

Electronic Supplementary information (ESI)

For

Self-assembly of a tetrahedral 58-nuclear barium vanadium oxide cluster

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1. Instrumentation

X-ray diffraction: Single-crystal X-ray diffraction studies were performed on a Nonius Kappa CCD Single-crystal X-ray diffractometer equipped with a graphite monochromator using MoK α radiation (wavelength $\lambda(\text{MoK}\alpha) = 0.71073\text{\AA}$).

UV-Vis spectroscopy: UV-Vis spectroscopy was performed on a Shimadzu UV-2401PC spectrophotometer or Varian Cary 50 spectrophotometer. All systems were used with standard cuvettes ($d = 10.0\text{ mm}$).

Thermogravimetry analysis (TGA): TGA was performed on a Setaram Setsys CS Evo, 30-1000°C @ 10K/min, 200 mL/min synthetic air, Graphite crucible 0.5 mL.

Atomic absorption spectroscopy: Atomic absorption spectroscopy analysis was performed on a Perkin Elmer 5100 PC spectrometer.

Cyclic Voltammetry (CV): CV was performed using an Ivium CompactStat potentiometer using a glassy carbon working electrode and platinum wire as counter electrode and pseudo-reference electrode. Ferrocene was used as internal reference. Dry solvents were used with $n\text{Bu}_4\text{NPF}_6$ as the electrolyte.

FT-IR spectroscopy: FT-IR spectroscopy was performed on a Shimadzu - FT-IR Prestige-21 spectrometer equipped with a Golden Gate-ATR-unit. Signals are given as wavenumbers in cm^{-1} using the following abbreviations: vs = very strong, s = strong, m = medium, w = weak and b = broad.

Elemental analysis: Elemental analysis was performed on a Euro Vector Euro EA 3000 Elemental Analyzer.

Nuclear Magnetic Resonance Spectroscopy (NMR): ^1H -NMR spectra were recorded on a JEOL JNM-EX270 FT NMR spectrometer. The solvent was DMSO- d_6 , it was used as internal reference, data is given as chemical shifts δ in ppm. ^{51}V -NMR spectra were recorded on a JEOL ECX 400JNM-EX270 FT-NMR spectrometer using DMSO- d_6 as solvent and sodium orthovanadate as external reference. Data is given as chemical shifts δ in ppm.

Mass spectrometry (MS): MS measurements were performed on a ultra-high resolution time-of-flight electrospray ionization UHR-TOF-ESI-MS Bruker Daltonik maXis capable of resolution of at least 40,000 FWHM. Detection was in negative-ion mode and the source voltage was 4 kV. The flow rates were 500 $\mu\text{L}/\text{hour}$. The drying gas (N_2) was held at 180 $^\circ\text{C}$. The machine was calibrated prior to every experiment via direct infusion of the Agilent ESI-TOF low concentration tuning mixture. Concentration was ca. 1×10^{-4} M.

General remarks: All chemicals were purchased from Sigma Aldrich or ACROS and were of reagent grade. $(^n\text{Bu}_4\text{N})_2[\text{H}_4\text{V}_{10}\text{O}_{28}]$ was synthesized as reported in reference S1. The chemicals were used without further purification unless stated otherwise.

2. Synthetic section:

2.1 Synthesis of $\text{H}_5[\text{Ba}_{10}(\text{NMP})_{14}(\text{H}_2\text{O})_8[\text{V}_{12}\text{O}_{33}]_4\text{Br}] \times \text{ca. } 11 \text{ NMP}$

$\text{BaBr}_2 \times 2\text{H}_2\text{O}$ (472 mg, 1.42 mmol, 2.1 eq) and $(^n\text{Bu}_4\text{N})_2[\text{H}_4\text{V}_{10}\text{O}_{28}]$ (400 mg, 0.68 mmol, 1.0 eq) were suspended in *N*-methyl-2-pyrrolidone (NMP, 20 ml). The reaction mixture was heated to 85 $^\circ\text{C}$ and the mixture turned brown. 6 M aqueous HBr (500 μl) was added. After cooling to room temperature, aqueous hydrogen peroxide (320 μl , 40 wt.-% in water) were added. The orange solution was stirred at room temperature for four days and a precipitate was centrifuged off. Diffusion crystallisation using ethyl acetate as diffusion solvent resulted in orange octahedral crystals. Yield: 257 mg (0.30 mmol, 21.1 % of crude product based on Ba).

Elemental analysis for $\text{Ba}_{10}\text{C}_{125}\text{H}_{246}\text{N}_{25}\text{V}_{48}\text{O}_{165}\text{Br}$ in wt.-% (calcd.): C 17.42 (17.38), N 3.86 (4.05), H 2.75 (2.87), Br 0.89 (1.11).

Flame atomic absorption spectroscopy (dried sample, in wt.-%) (calcd.): V: 33.94 (33.93), Ba 18.85 (19.06)

Characteristic IR bands (in cm^{-1}): 3421 (b), 2956(w), 2930 (w), 2876 (w), 1654 (s), 1647 (s), 1638 (s) 1508 (m), 1476 (w), 1458 (w), 1448 (w), 1421 (w), 1406 (m), 1305

(m), 1261 (m), 1229 (m), 1177 (w), 1116 (m), 952 (s), 897 (m), 835 (s), 758 (m), 662 (m), 608 (m), 521 (m), 449 (w).

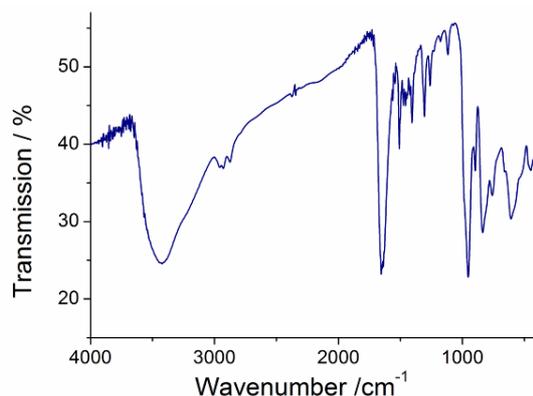


Figure S 1 FT-IR spectrum of $\text{H}_5[\text{Ba}_{10}(\text{NMP})_{14}(\text{H}_2\text{O})_8][\text{V}_{12}\text{O}_{33}]_4\text{Br}$ showing the characteristic V-O vibrational modes in the fingerprint region $< 1000 \text{ cm}^{-1}$ and solvent molecule based stretching vibrations around 3000 cm^{-1} as well as the NMP-based C=O mode at 1654 cm^{-1} .

UV-Vis spectroscopy

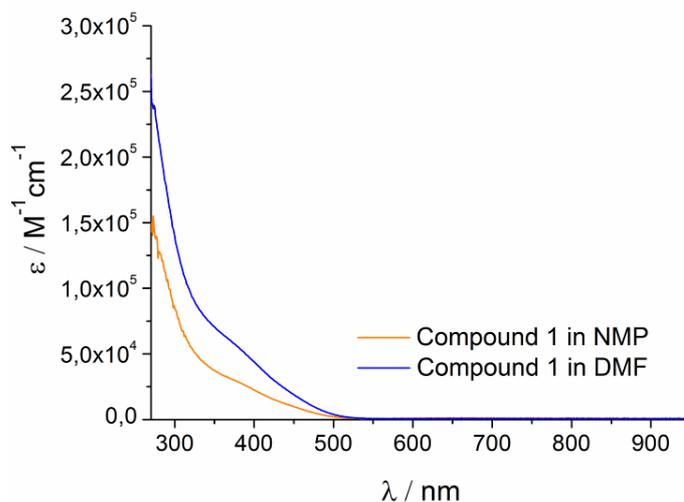


Figure S 2 UV-Vis spectra of compound **1** dissolved in NMP (orange) and DMF (blue).

3. Crystallographic information

Single-Crystal Structure Determination: Suitable single crystals of the **1** were grown and mounted onto the end of a thin glass fiber using Fomblin oil. X-ray diffraction intensity data were measured at 150 K on a Nonius Kappa CCD diffractometer [$\lambda(\text{Mo-K}\alpha) =$

0.71073 Å] equipped with a graphite monochromator. Structure solution and refinement was carried out using the SHELX-97 package^{S2} via WinGX.^{S3} Corrections for incident and diffracted beam absorption effects were applied using empirical^{S4} methods. Structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least-squares technique. Due to disorder, the NMP molecule based on N5 was modeled isotropically. The SQUEEZE^{S5} routine was applied to account for diffuse solvent molecules. Crystal data, data collection parameters and refinement statistics are listed in Table S1. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ; fax:(+44) 1223-336-033; or deposit@ccdc.cam.ac.uk. CCDC reference number 898056 (1).

Table S1: Summary of the crystallographic information

	Compound 1
Formula	Ba ₁₀ Br ₁ C ₁₂₅ H ₂₄₆ N ₂₅ O ₁₆₅ V ₄₈
M_r , g mol ⁻¹	8637.7
crystal system	Orthorhombic
space group	<i>F</i> ddd
<i>a</i> [Å]	34.779(4)
<i>b</i> [Å]	38.186(4)
<i>c</i> [Å]	47.980(5)
α [°]	90
β [°]	90
γ [°]	90
ρ_{calc} [g cm ⁻³]	1.618
<i>V</i> [Å ³]	63721(11)
<i>Z</i>	8
μ (MoK α) mm ⁻¹	2.745
<i>T</i> [K]	150(2)
no. rflns (measd)	121894
no. rflns (unique)	16262
no. params	732
<i>R</i> 1 ($I > 2\sigma(I)$)	0.0592
<i>wR</i> 2 (all data)	0.1938
Goof	1.091
Max/min resd. e-density	2.111 / -0.73

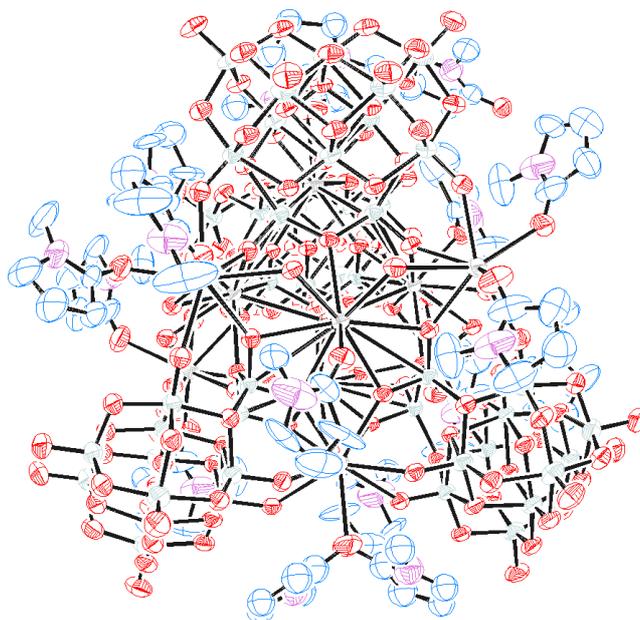


Figure S 3: ORTEP-plot of compound **1**, probability ellipsoids given at 50 %. The NMP molecule based on N5 was refined isotropically due to disorder. The remainder of the structure was refined anisotropically to satisfactory R values.

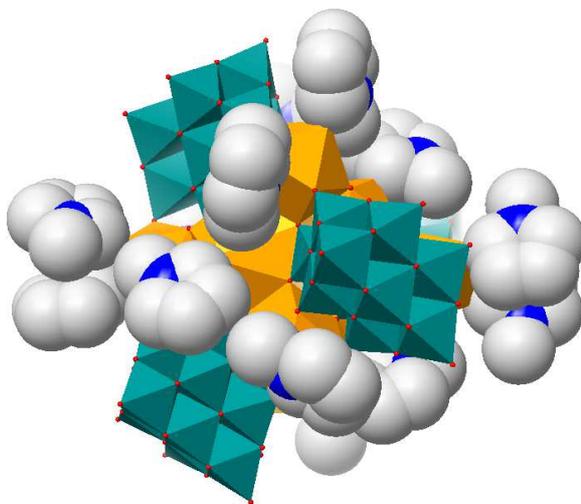


Figure S 4: Space-filling representation showing the “encapsulation” of the cluster by the organic NMP ligands.

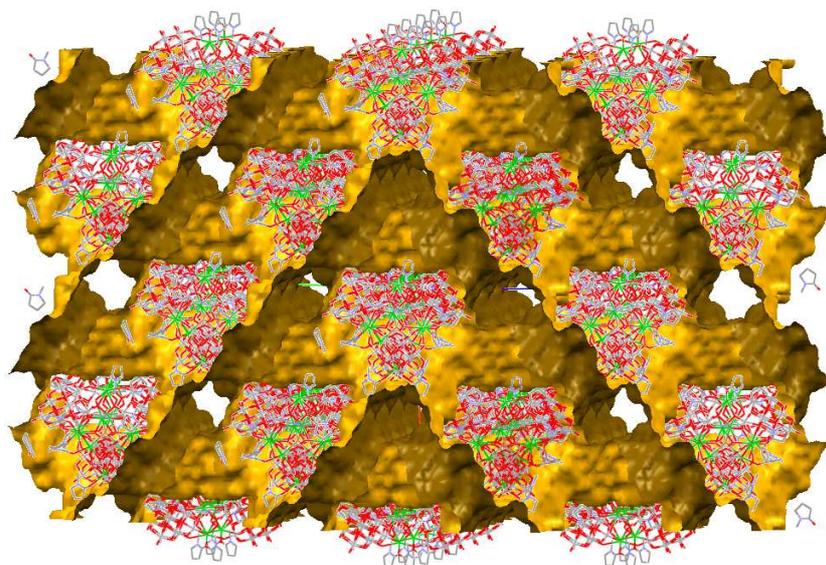


Figure S 5: Crystallographic packing diagram showing the solvent-accessible voids (ca. 34.4 vol.-% of the unit cell) observed within the crystal lattice of **1**. Void space highlighted in yellow. The void space can accommodate ca. 20 molecules of NMP per cluster formula unit. Based on thermogravimetric and elemental analyses, typical samples contain between 11-14 NMP solvent molecules (in addition to the eight NMP ligand molecules) per cluster unit. Loss of NMP is expected due to sample drying.

4. Mass spectrometry

ESI-MS measurements were performed on $\text{H}_5[\text{Ba}_{10}(\text{NMP})_{14}(\text{H}_2\text{O})_8][\text{V}_{12}\text{O}_{33}]_4\text{Br}$ (ca. 0.5 mM, solvent DMF/acetonitrile 1:4, v:v) in negative (-ve) ion mode.

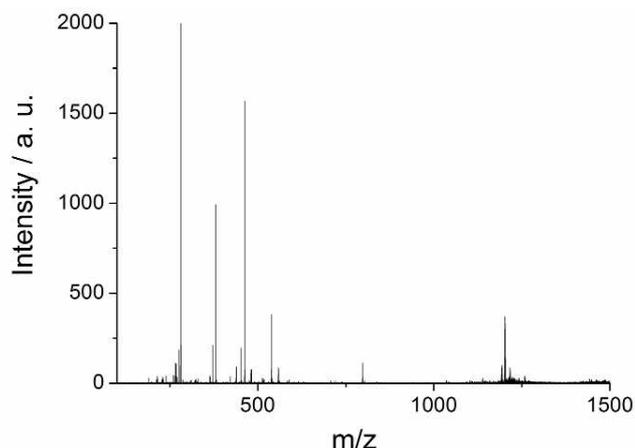


Figure S 6: Negative mode high resolution ESI mass spectrum of $\text{H}_5[\text{Ba}_{10}(\text{nmp})_{14}(\text{H}_2\text{O})_8(\text{V}_{12}\text{O}_{33})_4\text{Br}]$, ca. 1×10^{-4} M in acetonitrile / dimethyl formamide (4:1).

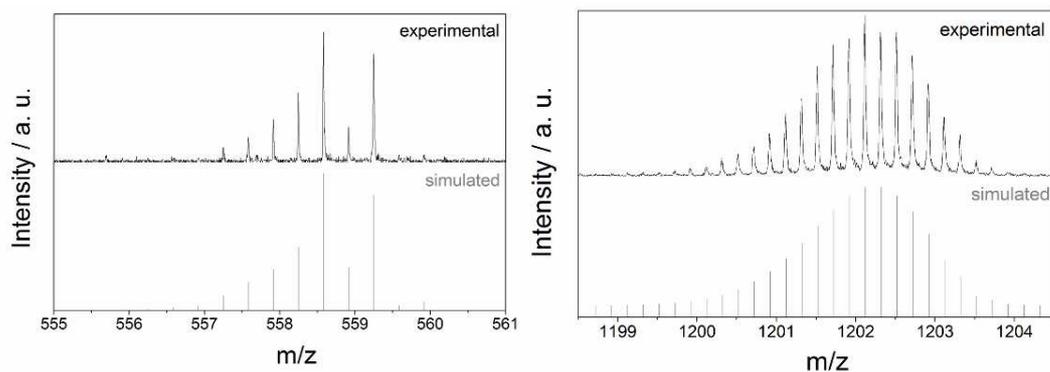


Figure S 7 Left: Comparison of the experimental and simulated signals for the low-intensity peak at $m/z = 558.58$ (calc: 558.58) assigned as $[\text{Ba}_2\text{V}_{12}\text{O}_{33}\text{V}_2\text{O}_5\text{Br}]^{3-}$. **Right:** Comparison of the experimental and simulated signals for the high-intensity peak at $m/z = 1202.12$ (calc: 1202.12) assigned as $[\text{Ba}_{10}[\text{V}_{12}\text{O}_{33}]_4\text{Br}]^{5-}$.

Table S 2 : Peak assignments for the ESI mass spectrum of $\text{H}_5[\text{Ba}_{10}(\text{nmp})_{14}(\text{H}_2\text{O})_8(\text{V}_{12}\text{O}_{33})_4\text{Br}]$

recorded m/z	calculated m/z	peak assignment
189.86 ^[a]	189.86	$[\text{V}_{12}\text{O}_{33}]^{6-}$
280.79 ^[a]	280.79	$[\text{V}_6\text{O}_{16}]^{2-}$
371.72 ^[a]	371.72	$[\text{V}_8\text{O}_{21}]^{2-}$
462.65 ^[a]	462.65	$[\text{V}_5\text{O}_{13}]^-$
539.60 ^[a]	539.60	$[\text{BaV}_{10}\text{O}_{27}]^{2-}$
558.58 ^[a]	558.58	$[\text{Ba}_2\text{V}_{12}\text{O}_{33}\text{V}_2\text{O}_5\text{Br}]^{3-}$
798.42 ^[a]	798.42	$[\text{Ba}_2\text{V}_{12}\text{O}_{33}\text{V}_2\text{O}_5]^{2-}$
1193.13 ^[b]	1193.15	$[\text{H}_2\text{Ba}_9[\text{V}_{12}\text{O}_{33}]_4\text{Br}(\text{H}_2\text{O})_5]^{5-}$
1202.12 ^[b]	1202.12	$[\text{Ba}_{10}[\text{V}_{12}\text{O}_{33}]_4\text{Br}]^{5-}$

^[a] Fragmentation product; ^[b] full cluster anion

6. Thermogravimetric analysis

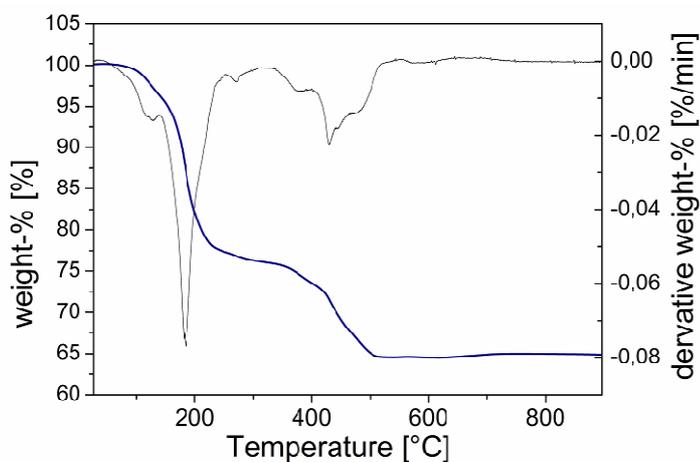


Figure S 8 Thermogravimetric analysis of compound **1**, indicating a first weight loss step (25 - 284 °C) corresponding to eight water molecules and 19 NMP molecules (11 NMP solvent molecules and 8 NMP ligand molecules) (observed: 23.47 wt.-%; calc: 23.47 wt.-%); the second weight loss step (284 - 442 °C) corresponds to the loss of six ligand NMP molecules (observed: 6.53 wt.-%, calc: 6.89 wt.-%). Above 442 °C the cluster anion decomposes and the third weight loss step can be assigned to 2.5 Ba(OH)₂ molecules, whereby the 5 protons from the cluster might serve as the proton source. The sublimation of Ba(OH)₂ was observed and a Ba(OH)₂ deposition was observed at the outlet valve (observed: 5.43 wt.-%; calc: 4.96 wt.-%).

7. Acidity determination

Aliquots of compound **1** were added and dissolved in water (15 ml) and the pH of the solution was measured using a pH probe (Mettler-Toledo FiveGo pH-meter).

Based on this analysis, ca. 0.3 protons are released per cluster unit.

8. Cyclic voltammetry

Cyclic voltammetry was performed to investigate the solution stability of $\{\text{Ba}_{10}\text{V}_{48}\}$ upon cycling between -1.8 and +0.8 V (against Fc/Fc^+). The voltammogram shown was recorded after 2 redox-cycles. No major changes were observed after 10 cycles.

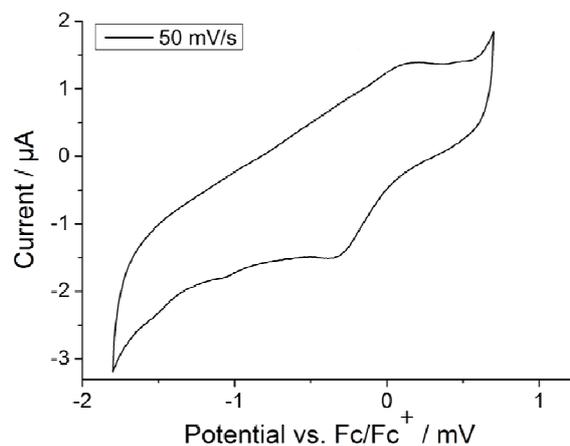


Figure S 9: Cyclovoltammogram of $\text{H}_5[\text{Ba}_{10}(\text{nmp})_{14}(\text{H}_2\text{O})_8(\text{V}_{12}\text{O}_{33})_4\text{Br}]$ (ca. 0.8 mM) in N,N-dimethyl formamide containing 0.1 M nBu_4NPF_6 . Scan rate: 50 mV/s, rest potential: 0.0 V. One quasi-reversible redox-wave is observed, centred at -0.1 V. Initial scan direction: to negative potentials.

9. NMR-spectroscopy

9.1. ^1H -NMR-spectroscopy

^1H -NMR spectroscopy was used to observe the NMP ligands present on the cluster and to investigate whether cluster-based protons can be observed. However, no cluster protons were observed in the ^1H -NMR spectrum, see below.

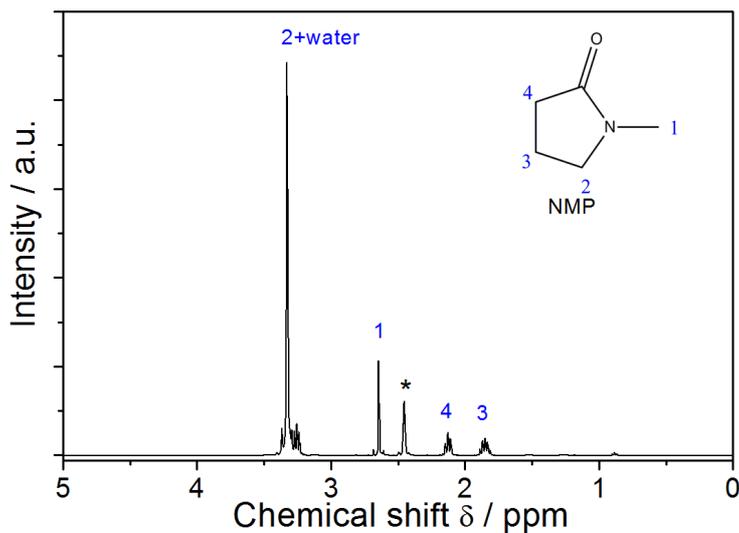


Figure S 10: ^1H -NMR spectrum of $\text{H}_5[\text{Ba}_{10}(\text{nmp})_{14}(\text{H}_2\text{O})_8(\text{V}_{12}\text{O}_{33})_4\text{Br}]$ in DMSO-d_6 ; solvent signal is marked with an asterisk (*). The signal for the methylene group 2 ($\delta = 3.3 - 3.4$ ppm) is overlaid by a water signal.

9.2 ^{51}V -NMR spectroscopy

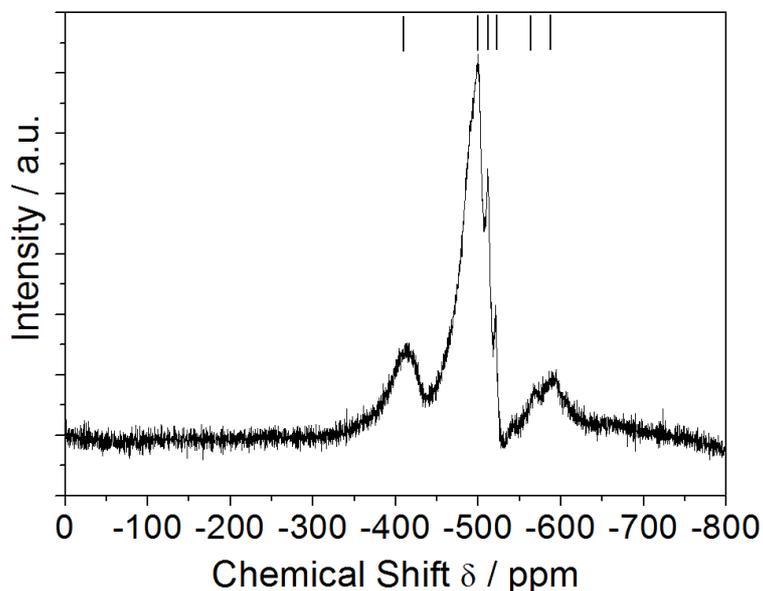


Figure S 11 ^{51}V -NMR spectrum of $\text{H}_5[\text{Ba}_{10}(\text{nmp})_{14}(\text{H}_2\text{O})_8(\text{V}_{12}\text{O}_{33})_4\text{Br}]$ in DMSO-d_6 . Six signals are tentatively observed in the range expected for octahedrally coordinated vanadium(V) centres ($\delta = -400 - 600$ ppm),^{S6} however, due to the low solubility of compound **1** (< 1 mM), the quality of the spectrum is low. No other signals were observed in the measured range ($\delta = -1500$ to $+1000$ ppm), suggesting that no degradation into a large number of degradation products is observed.

Table S3: ^{51}V -NMR chemical shifts

Chemical Shift /ppm
-411
-500
-512
-523
-567
-589

10. Literature references cited in Supporting Information

- S1 P. Roman, A. S. Jose, A. Luque, J. M. Gutierrez-Zorrilla, *Inorg. Chem.* 1993, **32**, 775.
- S2 G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112.
- S3 L. J. Farrugia, *J. Appl. Cryst.* 1999, **32**, 837.
- S4 R. H. Blessing, *Acta Crystallogr.* 1995, **A51**, 33.
- S5 A.L.Spek, *Acta Crystallogr.* 2009, **D65**, 148.
- S6 D. Rehder, *Bull. Mag. Res.* 1982, **4**, 33.