Electronic Supporting Information (ESI)

Conversion of a Cyclic Polyoxovanadate-Ethoxide Cluster to Its Lindqvist Congener: Thermodynamic vs Kinetic Products

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Experimental Details

General Considerations. All manipulations were carried out in the absence of water and oxygen in a UniLab MBraun inert atmosphere glovebox under an atmosphere of dinitrogen. Glassware was oven dried for a minimum of 4 h and cooled in an evacuated antechamber prior to use in the glovebox. Celite 545 (J. T. Baker) was dried in a Schlenk flask for at least 14 h at 150 °C under vacuum prior to use. 3 Å molecular sieves (Fisher Scientific) were activated using the same drying method. Anhydrous ethanol (200 proof) was purchased from Sigma-Aldrich and stored over activated 3 Å molecular sieves. All other solvents were dried and deoxygenated on a Glass Contour System (Pure Process Technology, LLC) and stored over activated 3 Å molecular sieves. $InCl_3$ was purchased from Strem Chemicals, Inc., and used as received. $VO(OC_2H_5)_3$ and $(^nBu_4N)BH_4$ were purchased from Sigma-Aldrich and used as received. $MnCl_2(THF)_{1.5}$ was prepared according to a previously reported method.[1]

^{1}H NMR spectra were recorded on a Bruker DPX-400 MHz spectrometer locked on the signal of deuterated solvents. All chemical shifts were reported relative to the peak of residual ^{1}H signal in the deuterated solvents. $CDCl_3$ and CD_2Cl_2 were purchased from Cambridge Isotope Laboratories, degassed by three freeze-pump-thaw cycles, and stored over activated 3 Å molecular sieves. Infrared (FT-IR, ATR) spectra of complexes were recorded on a Shimadzu IRAffinity-1 Fourier Transform Infrared spectrophotometer and were reported in wavenumbers (cm^{-1}). Electronic absorption measurements were recorded at room temperature in anhydrous dichloromethane in a sealed 1 cm quartz cuvette with an Agilent Cary 60 UV-Vis spectrophotometer. Mass spectrometry analyses were performed on an Advion Expression^L Compact Mass Spectrometer equipped with an electrospray probe and an ion-trap mass analyzer. Direct injection analysis was employed in all cases with a sample solution in acetonitrile. Single crystals were mounted on the tip of a thin glass optical fiber (goniometer head) and mounted on a XtaLab Synergy-S Dualflex diffractometer equipped with a HyPix-6000He HPC area detector for data collection at 173.00(10 K). The structure was solved using ShelXT and refined using ShelXL.[2-3] Elemental analyses were performed on a PerkinElmer 2400 Series II Analyzer at the CENTC Elemental Analysis Facility, University of Rochester.

Synthesis of $(VO)_6(OC_2H_5)_{12}(DCM)_{1.5}$
Method A. In a 150 mL glass pressure vessel, $VO(OC_2H_5)_3$ (1.504 g, 7.44 mmol, 5.0 eq) was dissolved in 60 mL of tetrahydrofuran. Solid $[^nBu_4N]BH_4$ (0.384 g, 1.49 mmol, 1.0 eq) and $MnCl_2(THF)_{1.5}$ (0.698 g, 2.98 mmol, 2.0 eq) were added to the yellow solution. The pressure vessel was sealed, removed from the glovebox, and stirred in an oil bath at 65 °C for 22 h. The resulting green reaction mixture was cooled to room temperature, and the vessel was returned to the glovebox. The reaction mixture was filtered over a bed of Celite (2 cm) on a medium porosity frit, and the volatiles were removed under reduced pressure. The solid was triturated with acetonitrile until the acetonitrile ran clear, and was subsequently washed with ethanol (5 mL x 3) to remove remaining impurities. The solid was triturated with small portions of dichloromethane (1 mL x 4) until the dichloromethane went from blue-green to bright-blue. The remaining blue solid was extracted with dichloromethane (10 mL). The volatiles were removed from the bright blue solution under vacuum, affording $(VO)_6(OC_2H_5)_{12}(DCM)_{1.5}$ as a light-blue solid (0.267 g, 20% based on $VO(OC_2H_5)_3$). Additional product could be isolated from the blue-green DCM fraction *via* recrystallization at -30 °C (0.110 g, 8% based on $VO(OC_2H_5)_3$), for a total of 0.377 g of $(VO)_6(OC_2H_5)_{12}(DCM)_{1.5}$ (28% based on $VO(OC_2H_5)_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.49 (-CH$_2$-, fwhh = 1170 Hz), -0.92 (-CH$_3$, fwhh = 625 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 4.52 (-CH$_2$-, fwhh = 1070 Hz), -0.88 (-CH$_3$, fwhh = 520 Hz). FT-IR (ATR, cm^{-1}): 2973, 2932-2880, 1443, 1377, 1354, 1263, 1159, 1092, 1053, 1026, 997 (V=O$_t$), 907, 887, 746. UV-vis (CH_2Cl_2): λ = 390 nm (ε = 94 M^{-1} cm^{-1}), 678 nm (shoulder, ε = 69 M^{-1} cm^{-1}), 772 nm (ε = 84 M^{-1} cm^{-1}). Elemental Analysis for $C_{24}H_{60}O_{18}V_6 \bullet 1½$ DCM (MW = 1069.77 g/mol) Calcd (%): C, 28.63; H, 5.94. Found (%): C, 28.73; H, 6.06.

Method B. A 48 mL glass pressure vessel was charged with $VO(OC_2H_5)_3$ (0.454 g, 2.25 mmol, 5.0 eq) and 18 mL of tetrahydrofuran. Solid $[^nBu_4N]BH_4$ (0.117 g, 0.45 mmol, 1.0 eq) and $InCl_3$ (0.101 g, 0.46 mmol, 1.0 eq) were added to the yellow solution. The pressure vessel was sealed, removed from the glovebox, and stirred in an oil bath at 65 °C for 22 h. The resulting brown reaction mixture was cooled to room temperature, and the vessel was returned to the glovebox. The reaction mixture was filtered over a bed of Celite (2 cm) on a medium porosity frit, and the volatiles were removed under reduced pressure. The solid was triturated with acetonitrile until the acetonitrile ran clear, followed by ethanol (5 mL). The resultant solid was extracted with dichloromethane (5 mL x 3) and filtered over a bed of Celite (2 cm) on a medium porosity frit. The volatiles were removed under vacuum, affording the product, $(VO)_6(OC_2H_5)_{12}(DCM)_{1.5}$, as a blue solid (0.028 g, 7% based on $VO(OC_2H_5)_3$). Characterization of the product matches that of **Method A**.

Conversion of Cyclic $(VO)_6(OC_2H_5)_{12}(DCM)_{1.5}$ to Lindqvist $V_6O_6(OC_2H_5)_{12}(MeCN)$
A 25 mL Teflon-lined Parr reactor was charged with $(VO)_6(OC_2H_5)_{12}(DCM)_{1.5}$ (0.150 g, 0.14 mmol) and 12 mL ethanol. The Parr reactor was sealed, removed from the glovebox, and heated in an oven at 125 °C for 18 h. The Parr reactor was allowed to cool to room temperature, then returned to the glovebox. The resulting brown solution was decanted from the blue solid, and the volatiles were removed under reduced pressure. The brown residue was extracted with acetonitrile (16 mL), filtered over a glass pipet packed with a glass fiber filter paper, and the volatiles were removed under reduced pressure. The brown residue was extracted with diethyl ether (10 mL) and filtered over a glass pipet packed with a glass fiber filter paper. The volatiles were removed under reduced pressure, affording the previously reported $V_6O_6(OC_2H_5)_{12}(MeCN)$ as a brown powder (0.057 g, 41% based on $(VO)_6(OC_2H_5)_{12}(DCM)_{1.5}$), which was confirmed by ^{1}H NMR analysis.[4] ^{1}H NMR analysis of the blue solid confirmed that it was unreacted $(VO)_6(OC_2H_5)_{12}(DCM)_{1.5}$.

Conversion of Cyclic $(VO)_6(OC_2H_5)_{12}(DCM)_{1.5}$ to Lindqvist $^nBu_4N[V_6O_6(OC_2H_5)_{12}(MeCN)]$
A 25 mL Teflon-lined Parr reactor was charged with $(VO)_6(OC_2H_5)_{12}(DCM)_{1.5}$ (0.142 g, 0.13 mmol, 1.0 eq), $(^nBu_4N)BH_4$, (0.051 g, 0.20 mmol, 1.5 eq), and 12 mL ethanol. The Parr reactor was sealed, removed from the glovebox, and heated in an oven at 125 °C for 3 h. The Parr reactor was allowed to cool to room temperature, then returned to the glovebox. The volatiles were removed from the resulting red-brown solution under reduced pressure. The brown residue was extracted with acetonitrile (6 mL), filtered over a glass pipet packed with a glass fiber filter paper, and the volatiles were removed under reduced pressure. The brown residue was extracted with dichloromethane (6 mL) and filtered over a glass pipet packed with a glass fiber filter paper. The volatiles were removed under reduced pressure, affording $(^nBu_4N)[V_6O_6(OC_2H_5)_{12}]$ as a brown powder (0.164 g, 100% based on $(VO)_6(OC_2H_5)_{12}(DCM)_{1.5}$). ^{1}H NMR and ESI-MS analyses match that of $(CoCp_2)[V_6O_6(OC_2H_5)_{12}]$ cluster.
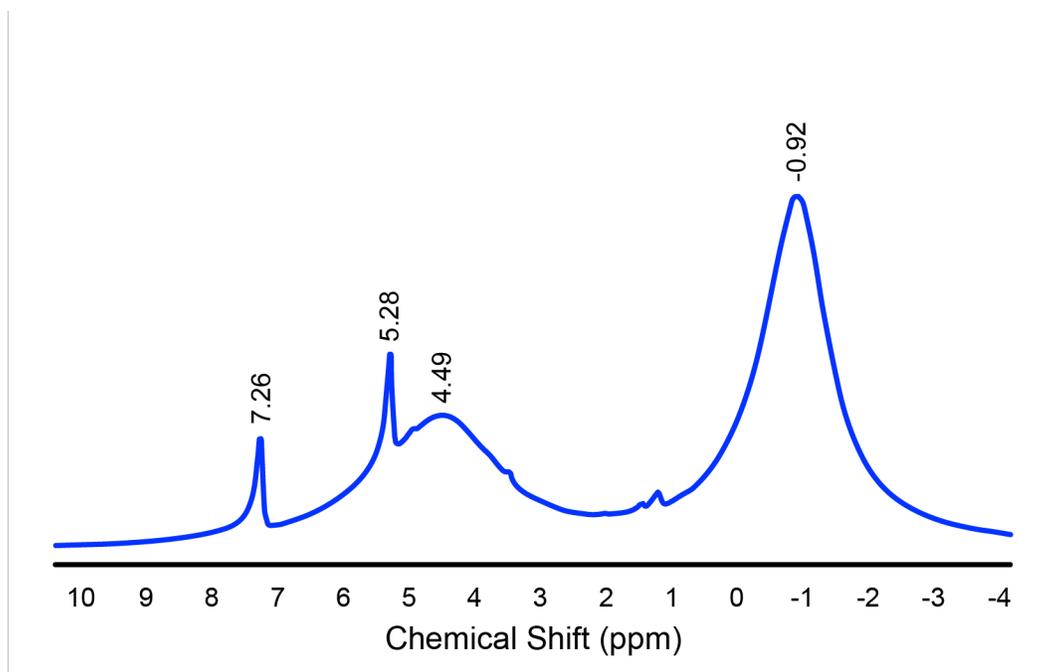
Figure S1. ^{1}H NMR spectrum of **[VO(OC$_2$H$_5$)$_2$]$_6$** (CDCl$_3$, 21 °C). Peaks: 7.26 (CHCl$_3$, reference), 5.28 (CH$_2$Cl$_2$), 4.49 (-CH$_2$-), -0.92 (-CH$_3$) ppm.

Table S1. Crystallographic parameters for **[VO(OC$_2$H$_5$)$_2$]$_6$**.

Compound	**(VO)$_6$(OC$_2$H$_5$)$_{12}$**
Emperical formula	C$_{24}$H$_{60}$O$_{18}$V$_6$
Formula weight	942.36
Temperature	173.00(10) K
Wavelength	1.54184 Å
Crystal system	Cubic
Space group	*Pa-3*
Unit cell dimensions	a = b = c = 16.36790(10) Å
	$\alpha = \beta = \gamma = 90°$
Volume	4385.09(8) Å^3
Z	4
Reflections collected	17780
Independent reflections	1567
Goodness-of-fit of F^2	1.071
Final R indices	*R*1 = 0.0293
[I>2sigma(I(]	*wR*2 = 0.0797

Table S2. Bond valence sum calculation for **[VO(OC$_2$H$_5$)$_2$]$_6$**. These results are consistent with a V^{IV} oxidation state assignment.

d$_{ij}$ (V=O, V-O)	V$_{ij}$ (V=O, V-O)[a]		
V1	V^{V}	V^{IV}	V^{III}
1.5861(13)	1.797175	1.707218	1.528144
1.9928(11)	0.598713	0.568744	0.509088
1.9912(12)	0.601308	0.571209	0.511294
1.9726(12)	0.632308	0.600658	0.537654
1.9777(12)	0.623652	0.592435	0.530294
BVS[b]	**4.253157**	**4.040264**	**3.616473**

[a] $V_{ij} = \exp[(R_{ij}-d_{ij})/B]$. V^{V}, R_{ij} = 1.803; V^{IV}, R_{ij} = 1.784; V^{III}, R_{ij} = 1.743. B = 0.37 for all.[5]
[b] Bond valence sum (BVS) = sum(V_{ij})
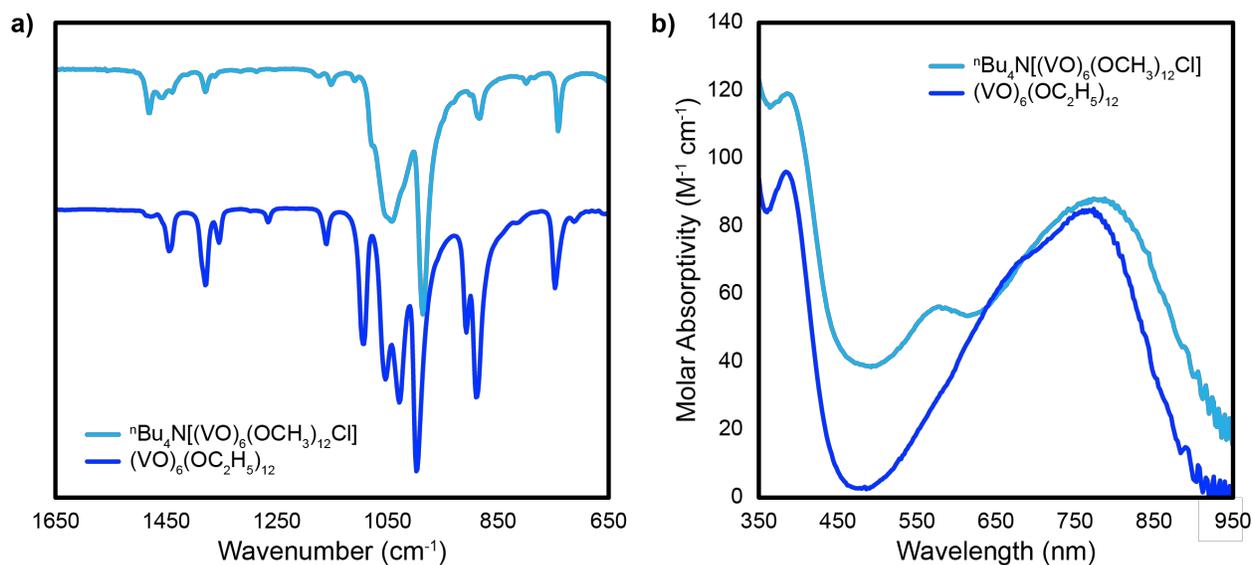
Figure S2. Spectroscopic characterization of **[VO(OC$_2$H$_5$)$_2$]$_6$**: a) infrared spectrum, plotted against the spectrum of **{[VO(OCH$_3$)$_2$]$_6$Cl}$^{-1}$**; electronic absorption spectrum (dichloromethane, 21 °C), plotted against the spectrum of **{[VO(OCH$_3$)$_2$]$_6$Cl}$^{-1}$** (acetonitrile, 21 °C). Note: the disparity of the solubilities between **[VO(OC$_2$H$_5$)$_2$]$_6$** and **{[VO(OCH$_3$)$_2$]$_6$Cl}$^{-1}$** prevented comparison of the electronic absorption spectra in the same solvent.
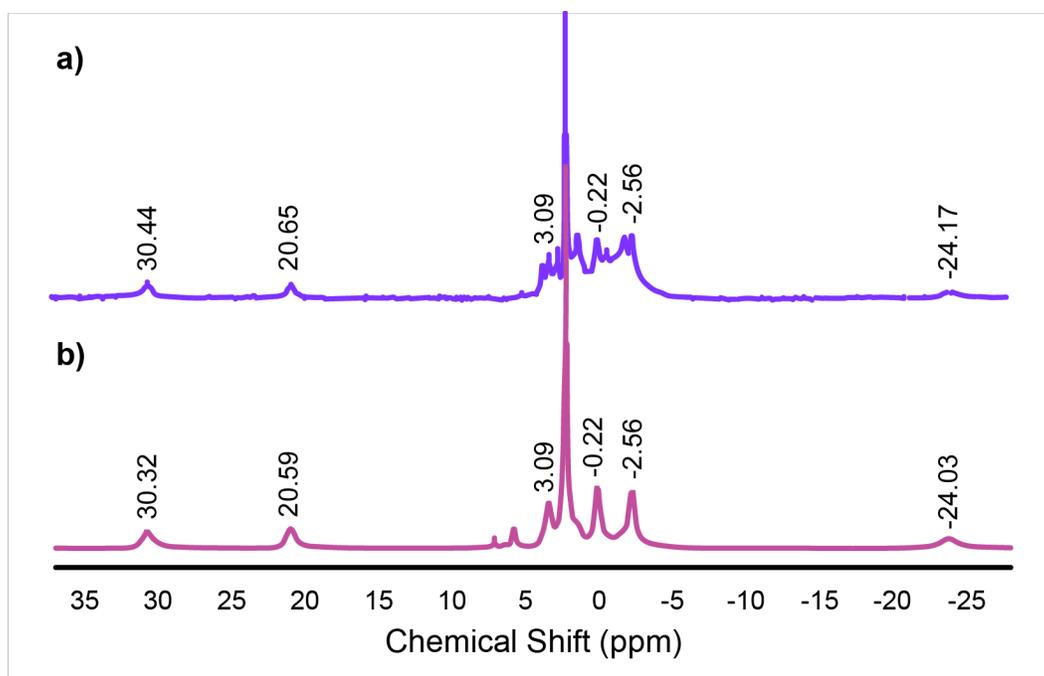
Figure S3. ^{1}H NMR spectrum of Lindqvist $V_6O_6(OC_2H_5)_{12}$ (CD$_3$CN, 21 °C) from a) heating **[VO(OC$_2$H$_5$)$_2$]$_6$** in ethanol (125 °C, 18 h) and b) independent synthesis.[4] Peaks: *ca*. 30 (-CH$_2$-), *ca*. 20 (-CH$_2$-), 3.09 (-CH3), 1.94 (CH$_3$CN, reference), -0.22 (-CH$_3$), -2.56 (-CH$_3$), *ca*. -24 (-CH$_2$-) ppm.
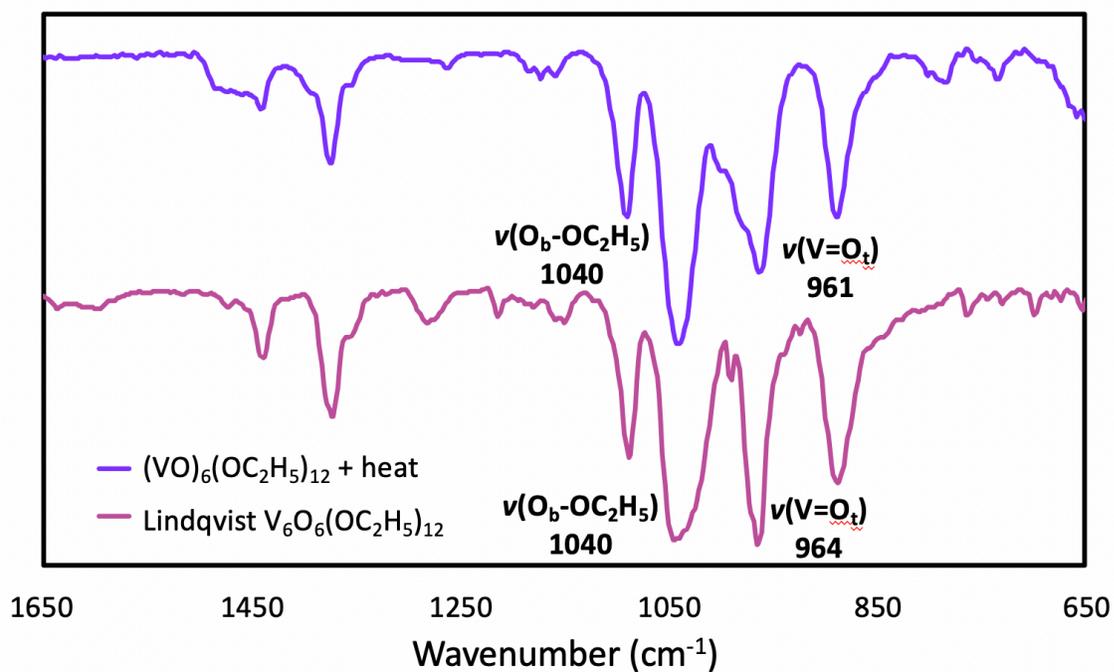
Figure S4. Infrared spectrum of Lindqvist $V_6O_6(OC_2H_5)_{12}$ from a) heating **[VO(OC$_2$H$_5$)$_2$]$_6$** in ethanol (125 °C, 18 h) and b) independent synthesis.[4] These spectra are distinctly different from that of the cyclic species (**Figure S2a**).
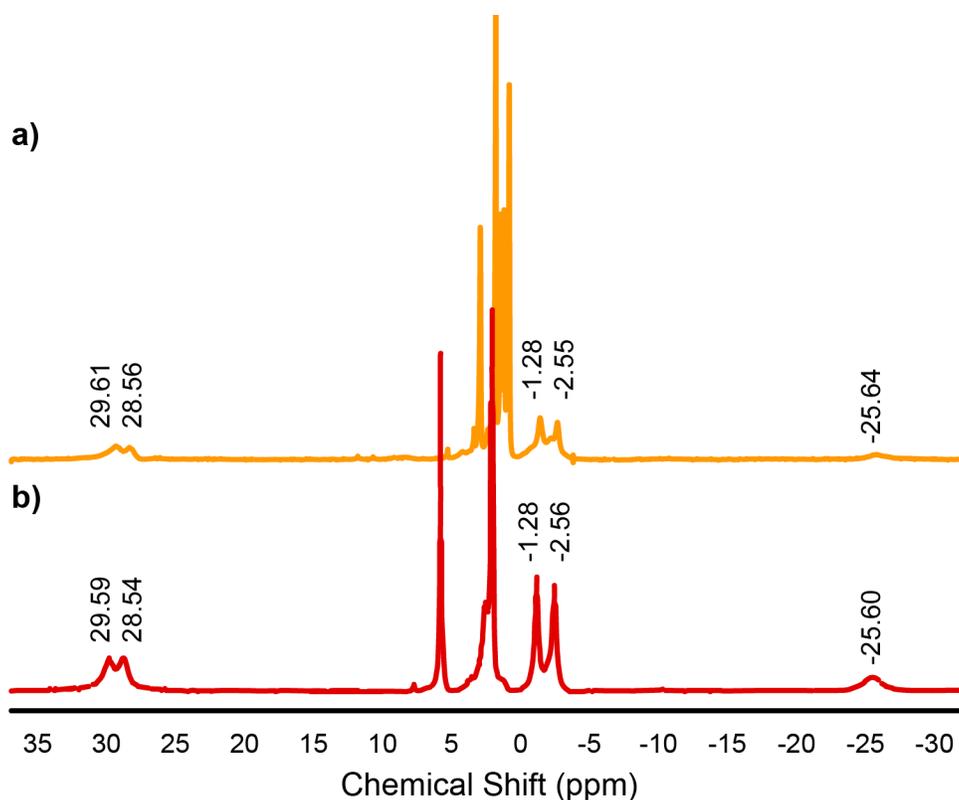
Figure S5. ^1H NMR spectrum of Lindqvist $[V_6O_6(OC_2H_5)_{12}]^-$ (CD_3CN, 21 °C) from a) heating **[VO(OC$_2$H$_5$)$_2$]$_6$** and (${}^nBu_4N)BH_4$ in ethanol (125 °C, 3 h) and b) independent synthesis. Peaks: *ca*. 29.6 (-CH$_2$-), *ca*. 28.5 (-CH$_2$-), 3.09, 1.94 (CH_3CN, reference), -1,28 (-CH$_3$), -2.56 (-CH$_3$), *ca*. -25.6 (-CH$_2$-) ppm. Note: a) has a ${}^nBu_4N^+$ cation (peaks: 3.06, 1.57, 1.33, 0.97 ppm), while b) has a cobaltocenium cation ($CoCp_2^+$, peaks: 5.66 ppm).
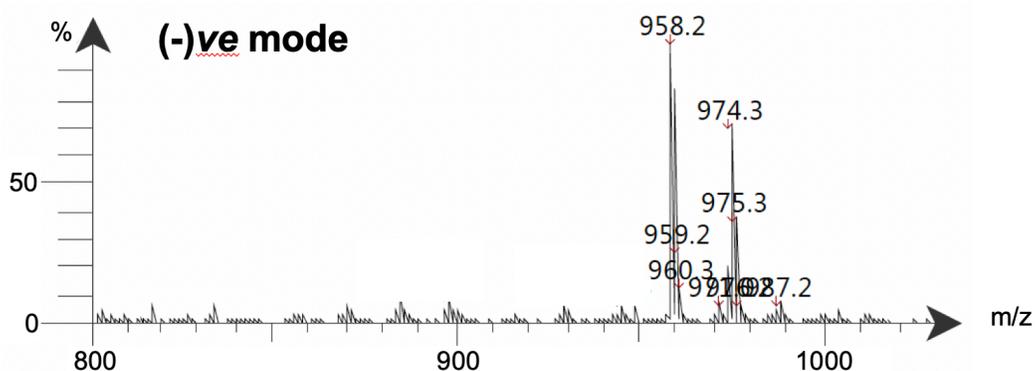
Figure S6. Electrospray-ionization mass spectrum (*-ve*) from heating **[VO(OC$_2$H$_5$)$_2$]$_6$** and (${}^nBu_4N)BH_4$ in ethanol (125 °C, 3 h). Peaks: 958 m/z = $[V_6O_7(OC_2H_5)_{12}]^-$, 975 m/z = $[V_6O_6(OC_2H_5)_{12}]^-$ + CH_3OH. Since the 1H NMR shows little to no $[V_6O_7(OC_2H_5)_{12}]^-$, the large $[V_6O_7(OC_2H_5)_{12}]^-$ signal in the ESI-MS is most likely from reaction of $[V_6O_6(OC_2H_5)_{12}]^-$ with atmospheric O_2/H_2O under the highly ionizing conditions in the instrument.
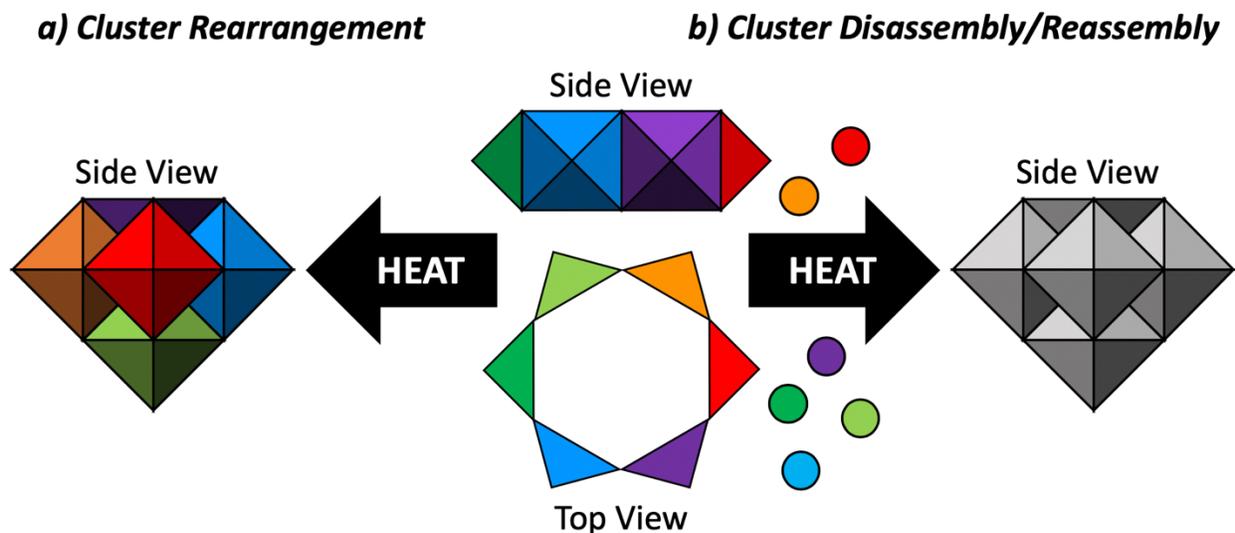
Figure S7. Possible mechanisms for the conversion of the cyclic **[VO(OC$_2$H$_5$)$_2$]$_6$** cluster to the Lindqvist configuration: a) rearrangement of the ring so that the vanadium linkages are maintained in the Lindqvist structure and b) complete disassembly of **[VO(OC$_2$H$_5$)$_2$]$_6$** into monomeric species, followed by reassembly to the Lindqvist conformation so that the vanadiums are scrambled.

References

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