

Hydrothermal Syntheses and Crystal Structure of Hybrid Material Based on Keggin Cluster Modified by Nickel Complex

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A new organic-inorganic hybrid compound based on the Keggin polyoxometalates modified by nickel and N-ligand organic moiety: $[\text{Ni}(\text{phen})_3]_2[\text{PMo}_{11}\text{V}^{\text{VI}}\text{Mo}^{\text{V}}\text{O}_{40}]$ (**1**) (phen = 1,10-phenanthroline) has been hydrothermally synthesized and characterized structurally. It crystallizes in the triclinic space group P-1 with $a = 12.203(2)$, $b = 13.907(2)$, $c = 14.438(3)$ Å; $\alpha = 104.859(2)$, $\beta = 108.777(2)$, $\gamma = 93.376(2)$, $V = 2215.3(7)$ Å³, $C_{72}\text{H}_{48}\text{N}_{12}\text{O}_{40}\text{PMo}_{12}\text{Ni}_2$, $M_r = 3020.85$, $Z = 1$, $D_c = 2.264$ g/cm³, $m = 2.164$ mm⁻¹, $F(000) = 1459$, $R = 0.0355$ and $wR = 0.0937$ for 6948 observed reflections with $I > 2\sigma(I)$. The compound **1** consists of discrete polyoxoanions $[\text{PMo}_{11}\text{V}^{\text{VI}}\text{Mo}^{\text{V}}\text{O}_{40}]^{4-}$ and counter cations $[\text{Ni}(\text{phen})_3]^{2+}$. The electrochemical property of compound **1** has been studied in the paper.

Keywords: Keggin structure, Polyoxometalates, Nickel, Hydrothermal synthesis, Electrochemical property.

INTRODUCTION

As an interesting class of metal oxide clusters, polyoxometalates (POMs) can be used as one kind of inorganic building blocks to build novel functional organic-inorganic solid materials, due to quite a number of valuable properties of these compounds such as catalysis, electrochemistry, photochemical and magnetism¹⁻⁴. Design and synthesis of novel functional organic-inorganic hybrid materials based on polyoxometalates (POMs) is still a challenge^{5,6}. Currently, modification of polyoxometalates with transition metal complexes of various organic groups under hydrothermal synthesis condition has been proven to be an effective route to prepare novel functional Keggin POM hybrids^{7,8}. Although many Keggin polyoxometalates modified by 3d transition metal complexes have been reported, Keggin polyoxo-metalates modified by nickel complexes ($[\text{Ni}(\text{phen})_3]^{2+}$) are few⁹⁻¹¹. In fact, our group has been focused on exploring the possible effect of N-ligand organic moiety in the crystal engineering of novel functional organic-inorganic hybrid materials based on polyoxometalates under hydrothermal conditions¹²⁻¹⁵. So, in this paper, as a continuation of our research, we report a novel organic-inorganic hybrid materials based on polyoxo-metalates: $[\text{Ni}(\text{phen})_3]_2[\text{PMo}_{11}\text{V}^{\text{VI}}\text{Mo}^{\text{V}}\text{O}_{40}]$ (**1**). The compound (**1**) consists of Keggin-type polyoxoanion $[\text{PMo}_{11}\text{V}^{\text{VI}}\text{Mo}^{\text{V}}\text{O}_{40}]^{4-}$ and counter cations $[\text{Ni}(\text{phen})_3]^{2+}$.

EXPERIMENTAL

General procedure: All chemicals were purchased commercially and used without further purification. Elemental analyses were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer (C, H and N); XPS analysis was performed on a VGESCALABMK II spectrometer with an $\text{MgK}\alpha$ (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during analysis. IR spectra were obtained on an Alpha Centaur FT/IR spectrometer with KBr pellet in the 4000-400 cm⁻¹ region. Thermogravimetric analyses were recorded in a dynamic nitrogen atmosphere with a heating rate of 10 °C/min using a Mettler TGA/SDTA851e thermal analyzer. Cyclic voltammograms were obtained with a CHI 660 electrochemical workstation at room temperature. Platinum gauze was used as counter electrode and Ag/AgCl electrode was reference. A chemically bulk-modified carbon paste electrode (CPE) was used as working electrode.

Synthesis of the title compound: A mixture of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (1 mmol, 0.242 g), MoO_3 (1 mmol, 0.144 g), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1 mmol, 0.2377 g), 1,10-phenanthroline (1 mmol, 0.198 g), pyridine (2 mL) and H_3PO_4 (2 mL, 85 %) was dissolved in 30 mL of water. The mixture was stirred for 2 h at room temperature and then heated in a 50 mL Teflon-lined stainless steel autoclave for 8 days at 180 °C. After slow cooling

to room temperature, the solid product containing black green block shaped crystals were isolated in 31 % yield (based on Ni).

For $C_{72}H_{48}N_{12}O_{40}PMo_{12}Ni_2$. Anal. Calcd (%): C, 28.63; H, 1.60; N, 5.56; found: C, 28.38; H, 1.94; N, 5.47. Infrared spectrum (KBr, ν_{\max} , cm^{-1}): 3750(w), 3440(s), 2937(w), 2350(w), 1643(s), 1531(s), 1440(s), 1072(s), 996(s), 898(s), 809(s), 728(s).

X-Ray crystallography: Black green single crystal of the title compound (0.32 mm \times 0.20 mm \times 0.18 mm) was put on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromated MoK_{α} radiation ($\lambda = 0.71073$ Å) by using a ϕ/ω scan technique at room temperature. 6948 independent reflections ($R_{int} = 0.0120$) in the range $2.53 < \theta < 24.00$ with $-13 \leq h \leq 13$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$ were collected at 273(2) K. The structure was solved by direct methods with SHELXS-97¹⁶.

The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restraints, while the non-hydrogen atoms were treated with common anisotropic displacement factors and included in the final refinement with geometrical restraints. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97¹⁷. The final agreement factor values are $R = 0.0355$ and $wR = 0.0937$. Crystallographic data and refinement parameters are listed in Table-1. CCDC 1013742 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.cam.ac.uk/data_request/cif.

TABLE-1
CRYSTALLOGRAPHIC DATA FOR $[Ni(phen)_3]_2[PMo_{11}^{VI}Mo^VO_{40}]$

Compound	$[Ni(phen)_3]_2[PMo_{11}^{VI}Mo^VO_{40}]$
Color/shape	Black green/block
Formula	$C_{72}H_{48}N_{12}O_{40}PMo_{12}Ni_2$
Formula weight	3020.85
Temperature (K)	273(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 12.203(2)$ Å, $b = 13.907(2)$ Å $c = 14.438(3)$ Å $\alpha = 104.859(2)^\circ$ $\beta = 108.777(2)^\circ$ $\gamma = 93.376(2)^\circ$
Z Volume, Å ³	1 2215.3(7)
Calculated density (mg/m ³)	2.264
Absorption coefficient (mm ⁻¹)	2.164
F(000)	1459
θ Range for data collection (°)	2.53–24.00
Reflections collected	14038
Independent reflection	6498 [$R_{int} = 0.0120$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6498/0/646
Goodness-of-fit on F^2	1.000
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0353$, $wR2 = 0.0937$
R indices (all data)	$R1 = 0.0383$, $wR2 = 0.0957$
Largest diff. peak and hole	1.410 and -0.922 e/Å ³

Preparation of (1)-CPE: Compound **1** modified carbon paste electrode (1)-CPE was prepared as follows: 96 mg of graphite powder and 4 mg of compound **1** was mixed and ground together by agate mortar and pestle to achieve a uniform mixture and then added to 0.5 mL petrolin with stirring. The homogenized mixture was packed into a glass tube with 1 mm inner diameter and the tube surface was wiped with pan paper. Electrical contact was established with copper rod through the back of the electrode.

RESULTS AND DISCUSSION

Description of the crystal structure: Single crystal X-ray diffraction analysis reveals that compound **1** consists of discrete polyoxoanions $[PMo_{11}^{VI}Mo^VO_{40}]^{4-}$ and counter cations $[Ni(phen)_3]^{2+}$ (Fig. 1). Selected bond lengths and angles are collected in Table-2. The polyoxoanion $[PMo_{11}^{VI}Mo^VO_{40}]^{4-}$ exhibits a disordered α -Keggin structure. The central P atom is surrounded by a cube of eight oxygen atoms with site half-occupied. The disordered $\{PO_4\}$ tetrahedron is located in the center of host cage with P-O distance of 1.467(6)–1.603(6) Å and O-P-O bond angle in the range of $103.2(3)$ – $115.9(3)^\circ$. All Mo atoms have a distorted $\{MoO_6\}$ octahedral environment. The Mo-O distances can be grouped into three sets: Mo-O_t (terminal) 1.647(4)–1.667(3) Å, Mo-O_b (bridge) 1.837(5)–1.874(5) Å and Mo-O_c (central) 1.922(5)–1.951(5) Å. The assignments of oxidation state for Mo atoms are consistent with their coordination geometries and confirmed by XPS spectra. In the experiment, by the introduction of the reducer pyridine, one out of twelve Mo centers is in the +5 oxidation state and the others are in the +6 oxidation state, resulting in a mixed valence polyoxometalate. In the structure of the title compound, there exists complex cation $[Ni(phen)_3]^{2+}$. Each Ni atom is coordinated by six nitrogen atoms from three phen ligands to form a distorted NiN_6 octahedron with an isolated complex cation. The Ni-N bond lengths range from 2.083(4) to 2.097(4) Å.

IR spectra: IR spectra of compound **1** were carried out over the rang from 4000 to 400 cm^{-1} (Fig. 2). The strong bands at 1072, 966, 898, 809 and 728 cm^{-1} are ascribed to $\nu_{as}(P-O)$, $\nu_{as}(Mo-O_d)$, $\nu_{as}(Mo-O_b-Mo)$, $\nu_{as}(Mo-O_c-Mo)$ and $\nu_{as}(Ni-N)$, respectively. The peaks at 3750–1080 cm^{-1} are characteristic for phenanthroline.

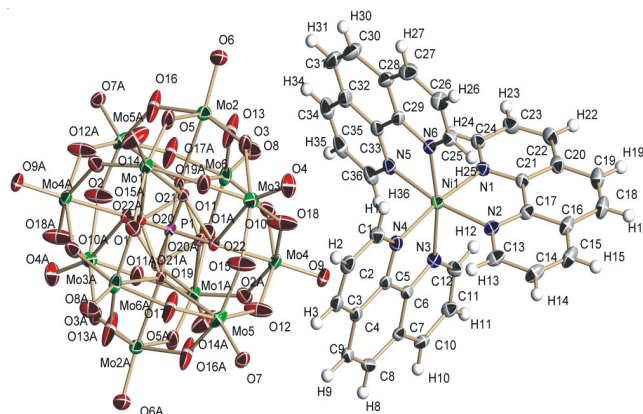


Fig. 1. Molecular structure of $[Ni(phen)_3]_2[PMo_{11}^{VI}Mo^VO_{40}]$ in the solid state. 30 % probability ellipsoids

TABLE-2
SELECTED BOND LENGTHS (Å), ANGLES (°), AND DIHEDRAL ANGLES (°) FOR
[Ni(phen)₃]₂[PMo₁₁^{VI}Mo^VO₄₀] WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond	d, (Å)	Bond	d, (Å)
Mo(1)-O(2)	1.855(4)	Mo(2)-O(13)	1.869(5)
Mo(3)-O(11)	1.848(5)	Mo(4)-O(18)	1.837(5)
Mo(5)-O(16)#1	1.874(5)	Mo(1)-O(11)	1.945(4)
Mo(2)-O(5)	1.926(5)	Mo(3)-O(18)	1.947(5)
Mo(4)-O(2)#1	1.951(5)	Mo(5)-O(15)	1.922(5)
Mo(1)-O(14)	1.647(4)	Mo(2)-O(6)	1.677(4)
Mo(3)-O(4)	1.657(4)	Mo(4)-O(9)	1.670(4)
Mo(5)-O(7)	1.667(3)	P(1)-O(21)#1	1.467(6)
P(1)-O(19)	1.603(6)	Ni(1)-N(6)	2.083(4)
Ni(1)-N(4)	2.089(4)	Ni(1)-N(5)	2.094(4)
Ni(1)-N(2)	2.096(4)	Ni(1)-N(3)	2.097(4)
Ni(1)-N(1)	2.101(4)	N(2)-C(13)	1.325(7)
N(4)-C(5)	1.362(7)	C(31)-C(30)	1.318(11)
C(32)-C(31)	1.444(11)	-	-
Angle	ω, (°)	Angle	ω, (°)
O(22)-P(1)-O(19)#1	103.2(3)	O(21)#1-P(1)-O(20)	115.9(3)
O(9)-Mo(4)-O(10)	100.6(2)	O(8)-Mo(6)-O(13)	101.0(3)
O(6)-Mo(2)-O(3)	102.0(2)	O(4)-Mo(3)-O(18)	102.3(3)
O(7)-Mo(5)-O(16)#1	102.7(3)	O(7)-Mo(5)-O(17)	102.8(2)
O(14)-Mo(1)-O(5)	102.9(3)	O(4)-Mo(3)-O(15)	103.1(3)
C(5)-N(4)-Ni(1)	112.1(3)	C(29)-N(6)-Ni(1)	113.0(3)
N(6)-C(29)-C(33)	116.9(5)	N(3)-C(12)-C(11)	123.4(5)
N(2)-Ni(1)-N(1)	79.51(16)	N(4)-Ni(1)-N(2)	96.09(17)

Symmetry transformations used to generate equivalent atoms: #1 -x + 1, -y + 1, -z + 1

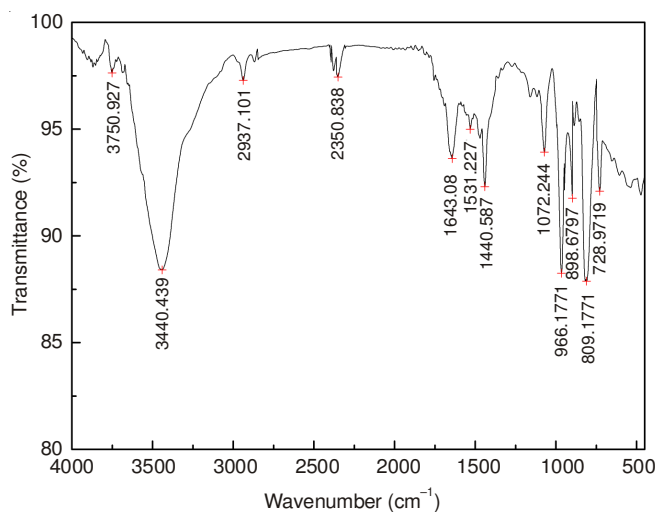


Fig. 2. IR spectra of [Ni(phen)₃]₂[PMo₁₁^{VI}Mo^VO₄₀]

Thermal analysis: The TG analyses were carried out over the temperature range from 20 to 800 °C. The TG curve of compound **1** shows continuous weight loss over the temperature range from 20 to 800 °C (Fig. 3). The region at about 35–730 °C with a mass loss of 64.4 % (calcd. 64.3 %) is due to release of phen molecules coordinated with Ni.

Cyclic voltammetry: The cyclic voltammetry of compound **1** was measured in the potential range from -0.2 to 0.55 V. The typical cyclic voltammetric behaviour of (1)-CPE was explored in 1 mol L⁻¹ H₂SO₄ aqueous solution at different scan rates. In Fig. 4, there are four reversible redox peaks appeared and mean peak potentials $E_{1/2} = (E_{pc} + E_{pa})/2$ are 0.359, 0.208 and -0.052V, respectively. Redox peaks I-I', II-II' and III-III' should be ascribed to three consecutive 2-electron processes of Mo,

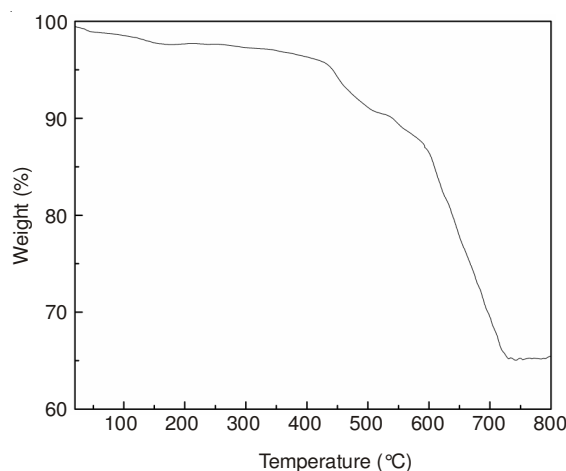


Fig. 3. TG curve of [Ni(phen)₃]₂[PMo₁₁^{VI}Mo^VO₄₀]

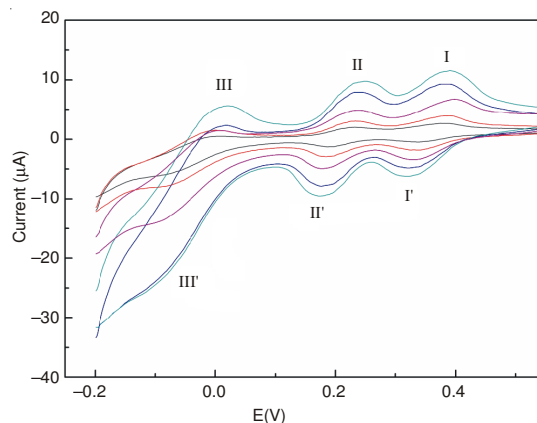


Fig. 4. Cyclic voltammograms for (1)-CPE was explored in 1 mol L⁻¹ H₂SO₄ aqueous solution at different scan rates. (from inner to outer: 0.02, 0.04, 0.06, 0.08, 0.10 V s⁻¹)

respectively. The cathodic peak potentials shift toward the negative and the corresponding anodic peak potentials to the positive direction. The peak-to-peak separation between the corresponding cathodic and anodic peaks increases with increasing scan rate, all but the mean peak potentials do not change.

Conclusion

In summary, a novel supramolecular organic-inorganic hybrid compound based on the Keggin polyoxometalates modified by nickel and 1,10-phenanthroline has been successfully prepared and structurally characterized. This work proves that the hydrothermal synthesis techniques is an effective route to prepare novel organic-inorganic hybrid materials based on polyoxometalates in combination with transition metal complexes of N-ligand organic moiety.

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