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We report the activation of nitrogen-containing oxyanions using an oxygen-deficient polyoxovanadate–alkoxide cluster. Reduction of NO_2^{1-} and NO_3^{1-} results in near-quantitative oxygen atom transfer to the coordinatively unsaturated V^{III} ion, and selective formation of NO. These results provide insight into possible mechanisms of oxyanion reduction by polyoxometalates.

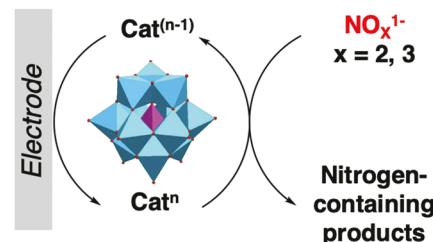
The conversion of nitrogen-containing oxyanions (e.g., NO_2^{1-} and NO_3^{1-}) to nitric oxide (NO) is an important process in the denitrification phase of the nitrogen cycle.¹ In nature, the reduction of these environmental contaminants is mediated by metalloenzymes (reductases) that catalyse the one and two-electron reduction of nitrite (NO_2^{1-}) and nitrate (NO_3^{1-}), respectively. Similarly, homo- and heterogeneous metal-oxide architectures have been shown to mediate these chemical transformations.² However, despite extensive understanding of the mechanism of NO_x^{1-} activation with bio-relevant systems, little is known about the pathways by which metal-oxide clusters mediate the deoxygenation of these substrates.

A particularly active class of compounds for the electrochemical reduction of NO_2^{1-} and NO_3^{1-} are polyoxometalates (POMs; Fig. 1).³ Indeed, the reactivity of reduced variants of these assemblies with nitrogen-containing oxyanions (in particular, NO_x^{1-}), is so ubiquitous that researchers often include the electrochemical response of new POM architectures in the presence of these substrates to assess the general reactivity of their systems.^{3–7} However, from the perspective of a coordination chemist, it is not inherently obvious how the oxide-terminated surfaces of these clusters might mediate the deoxygenation reactions invoked for POMs. The oxide terminated surfaces of these clusters,

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

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Polyoxometalates: Well-precedented electrocatalysts for NO_x^{1-} reduction



This work: Insights into possible mechanisms by which metal-oxide clusters mediate NO_x^{1-} reduction

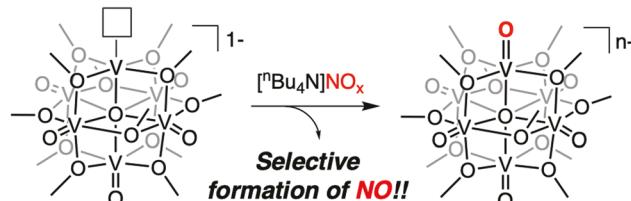


Fig. 1 Polyoxometalate clusters are well-established electrocatalysts for the reduction of NO_x^{1-} , however little is known about the mechanism by which these oxide-terminated surfaces mediate this transformation. Here, we present a surface-approach for probing possible reactive sites in these metal-oxide architectures.

composed of coordinatively saturated transition metal ions, leave little opportunities for inner-sphere reductive processes. To date, few reports have attempted to investigate the mechanism by which the reduction of NO_x^{1-} occurs in these systems, with exceptions relegated to heterometal-functionalized polyoxoanions, where substrate reduction occurs at the coordinatively unsaturated transition metal dopant.^{5,6,8,9}

In considering pathways by which this molecular transformation might occur, one can invoke a Mars Van-Krevelen type mechanism, where an oxygen-atom vacancy formed at the surface of a redox-active metal oxide generates an active site

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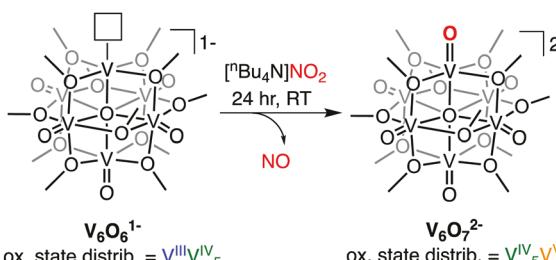
† Electronic supplementary information (ESI) available: ^1H NMR and infrared spectra of $\text{V}_6\text{O}_6^{1-}$ and $[\text{nBu}_4\text{N}]\text{NO}_2$ or $[\text{nBu}_4\text{N}]\text{NO}_3$, CoTPP control experiments, ^1H NMR and electronic absorption spectra of *in situ* nitrite and nitrate reduction with CoTPP, electronic absorption spectra and CV of $\text{V}_6\text{O}_6^{1-}$ *via* independent synthesis, ^1H NMR, electronic absorption, and CV spectra of substoichiometric nitrate reduction with $\text{V}_6\text{O}_6^{1-}$. See DOI: 10.1039/c9cc08230a

for reductive chemistries at the surface of a material.¹⁰ Indeed, the feasibility of this reaction as a step in NO_x^{1-} reduction by polyoxoanions is bolstered by independent studies from Launay¹¹ and Pope.¹² These studies cite the conversion of terminal oxido ligands at a face of a polyoxotungstate Keggin ion ($[\text{XW}_{12}\text{O}_{40}]^{n-}$) to datively bound aqua moieties under reducing conditions at low pH. The reactivity of the W^{IV} -aqua moieties, generated by the $6\text{e}^-/6\text{H}^+$ surface activation of the cluster, in organic solvent have demonstrated that these reduced entities are active toward oxygen atom transfer reactions (e.g., OAsR_3 , OSR_2 , ONPh).¹³ However, the stoichiometric reactivity of these reduced assemblies with nitrogen-containing oxyanions has not been studied.

Our laboratory has developed synthetic strategies for the isolation of oxygen-deficient, organofunctionalized polyoxovanadate assemblies.¹⁴ The polyoxovanadate-alkoxide (POV-alkoxide) clusters have many features similar to that of plenary POM motifs, however these complexes feature bridging alkoxide ligands that increase their solubility in organic solvents, providing handles for *in situ* analysis of reaction mixtures. Furthermore, reactivity in these systems is constrained to the terminal oxido moieties of the assembly.^{15,16} Our ability to generate and handle a cluster with a single oxygen atom vacancy at its surface prompted interest in understanding whether these reduced terminal positions in POMs might be active for the reduction of NO_x^{1-} .

To deepen our mechanistic understanding of the role of oxygen atom vacancies at the surface of POMs in the reduction of nitrogen-containing oxyanions, we opted to probe the reactivity of the previously reported, oxygen-deficient cluster, $[^n\text{Bu}_4\text{N}][\text{V}_6\text{O}_6(\text{OCH}_3)_{12}]$ ($\text{V}_6\text{O}_6^{1-}$), with NO_2^{1-} .¹⁴ We hypothesized that the one-electron reduction of NO_2^{1-} by the vanadium-oxide cluster would afford cleavage of an N–O bond, resulting in oxygen atom transfer from NO_2^{1-} to the reduced POV-alkoxide. This would lead to the release of NO, and formation of the dianionic, fully-oxygenated species, $[^n\text{Bu}_4\text{N}]_2[\text{V}_6\text{O}_7(\text{OCH}_3)_{12}]$ ($\text{V}_6\text{O}_7^{2-}$). Addition of one equivalent of tetrabutylammonium nitrite ($[^n\text{Bu}_4\text{N}][\text{NO}_2]$) in tetrahydrofuran (THF) resulted in a gradual colour change from brown/red to blue over the course of 24 h, consistent with cluster oxidation (Scheme 1). Analysis of the reaction mixture by ^1H NMR spectroscopy revealed formation of a fully-oxygenated POV-alkoxide cluster, as indicated by a single resonance located at ~ 24 ppm (Fig. S1, ESI†).

Assignment of the charge-state of a POV-alkoxide is not possible by ^1H NMR spectroscopy alone, given the similarities in spectra of clusters across a range of oxidation states. To verify



Scheme 1 Reduction of NO_2^{1-} with $\text{V}_6\text{O}_6^{1-}$.

the formation of $\text{V}_6\text{O}_7^{2-}$ following reaction of $\text{V}_6\text{O}_6^{1-}$ with NO_2^{1-} , characterization of the product was carried out *via* electronic absorption and infrared spectroscopies. These two analytical techniques have been reported to inform on the charge-state of the metal oxide cluster, as both contain diagnostic features that are sensitive to the oxidation state distribution of vanadyl moieties across the hexavanadate core.^{15–17} The electronic absorption spectrum of the product is largely featureless, with a weak absorption at 622 nm ($108 \text{ M}^{-1} \text{ cm}^{-1}$), which is attributed to a spin-forbidden $d_{xy}-d_{x^2-y^2}$ transition for V^{IV} ions within the Lindqvist cluster (Fig. 2).¹⁷ Notably, the lack of intervalence charge transfer (IVCT) bands associated with mixed-valent ($\text{V}^{IV/V}$) variants of the POV-alkoxide cluster ($[\text{V}^{IV-x}\text{V}_x^{V}(\text{OCH}_3)_{12}]^n$ ($n = -1, 0, +1$)) suggests that the product possesses an isovalent oxidation state distribution of vanadyl moieties, consistent with the electronic structure of $\text{V}_6\text{O}_7^{2-}$ ($[\text{V}_6^{IV}]$).¹⁷ The infrared spectrum of the product contains two absorption bands located at 937 cm^{-1} ($\text{V}=\text{O}; \text{O}_t = \text{terminal oxo}$) and 1059 cm^{-1} ($\text{O}_b-\text{CH}_3; \text{O}_b = \text{bridging oxo}$) (Fig. S3, ESI†). These energies are consistent with those reported for $\text{V}_6\text{O}_7^{2-}$.¹⁶

To evaluate the non-cluster containing products of the reaction of NO_2^{1-} with $\text{V}_6\text{O}_6^{1-}$, we turned our attention to detection of nitric oxide (NO). We opted to use cobalt(II) tetraphenylporphyrin (CoTPP) given its well-established affinity for NO.^{18,19} After conducting a series of control experiments (*via* electronic absorption spectroscopy, Fig. S4, ESI†) to confirm no reactivity between CoTPP and substrate or the parent and reduced clusters, we devised an *in situ* experiment where the NO scavenger complex was added directly to the reaction mixture. Similar to the results observed in the absence of CoTPP, complete consumption of the oxygen-deficient cluster was noted, along with formation of the NO-ligated CoTPP complex (confirmed by ^1H NMR, Fig. S5 and S6, ESI†).²⁰ Further analysis of the reaction mixture by electronic absorption spectroscopy revealed the expected bathochromic shift of the absorption feature diagnostic for NO–CoTPP.^{21–23}

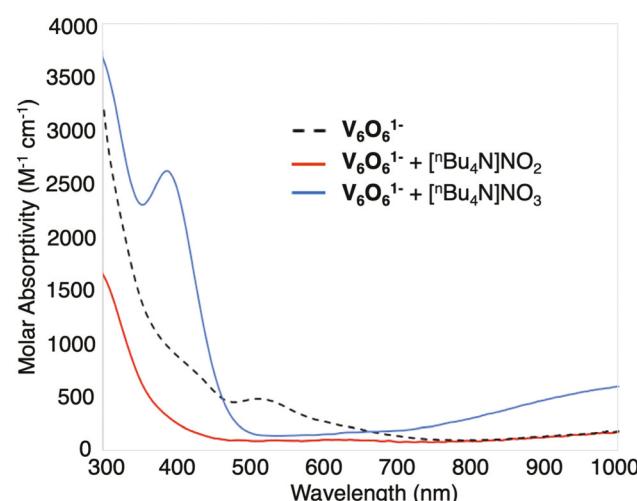


Fig. 2 Electronic absorption spectra of complex $\text{V}_6\text{O}_6^{1-}$ (black) and the reactions of $\text{V}_6\text{O}_6^{1-}$ with NO_2^{1-} (red) and NO_3^- (blue). See supporting information for detailed analysis (Fig. S2, ESI†).

Collectively, these data confirm formation of NO following reduction of nitrite by $\text{V}_6\text{O}_6^{1-}$ (Fig. S7, ESI†).

NO_2^{1-} activation mediated by metal complexes generally requires photolysis,^{24,25} protonation,²⁶ or the addition of other additives (e.g., PR_3 , SR_2)²⁷⁻²⁹ to facilitate N–O bond scission. Thus, the reactivity of the oxygen-deficient POV-alkoxide with this substrate is surprising. An exception was recently reported by Schelter and coworkers: addition of NO_2^{1-} to a pentavalent uranium complex ($\text{U}^{\text{V}}\text{Cl}_2(\text{N}(\text{SiMe}_3)_2)_3$) results in oxygen atom transfer (OAT) from NO_2^{1-} to the actinide centre.³⁰ Initial coordination of the substrate to the reduced uranium ion through its oxygen atom was supported by DFT calculations. Subsequent cleavage of the N–O bond of the oxyanion is facilitated by single electron transfer from uranium to the substrate, resulting in the release of NO and the formation of a new, one-electron oxidized uranium species with a terminal oxido ligand ($\text{U}^{\text{VI}}\text{OCl}(\text{N}(\text{SiMe}_3)_2)_3$). We invoke similar reactivity for our oxygen-deficient polyoxoanion. Addition of NO_2^{1-} results in the cleavage of the N–O bond, release of NO, and formation of a one-electron oxidized cluster with a new $\text{V}^{\text{IV}}=\text{O}$ bond at its surface (replacing the site-differentiated V^{III} centre).

Following the successful reduction of NO_2^{1-} , we set out to explore the activation of the more thermodynamically challenging substrate for deoxygenation, NO_3^{1-} . Molybdenum-containing nitrate reductases catalyse the reduction of NO_3^{1-} through a mechanism in which an oxygen atom is transferred from the oxyanion to a molybdenum(IV) centre.^{31,32} This results in the formation of NO_2^{1-} , with concurrent two-electron oxidation of the metal centre to form a $\text{Mo}^{\text{VI}}=\text{O}$ moiety. Drawing inspiration from enzymatic reduction of NO_3^{1-} , we opted to explore the reactivity of our reduced POV-alkoxide cluster with this substrate. We hypothesized that NO_3^{1-} activation would follow a similar pathway to that of the native enzyme, in that N–O bond cleavage would result in OAT to the site differentiated V^{III} centre, changing the overall oxidation state distribution of the cluster from $[\text{V}^{\text{III}}\text{V}^{\text{IV}}_5]^{1-}$ to $[\text{V}^{\text{IV}}_5\text{V}^{\text{V}}]^{1-}$. Similar OAT mechanisms for NO_3^{1-} reduction have been reported for d^{33,34} and f-block^{35,36} metal complexes.

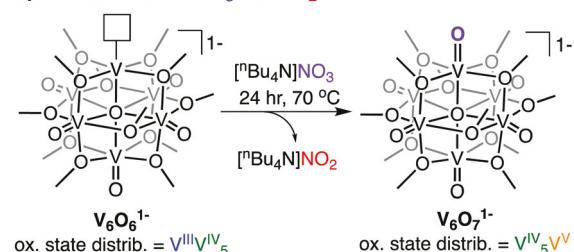
Addition of an equivalent of tetrabutylammonium nitrate ($[\text{Bu}_4\text{N}]\text{NO}_3$) to $\text{V}_6\text{O}_6^{1-}$ in THF at room temperature afforded minimal conversion to the oxidized POV-alkoxide (Fig. S8, ESI†). However, heating of this reaction mixture to 70 °C afforded a gradual colour change from brown/red to green over the course of 24 h. Analysis of the crude reaction mixture by ¹H NMR spectroscopy revealed formation of a fully-oxygenated POV-alkoxide (Fig. S9, ESI†).

Characterization of the cluster-containing product of the reaction of $\text{V}_6\text{O}_6^{1-}$ and $[\text{Bu}_4\text{N}]\text{NO}_3$ by IR spectroscopy revealed two strong absorption bands corresponding to $\nu(\text{V}=\text{O}_\text{t})$ and $\nu(\text{O}_\text{b}-\text{CH}_3)$, located at 953 and 1043 cm⁻¹, respectively (Fig. S10, ESI†). These infrared absorptions are substantially shifted from that of $\text{V}_6\text{O}_7^{2-}$ (937, 1055 cm⁻¹), however closely resemble values reported for the monoanionic POV-alkoxide, $[\text{Bu}_4\text{N}][\text{V}_6\text{O}_7(\text{OCH}_3)_{12}]$ ($\text{V}_6\text{O}_7^{1-}$; $\nu(\text{V}=\text{O}_\text{t})$: 953 cm⁻¹, $\nu(\text{O}_\text{b}-\text{CH}_3)$: 1047 cm⁻¹).^{14,16} To further discern the charge-state of the product of the reaction of NO_3^{1-} and $\text{V}_6\text{O}_6^{1-}$, electronic absorbance spectroscopy was employed (Fig. 2).

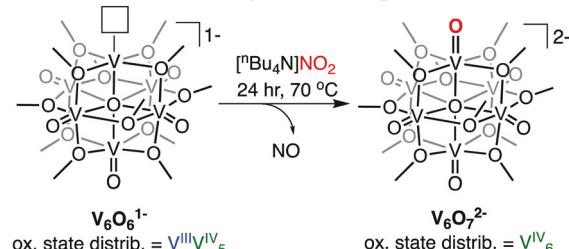
The spectrum of the crude product contains two IVCT bands located at 392 nm (2594 M⁻¹ cm⁻¹) and 1000 nm (605 M⁻¹ cm⁻¹). The presence of these absorbances are consistent with formation of a cluster with a mixed-valent $\text{V}^{\text{IV}/\text{V}}$ charge-state. However, further analysis revealed lower values of molar absorptivity for these features as compared to those reported for $\text{V}_6\text{O}_7^{1-}$ (392 nm (3583 M⁻¹ cm⁻¹) and 1000 nm (814 M⁻¹ cm⁻¹); Fig. S11, ESI†).¹⁴ This discrepancy suggests that the product of $\text{V}_6\text{O}_6^{1-}$ and $[\text{Bu}_4\text{N}]\text{NO}_3$ might in fact be a mixture of clusters with varying oxidation state distributions (namely complexes $\text{V}_6\text{O}_7^{1-}$ and $\text{V}_6\text{O}_7^{2-}$). Electrochemical analysis of the crude reaction mixture in acetonitrile revealed four quasi-reversible events, consistent with complete oxygen atom transfer from the substrate to the reduced scaffold (Fig. S12, ESI†).¹⁶ However, the open circuit potential (OCP) measurement of the sample revealed zero current at -0.61 V (vs. $\text{Fc}^{0/+}$) which is cathodically shifted from the OCP value for complex $\text{V}_6\text{O}_7^{1-}$ (-0.41 V vs. $\text{Fc}^{0/+}$). This shift provides further support for the formation of multiple charge states of the cluster-containing product upon NO_3^{1-} reduction.

Given that NO_2^{1-} reduction with $\text{V}_6\text{O}_6^{1-}$ occurs at room temperature, we posed that the observed mixture of $\text{V}_6\text{O}_7^{1-}$ and $\text{V}_6\text{O}_7^{2-}$ obtained from the activation of NO_3^{1-} might be a result of competitive reactions between the oxygen-deficient POV-alkoxide cluster and both nitrogen oxides (NO_2^{1-} being formed in solution following the two electron reduction of NO_3^{1-}). To assess whether the cluster was competent for the complete reduction of NO_3^{1-} to NO, a substoichiometric amount of $[\text{Bu}_4\text{N}]\text{NO}_3$ was added to $\text{V}_6\text{O}_6^{1-}$ (Scheme 2). Analysis by ¹H NMR spectroscopy revealed complete consumption of the oxygen deficient POV-alkoxide, despite addition of only one half of an equivalent of substrate (Fig. S13, ESI†). These results suggest that formation of NO_2^{1-} in solution upon the reduction of NO_3^{1-} is immediately followed by a reaction of this by-product with unreacted starting material ($\text{V}_6\text{O}_6^{1-}$). The OCP of the

Step 1: Reduction of NO_3^{1-} to NO_2^{1-}



Step 2: Reduction of in situ generated NO_2^{1-} to NO



Scheme 2 Reduction of NO_3^{1-} with $\text{V}_6\text{O}_6^{1-}$.

product (-0.59 V vs. $\text{Fc}^{0/+}$) compares favourably with the above result, confirming that a mixture of cluster-containing products are formed regardless of the number of equivalents of $[\text{Bu}_4\text{N}]\text{NO}_3$ added to $\text{V}_6\text{O}_6^{1-}$ (Fig. S14, ESI†). Finally, examination of the electronic absorption spectra of the *in situ* reaction of substrate, cluster, and CoTPP revealed formation of half an equivalent of NO (Fig. S15, ESI†).²¹

These results detailing the activation of NO_2^{1-} and NO_3^{1-} using oxygen-deficient POV-alkoxide clusters provide insight into a possible mechanism of electrocatalytic NO_x^{1-} activation (e.g., formation of an open-coordination site followed by NO_x^{1-} reduction at the reduced metal ion). However, it is worth noting that experiments probing the potential electrocatalytic activity of $\text{V}_6\text{O}_7^{1-}$ toward the reduction of NO_2^{1-} and NO_3^{1-} afforded no current response consistent with catalysis. The inactivity of the POV-alkoxide cluster suggests that bridging oxygen atoms found in plenary POM motifs likely play an important role in the reduction of NO_x^{1-} (POV-alkoxide clusters have only terminal oxygen sites available for small molecule activation).

In this work, we have expanded upon the reactivity of oxygen-deficient POV-alkoxide clusters toward small molecule activation by demonstrating their ability to facilitate NO_x^{1-} ($x = 2, 3$) reduction. Through spectroscopic analysis, we have shown that the one-electron reduction of NO_2^{1-} results in N–O bond cleavage and formation of a fully oxygenated cluster and nitric oxide. Furthermore, we present the reactivity of the O-deficient cluster with NO_3^{1-} , illustrating that these clusters can fully deoxygenate the more “inert” oxyanion, resulting in formation of NO. The additive-free, stoichiometric reactivity of the reduced metal ion embedded within the POV-alkoxide cluster toward N–O bond cleavage and oxygen atom transfer, demonstrates new reactivity for these oxygen-deficient species. These results provide insight into the mechanism by which metal oxides can facilitate molecular transformations of relevance to the activation of oxygenated substrates.

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Conflicts of interest

There are no conflicts to declare.

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