Chapter 2

THE LINDQVIST HEXAVANADATE: A PLATFORM FOR COORDINATION-DIRECTED ASSEMBLY

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ABSTRACT

The $\{V_6O_{19}\}$ hexavanadate adopting the classical Lindqvist POM structure has emerged as the most appealing candidate in the chemistry of polyoxovanadates (POVs) for multiple functionalization and derivatization. Various structural functionalities can be introduced on the ligand scaffold of Lindqvist POV, eventually allowing to construct diverse coordination assemblies finding application in catalysis. This chapter gives an overview of the methods of stabilization of the elusive bare $\{V_6O_{19}\}$ structure by different capping moieties and substituents, illustrates the main synthetic strategies toward the formation of fully-oxidized $\{V^V_{6}\}$, mixed-valence $\{V^{V/IV}_{6}\}$, and “fully-reduced” $\{V^{IV}_{6}\}$ trisalkoxohexavanadates, describes bis-(trisalkoxo)hexavanadates obtained by post-functionalization reactions, and details their reactivity toward transition metal and lanthanoid complexes.
Keywords: Lindqvist structure, polyoxovanadates, alkoxide ligands, inorganic–organic hybrid compounds

ABBREVIATIONS

acac    Acetylacetonate
bmimpm  Bis(1-methylimidazol-2-yl)-4-methoxyphen-1-ylmethanol
bpdo    4,4’-bis(pyridine-N-dioxide)
calix    p-tert-butylcalix[4]arene
DCC     N,N-dicyclohexylcarbodiimide
DCM     Dichloromethane
DMA     N,N-dimethylacetamide
DMF     N,N-dimethylformamide
DMAP    4-dimethylaminopyridine
dpa     2,2’-dipyridine amine
Fc      Ferrocenyl
NaACN   Sodium acenaphthalide
POM     Polyoxometalate
POV     Polyoxovanadate
TBA     Tetrabutylammonium
TEA     Tetraethylammonium
TMA     Tetramethylammonium
TPP     Meso-tetraphenylporphyrin

1. INTRODUCTION

The chemistry of polyoxovanadates (hereafter referred to as POVs) is a rapidly growing area of research in polyoxometalate (POM) molecular science because of the potential applicability of these polynuclear molecular vanadium oxides as well as their multidimensional assemblies to a wide range of traditional and interdisciplinary fields [1-5]. The inorganic–organic hybrid compounds constructed on their basis are the target of today’s research paving the way for competitive molecular materials with tunable chemical, biochemical, and physical responses [6]. Contrary to many bare POVs, which usually self-assemble in pH-controlled condensation reactions and display a strong reluctance toward their covalent expansion by organic and
organometallic moieties, the hexavanadate structure (abbreviated as \{V_6\}) of the \{MoO_{19}\} skeletal type is easily functionalized and derivatized in organic solutions. This opportunity to modify the metal-oxide environment, extensively developed for Mo and, even more, W, allows to study the underlying coordination chemistry of covalently expanded POVs [7], opening the door to rational synthesis of this class of compounds and their versatile applications.

The hexametalate \{MoO_{19}\} structure is named after the distinguished Swedish chemist Ingvar Fritz Lindqvist (Figure 1a) and consists of six \{MO_6\} octahedra fused around one central \(\mu_6\)-O ligand through common vertices and polyhedral edges. Besides \(\mu_6\)-O, the structure exhibits twelve bridging \(\mu_2\)-O ligands and six terminal O ligands (Figure 1b). The Lindqvist POMs with M = Mo and W have been regarded as clathrate-like structures, in which the internal oxygen atom carries the whole negative charge and the metal-oxide shell is neutral [8]. The clathrate-like model was proposed considering the elongation and the lower covalency in the M–\(\mu_6\)-O bonds compared to the M–\(\mu_2\)-O ones [8, 9]. Furthermore, density functional theory (DFT) calculations showed that the \{MoO_{18}\} cage without the central \(\mu_6\)-O atom exhibits enhanced stability with respect to other \{Mo_{2}O_{6}\}_{m} (m = 1–13) clusters, which is an important feature taking into account its role as a “host” agent [10].

Figure 1. a) Photograph of Prof. Dr. Ingvar Fritz Lindqvist. Reproduced with permission from Prof. Dr. Ylda Lindqvist (Karolinska Institute, Sweden); b) The Lindqvist core structure \{MoO_{19}\} (M = Nb, Ta, Mo, and W) is shown in a combined ball-and-stick and polyhedral representation. Color code: O, red spheres; M, gray spheres; MO_6, light-orange octahedra.
The discovery of these hexametalate structures dates back to 1950 when Lindqvist proposed the existence of the highly symmetrical \{M_6O_{19}\} motif with idealized \(O_h\) symmetry in the framework of his doctoral thesis [11]. In 1953 Lindqvist reported the crystal structure of a niobate analogue \([NbV_6O_{19}]^8^-\) [12], and in 1954 together with Aronsson confirmed that the same topology is adopted by the hexatantalate \([TaV_6O_{19}]^8^-\) [13]. Later on, the \{M_6O_{19}\} core structure was also demonstrated for other hexametalates containing W and mixed-addenda atoms (for example, \([V_2W_4O_{19}]^{4+}\)) [14-16]. The high thermal stability and redox activity of many Lindqvist-type hexametalates are remarkable features that over the past 65 years have attracted over 2000 fundamental and applied studies [17].

The Lindqvist polyoxoanions are often described as plenary or “saturated” POMs [18]. This description suggests that such POMs do not exhibit defect \((V_xO_y)\) sites and, therefore, cannot integrate additional addenda centers. Their chemical reactivity and inherent electronic and magnetic properties are typically altered by changes in the POM composition, the oxidation states of incorporated metal atoms, and the net charge of POM. For instance, Lindqvist POMs with low molecular charge such as \([Mo^{VI}_6O_{19}]^{2-}\) and \([W^{VI}_6O_{19}]^{2-}\) exhibit weak ionic interactions with dissolved cations. These interactions do not significantly affect the electronic structure of the polyoxoanion component, what allows the accurate prediction of spectra of these discrete, bare metal-oxide clusters in solution at the DFT level [19, 20]. The highly negatively charged Lindqvist POMs such as \([NbV_6O_{19}]^{8-}\) and \([TaV_6O_{19}]^{8-}\) show strong interactions toward electrophiles. The electrophilic cations typically bind to the bridging \(\mu_2-O\) atoms positioned at each polyhedral vertex of the Lindqvist POM [21].

In contrast to the bare \([M_6O_{19}]^{8-}\) polyoxoanions with \(M = Nb^{V}\) and \(Ta^{V}\), the lighter hexavanadate structure has not been reported yet. Bearing in mind that the Shannon-Prewitt ionic radius of \(V^{V}\) is 0.68 Å, which is smaller than that of other addenda atoms involved in constructing a Lindqvist POM structure (\(Nb^{V} = 0.78\) Å, \(Ta^{V} = 0.78\) Å, \(Mo^{VI} = 0.73\) Å, and \(W^{VI} = 0.74\) Å) [22], the hypothetical \([V_6O_{19}]^{8-}\) polyoxoanion with its high negative charge delocalized over the small molecular volume can thus be regarded as labile or not structurally stable [2, 23]. However, \([V_6O_{19}]\) fragments are part of POVs of larger nuclearity, such as \([V^{V}_{10}O_{28}]^{6-}\) and \([V^{V}_{13}O_{34}]^{3-}\), which were successfully isolated due to their lower molecular charge density. These two structures display highly dense-packing of \{VO_6\} octahedra, as illustrated in Figure 2.
Figure 2. A combined ball-and-stick and polyhedral representation of \([V^6V_{10}O_{28}]^{6-}\) (a) with a highlighted \([V_6O_{19}]\) fragment and \([V^3V_{13}O_{34}]^{3-}\) (b). Color code: O, red spheres; \(V^V\), orange spheres; \(V^O\)O, light-orange octahedra.

Figure 3. Structures where the elusive \([V^V_6O_{19}]^{8-}\) polyoxoanion is stabilized and its molecular charge is completely neutralized, partly compensated or “overcompensated” by (i) the four cationic \([\eta^5-C_5Me_5]M\)\(^{2+}\) grafted moieties with \(M = \text{Rh}\) or \(\text{Ir}\); (ii) the sixfold substitution of \(\mu_2-O^2\) with the \(\mu_2-\{\text{OR}\}\) ligands; (iii) the substitution of the \(\mu_2\)-oxo ligands with trisalkoxide ligands \(3O^2 \leftrightarrow \{\text{OCH}_2\text{CH}_2\text{CR}\}^3\) on opposite sides of the hexavanadate. The structures are shown in a combined ball-and-stick and polyhedral representation. Color code: C, black sticks; O, red spheres; \(V^V\), orange spheres; \(M\), purple spheres; \(V^O\)O, orange octahedra.
The challenges associated with the synthesis of $[V_{6}O_{19}]^{8-}$ with the purpose to use it as a modular building block for making hybrid materials guided the development of novel in situ approaches toward the stabilization of this polyoxoanion structure (Figure 3). These include: (A) grafting the cationic organometallic complexes $[(\eta^5-C_5Me_5)M]^2+$ (M = Rh and Ir); (B) derivatization with monodentate alkoxide ligands [OR]; (C) functionalization with trisalkoxide ligands or so-called triolates $\{[(OCH_2)CR]^3+$. The first two approaches are briefly discussed below.

**Approach A.** In 1989 the groups of Hayashi and Klemperer described the covalent attachment of cationic $[(\eta^5-C_5Me_5)M]^2+$ moieties with M = Rh and Ir to the $\{V_6O_{19}\}$ skeleton, which gave the neutral $\{[(\eta^5-C_5Me_5)M]_4(V_6O_{19})\}$ mixed-metal complexes soluble in dichloromethane (DCM), chloroform or toluene [24, 25]. The compounds were synthesized using the metavanadate $[V^V_2O_7]^-$ and dimeric $[M(\eta^5-C_5Me_5)Cl_2]_2$ precursors [24]. As was revealed by $^{17}$O NMR following $^{17}$O enrichment, the $\{[(\eta^5-C_5Me_5)M]_4(V_6O_{19})\}$ retains its overall structure in the pH range 6–8, while the bridging O atoms of this heterometallic complex are exchanged for the $^{17}$O atoms of the solvent ($^{17}$O-enriched water). Interestingly, at pH < 4 some of the $[(\eta^5-C_5Me_5)M]^2+$ moieties can be replaced by the $[(\eta^5-C_5Me_5)Ir]^2+$ ones and the formed multimetallic complexes $\{[(\eta^5-C_5Me_5)Rh]_4\{(\eta^5-C_5Me_5)Ir\}_z\{V_6O_{19}\}^\pm (z = 1, 2 \text{ and } 3)$ can be further separated using chromatographic methods.

**Approach B.** Another strategy to stabilize the $\{V_6O_{19}\}$ structural motif implies the formal substitution of its $\mu_2$-O ligands with monodentate alkoxide ligands $\mu_2\{OR\}^-$ (R = Me and Et). These monoalkoxohexavanadates are usually synthesized in methanol or ethanol, while the thermal requirements for the reactions can vary from room temperature to solvothermal conditions. The typical precursors in these reactions are esters of orthovanadic acid VO(OR)$_3$ (R$^*$ = Et and Bu$^*$).

The electrochemical and magnetic properties (due to the presence of vanadyl $[V^{IV}\text{O}]^{2+}$ groups with isotropic spin 1/2) of this class of organo-modified POVs are fine-tuned by adjustment of a number of substituted $\mu_2$-O ligands and the ratio of $V^{IV}$:$V^{V}$ redox couples, as demonstrated by a series of the $[V^{IV}_{n}V^{V}_{6-n}O_{19-n}(OR)_m]^{m-n-8}$ compounds [26-34].

Remarkably, Hartl and coworkers showed that the twelvefold-substituted hexavanadates $[V^{IV}_{n}V^{V}_{6-n}O_{17}(OR)_1]^{4-n}$ may undergo reversible reduction and oxidation (redox) processes [32, 33]. Increasing the number of $V^{IV}$ centers in $[V^{IV}_{n}V^{V}_{6-n}O_{17}(OR)_1]^{4-n}$ leads to lengthening of the bridging $\mu_2$-O–V and terminal V–O bonds, which consequently results in observable shifts in the corresponding infrared (IR) transmission bands. The quantum-mechanical
calculations at the DFT level forecasted that the $V^{IV}$ spin centers in a neutral, mixed-valence $[\text{V}^{IV}\text{V}^{V}\text{O}_7(\text{OMe})_{12}]$ structure are ferromagnetically coupled [35], a quite unusual observation in magnetochemistry of POVs that commonly exhibit predominant antiferromagnetic exchange interactions between the vanadium ions [6].

Interesting structural features of monoalkoxohexavanadates were revealed by the eightfold methoxo-substituted, mixed-valence $[\text{V}^{IV}_2\text{V}^{V}_4\text{O}_11(\text{OMe})_6]^2-$ displaying the temperature selective crystallization of diastereomers [28] and by a $[\text{V}^{IV}\text{O}(\text{bnimpm})(\text{acac})][\text{V}^{V}_{6}\text{O}_{13}(\text{OMe})_6]$ assembly exemplifying the noncovalent transoid ligation of two bulky, “fully-reduced” $[\text{V}^{IV}\text{O}(\text{bnimpm})(\text{acac})]^+$ complexes to the lower substituted, fully-oxidized $[\text{V}^{IV}_{6}\text{O}_{13}(\text{OMe})_6]^2-$ motif. The latter compound was synthesized by the reaction of bis(1-methylimidazol-2-yl)-4-methoxyphen-1-ylmethanol (= bnimpm), triethylamine ($\text{Et}_3\text{N}$), and [VO(acac)$_2$] (acac = acetylacetonate) in methanol solution [26]. The weak axial connectivity in $[\text{V}^{IV}\text{O}(\text{bnimpm})(\text{acac})]_2[\text{V}^{V}_{6}\text{O}_{13}(\text{OMe})_6]^2-$ can probably explain the irreversible electrochemical oxidation wave observed at 130 mV for this compound. Another complex $[\text{Pd}(\text{dpa})(\text{acac})][\text{V}^{V}_{6}\text{O}_{13}(\text{OMe})_6]$ (dpa = 2,2′-dipyridine amine) with electrostatic interactions between the cations and the hexavanadate dianion performed catalytic oxidation of diphenylmethane to benzophenone (oxidant: t-butylhydroperoxide) with conversion and selectivity of >95% [28]. It is noteworthy that POMs combined with Pd$^{II}$ complexes show generally good performance in homogeneous catalysis [36]. The synergy effects of both components in the catalytic cycle have not yet been investigated. The mixed-valence $[\text{V}^{IV}_5\text{V}^{V}\text{O}_7(\text{OMe})_{12}]^2+$ compound, in the presence of $[\text{Ru(bpy)}_3]^{2+}$ (bpy = 2,2′-bipyridine) as a photosensitizer and $\text{Na}_2\text{S}_2\text{O}_8$ as the sacrificial electron acceptor, catalyzes photoinduced water oxidation [37].

The electrochemical stability and reversibility of $[\text{V}^{IV}_n\text{V}^{V}_{6-n}\text{O}_{9-m}(\text{OR})_m]^{m-n-8}$ structures have indeed prompted their application in catalysis. However, one practical drawback still inhibiting a wide catalytic use of monoalkoxohexavanadates is that some of their representatives were shown to be susceptible to hydrolysis [2, 29]. This is however not the case for the Lindqvist-type hexavanadates stabilized by chelating trisalkoxide ligands. While the (post-)functionalization of monoalkoxohexavanadates with remote electron donating groups should be pursued to enrich their coordination chemistry, that of the trisalkoxo-capped congeners (approach C) is well-known and documented below. The high structural stability and tunability of trisalkoxohexavanadates enables control
over their redox and acid-base properties, making them attractive targets for synthesis. Significantly, they are reliable building blocks for the construction of hybrid \( \{V_6\} \)-based architectures. In the following sections, this chapter focuses on the major achievements and recent progress in the development of trisalkoxohexavanadate molecules toward their coordination-directed assemblies.

2. TRISALKOXOHEXAVANADATES

2.1. Trisalkoxohexavanadates with Small Group Substituents

2.1.1. Structural Archetypes

The twelve \( \mu_2\)-O ligands in the \( \{V_6O_{19}\} \) superoctahedron can be formally substituted with up to four trisalkoxide ligands. Today there are a number of structures with the general formula \( \{V_6O_{19-3x-y}(OH)_y(\text{OCH}_2)_3CR\}_x \) where \( x = 2, 3, \) and 4 tridentate ligands and \( R = \) organic substituent (\( –\text{Me}, –\text{Et}, –\text{CH}_2\text{OH}, –\text{CH}_2\text{Ph}, –\text{NH}_2, \) –NO\(_2 \) or –NMe\(_2 \)). In structures with two trisalkoxide ligands the hexavanadate skeleton can be capped in a transoid (\( \text{anti-} \)) or cisoid (\( \text{syn-} \)) fashion (Figure 4). Overall, the \( \text{bis}(\text{trisalkoxy}) \)-hexavanadates (= disubstituted species) featuring the \( \text{anti-} \)-capping coordination mode are the most common in this chemistry. The physicochemical properties of the \( \{V_6O_{19-3x-y}(OH)_y(\text{OCH}_2)_3CR\}_x \) structures are influenced by: (i) the number of chelating trisalkoxide ligands, (ii) the electron configuration of the V atoms [3\(d^0 \) (V\(_{\text{V}}\)), 3\(d^1 \) (V\(_{\text{IV}}\)), and 3\(d^2 \) (V\(_{\text{III}}\))], and (iii) the outer functionality of the trisalkoxide ligands (that is, the type of R substituents).

2.1.2. Synthetic Strategies for the Preparation

The preparation of \( \{V_6O_{19-3x-y}(OH)_y(\text{OCH}_2)_3CR\}_x \) is carried out using two methods: (1) condensation reactions of metavanadates [V\(_V\)O\(_4\)]\(^-\) or orthovanadates [V\(_V\)O\(_4\)]\(^3-\) with triols induced by reducing agents or acidification (for example, with HCl) at elevated temperatures (\( ca. \) 80°C) in aqueous solutions [38]; (2) post-condensation reactions of the highly soluble decavanadate [H\(_3\)V\(_{10}\)O\(_{28}\)]\(^3-\) with the (HOCH\(_2\))\(_3\)CR triols. The latter reaction type is represented by the synthesis of the fully-oxidized \( \text{anti-} \)[V\(_V\)\(_6\)O\(_{13}\) {(OCH\(_2\))\(_3\)CR\(_2\)}\(^2-\)] polyoxoanion (the insoluble V\(_2\)O\(_5\) byproduct can be readily removed by gravity filtration / decantation), which can be performed in
polar aprotic solvents such as acetonitrile, \(N,N\)-dimethylformamide (DMF), \(N,N\)-dimethylacetamide (DMA) or DCM at standard pressure [39-41]:

\[
2 \text{TBA}_2[H_2V_{10}O_{28}] \to 6 \text{HOCH}_2CR \to 3 \text{TBA}_2[V_6O_{13}((\text{OCH}_2)_3\text{CR})_2] \to 12 \text{H}_2\text{O} + \text{V}_2\text{O}_5
\]

Notably, the \(anti\)\([-\text{V}^V_6\text{O}_{13}((\text{OCH}_2)_3\text{CR})_2]\)^{2-} structures with \(R = \text{CH}_2\text{OH}\) and \(\text{NH}_2\) were widely used in the esterification and amidation post-functionalization reactions described in the section 2.2.2.

Figure 4. Lindqvist-type hexavanadate structures stabilized by two, three, and four trisalkoxide ligands. The structures are shown in a combined ball-and-stick and polyhedral representation. Hydrogen atoms are omitted for clarity. Color code: C, black sticks; O, red spheres; R substituents, black spheres; \(\text{VO}_6\), gray octahedra. The O atoms of trisalkoxide ligands have bigger red spheres. The oxidation state of the vanadium atoms in the \(\text{VO}_6\) octahedra is not defined.

Figure 5. \(Bis\)-(trisalkoxo)hexavanadates with different electron population of the vanadium atoms: a) \(anti\)\([-\text{V}^V_6\text{O}_{13}((\text{OCH}_2)_3\text{CCH}_2\text{OH})_2]\)^{2-}, b) \(syn\)\([-\text{V}^{IV}V^V_5\text{O}_{13}((\text{OCH}_2)_3\text{CCH}_2\text{OH})_2]\)^{3-}, and c) \(syn\)\([-\text{V}^{IV}_6\text{O}_7((\text{OCH}_2)_3\text{CCH}_2\text{OH})_2]\)^{2-}. The structures are shown in a combined ball-and-stick and polyhedral representation. Hydrogen atoms are omitted. Color code: C, black sticks; O, red spheres; \(\text{V}^{IV}\text{O}_6\), orange octahedra; \(\text{V}^{V}\text{O}_6\), sky-blue octahedra.
There are also scarce examples of the use of tetrOLS in (post-)condensation reactions. The fully-oxidized, mixed-valence, and “fully-reduced” bis-(trisalkoxo)hexavanadates (Figure 5) were obtained by reactions involving MVO₃ (M = NH₄ and Na) or TBA₃[HT₃V₁₀O₂₈] (TBA = tetrabutylammonium, Bu₄N⁺) and pentaerythritol as precursors [39, 42]. The “fully-reduced” syn-[VIV₆O₁₇(OH)₁₆{(OCH₂)₃CCH₂OH}₂]³⁻ polyoxoanion (Figure 5c) is afforded when the metavanadate is reduced with hydrazine to [VO(OH)₃]⁻ and the latter condenses with pentaerythritol [42]. If the obtained compound is treated in an aqueous solution with H₂O₂, after some hours one obtains a mixed-valence syn-[VIV₆O₁₃{(OCH₂)₃CCH₂OH}₂]⁵⁻ polyoxoanion (Figure 5b). Its structure contains one “fully-reduced” VIV center in the VO₆ octahedron situated between two adjoined trisalkoxide ligands in a syn fashion. The one-week exposure of this polyoxoanion to atmospheric oxygen leads to its fully oxidation, resulting in anti-[VIV₆O₁₃{(OCH₂)₃CCH₂OH}₂]⁷⁻ (Figure 5a). It is also noteworthy that this “fully-oxidized” polyoxoanion can be synthesized by lowering the pH of an aqueous NH₄VO₃/pentaerythritol solution to ca. 1.5 or by using TBA₃[HT₃V₁₀O₂₈] as precursor [39].

The synthesis of hexavanadates capped by three and four trisalkoxide ligands takes place in a higher temperature range (150 – 210°C) under solvo- or hydrothermal conditions [43, 44]. The “fully-reduced” [VIV₆O₁₇(OH)₁₆{(OCH₂)₃CMe}₁]²⁻ and [VIV₆O₁₇{(OCH₂)₃CEt}₁]²⁻ polyoxoanions and a mixed-valence [VIV₅VIV₆O₁₃(OH)₁₆{(OCH₂)₃CMe}₁]⁻ polyoxoanion were isolated from comproportionation reactions of VIII and VV precursors (V₂O₃, V₂O₅, and MVO₃ where M = Na and K) with the corresponding triols in aqueous solutions [43]. Reactions in the presence of NaBF₄ yielded [VIV₆O₁₇(OH)₁₆F{(OCH₂)₃CMe}₁]⁻ whose central μ₆-O atom is substituted by a μ₃-F. This demonstrates the potential of Lindqvist POP to enclose an atom other than μ₆-oxygen. For comparison, classical (bare) POP nanocans can encapsulate a variety of anions, such as Cl⁻, Br⁻, I⁻, HCOO⁻, MeCOO⁻, CN⁻, CO₃²⁻, NO⁻, NO₂⁻, N₃⁻, PO₄³⁻, SH⁻, SCN⁻, SO₃²⁻, SO₄²⁻, ClO₄⁻, VO₂²⁺, and VO₂F²⁻ [6].

Interestingly, the hexavanadate structure ligated by four trisalkoxide ligands showed the ability to incorporate the “highly-reduced” VIII atoms if the [VIIICl₃(THF)₃] precursor was used. A Lindqvist-like [(VIII)Cl₉O{(OCH₂)₃CR}₄]²⁺ polyoxoanion structure, in which six terminal O atoms are replaced by Cl ones, was chemically and structurally characterized [44]. The mixed-valence [VIIIIV₆O₁₃(OMe)₃(calix)(MeOH)]⁻ polyoxoanion where calix = p-tert-butylcalix[4]arene is also available [45].
2.1.3. Reactivity and Physicochemical Properties

According to $^{51}$V NMR studies, the fully-oxidized bis-(trisalkoxo)hexavanadates exhibit superior stability in solution. As demonstrated by the case study of anti-$^{V}_{V}^{V}_{V}O_{13}\{(OCH_{2})_{3}CR\}_{2}^{2-}$ [40, 46], the $^{51}$V NMR spectra of these polyoxoanions are characterized by a singlet around −500 ppm (versus VOCl$_3$ as external standard) because of the equivalence of all six V atoms. Some shielding effects governed by the nature of remote functional groups can be observed.

$^{17}$O NMR of anti-$^{V}_{V}^{V}_{V}O_{13}\{(OCH_{2})_{3}CMe\}_{2}^{2-}$ in $^{17}$O-enriched water indicate that only the bridging µ$_2$-O atoms are exchanged for $^{17}$O of the solvent [39], a situation also observed for the above-mentioned [$(\eta^5-C_5H_{5})Rh]_4(V_6O_{19})$ complex [24].

Depending on the formal oxidation states of the vanadium atoms, bis-(trisalkoxo)hexavanadates show different typical colors in solution: orange and red (fully-oxidized), greenish (mixed-valence), and dark green/blue (“fully-reduced”).

Characterization by UV/Vis spectroscopy in DMF and DCM reveals that anti-$^{V}_{V}^{V}_{V}O_{13}\{(OCH_{2})_{3}CR\}_{2}^{2-}$ polyoxoanions with R = −Me, −Et, −CH$_2$OH, −NO$_2$, −NMe$_2$, and −NHC(O)C=CH$_2$ exhibit two intense absorption bands in the region of 240–390 nm which can be assigned to ligand-to-metal (O→V) charge transfer (LMCT) [38, 39, 47]. A characteristic sign of the mixed-valence and “fully-reduced” species is intervalence charge transfer (IVCT) absorption bands in the region of 500–1000 nm.

The anti-$^{V}_{V}^{V}_{V}O_{13}\{(OCH_{2})_{3}CR\}_{2}^{2-}$ with, for example, R = −Me, −CH$_2$OH or −NO$_2$ exhibit reversible one-electron reduction [38-40]. Importantly, the redox potential is dependent on the type of isomerism and thus the redox potentials between the anti- and the syn-isomers for the reaction $^{V}_{V}^{V}_{V}O_{13}\{(OCH_{2})_3CCH_2OH\}_2^{2-} \rightleftharpoons [^{V}_{V}^{V}_{V}O_{13}((OCH_{2})_3CCH_2OH)]_2^{3-}$ (Figure 5a) vs $^{V}_{V}^{V}_{V}O_{13}((OCH_{2})_3CCH_2OH)]_2^{3-}$ (Figure 5b) are ca. 200 mV shifted with respect to one another (that is, 0.57 V for syn- and 0.37 V for anti-isomer):

$$\text{syn-}^{V}_{V}^{V}_{V}O_{13}((OCH_{2})_3CCH_2OH)]_2^{3-} \rightleftharpoons 0.57 \text{ V} \rightleftharpoons \text{syn-}^{V}_{V}^{V}_{V}O_{13}((OCH_{2})_3CCH_2OH)]_2^{3-}$$

$$\text{anti-}^{V}_{V}^{V}_{V}O_{13}((OCH_{2})_3CCH_2OH)]_2^{3-} \rightleftharpoons 0.37 \text{ V} \rightleftharpoons \text{anti-}^{V}_{V}^{V}_{V}O_{13}((OCH_{2})_3CCH_2OH)]_2^{3-}$$

The origin of this phenomenon can be traced to the stronger localization of a single $d^1$ electron in the syn-isomer (Figure 5b). The higher redox potential and the resulting higher stability toward oxidation explains why the syn-
\{\text{V}^{IV}\text{V}^5\} \text{ can be successfully isolated under oxidative conditions, in contrast to the } \text{anti-}{\{\text{V}^{IV}\text{V}^5\}}.

The hexavanadate polyoxoanions can be reduced selectively not only by electrochemical methods but also using specific reducing agents such as 1,1-methylphenylhydrazine (MePhNNH\textsubscript{2}), 1,2-diphenylhydrazine (PhHNNHPh), and sodium acenaphthalide (NaACN) in stoichiometric ratios. This is exemplified by the following scheme illustrating the adjustment of various \{\text{V}^{IV}_n\text{V}^{VI}_{6-n}\} redox states \((n = 2, 4 \text{ and } 6)\) when started from the fully-oxidized \([\text{V}^{V}_6\text{O}_{13}\{(\text{OCH}_2)\text{CMe}\}_2]\text{O}^2\) polyoxoanion with \(n = 0\) [39]:

![Scheme]

All compounds are isolable but their mixed-valence representatives tend to disproportionate.

Finally, the increasing number of \text{V}^{IV} \text{ centers in } \{\text{V}^{IV}_n\text{V}^{VI}_{6-n}\text{O}_{13-n}\text{OH}_n\{(\text{OCH}_2)\text{CMe}\}_2\}^2\text{ } (n = 2, 4, \text{ and } 6) \text{ was found to decrease the overall magnetic moment and to increase the antiferromagnetic coupling in these compounds [43].}

### 2.2. Higher (Post-)Functionalized \textit{Bis}-(Trisalkoxo)hexavanadates

Direct functionalization and post-functionalization methods [48, 49] can be used to access Lindqvist-type hexavanadates equipped with bulkier substituents on the trisalkoxide ligand scaffold. The direct functionalization implies the \textit{in situ} formation of the \{\text{V}_6\} structure from the interaction of the decavanadate precursor \(\text{TBA}_3[\text{H}_3\text{V}_{10}\text{O}_{28}]\) with the tris(hydroxymethyl) methane derivatives \((\text{HOCH}_2)_3\text{C-R}^{\text{bulky}}\) prefunctionalized with organic or organically tailored metal complex moieties \(= \text{R}^{\text{bulky}}\). The post-functionalization route represents a consecutive structural growth of directly functionalized hexavanadates as a result of exposure of functional termini of their trisalkoxide ligands to various organic and inorganic compounds. Depending on the chosen pathway, several different types of symmetric and asymmetric higher (post-)functionalized \textit{anti-}{\{\text{V}_6\}} structures can be obtained and they are exemplified below.
2.2.1. Direct Functionalization

The direct functionalization is the preferred method for the preparation of symmetrically functionalized \( \{V_6\} \). The most common synthon in these syntheses is tris(hydroxymethyl)aminomethane (HOCH\(_2\))CNH\(_2\) which reacts with alkyl halides or carboxylic acids and their derivatives containing carboxyethyl and formyl / acyl halide groups to give the secondary amine- or amide-elaborated triols in high yields. These resulting organic compounds are quite stable and form in combination with TBA\(_3\)[H\(_3\)V\(_{10}\)O\(_{28}\)] the \( \{V_6\} \) species under mild conditions. The structures of the latter are thus distinguished by the type of binding of the \(-C(\text{CH}_2\text{O})_3\)-ligated hexavanadate core to the remote functional group, through a \(-\text{NH}^-\) or \(-\text{NH}(\text{C}=\text{O})^-\) unit. It is noteworthy that the synthesis of the triolate \((\text{OCH}_2)_2\text{CR})^3^-\) capped hexavanadates furnished with small peripheral group substituents (R) such as \(-\text{Me} , -\text{Et} , -\text{CH}_2\text{OH} , -\text{CH}_2\text{Ph} , -\text{NH}_2, -\text{NO}_2\) or \(-\text{NMe}_2\) is described by this direct pathway of formation.

Amine binding unit. A condensation of (HOCH\(_2\))CNH\(_2\) with the 4-(chloromethyl)benzoic acid in water affords the HOOC-4-C\(_6\)H\(_2\)CH\(_2\)NHC(CH\(_2\)OH)\(_3\) triol, which further reacts with TBA\(_3\)[H\(_3\)V\(_{10}\)O\(_{28}\)] in DMA to yield a redox-active TBA\(_2\)[V\(_6\)O\(_{13}\]{(OCH\(_2\))CNHCH\(_2\)C\(_6\)H\(_4\)-4-COOH}]\(_2\) compound [47].

Amide binding unit. The reactions of TBA\(_3\)[H\(_3\)V\(_{10}\)O\(_{28}\)] with the presynthesized triols CH\(_2\)=CH(O)CNHC(CH\(_2\)OH)\(_3\), Py-3-(O)CNHC(CH\(_2\)OH)\(_3\) (Py = C\(_4\)H\(_2\)N, pyridyl), Py-4-(O)CNHC(CH\(_2\)OH)\(_3\), and Terpy-(O)CNHC(CH\(_2\)OH)\(_3\) (Terpy = C\(_{15}\)H\(_{10}\)N\(_3\), terpyridyl) give TBA\(_2\)[V\(_6\)O\(_{13}\]{(OCH\(_2\))CNHC(O)CH=CH\(_2\)]\(_2\) [40], TBA\(_2\)[V\(_6\)O\(_{13}\]{(OCH\(_2\))CNHC(O)-3-Py}]\(_2\) [50], TBA\(_2\)[V\(_6\)O\(_{13}\]{(OCH\(_2\))CNHC(O)-4-Py}]\(_2\) [46], and TBA\(_2\)[V\(_6\)O\(_{13}\]{(OCH\(_2\))CNHC(O)-Terpy}]\(_2\) [51], respectively. The central, fully-oxidized components of the compounds [V\(_{\text{V}6}\)O\(_{13}\]{(OCH\(_2\))CNHC(O)-3-Py}]\(_2\)\(^2^-\) and [V\(_{\text{V}6}\)O\(_{13}\]{(OCH\(_2\))CNHC(O)-4-Py}]\(_2\)\(^2^-\) as well as [V\(_{\text{V}6}\)O\(_{13}\]{(OCH\(_2\))CNHC(O)-4-Py}]\(_2\)\(^2^-\) were shown to act as feature building blocks in coordination chemistry, which is shown in the next section.

This family of compounds is represented by another inorganic-organic hybrid compound, which is however decorated with pendant metal complex moieties. A ferrocenyl (Fc)-terminated triad compound TBA\(_2\)[V\(_6\)O\(_{13}\]{(OCH\(_2\))CNHC(O)Fe}]\(_2\)\(_2\) was synthesized by the reaction of TBA\(_3\)[H\(_3\)V\(_{10}\)O\(_{28}\)] with the (C\(_5\)H\(_5\))Fe(C\(_6\)H\(_4\)-4-(O)CNHC(CH\(_2\)OH)\(_3\)) triol in DMA (Figure 6) [52]. The triol was obtained by condensation of the formylferrocene fluoride with (HOCH\(_2\))CNH\(_2\) in the presence of 4-(dimethylamino)pyridine (DMAP) and Et\(_3\)N in DMF.
Figure 6. The synthesis of the ferrocenyl-decorated triol and the TBA$_2$[V$_6$O$_{13}${(OCH$_2$)$_3$C$\text{NHC(O)}$Fc}$]$_2$] compound.

The TBA$_2$[V$_6$O$_{13}${(OCH$_2$)$_3$C$\text{NHC(O)}$Fc}$]$_2$] compound shows an electrochemically irreversible single oxidation wave and is characterized by the absence of electronic communication between the ferrocenyl groups and the bridging hexavanadate core. This electrochemical oxidation is likely to occur at the V$_6$ constituent and does not engage the Fc moieties because the upper occupied molecular orbitals (including the highest occupied molecular orbital, HOMO) are delocalized over the former. According to quantum mechanical calculations at the DFT level, the O–V–O bonding situation in [V$_6$O$_{13}${(OCH$_2$)$_3$C$\text{NHC(O)}$Fc}$]$_2$]$_2$ is described by the formalism of the 3-center-4-electron ‘hyperbonds’. The electrochemistry of [V$_6$O$_{13}${(OCH$_2$)$_3$C$\text{NHC(O)}$Fc}$]$_2$]$_2$ is thus in contrast to that of other herein-described trisalkoxohexavanadates with small peripheral group substituents, usually exhibiting reversible or quasi-reversible redox behavior.

2.2.2. Post-Functionalization

The preformed bis-(trisalkoxo)hexavanadate dianionic structures usually undergo post-functionalization at the trisalkoxide termini, using esterification or amidation reactions. A post-functionalization of [V$_6$O$_{13}${(OCH$_2$)$_3$CR}$]$_2$]$_2$ with the trialkylsilyl chloride or triflate, which results in the silylated molecule
[V\textsubscript{6}O\textsubscript{11}(OR”)\textsubscript{2}((OCH\textsubscript{2})\textsubscript{3}CR)\textsubscript{2}] (R” = –SiMe\textsubscript{3}, –SiMe\textsubscript{2}Bu) with a neutral charge, is also available [39].

The synthesis of TBA salts of [V\textsubscript{6}O\textsubscript{13}((OCH\textsubscript{2})\textsubscript{3}CCH\textsubscript{2}OC(O)R)\textsubscript{2}]\textsuperscript{2–} in acetonitrile using DMAP-catalyzed esterification of the [V\textsubscript{6}O\textsubscript{13}((OCH\textsubscript{2})\textsubscript{3}CCH\textsubscript{2}OH)\textsubscript{2}]\textsuperscript{2–} with acid anhydrides (RCO)\textsubscript{2}O (aliphatic R = –Me, –Et, –C\textsubscript{6}H\textsubscript{11}, and –C\textsubscript{7}H\textsubscript{35}) in the presence of Et\textsubscript{3}N serves as a good example of the post-functionalization method [53].

The amidated products were synthesized by the reaction of [V\textsubscript{6}O\textsubscript{13}((OCH\textsubscript{2})\textsubscript{3}CNH\textsubscript{2})\textsubscript{2}]\textsuperscript{2–} with, for example, anthracene-2,3-dicarboxylic acid anhydrides in DMA and they were used as redox-active detection or oxidation agents for thioureas, amines, and aldehydes [54]. Although the {V\textsubscript{6}} is reduced under non-oxidative conditions, its fully-oxidized form can easily be regenerated by changing the atmosphere to air.

A stepwise consecutive post-functionalization including esterification and amidation was the subject of a recent study [55]. This implies an esterification of [V\textsubscript{6}O\textsubscript{13}((OCH\textsubscript{2})\textsubscript{3}CCH\textsubscript{2}OH)\textsubscript{2}]\textsuperscript{2–} with succinic anhydride in the presence of DMAP and the subsequent amidation of the produced carboxylic acid-terminated [V\textsubscript{6}O\textsubscript{13}((OCH\textsubscript{2})\textsubscript{3}CCH\textsubscript{2}OC(O)CH\textsubscript{2}CH\textsubscript{2}COOH)\textsubscript{2}]\textsuperscript{2–} with the primary aliphatic or aromatic amines RNH\textsubscript{2} (R = –C\textsubscript{6}H\textsubscript{7}, –C\textsubscript{6}H\textsubscript{5}, –CH\textsubscript{2}CH=CH\textsubscript{2}, –C\textsubscript{6}H\textsubscript{6}Me, and –(C\textsubscript{6}H\textsubscript{4})Me-p) in the presence of 2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline. The obtained products are the symmetrical anti-[V\textsubscript{6}O\textsubscript{13}((OCH\textsubscript{2})\textsubscript{3}CCH\textsubscript{2}OC(O)CH\textsubscript{2}CH\textsubscript{2}C(O)NH)\textsubscript{2}]\textsuperscript{2–} trisalkoxohexavanadates.

Such nanosized anti-{V\textsubscript{6}} structures with long alkyl tails are regarded as polyoxoanionic surfactants. An interesting example of these is the asymmetrical trisalkoxohexavanadate [V\textsubscript{6}O\textsubscript{13}((OCH\textsubscript{2})\textsubscript{3}CNH\textsubscript{2}C\textsubscript{6}H\textsubscript{5}COOC\textsubscript{10}H\textsubscript{13})\textsubscript{2}]\textsuperscript{2–} (single-tailed {V\textsubscript{6}}-based surfactant) isolated from the reaction of cetyl 4-(chloromethyl)benzoate and TBA\textsubscript{2}[V\textsubscript{6}O\textsubscript{13}((OCH\textsubscript{2})\textsubscript{3}CNH\textsubscript{2})\textsubscript{2}] in DMF in the presence of tetrabutylammonium hydroxide in methanol [56]. Interestingly, the TBA countercations of the product can be exchanged for H\textsuperscript{+} by using a biphasic ion exchange technology. In aqueous solutions, the proton-counterbalanced polyoxoanionic molecules were shown to undergo stepwise hierarchical self-assembly to form micelle structures. Further process includes a spontaneous coagulation of these micelles into one-dimensional (1D) anisotropic nanobelt-like structures with the nanoscale thickness of ca. 20 nm. The 1D architecture is stable in acetonitrile and exhibits heterogeneous catalytic activity for the oxidation of organic sulfides with H\textsubscript{2}O\textsubscript{2}, yielding sulfide monoxides and sulfones.
Figure 7. Structures of the symmetrical (a) and asymmetrical (b) trisalkoxohexavanadate structures with pyrene termini, $\text{[V}_6\text{O}_{13}\{((\text{OCH}_2)_3\text{CNHC(O)CH}_2\text{CH}_2\text{CH}_2\text{Me})_2\}_2\}^{2-}$ and $\text{[V}_6\text{O}_{13}\{((\text{OCH}_2)_3\text{CNH}_2\{((\text{OCH}_2)_3\text{CNHC(O)CH}_2\text{CH}_2\text{CH}_2\text{Me})_2\}_2\}^{2-}$, respectively. The TBA salts of these dianionic amphiphilic molecules were synthesized using TBA$_2$[V$_6$O$_{13}${(OCH$_2$)$_3$CNH$_2$}] and 1-pyrenebutyric acid $N$-hydroxysuccinimide ester in the adjusted stoichiometric ratio. Color code: C, black sticks; N, blue spheres; O, red spheres; V$^6$O$_{10}$, orange octahedra.

Figure 8. Condensation of [Mo$^{VI}$O$_{19}$]$^{2-}$ with [V$^6$O$_{13}${(OCH$_2$)$_3$CNH$_2$}]$_2$$^{2-}$ toward the hybrid [V$^6$O$_{13}${(OCH$_2$)$_3$CNMo$_6$O$_{18}$}]$$^{6-}$ polyoxoanion in an anhydrous acetonitrile/pyridine mixed solution. Its structure is shown in a combined ball-and-stick and polyhedral representation. Color code: H, white; C, black sticks; N, blue spheres; O, red spheres; Mo, black spheres; V$^6$O$_{10}$, orange octahedra.

The TBA salt of a symmetrical trisalkoxohexavanadate $\text{[V}_6\text{O}_{13}\{((\text{OCH}_2)_3\text{CCH}_2\text{OC(O)}(\text{CH}_2)_{16}\text{Me})_2\}_2$$^{2-}$ (double-tailed {V$_6$}-based surfactant) was synthesized by the esterification reaction of TBA$_2$[V$_6$O$_{13}${(OCH$_2$)$_3$CCH$_2$OH}]$_2$ with the stearic acid Me(CH$_2$)$_{16}$COOH in acetonitrile [56], in the presence of $N$-$N$-dicyclohexylcarbodiimide (DCC) and DMAP as Steglich reagents [57]. In acetone-water solutions, the
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TBA$_2$[V$_6$O$_{13}${(OCH)$_3$CCH$_2$OC(O)(CH$_2$)$_{16}$Me}]$_2$ produces vesicles with controllable self-assembly behavior. When the TBA countercations are exchanged for H$^+$ or Na$^+$, the resulting compounds show blue luminescence emission bands at 392 nm, 409 nm, and 429 nm (excited at 335 nm). Such fluorescence properties are very rare in POM chemistry if no Eu$^{3+}$ ions are involved. In the subfield of POVs, fluorescence was besides observed for a host-guest TEA$_2$[V$_{14}$O$_{36}$Cl] compound (TEA$^+$ = Et$_4$N$^+$) [58]. Furthermore, the symmetrical and asymmetrical [V$_6$] polyoxoanions with pyrene termini (Figure 7), which exist with TBA, TMA (= Me$_4$N$^+$), TEA, and H$^+$ countercations and aggregate into the spherical vesicular structures in aqueous DMSO solutions, showed pH-dependent fluorescence properties [41]. However, fluorescence of these compounds is due to the attached pyrene fluorophores.

A few other examples of bis-(trisalkoxo)hexavanadates were obtained by using nonclassical post-functionalization approaches. An interesting type of reaction engaging Lindqvist-type hexavanadate and hexamolybdate dianions was reported [59]. Condensation of TBA$_2$[V$_6$O$_{13}${(OCH)$_3$C}2CNH$_2$]$_2$ with TBA$_2$[Mo$_6$O$_{19}$] in the presence of DCC afforded a TBA$_6$[V$_6$O$_{13}${(OCH)$_3$CNMo$_6$O$_{18}$}]$_2$ compound with the photochromic behavior under sunlight illumination. This compound is a covalently imido-bonded triad consisting of one central hexavanadate and two adjoined hexamolybdate ions (Figure 8). Remarkably, it shows reversible redox properties characterized by one-electron reversible reduction of [V$_6$] and of two [Mo$_6$O$_{19}$]$_2^-$ constituents in the triad. This thus contrasts with the electrochemical behavior of the above-mentioned TBA$_2$[V$_6$O$_{13}${(OCH)$_3$C}2CNH(O)Fe]$_2$ compound [52].

Hasenknopf, Ruhlmann and coworkers synthesized and characterized a series of discrete inorganic-organic hybrid materials consisting of the bis-(trisalkxo)hexavanadate and metalloporphyrin components [60]. In these discrete compounds the pyridyl termini of the redox-responsive anti-[V$_V$O$_{13}${(OCH)$_3$CCH$_2$OC(O)-4-Py}]$_2^2-$ or anti-[V$_V$O$_{13}${(OCH)$_3$CNHC(O)-4-Py}]$_2^2-$ axially coordinate to the Ru$^{II}$ atom of [Ru(CO)TPP] with TPP = meso-tetraphenylporphyrin (Figure 9). This assembling however influences badly the electrochemical properties of the whole system, making the redox reactions irreversible. The composition and structure of these mixed-metal coordination complexes were established by elemental analysis, IR, and ($^1$H, $^{13}$C)-NMR spectroscopy. Single-crystal X-ray diffraction studies are not available.
Figure 9. Proposed structure of the mixed-metal [Ru(CO)TPP]₆{V₆} compound. V²O₆ are shown as orange octahedra.

Figure 10. A segment of the copolymeric film containing anti-[V₆O₁₃{(OCH₂)₃CNHC(O)-4-Py}₂]²⁻ and zinc-β-octaethylporphyrin. V²O₆ are shown as orange octahedra.

The electrooxidation-driven formation of {V₆}-metalloporphyrin copolymeric films was described as well [61]. The latter consist of the anti-[V₆O₁₃{(OCH₂)₃CNHC(O)-4-Py}₂]²⁻ building blocks whose pyridyl termini are covalently bonded to the opposite meso positions in zinc-β-octaethylporphyrin (Figure 10). These films obtained via electropolymerization of porphyrin in the presence of {V₆} were studied by UV/Vis spectroscopy, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), electrochemical quartz crystal microbalance, and cyclic voltammetry (CV).
3. COORDINATION ASSEMBLIES

The structures of redox-active bis-(trisalkoxo)hexavanadates with peripheral, not sterically hindered connecting groups such as pyridyl (Py) or carboxylate (COO) can be remarkably extended to coordination assemblies by using a suitable metal cation linker. Up to now, a triangular coordinated superstructure, coordination polymers and a network differing in their lateral dimensions (from zero dimensional, 0D to three dimensional, 3D) were described and they are illustrated below.

3.1. Triangular Coordinated Superstructure

The groups of Hanan and Hasenknapf succeeded in the synthesis of a discrete (0D) trimeric assembly consisting of three 3-pyridyl terminated bis-(trisalkoxo)hexavanadate building blocks anti-[V\text{VI}_6O_{13}\{OCH_2\}_3CNHC(O)-3-Py\}_2]^2- arranged in a cyclic manner through three PdCl\text{II} transoid linking entities (Figure 11) [50]. This inorganic-organic hybrid solid was isolated from the reaction of the fully-oxidized TBA$_2$[V\text{VI}_6O_{13}\{OCH_2\}_3CNHC(O)-3-Py\}_2] complex with [PdCl\text{II}(MeCN)$_2$] in DMA. Although the single-crystal X-ray structure of the compound has not been determined, its composition and construction were investigated by elemental analysis, pulsed-field gradient NMR spectroscopy and high-resolution electrospray ionization (HR-ESI) mass spectrometry.

![Figure 11. Synthesis of the proposed Pd\text{II}-directed, trimeric assembly. Color code: C, black sticks; N, blue spheres; O, red spheres; V\text{VI}_6O_{13}, orange octahedra.](image-url)
3.2. 1D Coordination Polymers

Hill and coworkers reported the synthesis and characterization of a series of redox-active, isostructural zwitterionic coordination polymers [M(DMF)$_2$(H$_2$O)$_2$(V$_6$O$_{13}$){(OCH$_2$)$_3$CNNHC(O)-4-Py)$_2$}], composed of the fully-oxidized anti-[V$_6$O$_{13}${(OCH$_2$)$_3$CNNHC(O)-4-Py}$_2$]$^{2-}$ polynuclear anion and divalent transition metal cations (M = Mn$^{2+}$, Co$^{2+}$, Ni$^{2+}$, or Zn$^{2+}$ [46]. The interconnection of {V$_6$} and M$^{2+}$ into one-dimensional (1D) linear chains is attained due to the specific coordination vectors of the pendant 4-pyridyl groups (180°), which are different to those indicated by Hanan, Hasenknopf and coworkers for the 3-pyridyl groups (60°; see Figure 11) in a similar {V$_6$} building block. Each M$^{2+}$ ion adopts a sixfold coordination environment of two DMF, two water and two 4-pyridyl ligands (Figure 12). The crystal structure additionally displays extensive hydrogen bonds between the 1D chains, which in particular engage CH units of the 4-pyridyl rings. The composition and structure of these inorganic-organic hybrid solids with a slight solubility in polar aprotic solvents (DMSO, DMF or MeCN) were revealed by elemental analysis, $^1$H and $^{51}$V NMR, IR and UV/Vis spectroscopy, thermogravimetric analysis (TGA) as well as powder and single-crystal X-ray diffraction. Their reversible reduction by phenylhydrazine and NaBH$_4$ in CCl$_4$ as well as reoxidation without decomposition by O$_2$, Br$_2$, Ce$^{IV}$ or S$_2$O$_8^{2-}$ were observed.

![Figure 12. Synthesis of the [Co(DMF)$_2$(H$_2$O)$_2$(V$_6$O$_{13}$){(OCH$_2$)$_3$CNNHC(O)-4-Py}$_2$]](abbreviated as {V$^{IV}$-Py-Co$^{II}$}) zwitterionic coordination polymer from pyridyl-terminated bis-(trisalkoxy)hexavanadate and Co(NO$_3$)$_2$ precursors in the bi-layered solutions or mixtures of DMF/MeOH or MeCN. A segment of the polymeric solid-state structure of {V$^{IV}$-Py-Co$^{II}$} is shown. Color code: C, black sticks; N, blue spheres; O, red spheres; Co, purple spheres; V$^{IV}$O$_6$, orange octahedra.]
It is also noteworthy that the TBA₂[V₆O₁₃{(OCH₂)₃CNHCH₂C₆H₄-4-COOH}]₂ compound then allowed to react with Co(NO₃)₂·6H₂O and 4,4'-bipyridine in a DMSO/DMF mixed solvent gives a ladder-like \{V\textsubscript{V₆}COO-Co\textsuperscript{II}\}, microporous coordination polymer (characterized by elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction) catalyzing the O₂-based oxidation of thiols (R–SH) to disulfides (R–SS–R, R = Pr') [62]. This type of aerobic oxidation was found to be catalyzed by another 3D porous coordination network presented in the following subsection.

### 3.3. 3D Coordination Network

Han and Hill described a pillared layer-type coordination network \{V\textsubscript{V₆}COO-Tb\textsuperscript{III}\}, which was obtained by the reaction of a benzoic acid-terminated bis-(trisalkoxy)hexavanadate compound TBA₂[V₆O₁₃{(OCH₂)₃CNHCH₂C₆H₄-4-COOH}]₂ with 4,4'-bis(pyridine-N-dioxide) (= bpdo) and Tb(NO₃)₃ (Figure 13) [47]. The produced compound has a slight solubility in DMSO, DMF or DMA.

![Figure 13. Synthesis of the \{V\textsubscript{V₆}COO-Tb\textsuperscript{III}\}, porous coordination network from the anti- \{V\textsubscript{V₆}O₁₃{(OCH₂)₃CNHCH₂C₆H₄-4-COOH}\}₂\textsuperscript{2-} and the bpdo and Tb(NO₃)₃ reactants in a DMF/ethylene glycol mixed solvent. Color code: C, black sticks; N, blue spheres; O, red spheres; Tb, purple spheres; V\textsuperscript{V₆}O₆, orange octahedra.](imageURL)
Figure 14. Catalytic cycle for the aerobic oxidation of R–SH to R–SS–R (R = Pr\(^n\)) using the \{\(V_{6b}^V\)-COO-Tb\(^{III}\)\}\(_y\) porous coordination network (only a segment is shown) as catalyst. Color code: C, black sticks; N, blue spheres; O, red spheres; Tb, purple spheres; \(V_{6b}^V\), orange octahedra.

In this crystal structure the two-dimensional (2D) layers created by Tb\(^{III}\) ions and bpdo connectors are bridged by the redox-active, fully-oxidized anti-\{\(V_{6b}\)\} building blocks to result in a 3D open framework. The linkage is enabled by a bidentate chelating coordination of the terminal carboxylate groups of \{\(V_{6b}\)\} to Tb\(^{III}\) (see magnifier in Figure 13). The largest microporous channel exhibits dimensions of 8.0 Å (longest) and 5.2 Å (shortest). Solvent molecules were found to reside in large pores of the network. The \{\(V_{6b}^V\)-COO-Tb\(^{III}\)\}\(_y\) inorganic-organic hybrid material was characterized by elemental analysis, IR, powder and single-crystal X-ray diffraction, and TGA. According to TGA, the compound possesses a limited thermal stability. As illustrated in Figure 14, it shows catalytic activity for heterogeneous aerobic oxidation of R–SH to R–SS–R (R = Pr\(^n\)) under mild conditions and is not decomposed under turnover conditions. Sulfoxidation by peroxides using \{\(V_{6b}^V\)-COO-Tb\(^{III}\)\}\(_y\) as catalyst was also studied.

CONCLUSION

The synthetic accessibility, structural robustness and tunability, stability toward hydrolysis, sufficient solubility in organic solvents, excellent redox
activity, and fluorescence properties of Lindqvist-type trisalkoxohexavanadates open up vast prospects in the development of smart composite materials on their basis. Current methods to generate discrete or periodic structures involves the use of well-defined trisalkoxide ligands which are capable of derivatization and post-functionalization as well as transition metal and lanthanoid cations as linkers. Other reliable methods for accessing the discrete $\{V_6\}$-based supramolecules and their self-assembled macrostructures [63, 64] are being developed. The directed synthesis of donor–acceptor molecular systems with the homo- or heterovalent V atoms and the understanding of their structure-property relations and the associated electron transfer mechanisms represent here an interesting challenge for further investigation. Application in the broad fields of (photo-)redox catalysis, redox-flow batteries, nanophotonics, fluorescence markers, and next-generation information technology, including resistive switching and multilevel state processing is envisaged.

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