

Supporting Information

A Multi-component Polyoxometalate and its Catalytic Performance for CO₂ Cycloaddition Reactions

Shumin Chen, Ying Liu, Jipeng Guo, Pengzhen Li, Zhiyuan Huo, Pengtao Ma,
Jingyang Niu*† and Jingping Wang*†

† Key Laboratory of Polyoxometalate Chemistry of Henan Province, Institute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, P. R. China

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1. Experimental Section

1.1 Materials and Methods

All chemicals used for synthesis were purchased and without any further purification. Elemental analyses were performed by using a Perkin-Elmer 2400-II CHNS/O analyzer. The FT-IR spectra were recorded on a Bruker VERTEX 70 IR spectrometer (using KBr pellets) in the range of 4000–400 cm^{-1} . Thermogravimetric analyses were measured on Mettler–Toledo TGA/SDTA851^e instrument with a heating rate of 10 $^{\circ}\text{C min}^{-1}$ from 25 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$ in N_2 flow. XPS were recorded by an Axis Ultra (Kratos, U.K.) photoelectron spectroscope with Al $K\alpha$ (1486.7 eV) irradiation. EPR spectra were carried out using Bruker EMX-10/12 variable-temperature apparatus. GC chromatogram was obtained on Bruker 450-GC (flame ionization detector) instrument equipped with a 30 m column (GsBP-5, 0.25 mm internal diameter and 0.25 μm film thickness) with nitrogen as carrier gas.

1.2 Synthesis

(NH₄)₁₀[Co₈(H₂O)₁₀V₁₀Mo₂₃O₁₀₄(OH)₆] 34.5H₂O (1): (NH₄)₆Mo₇O₂₄ 4H₂O (0.32g, 0.260mmol) was dissolved in 25 mL water, then NH₄VO₃(0.15g, 1.280mol) and CoCl₂ 2H₂O (0.17 g, 1.000 mmol) were successively added at room temperature with stirring until the mixture became homogeneous. The pH of the solution was adjusted to 4.7 by addition of 4M HCl. Then the solution was stirred at room temperature for 1.5h. Finally, the solution was filtered into a beaker. Slow evaporation of the solvent at room temperature led to brown crystals of **1** suitable for X-ray diffraction after 4 weeks. Yield: ca.29.4% (based on Mo). **Elemental analysis calcd (%) for 1:** H 2.29, N 2.36, Co 7.94, V 8.58, Mo 37.18. **Found:** H 1.87, N 2.91, Co 7.67, V 8.92, Mo 36.92. IR spectra (KBr pellet): 1619(s), 1403(s), 922(w), 862(s), 829(w), 798(m), 654(s) and 517(m) cm^{-1} .

1.3 X-ray Crystallography

The crystallographic data for compound **1** was given in Table S1. A good-quality single-crystal with dimensions of **0.32 × 0.22 × 0.18 mm³** was mounted on a glass fiber. Intensity data were collected on Bruker APEX-II CCD detector at 296(2) K with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Direct methods were used to solve the structures and to locate the heavy atoms using the SHELXTL-97 program package. The remaining atoms were found from successive full-matrix least-squares refinements on F^2 and Fourier syntheses. Lorentz polarization and empirical absorption corrections were applied. No hydrogen atoms associated with water molecules were located from the difference Fourier map. A summary of crystal data and structure refinements for compound **1** is provided in Table S1. CSD-number 429071, contains supplementary crystallographic data for this paper. The data can be obtained free of charge from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [fax, (+49)7247-808-666; e-mail, crysdata@fiz-karlsruhe.de; web site, http://www.fiz-karlsruhe.de/depositing_crystal_structures.html?&L=0].

Table S1. Crystal Data and Structure Refinement for 1

1	
Empirical formula	$\text{Co}_8\text{H}_{135}\text{Mo}_{23}\text{N}_{10}\text{O}_{154.5}\text{V}_{10}$
Formula weight	5935.64
Temperature/K	296.15
Crystal system	Orthorhombic
Space group	<i>Pnmm</i>
<i>a</i> /Å	28.1420(16)
<i>b</i> /Å	24.2136(13)
<i>c</i> /Å	25.7921(14)
α (°)	90.00°
β (°)	90.00°
γ (°)	90.00°
<i>V</i> /Å ³	17575.2(17)
<i>Z</i>	4
<i>F</i> (000)	11412.0
ρ_{calc} / g cm ⁻³	2.243
μ / mm ⁻¹	2.922
Refl. collected	88020
Independent refl.	15773
GOOF	1.117
<i>R</i> (int)	0.0672
Final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	$R_1 = 0.0778, \omega R_2 = 0.2161$
<i>R</i> indices (all data)	$R_1 = 0.1106, \omega R_2 = 0.2475$

1.4 Bond Valence Sum (BVS) Calculations.**Table S2. The bond valence sum calculations of the Mo and Co atoms.**

Atom	Bond	Valence	Atom	Bond	Valence	Atom	Bond	Valence
Code	Valence	state	Code	Valence	state	Code	Valence	state
Mo1	6.03	6	Mo7	6.22	6	Mo13	6.31	6
Mo2	5.98	6	Mo8	5.85	6	Co1	2.08	2
Mo3	5.98	6	Mo9	6.14	6	Co2	2.09	2
Mo4	5.89	6	Mo10	6.12	6	Co3	2.06	2
Mo5	5.87	6	Mo11	5.90	6	Co4	2.10	2
Mo6	6.11	6	Mo12	6.07	6			

Table S3. The bond valence sum calculations of the V atoms.

Atom Code	BVS			Bond Valence
	V(III)	V(IV)	V(V)	
V1	4.45	4.97	5.23	5
V2	4.46	4.98	5.24	5
V3	4.26	4.76	5.01	5
V4	4.25	4.74	4.99	5
V5	4.24	4.74	4.97	5
V6	3.98	4.45	4.68	5

Table S4. The bond valence sum calculations of the oxygen atoms on polyoxoanions in 1.

Oxygen Code	Bond Valence	Protonation Degree
O7	1.317	1
O14	1.287	1
O56	1.216	1
O58	1.391	1

1.5 Synthesis Discussion

The title compound was isolated from aqueous solution under mild conditions. The mixture of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and NH_4VO_3 is bright yellow suspension liquid. After the addition of $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ with vigorous stirring, the colour of the reactions changes to reddish brown clear solution. Then, the pH value was adjusted to 4.7 by 4M HCl. For this reaction system, pH value was optimized to be within the range of 4.6-5.1.

2. Additional Structural Figures.

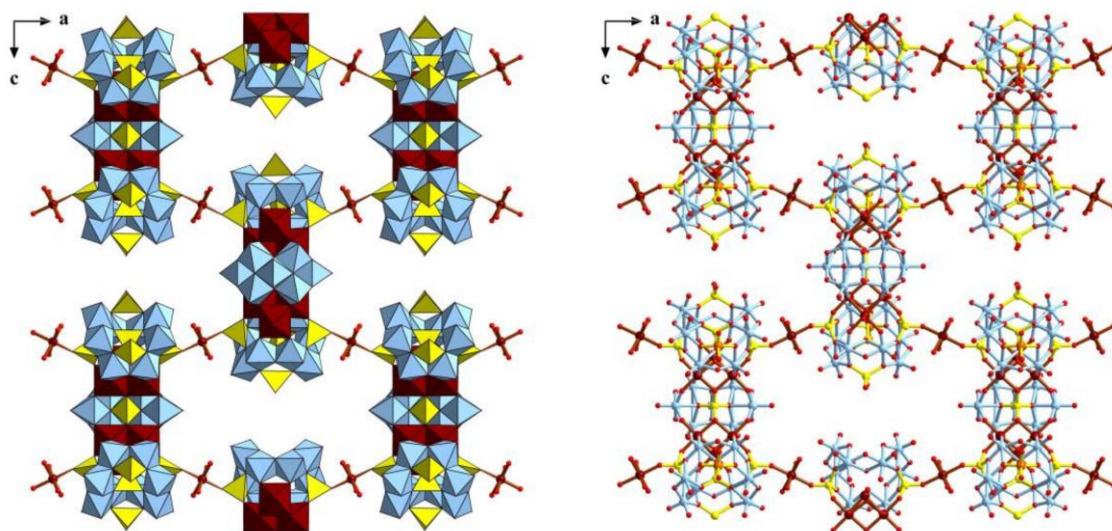


Figure S1. The 2D network of 1 along the *b* axis. The atoms of Co, V and Mo is brown, yellow and sky blue. The MoO_6 , VO_4 and CoO_6 polyhedra is shown in sky blue, yellow and brown, respectively.

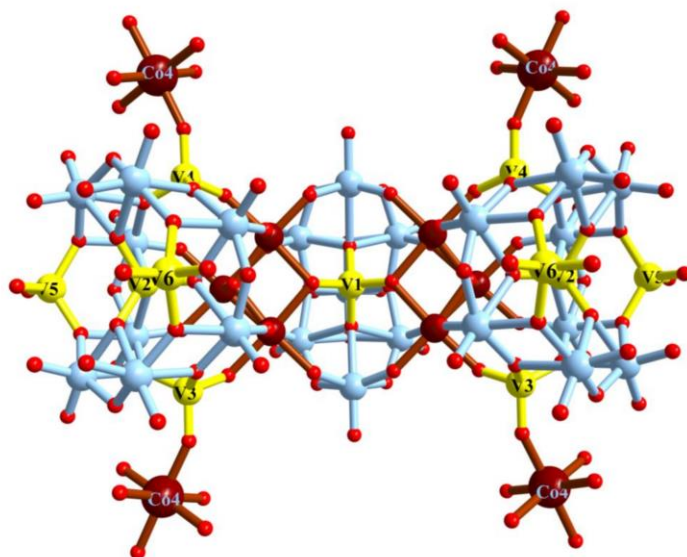


Figure S2. Ball-and-stick representation of $\{\text{Co}_6\text{V}_{10}\text{Mo}_{23}\}$ and 4 $\{\text{Co}(\text{H}_2\text{O})_4\}$

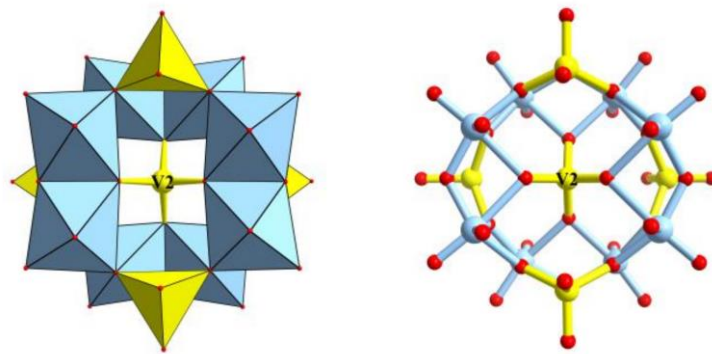
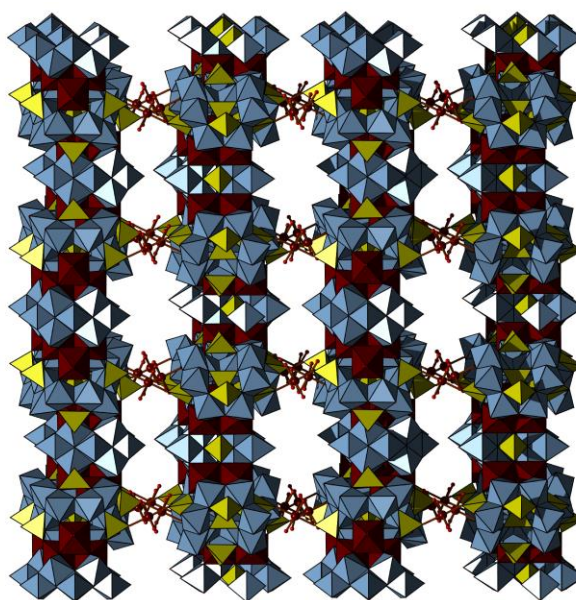


Figure S3. Polyhedral and ball-and-stick representation of $\{V_{4.5}Mo_8O_{40}\}$



FigureS4. The 3D network of 1 along the *b* axis.

3. Additional measurements of **1**

3.1 IR spectrum

In the IR spectrum of **1**, the bands at 1619 and 1403 cm^{-1} are ascribed to NH_4^+ stretching vibrations.¹ The strong bands at 922, 862 and 829 cm^{-1} are associated with M–Ot (M represents Mo or V),² The bands in the 798 cm^{-1} region are attributed to vibration of Mo–O–V.³ The band at 654 cm^{-1} is assigned to vibration of $\nu(\text{Mo–O}_b)$.⁴

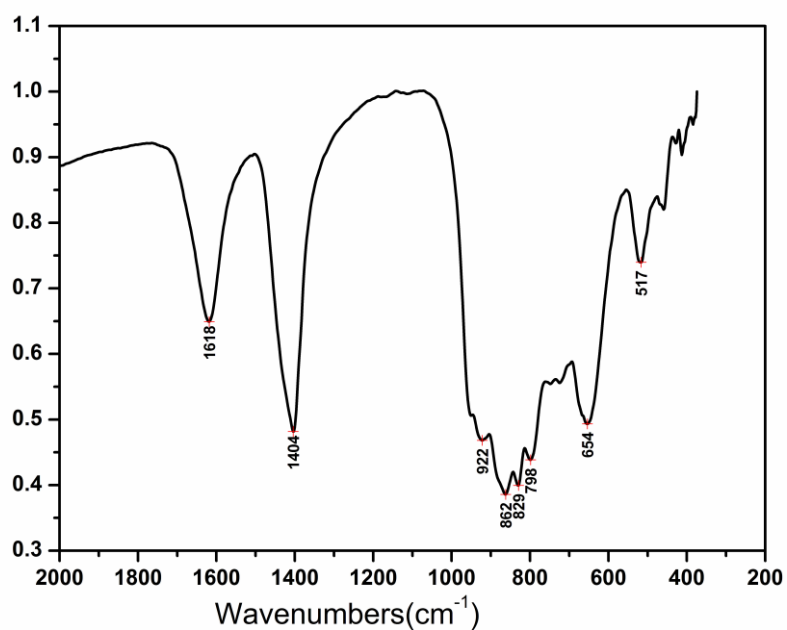


Figure S5. The IR spectrum of **1**

3.2 Thermogravimetric analyses

The TG curve of compound **1** exhibits two steps of weight loss in the temperature range 25–600 °C. First, it gradually loses 34.5 crystalline water molecules in the range 25–150 °C. The observed weight loss 7.20% is lower than the ideal 10.46%, which was attributed to efflorescence of the crystal. The second stage, which occurs from 150–600 °C, is attributed to the loss of 10 ammonia molecules, 10 coordinated water molecules and the decomposition of the polyoxoanions, and the observed total weight loss of 8.40% can compare with the calculated value of 8.32%.

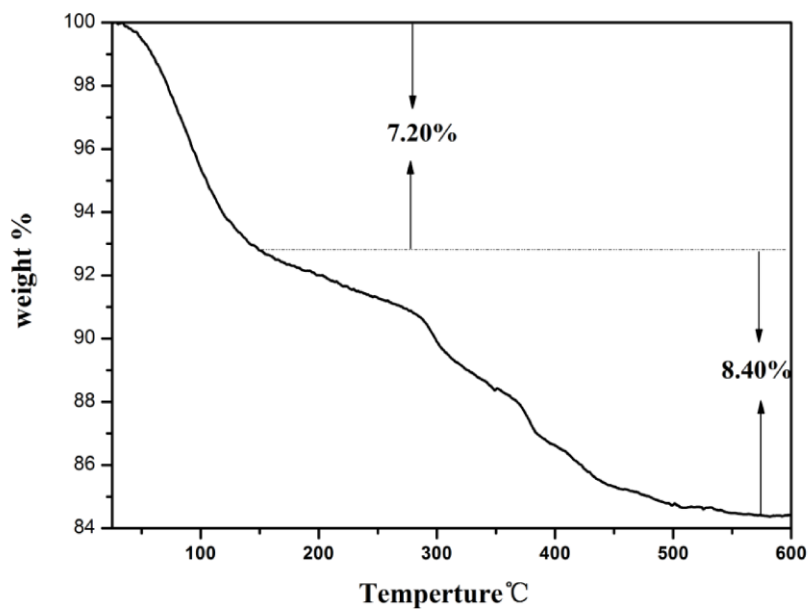


Figure S6. Thermogravimetric analysis (TGA) curve of 1.

4. IR spectra of catalyst

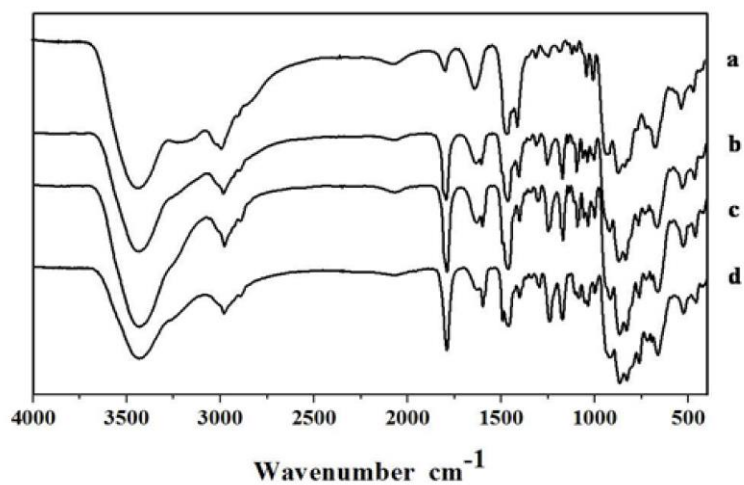


Figure S7. IR spectra of 1 before and after the recycling tests. a) IR spectra of 1 and ionic liquid of pyrrolidinium bromide; b) IR spectra of the sample tested 1st run; c) IR spectra of the sample tested 2nd run; d) IR spectra of the sample tested 3rd run.

5. References

1. W.B Yang, C.Z. Lu, X.P. Zhan and Y. Q. Yu, *J. Clust. Sci.*, 2003, **14**, 391.
2. J. W. Cui, X. B. Cui, J. N. Xu and H. H. Yu, *J. Mol. Struct.*, 2008, **891**, 35.
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4. Y. Y. Yang, L. Xu, G. G. Gao and F.Y. Li, *Eur. J. Inorg. Chem.*, 2009, 1460.