Supplementary Material (ESI) for Chemical Communications

Combination between Lacunary Polyoxometalates and High-Nuclear Transition Metal Clusters Under Hydrothermal Conditions: I. From Isolated Cluster to 1-D Chain

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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. 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 ºC/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 0.5T for **3** and **4** on polycrystalline samples with a Quantum Design PPMS-9T magnetometer. The experimental susceptibilities were corrected for the Pascal's constants. The optical diffuse reflectance spectra of powdered **3** and **4** were measured at room temperature using a Perkin-Elmer Lambda 900 Uv-vis spectrophotometer equipped with an integrating sphere attachment and $BaSO_4$ as reference.

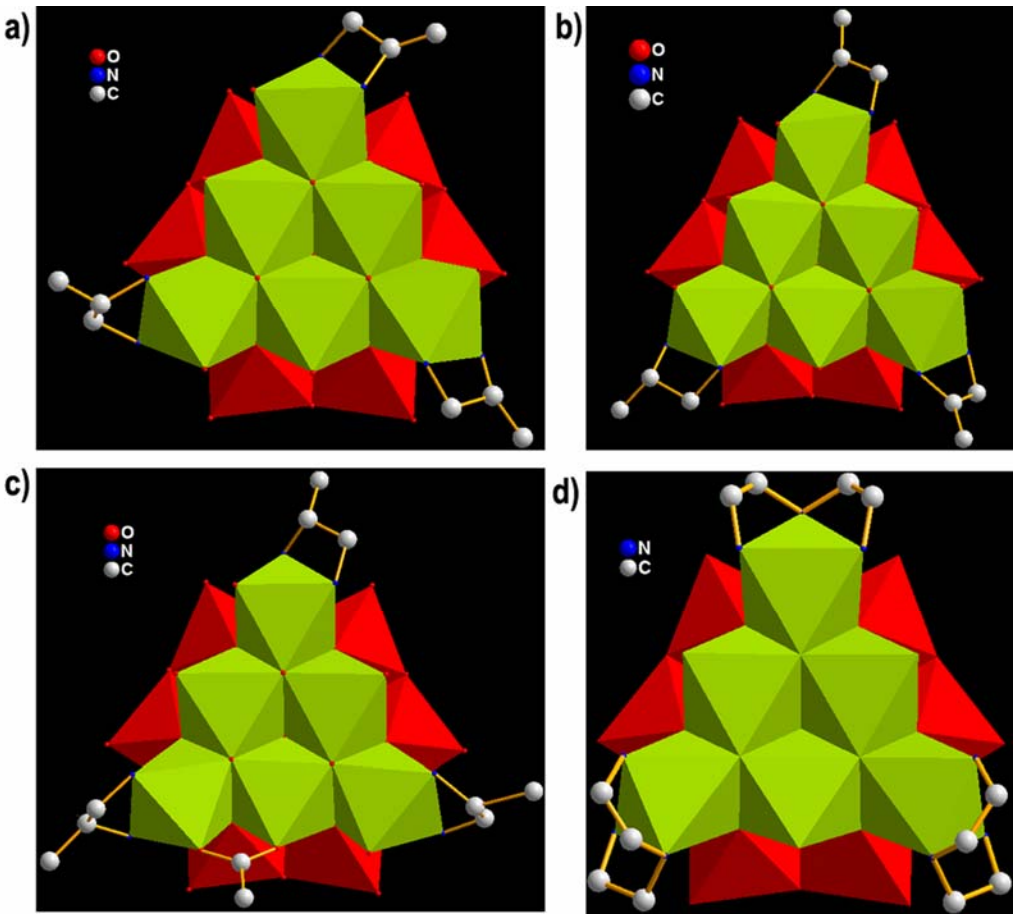

Figure S1. Polyhedral representations of the large hybrid cluster anions of $[Ni_6(\mu_3\text{-}OH)_3(H_2O)_6(enMe)_3(B\text{-}\alpha\text{-}SiW_9O_{34})]$ in **1** (a), $[Ni_6(\mu_3\text{-}OH)_3(H_2O)_6(enMe)_3(B\text{-}\alpha\text{-}SiW_9O_{34})]$ in **2** (b), and $[Ni_6(\mu_3\text{-}OH)_3(H_2O)_4(CH_3COO)(enMe)_3(B\text{-}\alpha\text{-}PW_9O_{34})]$ in **3** (c), as well as large cluster unit of $[Ni_6(\mu_3\text{-}OH)_3(H_2O)_2(dien)_3(B\text{-}\alpha\text{-}PW_9O_{34})]$ in **4** (d), respectively.

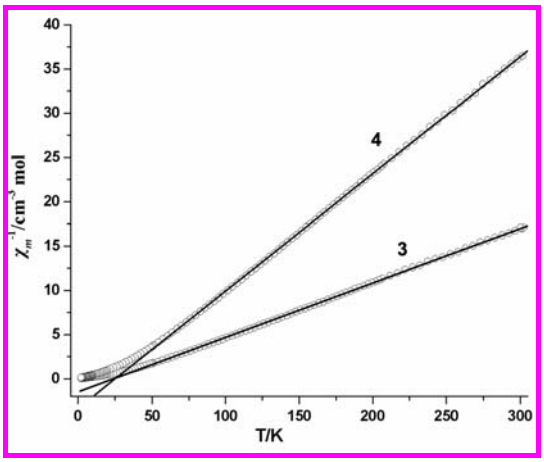

Figure S2. Temperature dependence of χ_m^{-1}(O) for **3** and **4**. The solid lines are the best-fit according to the Curve-Weiss law.

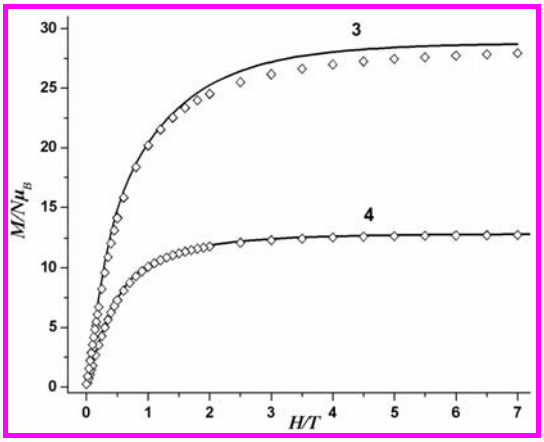

Figure S3. Magnetization measurement, in the reduced form of $M/N\mu_B$, in the field range 0 - 7 T at 2 K of **3** and **4**. The solid lines represent the simulation according to the values obtained from the fit of the susceptibility data.

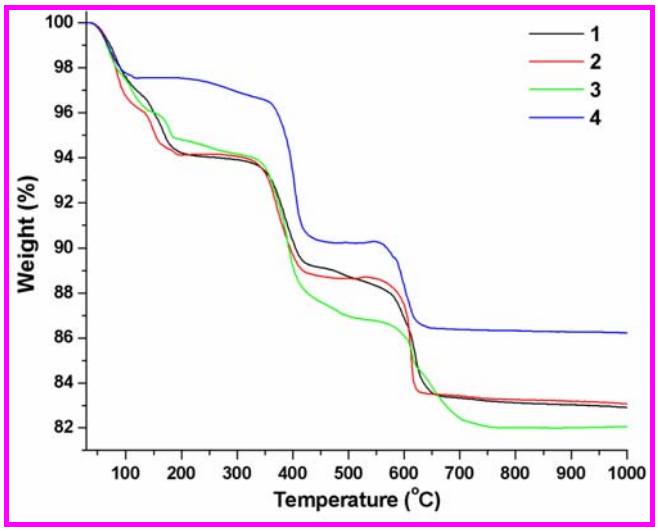

Figure S4. TGA curves of **1-4**

All the TG curves of **1-4** show three major weight loss stages, which are fallen in the regions about 43-210, 245-490 and 549-745 °C, respectively. The whole weight loss processes of **1-4** are attributed to the loss of water molecules and organic lignads. The observed total weight loss (**1**, 15.14%; **2**, 16.43%; **3**, 17.97%; **4**, 13.57%) is in agreement with the calculated value (**1**, 16.94%, corresponding to the loss of 35 water molecules and 6 enMe molecules; **2**, 16.52%, corresponding to the loss of 25 water molecules and 8 enMe molecules; **3**, 17.32%, corresponding to the loss of 23 water molecules, 2 CH_3COOH molecules and 8 enMe molecules; **4**, 14.55%, corresponding to the loss of 7.5 water molecules and 3 dien molecules, respectively).

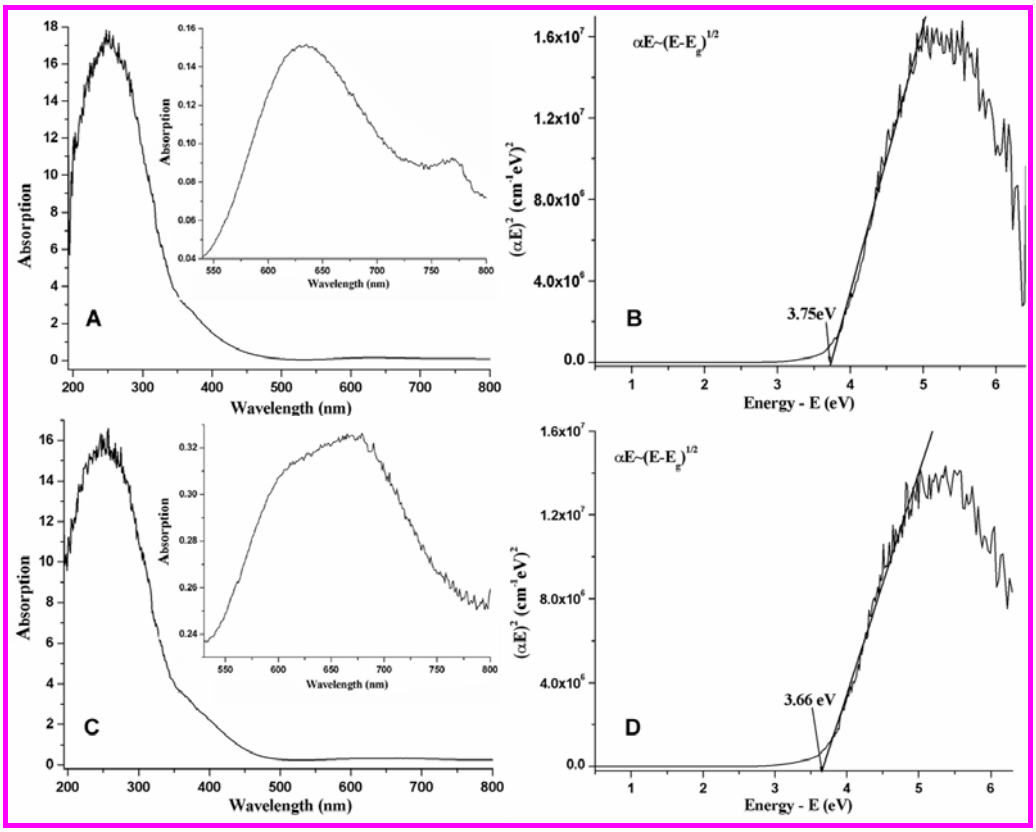

Figure S5. Optical absorption spectra of **3** (A) and **4** (C) and photon energy dependence of $(\alpha E)^2$ for **3** (B) and **4** (D).

Optical absorption spectra of **3** (Fig. S5A) and **4** (Fig. S5C) show one strong absorption bands at ca. 250 nm and a weak broad absorption bands among visible region (inset Fig. S5A, C), which are attributed to the charge transfer of O–W and the d–d transfers of Ni^{2+}, respectively. Based on the observed energy dependence function: $\alpha E = (E - E_g)^{1/2}$ (I. Kosacki, V. Petrovsky, H. U. Anderson, *Appl. Phys. Lett*, **1999**, *74*, 341; J. Tauc, in *Amorphous and Liquid Semiconductors*, edited by J. Tauc, Plenum, New York, **1974**, pp. 159–220), in which α is the absorption coefficient and E_g is the band gap energy, the E_g value can be determined by extrapolation from the linear portion of the absorption edge in a $(\alpha E)^2$ versus energy plot (Fig. S11B, D). The E_g of **3** and **4** are 3.75 and 3.66, respectively. The band gaps of compounds decrease with increasing dimensionality or complexity of the structures, as pointed out by Kanatzidis (E. A. Axtell, Y. Park, K. Chondroudis, M. G. Kanatzidis, *J. Am. Chem. Soc*. **1998**, *120*, 124) and Papavassiliou (G. C. Papavassiliou, *Prog Solid. State. Chem*. **1997**, *25*, 125). The band gap of **3** is slightly larger than that of **4**, which is consistent with their structural dimensionality.

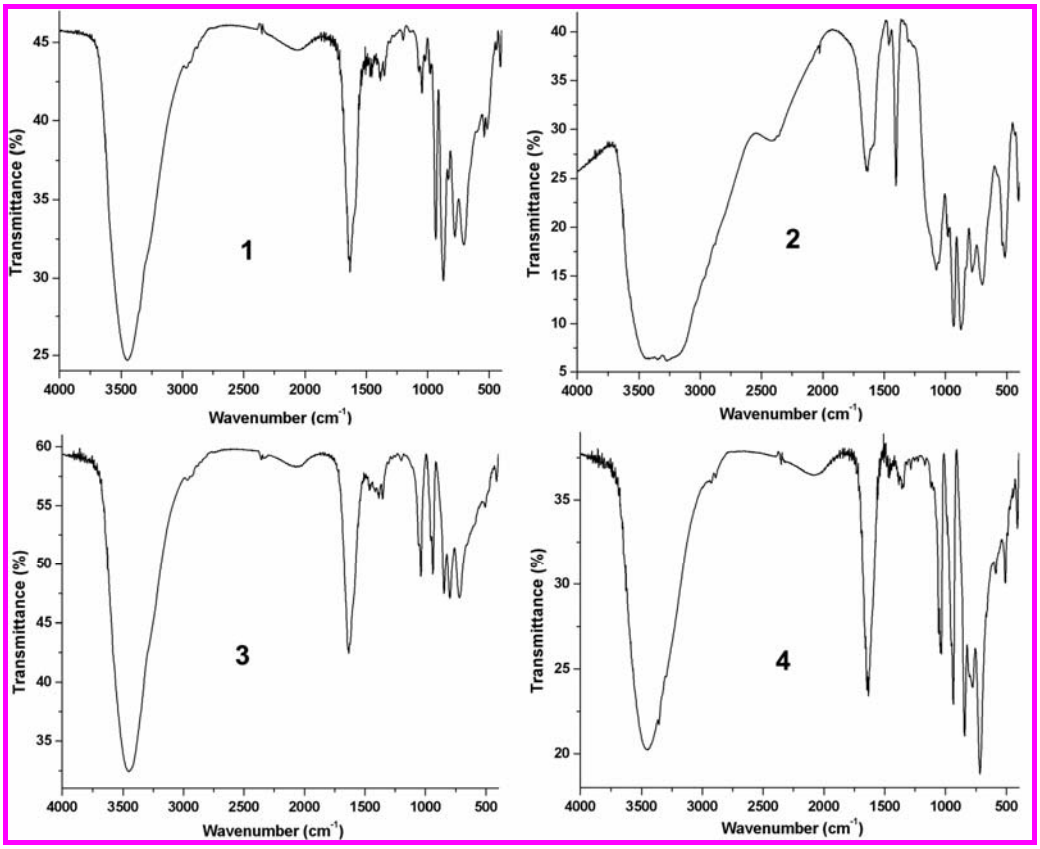

Figure S6. IR spectra of **1-4**.

Each of IR spectra of **1-4** exhibits an intense band at ca. 950 cm^{-1}, attributed to the ν (W=O), and features at ca. 1050 cm^{-1} due to ν (Si-O or P-O), bands in the 400-764 cm^{-1} region are characteristics of *ν* (M-O-M) (M = W or Ni) and *ν* (Ni-O). The characteristics of the NH_2 and CH_2 groups are fallen in the 1300-1500 and 2750-3300 cm^{-1} region.

The detailed description of disordered atoms in compounds 1-4.

Compound 1 (The plots and tables based on 1-622063.cif are given in Figure S7-9 and Table S1-3)

The atoms C4, C5, C7, C8 and C9 of two enMe ligands are disordered and each is modelled over two sites using PART instruction. The displacement and geometrical restraints have been applied to their anisotropic thermal parameters. The occupancies of disordered C4/C4A, C5/C5A, C7/C7A, C8/C8A and C9/C9A atoms are refined as 0.26/0.74, 0.26/ 0.74, 0.54/0.46, 0.54/0.46 and 0.54/0.46, respectively. The H atoms have been included in these disorder models. These disorder models and bond lengths and angles between these disordered atoms are shown in Figure S7-8 and Table S1-2. In addition, the atoms Ni7, OW7, OW8 and OW9 of isolated $[Ni(OW)_6]^{2+}$ complex in **1** are also disordered and modelled over two adjacent positions according to the splitting suggestion of SHELXL.lst file with occupancies of 0.22/0.28, 0.5/0.5, 0.5/0.5 and 0.5/0.5, respectively. It is notable that the Ni7 atom is situated on a center of symmetry (Figure S9 and Table S3). All of the above-mentioned disordered atoms have been refined anisotropically. The H atoms were not

added to all water molecules including the isolated water and terminal water ligands that coordinated to **Ni_6** core.

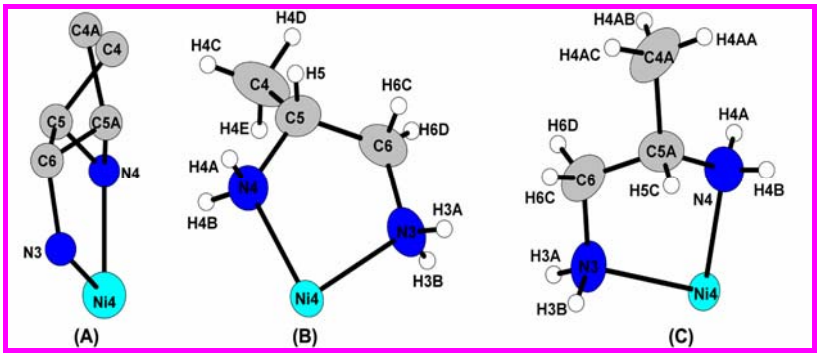

Figure S7. **(A)** View of the disordered model of enMe coordinated to the Ni4 atom of **Ni_6** core of **1**. All the H atoms are omitted for clarity. **(B)** and **(C)** ORTEP view of the two sets of separate disordered models of enMe including H atoms (50% thermal ellipsoids).

Table S1. The bond lengths and angles for the disordered C4 and C5 atoms, respectively.

Bond Lengths	**Å**	**Bond Lengths**	**Å**	**Bond Lengths**	**Å**
C4-C5	1.530	C6-N3	1.464	C5A-N4	1.489
C5-C6	1.525	C4A-C5A	1.547		
C5-N4	1.407	C5A-C6	1.503		
Bond Angles	**(deg)**	**Bond Angles**	**(deg)**	**Bond Angles**	**(deg)**
C4-C5-C6	106.4	N4-C5-C6	109.6	C4A-C5A-C6	108.3
C4-C5-N4	96.8	N4-C5A-C4A	113.8	C6-C5A-N4	106.6

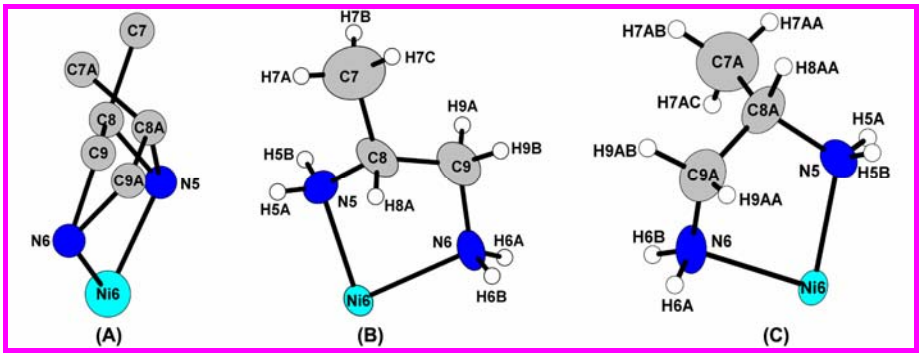

Figure S8. **(A)** View of the disordered model of enMe coordinated to the Ni6 atom of **Ni_6** core of **1**. All the H atoms are omitted for clarity. **(B)** and **(C)** ORTEP view of the two sets of separate disordered models of enMe including H atoms (50% thermal ellipsoids).

Table S2. The bond lengths and angles for the disordered C7, C8 and C9 atoms, respectively.

Bond Lengths	**Å**	**Bond Lengths**	**Å**	**Bond Lengths**	**Å**
C7-C8	1.534	C9-N6	1.513	C8A-N5	1.512
C8-C9	1.511	C7A-C8A	1.533	C9A-N6	1.450
C8-N5	1.514	C8A-C9A	1.529		
Bond Angles	**(deg)**	**Bond Angles**	**(deg)**	**Bond Angles**	**(deg)**

C7-C8-C9	116.8	N5-C8-C9	103.1	C7A-C8A-C9A	115.9
C7-C8-N5	113.0	N5-C8A-C9A	109.3	C7A-C8A-N5	101.4

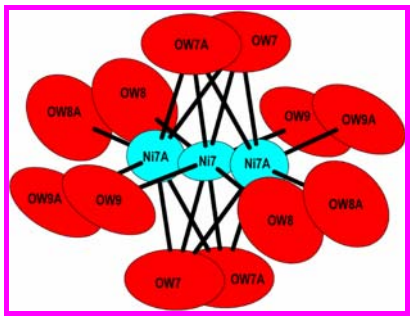

Figure S9. **(A)** ORTEP view of the disordered model of isolated $[Ni(OW)_6]^{2+}$ complex (50% thermal ellipsoids), showing the disordered Ni7 atom is located at the center of symmetry.

Table S3. The bond lengths and angles for the disordered Ni7, OW7, OW8 and OW9 atoms, respectively.

Bond Lengths	Å	Bond Lengths	Å	Bond Lengths	Å
Ni7-OW7	2.079	Ni7-OW9	2.017	Ni7A-OW8A	1.938
Ni7-OW7A	2.102	Ni7A-OW7	2.091	Ni7A-OW9A	1.999
Ni7-OW8	1.832	Ni7A-OW7A	2.375		

Compound 2 (The plots and tables based on 2-622064.cif are given in Figure S10-11 and Table S4-5)

The atoms C1, C2, C3, C4, C5 and C6 of two enMe ligands are disordered and each is modelled over two sites using PART instruction. The displacement and geometrical restraints have been applied to their anisotropic thermal parameters. The occupancies of disordered C1/C1A, C2/C2A, C3/C3A, C4/C4A, C5/C5A and C6/C6A atoms are refined as 0.30/0.70, 0.30/0.70, 0.30/0.70, 0.48/0.52, 0.48/0.52 and 0.48/0.52, respectively. The H atoms have been included in these disorder models. These disorder models and bond lengths and angles between these disordered atoms are shown in Figure S10-11 and Table S4-5, respectively. In addition, some isolated water molecules OW7, OW8, OW9 and OW11 in **2** are also disordered and modelled over two adjacent positions according to the splitting suggestion of SHELXL.lst file with occupancies of 0.5/0.5, 0.5/0.5, 0.25/0.25 and 0.25/0.25, respectively. All of the above-mentioned disordered atoms have been refined anisotropically. The H atoms were not added to all water molecules including the isolated water and terminal water ligands that coordinated to **Ni_6** core.

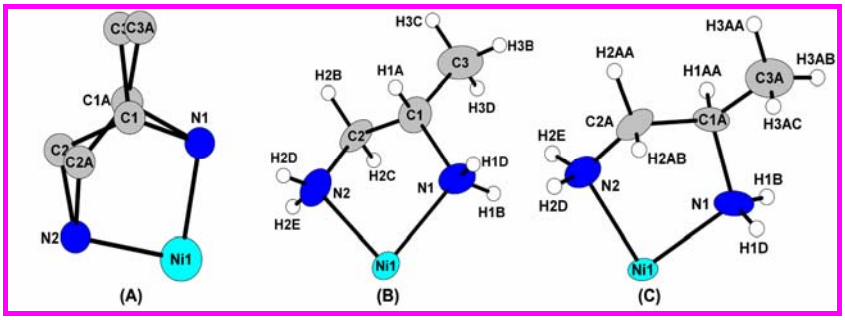

Figure S10. **(A)** View of the disordered model of enMe coordinated to the Ni1 atom of **Ni_6** core of **2**. All the H atoms are omitted for clarity. **(B)** and **(C)** ORTEP view of the two sets of separate disordered models of enMe including H atoms (50% thermal ellipsoids).

Table S4. The bond lengths and angles for the disordered C1, C2 and C3 atoms, respectively.

Bond Lengths	Å	Bond Lengths	Å	Bond Lengths	Å
C1-C3	1.529	C2-N2	1.511	C1A-N1	1.508
C1-C2	1.529	C3A-C1A	1.549	C2A-N2	1.524
C1-N1	1.486	C1A-C2A	1.521		

Bond Angles	(deg)	Bond Angles	(deg)	Bond Angles	(deg)
C3-C1-C2	102.4	N1-C1-C2	113.8	C3A-C1A-C2A	121.1
C3-C1-N1	110.3	N1-C1A-C3A	110.6	C2A-C1A-N1	105.6

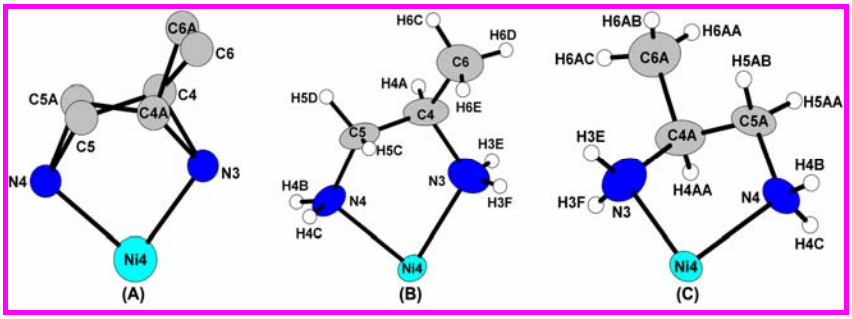

Figure S11. **(A)** View of the disordered model of enMe coordinated to the Ni4 atom of $\mathbf{Ni_6}$ core of **2**. All the H atoms are omitted for clarity. **(B)** and **(C)** ORTEP view of the two sets of separate disordered models of enMe including H atoms (50% thermal ellipsoids).

Table S5. The bond lengths and angles for the disordered C4, C5 and C6 atoms, respectively.

Bond Lengths	Å	Bond Lengths	Å	Bond Lengths	Å
C4-C6	1.538	C5-N4	1.511	C4A-N3	1.556
C4-C5	1.522	C4A-C6A	1.485	C5A-N4	1.473
C4-N3	1.452	C4A-C5A	1.521		
Bond Angles	**(deg)**	**Bond Angles**	**(deg)**	**Bond Angles**	**(deg)**
C6-C4-C5	102.8	N3-C4-C5	106.0	C6A-C4A-C5A	103.1
C6-C4-N3	106.2	N3-C4A-C6A	113.9	C5A-C4A-N3	104.8

Compound 3 (The plots and tables based on 3-622065.cif are given in Figure S12-14 and Table S6-8)

The atoms C2, C3 and C6 of two enMe ligands and C11 of one CH_3COO^- ligand are disordered and each is modelled over two sites using PART instruction. The displacement and geometrical restraints have been applied to their anisotropic thermal parameters. The occupancies of disordered C2/C2A, C3/C3A, C6/C6A and C11/C11A atoms are refined as 0.64/0.36, 0.64/0.36, 0.72/0.28, and 0.57/0.43, respectively. The H atoms have been included in these disorder models. These disordered atoms have been refined anisotropically. These disorder models and bond lengths and angles between these disordered atoms are shown in Figure S12-14 and Table S6-8. In addition, some isolated water molecules OW6, OW7, OW8, OW9 and OW11 in **3** are also refined with statistical disordered. The H atoms were not added to all water molecules including the isolated water and terminal water ligands that coordinated to $\mathbf{Ni_6}$ core.

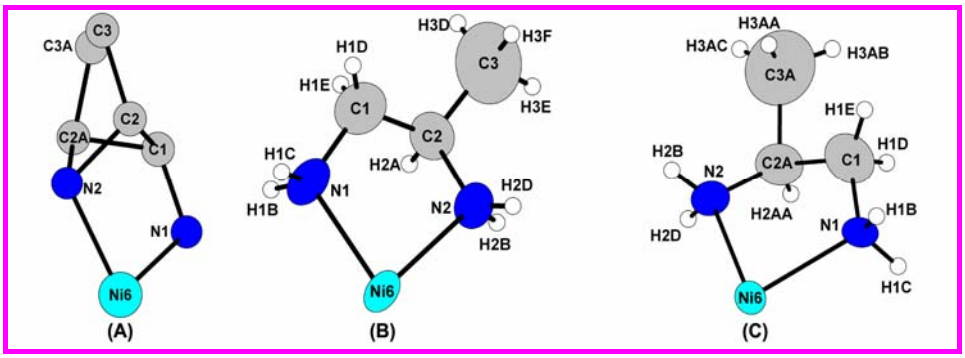

Figure S12. **(A)** View of the disordered model of enMe coordinated to the Ni6 atom of $\mathbf{Ni_6}$ core of **3**. All the H atoms on are omitted for clarity. **(B)** and **(C)** ORTEP view of the two sets of separate disordered models of enMe including H atoms (50% thermal ellipsoids).

Table S6. The bond lengths and angles for the disordered C2 and C3 atoms, respectively.

Bond Lengths	Å	Bond Lengths	Å	Bond Lengths	Å
C1-C2	1.526	C1-N1	1.466	C2A-N2	1.506
C2-C3	1.536	C1-C2A	1.535		
C2-N2	1.566	C2A-C3A	1.539		
Bond Angles	**(deg)**	**Bond Angles**	**(deg)**	**Bond Angles**	**(deg)**
C3-C2-C1	115.2	N2-C2-C1	101.8	C6A-C4A-C5A	103.1
C3-C2-N2	115.5	N3-C4A-C6A	113.9	C5A-C4A-N3	104.8

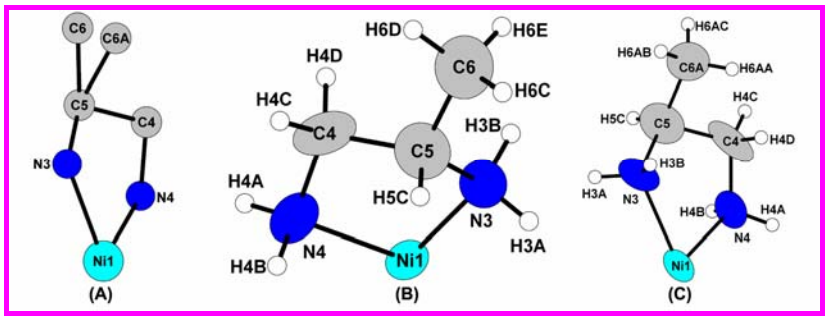

Figure S13. **(A)** View of the disordered model of enMe coordinated to the Ni1 atom of **Ni_6** core of **3**. All the H atoms are omitted for clarity. **(B)** and **(C)** ORTEP view of the two sets of separate disordered models of enMe including H atoms (50% thermal ellipsoids).

Table S7. The bond lengths and angles for the disordered C5 atom, respectively.

Bond Lengths	Å	Bond Lengths	Å	Bond Lengths	Å
C5-C6	1.553	C5-N3	1.447	C5-C6A	1.532
C4-C5	1.522	C4-N4	1.477		
Bond Angles	**(deg)**	**Bond Angles**	**(deg)**	**Bond Angles**	**(deg)**
C6-C5-C4	115.2	N3-C5-C4	108.1	C6A-C5-N3	114.2
C6-C5-N3	114.3	C6A-C5-C4	90.8		

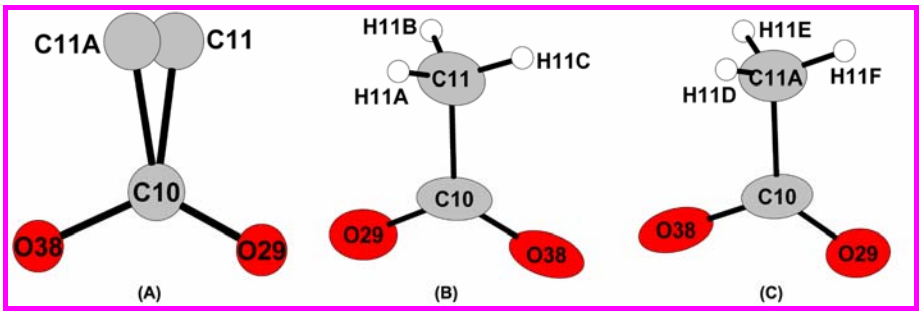

Figure S14. **(A)** View of the disordered model of CH_3COO ligand in **Ni_6** core of **3**. All the H atoms are omitted for clarity. **(B)** and **(C)** ORTEP view of the two sets of separate disordered models of CH_3COO ligand including H atoms (50% thermal ellipsoids).

Table S8. The bond lengths and angles for the disordered C11 atom, respectively.

Bond Lengths	Å	Bond Lengths	Å	Bond Lengths	Å
C11-C10	1.533	C11A-C10	1.544		
Bond Angles	**(deg)**	**Bond Angles**	**(deg)**	**Bond Angles**	**(deg)**
C11-C10-O38	120.4	C11A-C10-O38	105.3		
C11-C10-O29	111.6	C11A-C10-O29	125.6		

Compound 4 (The plots and tables based on 4-622066.cif are given in Figure S15 and Table S9)

The atoms C1 and C2 of one dien ligand are disordered and each is modelled over two sites using PART instruction. The displacement and geometrical restraints have been applied to their anisotropic thermal parameters. The occupancies of disordered C1/C1A and C2/C2A atoms are refined as 0.62/0.38 and 0.62/0.38, respectively. The H atoms have been included in these disorder models. These disorder models and bond lengths and angles between these disordered atoms are shown in Figure S15 and Table S9, respectively. These disordered atoms have been refined anisotropically. In addition, some isolated water molecules OW2 and OW4 in **4** are also disordered and modelled over two adjacent positions according to the splitting suggestion of SHELXL.lst file with occupancies of 0.5/0.5 and 0.25/0.25, respectively. The H atoms were not added to all water molecules including the isolated water and terminal water ligands that coordinated to $\mathbf{Ni_6}$ core.

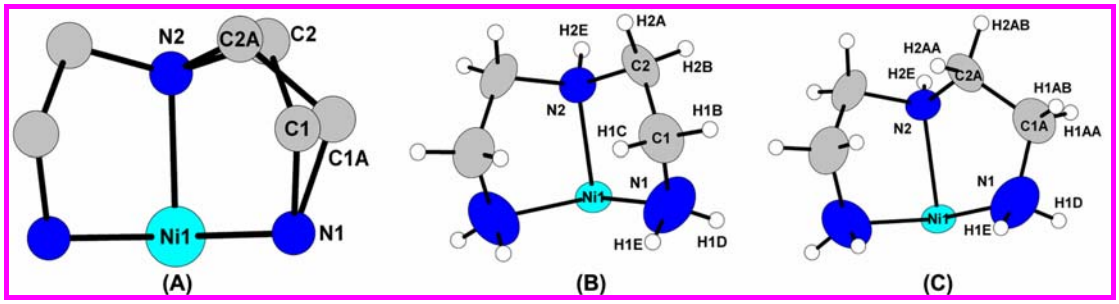

Figure S15. **(A)** View of the disordered model of dien coordinated to Ni1 atom of $\mathbf{Ni_6}$ core of **4**. All the H atoms are omitted for clarity. **(B)** and **(C)** ORTEP view of the two sets of separate disordered models of dien ligand including H atoms (50% thermal ellipsoids).

Table S9. The bond lengths and angles for the disordered C1 and C2 atoms, respectively.

Bond Lengths	**Å**	**Bond Lengths**	**Å**	**Bond Lengths**	**Å**
C1-C2	1.517	N1-C1	1.460	N2-C2	1.442
C1A-C2A	1.529	N1-C1A	1.482	N2-C2A	1.319
Bond Angles	**(deg)**	**Bond Angles**	**(deg)**	**Bond Angles**	**(deg)**
N2-C2-C1	109.2	N1-C1A-C2A	110.8		
N1-C1-C2	107.4	N2-C2A-C1A	110.4		