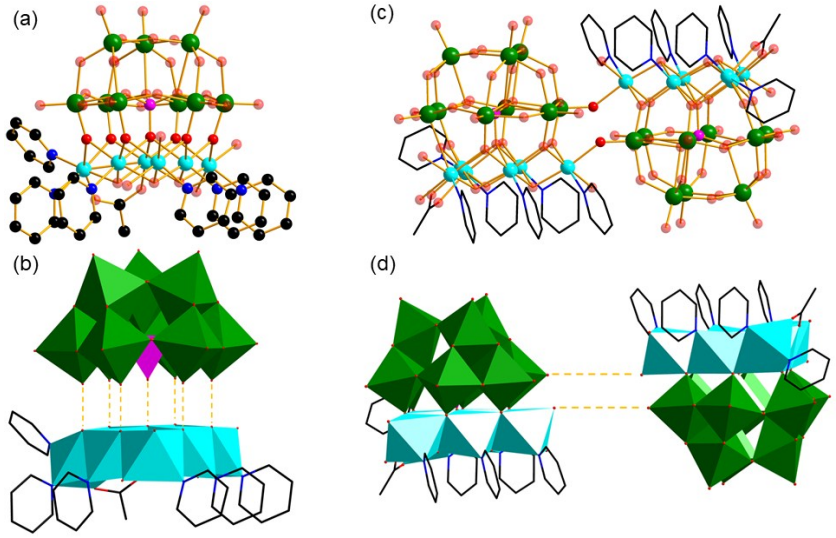


Fig. S6 The ball-and-stick (a) and polyhedral (b) of the connection between $[PW_9O_{34}]^{10-}$ anion and $\{Ni_6\}$ cluster containing ligands. The ball-and-stick (c) and polyhedral (d) of the connection between the $\{Ni_6(L')_6(CH_3COO)(H_2O)_3(\mu_3\text{-}OH)_3(HPW_9O_{34})\}$ subunits. H atoms and water molecules are omitted for clarity. Color codes: P, purple; W, green; Ni, sky blue; O, red; C, black; N, blue; WO_6, green; NiO_6, sky blue; PO_4, purple.

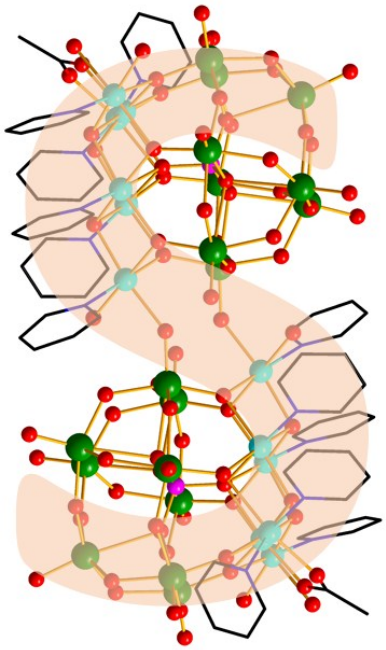


Fig. S7 The 'S-shape' structure of compound **3**. Color codes: P, purple; W, green; Ni, sky blue; O, red; C, black; N, blue.

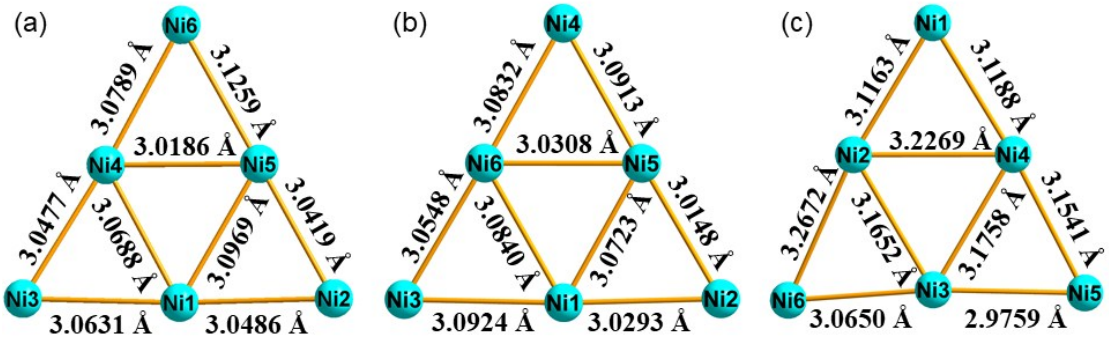


Fig. S8 The Ni···Ni distances in the $\mathbf{Ni_6}$ (a) of **1**, $\mathbf{Ni_6L(en)_2}$ (b) of **2**, and $\mathbf{Ni_6(L')_6Ac}$ (c) of **3**.

2. IR Spectra

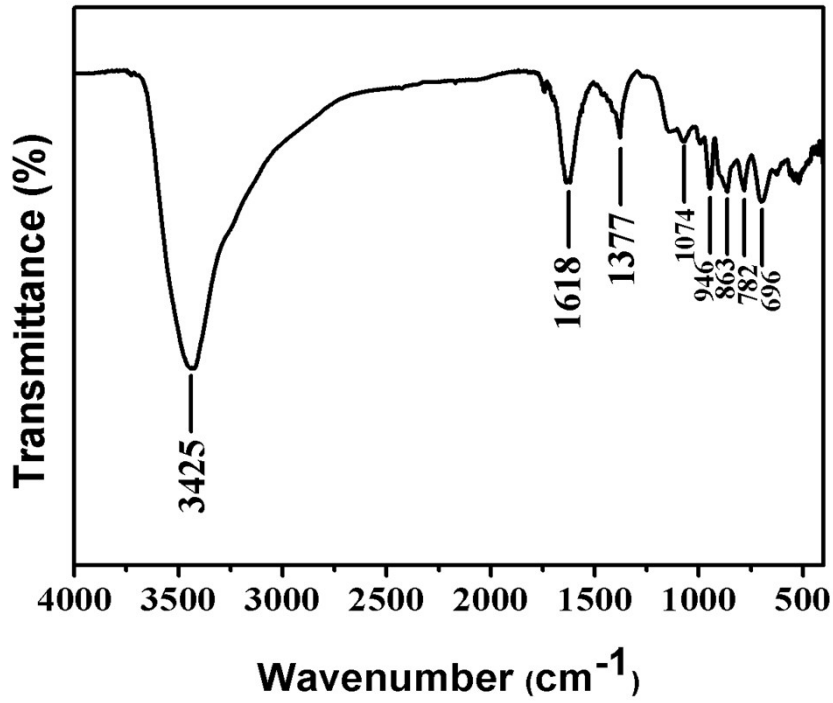


Fig. S9 The IR spectrum of compound **1**.

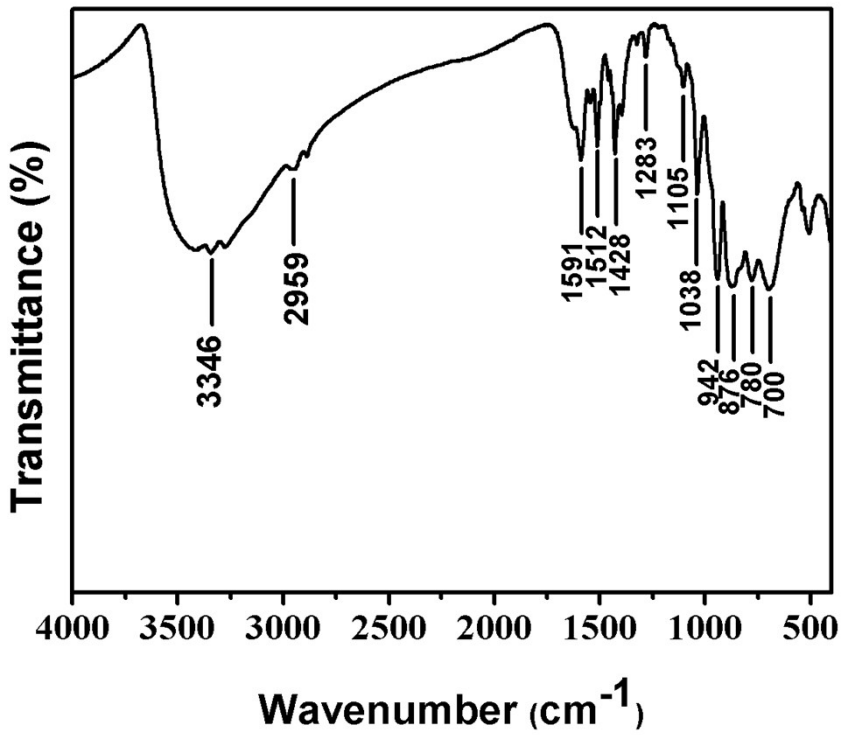


Fig. S10 The IR spectrum of compound **2**.

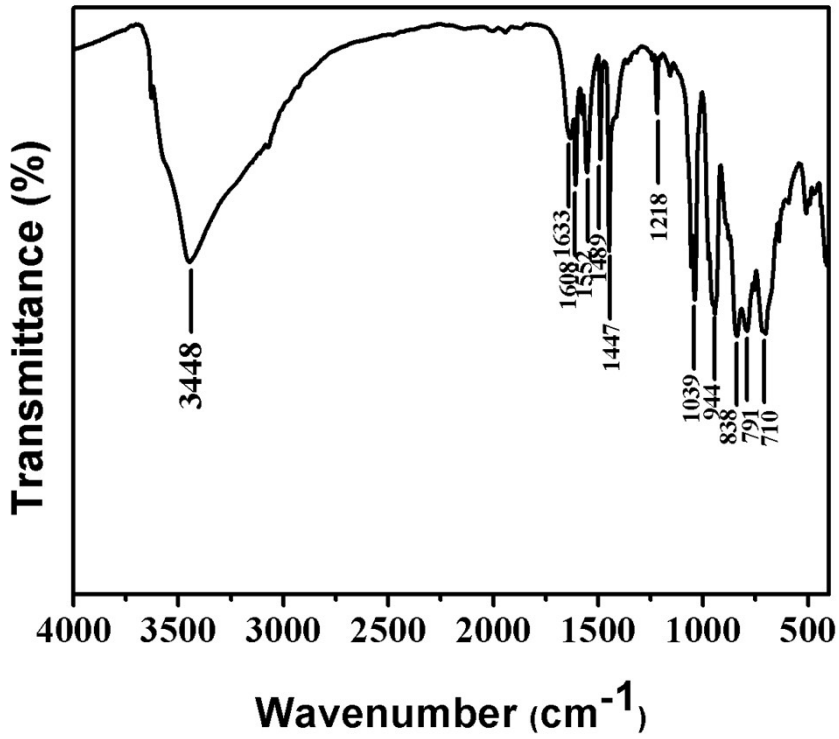


Fig. S11 The IR spectrum of compound **3**.

3. PXRD patterns

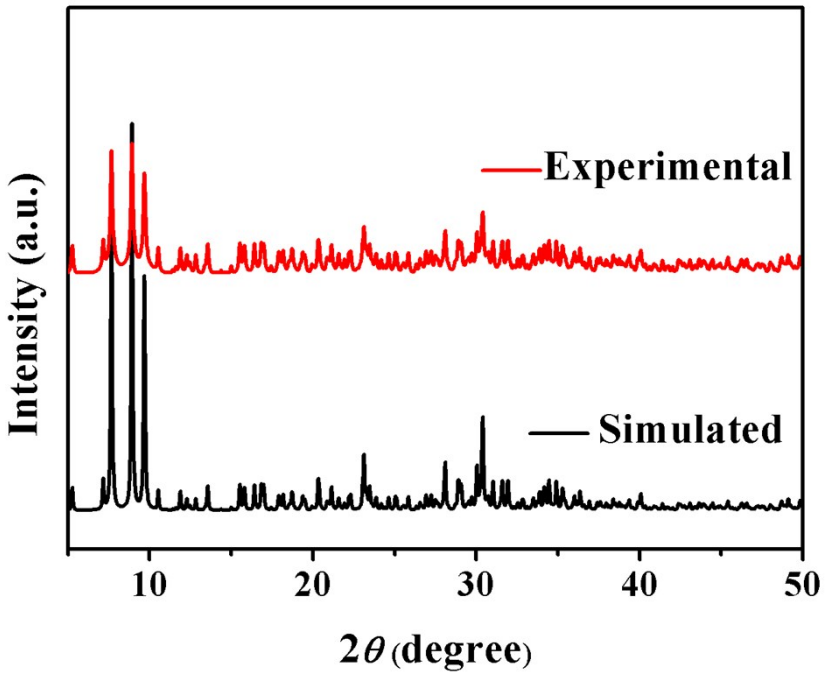


Fig. S12 Experimental and simulated PXRD patterns of **1**.

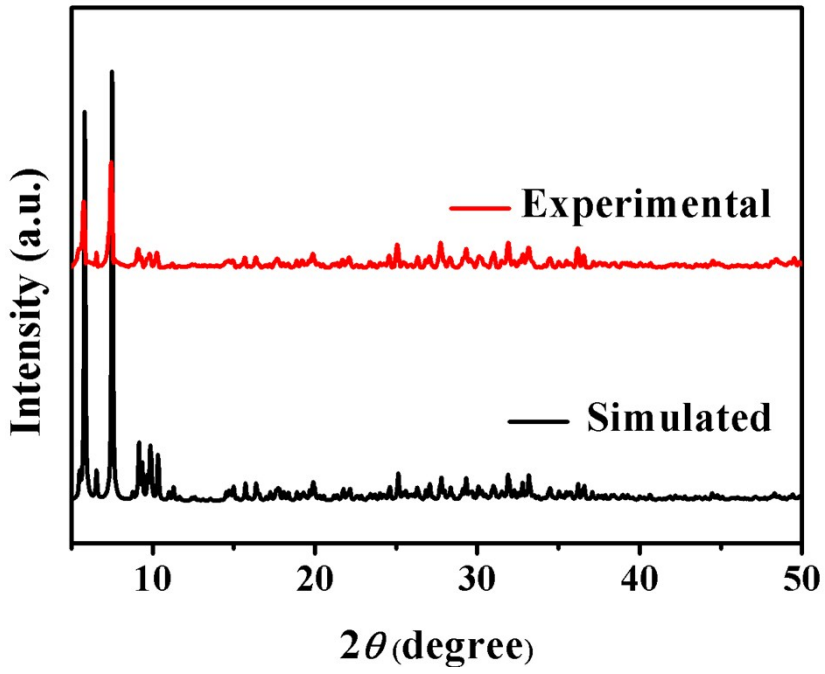


Fig. S13 Experimental and simulated PXRD patterns of **2**.

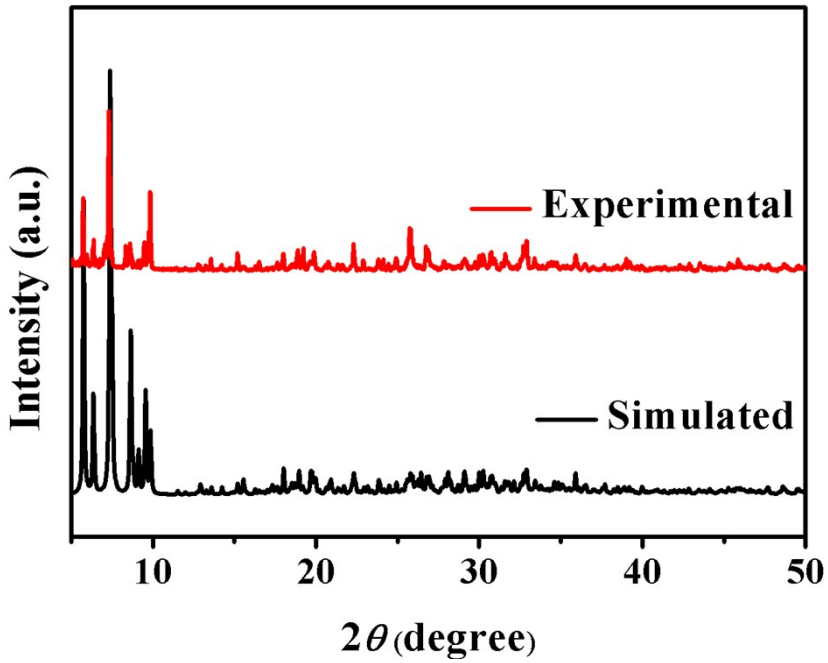


Fig. S14 Experimental and simulated PXRD patterns of **3**.

4. TGA

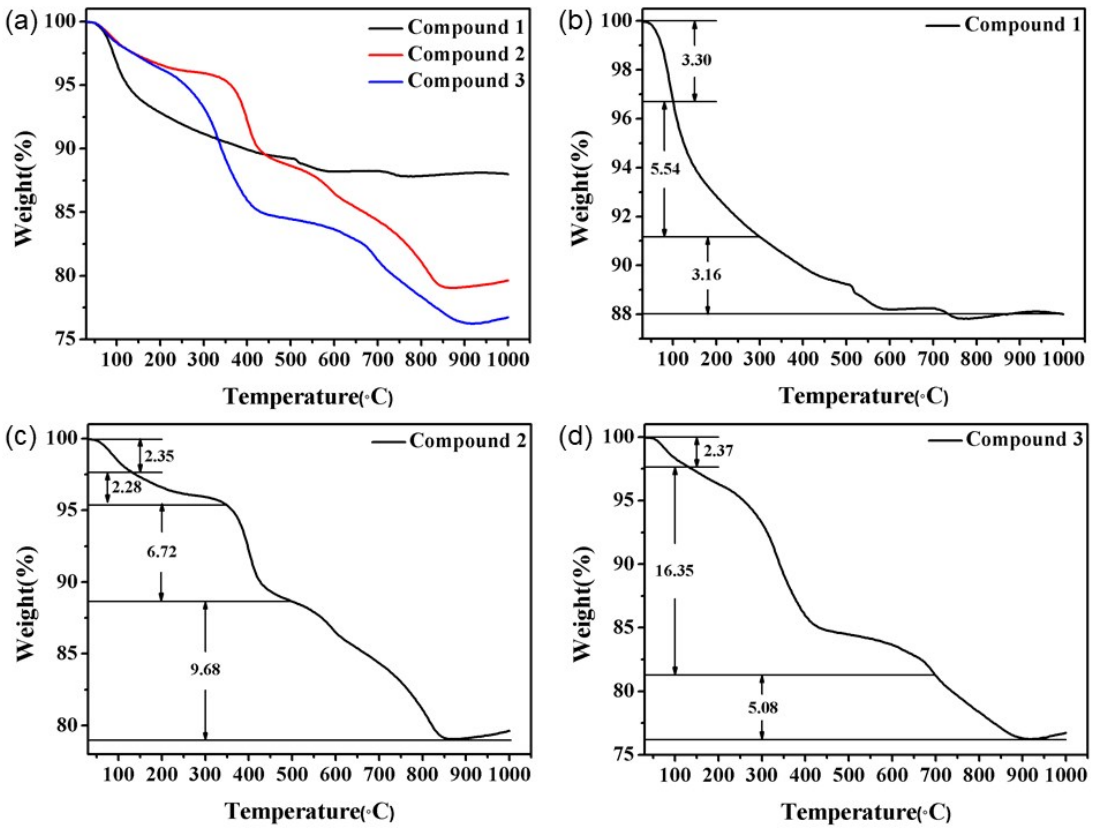


Fig. S15 The TG curve for **1**-**3**.

To investigate the thermal stability of **1**−**3**, the TG analyses were carried out under N_2 atmosphere from 25 to 1000 °C at a heating rate of 10 °C min^{-1} (Fig. S15). The TG curve of **1** shows three step weight loss processes (Fig. S15b). The first weight loss 3.30 (calcd 3.72 %) occurred in the range 30-100 °C is assigned to the release of 12 crystal water molecules. The second weight loss 5.54 (calcd 5.58 %) occurred in the range 100-300 °C belongs to 18 coordinated water molecules, following weight loss 3.16 in the range of 300–1000 °C is corresponded to the thermal decomposition of the main structure. The total weight loss of **1** is 11.99 %.

The TG curve of **2** shows four step weight loss processes (Fig. S15c). The first weight loss 2.35 (calcd 2.62 %) occurred in the range 30-130 °C is assigned to the release of 9 crystal water molecules. The second weight loss 2.28 (calcd 2.62 %) occurred in the range 130-350 °C belongs to 9 coordinated water molecules. The third weight loss 6.72 (calcd 6.80 %) in the range of 350–500 °C is corresponded to the decomposition of the organic ligands, following weight loss 9.68 in the range of 500–1000 °C is corresponded to the thermal decomposition of the main structure. The total weight loss of **2** is 21.03 %.

The TG curve of **3** shows three step weight loss processes (Fig. S15d). The first weight loss 2.37 (calcd 2.45 %) occurred in the range 30-130 °C is assigned to the release of 9 crystal water molecules. The second weight loss 16.35 (calcd 17.77 %) occurred in the range 130-700 °C belongs to 6 coordinated water molecules and the organic ligands. The third weight loss weight loss 5.08 in the range of 700–1000 °C is corresponded to the thermal decomposition of the main structure. The total weight loss of **3** is 23.80 %.

5. Nonlinear optical properties

Two-photon absorption (TPA) value containing TPA coefficient β and cross section σ were obtained through the open-aperture Z-scan technique femtosecond laser pulse and a Ti:95 sapphire system. The open-aperture Z-scan experiments of **1-3** and precursors ($Na_{10}[\alpha\text{-}SiW_9O_{34}]\cdot 18H_2O$, **$SiW_9$**; $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot 7H_2O$, **$PW_9$**) were performed at the concentration of 1.0×10^{-4} mol L^{-1} by employing the DMSO (DMSO = dimethyl sulfoxide) as solvent. The Figure 10 show the Z-scan curve, the red circles are the data of experiment and the solid line is the simulated curve modified under following equations (1) and (2)[1-3]:

$$T(z, s=1) = \sum_{m=0}^{\infty} \frac{[-q_0(z)]^m}{(m+1)^{3/2}} \quad (1)$$

$$q_0(z) = \frac{\beta I_0 L_{eff}}{1+x^2} \quad (2)$$

Where z is the sample position, I_0 is the input intensity of laser beam where z=0. $L_{eff} = (1 - e^{-\alpha L})/\alpha$ is the effective length while α and L are the linear absorption coefficient and the sample length respectively.

Then the molecular TPA cross section σ can be deduced through using equation (3) [4-6]:

$$\sigma = h\nu\beta / N_A d \times 10^{-3} \quad (3)$$

In which the N_A, *d* and *h* represent the Avogadro's constant, Planck's constant and the frequency of input intensity respectively.

Table S1 The third-order NLO data of reported relevant compounds

Compounds	β[a] ($cm \cdot GM^{-1}$)	σ[b] (GM)	Ref.
2	0.035	1552	This work
3	0.039	1843	This work
$[Ni(NTB^c)(H_2O)]_2(H_2P_2Mo_5O_{23})\cdot 9.25H_2O$	0.001655	758	7
$[Ni(H_2O)(NTB)]_2(PMo^{VI}{}_{11}Mo^{V}O_{40})\cdot 4.5H_2O$	0.001127	404	7
$[Ni(NTB)]_2(Mo_8O_{26})\cdot 9H_2O$	0.015925	673	7
$[Co(H_2O)_6]\{[C_3H_4N_2]_2[C_5NH_5]_{14}[H_{15}(Mo_2O_4)_8Co_{16}(PO_4)_{14}\text{-}(HPO_3)_{10}(OH)_3]\}\cdot 5H_2O$	0.01375	622	8
$[C_3H_5N_2]_4[C_5NH_5]_2[Ni(H_2O)_6]\{[C_3H_4N_2]_2[C_5NH_5]_{14}[H_{18}(Mo_2O_4)_8\text{-}Ni_{16}(PO_4)_{22}(OH)_6]\}\cdot 11H_2O$	0.0056	247	8
$[C_5NH_5]_8[C_3H_5N_2]_2\{[C_5NH_5]_9[H_{31}Mo_{12}O_{24}Co_{12}(PO_4)_{23}(H_2O)_4]\}\cdot 12H_2O$	0.00263	1058	9
(diimine)platinum(II) complex bearing 2-(benzothiazol-2'-yl)-9,9-diethyl-7-ethynylfluorene ligands	-	1000	10
$Na_2[(CH_3)_2NH_2]_3\{Na\subset[Ce^{III}(H_2O)(CH_3CH_2OH)(L\text{-}tartH_3)(H_2Si_2W_{19}O_{66})]\}\cdot 3.5H_2O$ (L-1)	0.00279	392	11
$[(CH_3)_2NH_2]_7\{Na\subset[Ce^{III}(H_2O)(CH_3CH_2OH)(D\text{-}tartH_3)(Si_2W_{19}O_{66})]\}\cdot 2.5H_2O$ (D-1)	0.01369	389	11

[a] the TPA absorption coefficient of the solution.

[b] the molecular TPA cross-section.

[c] NTB = tris(2-benzimidazylmethyl)amine

References

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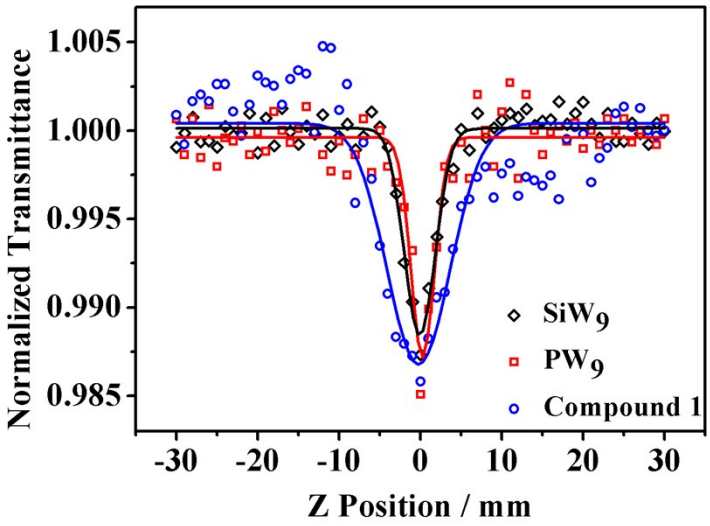

Fig. S16 Open aperture Z-scan data for **1** and precursors (**SiW_9** and **PW_9**). The dots are the experimental data and the solid curve represents the theoretical data.

Table S2 The Two-photon absorption (TPA) data

Compounds	β^a (cm·GM^{-1})	σ^b (GM)
1	0.00117	458
2	0.035	1552
3	0.039	1843
$Na_{10}[\alpha\text{-}SiW_9O_{34}]\cdot 18H_2O$(**$SiW_9$**)	0.00098	429
$Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot 7H_2O$(**$SiW_9$**)	0.00110	484

[a] the TPA absorption coefficient of the solution.

[b] the molecular TPA cross-section.

6. Magnetic property

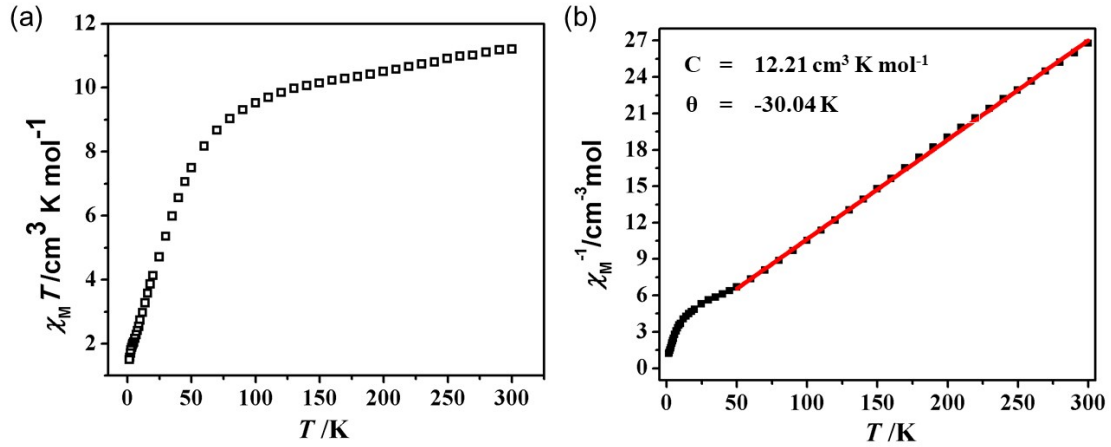

Fig. S17 (a) Plot of $\chi_M T$ vs T for **1**; (b) Temperature dependence of $1/\chi_M$ for compound **1**, the solid line is the best-fit line according to the Curie-Weiss law.

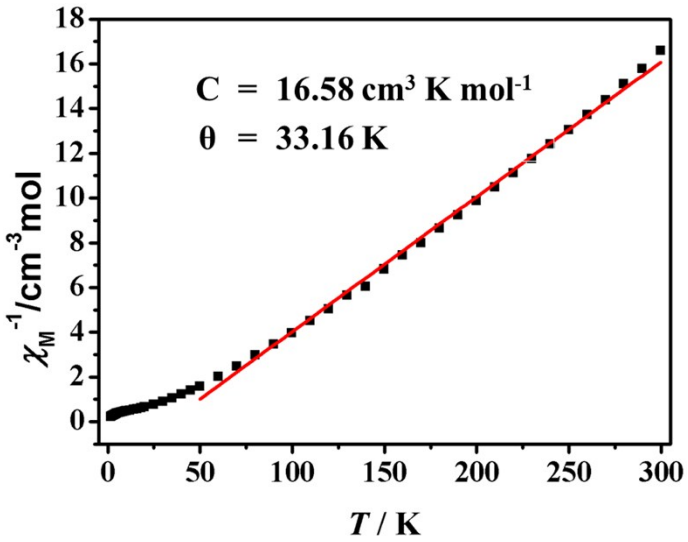

Fig. S18 Temperature dependence of $1/\chi_M$ for compound **2**; the solid line is the best-fit line according to the Curie-Weiss law.

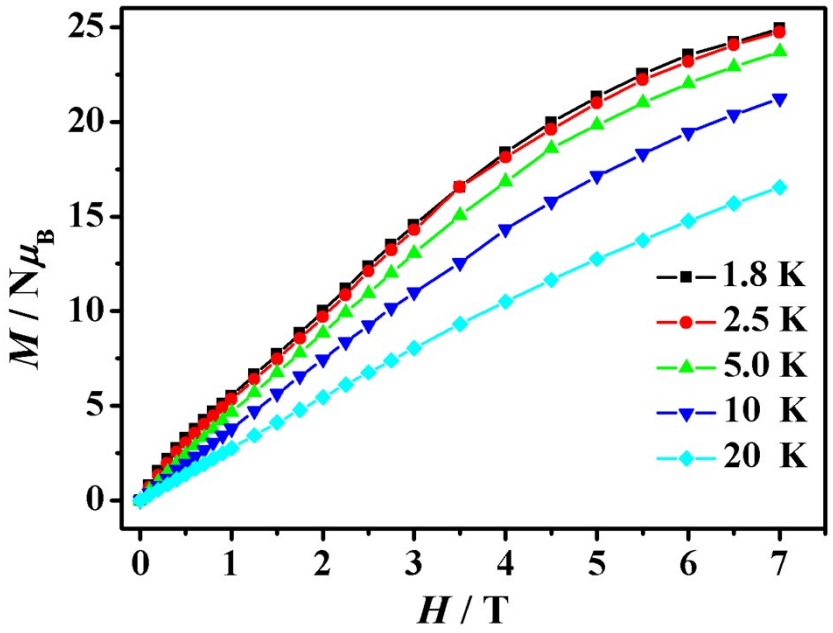

Fig. S19 Plot of M/Nμ_B vs H of **2**.

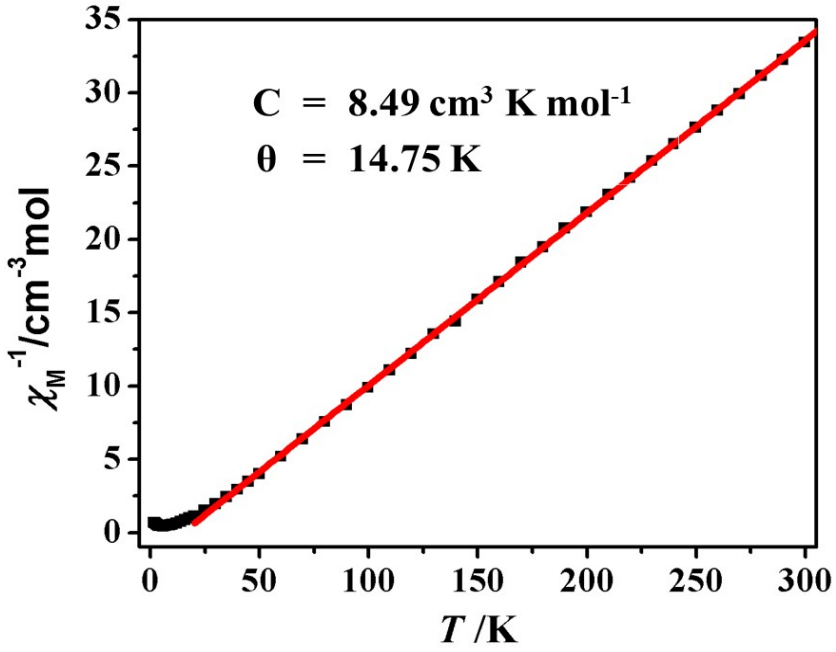

Fig. S20 Temperature dependence of $1/\chi_M$ for compound **3**; the solid line is the best-fit line according to the Curie-Weiss law.

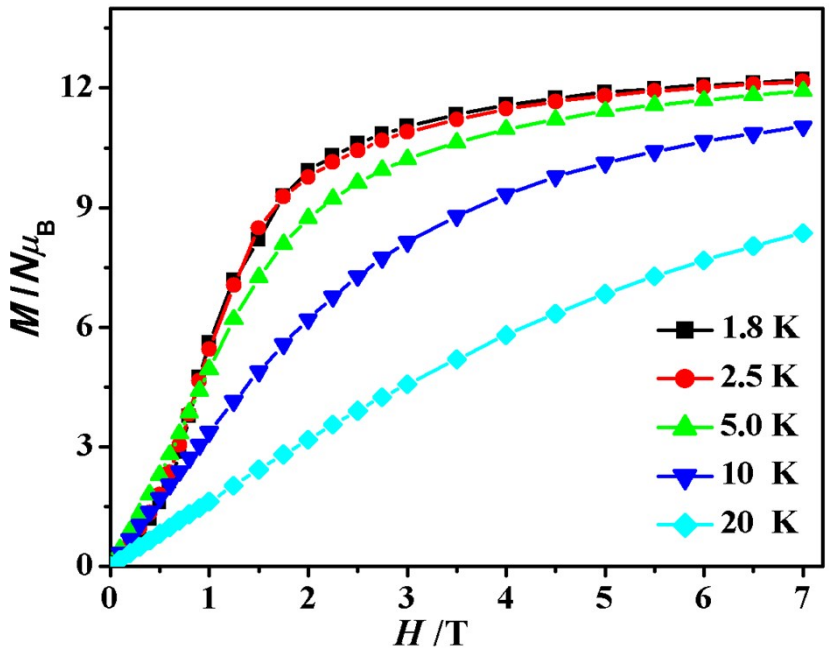

Fig. S21 Plot of M/Nμ_B vs H per Ni_6 unit of **3**.

7. Selected bond distances and angles

Table S3 Selected bond lengths for compound **1** (Å).

Ni(1)-O(28)	2.014(16)	Ni(2)-O(6)	2.030(16)	Ni(5)-O(3)	2.019(16)
Ni(1)-O(31)	2.029(16)	Ni(2)-O(28)	2.034(15)	Ni(5)-O(28)	2.039(16)
Ni(1)-O(2)$^{\#1}$	2.036(15)	Ni(2)-O(7W)	2.064(18)	Ni(5)-O(27)	2.060(15)
Ni(1)-O(11)$^{\#1}$	2.046(15)	Ni(2)-O(2W)	2.070(16)	Ni(5)-O(7)	2.071(16)
Ni(1)-O(7)	2.132(17)	Ni(2)-O(11)$^{\#1}$	2.096(16)	Ni(5)-O(5W)	2.096(17)
Ni(1)-O(1)	2.245(17)	Ni(2)-O(27)	2.110(16)	Ni(5)-O(10)	2.101(16)
Ni(3)-O(31)	1.988(16)	Ni(4)-O(3)	2.036(15)	Ni(6)-O(3)	2.014(16)
Ni(3)-O(22)	2.052(17)	Ni(4)-O(6W)	2.049(17)	Ni(6)-O(18)	2.039(16)
Ni(3)-O(2)$^{\#1}$	2.061(15)	Ni(4)-O(31)	2.062(17)	Ni(6)-O(1W)	2.059(18)
Ni(3)-O(9W)	2.072(19)	Ni(4)-O(7)	2.062(16)	Ni(6)-O(4W)	2.064(18)
Ni(3)-O(13)	2.074(18)	Ni(4)-O(13)	2.081(16)	Ni(6)-O(3W)	2.076(16)
Ni(3)-O(8W)	2.081(18)	Ni(4)-O(18)	2.084(17)	Ni(6)-O(10)	2.136(15)

Symmetry codes: #1 -x, -y+1, -z+1.

Table S4 Selected bond angles (°) for compound **1.**

O(28)-Ni(1)-O(31)	94.1(6)	O(6)-Ni(2)-O(28)	90.9(6)	O(31)-Ni(3)-O(22)	90.2(7)
O(28)-Ni(1)-O(2)$^{\#1}$	172.1(7)	O(6)-Ni(2)-O(7W)	93.1(7)	O(31)-Ni(3)-O(2)$^{\#1}$	81.8(6)
O(31)-Ni(1)-O(2)$^{\#1}$	81.4(6)	O(28)-Ni(2)-O(7W)	93.2(7)	O(22)-Ni(3)-O(2)$^{\#1}$	86.3(6)
O(28)-Ni(1)-O(11)$^{\#1}$	84.2(6)	O(6)-Ni(2)-O(2W)	90.2(7)	O(31)-Ni(3)-O(9W)	91.7(7)
O(31)-Ni(1)-O(11)$^{\#1}$	174.0(7)	O(28)-Ni(2)-O(2W)	178.9(7)	O(22)-Ni(3)-O(9W)	93.1(8)
O(2)$^{\#1}$-Ni(1)-O(11)$^{\#1}$	99.5(6)	O(7W)-Ni(2)-O(2W)	86.8(8)	O(2)$^{\#1}$-Ni(3)-O(9W)	173.4(7)
O(28)-Ni(1)-O(7)	82.2(6)	O(6)-Ni(2)-O(11)$^{\#1}$	87.2(6)	O(31)-Ni(3)-O(13)	84.4(7)
O(31)-Ni(1)-O(7)	83.9(7)	O(28)-Ni(2)-O(11)$^{\#1}$	82.4(6)	O(22)-Ni(3)-O(13)	168.7(7)
O(2)$^{\#1}$-Ni(1)-O(7)	90.8(6)	O(7W)-Ni(2)-O(11)$^{\#1}$	175.6(7)	O(2)$^{\#1}$-Ni(3)-O(13)	83.2(7)
O(11)$^{\#1}$-Ni(1)-O(7)	90.2(6)	O(2W)-Ni(2)-O(11)$^{\#1}$	97.6(7)	O(9W)-Ni(3)-O(13)	96.9(8)
O(28)-Ni(1)-O(1)	97.8(6)	O(6)-Ni(2)-O(27)	171.7(6)	O(31)-Ni(3)-O(8W)	176.9(7)
O(31)-Ni(1)-O(1)	96.7(6)	O(28)-Ni(2)-O(27)	83.8(6)	O(22)-Ni(3)-O(8W)	91.3(7)
O(2)$^{\#1}$-Ni(1)-O(1)	89.2(6)	O(7W)-Ni(2)-O(27)	93.6(7)	O(2)$^{\#1}$-Ni(3)-O(8W)	101.0(7)
O(11)$^{\#1}$-Ni(1)-O(1)	89.3(6)	O(2W)-Ni(2)-O(27)	95.1(7)	O(9W)-Ni(3)-O(8W)	85.5(8)
O(7)-Ni(1)-O(1)	179.5(6)	O(11)$^{\#1}$-Ni(2)-O(27)	85.8(6)	O(13)-Ni(3)-O(8W)	94.6(7)
O(3)-Ni(4)-O(6W)	94.6(7)	O(3)-Ni(5)-O(28)	97.4(6)	O(3)-Ni(6)-O(18)	82.3(7)
O(3)-Ni(4)-O(31)	99.2(6)	O(3)-Ni(5)-O(27)	175.0(6)	O(3)-Ni(6)-O(1W)	176.7(7)
O(6W)-Ni(4)-O(31)	93.5(7)	O(28)-Ni(5)-O(27)	85.0(6)	O(18)-Ni(6)-O(1W)	95.7(7)
O(3)-Ni(4)-O(7)	84.8(6)	O(3)-Ni(5)-O(7)	84.9(6)	O(3)-Ni(6)-O(4W)	97.7(7)
O(6W)-Ni(4)-O(7)	178.1(7)	O(28)-Ni(5)-O(7)	83.1(6)	O(18)-Ni(6)-O(4W)	177.5(7)
O(31)-Ni(4)-O(7)	84.9(6)	O(27)-Ni(5)-O(7)	91.0(6)	O(1W)-Ni(6)-O(4W)	84.2(7)
O(3)-Ni(4)-O(13)	174.8(6)	O(3)-Ni(5)-O(5W)	93.9(6)	O(3)-Ni(6)-O(3W)	94.4(7)
O(6W)-Ni(4)-O(13)	90.3(7)	O(28)-Ni(5)-O(5W)	93.1(7)	O(18)-Ni(6)-O(3W)	89.6(7)
O(31)-Ni(4)-O(13)	82.4(7)	O(27)-Ni(5)-O(5W)	90.3(6)	O(1W)-Ni(6)-O(3W)	88.1(7)
O(7)-Ni(4)-O(13)	90.5(6)	O(7)-Ni(5)-O(5W)	175.9(7)	O(4W)-Ni(6)-O(3W)	92.9(8)
O(3)-Ni(4)-O(18)	80.7(6)	O(3)-Ni(5)-O(10)	81.8(6)	O(3)-Ni(6)-O(10)	81.1(6)
O(6W)-Ni(4)-O(18)	92.2(7)	O(28)-Ni(5)-O(10)	174.0(6)	O(18)-Ni(6)-O(10)	83.3(6)
O(31)-Ni(4)-O(18)	174.3(6)	O(27)-Ni(5)-O(10)	95.3(6)	O(1W)-Ni(6)-O(10)	96.1(6)
O(7)-Ni(4)-O(18)	89.5(6)	O(7)-Ni(5)-O(10)	90.8(6)	O(4W)-Ni(6)-O(10)	94.3(7)
O(13)-Ni(4)-O(18)	97.1(7)	O(5W)-Ni(5)-O(10)	92.9(7)	O(3W)-Ni(6)-O(10)	172.0(7)
Ni(1)$^{\#1}$-O(2)-Ni(3)$^{\#1}$	96.7(6)	Ni(5)-O(10)-Ni(6)	95.1(6)	Ni(1)-O(28)-Ni(5)	99.7(6)
Ni(6)-O(3)-Ni(5)	101.6(7)	Ni(1)$^{\#1}$-O(11)-Ni(2)$^{\#1}$	94.8(6)	Ni(2)-O(28)-Ni(5)	96.6(6)
Ni(6)-O(3)-Ni(4)	99.0(7)	Ni(3)-O(13)-Ni(4)	94.3(7)	Ni(3)-O(31)-Ni(1)	99.4(7)
Ni(5)-O(3)-Ni(4)	96.2(6)	Ni(6)-O(18)-Ni(4)	96.6(7)	Ni(3)-O(31)-Ni(4)	97.6(7)
Ni(4)-O(7)-Ni(5)	93.8(7)	Ni(5)-O(27)-Ni(2)	93.7(6)	Ni(1)-O(31)-Ni(4)	97.2(7)
Ni(4)-O(7)-Ni(1)	94.0(6)	Ni(1)-O(28)-Ni(2)	97.7(7)	Ni(5)-O(7)-Ni(1)	94.9(7)

Symmetry codes: #1 -x,-y+1,-z+1.

Table S5 Selected bond lengths for compound **2** (Å).

Ni(1)-O(4)	1.998(8)	Ni(3)-O(1)	2.017(8)	Ni(5)-O(8)	2.006(9)
Ni(1)-O(1)	2.007(9)	Ni(3)-N(2)	2.056(10)	Ni(5)-O(4)	2.038(8)
Ni(1)-O(14)	2.052(8)	Ni(3)-O(21)$^{\#1}$	2.075(9)	Ni(5)-O(22)	2.065(8)
Ni(1)-O(17)	2.069(8)	Ni(3)-N(1)	2.076(11)	Ni(5)-O(28)	2.069(8)
Ni(1)-O(12)	2.125(8)	Ni(3)-O(23)	2.111(8)	Ni(5)-O(12)	2.093(8)
Ni(1)-O(2)$^{\#1}$	2.250(8)	Ni(3)-O(14)	2.147(8)	Ni(5)-O(1W)	2.110(8)
Ni(2)-O(4)	1.982(8)	Ni(4)-O(8)	2.006(8)	Ni(6)-O(1)	2.028(8)
Ni(2)-O(6)$^{\#1}$	2.062(8)	Ni(4)-N(4)	2.050(11)	Ni(6)-O(8)	2.041(8)
Ni(2)-O(13)	2.073(8)	Ni(4)-N(3)	2.062(11)	Ni(6)-O(30)	2.055(8)
Ni(2)-O(28)	2.077(8)	Ni(4)-O(3W)	2.111(10)	Ni(6)-O(23)	2.081(9)
Ni(2)-O(17)	2.079(8)	Ni(4)-O(30)	2.124(8)	Ni(6)-O(12)	2.083(8)
Ni(2)-O(10)	2.103(9)	Ni(4)-O(22)	2.149(8)	Ni(6)-O(2W)	2.117(9)
Ni(7)-N(6)	2.075(18)	Ni(7)-O(4W)	2.082(18)	Ni(7)-O(9W)	2.116(18)
Ni(7)-O(10W)	2.141(18)	Ni(7)-O(26)	2.179(10)	Ni(7)-N(5)	2.24(3)

Symmetry codes: #1 -x+1/2, -y+1/2, -z.

Table S6 Selected bond angles (°) for compound **2**.

O(4)-Ni(1)-O(1)	95.3(3)	O(4)-Ni(2)-O(6)$^{\#1}$	92.0(3)	O(1)-Ni(3)-N(2)	95.2(4)
O(4)-Ni(1)-O(14)	172.7(3)	O(4)-Ni(2)-O(13)	102.0(3)	O(1)-Ni(3)-O(21)$^{\#1}$	88.4(3)
O(1)-Ni(1)-O(14)	83.0(3)	O(6)$^{\#1}$-Ni(2)-O(13)	99.2(3)	N(2)-Ni(3)-O(21)$^{\#1}$	94.1(4)
O(4)-Ni(1)-O(17)	83.1(3)	O(4)-Ni(2)-O(28)	84.9(3)	O(1)-Ni(3)-N(1)	178.7(4)
O(1)-Ni(1)-O(17)	172.6(3)	O(6)$^{\#1}$-Ni(2)-O(28)	174.6(3)	N(2)-Ni(3)-N(1)	85.4(4)
O(14)-Ni(1)-O(17)	97.6(3)	O(13)-Ni(2)-O(28)	85.8(3)	O(21)$^{\#1}$-Ni(3)-N(1)	92.8(4)
O(4)-Ni(1)-O(12)	83.7(3)	O(4)-Ni(2)-O(17)	83.2(3)	O(1)-Ni(3)-O(23)	83.4(3)
O(1)-Ni(1)-O(12)	82.7(3)	O(6)$^{\#1}$-Ni(2)-O(17)	89.2(3)	N(2)-Ni(3)-O(23)	95.1(4)
O(14)-Ni(1)-O(12)	89.1(3)	O(13)-Ni(2)-O(17)	169.9(3)	O(21)$^{\#1}$-Ni(3)-O(23)	168.2(3)
O(17)-Ni(1)-O(12)	89.9(3)	O(28)-Ni(2)-O(17)	86.0(3)	N(1)-Ni(3)-O(23)	95.4(4)
O(4)-Ni(1)-O(2)$^{\#1}$	95.2(3)	O(4)-Ni(2)-O(10)	165.4(3)	O(1)-Ni(3)-O(14)	80.4(3)
O(1)-Ni(1)-O(2)$^{\#1}$	98.9(3)	O(6)$^{\#1}$-Ni(2)-O(10)	91.7(3)	N(2)-Ni(3)-O(14)	175.5(4)
O(14)-Ni(1)-O(2)$^{\#1}$	92.1(3)	O(13)-Ni(2)-O(10)	63.5(3)	O(21)#1-Ni(3)-O(14)	86.5(3)
O(17)-Ni(1)-O(2)$^{\#1}$	88.5(3)	O(28)-Ni(2)-O(10)	92.5(3)	N(1)-Ni(3)-O(14)	99.0(4)
O(12)-Ni(1)-O(2)$^{\#1}$	178.1(3)	O(17)-Ni(2)-O(10)	110.9(3)	O(23)-Ni(3)-O(14)	83.7(3)
O(8)-Ni(4)-N(4)	177.8(4)	O(8)-Ni(5)-O(4)	97.4(3)	O(1)-Ni(6)-O(8)	96.0(3)
O(8)-Ni(4)-N(3)	96.5(4)	O(8)-Ni(5)-O(22)	83.1(3)	O(1)-Ni(6)-O(30)	175.6(3)
N(4)-Ni(4)-N(3)	83.9(4)	O(4)-Ni(5)-O(22)	175.1(3)	O(8)-Ni(6)-O(30)	82.8(3)
O(8)-Ni(4)-O(3W)	92.3(4)	O(8)-Ni(5)-O(28)	175.5(3)	O(1)-Ni(6)-O(23)	83.9(3)
N(4)-Ni(4)-O(3W)	89.8(4)	O(4)-Ni(5)-O(28)	83.7(3)	O(8)-Ni(6)-O(23)	176.6(4)
N(3)-Ni(4)-O(3W)	94.6(4)	O(22)-Ni(5)-O(28)	95.4(3)	O(30)-Ni(6)-O(23)	97.0(3)
O(8)-Ni(4)-O(30)	82.0(3)	O(8)-Ni(5)-O(12)	85.2(3)	O(1)-Ni(6)-O(12)	83.3(3)
N(4)-Ni(4)-O(30)	97.4(4)	O(4)-Ni(5)-O(12)	83.5(3)	O(8)-Ni(6)-O(12)	84.6(3)
N(3)-Ni(4)-O(30)	176.4(4)	O(22)-Ni(5)-O(12)	91.6(3)	O(30)-Ni(6)-O(12)	92.3(3)
O(3W)-Ni(4)-O(30)	88.7(4)	O(28)-Ni(5)-O(12)	90.5(3)	O(23)-Ni(6)-O(12)	91.9(3)
O(8)-Ni(4)-O(22)	81.0(3)	O(8)-Ni(5)-O(1W)	97.1(3)	O(1)-Ni(6)-O(2W)	96.0(4)
N(4)-Ni(4)-O(22)	96.8(4)	O(4)-Ni(5)-O(1W)	91.3(3)	O(8)-Ni(6)-O(2W)	93.7(4)
N(3)-Ni(4)-O(22)	92.2(4)	O(22)-Ni(5)-O(1W)	93.5(3)	O(30)-Ni(6)-O(2W)	88.3(4)
O(3W)-Ni(4)-O(22)	170.9(4)	O(28)-Ni(5)-O(1W)	87.2(3)	O(23)-Ni(6)-O(2W)	89.8(4)
O(30)-Ni(4)-O(22)	84.3(3)	O(12)-Ni(5)-O(1W)	174.6(3)	O(12)-Ni(6)-O(2W)	178.1(3)
Ni(1)-O(1)-Ni(3)	100.4(4)	Ni(4)-O(8)-Ni(6)	99.3(4)	Ni(5)-O(22)-Ni(4)	94.3(3)
Ni(1)-O(1)-Ni(6)	99.7(4)	Ni(5)-O(8)-Ni(6)	97.0(3)	Ni(6)-O(23)-Ni(3)	93.6(3)
Ni(3)-O(1)-Ni(6)	98.1(3)	Ni(6)-O(12)-Ni(5)	93.1(3)	Ni(5)-O(28)-Ni(2)	93.3(3)
Ni(2)-O(4)-Ni(1)	99.2(3)	Ni(6)-O(12)-Ni(1)	94.3(3)	Ni(6)-O(30)-Ni(4)	95.1(3)
Ni(2)-O(4)-Ni(5)	97.2(4)	Ni(5)-O(12)-Ni(1)	93.5(3)	Ni(4)-O(8)-Ni(5)	100.8(4)
Ni(1)-O(4)-Ni(5)	99.2(3)	Ni(1)-O(14)-Ni(3)	94.8(3)	Ni(1)-O(17)-Ni(2)	93.8(3)

Symmetry codes: #1 -x+1/2, -y+1/2, -z.

Table S7 Selected bond lengths for compound **3** (Å).

Ni(1)-O(10)	2.042(11)	Ni(3)-O(5)	2.032(11)	Ni(5)-O(12)	2.010(11)
Ni(1)-N(6)	2.063(15)	Ni(3)-O(12)	2.032(11)	Ni(5)-N(4)	2.030(15)
Ni(1)-O(15)$^{\#1}$	2.082(12)	Ni(3)-O(8)	2.045(13)	Ni(5)-O(23)	2.104(12)
Ni(1)-O(21)	2.092(11)	Ni(3)-O(23)	2.047(12)	Ni(5)-O(4W)	2.117(13)
Ni(1)-O(30)	2.097(12)	Ni(3)-O(2)	2.065(11)	Ni(5)-O(5W)	2.132(13)
Ni(1)-O(3W)	2.170(12)	Ni(3)-O(11)	2.147(11)	Ni(5)-O(9)	2.144(11)
Ni(2)-O(5)	1.998(11)	Ni(4)-O(12)	2.022(11)	Ni(6)-O(5)	2.030(12)
Ni(2)-O(21)	2.049(11)	Ni(4)-O(30)	2.053(12)	Ni(6)-N(1)	2.079(17)
Ni(2)-O(10)	2.066(12)	Ni(4)-O(10)	2.058(12)	Ni(6)-O(2)	2.082(11)
Ni(2)-N(2)	2.070(16)	Ni(4)-N(5)	2.062(14)	Ni(6)-O(27)	2.082(15)
Ni(2)-O(31)	2.106(12)	Ni(4)-O(9)	2.108(12)	Ni(6)-N(3)	2.100(15)
Ni(2)-O(11)	2.251(11)	Ni(4)-O(11)	2.223(11)	Ni(6)-O(31)	2.372(12)

Symmetry codes:#1 -x+1, -y+1, -z+1.

Table S8 Selected bond angles (°) for compound **3**.

O(10)-Ni(1)-N(6)	98.1(5)	O(5)-Ni(3)-O(12)	94.0(5)	O(12)-Ni(5)-N(4)	98.3(6)
O(10)-Ni(1)-O(15)$^{\#1}$	171.9(4)	O(5)-Ni(3)-O(8)	91.7(5)	O(12)-Ni(5)-O(23)	81.8(5)
N(6)-Ni(1)-O(15)$^{\#1}$	89.1(5)	O(12)-Ni(3)-O(8)	92.7(4)	N(4)-Ni(5)-O(23)	178.8(6)
O(10)-Ni(1)-O(21)	81.1(4)	O(5)-Ni(3)-O(23)	173.7(5)	O(12)-Ni(5)-O(4W)	173.2(5)
N(6)-Ni(1)-O(21)	174.9(5)	O(12)-Ni(3)-O(23)	82.7(5)	N(4)-Ni(5)-O(4W)	88.5(6)
O(15)$^{\#1}$-Ni(1)-O(21)	92.0(4)	O(8)-Ni(3)-O(23)	93.8(5)	O(23)-Ni(5)-O(4W)	91.4(5)
O(10)-Ni(1)-O(30)	81.0(5)	O(5)-Ni(3)-O(2)	84.8(5)	O(12)-Ni(5)-O(5W)	89.6(5)
N(6)-Ni(1)-O(30)	96.0(5)	O(12)-Ni(3)-O(2)	175.7(5)	N(4)-Ni(5)-O(5W)	94.2(6)
O(15)$^{\#1}$-Ni(1)-O(30)	94.5(5)	O(8)-Ni(3)-O(2)	91.5(4)	O(23)-Ni(5)-O(5W)	87.0(5)
O(21)-Ni(1)-O(30)	88.9(4)	O(23)-Ni(3)-O(2)	98.1(5)	O(4W)-Ni(5)-O(5W)	89.1(6)
O(10)-Ni(1)-O(3W)	98.5(5)	O(5)-Ni(3)-O(11)	83.2(4)	O(12)-Ni(5)-O(9)	79.8(4)
N(6)-Ni(1)-O(3W)	86.4(5)	O(12)-Ni(3)-O(11)	82.6(4)	N(4)-Ni(5)-O(9)	92.6(6)
O(15)$^{\#1}$-Ni(1)-O(3W)	85.7(5)	O(8)-Ni(3)-O(11)	172.7(4)	O(23)-Ni(5)-O(9)	86.2(5)
O(21)-Ni(1)-O(3W)	88.6(5)	O(23)-Ni(3)-O(11)	91.1(5)	O(4W)-Ni(5)-O(9)	100.8(5)
O(30)-Ni(1)-O(3W)	177.5(5)	O(2)-Ni(3)-O(11)	93.2(4)	O(5W)-Ni(5)-O(9)	168.1(5)
O(5)-Ni(2)-O(21)	169.8(5)	O(12)-Ni(4)-O(30)	169.7(5)	O(5)-Ni(6)-N(1)	95.9(6)
O(5)-Ni(2)-O(10)	95.0(5)	O(12)-Ni(4)-O(10)	97.6(4)	O(5)-Ni(6)-O(2)	84.4(4)
O(21)-Ni(2)-O(10)	81.6(4)	O(30)-Ni(4)-O(10)	81.6(5)	N(1)-Ni(6)-O(2)	168.6(6)
O(5)-Ni(2)-N(2)	97.9(6)	O(12)-Ni(4)-N(5)	97.4(5)	O(5)-Ni(6)-O(27)	84.8(5)
O(21)-Ni(2)-N(2)	92.0(6)	O(30)-Ni(4)-N(5)	92.9(5)	N(1)-Ni(6)-O(27)	96.2(6)
O(10)-Ni(2)-N(2)	93.6(5)	O(10)-Ni(4)-N(5)	95.9(5)	O(2)-Ni(6)-O(27)	95.1(5)
O(5)-Ni(2)-O(31)	81.9(5)	O(12)-Ni(4)-O(9)	80.4(4)	O(5)-Ni(6)-N(3)	173.4(6)
O(21)-Ni(2)-O(31)	99.9(5)	O(30)-Ni(4)-O(9)	98.8(4)	N(1)-Ni(6)-N(3)	89.8(6)
O(10)-Ni(2)-O(31)	170.9(5)	O(10)-Ni(4)-O(9)	171.4(5)	O(2)-Ni(6)-N(3)	90.7(5)
N(2)-Ni(2)-O(31)	95.3(6)	N(5)-Ni(4)-O(9)	92.7(5)	O(27)-Ni(6)-N(3)	91.3(6)
O(5)-Ni(2)-O(11)	81.3(4)	O(12)-Ni(4)-O(11)	80.9(4)	O(5)-Ni(6)-O(31)	74.9(4)
O(21)-Ni(2)-O(11)	88.7(4)	O(30)-Ni(4)-O(11)	88.8(4)	N(1)-Ni(6)-O(31)	89.7(5)
O(10)-Ni(2)-O(11)	81.8(4)	O(10)-Ni(4)-O(11)	82.7(4)	O(2)-Ni(6)-O(31)	79.4(4)
N(2)-Ni(2)-O(11)	175.2(5)	N(5)-Ni(4)-O(11)	177.6(5)	O(27)-Ni(6)-O(31)	159.4(5)
O(31)-Ni(2)-O(11)	89.3(4)	O(9)-Ni(4)-O(11)	88.7(4)	N(3)-Ni(6)-O(31)	108.5(6)
Ni(3)-O(2)-Ni(6)	91.7(4)	Ni(1)-O(10)-Ni(2)	98.7(5)	Ni(5)-O(12)-Ni(3)	98.6(5)
Ni(2)-O(5)-Ni(6)	108.4(5)	Ni(4)-O(10)-Ni(2)	103.0(5)	Ni(4)-O(12)-Ni(3)	103.1(5)
Ni(2)-O(5)-Ni(3)	103.5(5)	Ni(3)-O(11)-Ni(4)	93.2(4)	Ni(2)-O(21)-Ni(1)	97.6(4)
Ni(6)-O(5)-Ni(3)	94.2(5)	Ni(3)-O(11)-Ni(2)	92.0(4)	Ni(3)-O(23)-Ni(5)	95.2(5)
Ni(4)-O(9)-Ni(5)	95.8(4)	Ni(4)-O(11)-Ni(2)	92.3(4)	Ni(4)-O(30)-Ni(1)	97.5(5)
Ni(1)-O(10)-Ni(4)	99.0(5)	Ni(5)-O(12)-Ni(4)	102.9(5)	Ni(2)-O(31)-Ni(6)	93.5(4)

Symmetry codes: #1 -x+1, -y+1, -z+1.

Table S9 Hydrogen bonds for **2** [Å and °].

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
N1—H1*C*···O7	0.9	2.58	3.225(16)	129
N1—H1*C*···O29	0.9	2.45	3.167(15)	137
N1—H1*D*···O10$^{\#1}$	0.9	2.06	2.951(15)	168
N2—H2*D*···O2*W*	0.9	2.26	3.066(16)	148
N3—H3*C*···O1*W*	0.9	2.45	3.260(16)	150
N4—H4*B*···O31	0.9	2.41	3.182(15)	143
N3—H3*B*···O7$^{\#2}$	0.9	2.4	3.262(15)	161
N3—H3*C*···O29$^{\#2}$	0.9	2.56	3.100(14)	119

Symmetry codes: #1 1/2-x, 1/2-y, -z; #2 1/2-x, 1/2+y, 1/2-z.

Table S10 Hydrogen bonds for **3** [Å and °].

D*—H···*A	***D*—H**	**H···*A***	***D*···*A***	***D*—H···*A***
C11—H11*A*···O16	0.93	2.39	3.32(3)	176
C15—H15*A*···O27	0.93	2.34	2.95(3)	123
C5—H5*A*···O24$^{\#1}$	0.93	2.47	3.10(2)	125
C19—H19*A*···O3$^{\#1}$	0.93	2.56	3.35(2)	143
C24—H24*A*···O29$^{\#1}$	0.93	2.54	3.42(2)	158
C28—H28*A*···O25$^{\#1}$	0.93	2.53	3.15(2)	124

Symmetry codes: #1 x, 3/2-y, -1/2+z.