

Conversion of NO_x^{1-} ($x = 2, 3$) to NO using an oxygen-deficient polyoxovanadate-alkoxide cluster

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Experimental Details

General Considerations. All manipulations were carried out in the absence of water and dioxygen using standard Schlenk techniques, or in a UniLab MBraun inert atmosphere drybox under a dinitrogen atmosphere except where specified otherwise. All glassware was oven-dried for a minimum of 3 hours and cooled in an evacuated antechamber prior to use in the drybox. All solvents were dried and deoxygenated on a Glass Contour System (Pure Process Technology, LLC) and stored over activated 3 Å molecular sieves purchased from Fisher Scientific prior to use. $[\text{Bu}_4\text{N}][\text{V}_6\text{O}_6(\text{OCH}_3)_{12}] (\text{V}_6\text{O}_6^{1-})$,¹ $[\text{Bu}_4\text{N}]_2[\text{V}_6\text{O}_7(\text{OCH}_3)_{12}] (\text{V}_6\text{O}_7^{2-})$,² and $[\text{Bu}_4\text{N}][\text{V}_6\text{O}_7(\text{OCH}_3)_{12}] (\text{V}_6\text{O}_7^{1-})$ ² were prepared according to previously published procedures. Tetrabutylammonium nitrite and tetrabutylammonium nitrate were purchased from Sigma Aldrich and stored in the drybox over P_2O_5 . 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine cobalt(II) (CoTPP) was purchased from Sigma Aldrich and used as received.

All ^1H NMR spectra were recorded at 400 MHz 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 H signal in deuterated solvents. CD_3CN was purchased from Cambridge Isotope Laboratories, degassed by three freeze–pump–thaw cycles, and stored in the drybox 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 are reported in wavenumbers (cm^{-1}). Electronic absorption measurements were recorded at room temperature in anhydrous acetonitrile or dichloromethane in a sealed 1 cm quartz cuvette with an Agilent Cary 60 UV-Vis spectrophotometer. Cyclic voltammetry experiments were recorded with a Bio-Logic SP200 potentiostat/galvanostat and the EC-Lab software suite. All measurements were performed in a three electrode system cell configuration that consisted of a glassy-carbon ($\phi = 3.0$ mm) as working electrode (CH Instruments, USA), a Pt wire as the counter electrode (CH Instruments, USA), and an Ag/Ag^+ non-aqueous reference electrode with 0.01 M AgNO_3 in 0.05 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ in acetonitrile (BASi, USA). All electrochemical measurements were performed at room temperature in a N_2 -filled drybox. Anhydrous acetonitrile that contained $[\text{Bu}_4\text{N}][\text{PF}_6]$ was used as the electrolyte solution.

Nitrite reduction with $\text{V}_6\text{O}_6^{1-}$. In a glovebox, a 20 mL scintillation vial was charged with $\text{V}_6\text{O}_6^{1-}$ (0.026 g, 0.026 mmol) and 6 mL tetrahydrofuran. $[\text{Bu}_4\text{N}]\text{NO}_2$ (0.008 g, 0.027 mmol, 1 equiv) was added to the solution as a solid. The reaction mixture was stirred for 24 hours at 21 °C, after which the product was filtered and the blue/grey solid was collected. The solid was washed with tetrahydrofuran (4 x 2 mL) and dichloromethane (4x 2mL) and then extracted with acetonitrile until the filtrate was colorless. The volatiles were removed under vacuum to yield $\text{V}_6\text{O}_7^{2-}$ (0.021 g, 0.016 mmol, 62%). Analytical data obtained for complex $\text{V}_6\text{O}_7^{2-}$ via standard characterization techniques match that obtained from previously reported synthesis.^{2,3}

Nitrate reduction with $\text{V}_6\text{O}_6^{1-}$, stoichiometric: In a glovebox, a 15 mL pressure vessel was charged with $[\text{Bu}_4\text{N}][\text{V}_6\text{O}_6(\text{OCH}_3)_{12}] (\text{V}_6\text{O}_6^{1-})$ (0.049 g, 0.048 mmol) and 6 mL tetrahydrofuran. $[\text{Bu}_4\text{N}]\text{NO}_3$ (0.015 g, 0.051 mmol, 1 equiv) was added to the pressure vessel as a solid, and the reaction vessel was sealed, removed from the glovebox, and placed in an oil bath and set to stir for 24 hours at 70 °C. After this time, the reaction vessel was brought back into the glovebox and the reaction was filtered to give a grey solid and green filtrate. Analytical data on crude reaction mixture by UV-Vis and CV revealed the product was a mixture of $\text{V}_6\text{O}_7^{2-}$ and $\text{V}_6\text{O}_7^{1-}$.

Nitrate reduction with $\text{V}_6\text{O}_6^{1-}$, sub-stoichiometric: In a glovebox, a 15 mL pressure vessel was charged with $[\text{Bu}_4\text{N}][\text{V}_6\text{O}_6(\text{OCH}_3)_{12}] (\text{V}_6\text{O}_6^{1-})$ (0.036 g, 0.035 mmol) and 6 mL tetrahydrofuran. $[\text{Bu}_4\text{N}]\text{NO}_3$ (0.005 g, 0.018 mmol, 0.5 equiv) was added to the pressure vessel as a solid, and the reaction vessel was sealed, removed from the glovebox, and placed in an oil bath and set to stir for 24 hours at 70 °C. After this time, the reaction vessel was brought back into the glovebox and the reaction was filtered to give a grey solid and green filtrate. Analytical data on crude reaction mixture by UV-Vis and CV revealed the product was a mixture of $\text{V}_6\text{O}_7^{2-}$ and $\text{V}_6\text{O}_7^{1-}$.

Capture of nitric oxide by CoTPP

To probe whether nitric oxide was produced in nitrite and nitrate reduction with $V_6O_6^{1-}$, 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine cobalt(II) (CoTPP) was added to the reaction mixture. CoTPP, a NO complexation agent, exhibits a highly characteristic shift in position of the absorption band ($\lambda_{\text{CoTPP,initial}} = 528$ nm in dichloromethane) following NO coordination.⁴⁻⁷ A calibration curve, collected in dichloromethane by Symes and coworkers, was used to qualitatively measure the amount of NO-ligated CoTPP formed.⁴

¹H NMR measurements were taken in two solvents, CD₃CN and CDCl₃. The ¹H NMR spectra in CDCl₃ was used to further assess (NO)CoTPP formation via the growth of new resonances at 8.91, 8.17, and 7.74 ppm, which match the previously reported spectra for the NO-ligated CoTPP complex.⁷ The insolubility of the (NO) CoTPP complex in CD₃CN afforded a spectra of solely the cluster-containing product following NO_x¹⁻ reduction.

Control experiments: Four 20 mL scintillation vials were charged with (1) CoTPP and $V_6O_6^{1-}$, (2) CoTPP and $V_6O_7^{2-}$, (3) CoTPP and [¹⁸Bu₄N]NO₂, (4) CoTPP and [¹⁸Bu₄N]NO₃, each in 6 mL tetrahydrofuran. The reactions mixtures were stirred for 24 hours at 50 °C, after which 0.01 mL was removed and diluted with 10 mL anhydrous dichloromethane. Electronic absorbance spectroscopy was used to measure the initial absorbance band of CoTPP and that of each reaction mixture (Figure S3).

Nitric oxide trapping via CoTPP for nitrite reduction: In a glovebox, a 20 mL scintillation vial was charged with $V_6O_6^{1-}$ (0.031 g, 0.031 mmol) and 6 mL tetrahydrofuran. CoTPP (0.009 g, 0.031 mmol, 1 equiv) was added to the solution as a solid. [¹⁸Bu₄N]NO₂ (0.009 g, 0.031 mmol, 1 equiv) was added to the solution as a solid. The reaction mixture was stirred for 24 hours at 21 °C, after which 0.01 mL was removed from the reaction mixture and diluted with 10 mL anhydrous dichloromethane. Electronic absorbance spectroscopy was used to measure the shift in wavelength following NO complexation to CoTPP ($\lambda_{\text{CoTPP,initial}} = 528$ nm in dichloromethane). ¹H NMR (400 MHz, CDCl₃) $\delta = 15.93$ (fwhh = 144 Hz), 13.12 (fwhh = 116 Hz), 9.94-9.75, 8.91 (fwhh = 68 Hz), 8.17 (fwhh = 56 Hz), 7.74 (fwhh = 96 Hz) ppm. ¹H NMR (400 MHz, CD₃CN) $\delta = 23.58$ (fwhh = 564 Hz), 3.09, 1.59, 1.36, 0.98 ppm. UV-Vis (CH₂Cl₂): 538 nm.

Nitric oxide trapping via CoTPP for nitrate reduction: In a glovebox, a 20 mL scintillation vial was charged with $V_6O_6^{1-}$ (0.035 g, 0.051 mmol) and 6 mL tetrahydrofuran. CoTPP (0.023 g, 0.035 mmol, 1 equiv) was added to the solution as a solid. [¹⁸Bu₄N]NO₃ (0.006 g, 0.019 mmol, 0.5 equiv) was added to the pressure vessel as a solid, and the reaction vessel was sealed, removed from the glovebox, and placed in an oil bath and set to stir for 24 hours at 70 °C. After this time, the reaction vessel was brought back into the glovebox and 0.01 mL was removed from the reaction mixture and diluted with 10 mL anhydrous dichloromethane. Electronic absorbance spectroscopy was used to measure the shift in wavelength following NO complexation to CoTPP ($\lambda_{\text{CoTPP,initial}} = 528$ nm in dichloromethane). ¹H NMR (400 MHz, CDCl₃) $\delta = 15.96$ (fwhh = 104 Hz), 13.15 (fwhh = 100 Hz), 9.95-9.74, 8.91 (fwhh = 56 Hz), 8.17 (fwhh = 68 Hz), 7.74 (fwhh = 52 Hz) ppm. ¹H NMR (400 MHz, CD₃CN) $\delta = 23.51$ (fwhh = 468 Hz), 3.23, 1.74, 1.49, 1.11 ppm. UV-Vis (CH₂Cl₂): 534 nm. Note: this procedure was repeated using stoichiometric amounts of nitrate which resulted in the same shift in the electronic absorption spectra to 534 nm in dichloromethane.

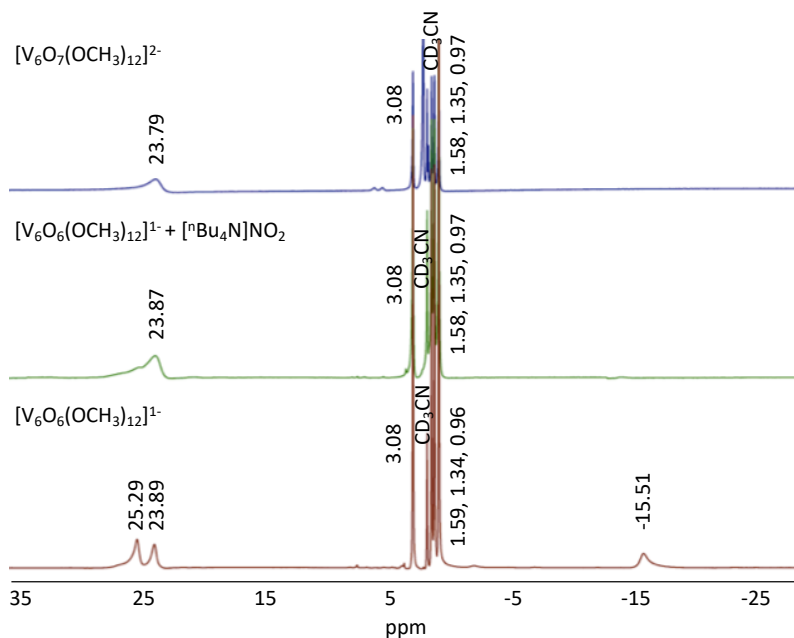


Figure S1. ^1H NMR spectra of $\text{V}_6\text{O}_6^{1-}$ (bottom, red), $\text{V}_6\text{O}_6^{1-} + [\text{nBu}_4\text{N}]\text{NO}_2$ after stirring at 21 °C for 24 hours (middle, green), and $\text{V}_6\text{O}_7^{2-}$ (top, blue, CD_3CN).

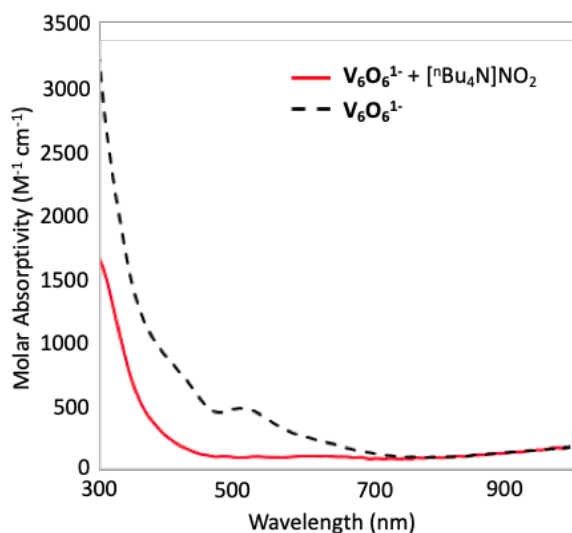


Figure S2. Electronic absorption spectra of $\text{V}_6\text{O}_6^{1-}$ (black) and $\text{V}_6\text{O}_6^{1-} + [\text{nBu}_4\text{N}]\text{NO}_2$ after stirring at 21 °C for 24 hours (red). The spectra of the cluster reacted with NO_2^{1-} shows no intervalence charge transfer bands, suggesting formation of an isovalent POV-alkoxide cluster, $[\text{V}^{\text{IV}}_6\text{O}_7(\text{OCH}_3)_{12}]^{2-}$.

Author's Note (explanation of the data presented for $\text{V}_6\text{O}_6^{1-}$): While complex $\text{V}_6\text{O}_6^{1-}$ is a mixed-valent species (ox. state distrib: $\text{V}^{\text{III}}\text{V}^{\text{IV}}_5$), this cluster does not possess intervalence charge transfer (IVCT) bands given limited electronic communication between the site differentiated V^{III} ion and the remainder of the vanadium-oxide scaffold. Given that the vanadium ion that differs in oxidation state is valence trapped, we would not expect to see IVCT bands in this spectrum. Indeed, the only feature observed in the spectrum of $\text{V}_6\text{O}_6^{1-}$ is a weak band at 526 nm, assigned to ligand field transitions for the charge-localized V^{IV} ions. For more information on the electronic absorption spectrum of $\text{V}_6\text{O}_6^{1-}$, please refer to the original report (*J. Am. Chem. Soc.* 2018, **140**, 8424-8428)

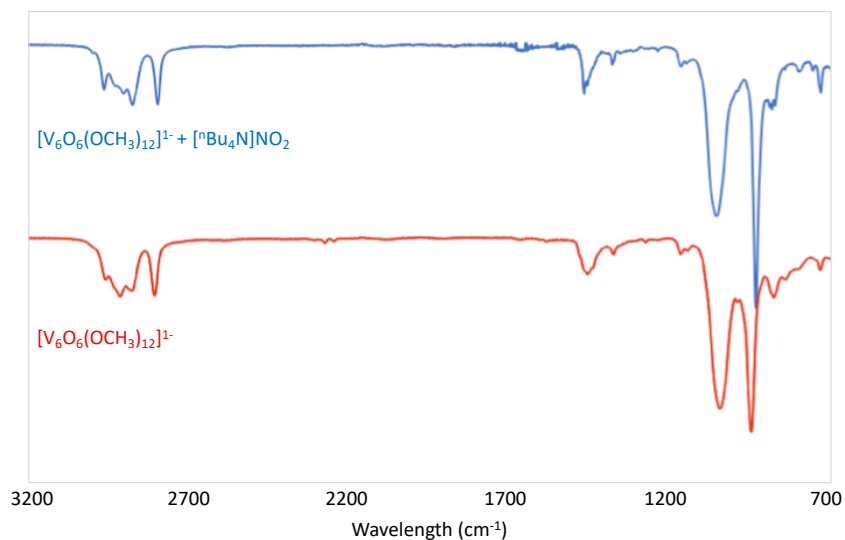


Figure S3. Infrared spectra of $V_6O_6^{1-}$ (bottom, red) and $V_6O_6^{1-} + [^nBu_4N]NO_2$ after stirring at 21 °C for 24 hours (top, blue, CD_3CN).

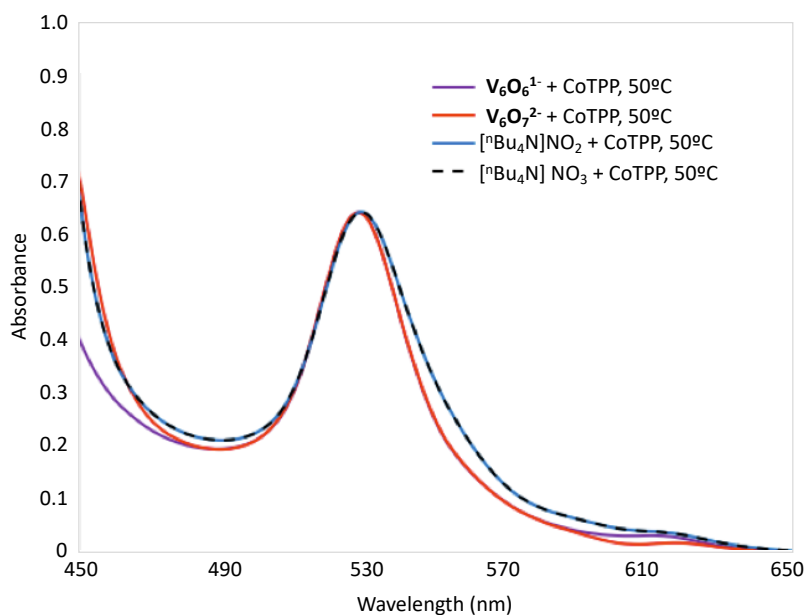


Figure S4. Electronic absorption spectra of CoTPP control experiments including reactions with $V_6O_6^{1-}$ (purple), $V_6O_7^{2-}$ (red), $[^nBu_4N]NO_2$ (blue), and $[^nBu_4N]NO_3$ (black, dotted). Reagents were allowed to stir in THF at 50°C for 24 hours. Electronic absorption spectra taken in dichloromethane.

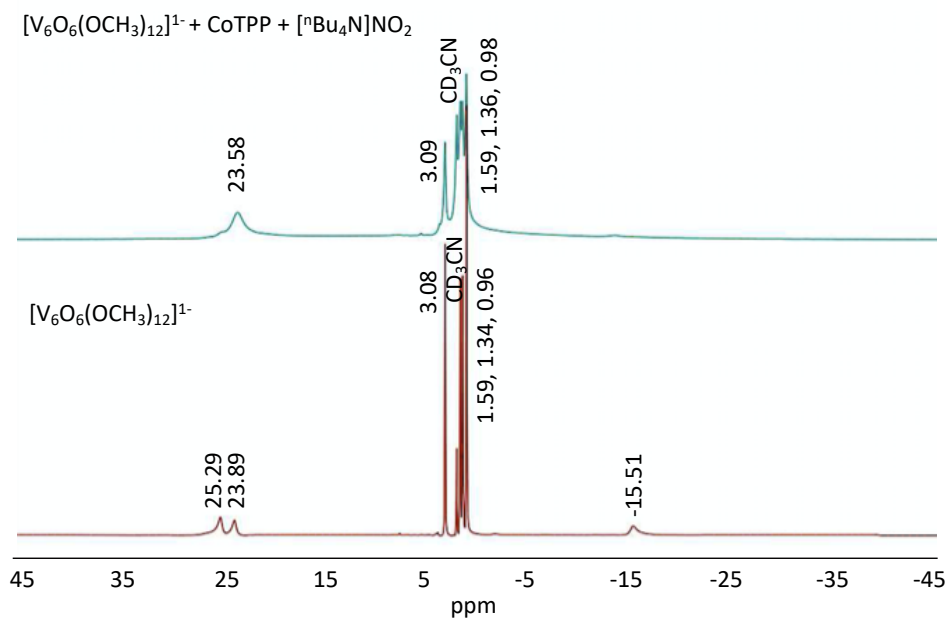


Figure S5. Paramagnetic region of the ^1H NMR spectra of $\text{V}_6\text{O}_6^{1-} + [\text{nBu}_4\text{N}]\text{NO}_2 + \text{CoTPP}$ after stirring at 21 °C for 24 hours (CD_3CN).

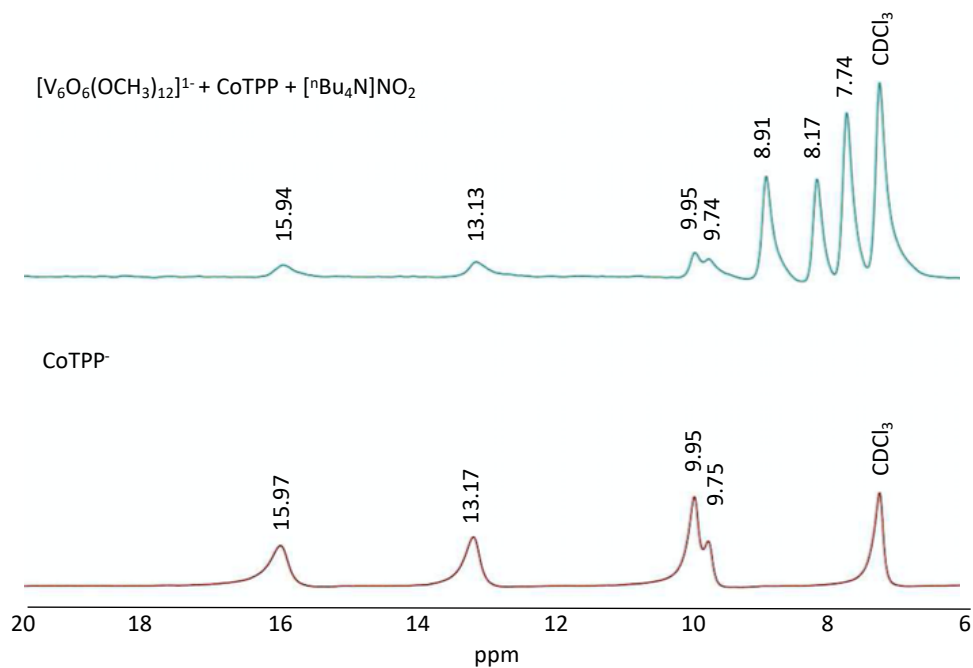


Figure S6. Diamagnetic region of the ^1H NMR spectra of $\text{V}_6\text{O}_6^{1-} + [\text{nBu}_4\text{N}]\text{NO}_2 + \text{CoTPP}$ after stirring at 21 °C for 24 hours (CDCl_3).

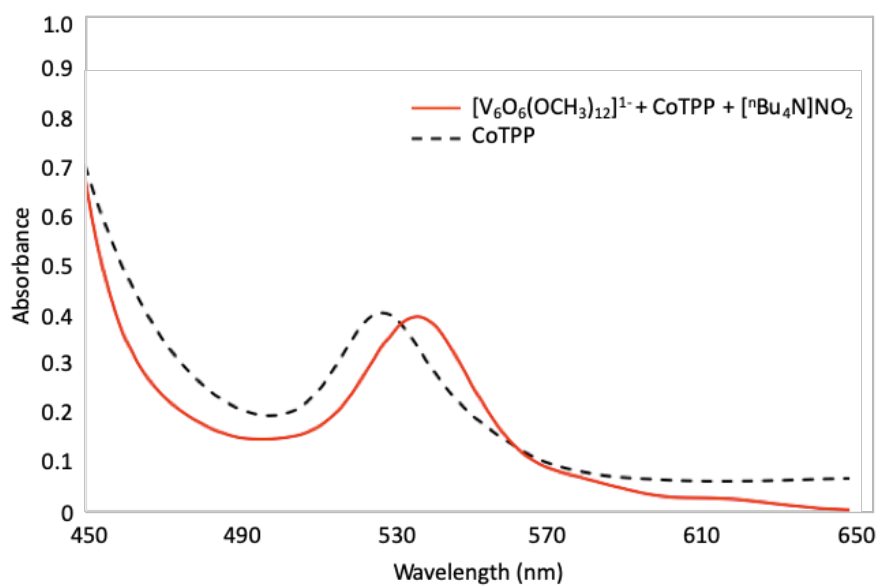


Figure S7. Electronic absorption spectra of $V_6O_6^{1-}$ + $[nBu_4N]NO_2$ + CoTPP after stirring at 21 °C for 24 hours taken in dichloromethane.

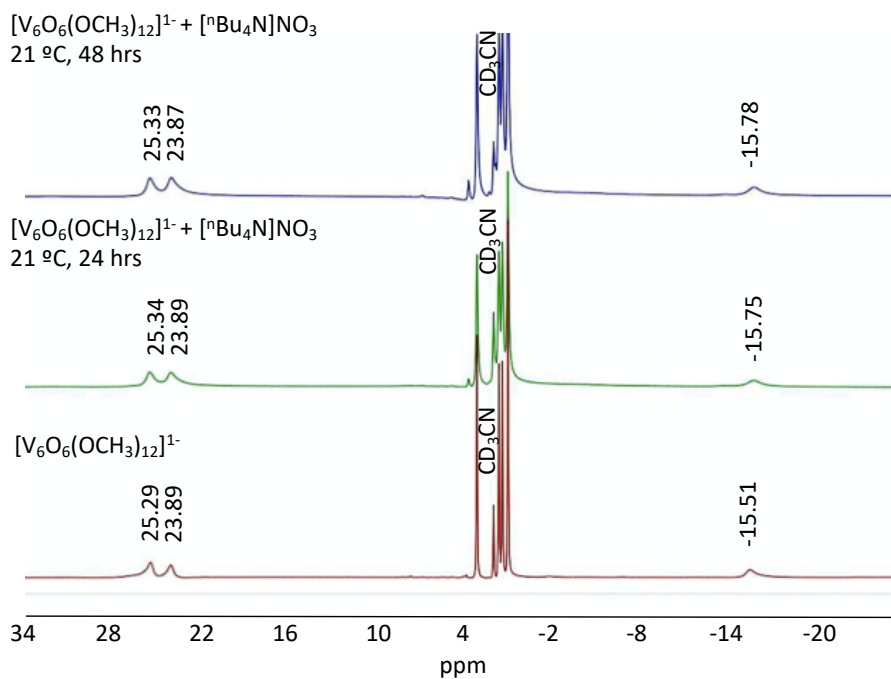


Figure S8. 1H NMR spectra of $V_6O_6^{1-}$ + $[nBu_4N]NO_3$ after stirring at 21 °C for 48 hours (CD_3CN).

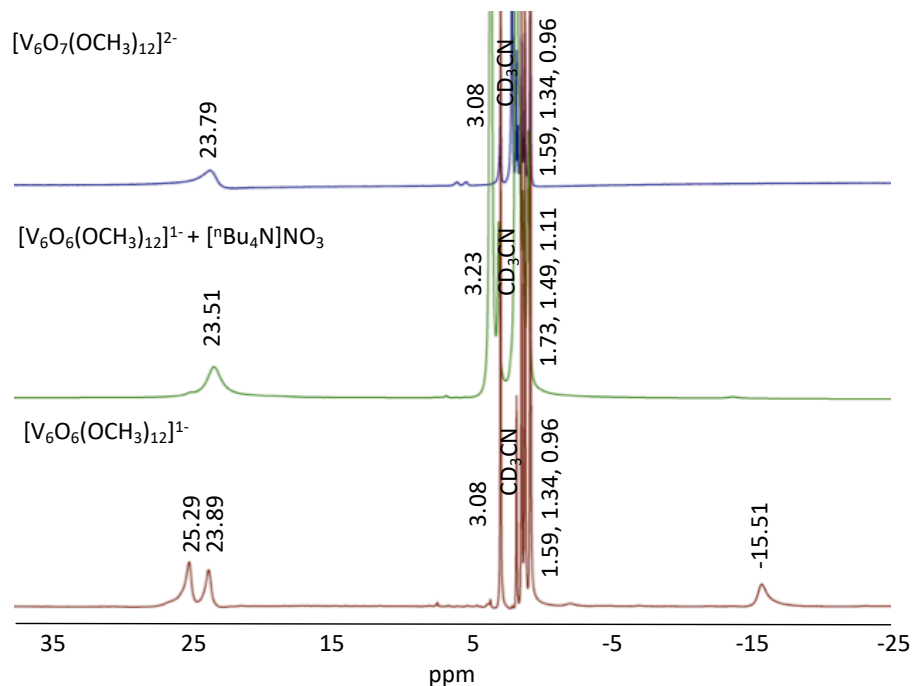


Figure S9. ^1H NMR spectra of $\text{V}_6\text{O}_6^{1-}$ (bottom, red), $\text{V}_6\text{O}_6^{1-} + [\text{nBu}_4\text{N}]\text{NO}_3$ after stirring at $70\text{ }^\circ\text{C}$ for 24 hours (middle, green), and $\text{V}_6\text{O}_7^{2-}$ (top, blue, CD_3CN).

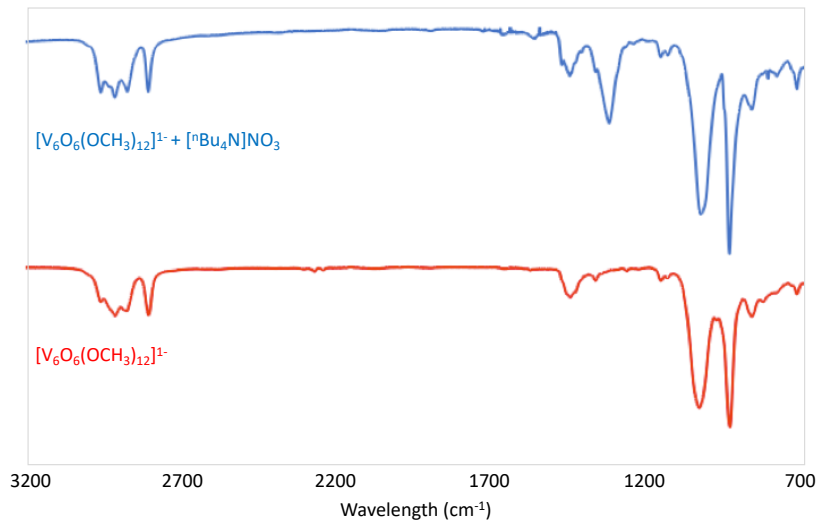


Figure S10. Infrared spectra of $\text{V}_6\text{O}_6^{1-}$ (bottom, red) and $\text{V}_6\text{O}_6^{1-} + [\text{nBu}_4\text{N}]\text{NO}_3$ after stirring at $70\text{ }^\circ\text{C}$ for 24 hours (top, blue).

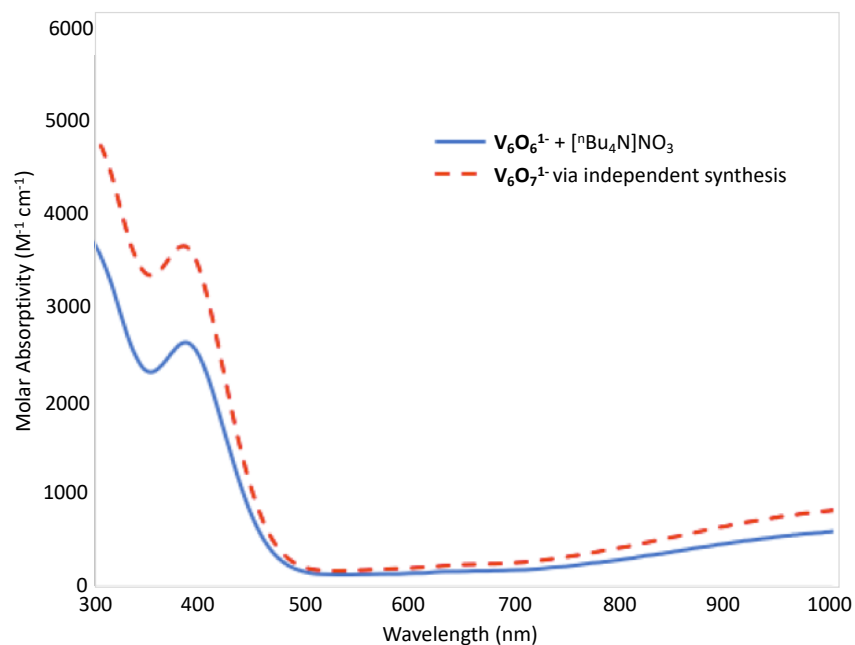


Figure S11. Comparison of the electronic absorption spectrum of the product of V₆O₆¹⁻ + [nBu₄N]NO₃ (blue) and V₆O₇²⁻ isolated via independent solvothermal synthesis (red, dotted), collected in acetonitrile.

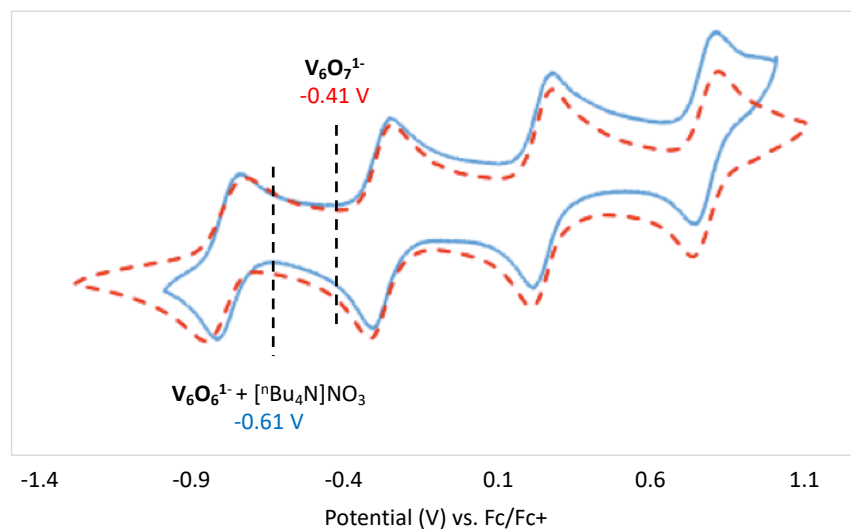


Figure S12. Comparison of the cyclic voltammograms of the product of V₆O₆¹⁻ + [nBu₄N]NO₃ (blue) and V₆O₇²⁻ isolated via independent solvothermal synthesis (red, dotted), collected in acetonitrile.

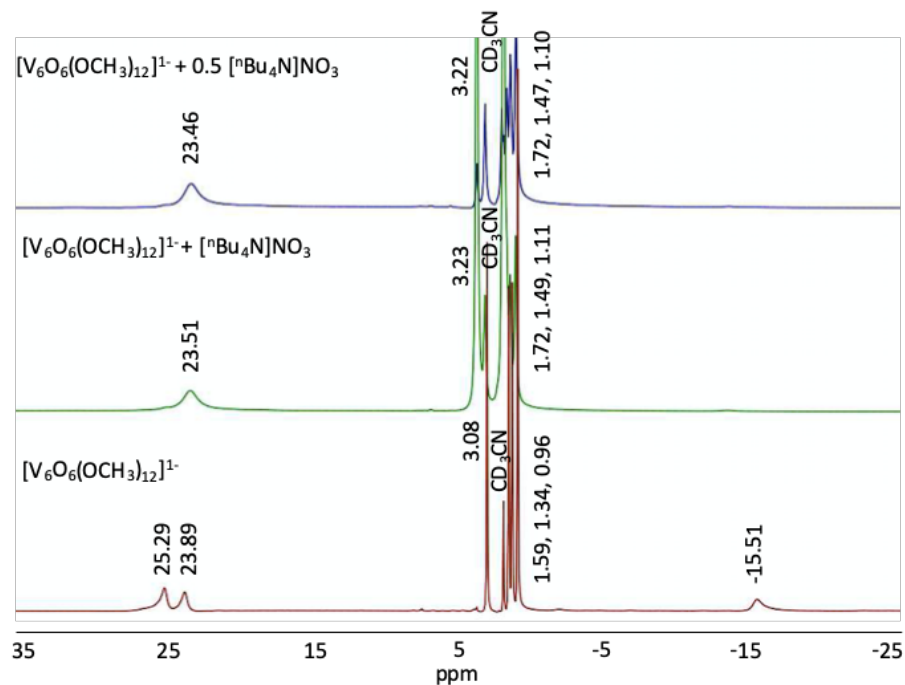


Figure S13. Comparison of the ^1H NMR spectra of $\text{V}_6\text{O}_6^{1-}$ (bottom, red) and the stoichiometric (middle, green) and sub-stoichiometric (top, blue) nitrate reduction reactions after stirring at 70°C for 24 hours (CD_3CN).

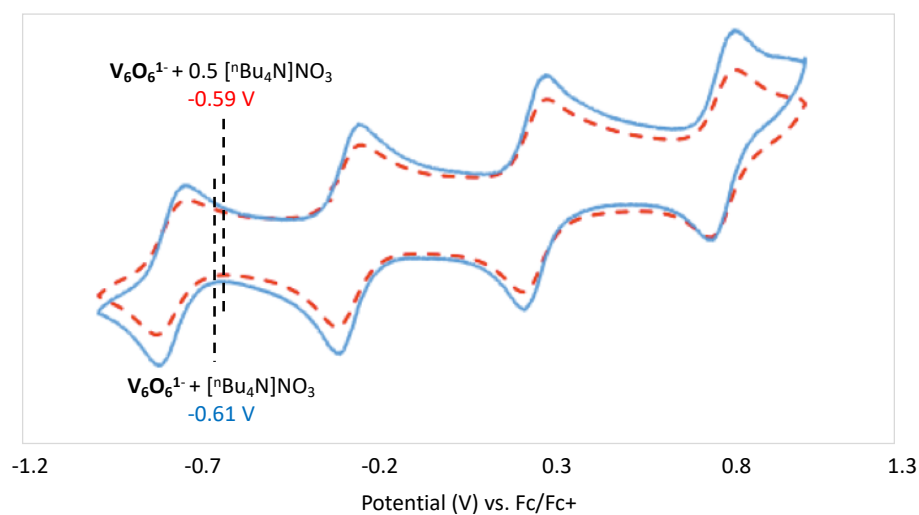


Figure S14. Comparison of the cyclic voltammograms of the stoichiometric (blue) and sub-stoichiometric (red) nitrate reduction reactions, collected in acetonitrile.

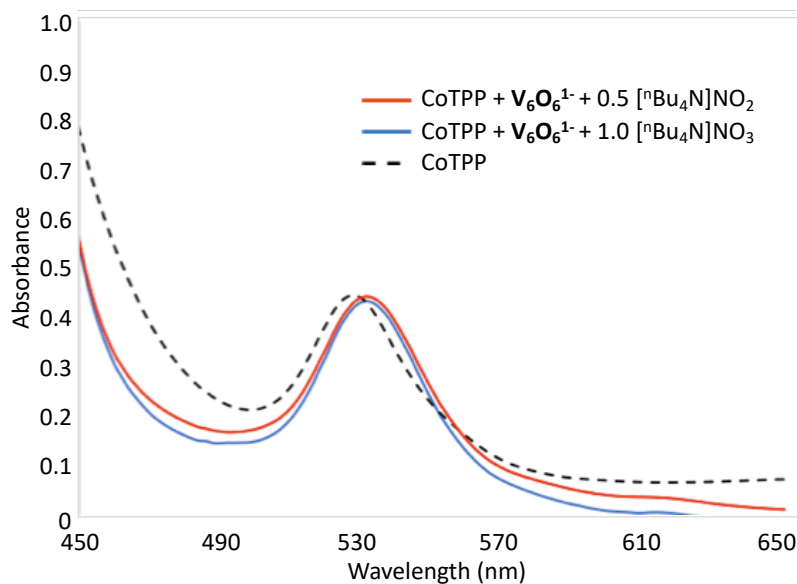


Figure S15. Electronic absorption spectra comparing CoTPP (black, dotted) and the reaction of substoichiometric (red) and stoichiometric (blue) equivalents of $[\text{nBu}_4\text{N}]\text{NO}_3$, $\text{V}_6\text{O}_6^{1-}$, and CoTPP after stirring at 70 °C for 24 hours. Spectra collected in dichloromethane.

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