

Electronic Supplementary Information (ESI)

A Large Spin, Magnetically Anisotropic, Octanuclear Vanadium(III) Wheel

Maurice G. Sorolla II,^a Xiqu Wang,^a Tatyana Makarenko,^a and Allan J. Jacobson*^a

^a Department of Chemistry and Texas Center for Superconductivity, University of Houston, Texas 77204, USA

I. EXPERIMENTAL

Synthesis of $[(\text{CH}_3)_2\text{NH}_2]_{17.4}[\text{V}_8(\text{OH})_8(\text{SO}_4)_{16}][\text{SO}_4]_{0.7}$ **1.** A mixture of DMF/concentrated sulfuric acid/anhydrous VOSO_4 with 50:7:1 mole ratio was sonicated for 15 minutes. After nine days of solvothermal reaction in a Teflon-lined autoclave at 130 °C, large dark green columnar crystals of **1** (45% yield) were acquired (Figure S1). The precursor VOSO_4 was obtained by heating $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ at 400 °C for two hours. The crystals of **1** could also be produced starting from $\text{V}_2(\text{SO}_4)_3$ instead of VOSO_4 . Calcd (found): C 14.2 (14.2), H 5.0 (5.0), N 8.3 (8.2). SEM-EDS analysis of the crystal samples confirmed the presence of V and S, and no impurities heavier than Na were detected.

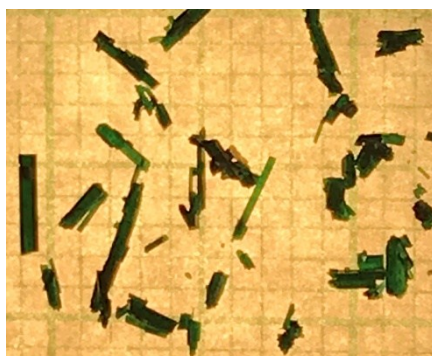


Figure S1. Photograph of the crystals of **1**. The length of the smallest squares in the grid is 1 mm.

Crystallography. A dark green prism with the approximate dimension $0.41 \times 0.32 \times 0.22 \text{ mm}^3$ was mounted on a Bruker DUO platform diffractometer equipped with a 4K CCD APEX II detector and measured using Mo K_α radiation at 123 K. The reflections were collected using a narrow-frame algorithm with scan widths of 0.25° in ω and an exposure time of 40 seconds per frame at 8 cm detector distance. Initial indexing of the reflections gave a monoclinic primitive cell with $a = 11.061 \text{ \AA}$, $b = 47.299 \text{ \AA}$, $c = 22.573 \text{ \AA}$, $\beta = 93.17^\circ$. Inspection of the measured frames revealed weak but sharp superstructure reflections that indicate a monoclinic C-centered lattice with $a_{\text{sup}} = 2a$, $b_{\text{sup}} = 2b$, $c_{\text{sup}} = -a-c$. Data were integrated using the Bruker Apex-II software package, with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. The data were scaled, and an empirical absorption correction was applied with the program SADABS of the package. While the substructure was readily determined, our effort to solve the superstructure has been

unsuccessful. The substructure was solved by using the program SHELXT 2014 and refined with SHELXL 2018. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically with riding parameters. Several sulfate and dimethyl ammonium groups were found split with fractional occupancies, probably due to the unresolved superstructure. Some highly disordered solvent species mainly located close to the center of the $V_8(OH)_8(SO_4)_{16}$ ring were treated with the program PLATON/SQUEEZE that indicates 97 electrons per unit cell were “squeezed.”

The final structure data in CIF format were deposited to the Cambridge Crystallographic Data Centre with the deposition number CCDC 1871701.

Table S1. Crystal data and structure refinement for **1**

Empirical formula	$V_8S_{16.7}O_{74.8}N_{16.7}C_{33.4}H_{141.2}$	
Formula weight	2918.8	
Temperature	123(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P 2_1/n$	
Unit cell dimensions	$a = 11.0605(7)$ Å	
	$b = 47.299(3)$ Å	$\beta = 93.175(5)^\circ$
	$c = 22.5731(14)$ Å	
Volume	11791.1(12) Å ³	
Z	4	
Density (calculated)	1.644 g/cm ³	
Absorption coefficient	1.008 mm ⁻¹	
F(000)	6036	
Crystal size	0.41 x 0.32 x 0.22 mm ³	
Theta range for data collection	1.576 to 28.161°.	
Index ranges	$-14 \leq h \leq 14, -61 \leq k \leq 14, -29 \leq l \leq 29$	
Reflections collected	50,077	
Independent reflections	28,226 [R(int) = 0.0332]	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	28,226 / 5,705 / 1706	
Goodness-of-fit on F ²	0.977	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0639, wR_2 = 0.1959$	
R indices (all data)	$R_1 = 0.0900, wR_2 = 0.2033$	
Largest diff. peak and hole	1.361 and -0.841 e.Å ⁻³	

Magnetic Measurements. Magnetic measurements of the crushed crystal samples were performed using a Quantum Design Model 6000 VSM magnetometer. The temperature dependence of the magnetic susceptibility was obtained under an applied magnetic field of 0.1 T in the temperature range from 2 to 300 K. The zero-field cooled and field cooled curves overlap. Magnetization measurements at 2 K were recorded between 0 to 8 T and no hysteresis was observed. Variable temperature-variable field measurements were taken from 2 to 7 K and 1 to 8 T. Diamagnetic corrections were estimated from Pascal tables.

II. Crystal Structure

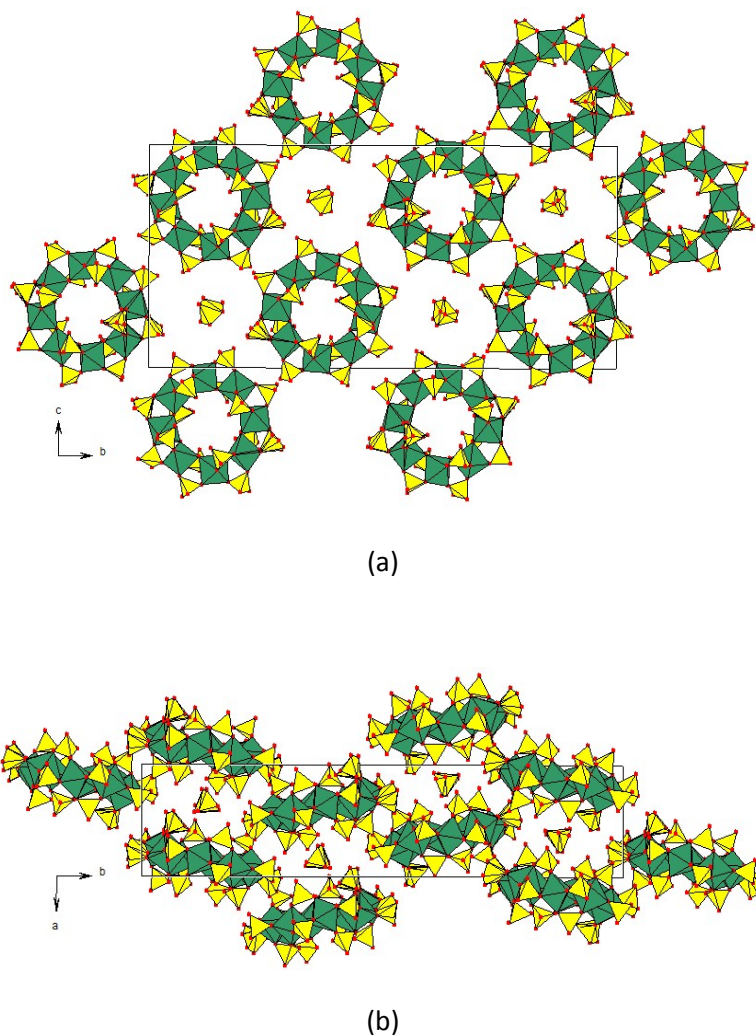


Figure S2. Crystal Structure of **1** along (a) *bc* plane, and (b) *ab* plane. VO_6 and SO_4 are represented by green and yellow polyhedra, respectively. For clarity, C, N, and H atoms are not shown.

III. THERMOGRAVIMETRIC ANALYSIS

To confirm the vanadium content of the crystals, thermogravimetric analysis (TGA 2050, TA Instruments) under helium was performed up to 700 °C at a heating rate of 1 °C/min (Figure S3). The experimental mass loss (79 %) is consistent with that expected from the decomposition to V_2O_3 (79 %).

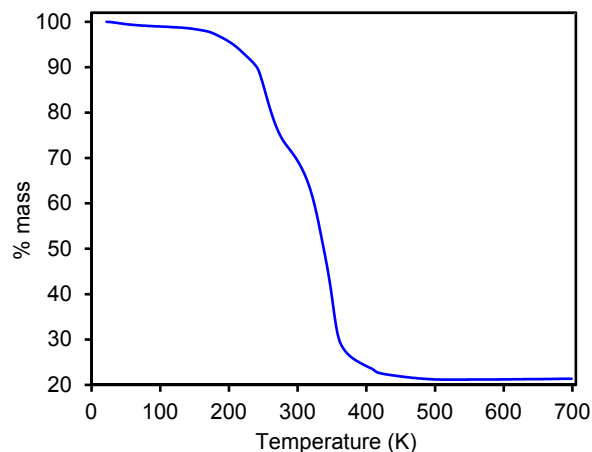


Figure S3. Thermogravimetric analysis of **1** under a helium gas flow.

IV. IR SPECTROSCOPY

IR spectrum of the crushed crystal samples of **1** was recorded using a Thermo Scientific Nicolet iS10 spectrometer (Figure S4). Table S2 lists the tentative peak assignments of the inorganic core. The peaks above 1400 cm^{-1} could be assigned to the organic guests, $[(CH_3)_2NH_2]^+$ cations. The O-H stretch is located at 3405 cm^{-1} .

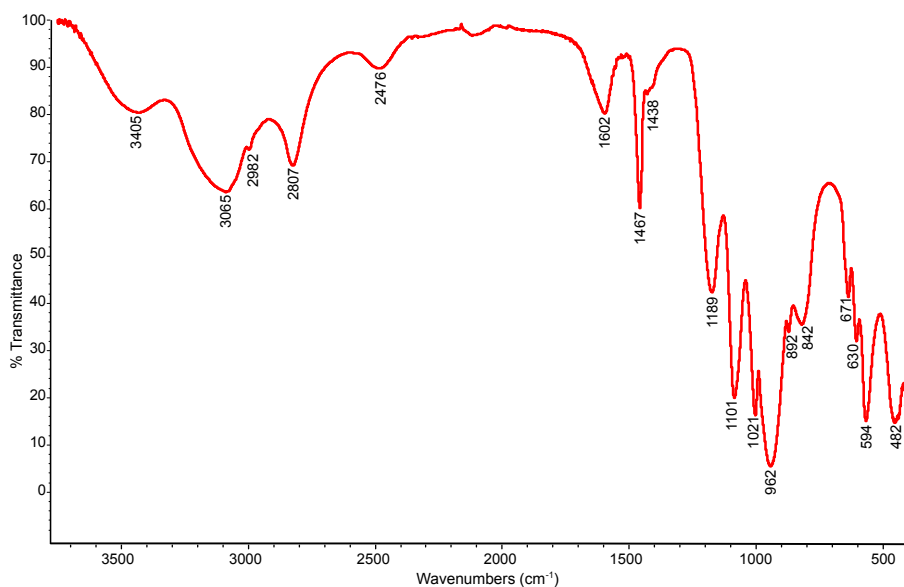


Figure S4. IR spectrum of **1**.

Table S2. Peak assignments of the inorganic core

IR Peaks	Tentative Assignment
441	$\nu_2(\text{SO}_4)$, $\nu(\text{V-O-S})$
482	
594	$\nu_4(\text{SO}_4)$, $\nu(\text{V-O-V})$
630	
671	
842	$\nu(\text{V-O-V})$
892	
962	$\nu_1(\text{SO}_4)$
1021	$\nu_1(\text{SO}_4)$, $\nu(\text{V-O-H})$
1101	$\nu_3(\text{SO}_4)$
1189	

V. BOND VALENCE SUM (BVS) CALCULATIONS

Table S3. Oxidation states assignment of the vanadium ions

Site	BVS			Assignment
	V(III)	V(IV)	V(V)	
V1	3.04	3.40	3.58	V(III)
V2	2.93	3.28	3.45	V(III)
V3	3.01	3.37	3.54	V(III)
V4	3.02	3.38	3.56	V(III)
V5	3.01	3.37	3.54	V(III)
V6	2.99	3.35	3.52	V(III)
V7	3.04	3.39	3.57	V(III)
V8	2.97	3.32	3.50	V(III)

Parameters used for the BVS calculations¹

	V(III)	V(IV)	V(V)
R_o	1.743	1.784	1.803
b	0.37	0.37	0.37

Reference

- 1 N. E. Brese and M. O'Keeffe, *Acta Cryst.*, 1991, **B47**, 192.