A Rare Two-dimensional Network Based on 2,2′-Biimidazole Bridged Double $[PW_{11}O_{39}Ni]^{5-}$ Polyanions

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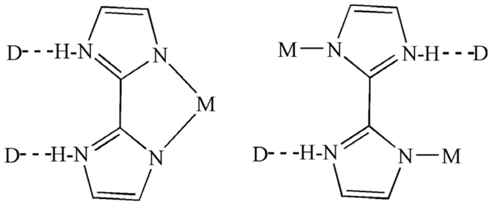
A novel two-dimensional complex based on the mono-vacant Keggin anion $[PW_{11}O_{39}]^{7-}$, $[Ni(BIIM)_3]_3[\{Ni(BIIM)_2\}_2(PNiW_{11}O_{39})_2(BIIM)]\cdot H_2O$ (BIIM = 2,2′-biimidazole), was hydrothermally synthesized and characterized by elemental and thermo-gravimetric analysis, IR and UV spectroscopy. Each $[PW_{11}O_{39}]^{7-}$ anion captures an Ni^{2+} ion forming a $[PNiW_{11}O_{39}]^{5-}$ polyanion, two of which are linked together by a BIIM ligand into a $[(PNiW_{11}O_{39})_2(BIIM)]^{10-}$ polyanion supporting two $Ni(BIIM)_2{}^{2+}$ units through two terminal oxygen atoms and affording a complicated $[\{Ni(BIIM)_2\}_2(PNiW_{11}O_{39})_2(BIIM)]^{6-}$ heteropolyanion. Each of these units is further attached to four surrounding equivalent units by their own $Ni(BIIM)_2{}^{2+}$ linkers into a two-dimensional brick wall-like network with (6,3) topology.

Key words: Polyoxometalate, Crystal Structure, Keggin, Topology

Introduction

During the past decades, polyoxometalates have been successfully introduced into the field of organic-inorganic hybrids as important inorganic building blocks due to their structural characteristics and potential applications in chemistry, physics and material science [1]. Moreover, their introduction has greatly promoted the development of hybrid materials so that lots of related complexes have been reported. Among these, hybrid compounds are mainly dominated by saturated polyoxometalates, namely $XM_{12}\{[PM_{12}O_{40}]^{3-}$ (M = Mo, W) [2 – 6], $[XM_{12}O_{40}]^{4-}$ (X = Si, Ge; M = Mo, W) [7, 8] and $[BW_{12}O_{40}]^{4-}$ [9, 10]$\}$ because of their higher negative charges and higher symmetry. However, hybrids based on mono-vacant Keggin anions such as XW_{11} ($[PW_{11}O_{39}]^{3-}$ [11, 12] and $[SiW_{11}O_{39}]^{8-}$ [12 – 16]) have been less observed, where XW_{11} anions are mainly connected by metal-organic linkers into a two-dimensional structure. After losing a $\{W{=}O\}^{4+}$ group from a saturated XW_{12} anion, although the XW_{11} anion still retains its large size and high negative charges, it possesses an active gap so that rare earth, alkaline earth or transition metals can be captured easily. Moreover, these captured metals are more difficult to coordinate to other organic ligands.



Scheme 1. Interaction modes of 2,2′-biimidazole (BIIM; D = acceptor, M = metal).

On the other hand, the type of coordinating organic ligands in those hybrids is limited to diethylenetriamine, ethylenediamine, DMSO, 4,4′-bipy, and 2,2′-bipy, obviously distinct from those nitrogen-rich ligands in Keggin-based compounds, which also indicates that metal ions captured by XW_{11} are not modified by organic ligands. Therefore, the rational selection for organic ligands takes the key role for constructing and expanding XW_{11}-based complexes.

In this paper, 2,2′-biimidazole (BIIM) is selected because it possesses two nitrogen coordination sites and two NH donors. Both nitrogen coordination sites have strong donor abilities and flexible coordination modes regarding the metal geometry or metal to ligand ratio, and can function not only in bidentate ligands chelating a transition metal, but also in bis(mono-dentate)

Table 1. Crystallographic data for $[Ni(BIIM)_3]_3$-$[\{Ni(BIIM)_2\}_2(PNiW_{11}O_{39})_2(BIIM)]\cdot H_2O$ (**1**).

Molecule formula	$C_{84}H_{84}N_{56}Ni_7O_{79}P_2W_{22}$
M_r	7659.68
Crystal size, mm^3	$0.15 \times 0.11 \times 0.08$
Crystal system	monoclinic
Space group	$C2/c$
a, Å	29.111(6)
b, Å	26.407(5)
c, Å	25.128(8)
β, deg	123.076(2)
V, Å^3	16186(7)
Z	4
D_{calcd}, g cm^{-3}	3.14
μ(Mo$K\alpha$), mm^{-1}	16.5
$F(000)$, e	13864
Refl. measured / unique / R_{int}	82458 / 15888 / 0.1296
Param. refined	1127
$R1$ / $wR2$ $[I \geq 2\sigma(I)]$[a, b]	0.0549 / 0.1280
$R1$ / $wR2$ (all data)[a]	0.1332 / 0.1586
GoF (F^2)[c]	0.931
$\Delta\rho_{fin}$ (max / min,) e Å^{-3}	4.10 / −3.65

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2, 0) + 2F_c{}^2)/3$; [c] $\mathrm{GoF} = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$.

units by bridging two transition metal ions. Additionally, two -NH donors can interact with hydrogen bonding acceptors *via* hydrogen bonds (Scheme 1) [17]. Herein we present the title compound $[Ni(BIIM)_3]_3$-$[\{Ni(BIIM)_2\}_2(PNiW_{11}O_{39})_2(BIIM)]\cdot H_2O$ (**1**).

Experimental Section

General

All chemicals were of reagent grade as received from commercial sources and used without further purification. C, H, N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The infrared spectrum was recorded from KBr pellets on a Nicolet 170SXFT-IR spectrometer in the range of 400 – 4000 cm^{-1}. The UV spectrum was obtained on a Shimazu UV-250 spectrometer in the range 190 – 400 nm. TG measurements were performed on a Perkin-Elmer7 thermal analyzer in flowing nitrogen gas with a heating rate of 10 °C min^{-1}.

Synthesis of $[Ni(BIIM)_3]_3[\{Ni(BIIM)_2\}_2(PNiW_{11}O_{39})_2$-$(BIIM)]\cdot H_2O$ (1)

A mixture of $Na_2WO_4\cdot 2H_2O$ (1.0 g, 3.2 mmol), BIIM (0.13 g, 0.25 mmol), $NiCl_2\cdot 6H_2O$ (0.08 g, 0.34 mmol), $Ni(Ac)_2\cdot 4H_2O$ (0.13 g, 0.52 mmol), and H_2O (20 mL) was sealed in a Teflon-lined stainless-steel reactor and heated at 160 °C for 4 d with starting pH = 3 adjusted with hydrochloric acid (6 mol L^{-1}). After cooling slowly to room temperature for 24 h, slightly yellow crystals were obtained, filtered, washed several times with distilled water and dried in air. – Elemental analysis: calcd. C 13.17, H 1.11, N 10.24; found C 13.40, H 1.32, N 10.01.

Table 2. Selected bond lengths (Å) and angles (deg.) of **1**[a].

P(1)–O(37)	1.520(12)	P(1)–O(36)	1.539(11)
P(1)–O(38)	1.526(12)	P(1)–O(39)	1.548(11)
W(1)–O(1)	1.701(13)	W(2)–O(2)	1.725(12)
W(3)–O(3)	1.718(12)	W(4)–O(4)	1.703(12)
W(5)–O(5)	1.712(13)	W(6)–O(6)	1.716(13)
W(7)–O(7)	1.718(12)	W(8)–O(8)	1.717(11)
W(9)–O(9)	1.699(12)	W(10)–O(10)	1.739(11)
W(11)–O(11)	1.696(13)	Ni(1)–N(1)	1.991(14)
Ni(1)–O(20)	2.006(12)	Ni(1)–O(18)	2.036(12)
Ni(1)–O(34)	2.013(12)	Ni(1)–O(15)	2.044(12)
Ni(1)–O(36)	2.249(11)	Ni(2)–N(4)	2.056(14)
Ni(2)–N(7)	2.058(14)	Ni(2)–N(3)	2.101(15)
Ni(2)–N(8)	2.073(15)	Ni(2)–O(3)	2.147(12)
Ni(2)–O(8c)	2.199(12)	Ni(3)–N(21)	2.080(18)
Ni(3)–N(22)	2.106(19)	Ni(3)–N(17)	2.116(17)
Ni(3)–N(25)	2.114(18)	Ni(3)–N(18)	2.122(16)
Ni(3)–N(26)	2.132(19)	Ni(4)–N(11b)	2.062(16)
Ni(4)–N(11)	2.062(16)	Ni(4)–N(15b)	2.08(2)
Ni(4)–N(15)	2.08(2)	Ni(4)–N(12)	2.107(18)
Ni(4)–N(12b)	2.107(18)	O(37)–P(1)–O(38)	109.2(6)
O(37)–P(1)–O(36)	110.0(6)	O(37)–P(1)–O(39)	109.9(6)
O(38)–P(1)–O(36)	110.1(6)	O(38)–P(1)–O(39)	108.1(6)
O(36)–P(1)–O(39)	109.6(6)	N(1)–Ni(1)–O(20)	97.3(5)
N(1)–Ni(1)–O(34)	95.0(5)	N(1)–Ni(1)–O(18)	94.9(5)
O(20)–Ni(1)–O(34)	88.1(5)	O(20)–Ni(1)–O(18)	167.9(5)
N(1)–Ni(1)–O(15)	97.9(6)	O(34)–Ni(1)–O(18)	90.4(5)
O(20)–Ni(1)–O(15)	92.2(5)	O(18)–Ni(1)–O(15)	86.7(5)
O(34)–Ni(1)–O(15)	167.0(5)	N(1)–Ni(1)–O(36)	170.1(5)
O(34)–Ni(1)–O(36)	90.1(4)	O(20)–Ni(1)–O(36)	91.4(4)
O(15)–Ni(1)–O(36)	76.9(4)	O(18)–Ni(1)–O(36)	76.6(4)

[a] Symmetry transformations used to generate equivalent atoms as in Fig. 1: (c) $x, -y+1, z+1/2$; (b) $-x, y, -z+1/2$.

Crystal structure determination

The data collection was made on a Bruker SMART APEX CCD area detector diffractometer using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at 293(2) K. The intensities were corrected empirically for absorption. The structure was solved by Direct Methods and refined by full-matrix least-squares routines on F^2 using the SHELX-97 program suite [18]. All non-hydrogen atoms were refined anisotropically. Crystallographic data are listed in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC 847708 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.com.ac.uk/data_request/cif.

Results and Discussion

Crystal and molecular structure of $[Ni(BIIM)_3]_3$-$[\{Ni(BIIM)_2\}_2(PNiW_{11}O_{39})_2(BIIM)]\cdot H_2O$

Hydrothermal syntheses are affected by many factors, such as the starting pH value, the original reaction

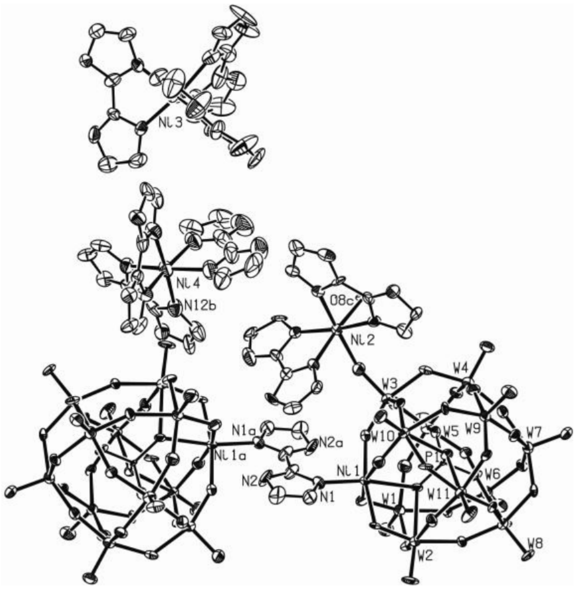


Fig. 1. Partial view of the crystal structure of **1**, showing the atom numbering scheme. Water and hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 30 % probability level (symmetry codes: (a) $-x+1/2$, $-y+1/2$, $-z$; (b) $-x$, y, $-z+1/2$; (c) x, $-y+1$, $z+1/2$).

materials and the temperature. During our preparation of the compound, we found that it is not sensitive to the reaction temperature in the range 150 – 170 °C but to the starting pH value. If the pH value was adjusted to 5 – 6, no perfect crystals were obtained except for some pink vitreous pieces. When the pH value was changed to 1 – 2, a product with Keggin structure was formed. The starting pH value usually controlled at 3 is propitious to the formation of the final product.

As shown in Fig. 1, the complex is composed of three isolated $[Ni(BIIM)_3]^{2+}$ cations, one $[\{Ni(BIIM)_2\}_2(PNiW_{11}O_{39})_2(BIIM)]^{6-}$ heteropolyanion in which BIIM is placed around an inversion center, and one discrete water molecule. In the isolated $[Ni(BIIM)_3]^{2+}$ cations, each Ni^{2+} cation is coordinated by six N atoms from three BIIM ligands with a distorted octahedral geometry [Ni(3)–N range 2.078(18) – 2.134(19) Å; Ni(4)–N range 2.060(16) – 2.104(18) Å]. In the $[\{Ni(BIIM)_2\}_2(PW_{11}O_{39}Ni)_2(BIIM)]^{6-}$ heteropolyanion, each PW_{11} unit in the $[(PNiW_{11}O_{39})_2(BIIM)]^{10-}$ anion is decorated by one $[Ni(BIIM)_2]^{2+}$ cation *via* a terminal oxygen atom. $Ni(2)^{2+}$ is coordinated by four N atoms from two BIIM ligands and two oxygen atoms from two $[PW_{11}O_{39}]^{7-}$ anions in form of a distorted octahedron, in which the O(3) and N(8) atoms are at the apical positions, and the O(8c), N(3), N(4), and N(7) atoms at the equatorial positions [Ni(2)–N = 2.059(14) – 2.104(11) Å, Ni(2)–O = 2.148(12) – 0.196(11) Å]. The $[(PW_{11}O_{39}Ni)_2(BIIM)]^{10-}$ anion can be considered as two equivalent $[PW_{11}O_{39}Ni]^{5-}$ anions bridged by the BIIM ligand. The surface of each PW_{11} unit is decorated by one $[Ni(BIIM)_2]^{2+}$ linker. Each $[\{Ni(BIIM)_2\}_2(PW_{11}O_{39}Ni)_2(BIIM)]^{6-}$ anion links four neighboring units through two terminal oxygen atoms [O(3) and O(8c)] into an infinite two-dimensional network (Fig. 2). If each $[PW_{11}O_{39}Ni]^{5-}$ anion is considered as a three-connected node, a brick wall-like (6, 3) network can be recognized (Fig. 3). In previously reported mono-substituted Keggin polyanions, Ni^{2+}-substituted Keggin anions have been rarely seen [19]. Moreover, double $XW_{11}M$ clusters

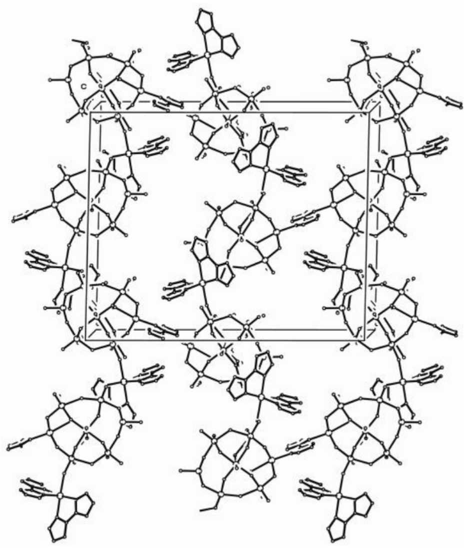


Fig. 2. View of the two-dimensional network in the (100) plane of **1**.

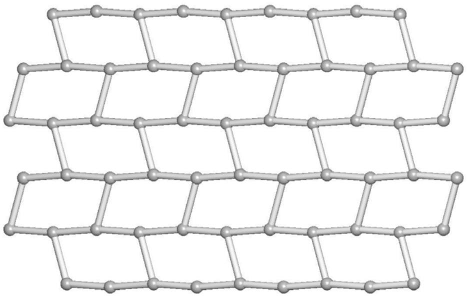


Fig. 3. Schematic view of the (6, 3) net in the crystal structure of **1**.

supported by the organic ligand BIIM have never been observed.

*IR spectrum of **1***

The IR spectrum exhibits absorption peaks in the 1426–1621 cm^{-1} region associated with the 2,2′-biimidazole ligands. Bands at 1072 and 1060 cm^{-1} are characteristic of P–O stretching vibrations. The peak at 963 cm^{-1} corresponds to $\nu(\mathrm{W–O_t})$, that at 877 cm^{-1} is attributed to $\nu(\mathrm{W–O}_b)$, and those at 813 and 757 cm^{-1} are related to $\nu(\mathrm{W–O}_c)$. The P–O and W–O_c bands are split into two bands since they are non-equivalent after a Ni atom substitutes for a W atom, an obvious difference from the single signal in the complete Keggin anion $[PW_{12}O_{10}]^{3-}$ [19, 20].

*Thermal properties of **1***

A thermo-gravimetric analysis (TGA) was carried out under an atmosphere of N_2. The first rapid weight loss step of 2.0 % from r. t. to 290.1 °C (calcd. 0.3 %) corresponds to the loss of water. The large deviation is attributed to the humidification of the sample. The second weight loss of 35.4 % (calcd. 33.2 %) can be observed from 390.1 to 717.6 °C, attributed to the decomposition of the 2,2′-biimidazole ligands.

*UV spectrum of **1***

The UV spectrum of the title complex exhibits an intense absorption peak at 272 nm corresponding to a charge-transfer absorption of $O_{b,c} \rightarrow W$, which is distinct from two wide intense absorption peaks in the Keggin anion [21]. If one $\{W{=}O\}^{4+}$ group is substituted by Ni^{2+} the charge-transfer absorption of $O_t \rightarrow W$ disappears.

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