**Supplementary Information** 

# Sulfur-Centred Polyoxoniobate-based 3D Organic-Inorganic Hybrid Compound and its Magnetic Behavior

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#### **Materials and Methods**

Elemental analyses (C, H and N) were measured on a ELEMENTAR vario EL cube Elmer CHN elemental analyzer; elemental analysis for S element was conducted on CS-2800 elemental analyzer; elements Nb, V and Co were determined with a Thermo iCAP 6000 atomic emission spectrometer. IR spectrum was collected in the range 40000-400 cm<sup>-1</sup> with KBr pellets dispersed with sample on a Nicolet 170SXFT-IR spectrophotometer. Powder Xray diffraction measurement was recorded radiation ranging from 5 to 50° at room temperature on a Shimadzu XRD-6000 X-ray diffractometer with Cu-K $\alpha$  ( $\lambda$  = 1.5418 Å). The energy dispersive spectrum (EDS) was collected on a H-8100 TEM spectrometer operating at 200 kV accelerating voltage. The X-ray photoelectron spectra (XPS) analyses were collected on a PHI Quantera SXM spectrometer with Al K $\alpha$  radiation as the X-ray source (1486.7 eV) and a pass energy of 55 eV, respectively. The pressure inside the analyzer was maintained at 10<sup>-9</sup> Torr.

#### Synthetic procedures

All common laboratory chemicals were reagent grade, purchased from commercial sources and used without further purification. Oxosulfatovanadate precursor was purchased from Energy Chemistry Cor. Hexaniobate precursor K<sub>7</sub>HNb<sub>6</sub>O<sub>19</sub>·8H<sub>2</sub>O was prepared according to the literature method (C. M. Flynn, G. D. Stucky, *Inorg. Chem.***1969**, 8, 332-334) and was identified by IR spectra and TGA. A mixture of K<sub>7</sub>HNb<sub>6</sub>O<sub>19</sub>·8H<sub>2</sub>O (0.15 g, 0.12 mmol), V<sub>2</sub>O<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub> (0.1g, 0.23 mmol), 2CoCO<sub>3</sub>·3Co(OH)<sub>2</sub>·H<sub>2</sub>O (0.28 g, 0.55 mmol) was dispersed in 8 mL of water, followed by adding 0.5 mL ethylenediamine. The mixture was transferred into a 23 ml stainless-steel autoclave and heated at 140 °C for 144 hours. After cooling to room temperature, block-shaped dark brown crystals of **1** were isolated by hand under the microscope. Yield: ~ 3.57% based on V. Anal. Calc. for C<sub>16</sub>H<sub>80.75</sub>N<sub>16</sub>Co<sub>4</sub>Nb<sub>8</sub>O<sub>55.5</sub>SV<sub>9.75</sub>: C, 6.54%; H, 2.87%; N, 7.52%; S, 0.91%; Co, 8.35%; V, 17.03%; Nb, 25.53%; Found: C, 6.64%; H, 2.80%; N, 7.75%; S, 1.11%; Co, 8.15%; V, 17.17%; Nb, 25.69%. IR (KBr, cm<sup>-1</sup>): 3423(s), 3351(s), 3262(s), 3212(s), 2961(w), 2883(w), 1637(m), 1587(s), 1459(m), 1384(m), 1325(w), 1282(w), 1155(w), 1121(w), 1057(s), 1007(s), 962(s), 878(s), 862(s), 775(m), 699(s), 624(s), 501(m).

#### **Crystallography details**

Crystal data for compound **1** were collected at 293(2) K on Bruker APEX-II CCD detector with graphite monochromatic Mo  $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å). The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  using the SHELX program.<sup>1</sup> Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at the calculated positions. CCDC-1417485 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crytallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk)

<sup>1</sup> G.M. Sheldrick, SHELXS-97, *Program for Crystal Structure Solution*, Göttingen University, Germany, 1997.

### **Magnetic Measurements**

Magnetic susceptibility data were taken on Quantum Design MPMS-XL7. Direct current(dc) magnetic susceptibility measurements were carried out on the crystalline samples crushed from single crystals under the applied field 1000 Oe in the temperature range 2-300 K. Alternate current (ac) magnetic susceptibility measurements were carried out under the zero dc field and 3.5 Oe oscillating ac field. The crystalline sample was compacted and immobilized into a cylindrical PTFE sample holder. Diamagnetic corrections were applied by using Pascal constants and diamagnetisms of the sample holder.

## Table S1 Crystallographic parameters for 1<sup>a</sup>.

Compound	1
Empirical Formula	$C_{16}H_{80.25}N_{16}Co_4Nb_8O_{55.5}SV_{9.75}$
Crystal system	Orthorhombic
Space group	Pnma
	a = 23.9036(8) Å, α = 90 °
Unit cell dimensions	b = 21.2261(6) Å, β = 90 °
	c = 18. 0968(4) Å, γ = 90 °
Volume	9182.0(5) Å <sup>3</sup>
Z	1
Mr	2893
Calculated density	2.032 Mg/m <sup>3</sup>
Absorption coefficient	2.704 mm <sup>-1</sup>
F(000)	5433
Temperature (K)	293(2)
Theta range for data collection	2.95 to 29.52°
Reflections collected/unique	38655/8325
R(int)	0.0871
Completeness to theta =25.00	99.7%
Absorption correction	Semi-empirical from equivalents
Final R indices [I>2sigma(I)]	R1 = 0.0996, wR2 = 0.2783
R indices (all data)	R1 = 0.1409 , wR2 = 0.3177
Goodness-of-fit on F <sup>2</sup>	1.038

 ${}^{a}R_{I} = \Sigma [IF_{0}I - IF_{c}II/\Sigma IF_{0}]; {}^{b}wR_{2} = \Sigma [w(F_{0}^{2} - F_{c}^{2})^{2}]/\Sigma [w(F_{0}^{2})^{2}]^{1/2}$ 

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Bond types	Bond lengths	Bond types	Bond lengths	Bond types	Bond lengths	
Nb1-O3	1.921(11)	V2-016	1.63(2)	Co1-O14_a	2.067(11)	
Nb1-O4	1.998(11)	V2-023	1.955(11)	Co1-O20	2.151(13)	
Nb1-O6	1.736(17)	V2-09_j	1.963(11)	Co1-N1	2.141(17)	
Nb1-O3_j	1.921(11)	V2-023_j	1.955(11)	Co1-N2	2.124(18)	
Nb1-O4_j	1.998(11)	V3-01	1.948(12)	Co1-N3	2.182(19)	
Nb2-O2	2.003(11)	V3-O2	1.967(11)	Co1-N4	2.107(18)	
Nb2-O3	1.921(11)	V3-011	1.931(12)	Co2-O8_c	2.100(17)	
Nb2-014	1.735(11)	V3-018	1.614(11)	Co2-O6	2.148(17)	
Nb2-O22	1.916(12)	V3-024	1.957(12)	Co2-N7	2.149(14)	
Nb2-O24	2.013(11)	V4-012	1.930(13)	Co2-N7_j	2.149(14)	
Nb2-O26	2.54(2)	V4-013	2.033(19)	Co2-N8	2.140(14)	
Nb2-027	2.53(2)	V4-019	2.01(2)	Co2-N8_j	2.140(14)	
Nb3-08	1.713(17)	V4-021	1.57(2)	Co3-O15	2.113(11)	
Nb3-O22	1.954(12)	V4-012_j	1.930(13)	Co3-O15_f	2.113(11)	
Nb3-O23	1.995(11)	V5-01	1.970(12)	Co3-N5	2.131(16)	
Nb3-O22_j	1.954(12)	V5-O9	2.010(11)	Co3-N5_f	2.131(16)	
Nb3-O23_j	1.995(11)	V5-O10	1.610(13)	Co3-N6	2.143(15)	
Nb4-01	1.966(11)	V5-023	1.930(11)	Co3-N6_f	2.143(15)	
Nb4-O9	1.949(12)	V5-024	1.953(12)	S1-O28	1.35(2)	
Nb4-012	1.949(12)	V6-O2	1.950(12)	S1-O26	1.48(2)	
Nb4-O19	1.945(7)	V6-O4	1.940(11)	S1-027	1.32(3)	
Nb4-O20	1.722(13)	V6-O5	1.967(11)	S1-027_j	1.32(2)	
Nb5-O5	1.957(11)	V6-011	1.957(12)	S1-O29	1.31(2)	
Nb5-O11	2.018(11)	V6-015	1.634(12)	S1-O26_j	1.48(2)	
Nb5-O12	1.958(12)	V7-022	2.060(17)			
Nb5-O13	1.928(6)	V7-025	1.60(7)			
Nb5-017	1.677(13)	V7-03_j	2.056(17)			
V1-O4	1.983(11)	V7-022_j	2.060(17)			
V1-05	1.954(11)	V7-03	2.056(17)			
V1-07	1.614(17)	V8-02W	2.30(3)			
V1-04_j	1.983(11)	V8-O3W	1.91(4)			
V1-05_j	1.954(11)	V8-O4W	2.13(4)			
V2-09	1.963(11)	V8-01W	2.06(5)			

Table S2 The selected bond lengths for 1.

a = 1/2-x,2-y,-1/2+z; c = -1/2+x,3/2-y,3/2-z; f = -x,2-y,1-z; j = x,3/2-y,z

Table **S3**. The bond valance sum calculation for compound **1**.

V site	V1	V2	V3	V4	V5	V6	V7	V8
BVS	4.01	4.01	4.13	4.18	4.06	4.03	3.55	2.5
assigne d O.S.	4	4	4	4	4	4	4	3
Co site	Co1	Co2	Co3					
BVS	2.76	2.69	2.75					
assigne d O.S.	3	3	3					

Fig. S1 Digital photograph of 1.



Fig. S2 The EDX spectrum of 1, which gives the compositional information.



**Fig. S3** Representation of the central  $\{SO_4\}$  in (a) ball-and-stick and (b) polyhedral drawings, where oxygen atoms labeled O26 and O27 atoms are somewhat disordered. Symmetry code: x, 3/2-y, z.



Fig. S4 Structural comparisons between the  ${SNb_8V_{9.25}O_{45.25}}$  (a, b, c) and  ${XNb_8V_8O_{44}}$  (X = P, As, V) reported by Wang (d, e, f).



Fig. S5 Representation of the solvated vanadium cation  $\{V(H_2O)_6\}^{5+}$  in (a) ball-and-stick and (b) polyhedral drawings.



**Fig. S6** Representation of Co3 complex acting as bridge to connect the polyanion  $\{SNb_8V_{9.25}O_{45.25}\}$  through Co-O-V linkage into a zigzag chain along the *c*-axis in (a) ball-and-stick and (b) mixed ball-and-stick and polyhedral drawings.



Fig. S7 The 2D layer constructed by the polyanion  $\{SNb_8V_{9.25}O_{45.25}\}$  and cobalt complex along the *ab* plane.



Fig. S8 The schematic view of the 3D topology.



**Fig. S9** The PXRD pattern of **1**. The phase purity of **1** was confirmed by the well match of the experimental powder pattern (line in black) with the simulated one (line in grey).



**Fig. S10** The FT - IR spectrum in the range 2000-500 cm<sup>-1</sup> for **1**. Peaks at 878 cm<sup>-1</sup> and 699 cm<sup>-1</sup> can be attributed to Nb=O<sub>t</sub> and Nb-O<sub>b</sub> vibrations. Peaks centered at 962 cm<sup>-1</sup> and 777 cm<sup>-1</sup> can be assigned to  $V^{IV}=O_t^2$  and V-O<sub>b</sub> vibrations, respectively. The vibration band at 1003 cm<sup>-1</sup> can be attributed to V-OH<sub>2</sub> of {V(H<sub>2</sub>O)<sub>6</sub>}<sup>5+.3</sup> The band at 862 cm<sup>-1</sup> is likely due to the coordinated water molecules of the solvated vanadium cations.<sup>3</sup>



**Fig. S11** The Uv/vis/NIR spectra of compound **1**. The characteristic band of 580 nm is attributed to the  $d \rightarrow d$  transition of octahedral Co<sup>2+</sup> ion.



- <sup>2</sup> M. Wendt, U. Warzok, C. Nather, J. V. Leusen, P. Kogerler, C. A. Schalley and W. Bensch, *Chem. Sci.*, 2016, **7**, 2684.
- <sup>3</sup> S. Cevik, B. Sasmaz, C. Yenikaya, F. Colak, M. Sari and O. Buyukagungor, *Russ. J. Inorg. Chem.*, 2010, **50**, 494.

**Fig. S12** The XPS survey spectrum for **1**. The binding energies were obtained with reference to the C 1s at 284.8 eV. The plot displays signals attributable to Nb3d, V2p, Co2p, S2p, C1s, N1s.



**Fig. S13** The XPS V2p spectrum of **1**, where two peaks at 515.40 eV and 516.63 eV corresponding to  $V^{IV}$  and  $V^{V}$  species, respectively are observed.



**Fig. S14** The XPS Co2p spectrum of **1**, where two well-resolved peaks at 781.8 and 796.76 eV with satellite structures are found, and this is characteristic for Co ions in +2 oxidation state.



**Fig. S15** The XPS S2p spectrum of **1**, where two peaks centered around 167.98 eV and 169.16 eV are fitted, corresponding to S2p3/2 and S2p1/2, respectively.



**Fig. S16** The FT-IR spectra of the fresh sample and the sample exposed in air for a month. The difference indicates that **1** is not air-stable and the structural change is possibly due to the oxidation of  $V^{IV}$  by  $O_2$ .



**Fig. S17** The FT-IR spectra in the range 2000-500 cm<sup>-1</sup> for **1** at various pH values. The results suggest that **1** as a solid is stable in aqueous solution in the pH range 7.0-11.0.



Fig. S18 Temperature dependence of X of 1 under applied dc field 1000 Oe.



Fig. S19 Field dependence of the magnetization for 1. The inset shows the hysteresis for 1 at 2 K. The magnetization of 1 at 70 kOe is 5.92 N $\beta$  at temperature 2 K, much lower than the expected saturation value (*Ms* = 8.66 N $\beta$ , S' = 1/2, and g' = 4.33 for octahedral Co<sup>II</sup>, assuming the {V<sup>VI</sup><sub>8</sub>} cluster makes no contribution). The clear hysteresis loop at 2.0 K gives a coercive field of *H*c ≈ 0.68 kOe and a remnant magnetization of *M*r = 0.30 N $\beta$ . The canting angle can be estimated to be 1.98° based on the equation  $\alpha = \tan^{-1}(Mr/Ms)$ .



**Fig. S20** Arrhenius plot of the relaxation time  $\tau$  vs reciprocal temperature of **1**. The frequency shift parameter can be estimated by the equation  $\phi = \Delta T_p/[T_p\Delta(\log \omega)]$ , where  $\Delta T_p$  is the shift of peak in  $\chi'$ ,  $T_p$  is the peak temperature, and  $\omega$  is the applied frequency. As a result, the value of  $\phi = 0.03$  is determined. The relaxation times were calculated by the equation  $\tau = 1/(2\pi v)$ . The relaxation times obey the Arrhenius law [ $\tau = \tau_0 \exp(\Delta_{\tau}/\kappa_B T)$ ] ( $\kappa_B$  is the Boltzmann constant and  $\tau_0$  a pre-exponential factor) and the resulting relaxation barrier ( $\Delta_{\tau}/\kappa_B$ ) and  $\tau$  is 576 K and 1.27 × 10<sup>-21</sup> s, respectively.

