Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for compound 1

Experimental Section

Materials and measurements

All the chemicals used were of reagent grade without further purification. C, H, N elemental analyses were carried out on a Perkin-Elmer 2400 CHN elemental Analyzer. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer SPECTRUM ONE FTIR spectrophotometer. UV-vis spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Powder XRD patterns were obtained with a Scintag X1 powder diffractometer system using Cu Kα radiation with a variable divergent slit and a solid-state detector. Electron spin resonance (ESR) spectra were performed on a JEOL JES-FA200 spectrometer operating in the X-band mode. The g value was calculated by comparison with the spectrum of 1,1-diphenyl-2-picrylhydrazyl (DPPH), whereas the spin concentrations were determined by comparing the recorded spectra with that of a Mn marker and DPPH, using the built-in software of the spectrometer.

Experiment

Compound **1** was synthesized hydrothermally by reacting of $K_7HNb_6O_{19}\cdot 13H_2O$ (0.050g, 0.03mmol) was added to 10 mL of H_2O at room temperature and stirred until dissolution. Sb_2O_3 (0.100g, 0.37mmol) and V_2O_5 (0.075g, 0.41mmol) were added to the solution, which was further stirred for 90 minutes. $CoSO_4\cdot 7H_2O$ (0.281g, 1.0mmol), phen (0.100g, 0.50mmol) and 2,2'-bpy (0.156g, 1.0mmol) were added to the solution and stirred for another 30 minutes. 1.5ml en was then slowly dropwise added to the suspension until the pH reached a value of 9.5, and then the suspension was sealed in a Teflon-lined stainless bomb and heated at 160°C for 120 hours. Macroscopic black diamond block crystals of **1** were filtered off, washed with water, and air-dried at room temperature (ca.68.5% yield based on V). Calcd. For $C_{68}H_{48}Co_2N_{12}O_{50}Sb_8V_{14}$: Sb, 26.74; Co, 3.24; V, 19.58; C, 22.95; H, 1.67; N, 4.61%; Found: Sb, 26.65; Co, 3.08; V, 19.51; C, 22.36; H, 1.26; N, 4.39. The addition of $K_7HNb_6O_{19}\cdot 13H_2O$ is important for the preparation of compound **1**. while it is absent in the product, $K_7HNb_6O_{19}\cdot 13H_2O$ is required for the synthesis of compound **1**. It should be noted that such a phenomenon is not unusual in hydrothermal preparations.[1]

X-ray crystallography

The reflection intensity data for compound **1** were measured on an Agilent Technology SuperNova Eos Dual system with a Mo K_α (λ = 0.71073Å) microfocus source and focusing multilayer mirror optics. The crystal showed no evidence of crystal decay during the data collection. Data reduction was performed using CrysAlisPro. Refinements were carried out with SHELXS-2014/7[2] and SHELXL-2014/7[2] using WinGX via the full matrix least-squares on F_2 method. In the final refinements, all atoms were refined anisotropically in compounds **1**. The hydrogen atoms of phen and 2,2'-bpy ligands in the compound were placed in calculated positions and included in the structure factor calculations but not refined. In the heavy-atom structure with reflection data from a poor-quality crystal it was not possible to see clear electron-density peaks in difference maps which would correspond with acceptable locations for the various H atoms bonded to water oxygen atoms. The refinement was then completed with no allowance for these water H atoms in the model; CCDC number: 1537169 for **1**. A summary of the crystallographic data and structure refinements for compound **1** is given in Table s1.

There are some unusually high residual electron densities in the CIF file of compound 1, which are due to minor disorder of one of the two crystallographically non-equivalent metal-oxide clusters in the structure. The disorder could not be fully resolved, for its partial rationalisation see CCDC-1552111.

Table s1. Crystal data and structure refinement for compound **1**.

Empirical formula	$C_{69.6}H_{60.5}Co_2N_{12}O_{48.25}Sb_8V_{14}$
Formula weight	3642.02
Crystal system	Tetragonal
space group	I 41/a
a (Å)	19.81131(15)
b (Å)	19.81131(15)
c (Å)	56.5195(5)
Volume (Å^3)	22183.2(4)
Z	8

Calculated density ($Mg\cdot m^{-3}$)	2.181
Absorption coefficient (mm^{-1})	3.405
F(000)	13857
Theta range for data collection	2.921 to 29.097 deg.
Limiting indices	-24<=h<=15 -27<=k<=10 -70<=l<=67
Reflections collected / unique	25893 / 12639 [R(int) = 0.0342]
Completeness to theta = 25.242	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12639 / 36 / 723
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	$R_1 = 0.0664 wR_2 = 0.1799$
R indices (all data)	$R_1 = 0.0936$ $wR_2 = 0.2113$

BVS calculations of V and Sb in compound 1

Table s2. Calculation results of vanadium in compound **1**[3]

V1	V2	V3	V4	V5	V6	V7	V8
4.09	3.95	3.93	4.02	3.99	3.94	4.06	3.90

$V_i=\sum(B_i/1.77)^{-5.2}$

Table s3. Calculation result of antimony in compound **1** [3]

Sb1	Sb2	Sb3	Sb4
2.75	2.75	2.75	2.70

$V_i=\sum(Bi/1.91)^{-4.5}$

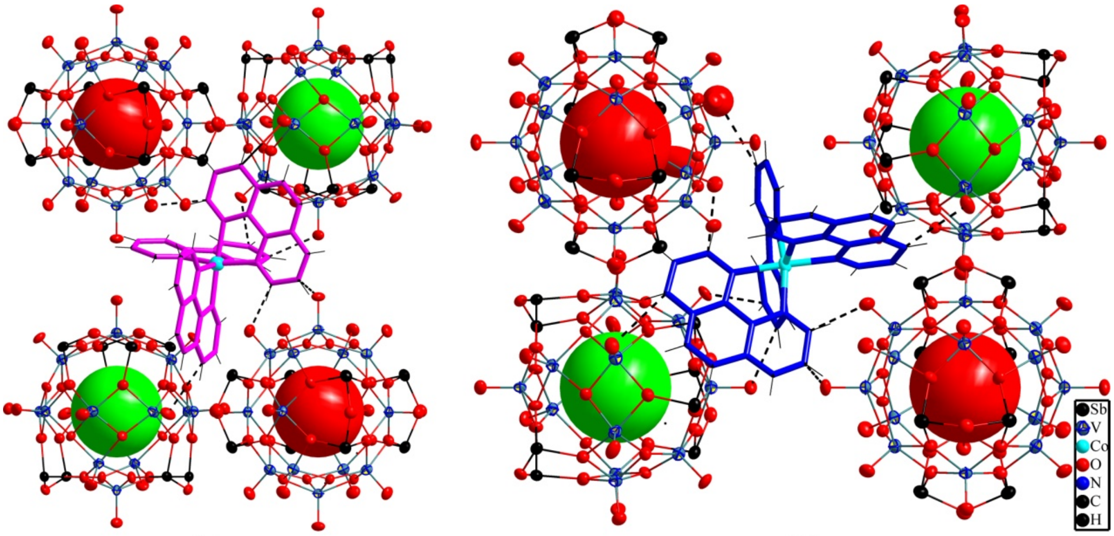

Fig. s1 (a) C-H···O hydrogen bonding interactions between Δ-$[Co(phen)_2(2,2\text{-}bpy)]^{2+}$ and $V_{14}Sb_8$ clusters; (b) C-H···O hydrogen bonding interactions between Λ-$[Co(phen)_2(2,2\text{-}bpy)]^{2+}$ and $V_{14}Sb_8$ clusters. The Δ-$[Co(phen)_2(2,2\text{-}bpy)]^{2+}$ complex is represented by purple wires, and the Λ-$[Co(phen)_2(2,2\text{-}bpy)]^{2+}$ complex is represented by blue wires. The red big ball represents the α-$V_{14}Sb_8$ shell, and the green big ball represents the β-$V_{14}Sb_8$ shell.

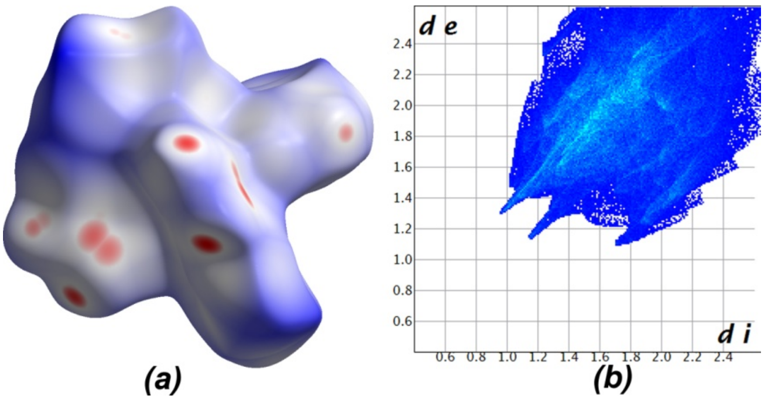

Fig. s2 (a) Hirshfeld-surface for the $[Co(phen)_2(2,2\text{-}bpy)]^{2+}$ in compound **1** with d_{norm} plotted for all short intermolecular contacts, (b) Hirshfeld 2D fingerprint plot for the $[Co(phen)_2(2,2\text{-}bpy)]^{2+}$ complex Hirshfeld-surface shown in (a). Color code: red: short intermolecular contacts, blue: long intermolecular contacts.

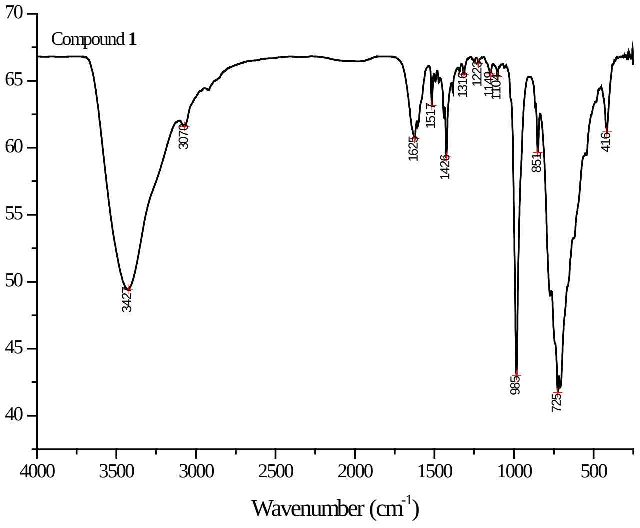

Fig. s3 IR spectrum of compound **1**.

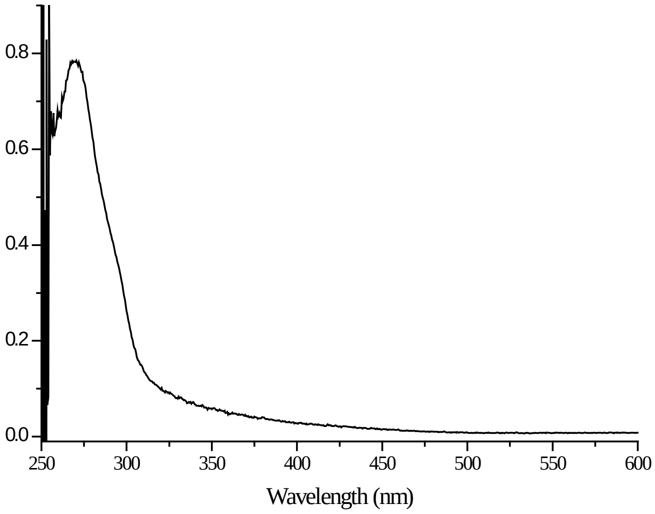

Fig. s4 UV-Vis spectrum of compound **1**.

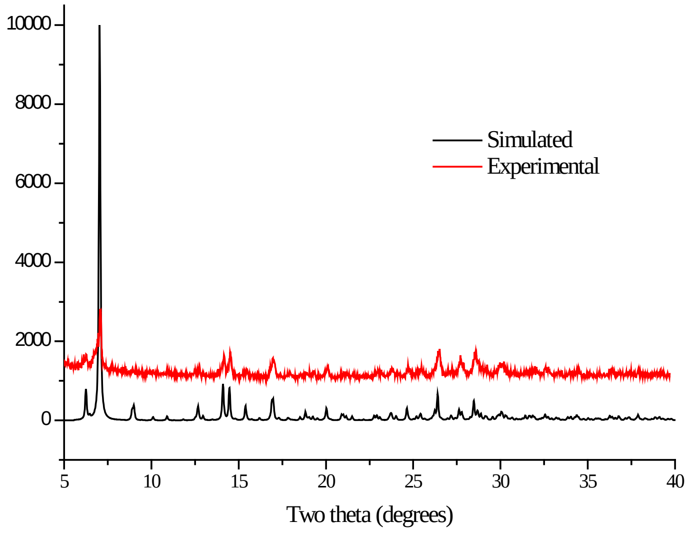

Fig. s5 Simulated and experimental XRD patterns of compound **1**.

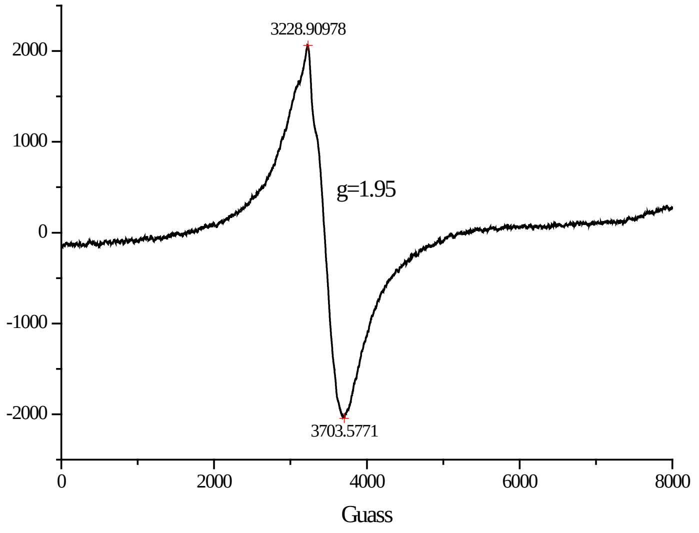

Fig. s6 ESR spectrum of compound **1**.

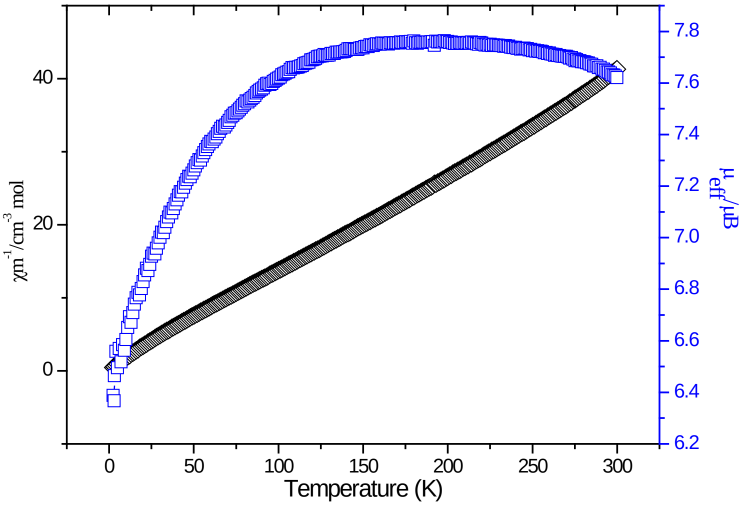

Fig. s7 Plots of μ_{eff} (□) and χ_m^{-1} (◇) versus T for **1**.

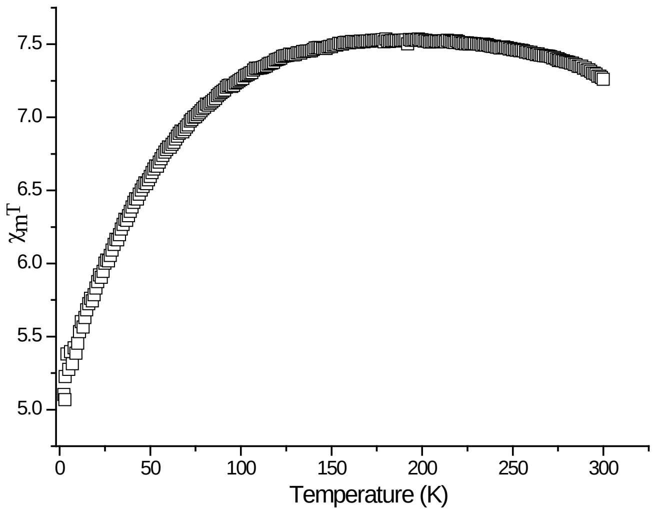

Fig. s8 Plots of χ $_m$·T (☐) versus T for **1**.

References:

1. P. J. Hagraman and J. Zubieta, *Inorg. Chem.*, 2000, **39**, 3252.
2. G. Sheldrick, *Acta Crystallogr., Sec. A.*, 2008, **64**, 112.
3. I. D. Brown, *in Structure and Bonding in Crystals, edited by M. O'Keefe, A. Navrotsky*, Academic Press, New York, 1981.