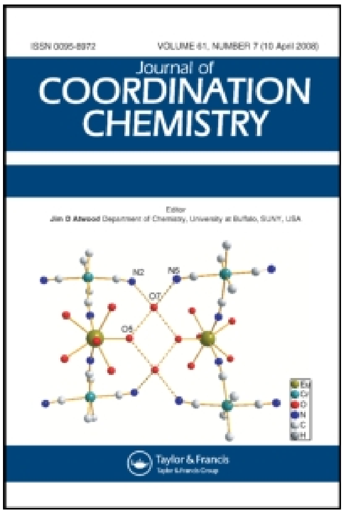

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Two new supramolecular compounds based on Ni(II)-Schiff-base and Keggin-type [PMo$_{12}$O$_{40}$]$^{3-}$

Meilin Wei[a]; Pengfei Zhuang[a]; Ruiping Sun[a]
[a] College of Chemistry and Environmental Science, Henan Normal University, Xinxiang 453007, P.R. China

First published on: 19 August 2010

To cite this Article Wei, Meilin , Zhuang, Pengfei and Sun, Ruiping(2010) 'Two new supramolecular compounds based on Ni(II)-Schiff-base and Keggin-type [PMo$_{12}$O$_{40}$]$^{3-}$', Journal of Coordination Chemistry, 63: 19, 3384 — 3392, First published on: 19 August 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.512384

URL: http://dx.doi.org/10.1080/00958972.2010.512384

Journal of Coordination Chemistry
Vol. 63, No. 19, 10 October 2010, 3384–3392

Two new supramolecular compounds based on Ni(II)-Schiff-base and Keggin-type $[PMo_{12}O_{40}]^{3-}$

MEILIN WEI*, PENGFEI ZHUANG and RUIPING SUN

College of Chemistry and Environmental Science, Henan Normal University,
Xinxiang 453007, P.R. China

(*Received 1 February 2010; in final form 16 June 2010*)

Two polyoxometalate-templated nickel-Schiff-base compounds, $\{[Ni(L)_2]_2[PMo_{12}O_{40}][Cl]\cdot 1.5DMF\cdot H_2O\}_n$ (**1**) and $\{[Ni(L)_2]_2[PMo_{12}O_{40}][Cl]\cdot DMSO\cdot CH_3OH\cdot 0.5H_2O\}_n$ (**2**) (where L is 1,4-*bis*(4-imidazolyl)-2,3-diaza-1,3-butadiene), were synthesized *in situ* from Ni^{2+} and L in $H_2O/DMF/CH_3OH$ or $H_2O/DMSO/CH_3OH$ at room temperature and characterized by elemental analysis, infrared spectroscopy, and single-crystal X-ray diffraction analysis. The results of the single-crystal X-ray diffractions suggested that both compounds have the same packing of the Ni(II)-Schiff-base cation layer and Keggin anion layer. Thermogravimetric analyses suggested that two supramolecular compounds have similar thermal stabilities based on the same packing of the cation and anion layers.

Keywords: Supramolecular compound; Metal Schiff-base; Crystal structure; Polyoxometalate

1. Introduction

Construction of supramolecular assemblies from organic and/or inorganic molecular building blocks has evolved rapidly in coordination chemistry, crystal engineering, and materials science [1–3]. Metal Schiff-base complexes are excellent candidates to construct supramolecular compounds due to their applications [4, 5]. At the same time, polyoxometalates (POMs), as anionic metal-oxide clusters with many applications, are an outstanding class of functional inorganic building blocks in the construction of supramolecular compounds [6–11]. The introduction of metal Schiff-base into the chemistry of POMs opens a new direction for supramolecular compounds and hybrid materials. However, reports on the combination of these two interesting fields, to prepare new hybrid materials, have been unexplored [12–14]. A prominent subclass of POMs is polyoxomolybdates which present a range of intriguing topologies and structures, and whose spherical surfaces give an opportunity for forming coordination bonds or hydrogen bonds [15]. Representative examples include $[Cu(DF)_2]_3[PMo_{12}O_{40}]$ [15d], $[Cu^{I}(bpy)_2]_2\{[Cu^{II}(bpy)]_2PMo_3^{V}Mo_9^{VI}O_{40}\}$ [15c], and $[HN(C_2H_5)_3]_3[PMo_{12}O_{40}]$ [15a]. In addition, polyoxomolybdates are suitable building blocks for POM-metal-Schiff-base compounds [12–14]. To understand the correlation

---

*Corresponding author. Email: weimeilin@henannu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2010.512384

of the influence of polyanions on the resultant structures in different solvents, herein, Ni^{2+} ions, 1,4-*bis*(4-imidazolyl)-2,3-diaza-1,3-butadiene and Keggin-type $[PMo_{12}O_{40}]^{3-}$ polyanions were chosen to construct POM-metal-Schiff-base compounds. Such composite materials present the opportunity to generate *in situ* novel nanoscopic assemblies from small units and have potential for use in materials science by incorporation of their own physical and chemical properties.

2. Experimental

2.1. *Materials and measurements*

All organic solvents and materials, used for syntheses, were of reagent grade and used without purification. According to a literature method [16], α-$H_3PMo_{12}O_{40} \cdot 6H_2O$ was prepared and it was characterized by infrared (IR) spectrum and thermogravimetric (TG) analysis. According to literature method, 1,4-*bis*(4-imidazolyl)-2,3-diaza-1,3-butadiene was synthesized [17]. Elemental analyses were carried out on a Perkin Elmer 240C analyzer for C, H, and N. IR spectra were recorded on a VECTOR 22 Bruker spectrophotometer with KBr pellets from 400 to 4000 cm^{-1}. TG analyses were carried out on a Perkin Elmer thermal analyzer in an atmosphere of N_2 with a heating rate of 10°C min^{-1}.

2.2. *Synthesis of* $\{[Ni(L)_2]_2[PMo_{12}O_{40}][Cl] \cdot 1.5DMF \cdot H_2O\}_n$ *(1)*

The formation of heteropolyacid nickel salts was accomplished by neutralization of α-$H_3PMo_{12}O_{40} \cdot 6H_2O$ (40 mg, 0.02 mmol) and by adding $NiCl_2 \cdot 6H_2O$ (8 mg, 0.03 mmol) dissolved in water (2 mL). The solution was heated at 80°C in a water bath. Yellow crystals were formed by cooling the saturated solution and slow evaporation at room temperature, and characterized by IR spectrum. Compound **1** was prepared by the layering method. A buffer layer of a solution (10 mL) methanol : water (1 : 1, v/v) was carefully layered over 4 mL of a DMF solution of L (12 mg, 0.06 mmol), and then a methanol solution (4 mL) of resultant heteropolyacid nickel salts was carefully layered over the buffer layer. Black block crystals appeared after 2 weeks and were collected. Yield: 77% based on α-$H_3PMo_{12}O_{40} \cdot 6H_2O$. Anal. Calcd for $C_{36.5}H_{44.5}N_{25.5}O_{42.5}Ni_2Mo_{12}PCl$ (%): C, 15.34; H, 1.56; N, 12.50. Found (%): C, 15.16; H, 1.47; N, 12.35. IR (KBr) ν, cm^{-1}: four characteristic vibrations resulting from heteropolyanions with the Keggin structure: 786 ν(Mo–Oc), 878 ν(Mo–Ob), 950 ν(Mo=Ot), and 1075 ν(P–Oa); and vibrations resulting from the L molecules: 3367 ν(N–H), 3125 ν(=C–H), and 1617 ν(C=N).

2.3. *Synthesis of* $\{[Ni(L)_2]_2[PMo_{12}O_{40}][Cl] \cdot DMSO \cdot CH_3OH \cdot 0.5H_2O\}_n$ *(2)*

Compound **2** was prepared in the same way as for **1** using DMSO instead of DMF. Black crystals appeared after 2 weeks and were collected. Yield: 75% based on α-$H_3PMo_{12}O_{40} \cdot 6H_2O$. Anal. Calcd for $C_{35}H_{43}N_{24}O_{42.5}Ni_2Mo_{12}PClS$ (%): C, 14.75; H, 1.51; N, 11.80. Found (%): C, 14.66; H, 1.40; N, 11.65. IR (KBr) ν, cm^{-1}: four

Table 1. Crystal data and structure refinements for **1** and **2**.

	1	**2**
Empirical formula	$C_{36.5}H_{44.5}N_{25.5}O_{42.5}Ni_2Mo_{12}PCl$	$C_{35}H_{43}N_{24}O_{42.5}Ni_2Mo_{12}PClS$
Formula weight	2855.60	2847.11
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	14.625(10)	14.882(7)
b	22.914(17)	22.299(10)
c	15.183(11)	15.330(7)
β	113.633(12)	113.677(7)
Volume (Å^3), Z	4661(6), 2	4659(4), 2
Calculated density (g cm^{-3})	2.034	2.030
Absorption coefficient (mm^{-1})	2.083	2.105
$F(000)$	2748	2738
Reflections measured	22,228	22,036
Independent reflection	8195 [$R(\text{int}) = 0.0596$]	8151 [$R(\text{int}) = 0.0595$]
Parameter refined	569	555
Goodness-of-fit on F^2	0.988	1.035
Final R indices [$I \geq 2\sigma(I)$]	$R_1 = 0.0786$, $wR_2 = 0.1599$	$R_1 = 0.0983$, $wR_2 = 0.2054$
Largest difference peak and hole (e Å^{-3})	1.394 and −0.787	2.097 and −1.255

characteristic vibrations resulting from heteropolyanions with the Keggin structure: 786 ν(Mo–Oc), 877 ν(Mo–Ob), 951 ν(Mo=Ot), and 1074 ν(P–Oa); and vibrations resulting from the L molecules: 3367 ν(N–H), 3124 ν(=C–H), and 1616 ν(C=N).

2.4. *Crystal structure and determination*

Intensity data of **1** and **2** were collected on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using SMART and SAINT [18]. The structure was solved by direct methods and refined on F^2 by using full-matrix least-squares method with SHELXTL version 5.1 [19]. For **1** and **2**, all non-hydrogen atoms except disordered atoms of the L, Cl^{-1} and solvent molecules were refined anisotropically; C4, C5, N3, N4, C4′, C5′, N3′, and N4′ of L were refined disordered with the site occupancy factors (SOF) being fixed at 0.5. Hydrogens of organic molecules were localized in their calculated positions and refined using a riding model. Hydrogens of water were not treated. The crystal parameters, data collection and refinement results for both compounds are summarized in table 1. The selected bond lengths and angles are listed in tables 2 and 3, respectively. The hydrogen bond parameters are listed in table 4.

3. Results and discussion

3.1. *Structure description*

Molecular structures of **1** and **2**, $\{[Ni(L)_2]_2[PMo_{12}O_{40}][Cl] \cdot 1.5DMF \cdot H_2O\}_n$ and $\{[Ni(L)_2]_2[PMo_{12}O_{40}][Cl] \cdot DMSO \cdot CH_3OH \cdot 0.5H_2O\}_n$, were confirmed by X-ray

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

P(1)–O(1)	1.531(10)	Ni(1)–N(9)	2.063(7)	O(6)–Mo(1)–O(3)	64.0(3)
P(1)–O(4)	1.510(8)	Ni(1)–N(3)	2.150(13)	O(7)–Mo(1)–O(3)	90.8(3)
P(1)–O(2)	1.550(10)	O(1)–P(1)–O(2)	105.7(5)	N(4′)–Ni(1)–N(5)	71.4(5)
P(1)–O(3)	1.442(10)	O(4)–P(1)–O(2)	106.0(5)	N(12)–Ni(1)–N(5)	91.4(3)
Mo(1)–O(9)	1.659(7)	O(3)–P(1)–O(2)[#1]	108.6(6)	N(12)–Ni(1)–N(2)	92.4(3)
Mo(1)–O(6)	1.876(8)	O(4)–P(1)–O(3)[#1]	112.0(5)	N(4′)–Ni(1)–N(8)	95.1(4)
Mo(1)–O(7)	1.915(7)	O(1)–P(1)–O(4)	108.5(5)	N(5)–Ni(1)–N(8)	90.4(3)
Mo(1)–O(5)	1.890(6)	O(1)–P(1)–O(3)[#1]	115.5(5)	N(2)–Ni(1)–N(8)	88.2(3)
Mo(1)–O(8)	1.915(7)	O(6)–Mo(1)–O(7)	88.0(3)	N(12)–Ni(1)–N(9)	89.4(4)
Mo(1)–O(4)	2.407(10)	O(6)–Mo(1)–O(5)	89.1(3)	N(5)–Ni(1)–N(9)	95.4(3)
Mo(1)–O(3)	2.481(9)	O(7)–Mo(1)–O(8)	87.0(3)	N(2)–Ni(1)–N(9)	95.7(3)
Ni(1)–N(4′)	2.009(13)	O(5)–Mo(1)–O(8)	86.1(3)	N(8)–Ni(1)–N(9)	78.7(3)
Ni(1)–N(12)	2.021(7)	O(6)–Mo(1)–O(4)	93.8(3)	N(2)–Ni(1)–N(3)	73.8(4)
Ni(1)–N(5)	2.033(10)	O(7)–Mo(1)–O(4)	65.2(3)	N(12)–Ni(1)–N(3)	95.5(4)
Ni(1)–N(2)	2.037(8)	O(5)–Mo(1)–O(4)	91.3(3)	N(5)–Ni(1)–N(3)	94.8(4)
Ni(1)–N(8)	2.064(8)	O(8)–Mo(1)–O(4)	63.2(3)	N(8)–Ni(1)–N(3)	96.4(4)

[#1] $-x+1$, $-y+2$, and $-z$.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

P(1)–O(1)	1.515(13)	Ni(1)–N(9)	2.083(11)	O(6)–Mo(1)–O(3)	63.4(4)
P(1)–O(4)	1.526(11)	Ni(1)–N(3)	2.192(13)	O(7)–Mo(1)–O(3)	93.2(3)
P(1)–O(2)	1.558(12)	O(1)–P(1)–O(2)	108.7(7)	N(4′)–Ni(1)–N(5)	71.2(6)
P(1)–O(3)	1.535(11)	O(4)–P(1)–O(2)	107.7(6)	N(12)–Ni(1)–N(5)	92.8(4)
Mo(1)–O(9)	1.659(7)	O(3)–P(1)–O(2)[#1]	107.1(6)	N(12)–Ni(1)–N(2)	90.3(4)
Mo(1)–O(6)	1.876(8)	O(4)–P(1)–O(3)[#1]	109.6(7)	N(4′)–Ni(1)–N(8)	94.9(5)
Mo(1)–O(7)	1.896(8)	O(1)–P(1)–O(4)	110.6(6)	N(5)–Ni(1)–N(8)	91.1(4)
Mo(1)–O(5)	1.914(8)	O(1)–P(1)–O(3)[#1]	112.9(6)	N(2)–Ni(1)–N(8)	87.8(4)
Mo(1)–O(8)	1.917(8)	O(6)–Mo(1)–O(7)	91.1(4)	N(12)–Ni(1)–N(9)	89.4(4)
Mo(1)–O(4)	2.461(12)	O(6)–Mo(1)–O(5)	88.5(3)	N(5)–Ni(1)–N(9)	94.4(5)
Mo(1)–O(3)	2.473(9)	O(7)–Mo(1)–O(8)	85.8(4)	N(2)–Ni(1)–N(9)	94.8(4)
Ni(1)–N(4′)	1.997(16)	O(5)–Mo(1)–O(8)	85.5(4)	N(8)–Ni(1)–N(9)	78.4(4)
Ni(1)–N(12)	2.029(8)	O(6)–Mo(1)–O(4)	95.5(4)	N(2)–Ni(1)–N(3)	75.5(5)
Ni(1)–N(5)	2.030(12)	O(7)–Mo(1)–O(4)	65.1(4)	N(12)–Ni(1)–N(3)	96.3(4)
Ni(1)–N(2)	2.040(10)	O(5)–Mo(1)–O(4)	91.8(4)	N(5)–Ni(1)–N(3)	95.1(5)
Ni(1)–N(8)	2.063(10)	O(8)–Mo(1)–O(4)	62.4(4)	N(8)–Ni(1)–N(3)	95.3(4)

[#1] $-x+1$, $-y+1$, and $-z+2$.

Table 4. Selected hydrogen bond lengths (Å) in **1** and **2**.

D–H···A	d(D–H)	d(H···A)	∠D–H···A	d(D···A)	Symmetry
1					
N(1)···H(1A)···N(4)	0.860	2.221	150.44	2.999	$(x, -y+3/2, z+1/2)$
N(1)···H(1A)···N(3′)	0.860	2.450	148.12	3.213	$(x, -y+3/2, z+1/2)$
N(6)···H(6A)···Cl(2)	0.860	1.993	156.89	2.805	$(x-1, y, z-1)$
N(7)···H(7A)···Cl(1)	0.860	1.918	165.12	2.758	$(x-1, y, z-1)$
N(11)···H(11A)···O(23)	0.860	2.055	164.81	2.894	$(x, -y+3/2, z-1/2)$
2					
N(1)···H(1A)···N(4)	0.860	2.224	150.66	3.004	$(x, -y+3/2, z+1/2)$
N(1)···H(1A)···N(3′)	0.860	2.435	149.90	3.208	$(x, -y+3/2, z+1/2)$
N(6)···H(6A)···Cl(2′)	0.860	2.073	150.42	2.852	$(x-1, y, z-1)$
N(6)···H(6A)···Cl(2)	0.860	2.339	150.81	3.118	$(x-1, y, z-1)$
N(7)···H(7A)···Cl(1)	0.860	1.929	172.53	2.784	$(x-1, y, z-1)$
N(11)···H(11A)···O(23)	0.860	1.945	160.79	2.772	$(x-1, y, z-1/2)$

single crystal structure analyses. Single crystal X-ray diffractions suggested the compounds crystallized in monoclinic space group $P2_1/c$ and had the same packing of the metal Schiff-base cation layer and Keggin anion layer, the same Cl^- serving as counter-anion and different solvent molecules. Figure 1 shows the unit of **1** with atom numbering scheme and **2** has the same atom numbering. Each molecular unit of **1** consists of two $[Ni(L)_2]^{2+}$, one $[PMo_{12}O_{40}]^{3-}$, one Cl^- anion, one and a half DMF, and one crystal water. Each molecular unit of **2** consists of two $[Ni(L)_2]^{2+}$, one $[PMo_{12}O_{40}]^{3-}$, Cl^- anion, one DMSO, half a crystal water, and one methanol. The polyoxoanion $[PMo_{12}O_{40}]^{3-}$ is wholly enwrapped by the two $[Ni(L)_2]^{2+}$ moieties, connected *via* electrostatic attraction. The novelty of **1** and **2** is based on the fact that $[Ni(L)_2]^{2+}$ serves as the cation and the molecular structure contains two cations per polyanion instead of only one, rarely seen in POM-metal-Schiff-base chemistry [13, 14].

In $[Ni(L)_2]^{2+}$, as shown in figure 1, the Ni^{2+} is linked to two L in a distorted octahedral geometry, coordinated by two nitrogens (N(9), N(3) or N(4′)) from two different imine groups and four nitrogens (N(2), N(5), N(8), and N(12)) from four imidazole rings. Coplanar N(2), N(9), N(5), N(3) or N(2), N(9), N(5), N(4′) form the equatorial plane, N(12) and N(8) are axial. The average Ni(1)–N bond length is 2.054 Å for **1** and 2.035 Å for **2**, respectively. The dihedral angle between N(6) ring (the N(6)-containing imidazole ring) and N(1) ring (the N(1)-containing imidazole ring) of one L ligand is 10.2° for **1** and 11.6° for **2**; that between N(7) ring (the N(7)-containing imidazole ring) and N(11) ring (the N(11)-containing imidazole ring) of the other L is 3.3° for **1** and 12.3° for **2**, indicating that the two imidazole groups of each ligand are almost coplanar. The torsion angle between C(4)–N(3)–N(4)–C(5) is −179.6° for **1** and −172.9° for **2**, that between C(4′)–N(3′)–N(4′)–C(5′) is 174.0° for **1** and 178.0° for **2**, and that between C(12)–N(9)–N(10)–C(13) is −179.9° for **1** and 176.9° for **2**, respectively. The $[Ni(L)_2]^{2+}$ are generated *in situ* from Ni^{2+} and L in $H_2O/DMF/CH_3OH$ or $H_2O/DMSO/CH_3OH$ solvents at room temperature, different from the reaction system of $[N(CH_3)_4]_2[Mn(Salen)(DMF)_2]_2[\beta\text{-}Mo_8O_{26}] \cdot 2DMF$ based on ready-made metal Schiff-base building blocks $[MnIII(Salen)(DMF)_2]^+$ [13] and that of the $[Ag_2L_2][(n\text{-}C_4H_9)_4N][PMo_{12}O_{40}] \cdot H_2O \cdot 0.5CH_3OH \cdot 0.25DMF$ based on $[Ag_2L_2]^{2+}$ [14]. As far as we know, this method has not been used before in POM-based chemistry. As shown in figure 2, $[NiL_2]^{2+}$ monomers form a zigzag chain through hydrogen bonds between uncoordinated nitrogen N(1C) of imidazole from one $[NiL_2]^{2+}$ and nitrogens N(4A) and N(3′A) of imine groups from adjacent $[NiL_2]^{2+}$. The Ni1A $\cdots$ Ni1C separation between two adjacent $[NiL_2]^{2+}$ monomers in the chain is 9.7 Å. Packing of the chains revealed that each chain interacted with neighboring chains *via* weak π–π and N–H $\cdots$ π interactions to form a 3-D cationic network (figure 3). The interacting N(7) rings, related by π–π interactions, were antiparallel with a center-to-center separation of 4.8 Å. For N–H $\cdots$ π interactions between imidazole rings, the distance of N(7) $\cdots$ M (M is the center of the imidazole ring) was 4.4 Å. The Ni1P $\cdots$ Ni1F separation between two adjacent chains is 10.6 Å and the Ni1P $\cdots$ Ni1C separation is 12.0 Å.

In the unit cells of **1** and **2**, the metal Schiff-base cation layer and Keggin anion layer are regularly arranged along the *a*-axis. Every Keggin anion is surrounded by two complex cations. The cationic layer with formula $[NiL_2]_n^{2n+}$ is formed by cationic chains with two successive cationic layers antiparallel to each other. The difference is interlaced ring direction of the $[NiL_2]^{2+}$ monomer. The anionic layer $[NiL_2]_n^{3n-}$ is formed by isolated Keggin polyanions. So, the whole packing arrangement of two compounds can

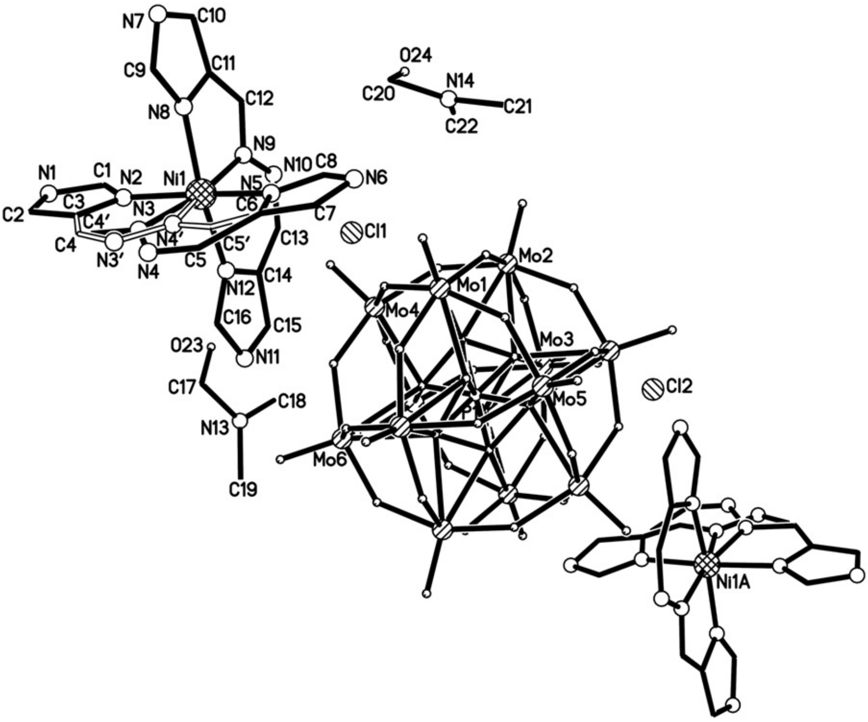

Figure 1. The ball-and-stick representation of the structural unit of **1**, as well as representative coordinated cation $[Ni(L)_2]^{2+}$ unit in the title compounds. All hydrogens and some solvent molecules have been omitted for clarity.

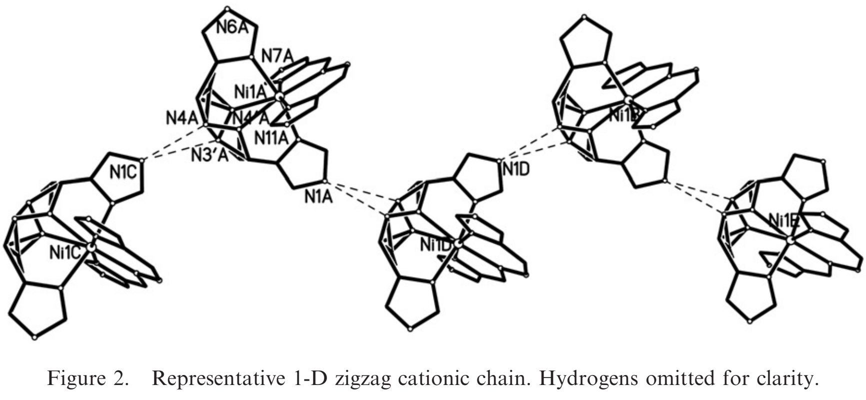

Figure 2. Representative 1-D zigzag cationic chain. Hydrogens omitted for clarity.

be viewed as "AAB" style (as shown in figure 4). The cohesion between the two layers is from electrostatic forces, π–π and N–H $\cdots \pi$ interactions. L hardly dissolved in usual organic solvent, such as CH_3OH, and slightly dissolved in DMF and DMSO so we selected H_2O/DMF/CH_3OH or H_2O/DMSO/CH_3OH mixture solvents to prepare **1** and **2** based on the layer method. The results of the single crystal X-ray diffractions suggest

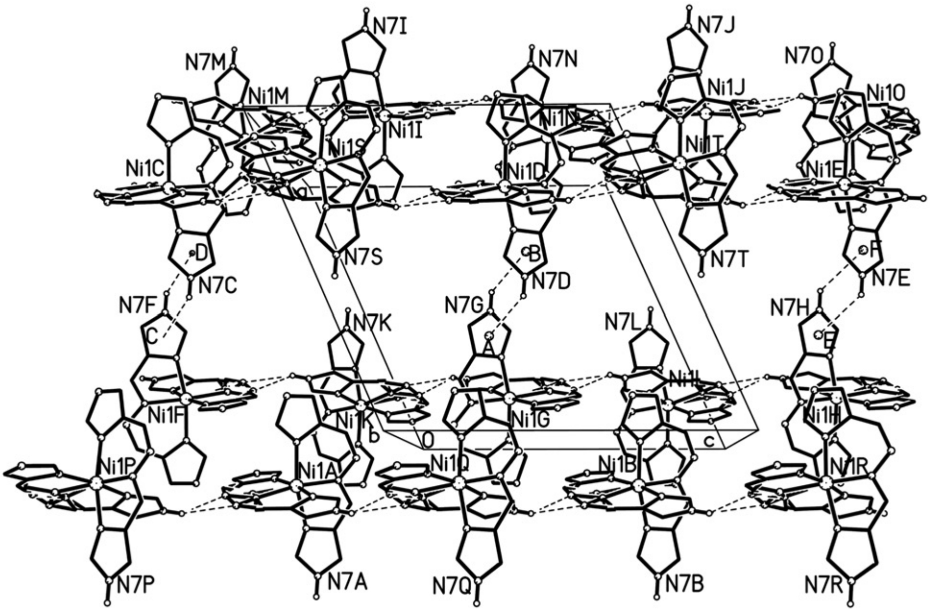

Figure 3. Packing of cationic chains along the *a*-axis. Hydrogens omitted for clarity.

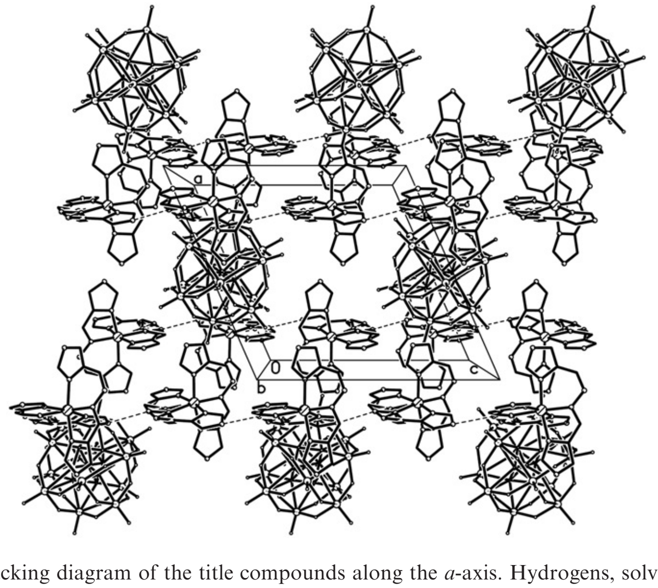

Figure 4. The packing diagram of the title compounds along the *a*-axis. Hydrogens, solvent, and Cl^- have been omitted for clarity.

that two composite compounds have the same packing of the Ni(II)-Schiff-base layer and Keggin layer; that DMF in **1** stays inside the voids based on the hydrogen bond between its O(23) and N(11) from L, and the DMSO in **2** also stays inside the voids based on the hydrogen bond between its oxygen O(23) and N(11) from L. Water or methanol also fill voids just as solvent. Consequently, solvent molecules are unimportant for the crystal structures of two compounds. The Cl^- serves as counter-anion residing near $[PMo_{12}O_{40}]^{3-}$ and $[NiL_2]^{2+}$ for charge balance.

In **1**, the P–O and Mo–O bond lengths are 1.442(10)–1.550(10) and 1.632(6)–2.511(10) Å, respectively, and in **2**, 1.515(13)–1.558(12) and 1.617(8)–2.508(13) Å, respectively. The O–P–O angles are 105.7(5)–115.5(5)° for **1** and 107.1(6)–112.9(6)° for **2**. All these results indicate that $[PMo_{12}O_{40}]^{3-}$ has a normal Keggin structure [11, 14].

3.2. *TG analyses*

TG analysis of the powder from crystalline **1** in an atmosphere of N_2 (Supplementary material) shows a slow weight loss of 3.96% from 25°C to 250°C, corresponding to one water and one and a half DMF molecules (Calcd 3.83%). The anhydrous product begins to decompose at 250°C. TG analysis of **2** shows a slow weight loss of 4.13% at 25−270°C, corresponding to one methanol, half a water and one DMSO (Calcd 4.18%); the anhydrous product begins to decompose at 270°C. TG analyses suggest that compounds have similar thermal stabilities based on the same packing of the Ni(II)-Schiff-base cation layer and Keggin anion layer.

4. Conclusions

We constructed two layered supramolecular compounds by *in situ* combining two traditional but distinct building blocks, metal Schiff-base cations and Keggin-type anions. This research represents a new and rare example of introducing the metal Schiff base generated *in situ* into POMs chemistry, opening a pathway for design and synthesis of multifunctional hybrid materials based on metal Schiff-base complexes and POMs.

Supplementary material

Crystallographic data for **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre, CCDC-764012 (**1**) and CCDC-764013 (**2**). The data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223/336 033; Email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk/conts/retrieving.html

Acknowledgments

This study is supported by the National Natural Science Foundation of China (grant no. 20971038) and the Natural Science Foundation of the Education Department of Henan Province (no. 2009A 150015).

References

[1] J.C. MacDonald, G.M. Whitesides. *Chem. Rev.*, **94**, 2383 (1994).

[2] N.L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, O.M. Yaghi. *J. Am. Chem. Soc.*, **127**, 1504 (2005).

[3] B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001).

[4] H. Miyasaka, A. Saitoh, S. Abe. *Coord. Chem. Rev.*, **251**, 2622 (2007).

[5] K.C. Gupta, A.K. Sutar. *Coord. Chem. Rev.*, **252**, 1420 (2008).

[6] D. Long, E. Burkholder, L. Cronin. *Chem. Soc. Rev.*, **36**, 105 (2007).

[7] C. Jiang, A. Lesbani, R. Kawamoto, S. Uchida, N. Mizuno. *J. Am. Chem. Soc.*, **127**, 14240 (2006).

[8] Y.-G. Li, L.-M. Dai, Y.-H. Wang, X.-L. Wang, E.-B. Wang, Z.-M. Su, L. Xu. *Chem. Commun.*, 2593 (2007).

[9] J. Kang, B. Xu, Z. Peng, X. Zhu, Y. Wei, D.R. Powell. *Angew. Chem., Int. Ed.*, **44**, 6902 (2005).

[10] X.-J. Kong, Y.-P. Ren, P.-Q. Zheng, Y.-X. Long, L.-S. Long, R.-B. Huang, L.-S. Zheng. *Inorg. Chem.*, **45**, 10702 (2006).

[11] (a) M.-L. Wei, C. He, W.-J. Hua, C.-Y. Duan, S.-H. Li, Q.-J. Meng. *J. Am. Chem. Soc.*, **128**, 13318 (2006); (b) M.-L. Wei, C. He, Q.-Z. Sun, Q.-J. Meng, C.-Y. Duan. *Inorg. Chem.*, **46**, 5957 (2007); (c) M.-L. Wei, R.-P. Sun, K. Jiang, L. Yang. *J. Coord. Chem.*, **61**, 3800 (2008); (d) M.-L. Wei, H.Y. Xu, R.-P. Sun. *J. Coord. Chem.*, **62**, 1989 (2009); (e) M.-L. Wei, H.Y. Xu, R.-P. Sun. *Chin. J. Struct. Chem.*, **28**, 978 (2009).

[12] V. Mirkhani, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Baltork, N. Rasouli. *Inorg. Chem. Commun.*, **10**, 1537 (2007).

[13] Y.W. Li, Y.H. Wang, Y.G. Li, E.B. Wang. *Inorg. Chem. Commun.*, **12**, 112 (2009).

[14] M.-L. Wei, R.-P. Sun, P.-F. Zhuang, Y.-H. Yang. *Russian J. Coord. Chem.*, **35**, 885 (2009).

[15] (a) S.-Y. Shi, J.-N. Xu, W.-Y. Ma, X.-B. Cui, Y. Wang, G.-W. Wang, J.-Q. Xu. *J. Coord. Chem.*, **62**, 3885 (2009); (b) H.-L. Chen, Y. Ding, X.-X. Xu, E.-B. Wang, W.-L. Chen, S. Chang, X.-L. Wang. *J. Coord. Chem.*, **62**, 347 (2009); (c) X.-J. Wang, X.-M. Lu, P.-Z. Li, X.-H. Pei, C.-H. Ye. *J. Coord. Chem.*, **61**, 3753 (2008); (d) X.-M. Chen, D.-S. Wang, Q.-Z. Luo, R. Wang. *J. Coord. Chem.*, **62**, 3895 (2009).

[16] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot. *Inorg. Chem.*, **22**, 207 (1983).

[17] Q.Z. Sun, Y. Bai, G.J. He, C.Y. Duan, Q.J. Meng. *Chem. Commun.*, 2777 (2006).

[18] *SMART and SAINT*, *Area Detector Control and Integration Software*, Siemens Analytical X-ray Systems, Inc., Madison, WI (1996).

[19] G.M. Sheldrick. (*SHELXTL Version 5.1*), *Software Reference Manual*, Bruker AXS, Inc., Madison, WI (1997).