Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Synthesis, Characterization, DFT Calculations, and Reactivity Study of a Nitrido-Bridged Dimeric Vanadium(IV) Complex

Adriana Lugosan,[a] *Thomas Cundari,*[b] *Kristin Fleming,*[a] *Diane A. Dickie,*[c§] *Matthias Zeller,*[d] *Jack Ghannam,*[a] *Wei-Tsung Lee*[a*]

[a] Department of Chemistry and Biochemistry, Loyola University Chicago, Chicago, IL 60660, United States.

[b] Department of Chemistry, Center for Advanced Scientific Computing and Modeling (CASCaM), University of North Texas, Denton, TX 76203, United States

[c] Department of Chemistry, Brandeis University, Waltham, MA 02453, United States.

[d] Department of Chemistry, Purdue University, West Lafayette, IN 47907, United States.

[§] Current Address: Department of Chemistry, University of Virginia, Charlottesville, VA 22904, United States.

Table of Contents

Table S1. Selected Bond Distances (Å) and Angles (°) for **1–3**.[a]

1		**2**		**3**[b]	
V1–N1	2.1357(14)	V1–N1	2.1156(16)	V1–N1	2.172(2)
V1–N3	1.8961(15)	V1–N3	1.9097(15)	V1–N3	2.064(2)
V1–N5	2.1298(14)	V1–N5	2.1228(16)	V1–N5	2.189(3)
V1–Cl1	2.2783(5)	V1–N6	1.9721(17)	V1–N6	1.641(3)
V1–Cl2	2.3088(5)	V1–N9	1.9379(17)	V1–N6#1	1.997(2)
N1–V1–N3	89.24(6)	N1–V1–N3	89.26(6)	N1–V1–N3	81.58(9)
N3–V1–N5	89.37(6)	N3–V1–N5	89.66(6)	N3–V1–N5	83.40(9)
N1–V1–N5	176.83(5)	N1–V1–N5	176.95(6)	N1–V1–N5	134.04(10)
N3–V1–Cl1	113.99(5)	N3–V1–N6	115.09(7)	N3–V1–N6	100.42(10)
N3–V1–Cl2	113.84(5)	N3–V1–N9	117.96(7)	N3–V1–N6#1	172.36(10)
Cl1–V1–Cl2	132.179(19)	N6–V1–N9	126.93(7)		
		N6–N7–N8	175.9(2)		
		N9–N10–N11	175.6(2)		
		V1–N6–N7	135.90(14)		
		V1–N9–N10	139.81(15)	N6···N6#1	2.515(3)
				V1···V1#1	2.6546(11)
τ_5[1]	0.74	τ_5	0.83	τ_5	0.64

[a] Numbers in parentheses are standard uncertainties in the last significant Fig.s. Atoms are labeled as indicated in Fig. 1, 2, and 3. [b] Symmetry operations: #1 = = -x, 1-y, 1-z.

Table S2. X-ray Crystallographic Data for **1–4**.

	1	**2**	**3**	**4**
Chemical formula	$C_{32}H_{40}Cl_2N_5V\cdot C_7H_8$	$C_{32}H_{40}N_{11}V\cdot C_7H_8$	$C_{64}H_{80}N_{12}V_2\cdot 2(C_4H_{10}O)$	$C_{64}H_{80}ClN_{10}O_2V_2\cdot C_4H_8O$
M_r	708.66	721.82	1267.51	1230.81
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Temperature (K)	100	120	120	100
a (Å)	11.5972 (2)	15.0518 (4)	11.7050 (12)	10.5713 (9)
b (Å)	14.7064 (3)	14.5044 (4)	12.9909 (14)	16.0342 (11)
c (Å)	21.9685 (5)	17.2485 (4)	13.1353 (15)	19.4152 (15)
α (°)	90	90	96.537 (7)	94.679 (6)
β (°)	95.6135 (16)	92.868 (2)	110.688 (6)	95.011 (6)
γ (°)	90	90	106.507 (7)	99.765 (5)
V (Å^3)	3728.83 (13)	3760.93 (17)	1739.7 (3)	3215.2 (4)
Z	4	4	1	2
Radiation type	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	3.80	0.308	0.32	3.24
Crystal size (mm)	0.22 × 0.21 × 0.16	0.29 × 0.24 × 0.07	0.38 × 0.32 × 0.06	0.20 × 0.04 × 0.04
T_{min}, T_{max}	0.441, 0.582	0.87, 0.98	0.82, 0.98	0.662, 0.881
[$I > 2\sigma(I)$] reflections	6843	6471	4226	62964
R_{int}	0.037	0.052	0.092	n/a
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.618	0.667	0.626	0.618
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.096, 1.07	0.046, 0.112, 1.02	0.056, 0.131, 1.00	0.109, 0.343, 1.09
No. of reflections	7200	9303	7133	62964
No. of parameters	501	471	450	843
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.48, −0.48	0.40, −0.43	0.47, −0.56	1.51, −0.90

Special refinement details:

In the structure of **1**, a toluene molecule is disordered with two alternative orientations. The two moieties were restrained to have similar geometries, and U^{ij} components of ADPs were restrained to be similar for atoms closer than 2.0 Å. Subject to these conditions the occupancy ratio refined to 0.852(5) to 0.148(5).

In the structure of **3**, an isopropyl group and a solvate ether molecule were refined as disordered. Equivalent atoms within the major and minor moieties of the isopropyl group were constrained to have identical ADPs. The occupancy ratio refined to 0.561(12) to 0.439(12). In the ether molecule, O1 and methyl C atom C33 were omitted from the disorder. The occupancy ratio refined to 0.519(8) to 0.481(8).

For **4**, the crystal under investigation was found to be non-merohedrically twinned. HKL3000 lacks the ability to simultaneously integrate more than one twin domain. Rigaku programs compatible with the diffractometer (twinsolve) gave unsatisfactory results. With no usable data set obtainable through simultaneous integration of both twin domains, the data were instead handled as if not twinned, with only the major domain integrated, and converted into an hklf 5 type format hkl file after integration using the "Make HKLF5 File" routine as implemented in WinGX.[2] The twin law and matrix were obtained using the program ROTAX as implemented in WinGX. The twin operation was identified as a 180° rotation around the reciprocal b-axis, the twin matrix as -1.000 0.000 0.000, 0.540 1.000 0.160, 0.000 0.000 -1.000

The Overlap R1 and R2 values in the "Make HKLF5 File" routine used were 0.11, i.e. reflections with a discriminator function less or equal to overlap radius of 0.11 were counted overlapped, all others as single. The discriminator function used was the "delta function on index non-integrality". No reflections were omitted.

The structure was solved using direct methods with all reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the overlapping ones) as obtained from WinGX, resulting in a BASF value of 0.216(4).

No R_{int} value is obtainable for the hklf 5 type file using the WinGX routine.

The terminal Cl and O atoms of a Cl−V−O−V=O unit are disordered in a close to 1:1 ratio. The U^{ij} components of ADPs of the V atoms and disordered V and O atoms were restrained to be similar, and the V=O bond distances were restrained to be similar as well. The occupancy ratio refined to 0.496(12) to 0.504(12).

A THF molecule was refined as disordered over two orientations. The two moieties were restrained to have similar geometries. All O−C and C−C bond distances were restrained to be similar, and all 1,3 distances to be at least 2.40(2) Å. The occupancy ratio refined to 0.37(1) to 0.63(1).

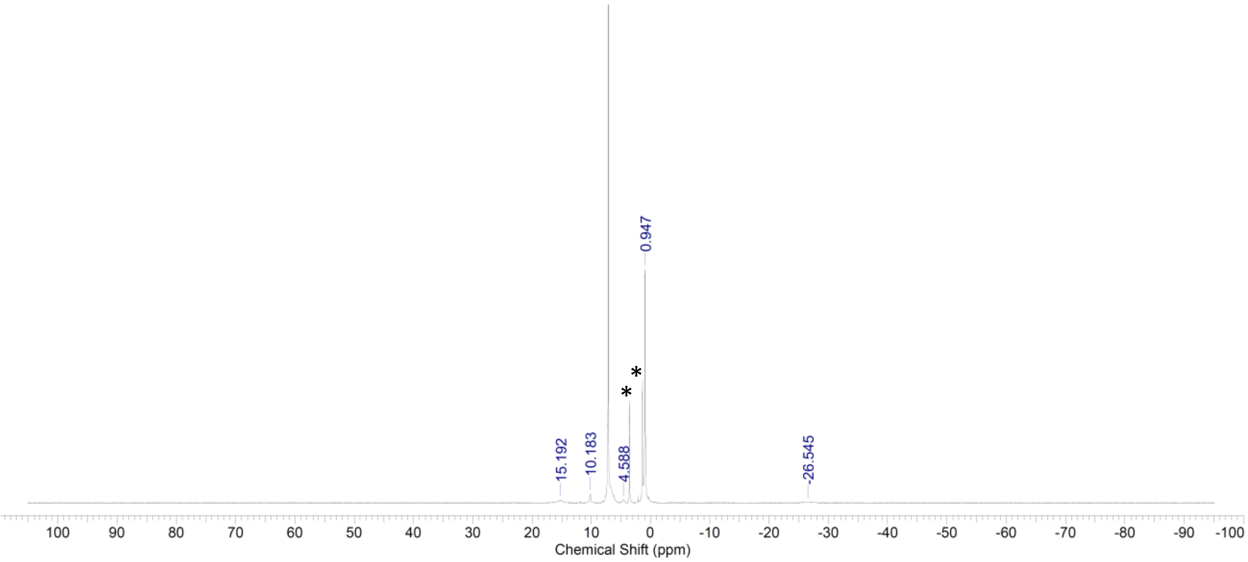

Fig. S1. ^{1}H NMR spectrum of **1**. * Solvent residual peaks.

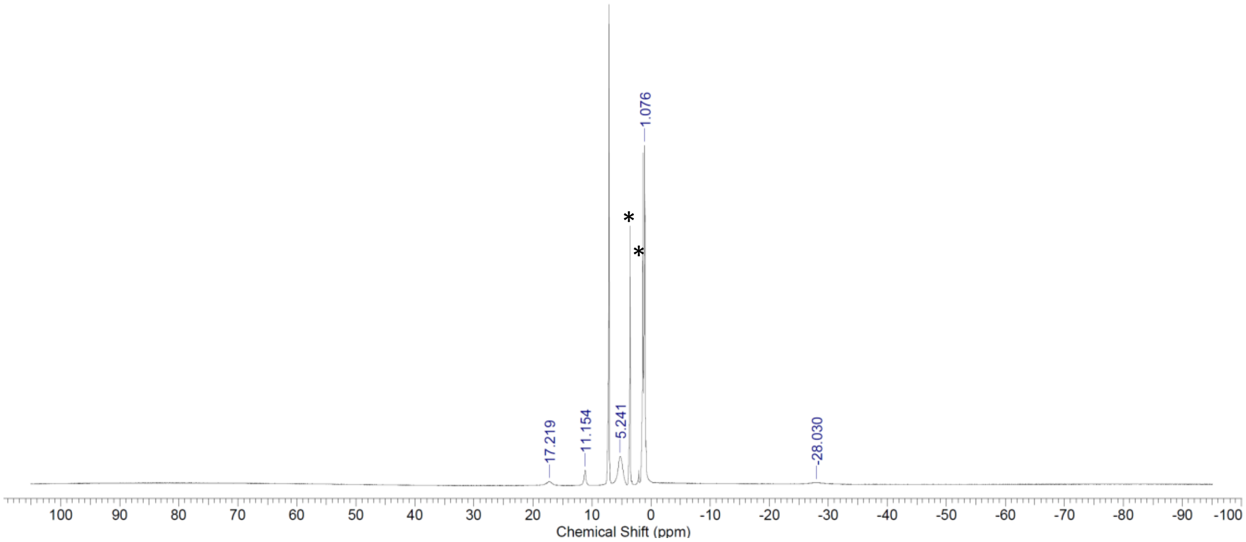

Fig. S2. ^{1}H NMR spectrum of **2**. * Solvent residual peaks.

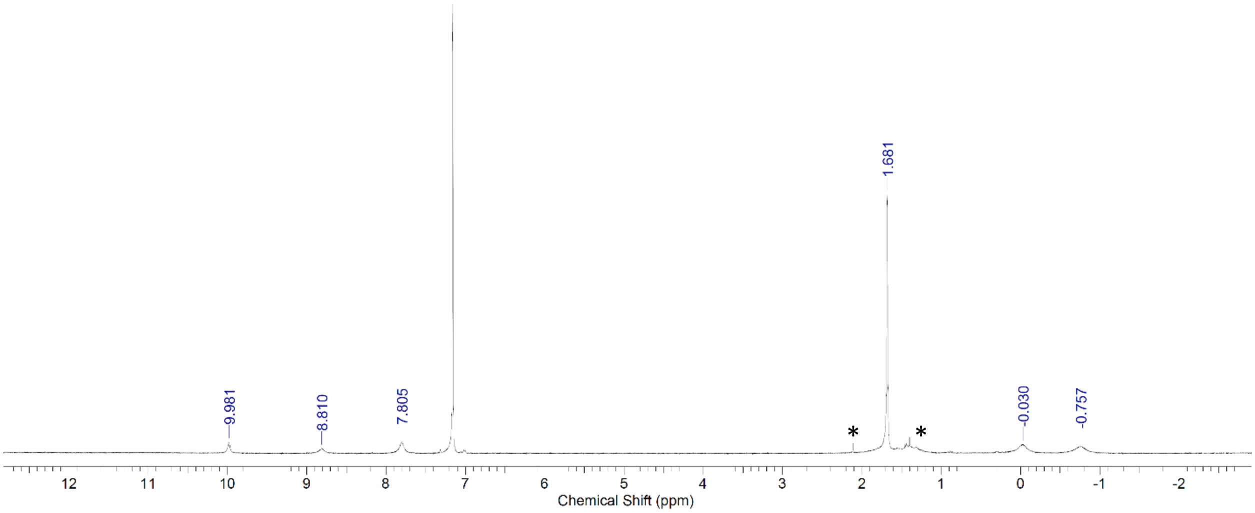

Fig. S3. ^{1}H NMR spectrum of **3**. * Solvent residual peaks.

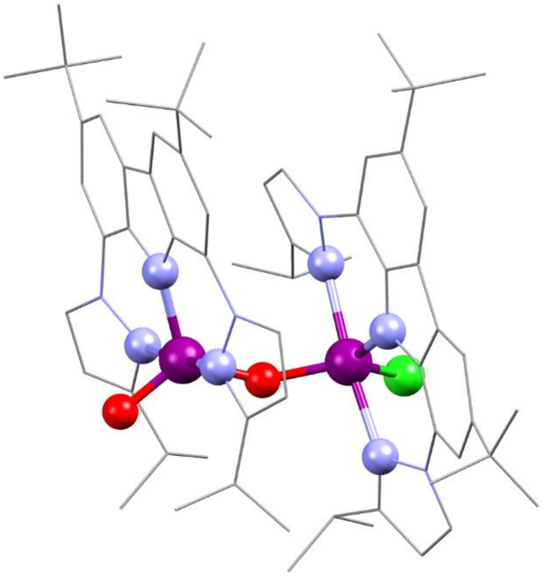

Fig. S4. Molecular structure of **4**. Most of atoms are shown in wireframe and hydrogen atoms are omitted for clarity. Color key: purple = V, blue = N, gray = C, green = Cl, red = O.

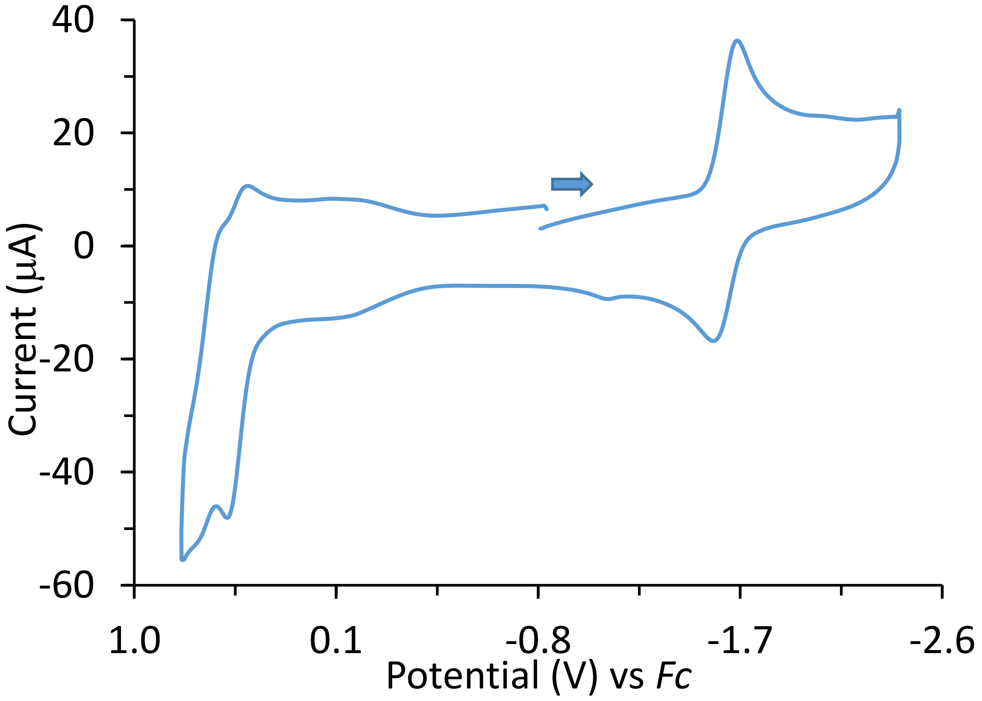

Fig. S5. Cyclic voltammogram of **1** (1mM). Scan rate = 100 mV/s. The arrow indicates the initial scan direction.

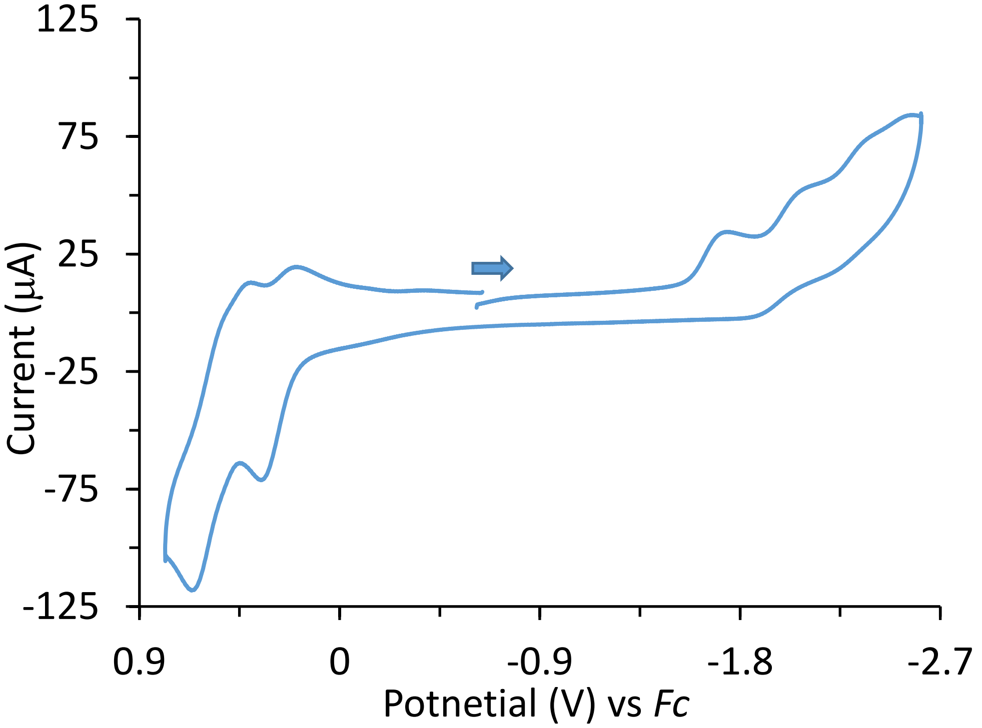

Fig. S6. Cyclic voltammogram of **2** (1mM). Scan rate = 100 mV/s. The arrow indicates the initial scan direction.

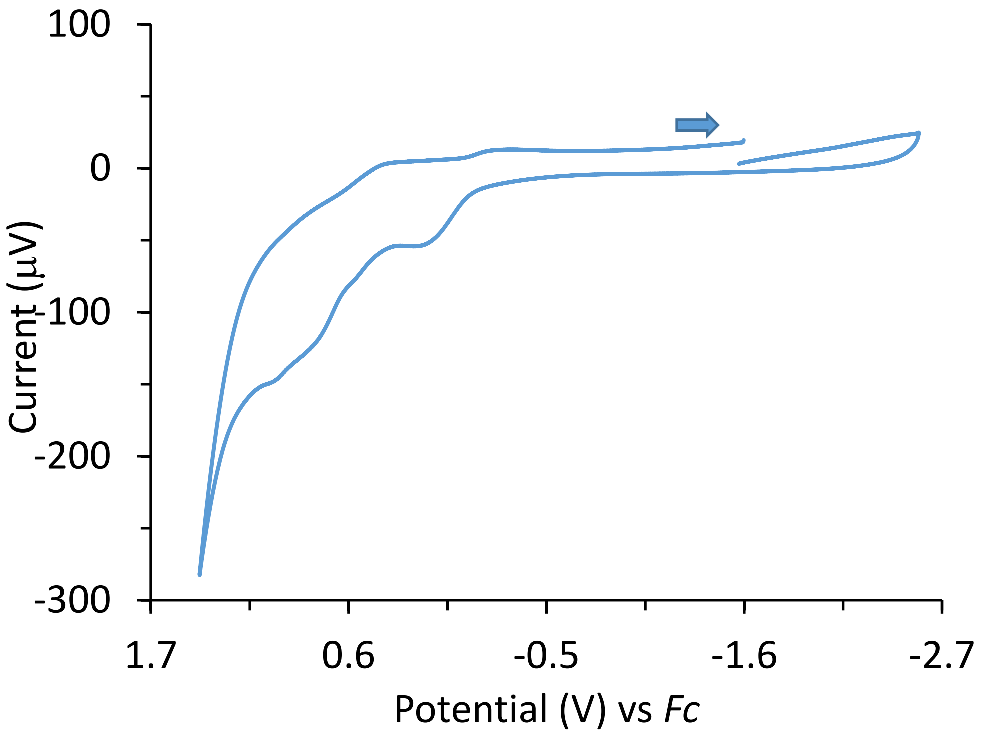

Fig. S7. Cyclic voltammogram of **3** (1mM). Scan rate = 100 mV/s. The arrow indicates the initial scan direction.

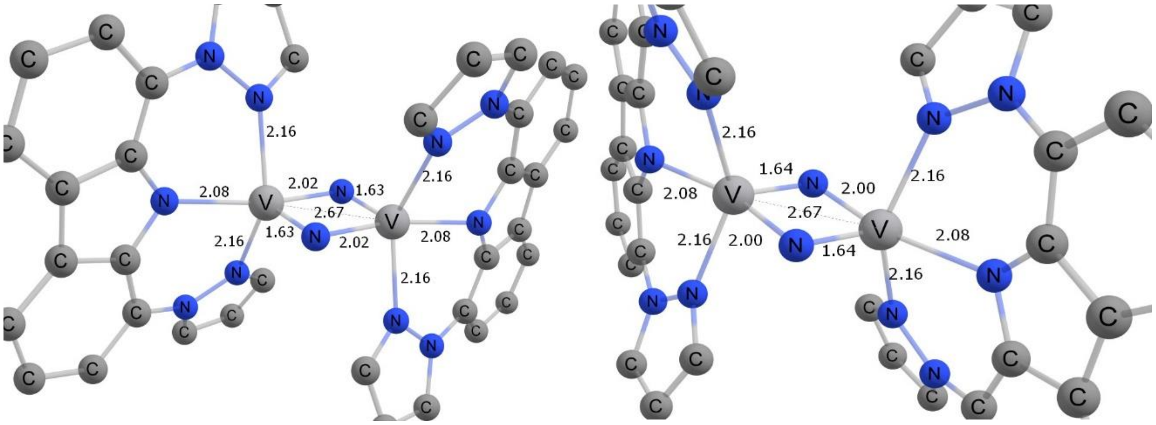

Fig. S8. Computed structures of singlet $[\{Cz^{H}(Pyr^{iPr})_2\}V]_2(\mu\text{-}N)_2$ (left) and triplet $[\{Cz^{H}(Pyr^{iPr})_2\}V]_2(\mu\text{-}N)_2$ (right).

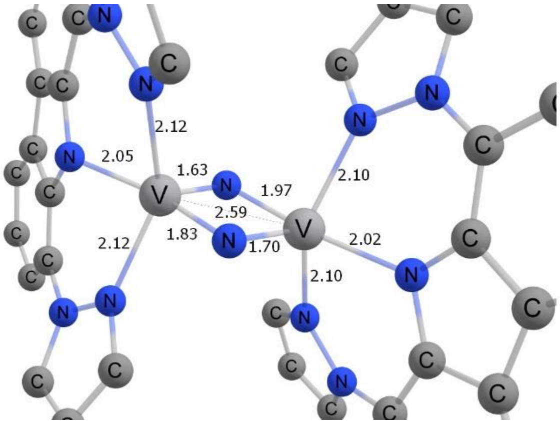

Fig. S9. Computed structure of doublet [[{Cz^{H}(Pyr^{iPr})$_2$}V]$_2$(μ-N)$_2$]$^+$.

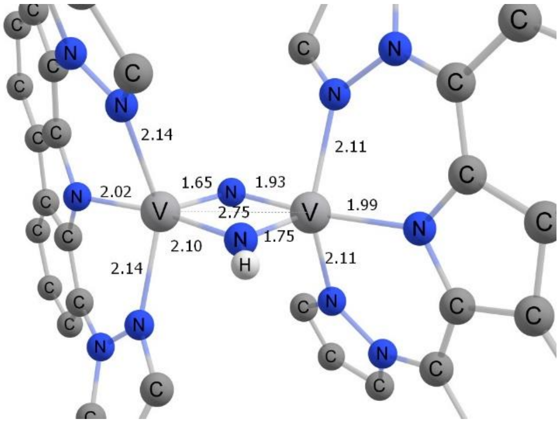

Fig. S10. Computed structure of triplet [[{Cz^{H}(Pyr^{iPr})$_2$}V]$_2$(μ-N)(μ-NH)]$^+$.

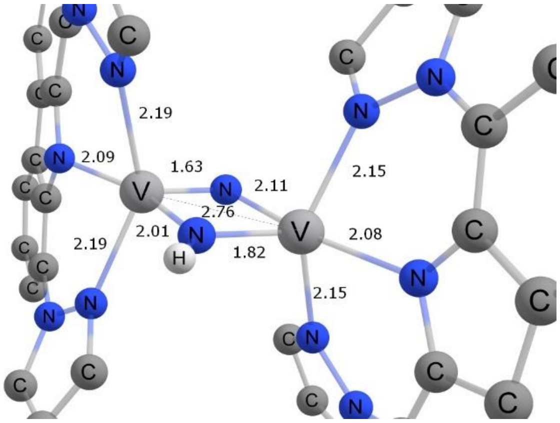

Fig. S11. Computed structure of quartet [[{Cz^{H}(Pyr^{iPr})$_2$}V]$_2$(μ-N)(μ-NH)].

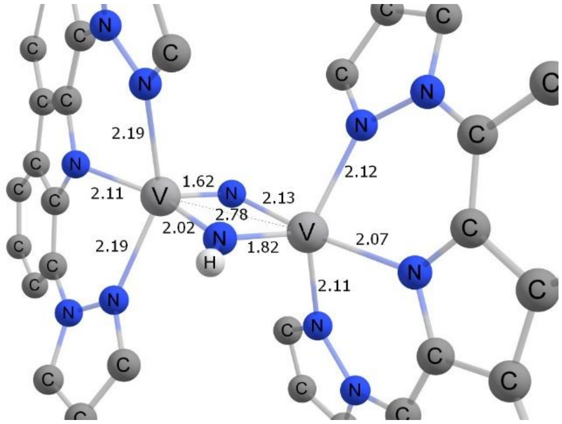

Fig. S12. Computed structure of triplet $[[\{\mathrm{Cz}^{\mathrm{H}}(\mathrm{Pyr}^{i\mathrm{Pr}})_2\}\mathrm{V}]_2(\mu\text{-N})(\mu\text{-NH})]^{-}$.

References

1. Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C., Synthesis, Structure, and Spectroscopic Properties of Copper(II) Compounds Containing Nitrogen–Sulphur Donor Ligands; the Crystal and Molecular Structure of Aqua[1,7-bis(N-methylbenzimidazol-2′-yl)-2,6-dithiaheptane]copper(II) Perchlorate. *J. Chem. Soc., Dalton Trans.* **1984**, 1349-1356.

2. Farrugia, L., WinGX and ORTEP for Windows: An Update. *J. Appl. Crystallogr.* **2012,** *45*, 849-854.