

Electronic Supplementary Information

Three intersecting $\{V_{12}\}$ rings: $\{V_{30}Sb_8\}$, an ultra-large polyoxovanadate cluster shell

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Synthesis of $(NH_4)_{12}[V_{30}Sb_8O_{78}] \cdot 10H_2O$ (**1**)

900.6 mg (7.7 mmol) NH_4VO_3 and 600 mg (2 mmol) Sb_2O_3 were mixed with 4 mL of a mixture of N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine and water (38 % amine), resulting in a pH of *ca.* 10. The reaction mixture was heated in a PTFE-lined autoclave for 10 d at 150 °C, after which the pH remained at *ca.* 10. In the reaction product, small amounts of deep red crystals were observed which were manually separated. The crystals were washed with water, ethanol and acetonitrile and stored in a desiccator. A large number of syntheses were performed varying several reactions parameters but the yield was always very low, and even in some batches no red crystals could be observed. We note that only the above-stated $NH_4VO_3:Sb_2O_3$ molar ratio of 3.85:1 yielded crystalline **1**.

Elemental analysis: calcd. for $H_{68}N_{12}O_{100}Sb_8V_{30}$: H, 1.58; N, 3.87; Found: H, 1.51; N, 3.98 %.

Single-crystal X-ray diffraction structure determination

Data collection was performed using an Imaging Plate Diffraction System (IPDS-1) from STOE & CIE with Mo-K α radiation. A numerical absorption correction was performed with X-Red X-Shape as part of the program package X-Area. All non-hydrogen atoms were refined with anisotropic displacement parameters. One N atom can be clearly located because all H atoms were found in the difference map. For this N atom the N-H hydrogen atoms were located in difference map, their bond lengths were set to ideal values and finally they were refined isotropically with $U_{iso}(H) = 1.5 U_{eq}(N)$ using a riding model. The second N atom was arbitrarily assigned to a position that seems to be not fully occupied, and one cannot exclude that it corresponds to a water O atom. After structure refinement there are a few residual

electron density peaks indicating for disordered water molecules. Their contribution to the electron density map was removed using the Squeeze option in Platon, leading to a solvent-accessible void volume of 537 Å³ and an electron count of 178. These data account for about 10 crystal water molecules in the structure of the title compound. We note that two small residual electron density maxima are found within the central cavity of the {V₃₀Sb₈} cluster with distances to cluster O atoms of about 2.74 Å, indicating altogether one disordered water molecule. For this water molecule the O-H hydrogen atoms cannot be located, and upon anisotropic refinement using a split model, very large components of the anisotropic displacement parameters are observed indicating for larger static or dynamic disorder. Therefore, as we could not unambiguously confirm this group, its contribution to the electron density was removed using Squeeze. Selected crystal data and details of the structure refinements are given in Table S1, an Ortep plot in Figure S1 and selected bond lengths in Table S2. Bond valence sums for V and Sb are given in Table S3.

CSD 2088762 contains the supplementary crystallographic data for this paper. These data can be obtained free charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Selected crystal data and results of the structure refinements for **1**.

Compound	1
Sum formula	H ₄₈ N ₁₂ O ₉₀ Sb ₈ V ₃₀
MW / g mol ⁻¹	3966.70
Crystal system	Tetragonal
Space group	<i>I4/m</i>
Wavelength / Å	0.71073
<i>a</i> / Å	16.2776(7)
<i>b</i> / Å	16.2776(7)
<i>c</i> / Å	17.7520(9)
α	90°
β	90°
γ	90°
<i>V</i> / Å ³	4703.6(5)
<i>T</i> / K	293
<i>Z</i>	2
<i>D</i> _{calc} / g cm ⁻³	2.801
μ / mm ⁻¹	5.177
Crystal size / mm ³	0.06 × 0.08 × 0.10
<i>T</i> _{min/max}	0.4385/0.4809
θ _{max}	27.992

Refl. collected	14821
Unique refl.	2925
R_{int}	0.0616
Refl. [$F_o > 4\sigma(F_o)$]	2229
Parameters	161
$R_1[F_o > 4\sigma(F_o)]$	0.0415
wR_2 (for all data)	0.1072
GOF	1.034
$\Delta\rho_{max}, \Delta\rho_{min} / e\text{\AA}^{-3}$	2.455, -0.899

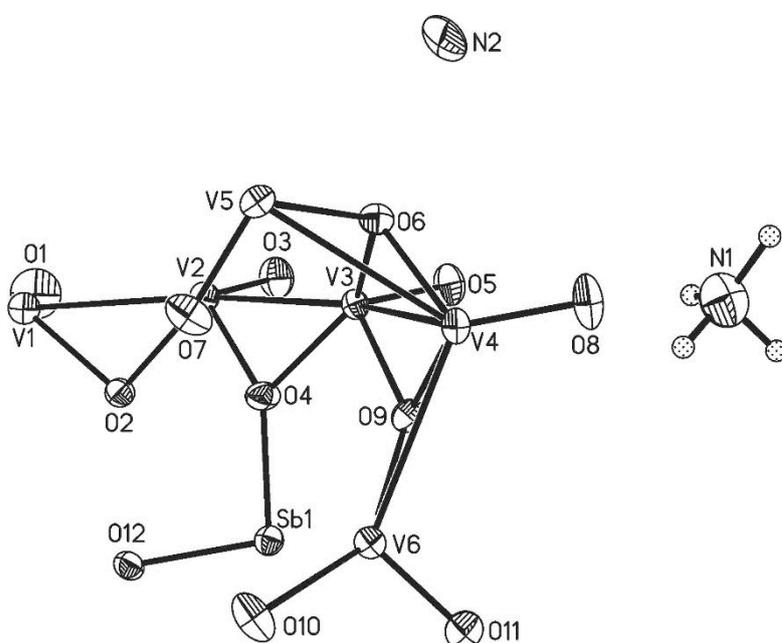


Figure S1. View of the asymmetric unit of **1** with labelling and displacement ellipsoids drawn at the 50% probability level.

Table S2. Bond lengths (in Å) for **1**. Symmetry transformations used to generate equivalent atoms: #1 $x, y, -z+1$; #2 $-y+1, x+1, z$; #3 $y-1, -x+1, z$; #4 $-x, -y+2, z$; #5 $-y+1, x+1, -z+1$.

Sb(1)-O(10)#1	1.959(5)	V(3)-O(4)	1.971(4)
Sb(1)-O(12)	1.961(4)	V(3)-O(12)#2	2.007(4)
Sb(1)-O(4)	1.970(4)	V(3)-V(4)	2.9192(11)
V(1)-O(1)	1.608(10)	V(4)-O(8)	1.621(6)
V(1)-O(2)	1.938(4)	V(4)-O(6)#1	1.950(4)
V(1)-O(2)#2	1.938(4)	V(4)-O(6)	1.950(4)
V(1)-O(2)#3	1.938(4)	V(4)-O(9)#1	1.952(4)

V(1)-O(2)#4	1.938(4)	V(4)-O(9)	1.952(4)
V(1)-V(2)	2.8813(12)	V(4)-V(5)	2.8274(19)
V(1)-V(2)#2	2.8813(12)	V(4)-V(6)	2.8839(19)
V(1)-V(2)#4	2.8813(12)	V(5)-O(7)	1.606(7)
V(1)-V(2)#3	2.8813(12)	V(5)-O(6)#1	1.953(4)
V(2)-O(3)	1.614(5)	V(5)-O(6)	1.953(4)
V(2)-O(2)#2	1.914(4)	V(5)-O(10)#2	1.958(4)
V(2)-O(2)	1.928(4)	V(5)-O(10)#5	1.958(4)
V(2)-O(12)#2	1.981(4)	V(5)-V(6)#2	3.0310(19)
V(2)-O(4)	1.982(4)	V(6)-O(11)	1.607(6)
V(2)-V(3)	2.9429(14)	V(6)-O(9)#1	1.950(4)
V(3)-O(5)	1.619(4)	V(6)-O(9)	1.950(4)
V(3)-O(6)	1.931(4)	V(6)-O(10)#1	1.971(4)
V(3)-O(9)	1.955(4)	V(6)-O(10)	1.971(4)

Table S3. Bond valence sums for Sb and V centers in **1**.

V(1)	4.134	V(4)	3.991
V(2)	4.027	V(5)	4.024
V(3)	3.908	V(6)	3.988
Sb(1)	2.933		

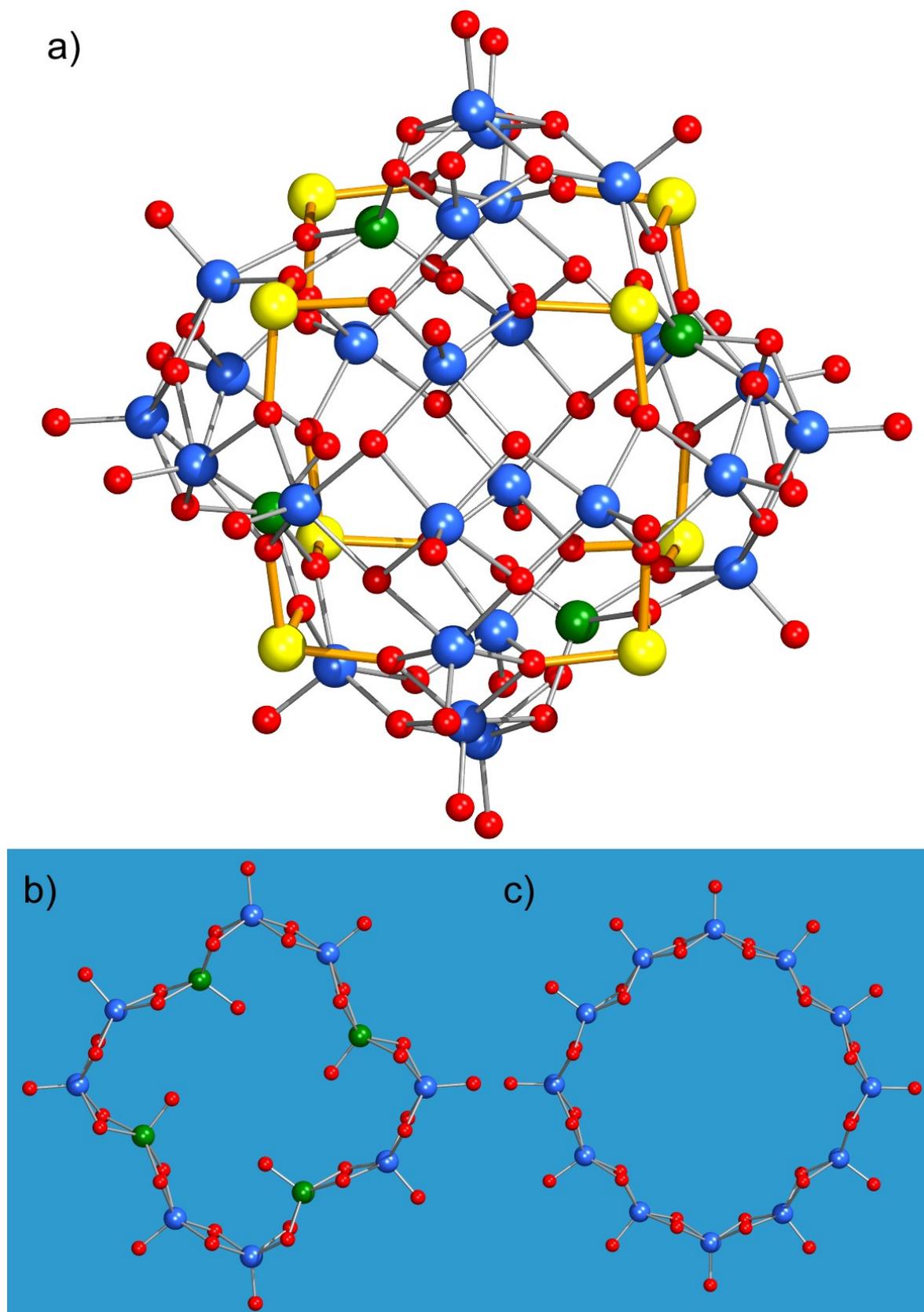


Figure S2. a) Ball-and-stick representation of the $\{V_{30}Sb_8\}$ cluster sphere in **1**. b) The $\{V_{12}\}$ ring featuring the four endo-oriented vanadyl groups. c) One of the other two $\{V_{12}\}$ rings will all-exo-oriented vanadyl groups. Color code: V_{exo} : blue, V_{endo} : green, Sb: yellow, O: red.

Measurements of magnetic properties

Magnetic data were recorded using a Quantum Design MPMS-5XL SQUID magnetometer. The polycrystalline **1** was compacted and immobilized into a cylindrical PTFE capsule. The data were acquired as a function of the magnetic field (0.1 – 5.0 Tesla at 2.0 K) and temperature (2.0–290 K at 0.1 Tesla) and were corrected for the diamagnetic contributions of the sample holder and the compound ($\chi_{m,dia} = -3.5 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$).

Powder X-ray diffraction

The XRPD measurements were performed with a Stoe Transmission Powder Diffraction System (STADI P) with Cu-K α 1 radiation and a Dectris Mythen 1K detector with a Johann-type Ge(111) monochromator from STOE & CIE.

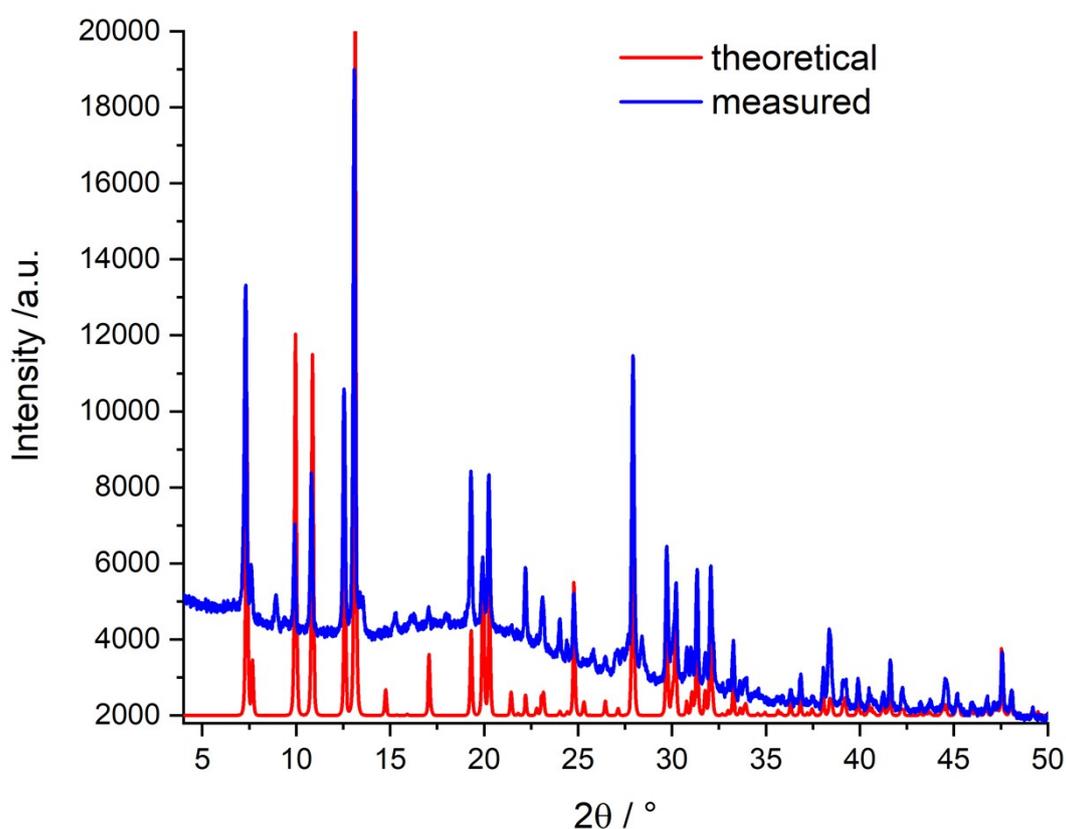


Figure S3. Comparison of experimental (blue) and simulated (red) powder diffraction patterns for **1**.