Supporting Information

Synthesis and Interconversion of V_4, V_7, and V_8 Oxide Clusters: Unexpected Formation of Neutral Heptanuclear Oxido(alkoxido)vanadium(V) Clusters $[V_7O_{17}(OR)(4,4'\text{-}^t\text{Bubpy})_3]$ (R = Et, $MeOC_2H_4$)

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Table S1. X-ray crystallographic data for 1, 2, and 3b.

	1·$4CH_2Cl_2$	**2**·$2CH_3OH·2H_2O$	**3b**·$CH_3OC_2H_4OH·2H_2O$
chemical formula	$C_{76}H_{104}Cl_8N_8O_{20}V_8$	$C_{42}H_{72}N_4O_{16}V_4$	$C_{60}H_{91}N_6O_{23}V_7$
formula weight	2140.86	1092.81	1621.00
dimension of crystals	0.49×0.38×0.29	0.66×0.31×0.15	0.28×0.21×0.17
crystal system	tetragonal	monoclinic	monoclinic
space group	$I4_1/a$ (#88)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a, Å	21.6694(5)	15.487(3)	16.149(3)
b, Å	21.6694(5)	9.647(2)	22.104(3)
c, Å	23.9946(7)	18.471(3)	22.140(4)
α, deg	90.0000	90.0000	90.0000
β, deg	90.0000	107.928(2)	108.769(3)
γ, deg	90.0000	90.0000	90.0000
V, $Å^3$	11267.0(5)	2625.7(8)	7483(2)
Z	4	2	4
ρ_{calcd}, g cm^{-3}	1.262	1.382	1.439
F(000)	4384	1144	3352
μ, cm^{-1}	8.788	7.557	9.089
trans. factors range	0.579–0.774	0.581–0.891	0.756–0.861
index ranges	$-22 \le h \le 28$	$-18 \le h \le 20$	$-20 \le h \le 20$
	$-28 \le k \le 25$	$-12 \le k \le 9$	$-28 \le k \le 28$
	$-31 \le l \le 26$	$-23 \le l \le 16$	$-28 \le l \le 28$
no. rflns measured	42681	19817	61078
no. unique rflns	13249	5972	16482
R_{int}	0.0442	0.0486	0.0610
no. rflns ($I > 2\sigma(I)$)	6450	5972	16951
no. params refined	271	297	848
*R*1 ($I > 2\sigma(I)$)[a]	0.0480	0.0507	0.0831
R (All cata)	0.0543	0.0609	0.1061
wR2 (All cata)[b]	0.1325	0.1444	0.2428
GOF[c]	1.155	1.072	1.094
max diff peak/hole, e $Å^{-3}$	0.35/−0.49	0.72/−0.71	1.60/−0.89

Table S2. Selected interatomic distances (Å) and angles (deg) for 1.

Interatomic distances (Å)			
V1–O1	1.5991(18)	V1−O4^{i}	2.0119(16)
V1−O4	1.8483(16)	V1−O3	1.9780(16)
V1−O4^{iii}	2.4101(18)	V1−O5	1.7927(17)
V2−O2	1.6080(18)	V2−O4^{i}	2.2128(16)
V2−O3	1.7247(16)	V2−O5^{iii}	1.8483(18)
V2−N1	2.155(2)	V2−N2	2.187(2)
V1···V1^{i}	2.8653(6)	V1···V2	3.0720(6)
Angles (deg)			
V1−O3−V2	111.95(8)	V1−O4−V1^{i}	95.76(7)
V1−O4−V1^{ii}	106.59(8)	V1−O4−V2^{i}	164.33(10)
V1^{i}–O4−V1^{ii}	101.37(7)	V1^{i}–O4−V2^{i}	93.17(7)
V1^{ii}–O4−V2^{i}	84.13(6)	V1−O5−V2^{ii}	116.77(9)
O4−V1−O4^{i}	80.01(7)	O4−V1−O4^{iii}	76.94(7)
O4^{i}–V1−O4^{iii}	74.17(6)	O3−V1−O4^{i}	77.37(7)
O3−V2−O4^{i}	77.51(7)	O4^{i}–V2−N1	79.36(7)

Symmetry operators: (i) −X+1, −Y+1/2+1, Z; (ii) −Y+1/4+1, X+1/4, −Z+1/4+1;
(iii) Y+3/4−1, −X+1/4+1, −Z+1/4+1.

Table S3. Selected interatomic distances (Å) and angles (deg) for 2.

Interatomic distances (Å)			
V1−O1	1.598(2)	V1−O3	1.9974(13)
V1−O4	1.8227(19)	V1−O5	1.8033(17)
V1−O6	2.2976(19)	V1−O6^{i}	2.0396(15)
V2−O2	1.618(2)	V2−O3^{i}	1.7110(16)
V2−O4	1.820(2)	V2−O6	2.2825(17)
V2−N1	2.1710(18)	V2−N2	2.162(3)
Angles (deg)			
V1−O3−V2^{i}	114.23(9)	V1−O4−V2	118.40(9)
V1−O6−V1^{i}	105.57(8)	V1−O6−V2	86.19(6)
O6−V2− N1	81.80(7)	O1−V1−O5	101.25(9)

Symmetry operators: (i) −X+1, −Y+1, −Z+1.

Table S4. Selected interatomic distances (Å) and angles (deg) for 3b.

Interatomic distances (Å)			
V1–O1	1.617(3)	V1–O8	1.713(3)
V1–O9	1.783(4)	V1–O10	1.785(4)
V2–O2	1.591(3)	V2–O11	1.766(3)
V2–O12	1.772(4)	V2–O18	1.794(4)
V3–O3	1.596(4)	V3–O8	2.508(4)
V3–O11	1.964(3)	V3–O13	1.864(4)
V3–O14	1.827(3)	V3–O15	1.951(3)
V4–O4	1.593(3)	V4–O8	2.584(3)
V4–O12	1.978(3)	V4–O13	1.808(4)
V4–O16	1.865(3)	V4–O17	1.948(4)
V5–O5	1.602(3)	V5–O8	2.213(3)
V5–O14	1.793(4)	V5–O16	1.795(3)
V5–N1	2.161(4)	V5–N2	2.132(4)
V6–O6	1.609(3)	V6–O9	1.818(4)
V6–O11	2.262(3)	V6–O15	1.730(3)
V6–N3	2.165(4)	V6–N4	2.149(4)
V7–O7	1.603(4)	V7–O10	1.827(3)
V7–O12	2.236(4)	V7–O17	1.732(3)
V7–N5	2.179(4)	V7–N6	2.167(4)
V3···V6	3.0636(10)	V4···V7	3.0586(13)
Angles (deg)			
O8−V1−O9	108.49(16)	O8−V1−O10	109.42(15)
O9−V1−O10	111.17(16)	O11−V2−O12	113.74(16)
O11−V2−O18	113.14(18)	O12−V2−O18	113.27(17)

O13−V3−O14	93.36(16)	O13−V4−O16	93.80(17)
O14−V5−O16	100.77(16)	O9−V6−O15	103.81(16)
O10−V7−O17	105.25(16)	V1−O8−V3	122.95(17)
V1−O8−V4	120.88(17)	V1−O8−V5	145.01(17)
V1−O9−V6	130.63(16)	V2−O11−V3	116.59(16)
V2−O11−V6	148.09(17)	V3−O8−V4	79.76(9)
V3−O13−V4	125.59(17)	V3−O8−V5	83.34(11)
V3−O11−V6	92.65(13)	V3−O14−V5	120.7(2)
V3−O15−V6	112.55(18)	V4−O8−V5	83.51(10)

Table S5. BVS calculations for vanadium atoms of 1, 2, and 3b.[a]

V complex		V1	V2	V3	V4	V5	V6	V7
1	V(IV)	4.78	4.80	–	–	–	–	–
	V(V)	**5.03**	**5.01**	–	–	–	–	–
2	V(IV)	4.82	4.83	–	–	–	–	–
	V(V)	**5.07**	**5.03**	–	–	–	–	–
3b	V(IV)	4.78	4.74	4.75	4.77	4.82	4.85	4.67
	V(V)	**5.03**	**4.99**	**5.00**	**5.02**	**5.02**	**5.05**	**5.03**

[a] BVS calculations were conducted using X-ray data of **1** (Table S2), **2** (Table S3), and **3b** (Table S4). Bond valence parameters: V(IV)−O (1.784 Å), V(V)−O (1.803 Å), and V−N (1.86 Å).[S1]

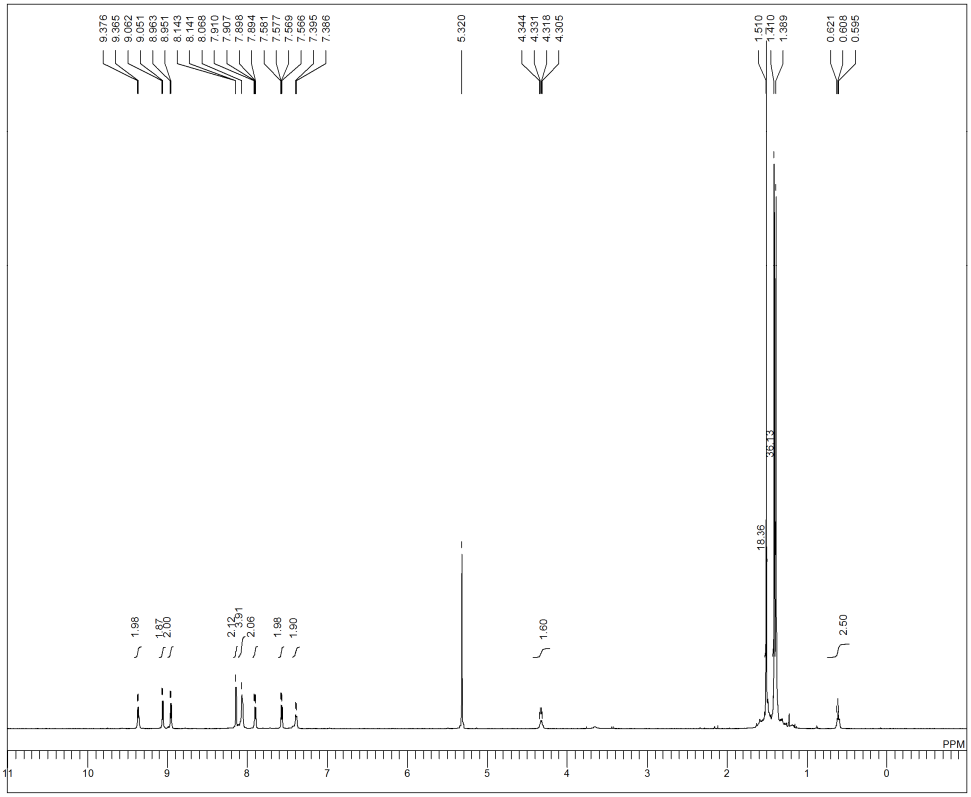

Figure S1. ^{1}H NMR (CD_2Cl_2) spectrum of $[V_7O_{17}(OEt)(4,4'\text{-}^t\text{Bubpy})_3]$ (3a).

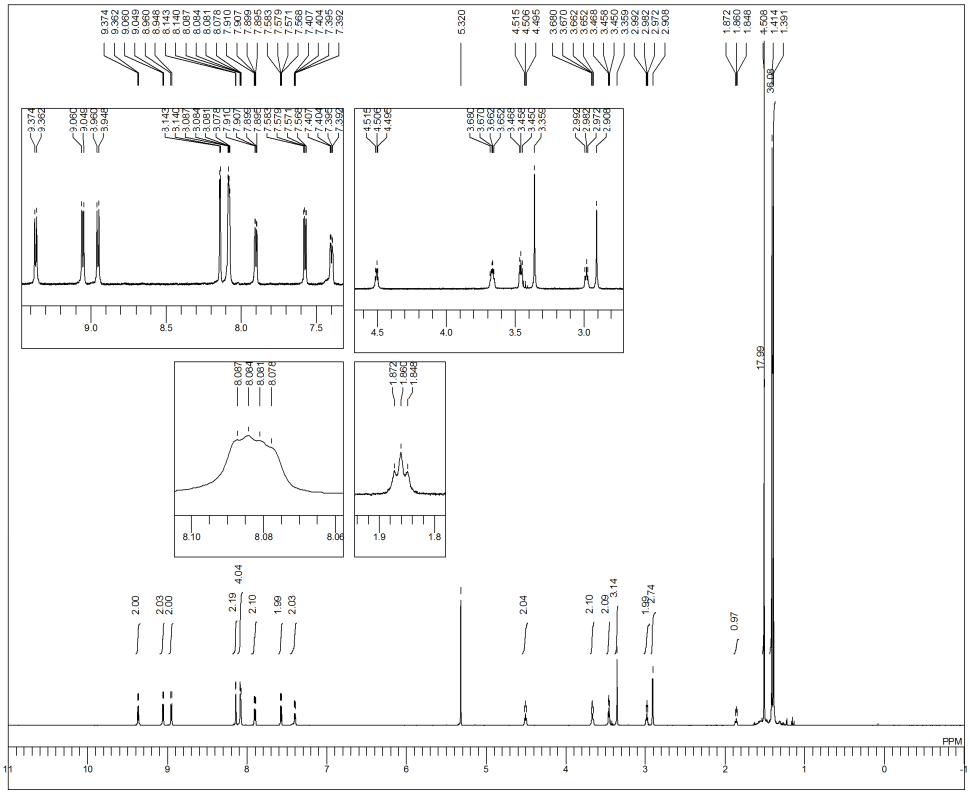

Figure S2. ^{1}H NMR (CD_2Cl_2) spectrum of $[V_7O_{17}(OC_2H_4OMe)(4,4'\text{-}^t\text{Bubpy})_3]$ $\cdot CH_3OC_2H_4OH$ ($3b\cdot CH_3OC_2H_4OH$).

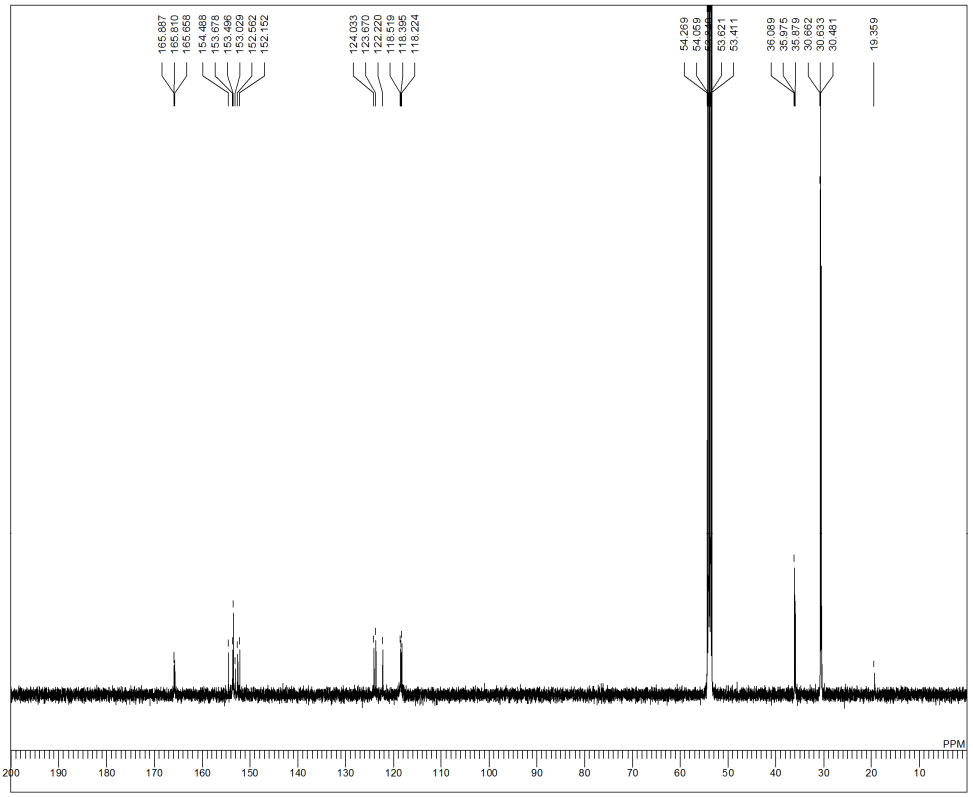

Figure S3. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) spectrum of $[V_7O_{17}(OEt)(4,4'\text{-}^{t}Bubpy)_3]$ (3a).

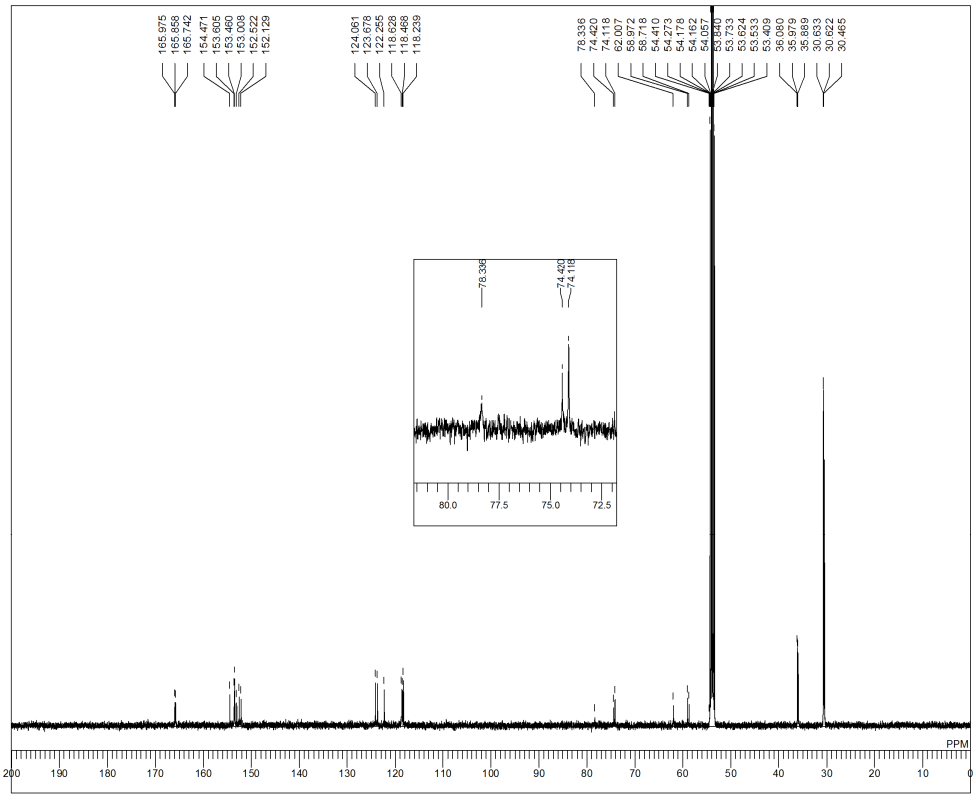

Figure S4. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) spectrum of $[V_7O_{17}(OC_2H_4OMe)(4,4'\text{-}^{t}Bubpy)_3]$ $\cdot CH_3OC_2H_4OH$ (3b$\cdot CH_3OC_2H_4OH$).

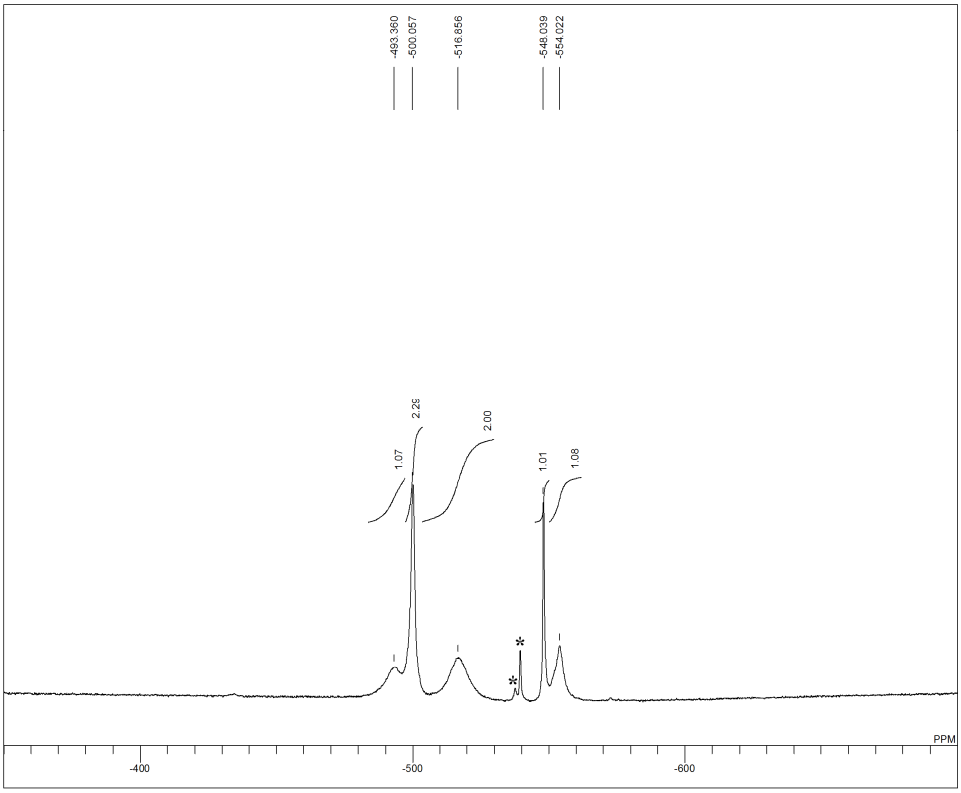

Figure S5. ^{51}V NMR (CD_2Cl_2) spectrum of [V_7O_{17}(OEt)(4,4'-^{t}Bubpy)$_3$] (3a). Signals with an asterisk are those of unidentified vanadium(V) species which may be generated from partial decomposition of 3a by trace amounts of water in CD_2Cl_2.

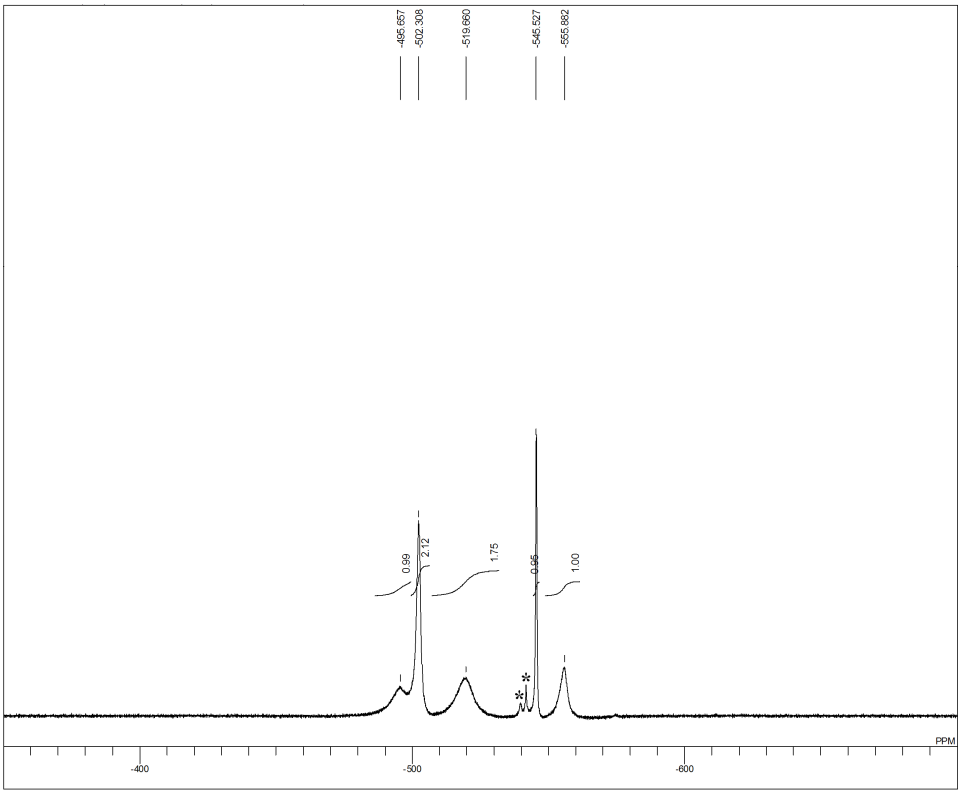

Figure S6. ^{51}V NMR (CD_2Cl_2) spectrum of [V_7O_{17}(OC_2H_4OMe)(4,4'-^{t}Bubpy)$_3$]·$CH_3OC_2H_4OH$ (3b·$CH_3OC_2H_4OH$). Signals with an asterisk are those of unidentified vanadium(V) species which may be generated from partial decomposition of 3b by trace amounts of water in CD_2Cl_2.

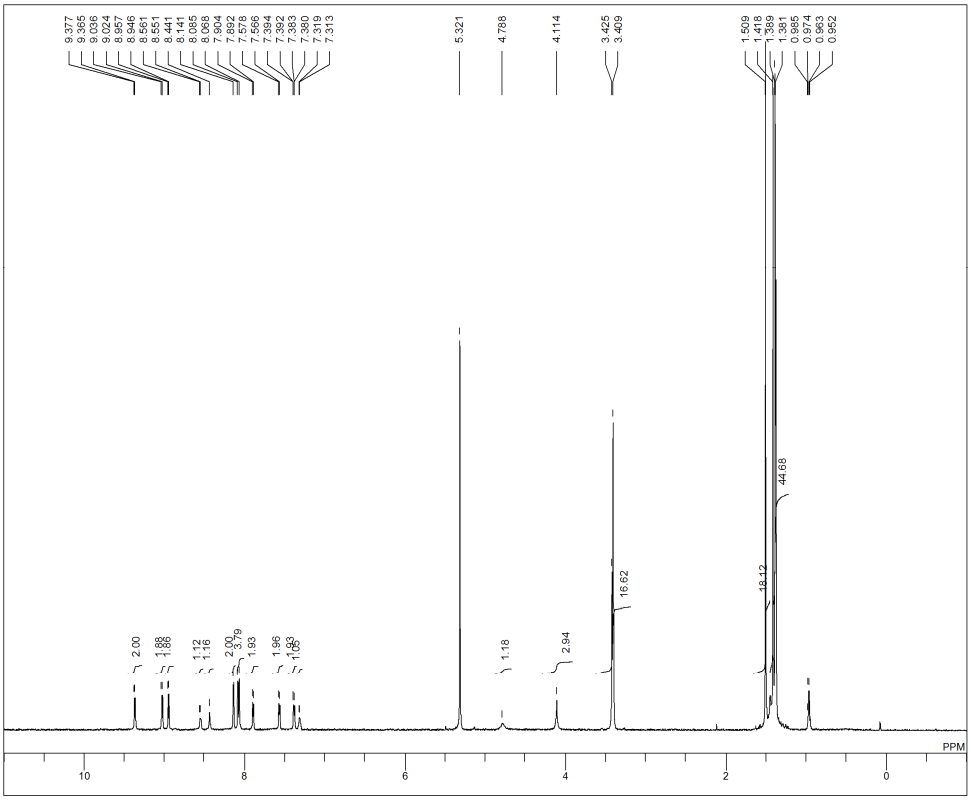

Figure S7. ^{1}H NMR spectrum of the CD_2Cl_2 solution of 2.

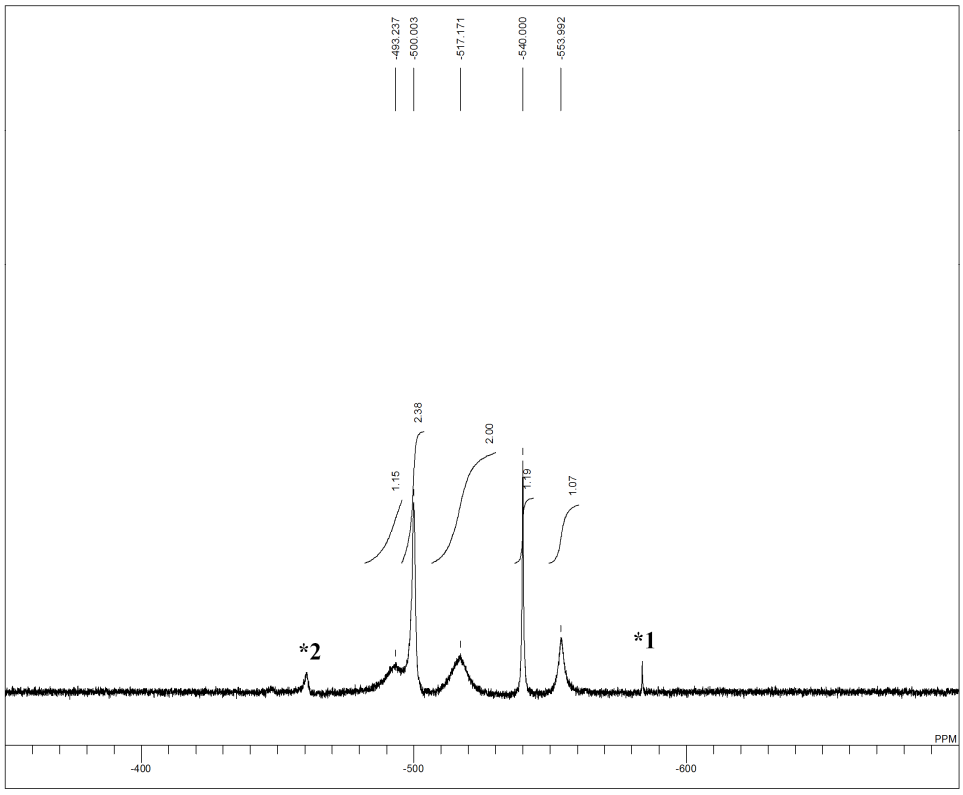

Figure S8. ^{51}V NMR spectrum of the CD_2Cl_2 solution of 2. The signal with a numbered asterisk (*1) has been tentatively assigned to $[VO(OMe)_3]$,[S2] and the signal with *2 is that of unidentified vanadium(V) species.

References

(1) Brese, N. E.; O'Keeffe, M. *Acta Crystallogr. Sect. B* **1991**, *47*, 192−197.

(2) Jiang, F.; Anderson, O. P.; Miller, S. M.; Chen, J.; Mahroof-Tahir, M.; Crans, D. C. *Inorg. Chem.* **1998**, *37*, 5439–5451.