Mechanistic insights into polyoxometalate self-assembly in organic solvent: Conversion of a cyclic polyoxovanadate-ethoxide to its Lindqvist congener

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Mechanistic insights into polyoxometalate self-assembly in organic solvent: Conversion of a cyclic polyoxovanadate-ethoxide to its Lindqvist congener

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We report the synthesis of a cyclic hexavanadate polyoxovanadate-alkoxide cluster, $[VO(OC_2H_5)_2]_6$, and its conversion, under solvothermal conditions, to an oxygen-deficient Lindqvist assembly, $[V_6O_6(OC_2H_5)_{12}]^n$ (n = 1–, 0). This study presents insights into the mechanism of organo-functionalized polyoxovandate-alkoxide formation, namely identifying essential intermediates and the source of the central μ_6-O^{2-} ligand.

Developing synthetic methods to precisely control the topology of polyoxometalates (POMs) would allow for targeting clusters with specific optical, magnetic, electrochemical, and catalytic properties.[1-3] Unfortunately, the majority of reported syntheses of these molecular metal oxide assemblies rely on serendipitous self-assembly processes. Few studies have focused on the underlying mechanisms that drive the formation of POM architectures,[4-14] rendering predictable and reproducible syntheses for these clusters a challenge for the field. The formation of polyoxovanadates (POVs) are of particular interest, as the structural and redox flexibility of vanadium makes the product distributions from these reactions difficult to predict and control.[8, 15-16] While a handful of investigations have probed the role of pH-dependant hydrolysis in the aggregation of monomeric vanadium precursors,[5-6, 17-19] similar studies investigating the formation of POVs in organic solvent have not been performed. This dearth of knowledge renders the development of synthetic methodologies for organofunctionalized POV clusters particularly conspicuous.

Polyoxovanadate-alkoxide (POV-alkoxide) clusters have emerged as an important class of metal oxide assemblies in recent years due to their unique physicochemical properties (Figure 1).[20-25] However, the solvothermal self-assembly of these mixed-valent assemblies has thus far prevented the application of general functionalization procedures to rationally

tune their properties. Furthermore, the "black box" nature of solvothermal reaction conditions, coupled with the paramagnetism of the intermediates and products, complicates mechanistic studies.

One method that has proven broadly successful for gaining insight into the mechanism of POM formation is the alteration of reaction conditions to isolate kinetic products that could be potential intermediates in the generation of the final, thermodynamically-stable cluster.[4, 9] In line with this research strategy, we have initiated a series of investigations studying POV cluster formation at low temperatures. Previously, our research group has reported the formation of a cyclic, chloride-

Previously Reported Syntheses of POV-alkoxide Clusters

$[V_6O_6(OC_2H_5)_{12}]^n$
Hartl (2003)

$\{[VO(OCH_3)_2]_6Cl\}^{1-}$
Matson (2019)
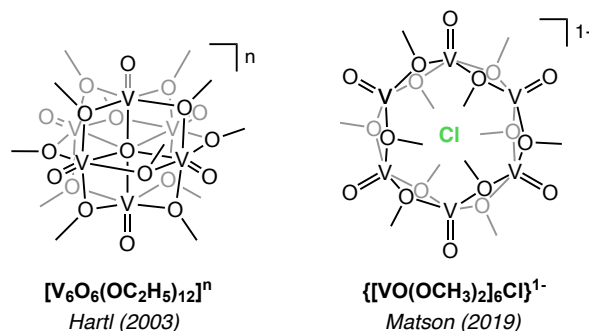
This Work: Mechanistic Insight into Formation of Lindqvist Assembly via Isolation of Cyclic Hexavanadate Cluster
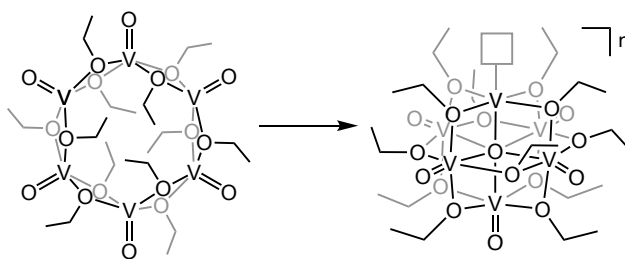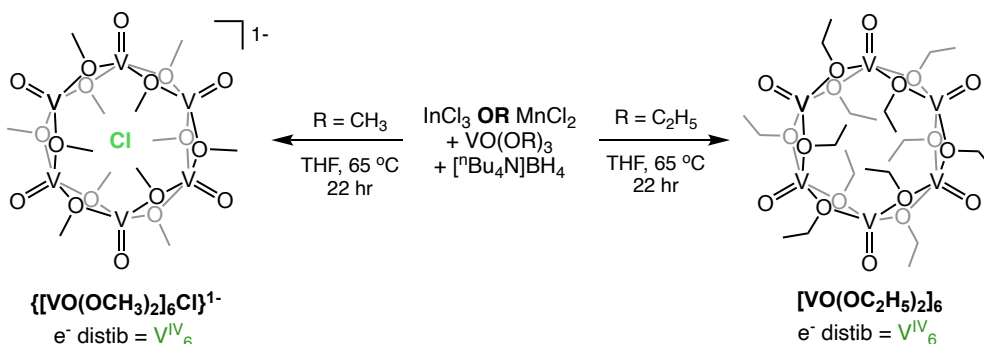
Figure 1. Previous examples of self-assembled POV-alkoxide clusters.[20, 26] The current study highlights kinetic and thermodynamic products of cluster formation, that shed light into the mechanism of self-assembly of POV-alkoxide clusters.

Scheme 1. Synthesis of cyclic clusters **{[VO(OCH₃)₂]₆Cl}¹⁻** and **[VO(OC₂H₅)₂]₆**.

{[VO(OCH₃)₂]₆Cl}¹⁻
e⁻ distib = V^{IV}₆

[VO(OC₂H₅)₂]₆
e⁻ distib = V^{IV}₆

templated, POV-methoxide cluster, [ⁿBu₄N]{[VO(OCH₃)₂]₆Cl} (Figure 1, **{[VO(OCH₃)₂]₆Cl}¹⁻**),[26] generated at low temperatures and pressures. Given the molecular composition of this cluster, we postulated that the arrangement of the six vanadyl moieties may serve as an intermediate in the formation of Lindqvist assemblies. However, the chloride ion embedded within the centre of this cluster rendered the elemental composition of the product of solvothermal synthesis a concern. Thus, we opted to expand our library of cyclic POV assemblies to ethoxide congeners, driven by the hypothesis that the increased length of the alkoxide ligands would alter the favourability of chloride intercalation in the cyclic assembly.

Using the reactions conditions optimized for the **{[VO(OCH₃)₂]₆Cl}¹⁻** synthesis as a starting point, one equivalent of InCl₃ was reacted with five equivalents of VO(OC₂H₅)₃ and one equivalent of [ⁿBu₄N]BH₄ in tetrahydrofuran (Scheme 1). Unlike the methoxide cluster, which precipitates from the reaction mixture as a blue solid, the analogous reaction using VO(OC₂H₅)₃ as a starting material resulted in a homogeneous brown solution. Following work-up, a bright, blue solid, similar in colour to **{[VO(OCH₃)₂]₆Cl}¹⁻**, was isolated. Notably, the solubilities of the resultant precipitant and complex **{[VO(OCH₃)₂]₆Cl}¹⁻** are drastically different; whereas the ethoxide product is readily soluble in dichloromethane and insoluble in acetonitrile, the inverse was noted for **{[VO(OCH₃)₂]₆Cl}¹⁻**. The observed decrease in solubility of the ethoxide derivative in polar organic solvents could be a result of the longer alkyl chains on the bridging alkoxides, consistent with changes in the physicochemical properties of POV-alkoxide clusters reported previously by our group.[24-25] Alternatively, this change in solubility could arise from the absence of the central chloride ion, rendering the cluster neutral in its overall charge.

To gain a better understanding of the chemical composition of the ethoxide product, electrospray-ionization mass-spectrometry (ESI-MS) and ¹H NMR spectroscopy were performed on the isolated blue solid. Interestingly, in contrast to its chloride-template methoxide-bridge congener, no cluster signals were observed in the ESI-MS, suggesting the product is neutral in charge and challenging to ionize. This supposition is further supported by the absence of signals for a tetrabutylammonium cation in the ¹H NMR spectrum (CDCl₃, Figure S1). Two broad resonances located at 4.49 and -0.88 ppm were observed in the ¹H NMR spectrum, which were assigned to the -CH₂- and -CH₃ hydrogens of the bridging ethoxides

ligands, respectively. This two-signal pattern in the ¹H NMR spectrum indicates that the cluster is highly symmetric, with all ethoxide groups chemically equivalent to one another.

To unambiguously determine the molecular structure of the ethoxide cluster, crystals suitable for single crystal X-ray analysis were grown from a concentrated dichloromethane solution at −30 °C (Figure 2, Table S1). Refinement of the data revealed a cyclic structure composed of six "[VO(OC₂H₅)₂]" subunits, similar to that reported for its methoxide congener.[26] Notably, the cyclic POV-ethoxide cluster, **[VO(OC₂H₅)₂]₆**, does not contain a guest-anion. This structural variation matches the observations noted during the cluster purification (*vide supra*). The **[VO(OC₂H₅)₂]₆** cluster co-crystallized with solvent that could not be identified *via* structural analysis; however, elemental analysis and the presence of dichloromethane in the ¹H NMR spectrum (Figure S1) suggest that this solvent is likely dichloromethane. Bond valence sum calculations revealed an oxidation state distribution of [V^{IV}₆] for the cluster (Table S2), similar to that of **{[VO(OCH₃)₂]₆Cl}¹⁻**. Additionally, the presence of low intensity, V^{IV} d-d transition in the electronic absorption spectrum of (VO)₆(OC₂H₅)₁₂, and the similar energies of the v(V=Oₜ) transition in the infrared spectra of the methoxide and ethoxide clusters, confirm the isovalent V^{IV} electronic structure of the ethoxide species (Figure S2).

As mentioned above, a major difference between the ethoxide and methoxide cyclic structures is the absence of a chloride ion encapsulated in the centre of the ethoxide species. Previous studies exploring the synthesis of **{[VO(OCH₃)₂]₆Cl}¹⁻**,[26]

top view
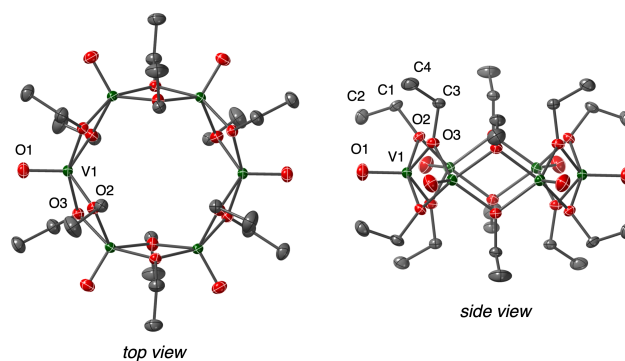
side view

Figure 2. Molecular structure of [VO(OC₂H₅)₂]₆ shown with 50% probability ellipsoid (top and side view). Hydrogen atoms have been omitted for clarity.
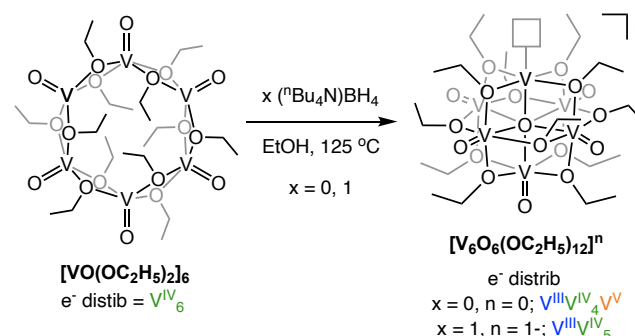
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and other chloride-containing, POV assemblies, report that the anion is essential for their formation.[16, 27] The chloride interacts with open coordination sites of the vanadium centres and directs the condensation the POV to curve and surround the anion, resulting in the formation of closed three-dimensional structures. For this reason, we propose that a chloride ion similarly templates the formation of **[VO(OC$_2$H$_5$)$_2$]$_6$**. However, in the case of the cyclic POV-ethoxide cluster, the anion dissociates from the final structure.

Justification for this hypothesis can be obtained through crystallographic analysis: since the structures of **{[VO(OCH$_3$)$_2$]$_6$Cl}$^{1-}$** and **[VO(OC$_2$H$_5$)$_2$]$_6$** are almost identical, only subtle changes imparted by the bridging ethoxide ligands are required to overcome the low-energy barriers that keep the chloride ion in place. For instance, the increased steric bulk of the ethyl chains forces these groups to point away from the centre of the **[VO(OC$_2$H$_5$)$_2$]$_6$** cluster, thus providing a channel through which the anion can pass. In addition to these steric effects, the bridging alkoxides could decrease the electrophilicity of the V^{IV} centres, which would in turn weaken the Lewis acid-base interaction between the POV ring and the nucleophilic chloride ion. A similar inductive effect was also observed in the Lindqvist POV-alkoxides, V$_6$O$_7$(OR)$_{12}$ (R = CH$_3$ or C$_2$H$_5$), where the slight increase in the partial negative charge on the ethoxide groups imparted oxidative stability to the overall V$_6$O$_7$(OC$_2$H$_5$)$_{12}$ cluster.[22, 24]

Unfortunately, only an 8 % yield resulted from the **[VO(OC$_2$H$_5$)$_2$]$_6$** synthesis with InCl$_3$. There is literature precedent suggesting that additional reducing equivalents are necessary to drive cluster formation in the ethoxide-bridged POVs.[22] As such, to achieve a better yield from our reductive polymerization reaction, we tried exchanging InCl$_3$ for a redox-active metal. The tetrahydrofuran adduct of MnCl$_2$ was selected due to the rich redox chemistry of manganese and the similarity of the ionic radii of Mn^{II} and In^{III} (0.83 and 0.80, respectively).[28] Following optimization of reaction conditions, we found that heating of two equivalents of the Mn^{II} salt with five equivalents of VO(OC$_2$H$_5$)$_3$ and one equivalent of [^{n}Bu$_4$N]BH$_4$ in tetrahydrofuran improved the yield of the cyclic POV-ethoxide cluster (28 %).

With complex **[VO(OC$_2$H$_5$)$_2$]$_6$** in hand, we turned to exploring the reactivity of the cyclic POV-ethoxide cluster. Specifically, the presence of six, low-valent vanadium ions held in close proximity by bridging ethoxide ligands suggested that **[VO(OC$_2$H$_5$)$_2$]$_6$** might be an intermediate formed *en route* to the plenary Lindqvist hexavanadate (e.g. V$_6$O$_7$(OC$_2$H$_5$)$_{12}$). To test this hypothesis, **[VO(OC$_2$H$_5$)$_2$]$_6$** was subjected to solvothermal conditions (ethanol, 125 °C, 18 h, Scheme 2). Under these conditions, a brown species was produced (41 %). The product was separated from unreacted starting material *via* extraction with acetonitrile. The six peaks in the ^{1}H NMR spectrum (three -CH$_2$-, three -CH$_3$) identified the product as the previously reported, oxygen-deficient, Lindqvist cluster, **[V$_6$O$_6$(OC$_2$H$_5$)$_{12}$]^0** (Figure S3).[29] The infrared spectrum of product also matches that of **[V$_6$O$_6$(OC$_2$H$_5$)$_{12}$]^0** (Figure S4), confirming both the structural change to the Lindqvist configuration and the oxidation state assignment as the neutral cluster.

Scheme 2. Conversion of the cyclic cluster, [VO(OC$_2$H$_5$)$_2$]$_6$, to the oxygen deficient POV-ethoxide cluster, [V$_6$O$_6$(OC$_2$H$_5$)$_{12}$]^n (n = 1–, 0).

[VO(OC$_2$H$_5$)$_2$]$_6$
e$^-$ distib = V^{IV}$_6$

[V$_6$O$_6$(OC$_2$H$_5$)$_{12}$]^n
e$^-$ distrib
x = 0, n = 0; V^{III}V^{IV}$_4$V^V
x = 1, n = 1-; V^{III}V^{IV}$_5$

The significant amount of unreacted starting material suggested that that the conversion from the cyclic cluster to its Lindqvist congener at temperatures relevant to previously reported POV-ethoxide formation is challenging. We postulated that this is due to the fact that the electronic structure of the mono-vacant, Lindqvist POV-ethoxide cluster has been shown to possess and oxidation state distribution of [V^{III}V^{IV}$_4$V^V].[29] The site-differentiation of a single vanadium ion caused by the conversion of a terminal oxo moiety to the μ_6-O^{2-} ligand requires reduction of a said metal (V^{IV} → V^{III}). In the absence of an external reductant, the generation of the V^{III} centre is achieved by the disproportionation of two of the V^{IV} ions to V^V and V^{III}. This electronic reorganization within the cluster, coupled to the structural rearrangement from edge-sharing square-pyramidal vanadate moieties to the corner-sharing octahedra in the Lindqvist motif, renders the conversion between the POV-alkoxides challenging.

To obviate the disproportionation step of this reaction, we explored the formation of the Lindqvist assembly in the presence of an external reductant. Indeed, addition of [^{n}Bu$_4$N]BH$_4$ to the solvothermal reaction resulted in complete consumption of the starting material and formation of a brown product within 3 h (quantitative yield, Scheme 2). ^{1}H NMR and ESI-MS analysis of the isolated solid confirmed the formation of the mono-anionic, oxygen deficient POV-ethoxide cluster, [^{n}Bu$_4$N][V$_6$O$_6$(OC$_2$H$_5$)$_{12}$] (**[V$_6$O$_6$(OC$_2$H$_5$)$_{12}$]$^{1-}$**, Figure S5-S6).[30] The improvement in yield and shortened reaction time confirms our hypothesis that eliminating disproportionation during conversion lowers the activation barrier for the formation of the Lindqvist product.

The formation of the cyclic hexavanadate cluster at low temperature suggests that this compound is a kinetic intermediate accessed in cluster formation. Subjecting this low-valent cyclic assembly to temperatures reported to result in self-assembly of Lindqvist-shaped POV-alkoxide clusters results in the conversion of **[VO(OC$_2$H$_5$)$_2$]$_6$** to **[V$_6$O$_6$(OC$_2$H$_5$)$_{12}$]$^{1-}$**, indicating that the Lindqvist species is the thermodynamically preferred product. This result is notable, given that mechanisms of POM formation have been predominantly focused on pH controlled hydrolysis pathways that are operative in aqueous solution.[4-8, 11] These types of condensation steps cannot be invoked in the self-assembly of POV-alkoxide clusters reported here in organic solvents in the absence of moisture. As such,

mapping of the POV-alkoxide speciation under various conditions will be necessary in studying these poorly understood aggregation pathways. Utilizing kinetic control to isolate intermediates in the formation of thermodynamically-stable POV-alkoxide clusters proves to be an effective method for elucidating critical steps that control the formation of various metal oxide assemblies.

Though a mechanism for the structural rearrangement of the hexavanadate-ethoxide species (e.g. rearrangement of the ring vs complete disassembly and reassembly, Figure S7) cannot be identified at this time, our results suggest that the generation and subsequent polymerization of $[V^{IV}O(OC_2H_5)_2]$ units under reducing conditions are important steps in the synthesis of Lindqvist POV-alkoxides. Additionally, the conserved elemental formula for the two POV clusters indicates that one of the terminal vanadyl oxygens in the cyclic structure is the source of the central μ_6-oxo in the Lindqvist form. The plenary, fully-oxygenated motif, $[V_6O_7(OC_2H_5)_{12}]^{1-}$, can subsequently be accessed through reaction of the oxygen-deficient POV-alkoxide with water or oxygen.[31]

In this work, we have described the synthesis of a cyclic hexavanadate-ethoxide cluster and its subsequent conversion to the Lindqvist form when subjected to higher temperatures. Future studies will focus on elucidating the mechanism of this transformation in the context of understanding the conditions that drive the formation of specific structures. Additionally, the **[VO(OC₂H₅)₂]₆** cluster will be used as a source of "$V^{IV}O(OC_2H_5)_2$" in attempts at assembling novel POV-ethoxide frameworks. As such, the cyclical hexavanadate reported here has the potential to expand both the variety of POV motifs and the knowledge base to develop methods for their rational design.

Conflicts of interest

There are no conflicts to declare.

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