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### Controlling Metal-to-Oxygen Ratios via M=O Bond Cleavage in Polyoxovanadate Alkoxide Clusters

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**S** Supporting Information

ABSTRACT: In this manuscript, we further investigate the use of Lindqvist polyoxovanadate alkoxide (POV-alkoxide) clusters as homogeneous molecular models of reducible metal oxides (RMO), focusing on the structural and electronic consequences of forming one or two oxygen-deficient sites. We demonstrate the reactivity of a neutral POV-alkoxide cluster,  $[V_6O_7(OCH_3)_{12}]^0$ , with a reductant, revealing routes for controlling metal-to-oxygen ratios in self-assembled polynuclear ensembles through post-synthetic modification. The outlook of this science is bolstered by the fact that, in both cases, O-atom removal reveals reduced V ions at the surface of the cluster. Extending our entry into small-molecule activation mediated by surface defect sites, we report the reactivity of mono- and divacant clusters with a model substrate, tert-butyl



isocyanide, demonstrating the electronic consequences of small-molecule coordination to reduced ions in RMO materials.

#### INTRODUCTION

Reducible metal oxides (RMOs) are prominent materials that act as functional components in many industrially relevant heterogeneous processes.<sup>1-3</sup> Theoretical investigations have revealed that surface defects in these materials, such as O-atom vacancies, act as active sites in catalysis for the activation of small molecules.<sup>4</sup> Despite progress in the development of RMOs as catalysts, an understanding of the factors that influence the formation and reactivity of O-atom vacancies remains a significant gap in knowledge. In particular, the optimization of RMOs for the conversion of small, inert substrates to energy-rich chemical fuels has been hampered by a limited spectroscopic understanding of the role of singleatom vacancies on extended surfaces during catalysis (vide infra). Recent advances in microscopy probing single-atom vacancies on the surface of bulk materials remain limited by challenging sample preparation,<sup>5</sup> poor resolution,<sup>6,7</sup> thermal drift,<sup>8,9</sup> misassignment of signals, and artifact generation.<sup>10</sup> Furthermore, the lack of in situ analysis limits opportunities to characterize reactive intermediates.<sup>5</sup> Thus, to provide insight into the formation of reactive defect sites and their role in substrate activation, our research group has focused on probing the chemistry of O-atom vacancies using homogeneous cluster complexes as models for bulk RMOs.

One class of compounds well-suited for modeling the surface chemistry and activity of bulk RMO materials is polyox-ometalates (POMs).<sup>11–13</sup> These polynuclear clusters are threedimensional molecular fragments of metal oxides that consist of multiple transition-metal oxyanions linked together by bridging oxide units. Although many examples of these metal

oxide clusters have been reported, access to structurally related assemblies with controlled metal-to-oxygen ratios remains challenging. This is principally due to well-established synthetic procedures for the formation of metal oxide clusters, which nominally invoke self-assembly protocols.<sup>14</sup> Most commonly, synthetic chemists manipulate the structures of plenary motifs (e.g., Keggin, Dawson, Anderson POM ions) via basic degradation, affording the formation of mono-, di-, and trilacunary clusters.<sup>15</sup> In this approach, entire [MO<sub>4</sub>]<sup>n-</sup> subunits are removed from the surface of a POM structure. While this strategy does lead to the controlled formation of POMs with new metal-to-oxygen ratios, the nucleophilic, oxygen-terminated surfaces of the lacunary clusters do not appropriately model surface defects (i.e., reduced metal ions) invoked in small-molecule activation involving heterogeneous catalysts.

Interested in investigating the consequences of defect formation at the surface of well-defined metal oxide materials, our research group has been studying the O-atom-transfer (OAT) reactivity of POMs, targeting removal of terminal oxo moieties with retention of the polynuclear core.<sup>16</sup> Specifically, organo-functionalized polyoxovanadate ions,  $[V_6O_7(OCH_3)_{12}]^n$  (n = 0, 1-), have captured our interest because of their distinct physical and electrochemical proper-ties (Figure 1).<sup>14,17,18</sup> Their composition features 6 terminal

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**Figure 1.** POV-alkoxide clusters as models for vacancy formation in RMOs.

vanadyl ions and 12 bridging oxygen-donating alkoxo ligands, constructing stable mixed-valent  $(V_n^V V_{6-n}^{V})^{V}$  where n = 0-4) clusters that resemble redox-active metal oxide supports.<sup>18</sup> Additionally, the solubility of these clusters in an organic solvent renders them amenable to in situ analysis via spectroscopies reserved for homogeneous systems. Furthermore, extensive chemical and electrochemical studies on polyoxovanadate alkoxide (POV-alkoxide) clusters have demonstrated the cluster's ability to redistribute electron density following oxidative or reductive transformations, making these homogeneous materials ideal systems for modeling the diffuse electronic structure of semiconducting RMOs.<sup>16,19-21</sup> While our systems certainly do not constitute absolute structural mimics of the surface of an extended material, we believe that the similarities in the electronic structures of the two systems justify further work into the study of their chemistry.

We recently disclosed the formation of a single O-atom vacancy at the surface of a POV–alkoxide cluster, marking the first report of an unsupported (i.e., "ligand-free") polynuclear metal oxide assembly with a reduced ion formed as a result of M=O bond cleavage.<sup>16</sup> Our initial results demonstrated that the addition of a single equivalent of V(Mes)<sub>3</sub>(THF) (Mes = 2,4,6-trimethylphenyl; THF = tetrahydrofuran) to the

monoanionic form of the cluster  $[^{n}Bu_{4}N][V_{6}O_{7}(OCH_{3})_{12}]^{-1}$  $(1-V_6O_7)$  resulted in OAT to the reductant and the isolation of a reduced polyoxovanadate compound,  $[^{n}Bu_{4}N][V_{6}O_{6}(OCH_{3})_{12}]^{-}$  (2-V<sub>6</sub>O<sub>6</sub><sup>-</sup>; Scheme 1). Herein, we extend upon our initial report, targeting controlled formation of multiple vacant sites within a POV-alkoxide assembly. A correlation between the electronic structure of the parent POV-alkoxide cluster and number of vacant sites reveals predictable routes to structurally related clusters with controlled metal-to-oxygen ratios. Finally, we summarize an entry into modeling the surface chemistry of defect sites with small-molecule substrates. Exploration of the coordination chemistry of isonitrile ligands with reduced, site-differentiated V ions embedded *directly* within the polyoxovandate clusters provides a system for interrogating the initial steps in the mechanism of small-molecule activation in RMOs (i.e., substrate binding). Collectively, these results provide a distinct route to exploring the structural and electronic consequences of selective vacancy generation and substrate binding on metal oxide supports in heterogeneous catalysis.

#### RESULTS AND DISCUSSION

Correlating the Electronic Structure of POV–Alkoxides to OAT. The generation of a reduced polyoxovanadate assembly in our preliminary manuscript marked the first example of the creation of an oxygen-deficient site via M==O bond cleavage.<sup>16</sup> Evaluation of the electronic structure of the parent POV–alkoxide cluster, complex 1-V<sub>6</sub>O<sub>7</sub><sup>-7</sup>, and the oxygen-deficient product, 2-V<sub>6</sub>O<sub>6</sub><sup>-7</sup>, by electronic absorption spectroscopy revealed a loss of intervalence charge-transfer (IVCT) bands associated with electron transfer between V<sup>IV</sup>/ V<sup>V</sup> ions. The removal of an O atom, coupled with the loss of IVCT bands, indicates a two-electron reduction of the single V<sup>V</sup> center in 1-V<sub>6</sub>O<sub>7</sub><sup>-7</sup> (electronic distribution: V<sup>V</sup>V<sup>IV</sup><sub>5</sub>) to V<sup>III</sup> in the reduced cluster (2-V<sub>6</sub>O<sub>6</sub><sup>-7</sup>; electronic distribution: V<sup>IV</sup><sub>5</sub>V<sup>III</sup>). To experimentally evaluate the relationship between the electronic structure of the parent POV–alkoxide cluster,

Scheme 1. Reactivity of POV–Alkoxide Clusters across Three Different Oxidation States, with the Vacancy Formation Correlated to the Number of  $V^{V}$  Ions in the Starting Material



specifically the number of V<sup>V</sup> ions in the starting material, and V=O bond cleavage, we attempted the formation of multiple vacant sites via the addition of excess reductant to complex 1-V<sub>6</sub>O<sub>7</sub><sup>-</sup>. A subsequent V=O cleavage event at a tetravalent vanadyl ion would necessitate transient formation of a V<sup>II</sup> center, likely unfavorable in the oxidizing environment of the POM. Consistent with our hypothesis, despite the addition of multiple equivalents of V(Mes)<sub>3</sub>(THF) to 1-V<sub>6</sub>O<sub>7</sub><sup>-</sup> and prolonged heating of the reaction mixture, the sole formation of complex 2-V<sub>6</sub>O<sub>6</sub><sup>-</sup> was observed (Figure S1).

To probe the influence of the number of V<sup>V</sup> ions present in the starting material to vacancy formation, a control experiment was conducted with the fully reduced, dianionic POV– alkoxide cluster [ ${}^{n}Bu_{4}N$ ]<sub>2</sub>[V<sub>6</sub><sup>IV</sup>O<sub>7</sub>(OCH<sub>3</sub>)<sub>12</sub>]<sup>2-</sup> (3-V<sub>6</sub>O<sub>7</sub><sup>2-</sup>; Scheme 1). The oxidation state distribution of V ions across the Lindqvist core is V<sup>IV</sup><sub>6</sub>, presenting an opportunity to evaluate potential OAT from a tetravalent V ion imbedded within an isovalent vanadate cluster. As expected, the addition of V(Mes)<sub>3</sub>(THF) to 3-V<sub>6</sub>O<sub>7</sub><sup>2-</sup> yielded no reaction, providing further support of the hypothesis that the presence of V<sup>V</sup> ions within the POV–alkoxide cluster is a determinant in OAT (Figure S2).

**Synthesis of a POV–Alkoxide Cluster with Multiple O-Atom Vacancies.** Theoretical investigations on the role of surface defects have revealed the importance of O-atom vacancies on the activity of RMO catalysts.<sup>22</sup> Studies featuring the synthesis and characterization of oxygen-deficient metal oxides have demonstrated that *multiple* oxygen vacancies are created on the surface of the heterogeneous catalyst via current techniques such as surface annealing,<sup>10,23</sup> electron bombardment,<sup>10,23</sup> or hydrothermal syntheses.<sup>23</sup> Therefore, the generation of a POV–alkoxide model system that allows for the investigation of the effect of variable numbers of O-atom vacancies on the electronic structure of RMOs is coveted because this would more aptly describe the surface composition of the bulk solid.

Given the apparent relationship between the vacancy generation and number of available V<sup>V</sup>=O moieties in the Lindqvist core, we shifted our focus to the neutral POValkoxide,  $[V_6O_7(OCH_3)_{12}]^0$  (4-V<sub>6</sub>O<sub>7</sub><sup>0</sup>). We hypothesized that the electronic distribution of the neutral cluster  $4 \cdot V_6 O_7^{0}$  $(V_{2}^{V}V_{4}^{IV})$  would support the generation of either a single or multiple oxygen-deficient site(s), due to the *two* accessible  $V^V$ centers in the hexavanadate core. Upon exposure of  $4-V_6O_7^{0}$  to 2 equiv of  $V(Mes)_3(THF)$ , a color change to brown-red was observed, consistent with the generation of an oxygen-deficient cluster (Scheme 1). Analysis of the reaction mixture by electrospray ionization mass spectrometry (ESI-MS, positive mode) revealed a single peak corresponding to m/z 758. This molecular weight is consistent with formation of the desired product,  $[V_6O_5(OCH_3)_{12}(MeCN)_2]^0$  (5- $V_6O_5^0$ ; Figure S3). While the product of the reaction is proposed to be neutral in charge, we justify the observation of the parent ion in the positive mode as a result of one-electron oxidation of the cluster under the high voltages associated with electrospray ionization.<sup>16,24,36–39</sup> Further support of OAT was obtained via analysis of the crude reaction mixture by <sup>1</sup>H NMR spectroscopy. Formation of the anticipated diamagnetic byproduct,  $OV(Mes)_3$ , was observed, along with a series of new paramagnetic resonances, ranging from 85.31 to -22.46 ppm (Figure S4). Unlike the three signals observed for the monovacant cluster,<sup>16</sup>  $2-V_6O_6^-$ , the product of this reaction has six resonances, five assigned to the  $O-CH_3$  ligands and the

sixth associated with solvent bound to the cluster ( $CH_3CN$ ), suggesting the formation of a cluster with reduced molecular symmetry. The <sup>1</sup>H NMR spectrum obtained for  $5-V_6O_5^{0}$  is consistent with selective formation of the *cis*-vacancy product upon removal of the second O atom.

To confirm the formation of complex  $5 \cdot V_6 O_5^{0}$  (electronic distribution:  $V^{IV}_4 V^{III}_2$ ), analyses via IR and electronic absorption spectroscopies were conducted. IR spectroscopy of POV–alkoxide clusters has been demonstrated to be a useful tool for cluster charge-state analysis via examination of the stretching frequencies of the characteristic metal–oxygen bonds of the Lindqvist core  $[\nu(V=O_t) \text{ and } \nu(O_b-CH_3); O_t = \text{terminal oxo and } O_b = \text{bridging oxo}].^{16,19,20,24}$  Upon removal of two surface O atoms from  $4 \cdot V_6 O_7^{0}$ , two strong absorption bands were observed in the IR spectrum, corresponding to the  $\nu(V=O_t)$  (964 cm<sup>-1</sup>) and  $\nu(O_b-CH_3)$  (1038 cm<sup>-1</sup>) stretching frequencies of  $5 \cdot V_6 O_5^{0}$  (Figure 2a). The V=O\_t



Figure 2. (a) IR spectra of complexes  $4-V_6O_7^{0}$ ,  $5-V_6O_5^{0}$ , and  $6-V_6O_6^{0}$ . (b) Electronic absorption spectra of complexes  $4-V_6O_7$ ,  $5-V_6O_5^{0}$ , and  $6-V_6O_6^{0}$  collected in MeCN.

and  $O_b-CH_3$  stretching frequencies are shifted from  $4-V_6O_7^0$  (V= $O_v$  966 cm<sup>-1</sup>;  $O_b-CH_3$ , 1009 cm<sup>-1</sup>), confirming the formation of a reduced cluster core. Specifically, the changes in the energy differences between  $\nu$ (V= $O_t$ ) and  $\nu$ ( $O_b-CH_3$ ) for complexes  $4-V_6O_7^0$  ( $\Delta = 43$  cm<sup>-1</sup>) and  $5-V_6O_5^0$  ( $\Delta = 74$  cm<sup>-1</sup>) are reminiscent of the separation between similar bands in the IR spectra of reduced and oxidized POV-alkoxide clusters previously reported by our group<sup>16,24</sup> and others.<sup>18-20</sup>

Furthermore, the reduction in the intensity of  $\nu$ (V=O<sub>t</sub>) in the complex 5-V<sub>6</sub>O<sub>5</sub><sup>0</sup> compared to that of complex 4-V<sub>6</sub>O<sub>7</sub><sup>0</sup> is indicative of the removal of two vanadyl O atoms.

Further evidence supporting the reduction of the hexavanadate core was obtained via analysis of  $5 \cdot V_6 O_5^{0}$  via electronic absorption spectroscopy (Figure 2b). The absorption spectra of the parent cluster  $4 \cdot V_6 O_7^{0}$  (electronic distribution:  $V_2^V V_2^{IV_4}$ ) contain two IVCT bands assigned to charge transfer between  $V^{IV}$  and  $V^V$  metal centers (386 nm,  $\varepsilon = 6975 \text{ M}^{-1} \text{ cm}^{-1}$ ; 998 nm,  $\varepsilon = 1375 \text{ M}^{-1} \text{ cm}^{-1}$ ). A loss of these IVCT bands associated with electron transfer between  $V^V$  (d<sup>0</sup>) and  $V^{IV}$  (d<sup>1</sup>) centers in the mixed-valent starting material is observed upon the formation of  $5 \cdot V_6 O_5$ , consistent with a reduction of all d<sup>0</sup> vanadyl moieties to  $V^{III}$  ions upon the removal of two surface O atoms. An additional weak transition is observed in the electronic absorption spectrum, centered at 524 nm ( $\varepsilon = 468$  $M^{-1} \text{ cm}^{-1}$ ). A similar band was observed in the spectrum of  $2 \cdot V_6 O_6^-$  (526 nm,  $\varepsilon = 473 \text{ M}^{-1} \text{ cm}^{-1}$ ) and is assigned to a spinforbidden, d–d excitation of a  $V^{IV}$  ion.<sup>16</sup>

Crystals suitable for structural analysis were grown from the slow diffusion of diethyl ether into a concentrated THF solution of  $5-V_6O_5^{0}$ . Refinement of the data revealed the expected Lindqvist structure with two O-atom vacancies formed on *cis*-V ions (Figure 3 and Table 1; for full



**Figure 3.** Molecular structures of  $5-V_6O_6^{0}$  (left) and  $6-V_6O_6$  (right) shown with 50% probability ellipsoids. H atoms and solvent molecules coordinated to the cluster have been removed for clarity. In the case of complex  $6-V_6O_6^{0}$ , the asymmetric unit cell contains half of the POV–alkoxide cluster located at a crystallographic inversion center.

Table 1. Structural Parameters of Complexes  $4-V_6O_7^{0,18}$  5- $V_6O_5^{0,0}$ , and  $[V_6O_6(OCH_3)_{12}(OTf)]^{16}$ 

bond	4-V <sub>6</sub> O <sub>7</sub> <sup>0</sup>	$5 - V_6 O_5^{0} (E = N)$	$[V_6O_6(OCH_3)_{12}(OTf)] (E = O)$
$V_v$ –E (Å)		2.112(2), 2.104(3)	2.052(8)
$V_v - O_c$ (Å)		2.0666(17), 2.0760(17)	2.079(4)
$V_v - O_b - V_c(avg.)$ (deg)		105	105
$V_v - O_b - V_v$ (deg)		96.78	
$V-O_c(avg.)$ (Å)	2.25	2.3686	2.317
$V_t \!\!=\!\! O_t(avg.) \ (\text{\AA})$	1.60	1.605	1.585

crystallographic parameters, see Table S1). Each reduced V center  $(V_v)$  has a bound acetonitrile (MeCN), occupying the vacant site. While crystallization was not conducted in the presence of MeCN, characterization of the cluster was

performed using CD<sub>3</sub>CN, affording an opportunity for the more strongly coordinating MeCN ligand to bind to the cluster. We postulate that MeCN makes for a better ligand to the complex  $5 - V_6 O_5^0$ , in comparison to THF, as a result of the reduced steric bulk of the solvent at the coordinating atom. Analysis of the intracluster V<sub>v</sub>-O bond distances reveals that, upon removal of two surface O atoms, the reduced V ions pucker toward the center of the cluster, resulting in shortened  $V_v - O_c$  bonds  $[O_c = central u_6 - O atom, 2.0666(17) and$ 2.0760(17) Å]. These bond lengths compare well with similar metrics in the previously reported O-atom-vacancy-containing product,  $[V_6O_6(OCH_3)_{12}OTf]$  (OTf = trifluoromethylsulfonate), with a  $V_v - O_c$  distance of 2.08(4) Å.<sup>16</sup> Likewise, to accommodate the movement of the reduced ions toward the center of the cluster, the  $V_{y}-O_{b}-V_{t}$  (V<sub>t</sub> = terminal vanadyl ion) bond angles are contracted, averaging  $\sim 105^{\circ}$ .

Each V ion resolved in the crystal structure of  $5 \cdot V_6 O_5^{00}$  occupies a distinct position in the unit cell. This allows for bond-valence-sum (BVS) calculations to be performed for this POV–alkoxide cluster, shedding insight into the oxidation state distributions of V centers across the Lindqvist core (Table S2). Unsurprisingly, our calculations suggest that the two reduced metal centers can be assigned as V<sup>III</sup>, while the remaining vanadyl sites occupy a tetravalent oxidation state. A charge distribution of V<sup>IV</sup><sub>4</sub>V<sup>III</sup><sub>2</sub> for complex  $5 \cdot V_6O_5^{00}$  is consistent with its electronic absorption spectrum, which bears no IVCT bands (vide supra). As in the case of [V<sub>6</sub>O<sub>6</sub>(OCH<sub>3</sub>)<sub>12</sub>OTf], the BVS values calculated for individual V ions deviate from the integer values of the anticipated valence states, consistent with the established electronic communication between V ions across the Lindqvist core.<sup>16</sup>

Sole formation of the cis-vacancy product is surprising. While formation of a second vacant site cis to the original Oatom vacancy is statistically favored, we note that we never observe additional resonances in the <sup>1</sup>H NMR spectrum that would be consistent with the formation of a trans-vacancy product. Because the parent POV-alkoxide cluster is a wellestablished Robin and Day class II delocalized system,<sup>25</sup> IVCT processes prevent localization of the oxidation states throughout the cluster (supported by BVS calculations and electronic characterization of  $4-V_6O_7^{(0)}$ ). Thus, the selective generation of the cis product can be justified by the observed structural perturbations of  $5-V_6O_5^0$ , which require truncation of the  $V_v - O_c$  bond distance. Positioning the vacant sites *cis* to one another allows for the formation of a "square" V<sub>2</sub>O<sub>2</sub> site with enhanced stability, as observed in the " $V_v - O_b - V_v$ " (V1-O-V2) bond angles of  $5-V_6O_5^0$  (Figure 4 and Table 1). However, we cannot rule out an electronic influence, in which



**Figure 4.** Portion of  $5 \cdot V_6 O_5^0$  with other atoms in the POV–alkoxide cluster removed to highlight distortion of the V–O<sub>b</sub>–V bond angle compared to the starting material  $4 \cdot V_6 O_7^0$ .

case the V<sup>V</sup> center remaining after reduction of the *first* vanadyl moiety to yield a monovacant cluster is localized to the equatorial plane of the remaining vanadyl ions. This indeed is apparent in the BVS calculations previously reported for [V<sub>6</sub>O<sub>6</sub>(OCH<sub>3</sub>)<sub>12</sub>OTf], where oxidation of the monovacancy-containing complex **2-V<sub>6</sub>O<sub>6</sub>**<sup>-</sup> is exclusively localized to vanadyl ions positioned *cis* to the reduced V ion.<sup>16</sup>

Accessing a Neutral POV-Alkoxide Cluster with a Single O-Atom Vacancy. The ability to remove two O atoms from the POV-alkoxide cluster confirms our hypothesis that the number of possible oxygen vacant sites is dependent on the available V<sup>V</sup> moieties in the cluster core. Intrigued by whether we could selectively form a cluster containing a single vacancy from the neutral POV-alkoxide precursor, we shifted our focus to probing the generation of a neutral, monovacant cluster via V=O bond cleavage of  $4 \cdot V_6 O_7^{0}$ . The addition of 1 equiv of V(Mes)<sub>3</sub>(THF) to  $4 \cdot V_6 O_7^{0}$  resulted in an instantaneous color change from green to red-brown, suggesting vacancy formation (Scheme 1). Analysis of the crude product by <sup>1</sup>H NMR spectroscopy revealed a mixture of the anticipated diamagnetic byproduct OVMes<sub>3</sub>, small amounts of complex 5- $V_6O_5^0$ , and three new paramagnetically shifted and broadened resonances ( $\delta$  25.44, 18.27, and -12.69; Figure S5). A similar three-peak pattern was observed in the <sup>1</sup>H NMR spectra of  $2-V_6O_6^{-}$ , suggesting that the newly shifted resonances correspond to the formation of a product with a similar reduction in the molecular symmetry  $(O_h \rightarrow C_{4\nu})$ , albeit in a different charge state.<sup>16</sup> These qualifications fit well with formation of the desired product, the neutral monovacant cluster  $[V_6O_6(OCH_3)_{12}(MeCN)]^0$  (6-V<sub>6</sub>O<sub>6</sub><sup>0</sup>). However, adjusting the reaction conditions by altering the time, temperature, solvent, and equivalents of V(Mes)<sub>3</sub>(THF) added resulted in nominal changes in the purity of  $6-V_6O_6^{0}$ .

Given the challenges associated with the selective generation of  $6-V_6O_6^0$  via vacancy formation, attempts to access this molecule via the oxidation of  $2-V_6O_6^-$  were performed with 1 equiv of  $FcBF_4$  (Fc = ferrocenium; Scheme 1; confirmed by <sup>1</sup>H NMR; Figure S6). While this independent synthesis resulted in generation of the neutral species  $6-V_6O_6^{0}$  as the sole paramagnetic product, challenges in isolating this reactive complex from the byproduct  $[^{n}Bu_{4}N][BF_{4}]$  persisted. The enhanced purity associated with the oxidative preparation of 6- $V_6 O_6^{0}$  afforded opportunities to rigorously confirm the vacancy formation via X-ray crystallography, however, by selecting deep-brown crystals from co-crystallized translucent salts. Indeed, crystals suitable for analysis were grown from the slow diffusion of pentane into a concentrated THF solution of complex  $6 \cdot V_6 O_6^{0}$  synthesized via the oxidation of  $2 \cdot V_6 O_6^{-1}$ with 1 equiv of FcBF<sub>4</sub>. Structural refinement revealed the expected Lindqvist structure with a single O atom removed and replaced with MeCN (Figure 3; for full crystallographic parameters, see Table S3). The neutral monovacant cluster crystallized with a crystallographic inversion center, causing V=O/V-MeCN disorder. While this disorder within the unit cell resulted in unusable bond metrics for complex  $6-V_6O_6^{0}$ , structural analysis unambiguously confirms M=O bond cleavage.

To further investigate the perturbations in the electronic structure of  $6 \cdot V_6 O_6^{\ 0}$  (electronic distribution:  $V^V V^{IV}_4 V^{III}$ ), IR and electronic absorption spectroscopies were employed. In the IR spectrum of the highest purity sample of  $6 \cdot V_6 O_6^{\ 0}$ , two strong absorptions were observed, corresponding to the  $\nu$ (V= $O_t$ ) (968 cm<sup>-1</sup>) and  $\nu$ (O<sub>b</sub>-CH<sub>3</sub>) (1030 cm<sup>-1</sup>) frequencies

(Figure 2a). These features are significantly shifted from both the parent cluster,  $4-V_6O_7^{-0}$ , and the monovacant anionic cluster,  $2-V_6O_6^{-1}$  (Figure S7).<sup>16,20</sup> Previous reports have shown a correlation between the vibrational energies of both the  $\nu(V=O_t)$  and  $\nu(O_b-CH_3)$  stretching frequencies and the oxidation state distribution of vanadyl ions that compose the POV-alkoxide cluster.<sup>20</sup> For example, the monoanionic Lindqvist POV-alkoxide cluster  $1-V_6O_7$  has absorbance features at 953 cm<sup>-1</sup> [ $\nu$ (V=O<sub>t</sub>)] and 1047 cm<sup>-1</sup> ( $\nu$ (O<sub>b</sub>-CH<sub>3</sub>)). Upon oxidation of the hexavanadate cluster to 4- $V_6 O_7^{0}$ , the stretching frequencies shift to 964 and 1009 cm<sup>-1</sup>, respectively.<sup>16</sup> In the case of complex 6-V<sub>6</sub>O<sub>6</sub><sup>0</sup>, strong  $\nu$ (V=  $O_t$ ) and  $\nu(O_b - CH_3)$  frequencies are observed at 968 and 1030 cm<sup>-1</sup>, whereas the reduced species  $2-V_6O_6^-$  bears analogous features at 951 and 1047 cm<sup>-1</sup>, respectively.<sup>16</sup> These distinct shifts in  $\nu(V=O_t)$  and  $\nu(O_b-CH_3)$  are consistent with a oneelectron oxidation of  $2 \cdot V_6 O_6^-$  upon formation of the neutral species  $6 \cdot V_6 O_6^{0}$ . Evidence for the reduction of  $4 \cdot V_6 O_7^{0}$ through the removal of a single O atom is also obtained from electronic absorption spectroscopy (Figure 2b). The absorption spectrum of the monovacant complex consists of two IVCT bands, albeit with lower-intensity molar absorptivity values than those of the parent cluster 6-V<sub>6</sub>O<sub>6</sub><sup>0</sup> (394 nm,  $\varepsilon =$ 2766  $M^{-1}$  cm<sup>-1</sup>; 998 nm, 450  $M^{-1}$  cm<sup>-1</sup>). The decrease in the intensity of the IVCT bands is a result of the lower probability of electronic exchange between VV/VIV ions as a result of the reduction of one V<sup>V</sup> center to V<sup>III</sup>, further confirming the oxidation state assignment of V<sup>V</sup>V<sup>IV</sup><sub>4</sub>V<sup>III</sup>. The electronic absorption spectra of  $\mathbf{6-V_6O_6^{00}}$  also contain a small absorption at 530 nm ( $\varepsilon = 891 \text{ M}^{-1} \text{ cm}^{-1}$ ), corresponding to a spinforbidden  $d_{xv}(V^{IV}) - d_{x^2-v^2}(V^{IV})$  excitation.

Electronic Properties of Mono- and Divacant POV– Alkoxide Clusters. Interested in further understanding the electronic consequences of the removal of a second O atom from the surface of the POV–alkoxide cluster, the electrochemical profiles of complexes  $5 \cdot V_6 O_5^{\ 0}$  and  $6 \cdot V_6 O_6^{\ 0}$  were interrogated by cyclic voltammetry (CV; Figure 5). The opencircuit potential of  $5 \cdot V_6 O_5^{\ 0}$  (-0.39 V vs Fc/Fc<sup>+</sup>) suggests that the divacant molecule is in its most reduced state, consistent with the oxidation state distribution assignment predicted via BVS calculations and the electronic absorption spectrum ( $V_1^{V}_4 V_1^{W}_2$ ). Two oxidation events are observed, centered at



**Figure 5.** Cyclic voltammograms of complexes  $4 \cdot V_6 O_7^{0}$  (green).  $5 \cdot V_6 O_5^{0}$  (red), and  $6 \cdot V_6 O_6^{0}$  (blue) collected in DCM with 0.1 M [<sup>n</sup>Bu<sub>4</sub>N][PF<sub>6</sub>] as the supporting electrolyte.

 $E_{1/2}$  values of -0.305 and 0.256 V (vs Fc/Fc<sup>+</sup>). In comparison to the electrochemical profile of **6-V**<sub>6</sub>**O**<sub>6</sub><sup>0</sup>, which contains three reversible events ( $E_{1/2} = -0.704$ , -0.155, and +0.519 V vs Fc/Fc<sup>+</sup>), the removal of a second O atom further destabilizes the redox chemistry of the Lindqvist core. This result follows the trend seen in CV of the monovacant cluster, where reduction of the polyoxovanadate assembly results in the loss of a single redox event from the electrochemical profile of the initial polyoxovanadate assembly (Figure 5).

Previous work from our laboratory has established that POV-alkoxide clusters exhibit fast electron-transfer kinetics and quasi-reversible redox couples.<sup>21</sup> To evaluate the consequences of O-atom removal from the periphery of the hexavanadate cluster on the electrochemical properties of the Lindqvist core, we examined the reversibility, diffusion coefficients  $(D_0)$ , and electron-transfer rate constants  $(k_0)$  for all redox processes of  $5-V_6O_5^{0}$  and  $6-V_6O_6^{0}$  (Figures S8-S11 and Tables S4 and S5). Cyclic voltammograms of each event at scan rates varying from 100 to 2000 mV s<sup>-1</sup> were obtained to determine the relationship between the peak current  $(i_p)$  or peak separation  $(\Delta E_p)$  and scan rate. The increase of  $\Delta E_p$  with increasing scan rate indicates that each event for 5-V<sub>6</sub>O<sub>5</sub><sup>0</sup> and 6-V<sub>6</sub>O<sub>6</sub><sup>0</sup> is quasi-reversible (Figures S9a and S11a).<sup>21,26</sup> To determine the diffusion coefficient  $(D_0)$  associated with each redox couple of the vacant clusters, the Randles–Sevcik equation was used.<sup>21,27–29</sup> The comparable values of  $D_0$  for both  $4-V_6O_7^0$  and complexes  $5-V_6O_5^0$  and  $6-V_6O_6^0$  (~10<sup>-6</sup>) suggest that diffusion of the complexes through a solution is not influenced by the formation of up to two vacant sites. The Nicholson method was then used to determine the electrontransfer rate constant.<sup>21,30,31</sup> These calculations show that both of the resulting oxygen-deficient clusters  $5{\text{-}}V_6O_5{\,}^0$  and  $6{\text{-}}V_6O_6{\,}^0$ maintain  $k_0$  values comparable to that of 4-V<sub>6</sub>O<sub>7</sub><sup>0</sup> (Figures S12 and S13 and Table S6). The retention of fast electron-transfer rates following the removal of one or two surface O atom(s) suggests preservation of the delocalized electronic structure of the hexanuclear core upon vacancy formation. This is further supported by the IR spectra, electrochemical characterization, and BVS calculations of  $4-V_6O_7^{0}$ ,  $5-V_6O_5^{0}$ , and  $6-V_6O_6^{0}$ , which are consistent with extensive electron delocalization within both the parent cluster and reduced scaffolds.

Modeling Substrate Interaction with Vacant Sites: Reactivity of [V<sub>6</sub>O<sub>5</sub>(OCH<sub>3</sub>)<sub>12</sub>(MeCN)<sub>2</sub>]<sup>0</sup> and [V<sub>6</sub>O<sub>6</sub>(OCH<sub>3</sub>)<sub>12</sub>]<sup>-</sup> with Isocyanide. With increasing concerns on the environmental impact of chemical pollutants, the activation of energy-poor, gaseous molecules using metal oxide surfaces has become one of the most important industrial processes for the production of energy-rich chemical fuels.<sup>1,3</sup> Computational investigations on RMO-catalyzed small-molecule activation have determined that substrate binding to defect sites at the surface of these materials is a critical step in catalysis.<sup>22</sup> However, while a mechanistic understanding is crucial for the design of improved catalysts, the electronic consequences of substrate coordination to oxygen-deficient sites during catalysis remains poorly understood. In previous work, we have demonstrated that the vacant POV-alkoxide cluster  $2\text{-}V_6O_6^{-}$  is able to activate molecular oxygen, resulting in the quantitative formation of  $1-V_6O_7^-$  via the restoration of an O atom into the vacant site.<sup>16</sup> As such, we hypothesized that the mono- and divacant clusters could be used to model substrate binding at defect sites on heterogeneous surfaces, providing a means to explore the consequences of altering the metal-to-oxygen ratios on the reactivity of reduced V<sup>III</sup> centers.

The activation of CO by metal oxide supports is a wellestablished heterogeneous transformation used to mediate the emission of this toxic environmental contaminant.<sup>32,33</sup> We therefore began modeling substrate binding on bulk materials with the addition of an electron-rich carbon monoxide analogue, *tert*-butyl isocyanide (CN<sup>t</sup>Bu), to the divacant cluster. Treatment of **5-V<sub>6</sub>O<sub>5</sub><sup>0</sup>** with 2 equiv CN<sup>t</sup>Bu results in isolation of the desired product  $[V_6O_5(OCH_3)_{12}(CN^tBu)_2]^0$ 

## Scheme 2. Synthesis of $7\text{-}V_6O_6(CN^tBu)_2^0$ and $8\text{-}V_6O_6(CN^tBu)^-$



 $[7-V_6O_5(CN^tBu)_2^0]$  in excellent yield (Scheme 2, 91%). The <sup>1</sup>H NMR spectrum of complex 7- $V_6O_5(CN^tBu)_2^0$  is composed of five broad paramagnetic resonances that are slightly shifted from the parent cluster  $5-V_6O_5^0$  (Figure S14). Notably, we were not able to observe a sixth resonance assigned to the isonitrile *tert*-butyl moiety, likely because of fluxional coordination of this ligand in solution.

Analysis of the IR spectrum of 7-V<sub>6</sub>O<sub>5</sub>(CN<sup>t</sup>Bu)<sub>2</sub><sup>0</sup> reveals a new feature at 2195 cm<sup>-1</sup>, corresponding to  $\nu$ (C $\equiv$ N) of the isonitrile ligands bound to the site-differentiated V<sup>III</sup> ions (Figures 6 and S15). This value is substantially shifted from that of free CN<sup>t</sup>Bu (2133 cm<sup>-1</sup>), consistent with coordination of the substrate to the coordinatively unsaturated, electron-rich V<sup>III</sup> ion.<sup>34</sup> Indeed, the observed shift in  $\nu$ (C $\equiv$ N) resembles



Figure 6. IR spectra of  $CN^{t}Bu$ ,  $7-V_{6}O_{5}(CN^{t}Bu)_{2}^{0}$ , and  $8-V_{6}O_{6}(CN^{t}Bu)^{-}$ .

values reported for isonitrile ligands bound to other low-valent V ions, ranging from 2150 to 2200 cm<sup>-1.35</sup> Further analysis of the IR spectrum of  $7-V_6O_5(CN^tBu)_2^0$  reveals the characteristic  $\nu(V{=}O_t)$  and  $\nu(O_b{-}CH_3)$  vibrational modes observed in Lindqvist POV-alkoxide clusters (968 and 1049  $cm^{-1}$ , respectively; Figures 6 and S15). These values closely resemble those of complex  $5 - V_6 O_5^{0}$  (964 and 1038 cm<sup>-1</sup>), indicating retention of the structural integrity of the POV-alkoxide ensemble upon coordination of the isonitrile ligands. Likewise, the negligible shifts in both bands indicate limited changes in the electronic structure of the vanadyl core upon substrate coordination. Further support for this observation can be made through analysis of the electronic absorption spectrum of 7- $V_6O_5(CN^tBu)_2^0$ , which reveals no significant changes in the absorption features, following the addition of CN<sup>t</sup>Bu (Figure S16).

Likewise, we investigated the reactivity of CN<sup>t</sup>Bu with a monovacant cluster. In comparing the electrochemical profile of the mono- and divacant molecules, we observed that the electronic structure of  $5-V_6O_5^{0}$  resembles that of the *anionic* monovacant cluster,  $2-V_6O_6^{1-}$ , in that both are the mosir reduced state of the cluster  $(2-V_6O_6^{-}, V^{IV}_5V^{III}; 5-V_6O_5^{0}, V^{IV}_4V^{III}_2)$ .<sup>16</sup> Furthermore, challenges in isolating  $6-V_6O_6^{0}$  in appreciable amounts prompted the use of complex  $2-V_6O_6^-$  as the monovacant starting material. The addition of 1 equiv of  $CN^{t}Bu$  to  $2-V_{6}O_{6}^{-}$  resulted in isolation of the desired product  $[V_6O_6(OCH_3)_{12}(CN^tBu)]^-$  (8-V<sub>6</sub>O<sub>6</sub>(CN<sup>t</sup>Bu)<sup>-</sup>) in quantitative yield (Scheme 2, 98%). Analysis of the product by <sup>1</sup>H NMR spectroscopy reveals slight shifts of the three paramagnetic resonances observed in complex  $2-V_6O_6^-$ , indicating retention of the charge state of the Lindqvist core (Figure S17). These shifts in the paramagnetic signals are consistent with changes in the <sup>1</sup>H NMR spectrum observed upon the formation of  $7-V_6O_5(CN^tBu)$ , suggesting analogous isocyanide coordination to the anionic monovacant cluster. Further support for formation of the desired product was garnered via ESI-MS (positive mode), which revealed the presence of a new parent ion peak that corresponds to  $8-V_6O_6(CN^tBu)^ (m/z \ 921; \ 8-V_6O_6(CN^tBu)^- + Na + CH_3CN; Figure \ S18).$ 

The electronic consequences of substrate coordination to the surface defect site were evaluated using IR and electronic absorption spectroscopies. The IR spectrum of 8- $V_6O_6(CN^tBu)^-$  revealed, once again, no changes in the energies of the  $\nu(V=O_t)$  and  $\nu(O_b-CH_3)$  vibrational modes (951 and 1051 cm<sup>-1</sup>, respectively) from that of the starting material  $2 \cdot V_6 O_6^-$  (951 and 1047 cm<sup>-1</sup>, respectively; Figure \$15).<sup>16</sup> The lack of shifts observed in these transitions suggests a similar distribution of oxidation states of vanadyl ions following coordination of the isonitrile moiety at the sitedifferentiated V<sup>III</sup> ion. This is analogous to the observed lack of change in the electronic structure of the Lindqvist core upon coordination of two isonitrile entities in the case of 7- $V_6O_5(CN^tBu)_2^0$ . In addition to the vanadyl-based stretching frequencies, the IR spectrum of  $8-V_6O_6(CN^tBu)^-$  possesses a new transition located at 2189 cm<sup>-1</sup>, which was assigned to  $\nu(C \equiv N)$  of the new isonitrile ligand (Figure 6). Electronic absorption spectroscopy was used to further confirm the oxidation state distribution of complex  $8-V_6O_6(CN^tBu)^-$ . A comparison of the spectrum of the isonitrile-bound POValkoxide cluster to that of  $2\text{-}V_6O_6^-$  revealed no noticeable changes, indicating retention of the oxidation state distribution of the V ions  $(V_{5}^{IV}V_{5}^{III}; Figure S16)$ .

CV of the isonitrile-coordinated complexes  $(7-V_6O_5(CN^tBu)_2^0 \text{ and } 8-V_6O_6(CN^tBu)^-)$  was used to explore the electronic consequences of binding CN<sup>t</sup>Bu to the reduced V<sup>III</sup> center (Figure 7). In the case of the monovacant cluster,



**Figure 7.** Cyclic voltammograms of complexes  $2-V_6O_6^-$  (dark blue, solid),  $5-V_6O_5^0$  (red, solid),  $7-V_6O_5(CN^tBu)_2^0$  (orange, dashed), and  $8-V_6O_6(CN^tBu)^-$  (light blue, dashed) collected in DCM with 0.1 M [<sup>n</sup>Bu<sub>4</sub>N][PF<sub>6</sub>] as the supporting electrolyte.

the CV curve of the hexavanadate assembly following substrate coordination  $[8-V_6O_6(CN^tBu)^-]$  in dichloromethane (DCM) contains three quasi-reversible redox events, shifted anodically by ~0.10 V relative to the respective parent cluster. However, in the case of complex  $7-V_6O_5(CN^tBu)_2^{0}$ , in addition to a slight shift in the redox potential (~0.05 V), a third reversible electrochemical event was observed for the cluster upon coordination of isonitrile (+0.92 V). We justify the appearance of this more-oxidizing redox event as a result of stabilization of the cluster core in higher oxidation states due to the strong  $\sigma$ -donating properties of the two CN<sup>t</sup>Bu ligands.

Next, we examined the redox profile of  $7 \cdot V_6 O_5 (CN^t Bu)_2^0$  in DCM to study substrate coordination to the multivacant model. The CV spectrum of the parent cluster  $5-V_6O_5^{0}$ contains two quasi-reversible redox events centered at -0.305 and 0.256 V (vs Fc/Fc<sup>+</sup>). Similar redox events are observed in the electrochemical profile of 7-V<sub>6</sub>O<sub>5</sub>(CN<sup>t</sup>Bu)<sub>2</sub><sup>0</sup>, albeit shifted anodically by  $\sim 0.1$  V. These slight shifts are consistent with changes in the electrochemical profile observed in 8-V<sub>6</sub>O<sub>6</sub>(CN<sup>t</sup>Bu)<sup>-</sup> (vide supra). However, unlike the cyclic voltammogram of complex 8-V<sub>6</sub>O<sub>6</sub>(CN<sup>t</sup>Bu)<sup>-</sup>, the appearance of an *additional* oxidizing event, located at  $E_{1/2} = 0.9164$  V (vs  $Fc/Fc^+$ ), marks a notable change in the electrochemical profile of  $7 \cdot V_6 O_5 (CN^t Bu)_2^0$ . This surprising result suggests that the addition of two electron-rich CN<sup>t</sup>Bu ligands to the cis-V<sup>III</sup> sites of the molecular model results in the cooperative stabilization of higher oxidation state distributions of the polynuclear core.

#### CONCLUSION

In this work, we have demonstrated the selective formation of neutral mono- and divacant POV–alkoxide clusters. The formation of O-atom vacancies was found to be dependent on the number of available  $V^{V}$  ions in the hexavandate starting materials (e.g.,  $1-V_6O_7^-$  and  $4-V_6O_7^0$ ). This work presents an unprecedented route to controlling metal-to-oxygen ratios on Lindqvist POM clusters. The IR and electronic absorption

spectroscopies, as well as CV, established the retention of a high degree of electron delocalization following the formation of reduced V<sup>III</sup> centers. This is a significant result in light of the semiconducting properties of many RMO materials. Additionally, coordination of a carbon monoxide analogue, *tert*-butyl isocyanide, provides insight into the electronic consequences of substrate binding at these surface vacant sites in materials. Future work investigating POV–alkoxide clusters as molecular models for heterogeneous catalysts will expand upon probing the role of surface defects in small-molecule activation processes and is currently underway in our laboratory.

#### EXPERIMENTAL SECTION

**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 ovendried for a minimum of 3 h and cooled in an evacuated antechamber prior to use in the drybox. Unless otherwise noted, 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. [ $^{n}Bu_{4}N$ ]-[ $V_{6}O_{7}(OCH_{3})_{12}$ ]<sup>-</sup> ( $1-V_{6}O_{7}^{-}$ ),<sup>20</sup> [ $^{n}Bu_{4}N$ ]<sub>2</sub>[ $V_{6}O_{7}(OCH_{3})_{12}$ ]<sup>2-</sup> ( $3-V_{6}O_{7}^{-2}$ ),<sup>18</sup> [ $V_{6}O_{7}(OCH_{3})_{12}$ ]<sup>0</sup> ( $4-V_{6}O_{7}^{-0}$ ),<sup>18</sup> [ $^{n}Bu_{4}N$ ]-[ $V_{6}O_{6}(OCH_{3})_{12}$ ] ( $2-V_{6}O_{6}^{-}$ ),<sup>16</sup> [ $V_{6}O_{6}(OCH_{3})_{12}(OTf)$ ],<sup>16</sup> and V-(Mes)<sub>3</sub>(THF)<sup>40</sup> were prepared according to published procedures. Ferrocenium tetrafluoroborate was purchased from Sigma-Aldrich and used as received. Celite 545 (J. T. Baker) was dried in a Schlenk flask for 48 h under vacuum while heating to at least 150 °C prior to use in the glovebox. *tert*-Butyl isocyanide was purchased from Sigma-Aldrich and used as received.

<sup>1</sup>H NMR spectra were recorded at 500 and 400 MHz on Bruker DPX-500 and DPX-400 MHz spectrometers locked on the signal of deuterated solvents. All chemical shifts were reported relative to the peak of the residual H signal in deuterated solvents. CD<sub>3</sub>CN was purchased from Cambridge Isotope Laboratories, degassed by three freeze-pump-thaw cycles, and stored over fully activated 3 Å molecular sieves. IR [Fourier transform infrared (FT-IR) and attenuated total reflectance (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 MeCN in a sealed 1 cm quartz cuvette with an Agilent Cary 60 UV-vis spectrophotometer. Mass spectrometry analyses were performed on an Advion Expression<sup>L</sup> 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 MeCN. CV 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 glassy carbon ( $\emptyset = 3.0 \text{ mm}$ ) as the working electrode (CH Instruments, USA), a Pt wire as the counter electrode (CH Instruments, USA), and an Ag/Ag<sup>+</sup> nonaqueous reference electrode with 0.01 M AgNO<sub>3</sub> in 0.05 M [<sup>n</sup>Bu<sub>4</sub>N][PF<sub>6</sub>] in MeCN (BASi, USA). All electrochemical measurements were performed at room temperature in a N2-filled glovebox. Dry DCM that contained 0.1 M  $[^{n}Bu_{4}N][PF_{6}]$  was used as the electrolyte solution.

Single crystals of  $5-V_6O_5^{0}$  and  $6-V_6O_6^{0}$  were mounted on the tip of a thin glass optical fiber (goniometer head) and mounted on a XtaLab Synergy-S dual-flex diffractometer equipped with a HyPix-6000HE HPC area detector for data collection at 100.00(10) K. The structure was solved using *SHELXT-2018*/2<sup>41</sup> and refined using *SHELXL-2018/3.*<sup>42</sup> Elemental analyses were performed on a PerkinElmer 2400 series II analyzer, at the CENTC Elemental Analysis Facility, University of Rochester, Rochester. NY.

Synthesis of  $[V_6O_5(OCH_3)_{12}(MeCN)_2]$  (5- $V_6O_5^0$ ). In a glovebox, a 20 mL scintillation vial was charged with 4- $V_6O_7^0$  (0.050 g, 0.063 mmol) and 5 mL of THF. V(Mes)<sub>3</sub>(THF) (0.067 g, 0.139 mmol, 2.2 equiv) in 4 mL of THF was added dropwise to the solution with stirring. The color of the mixture immediately changed from green to red-brown. The reaction was stirred for an additional 1 h to ensure completion, after which the solvent was removed under reduced pressure to yield a red solid. The residue was stirred in diethyl ether (10 mL) for 30 min and then filtered over a bed of Celite (2 cm) to give a red/black solid. The red/black solid was continuously washed with diethyl ether until the filtrate ran clear, ensuring complete removal of the byproduct OV(Mes)<sub>3</sub>. The solid was then extracted with THF (5 mL  $\times$  3), and any volatiles were removed under vacuum to yield the product  $5 \cdot V_6 O_5^{0}$  as a red solid (90%). Crystals suitable for X-ray analysis were grown from the slow diffusion of diethyl ether into a concentrated solution of the product in THF. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN): δ 85.31, 27.10, 25.86, -1.80, -6.76, -22.46. FT-IR (ATR, cm<sup>-1</sup>): 1038 (O-CH<sub>3</sub>), 964 (V=O). UV-vis (CH<sub>3</sub>CN): 524 nm ( $\varepsilon$  = 468 M<sup>-1</sup> cm<sup>-1</sup>). Elem anal. Calcd for  $V_6O_{17}C_{16}H_{42}N_2 \cdot \frac{1}{4}C_4H_8O$  (MW = 858.17 g mol<sup>-1</sup>) : C, 23.79; H, 5.17; N, 3.26. Found: C, 23.63; H, 4.87; N, 3.11. Note: Crystals used for X-ray analysis were crushed up and dried under vacuum and subsequently submitted for elemental analysis.

Synthesis of  $[V_6O_6(OCH_3)_{12}(MeCN)]$  (6- $V_6O_6^0$ ). Method A. In a glovebox, a 20 mL scintillation vial was charged with  $4-V_6O_7^{0}$  (0.0602) g, 0.0762 mmol) and 6 mL of THF. V(Mes<sub>3</sub>)(THF) (0.0370 g, 0.0765 mmol, 1 equiv) in 4 mL of THF was added dropwise to the solution with stirring. The color of the mixture immediately changed from green to red-brown. The reaction was stirred for 2 h, after which the solvent was removed under reduced pressure to yield a brown solid. The residue was stirred in diethyl ether (10 mL) overnight and then filtered over a bed of Celite (2 cm) to give a brown solid. The solid was continuously washed with diethyl ether until the filtrate ran clear, ensuring complete removal of the byproduct OV(Mes)<sub>3</sub>. The solid was then extracted with THF (5 mL  $\times$  3), and any volatiles were removed under vacuum to yield a mixture of  $6-V_6O_6^{0}$  and  $5-V_6O_5^{0}$ . <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN): δ 25.44, 18.27, -12.69. FT-IR (ATR, cm<sup>-1</sup>): 1030 (O-CH<sub>2</sub>), 968 (V=O). UV-vis (CH<sub>2</sub>CN): 394 nm (ε = 2766 M<sup>-1</sup> cm<sup>-1</sup>), 530 nm ( $\varepsilon$  = 891 M<sup>-1</sup> cm<sup>-1</sup>), 998 nm ( $\varepsilon$  = 450 M<sup>-1</sup> cm<sup>-1</sup>). Elem anal. Calcd for V<sub>6</sub>O<sub>18</sub>C<sub>14</sub>H<sub>39</sub>N·<sup>1</sup>/<sub>4</sub>C<sub>4</sub>H<sub>8</sub>O (MW = 833.12 g mol-1): C, 21.62; H, 4.96; N, 1.68. Found: C, 21.81; H, 4.62; N, 1.38. Note: Crystals used for X-ray analysis were crushed up and dried under vacuum and subsequently submitted for elemental analysis.

Method B. In a glovebox, a 20 mL scintillation vial was charged with  $2 \cdot V_6 O_6^-$  (0.0501 g, 0.0493 mmol), FcBF<sub>4</sub> (0.0139 g, 0.0509 mmol, 1 equiv), and 6 mL of MeCN. The reaction was stirred for 3 h, after which the solvent was removed under reduced pressure to yield a brown solid. The solid was stirred in pentane (10 mL) for 30 min. The solid was then filtered and continuously washed with pentane until the filtrate ran clear. The solid was then extracted with DCM, and any volatiles were removed under vacuum to yield a mixture of 6- $V_6O_6^0$  and [<sup>n</sup>Bu<sub>4</sub>N][BF<sub>4</sub>]. Crystals suitable for X-ray analysis were grown from the slow diffusion of pentane into a concentrated solution of the product in THF. Note: Elemental analysis on this sample was not performed because of our inability to separate the tetrabutylammonium tetrafluoroborate salt from compound  $6 \cdot V_6O_6^0$ .

Synthesis of  $[V_6O_5(OCH_3)_{12}(CNC(CH_3)_3)_2]$   $[7-V_6O_5(CN^tBu)_2^0]$ . In a glovebox, a 15 mL pressure vessel was charged with 5- $V_6O_5^0$  (0.050 g, 0.060 mmol) and 5 mL of DCM. *tert*-Butyl isocyanide (15  $\mu$ L, 0.133 mmol, 2.2 equiv) was added to the solution with stirring. The reaction was stirred for 2 h at 70 °C, after which the solvent was removed under reduced pressure to yield a red solid. The residue was stirred in pentane (10 mL) for 30 min and then filtered over a bed of Celite (2 cm) to give a red solid. The solid was washed with 10 mL of pentane to remove any unreacted *tert*-butyl isocyanide. The solid was then extracted with DCM (5 mL × 3), and any volatiles were removed under vacuum to yield the product 7- $V_6O_5(CN^tBu)_2^0$  as a red solid (0.060 g, 0.066 mmol, 91%). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  27.20, 25.96, -1.11, -6.75, -19.69. FT-IR (ATR, cm<sup>-1</sup>): 2195 (C $\equiv$ N), 1049 (O-CH<sub>3</sub>), 968 (V=O). UV-vis (CH<sub>3</sub>CN): 532 nm ( $\varepsilon$  = 1871 M<sup>-1</sup> cm<sup>-1</sup>). Elem anal. Calcd for  $V_6O_{17}C_{22}H_{54}N_2\cdot^1/_4C_4H_8O~(MW$  = 942.33 g mol^-1): C, 29.32; H, 5.99; N, 2.97. Found: C, 29.40; H, 5.72; N, 2.66.

Synthesis of [ ${}^{n}Bu_{4}N$ ][ $V_{6}O_{6}(OCH_{3})_{12}(CNC(CH_{3})_{3}$ ]] (8- $V_{6}O_{6}(CN^{1}Bu)^{-}$ ). In a glovebox, a 15 mL pressure vessel was charged with 2- $V_{6}O_{6}^{-}$  (0.055 g, 0.0539 mmol) and 6 mL of DCM. *tert*-Butyl isocyanide (7.25  $\mu$ L, 0.0641 mmol, 1.2 equiv) was added to the solution with stirring. The reaction was stirred for 2 h, after which the solvent was removed under reduced pressure to yield 8- $V_{6}O_{6}(CN^{t}Bu)^{-}$  as a red solid (0.0579 g, 0.0527 mmol, 98%). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN):  $\delta$  25.41, 23.86, 3.07, 1.59, 1.35, 0.97, -15.87. FT-IR (ATR, cm<sup>-1</sup>): 2189 (C $\equiv$ N), 1051 (O-CH<sub>3</sub>), 951 (V $\equiv$ O). UV-vis (CH<sub>3</sub>CN): 430 nm ( $\varepsilon$  = 763 M<sup>-1</sup> cm<sup>-1</sup>), 522 nm ( $\varepsilon$ = 512 M<sup>-1</sup> cm<sup>-1</sup>). Elem anal. Calcd for  $V_{6}O_{18}C_{33}H_{81}N_{2}$ ·CH<sub>2</sub>Cl<sub>2</sub> (MW = 1184.58 g mol<sup>-1</sup>): C, 34.47; H, 7.06; N, 2.36. Found: C, 34.73; H, 7.11; N, 2.19.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00389.

<sup>1</sup>H NMR, ESI-MS (positive mode), UV–vis, and IR spectroscopic data for all complexes, crystallographic parameters of complexes  $5-V_6O_5^0$  and  $6-V_6O_6^0$ , BVS calculations of complex  $5-V_6O_5^0$ , and the diffusion parameters and electron-transfer rate constants for complexes  $4-V_6O_7^0$ ,  $5-V_6O_5^0$ , and  $6-V_6O_6^0$  (PDF)

#### **Accession Codes**

CCDC 1883474 and 1896509 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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B.E.P., A.A.F., and M.L.M. contributed to the experimental findings. All authors participated in data interpretation and analysis. The manuscript was written through contributions of B.E.P. and E.M.M. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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#### REFERENCES

(1) McFarland, E. W.; Metiu, H. Catalysis by doped oxides. *Chem. Rev.* **2013**, *113*, 4391–427.

(2) Lee, D. W.; Yoo, B. R. Advanced metal oxide (supported) catalysts: Synthesis and applications. J. Ind. Eng. Chem. 2014, 20, 3947–3959.

(3) Védrine, J. C. Heterogeneous catalysis on metal oxides. *Catalysts* **2017**, *7*, 341–366.

(4) Ruiz Puigdollers, A.; Schlexer, P.; Tosoni, S.; Pacchioni, G. Increasing oxide reducibility: the role of metal/oxide interfaces in the formation of oxygen vacancies. *ACS Catal.* **2017**, *7*, 6493–6513.

(5) Ek, M.; Ramasse, Q. M.; Arnarson, L.; Georg Moses, P.; Helveg, S. Visualizing atomic-scale redox dynamics in vanadium oxide-based catalysts. *Nat. Commun.* **2017**, *8*, 1–9.

(6) Lauhon, L. J.; Ho, W. Effects of temperature and other experimental variables on single molecule vibrational spectroscopy with the scanning tunneling microscope. *Rev. Sci. Instrum.* 2001, 72, 216–223.

(7) Bai, C. Scanning Tunneling Microscopy and Its Application, 2nd revised ed.; Shenghai Scientific & Technical Publishers: Shenghai, China, 2000; Vol. 2.

(8) Lapshin, R. V. Automatic drift elimination in probe microscope images based on techniques of counter-scanning and topography feature recognition. *Meas. Sci. Technol.* **2007**, *18*, 907–927.

(9) Marinello, F.; Balcon, M.; Schiavuta, P.; Carmignato, S.; Savio, E. Thermal drift study on different commercial scanning probe microscopes during the initial warming-up phase. *Meas. Sci. Technol.* **2011**, *22*, 094016.

(10) Diebold, U. The surface science of titanium dioxide. *Surf. Sci. Rep.* **2003**, *48*, 53–229.

(11) Hayashi, Y. Hetero and lacunary polyoxovanadate chemistry: Synthesis, reactivity and structural aspects. *Coord. Chem. Rev.* 2011, 255, 2270–2280.

(12) Wang, S. S.; Yang, G. Y. Recent advances in polyoxometalatecatalyzed reactions. *Chem. Rev.* **2015**, *115* (11), 4893–4962.

(13) Long, D. L.; Burkholder, E.; Cronin, L. Polyoxometalate clusters, nanostructures and materials: from self assembly to designer materials and devices. *Chem. Soc. Rev.* **2007**, *36*, 105–121.

(14) Yin, P.; Li, D.; Liu, T. Solution behaviors and self-assembly of polyoxometalates as models of macroions and amphiphilic polyoxometalate-organic hybrids as novel surfactants. *Chem. Soc. Rev.* **2012**, *41*, 7368–7383.

(15) Hutin, R.; Long, D.-L.; Cronin, L. Comprehensive Inorganic Chemistry II; Elsevier, 2013; Vol. 2.

(16) Petel, B. E.; Brennessel, W. W.; Matson, E. M. Oxygen-atom vacancy formation at polyoxovanadate clusters: homogeneous models for reducible metal oxides. *J. Am. Chem. Soc.* **2018**, *140*, 8424–8428. (17) Monakhov, K. Y.; Bensch, W.; Kögerler, P. Semimetal-functionalised polyoxovanadates. *Chem. Soc. Rev.* **2015**, *44*, 8443–8483.

(18) Spandl, J.; Daniel, C.; Brüdgam, I.; Hartl, H. Synthesis and structural characterization of redox active dodecamethoxoheptaoxohexavanadium clusters. *Angew. Chem., Int. Ed.* **2003**, *42*, 1163–1166. (19) Daniel, C.; Hartl, H. A mixed-valence  $V^{IV}/V^V$  alkoxopolyoxovanadium cluster series  $[V_6O_8(OCH_3)_{11}]^{n\pm}$  exploring the

influence of a  $\mu$ -Oxo ligand in a spin frustrated structure. J. Am. Chem. Soc. **2009**, 131, 5101–5114.

(20) Daniel, C.; Hartl, H. Neutral and cationic V<sup>IV</sup>/V<sup>V</sup> mixedvalence alkoxo-polyoxovanadium clusters  $[V_6O_7(OR)_{12}]^{n+}$  (R = – CH<sub>3</sub>–C<sub>2</sub>H<sub>5</sub>): structural, cyclovoltammetric and IR-spectroscopic investigations on mixed valency in a hexanuclear core. *J. Am. Chem. Soc.* **2005**, *127*, 13978–13987.

(21) VanGelder, L. E.; Kosswattaarachchi, A. M.; Forrestel, P. L.; Cook, T. R.; Matson, E. M. Polyoxovanadate-alkoxide clusters as multi-electron charge carriers for symmetric non-aqueous redox flow batteries. *Chem. Sci.* **2018**, *9*, 1692–1699.

(22) Mars, P.; van Krevelen, D. W. Oxidations carried out by means of vanadium oxide catalysts. *Chem. Eng. Sci.* **1954**, *3*, 41–59.

(23) Pan, X.; Yang, M.-Q.; Fu, X.; Zhang, N.; Xu, Y.-J. Defective TiO2 with oxygen vacancies: synthesis, properties and photocatalytic applications. *Nanoscale* **2013**, *5*, 3601–3614.

(24) Li, F.; Carpenter, S. H.; Higgins, R. F.; Hitt, M. G.; Brennessel, W. W.; Ferrier, M. G.; Cary, S. K.; Lezama-Pacheco, J. S.; Wright, J. T.; Stein, B. W.; Shores, M. P.; Kozimor, S. A.; Neidig, M. L.; Matson,

E. M. Polyoxovanadate-alkoxide clusters as a redox reservoir for iron. *Inorg. Chem.* **2017**, *56*, 7065–7080.

(25) Robin, M. B.; Day, P. Mixed Valence Chemistry—A Survey and Classification; World Scientific: New York, 1968; Vol. 10.

(26) Ortiz, M. E.; Núñez-Vergara, L. J.; Squella, J. A. Voltammetric determination of the heterogeneous charge transfer rate constant for superoxide formation at a glassy carbon electrode in aprotic medium. *J. Electroanal. Chem.* **2003**, *549*, 157–160.

(27) Liu, Q.; Shinkle, A. A.; Li, Y.; Monroe, C. W.; Thompson, L. T.; Sleightholme, A. E. S. Non-aqueous chromium acetylacetonate electrolyte for redox flow batteries. *Electrochem. Commun.* **2010**, *12*, 1634–1637.

(28) Sleightholme, A. E. S.; Shinkle, A. A.; Liu, Q.; Li, Y.; Monroe, C. W.; Thompson, L. T. Non-aqueous manganese acetylacetonate electrolyte for redox flow batteries. *J. Power Sources* **2011**, *196*, 5742–5745.

(29) Liu, Q.; Sleightholme, A. E. S.; Shinkle, A. A.; Li, Y.; Thompson, L. T. Non-aqueous vanadium acetylacetonate electrolyte for redox flow batteries. *Electrochem. Commun.* **2009**, *11*, 2312–2315. (30) Nicholson, R. S.; Shain, I. Theory of stationary electrode polarography. single scan and cyclic methods applied to reversible, irreversible, and kinetic Systems. *Anal. Chem.* **1964**, *36*, 706–723.

(31) Muhammad, H.; Tahiri, I. A.; Muhammad, M.; Masood, Z.; Versiani, M. A.; Khaliq, O.; Latif, M.; Hanif, M. A comprehensive heterogeneous electron transfer rate constant evaluation of dissolved oxygen in DMSO at glassy carbon electrode measured by different electrochemical methods. J. Electroanal. Chem. 2016, 775, 157–162.

(32) Nie, L.; Mei, D.; Xiong, H.; Peng, B.; Ren, Z.; Hernandez, X. I. P.; De La Riva, A.; Wang, M.; Engelhard, M. H.; Kovarik, L.; Datye, A. K.; Wang, Y. Activation of surface lattice oxygen in single-atom Pt/ CeO<sub>2</sub> for low-temperature CO oxidation. *Science* **2017**, *358*, 1419–1423.

(33) Cheng, T.; Xiao, H.; Goddard, W. A. Nature of the active sites for CO reduction on copper nanoparticles; suggestions for optimizing performance. *J. Am. Chem. Soc.* **2017**, *139*, 11642–11645.

(34) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley-Interscience: Hoboken, NJ, 2005.

(35) Silverman, L. D.; Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. Molecular structure and ligand-exchange reactions of trichlorotris(tert-butyl isocyanide)vanadium(III). Synthesis of the hexakis(tert-butyl isocyanide)vanadium(II) cation. *Inorg. Chem.* **1980**, *19*, 3379–3383.

(36) Meyer, R. L.; Brennessel, W. W.; Matson, E. M. Synthesis of a gallium-functionalized polyoxovanadate-alkoxide cluster: Toward a general route for heterometal installation. *Polyhedron* **2018**, *156*, 303–311.

(37) VanGelder, L. E.; Brennessel, W. W.; Matson, E. M. Tuning the redox profiles of polyoxovanadate-alkoxide clusters via heterometal installation: toward designer redox reagents. *Dalton Trans.* **2018**, *47*, 3698–3704.

(38) Li, F.; VanGelder, L. E.; Brennessel, W. W.; Matson, E. M. Selfassembled, iron-functionalized polyoxovanadate alkoxide clusters. *Inorg. Chem.* **2016**, *55*, 7332–7334.

(39) Zhang, T.; Sole-Daura, A.; Hostachy, S.; Blanchard, S.; Paris, C.; Li, Y.; Carbo, J. J.; Poblet, J. M.; Proust, A.; Guillemot, G. Modeling the oxygen vacancy at a molecular vanadium(III) silicasupported catalyst. J. Am. Chem. Soc. **2018**, 140, 14903–14914.

(40) Hamaed, A.; Mai, H. V.; Hoang, T. K. A.; Trudeau, M.; Antonelli, D. Functionalized porous silicas with unsaturated early transition metal moieties as hydrogen storage materials: comparison of metal and oxidation state. J. Phys. Chem. C 2010, 114, 8651–8660.

(41) Sheldrick, G. M. SHELXT, version 2018/2. Acta Crystallogr., Sect. A: Found. Adv. 2015, 71, 3–8.

(42) Sheldrick, G. M. SHELXL, version 2018/3. Acta Crystallogr. 2015, C71, 3-8.