Supporting Information

Synthesis, Structures, and Magnetic Properties of Metal-organic Polyhedra Based on Unprecedented $\{V_7\}$ Isopolyoxometalate Clusters

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1. Materials and Methods

All the reagents were obtained from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) measurement was recorded ranging from 5 to 40º at room temperature on a Siemens D5005 diffractometer with Cu-*Kα* (λ = 1.5418 Å). The C, H, and N elemental analyses were conducted on a Perkin-Elmer 2400CHN elemental analyzer. Thermogravimetric analysis (TGA) of the samples was performed using a Perkin-Elmer TG-7 analyzer heated from room temperature to 800 ºC under nitrogen at the heating rate of 10 °C·min^{-1}. IR spectrum was performed in the range 4000–400 cm^{-1} using KBr pellets on an Alpha Centaurt FT/IR spectrophotometer. Variable temperature magnetic susceptibility data were obtained in the temperature range of 2–300 K using a SQUID magnetometer (Quantum Design, MPMS-5) with an applied field of 1000 Oe. X-ray photoelectron spectroscopy analyses were performed on a VG ESCALABMKII spectrometer with an Al-K*α* (1486.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during the analysis.

2. Synthesis and Characterization

(1) Synthesis of **VMOP-16**:

VCl_3 (0.05 g) and H_2BDC (0.02 g) in a solvent mixture of DEF (N,N-Diethylformamide)/CH_3OH/H_2O (2:0.5:0.05 ml) were placed in a Parr Teflon-lined stainless steel vessel heated to 130 °C and held at this temperature for 2 days. After slow cooling to room temperature, yellowish-brown crystals were obtained (washed with DEF) with a yield of 35 % based on H_2BDC. Elemental analysis (%) cacld: C, 27.22; H, 4.31; N, 1.39. Found: C, 27.36; H, 4.05; N, 1.58. IR (KBr, cm^{-1}): 3444 (br), 2929 (w), 2813 (w), 2499 (w), 1577 (vs), 1396 (vs), 1070 (m), 953 (m), 848 (s), 744 (w), 567 (w).

(2) Synthesis of **VMOP-17**:

The synthetic procedure is similar to that of **VMOP-16** except that H_2BDC was replaced by H_2BDC-NH_2. VCl_3 (0.05 g) and H_2BDC-NH_2 (0.025 g) in solvent mixture of DEF (N,N-Diethylformamide)/CH_3OH/H_2O (2:0.5:0.05 ml) were placed in a Parr Teflon-lined stainless steel vessel heated to 130 °C and held at this temperature for 2 days. After slow cooling to room temperature, yellowish-brown crystals were obtained (washed with DEF) with a yield of 22 % based on H_2BDC-NH_2. Elemental analysis (%) cacld: C, 26.72; H, 4.39; N, 3.18. Found: C, 26.58;

H, 4.55; N, 3.02. IR (KBr, cm^{-1}): 3484 (w), 3374 (w), 2927 (w), 2815 (w), 2497 (w), 1565 (s), 1440 (w), 1382 (w), 1259 (w), 1072 (s), 958 (s), 852 (s), 763 (w), 532 (w).

Caution! A protective mask should be worn in the treatment of obtained **VMOP-16** and **VMOP-17** because of a very unpleasant smell.

3. Single-crystal X-ray Crystallography

The crystallographic data for **VMOP-16** and **VMOP-17** are given in Table S3 and S4. Intensity data were collected at 293 K on a Bruker APEX-II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Absorption corrections were applied using a multi scan technique. The structure was solved using SHELXS-2014[1] (direct methods) and refined using SHELXL-2014 (full-matrix least-squares on F2) contained in OLEX2[1,2]. Since the counter cations or disorder solvents cannot be exactly assigned from the weak reflections, the *SQUEEZE* program in *PLATON*[3] was used to calculate and estimate the possible numbers of the cations and solvents in the accessible void of two crystal structures. During the refinement, most of the non-H atoms were refined ansiotropically. Additionally, some restraints were used in the final refinement, including SIMU and DELU. CCDC 1490971 and 1490972 contain the supplementary crystallographic data for this paper.

Table S1. BVS results for the vanadium ions in **VMOP-16** and **VMOP-17**.

Atom	**BVS calc. for V(IV)**	**BVS calc. for V(V)**
for **VMOP-16**		
V1	**4.24**	4.46
V2	4.82	**5.07**
for **VMOP-17**		
V1	**4.37**	4.60
V2	4.91	**5.17**

Table S2. BVS results for the oxygen atoms of central VO_4 tetrahedrons in **VMOP-16** and **VMOP-17**.

Atom	**BVS value**
for **VMOP-16**	
O3	2.15
O1w	**0.66**
for **VMOP-17**	
O3	2.09
O1w	**0.85**

Table S3. Crystallographic data for **VMOP-16**

Empirical formula	$C_{102.5}H_{193.5}N_{4.5}O_{100.5}V_{28}$
Formula weight	4523.43
Crystal system	Cubic
Space group	*I-43m*
Temperature	293(2) K
Wavelength	0.71069 Å
Unit-cell dimensions	a = b = c =21.911(5) Å α = β =γ = 90 °
Volume	10519(7) $Å^3$
Z	2
Density (calculated)	1.428 g/cm^3
F(000)	4576
Limiting indices	-26<=h<=26, -23<=k<=26, -19<=l<=26
Theta range for data collection	1.859-24.979°
Reflections collected	29227
Independent reflections	1735 [R(int) = 0.0963]
Completeness to theta = 24.979°	99.4 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1735 / 17 / 98
Goodness-of-fit on F^2	1.015
Final R indices [I > 2sigma(I)]	R1 = 0.0435, wR2 = 0.0901
R indices (all data)	R1 = 0.0570, wR2 = 0.0951
Largest diff. peak and hole	0.322 and -0.459 eA^{-3}

Table S4. Crystallographic data for **VMOP-17**

Empirical formula	$C_{103}H_{201.5}N_{10.5}O_{101}V_{28}$
Formula weight	4629.55
Crystal system	Cubic
Space group	*I-43m*
Temperature	293(2) K
Wavelength	0.71073 Å
Unit-cell dimensions	a = b = c =21.954(12) Å α = β =γ = 90 °
Volume	10581.6(17) $Å^3$
Z	2
Density (calculated)	1.453 g/cm^3
F(000)	4690
Limiting indices	-25<=h<=26, -26<=k<=26, -26<=l<=19
Theta range for data collection	1.855 to 25.045°

Reflections collected	30780
Independent reflections	1757 [R(int) = 0.1185]
Completeness to theta = 25.045°	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1757/ 17 / 107
Goodness-of-fit on F^2	1.023
Final R indices [I > 2sigma(I)]	R1 = 0.0635, wR2 = 0.1433
R indices (all data)	R1 = 0.1007, wR2 = 0.1605
Largest diff. peak and hole	0.280 and -0.475 eA^{-3}

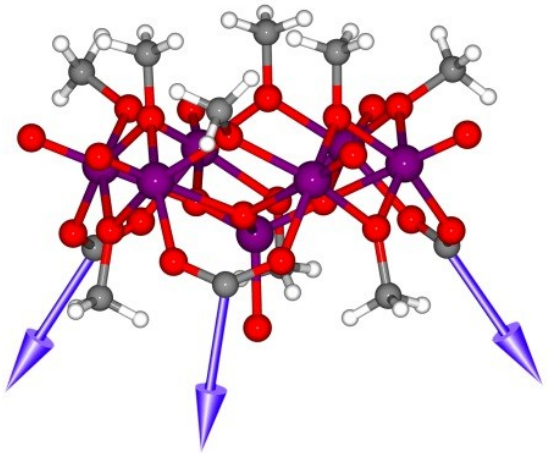

Figure. S1 The Ball-and-sticks view of 3-connected $\{V_7\}$ alkoxo-polyoxovanadate second building unit. Color codes: V, violet; S, light orange; O, red; C, gray; H, white.

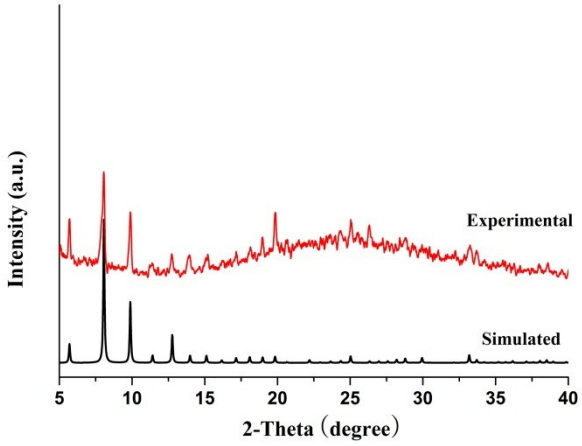

Figure S2. Experimental and simulated powder X-Ray diffraction patterns for **VMOP-16.**

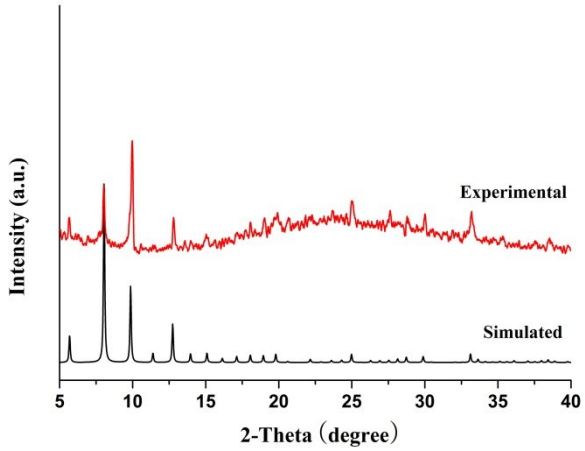

Figure S3. Experimental and simulated powder X-Ray diffraction patterns for **VMOP-17**.

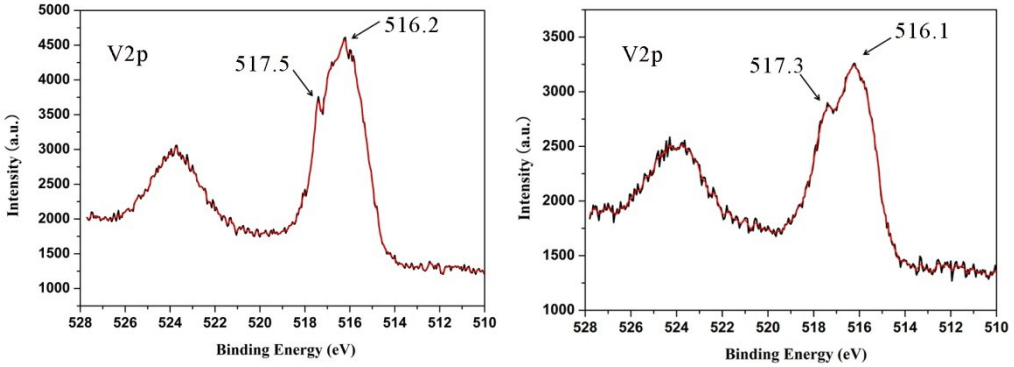

Figure S4. XPS spectra of **VMOP-16** (left) and **VMOP-17** (right)**.**

The XPS spectra of **VMOP-16** gives two peaks at 516.2 and 517.5 eV, which should be attributed to $V^{4+}2p3/2$ and $V^{5+}2p3/2$, respectively. For **VMOP-17**, there exist two peaks at 516.1 and 517.3 eV, which are assigned to $V^{4+}2p3/2$ and $V^{5+}2p3/2$, respectively.[4-6]

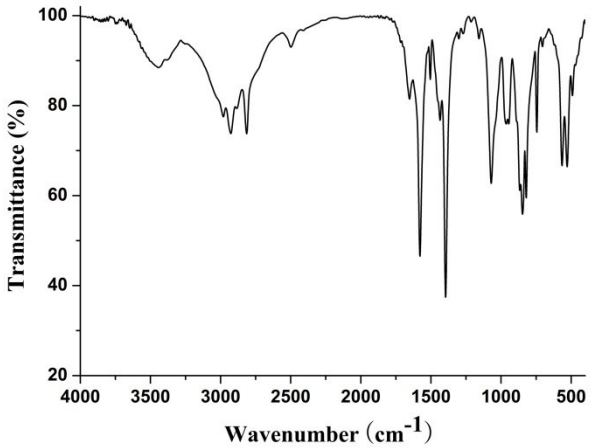

Figure S5. IR spectrum of **VMOP-16.**

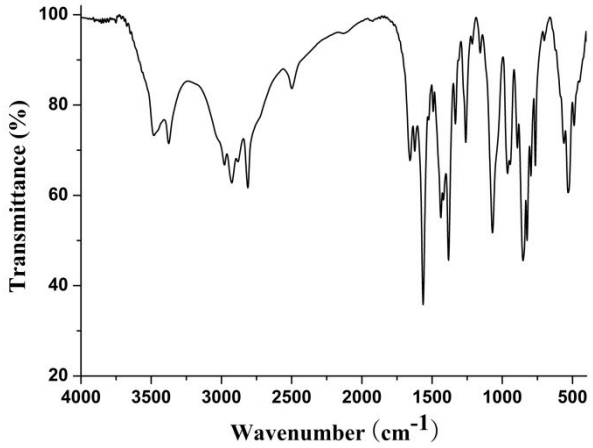

Figure S6. IR spectrum of **VMOP-17.**

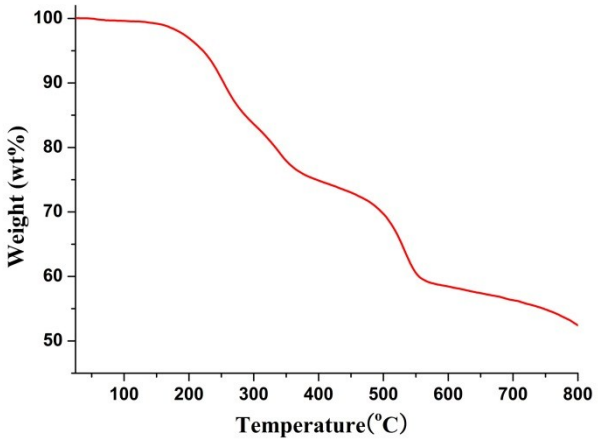

Figure S7. TGA curve of **VMOP-16**.

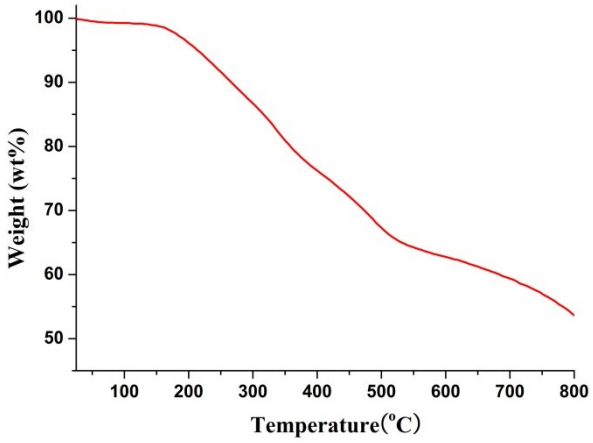

Figure S8. TGA curve of **VMOP-17**.

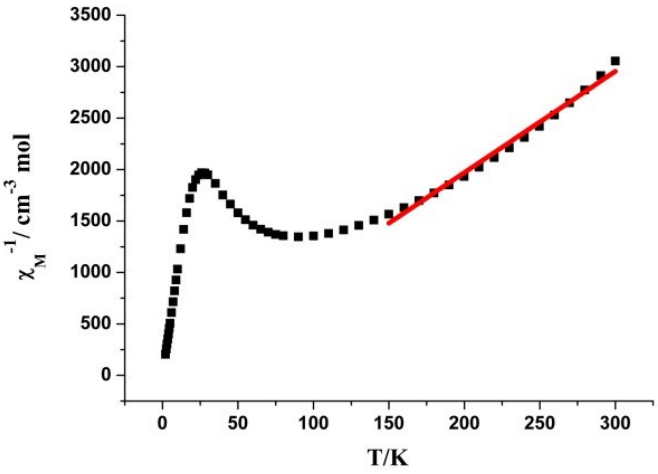

Figure S9. The temperature dependence of the inverse magnetic susceptibility χ_M^{-1} for **VMOP-16** between 2 and 300 K. The solid red line was generated from the best fit by the Curie-Weiss expression in the range of 150–300 K.

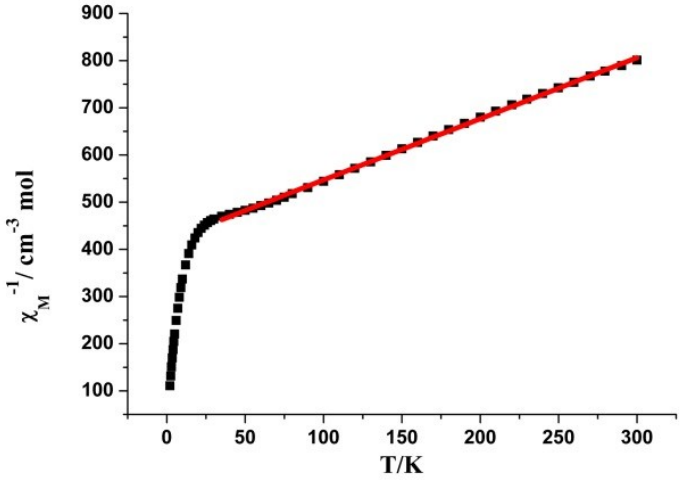

Figure S10. The temperature dependence of the inverse magnetic susceptibility χ_M^{-1} for **VMOP-17** between 2 and 300 K. The solid red line was generated from the best fit by the Curie-Weiss expression in the range of 35–300 K.

References

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