Vanadium redox reactivity with amidoxime ligands

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Supplemental Information

Cyclic voltammetry

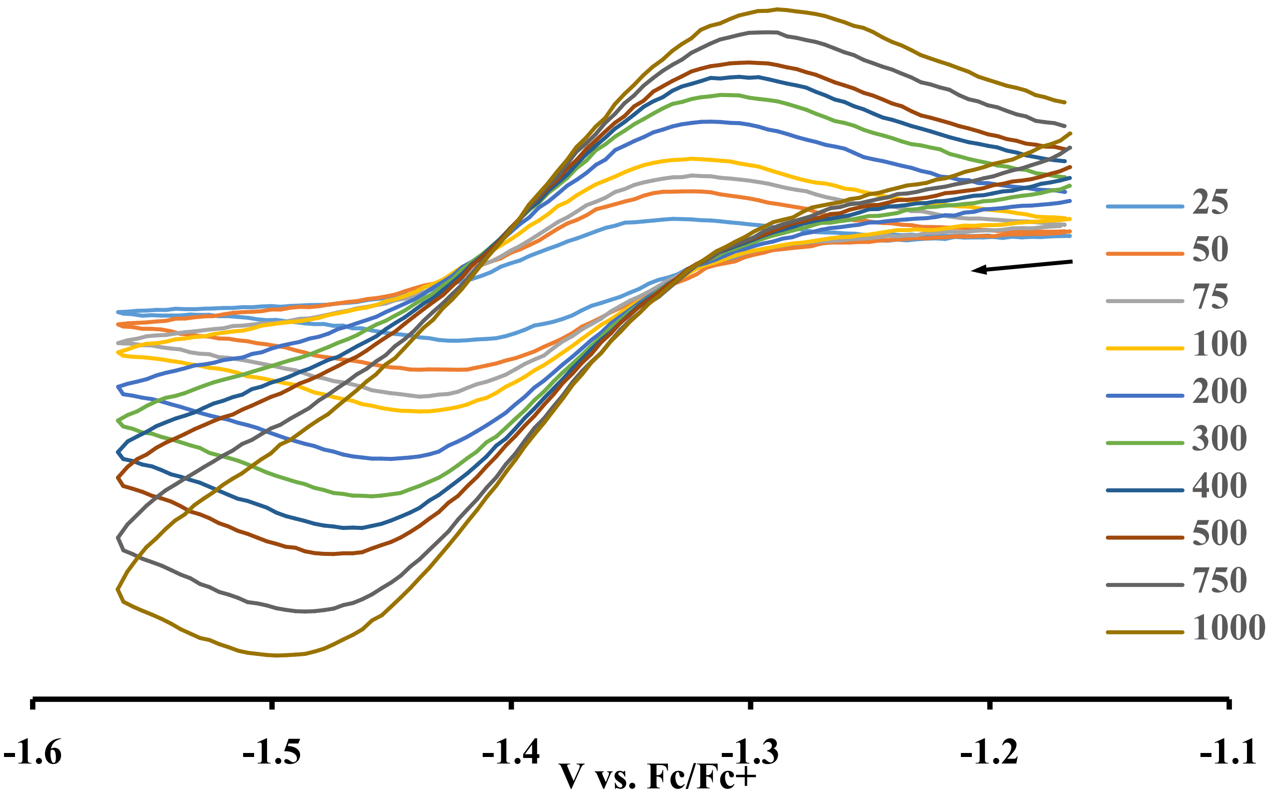

Figure S1: Reduction of [NEt$_4$][**1**] in DCM measured at different scan rates (in mV/s)

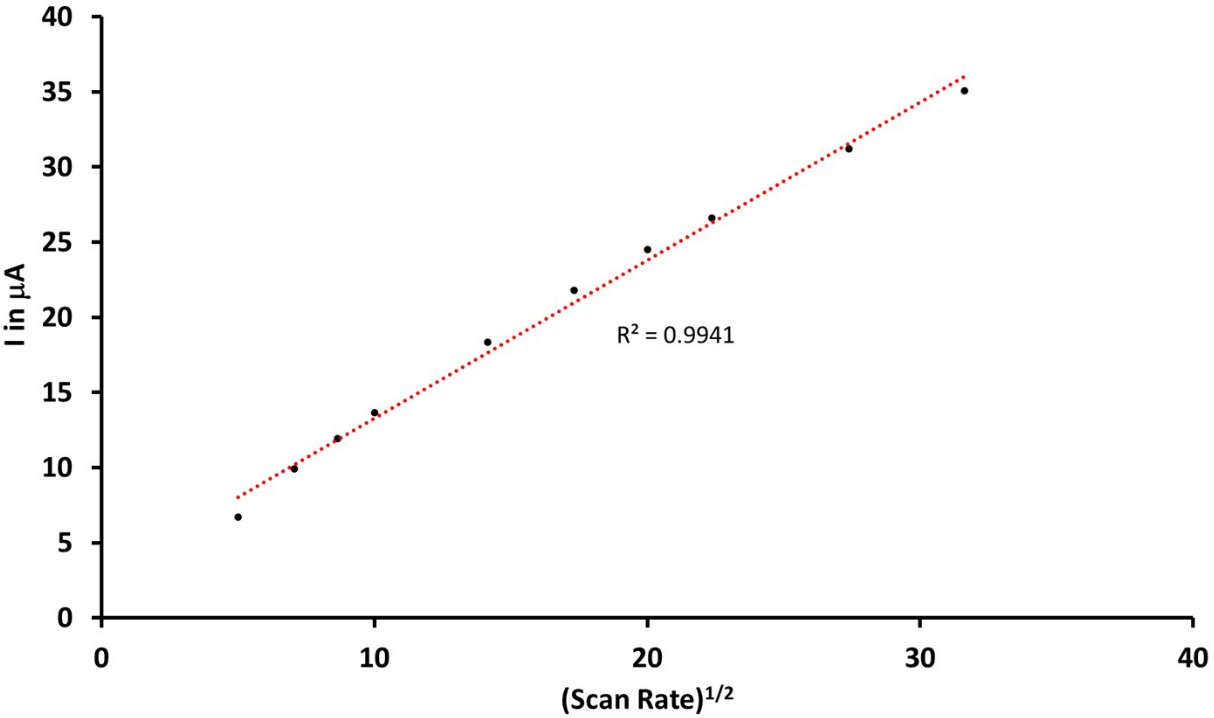

Figure S2: Linear plot of the flowing current vs the square root of the scan rate for the first reduction of [NEt_4][**1**] in DCM.

NMR Spectra

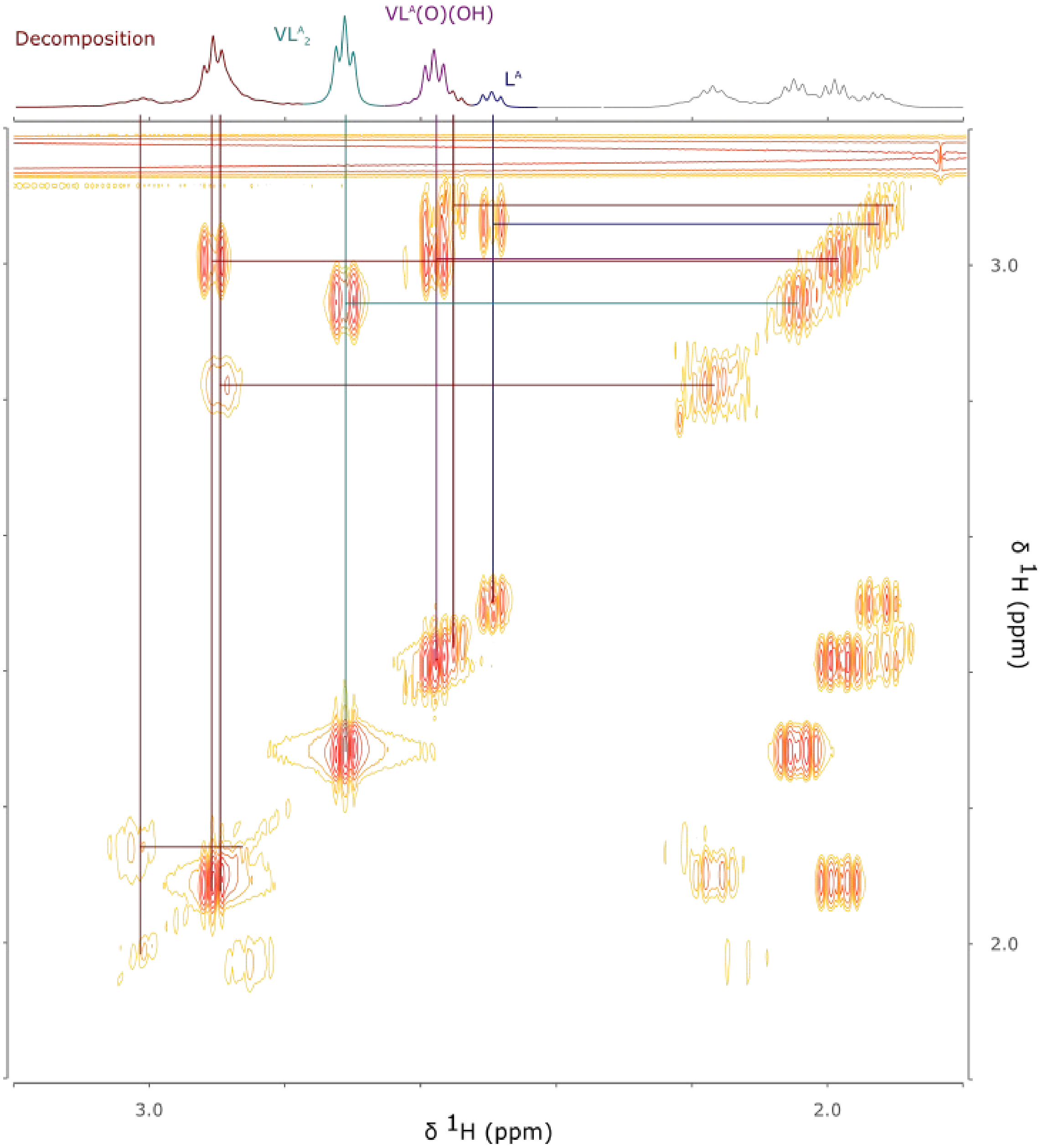

Figure S3: ^{1}H COSY NMR spectrum of 1:3 $\mathbf{L^A}$ – V(IV) mixture (also see main text, Figure 4)

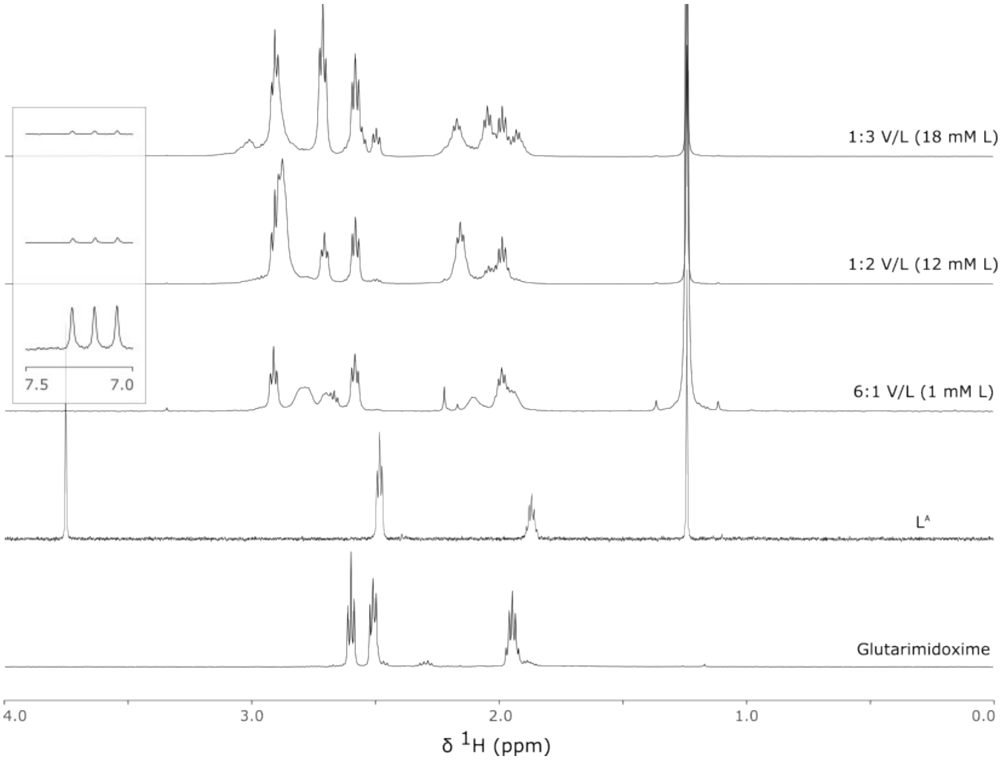

Figure S4: ^{1}H NMR spectra of $\mathbf{L^A}$ – V(IV) mixtures. The ligand spectrum contains dioxane as an additional internal standard.

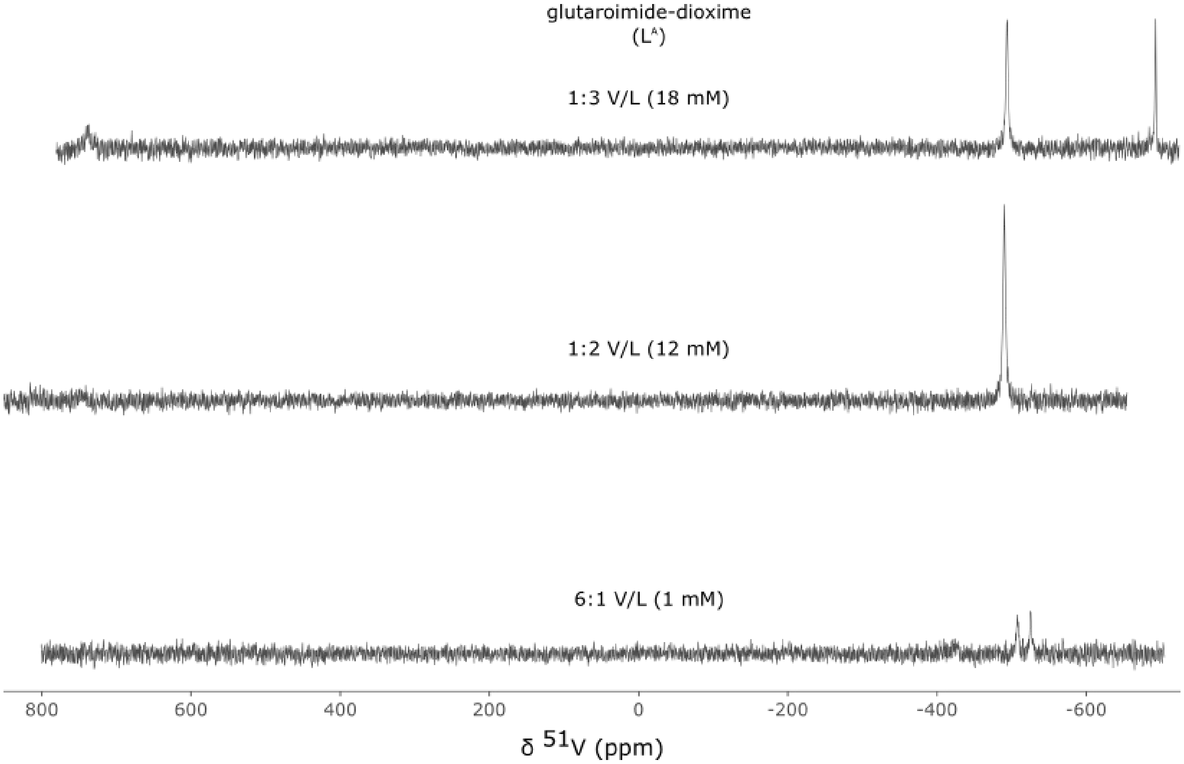

Figure S5: ^{51}V NMR spectra of $\mathbf{L^A}$ – V(IV) mixtures. Complex **1** is the signal at +740 ppm, complex **2** is at -460 ppm, and other signals are vanadates.

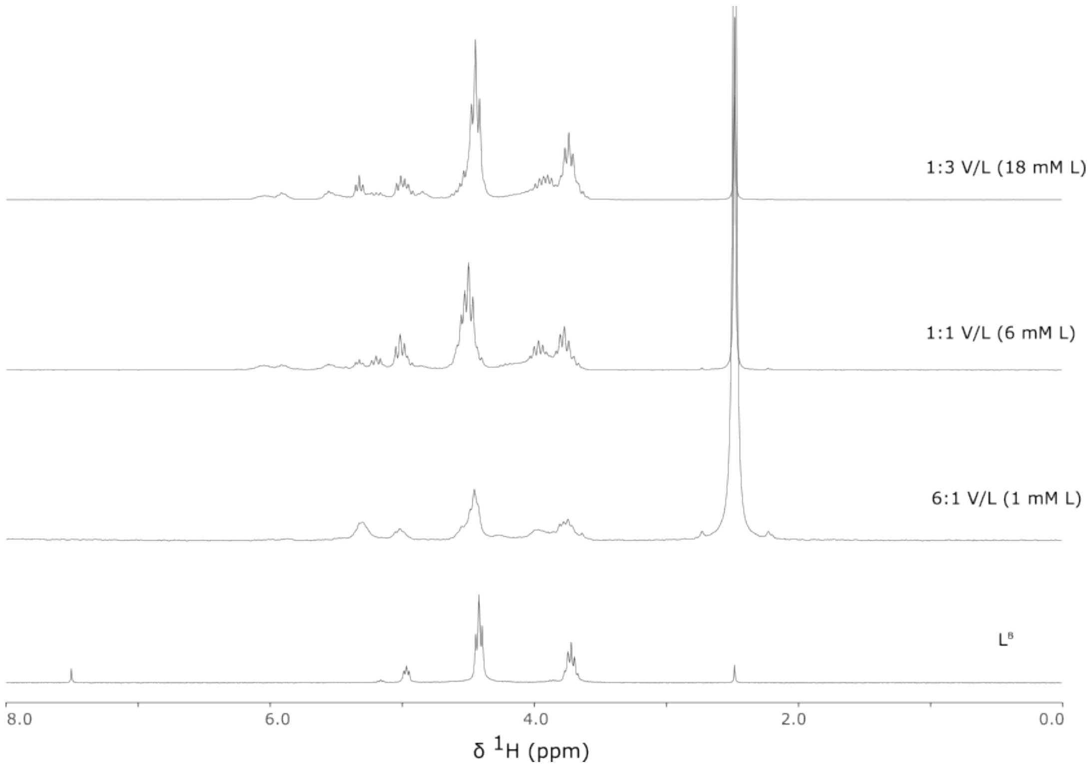

Figure S6: ^{1}H NMR spectra of $\mathbf{L^B}$ – V(IV) mixtures

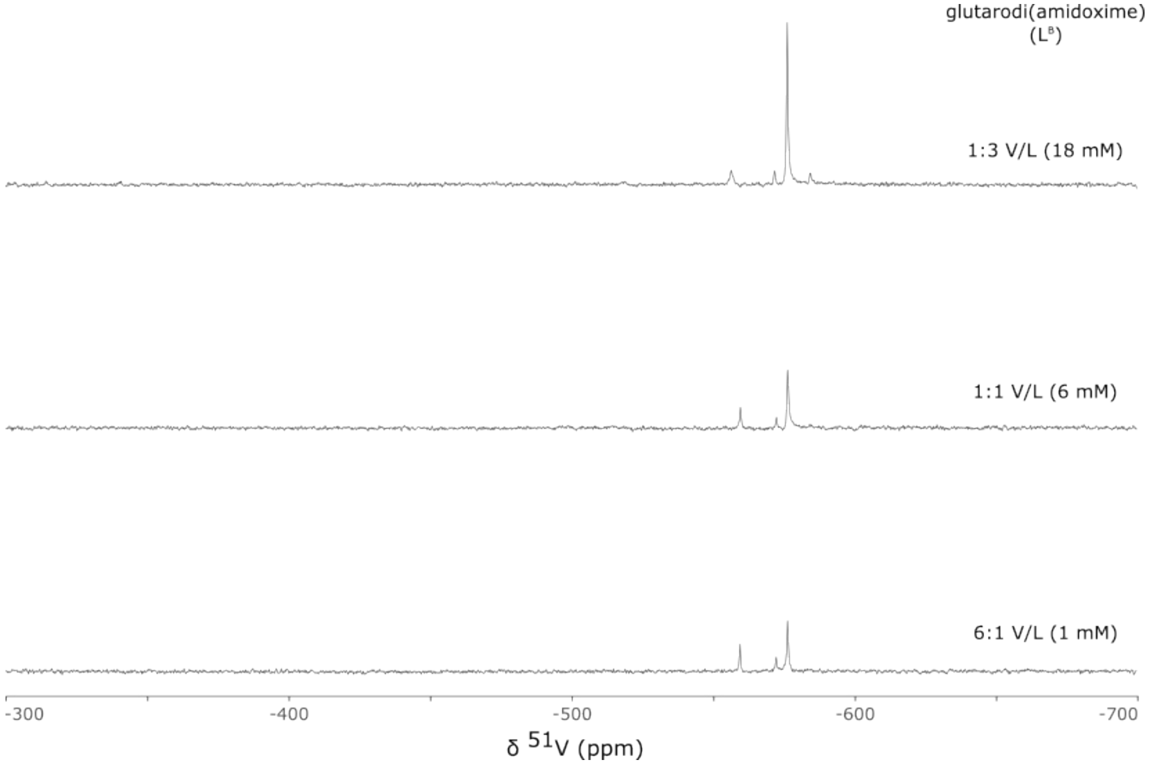

Figure S7: ^{51}V NMR spectra of $\mathbf{L^B}$ – V(IV) mixtures

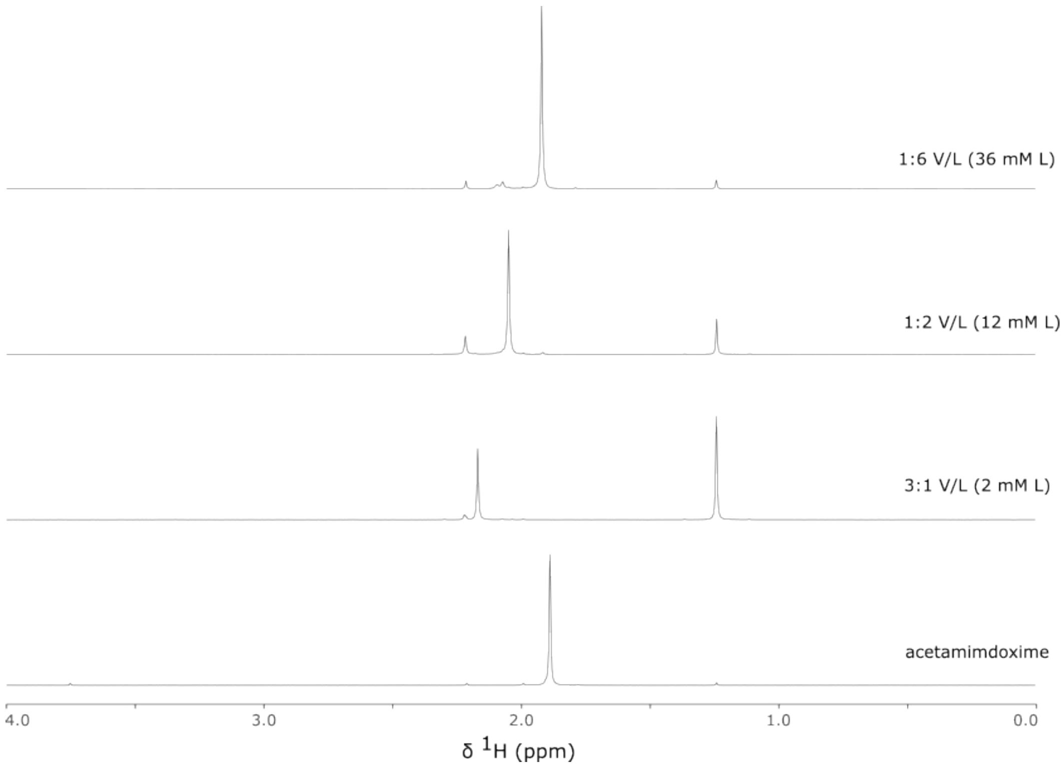

Figure S8: ^{1}H NMR spectra of acetamidoxime – V(IV) mixtures.

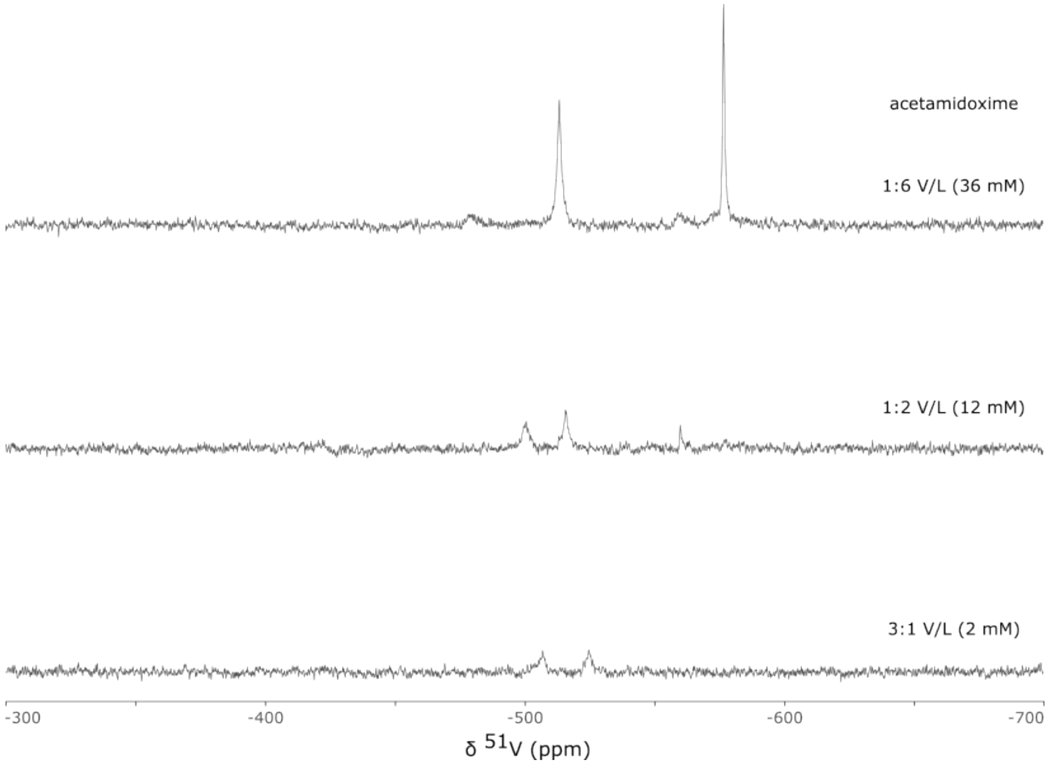

Figure S9: ^{51}V NMR spectra of acetamidoxime – V(IV) mixtures. All signals correspond to known V(V) vanadate species.

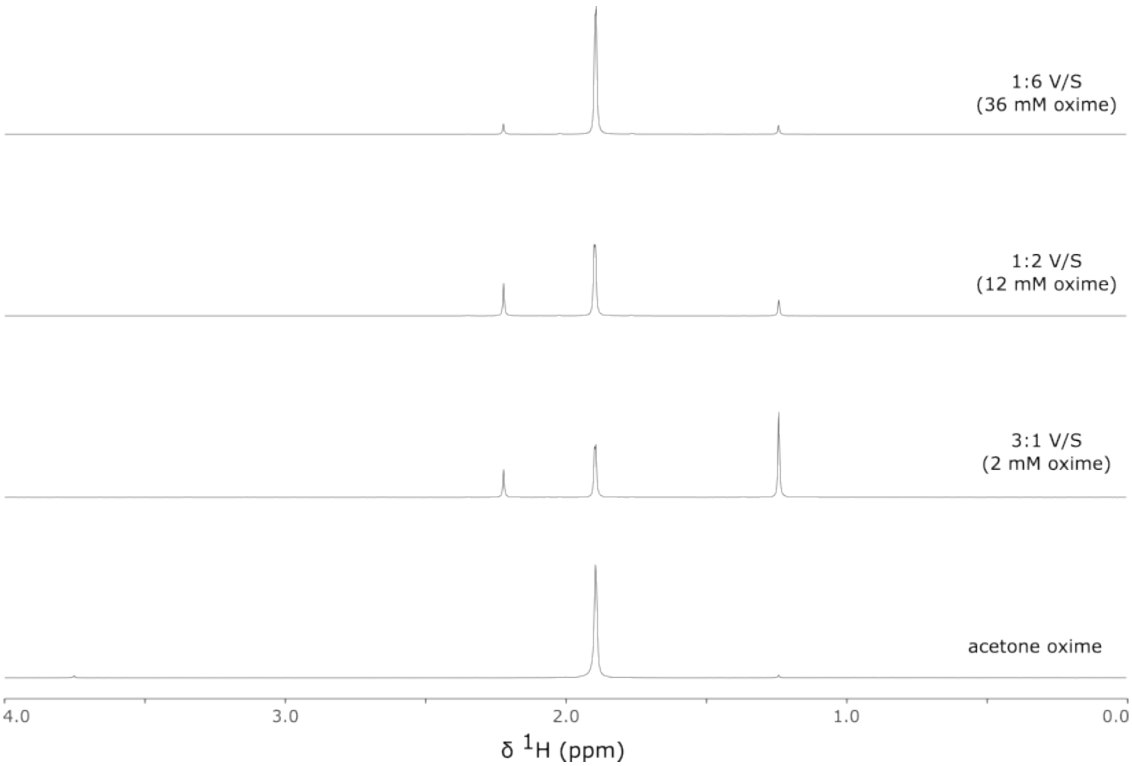

Figure S10: ^{1}H NMR spectra of acetone oxime – V(IV) mixtures. Only acetone and acetone oxime are observed.

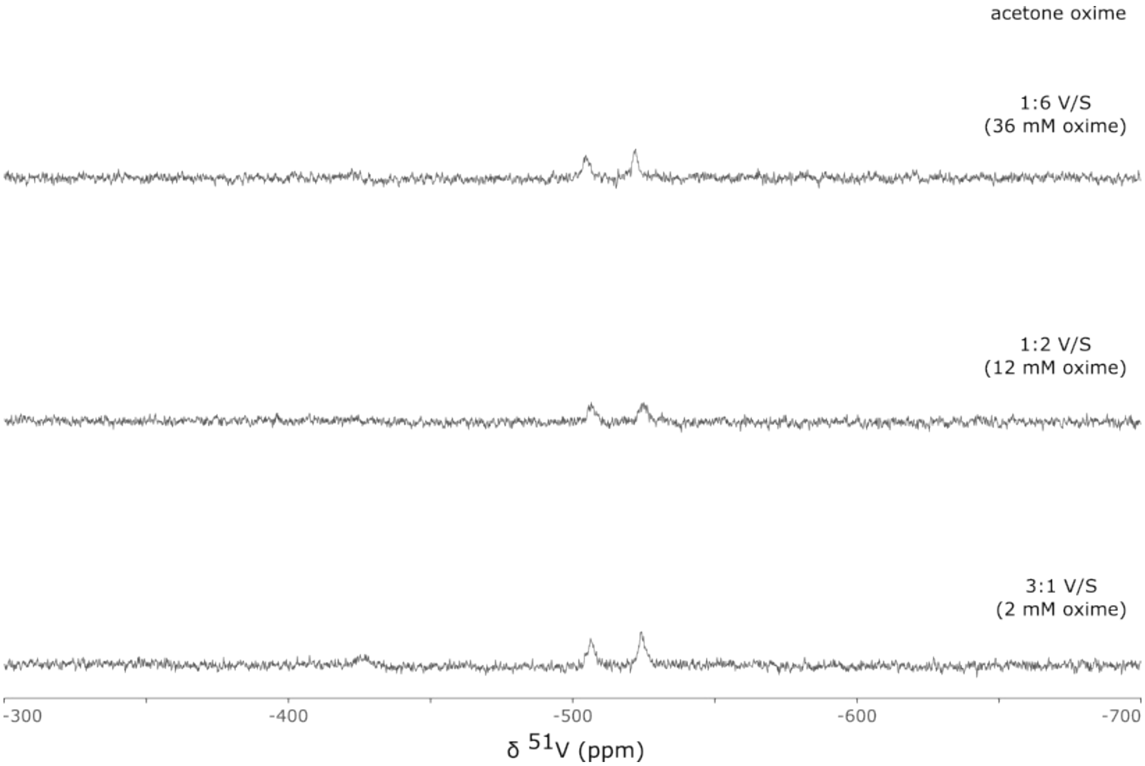

Figure S11: ^{51}V NMR spectra of acetone oxime – V(IV) mixtures. All signals correspond to known V(V) vanadate species.

Formation of vanadium dioxide colloid

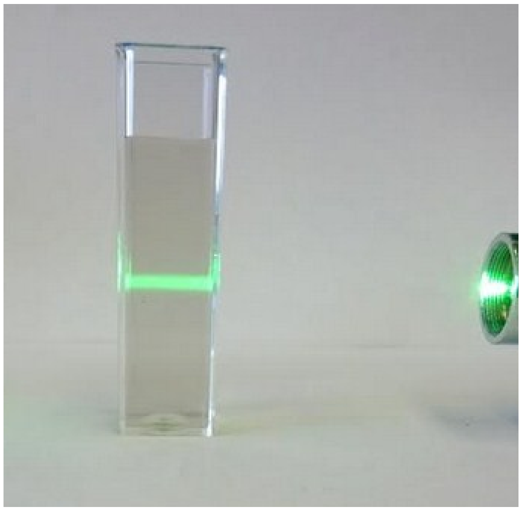

Image S1: Tyndall effect observed in V(IV) – acetone oxime reactions, forming colloidal VO_2

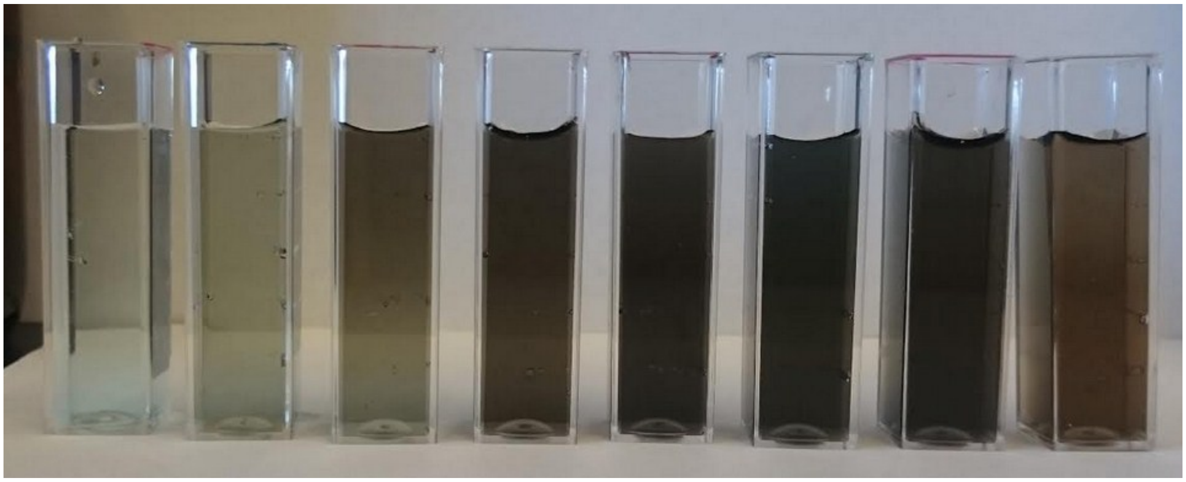

Image S2: Reaction appearance dependent on added base. 0.5 equivalents additional base added (with respect to V) from left to right; 0.5 eq. to 4.0 eq. Excess acetone oxime is present as the substrate. The dark color is due to colloidal VO_2.

Crystallography

X-ray structural determination was performed on a Bruker APEX diffractometer with a Bruker fixed-Chi 3-Circle goniometer, a Bruker SMART APEX II CCD detector, and a monochromatized fine-focus sealed Mo-kα X-ray source. A crystal was coated with paratone oil and mounted in a Kaptan loop, which was mounted on the goniometer with a nitrogen cryostream held at a temperature of 100 ± 0.5 K. Crystallography data was processed in the WinGX software package, solved using the SHELXTL software package and refined with the SHELXL software package, with semiempirical absorption correction with SADABS, included in SHELXTL.[1] All non-hydrogen and non-solvent atoms were refined anisotropically, and non-solvent hydrogens were placed using a riding model. Solvent oxygen atoms were refined isotropically and solvent hydrogens were not located. Details of crystallographic data are below in Table S1.

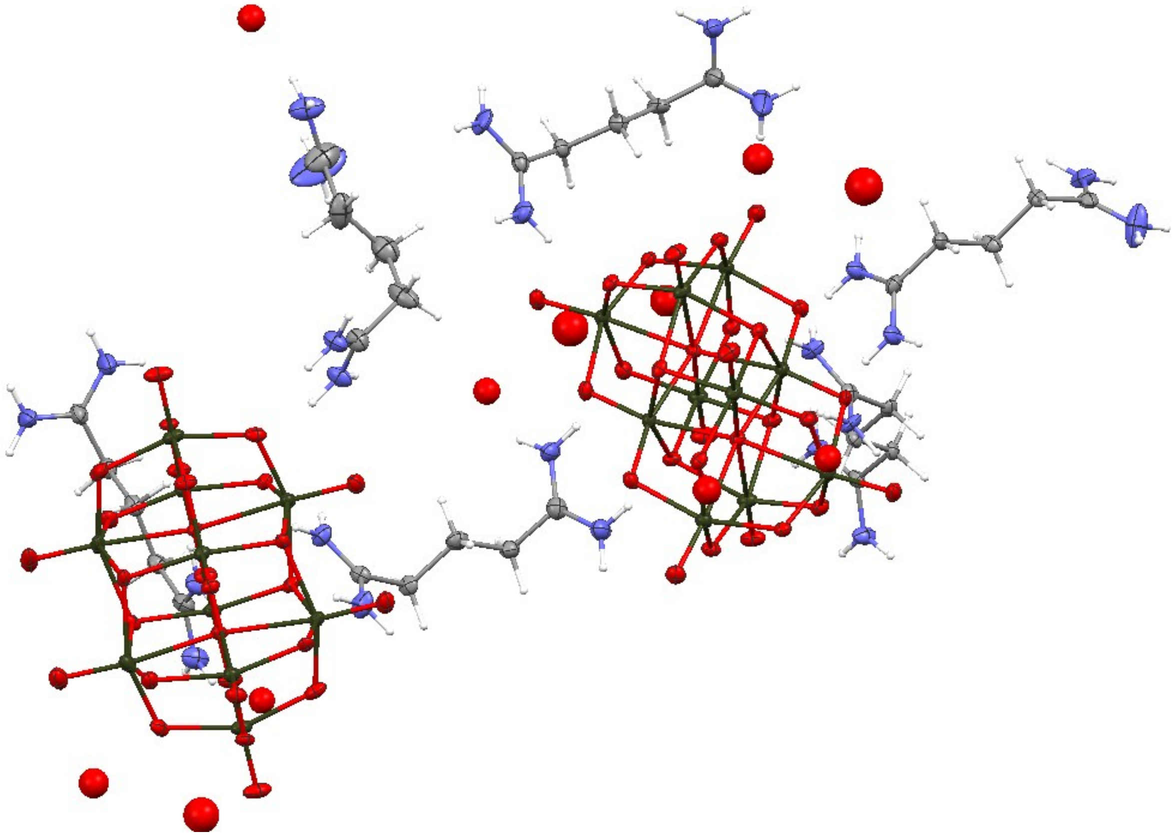

Figure S12: Crystal structure of glutaramidinium decavanadate ($[(H_2N)_2C(CH_2)_3C(NH_2)_2]_6[V_{10}O_{28}]_2{\cdot}11H_2O$).

Table S1: Crystallographic data for glutaramidinium decavanadate

Formula	$C_{40}H_{106}N_{24}O_{67}V_{20}$
Formula weight (g·mol^{-1})	2894.11
Space group	$Pna2_1$
a (Å)	18.6232(16)
b (Å)	37.606(3)
c (Å)	13.3441(11)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	9345.6(14)
Z	4
ρ_{calc} (g·cm^{-3})	2.057
μ (mm^{-1})	2.014
Crystal size (mm×mm×mm)	0.15×0.15×0.05
Crystal color and form	brown block
R1 ($I > 2\sigma(I)$)	0.0390
wR2 ($I > 2\sigma(I)$)	0.0952
R1 (all data)	0.0427
wR2 (all data)	0.0974
GoF	1.028
Largest difference peak/hole (e·Å^3)	1.303 / -0.655