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Review

Aryloxo and thiolato vanadium complexes as chemical models of the active site of vanadium nitrogenase

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Contents

Abstract

This review describes recent advances in the synthesis and structural characterization of O- and S-rich ligated vanadium complexes with coligands relevant to the dinitrogen fixation process. Two classes of vanadium complexes: phenolato and thiolato are demonstrated, in aspect of ability to binding nitrogenous species. Examination of their X-ray structures allowed one to correlate the influence of O- and S-ligands at the vanadium site on the ability to bind N_2-intermediates. In such simple systems, the interactions of the vanadium center with reduced and protonated N_2 intermediates may help us develop an understanding of how nitrogenase functions.
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Keywords: Aryloxides; Nitrogenase; Thiolates; Vanadium

1. Introduction

Nitrogen fixation has been a challenge both to biochemists and chemists because of the great difficult to explain how microorganisms engaging nitrogenase enzymes could convert dinitrogen to ammonia, whereas humans had to invent high pressure and high temperature chemical engineering to do it with any facility. Two discoveries: (i) the preparation of the first dinitrogen complex by Allen and Senoff [1] and (ii) the preparation of cell-free extracts of nitrogenase from the anaerobic *Clostridium pasteurianum* [2] stimulated intense activity in the chemical and biochemical fields. Since that time a large number of new dinitrogen fixation complexes were quickly discovered [3]. Biochemical studies up to 1985 had shown the Mo-nitrogenase to be a two-component enzyme, consisting of a Fe-protein and a MoFe-protein, which contained an Fe- and Mo-containing cofactor centre (FeMoco) [4–6]. During association of the two proteins,

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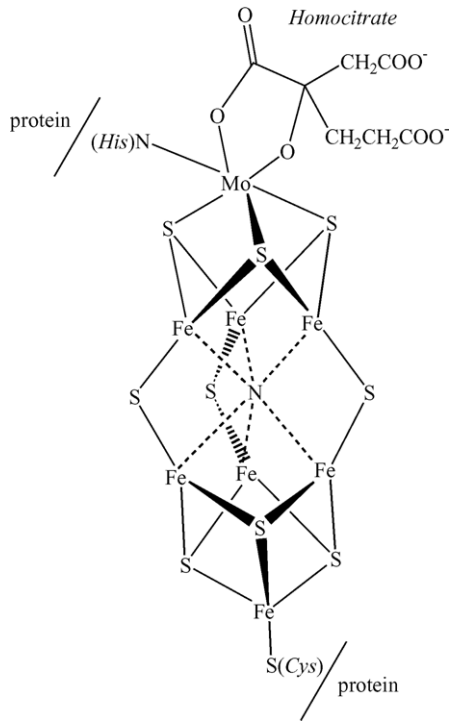


Fig. 1. Structure of the FeMo-cofactor including an interstitial nitride.

electrons are transferred from the Fe-protein to the active site in the MoFe-protein along with hydrolysis of adenosine triphosphate (ATP) [7]. Under optimal conditions the stoichiometry of dinitrogen fixation by Mo-nitrogenase is shown in Eq. (1).

$$N_2 + 8e^- + 8H^+ + 16MgATP = 2NH_4^+ + H_2 + 16MgADP + 16P_i \quad (1)$$

The active site where the N_2 binds and reacts is believed to be the FeMo cofactor. The X-ray structure of the Fe- and MoFe-proteins showed that the FeMoco contains a cluster constrained with seven iron atoms, nine sulfur atoms and the molybdenum atom (Fig. 1) [8]. The cluster is coordinated to the protein through the side chains of only two residues bound to the Fe and Mo atoms located at opposite ends of the cluster. The Mo atom in the cofactor is six coordinate with three inorganic sulfide ions, one nitrogen atom of the histidine and two oxygen atoms of the homocitrate group. However, recent analysis of the crystallographic structure of the MoFe protein at resolution up 1.16 Å revealed a previously unrecognized ligand, most plausibly nitrogen, coordinated to six iron atoms, in the center of the catalytically essential FeMoco [9]. This central atom completes an approximate tetrahedral coordination for all iron atoms. From the chemical point of view, the mode of coordination of the interstitial nitrogen atom in the MoFeco is not unusual and has chemical precedent in the Co carbonyl cluster [10]. This leads to the questions of how the nitrogen atom is inserted, and what is the location and mode of N_2 bonding to the cofactor. So far several models have been proposed and calculated for the interaction between N_2 and the cofactor (Fig. 2) [11]. Model C has most often been considered because the Mo atom lies on the periphery of the cofactor and could easily be reached by an incoming N_2 molecule. This proposal also has good chemical precedents in non-biological phosphine Mo, W, V systems, which bind and reduce dinitrogen under mild conditions [12,13].

Now, two more nitrogenases are known: one contains vanadium instead of Mo and other apparently has Fe as its only metal ions [14].

Vanadium nitrogenase was discovered considerably later than the Mo one [15]. The genetic and spectroscopic data demonstrate [16–20] that vanadium in a cofactor centre (FeVco) has a chemical environment very similar to that of

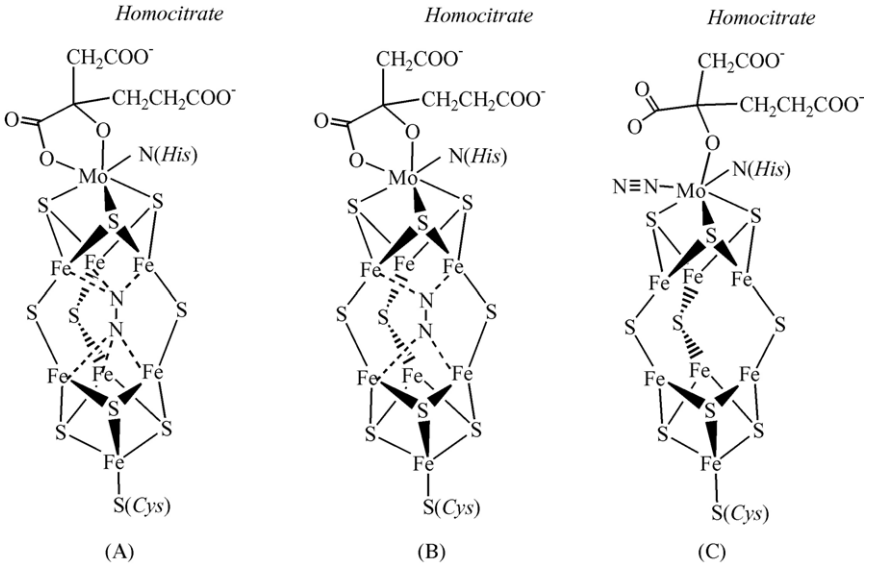


Fig. 2. Favorable binding modes for N_2 at the FeMo-cofactor. Redrawn from Ref. [40b].

molybdenum in FeMoco. The rate of electron transfer from the Fe protein to the VFe protein and its ATP dependence are very similar to those of Mo-nitrogenase. However, N_2 does not compete with protons as effectively as is the case with Mo-nitrogenase [6]. The limiting stoichiometry in vitro is as shown in Eq. (2).

$$N_2 + 12e^- + 14H^+ + 24MgATP = 2NH_4^+ + 3H_2 + 24MgADP + 24P_i \quad (2)$$

In addition, N_2H_4 is a minor product of dinitrogen reduction by V-nitrogenase [21]. Nevertheless, this nitrogenase is more effective in reducing N_2 at lower temperatures than Mo-nitrogenase.

To obtain insight into the role of vanadium and a reduction pathway relevant to nitrogenase chemists have been trying to synthesize FeV-clusters in which the coordination sphere of vanadium mimics the environment around the vanadium centre in VFeco [22–32]. Model VFe-clusters and their reactivity towards N_2-reduced derivatives have recently been reviewed [33]. Both stoichiometric and catalytic reduction of hydrazine using synthetic VFeS-based clusters are already well documented [23,30,31,33]. In addition, the cluster $[Me_4N][VFe_3S_4Cl_3(bpy)(PhNHNH_2)]$ has been isolated and the coordination of the $PhNHNH_2$ to the V site confirmed by X-ray crystallography [32]. Unfortunately, there is no crystallographical evidence for dinitrogen fixation either by vanadium or iron group metals of any synthetic VFe-clusters, although the formation of molecular nitrogen coordination vanadium and iron compounds is well documented. A series of N_2 bridging and end-on, mononuclear and dinuclear vanadium complexes has been reported and characterized [34–39]. Moreover, Shilov's group has discovered vanadium systems, some of them catalytic, which reduce N_2 to NH_3 and/or hydrazine in hydroxylic solvents such as methanol [40]. There is also iron-dinitrogen chemistry mainly developed by Sellmann, which has yielded functional models for nitrogenases [41]. So, from the point of view of nitrogenase function the question of which metal center in the cofactor is responsible for dinitrogen fixation is of great interest. There is strong circumstantial evidence indicating that N_2, or its reduction intermediate, and acetylene binds to the same site in the cofactor [42]. However, there is, as yet, no direct evidence relating the binding of N_2 or its reduction products to cofactors. A novel set of $^{1,2}H$ and ^{13}C ENDOR spectroscopic techniques allowed the first description of a trapped reduction product of propargyl alcohol as a metalla-cyclopropane ring to a single Fe atom of the Fe-S face of the FeMoco [43]. If this be so, the related question arises concerning the function of the molybdenum and vanadium.

Here we discuss results concerning isolation and characterization of vanadium complexes of aryloxo- and thiolato-ligands (Fig. 3) with coligands relevant to the dinitrogen fixation process.

2. Aryloxide vanadium complexes

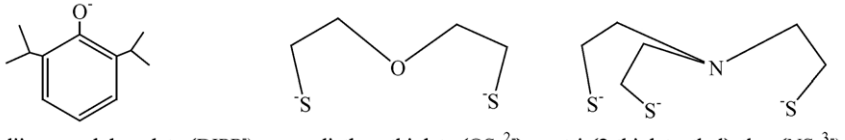
The development of vanadium coordination chemistry with aryloxo ligands is of particular interest because they can reduce dinitrogen under ambient conditions [44]. Systems based on the vanadium catecholates are capable of nitrogen fixation at high pH [45]. Semi-mechanistic analyses of these systems have been interpreted consistently as requiring N_2 to bridge end-on between two metal atoms. However, N_2-carring intermediates have not been isolated and characterized and how they actually function has not been established.

2.1. Synthesis of diisopropylphenolato vanadium complexes

The simplest synthetic route to vanadium(III) aryloxo complexes involves the reaction of $[VCl_3(THF)_3]$ with lithium or sodium salts of the desired phenol [46,47]. Using this methodology a family of diisopropylphenolato vanadium(III) complexes can be created as shown in Scheme 1. The solvent can be toluene or hexane in which LiCl or NaCl is not soluble and can be easily separated from well soluble vanadium diisopropylphenolates **1** [48], **2** [49] and **3** [46].

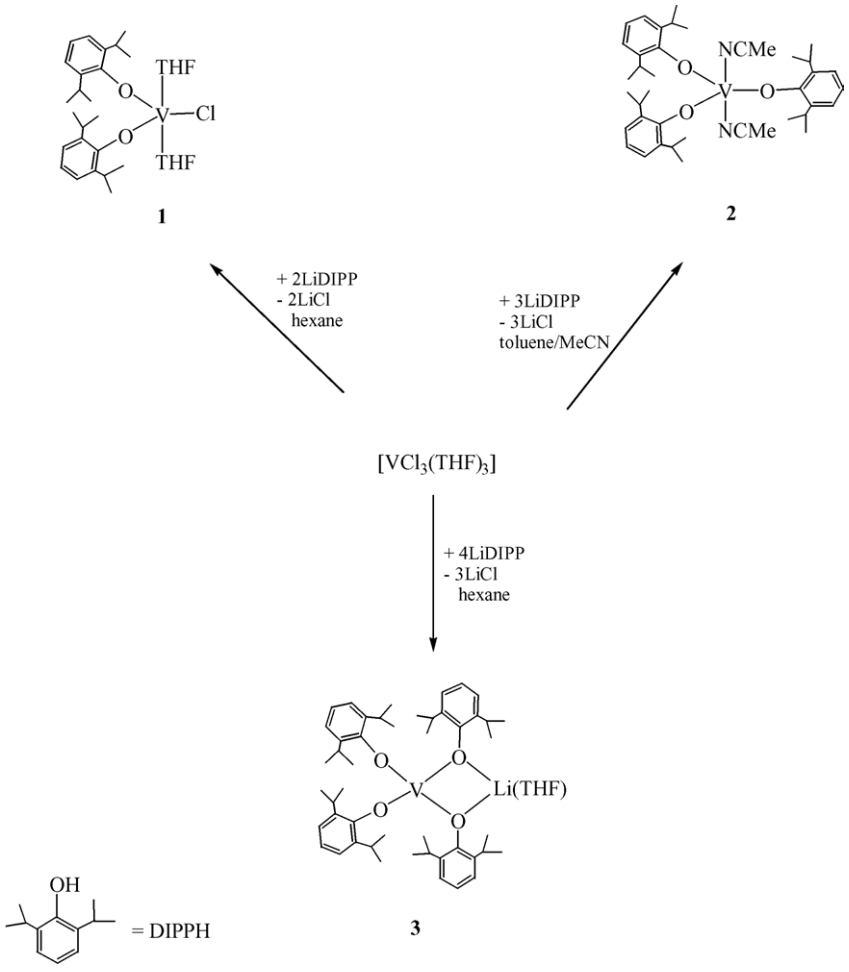
Both **1** and **2** have essentially trigonal bipyramidal geometry, with apical THF or CH_3CN ligands, respectively. The trigonal planes are occupied by the DIPP groups and the chloride. The DIPP ligands have their aromatic groups (related by a two-fold symmetry axis) in the 'up-down' configuration relative to the trigonal plane. Compound **3** has a rather rare, for V(III), distorted tetrahedral structure [50].

Compound **4** was obtained by three routes (Scheme 2), the first being accidental [48]. Treatment of compound **1** with $N_2(SiMe_3)_4$ involved loss of dinitrogen from a transient intermediate which could not be isolated. Compound **4** has an IR band at 1000 cm^{-1} assignable to (V=O). The origin of the V=O group has not been established, but is very likely a result of hydrolysis by adventitious water of the presumably very reactive species formed after loss of N_2 from an intermediate produced during the early stages of the reaction. There

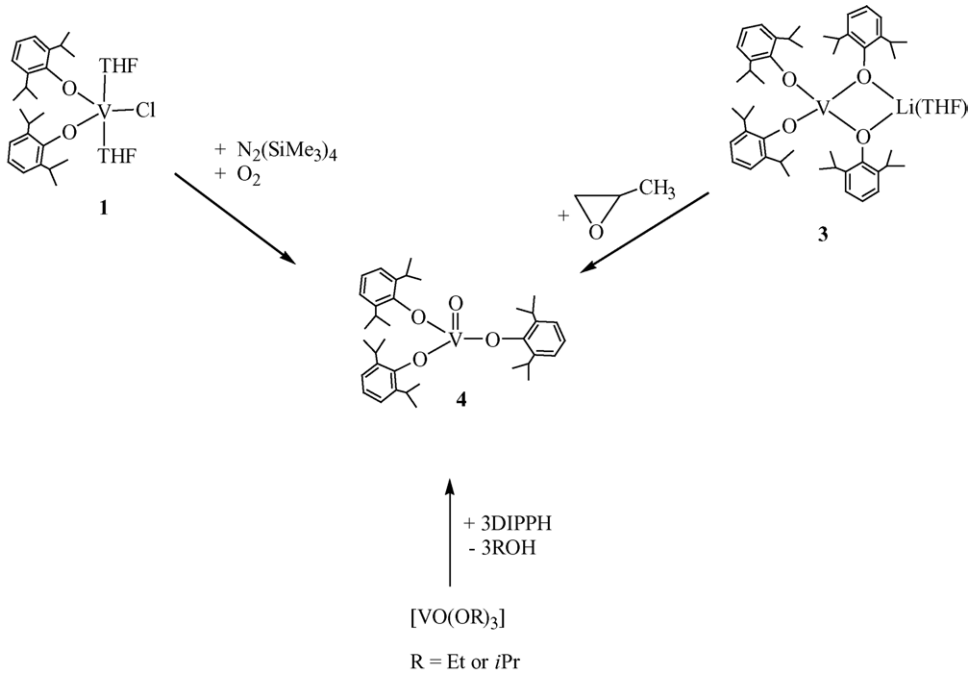


2,6-diisopropylphenolato ($DIPP^-$) oxydiethanethiolato (OS_2^{2-}) tris(2-thiolatoethyl)ether (NS_3^{3-})

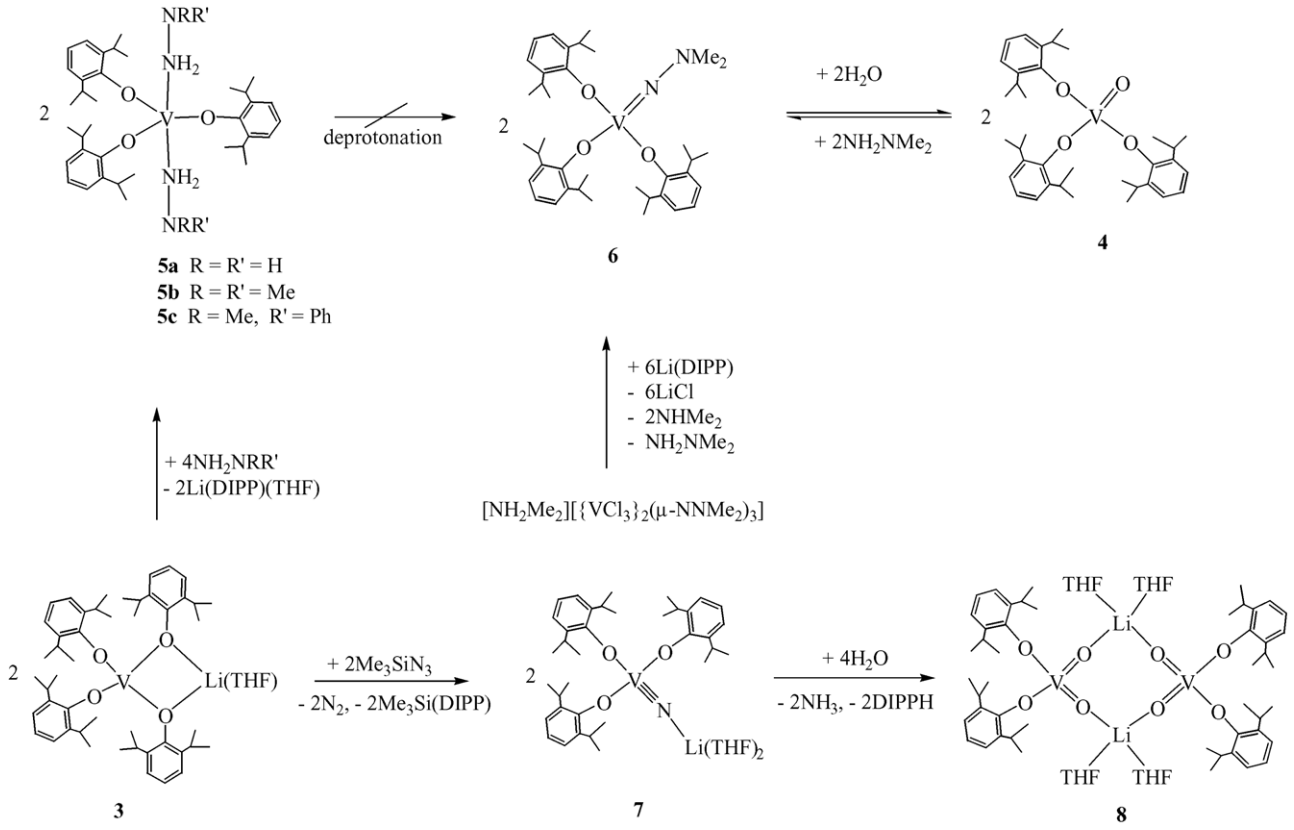
Fig. 3. Representations of the ligands employed in this work and their abbreviations.



Scheme 1.



Scheme 2.



Scheme 3.

must also be a step in the reaction sequence, which generates the third diisopropylphenolato group found at vanadium in **4**. In high yield, compound **4** can be obtained by treatment of [VO(*i*OPr)$_3$] with DIPPH or treatment of **3** with propylene oxide (Scheme 1). It has trigonal pyramidal geometry about vanadium with the vanadium atom 0.633(1) Å out of the plane of the three phenoxide oxygen atoms. The molecule of **4** shows disorder about a crystallographic two-fold symmetry axis. The vanadyl group is randomly disordered between sites related by this axis. This is a rare geometry for V(V) chemistry; alkoxide analogues are dimers with trigonal bipyramidal environments for the vanadium atoms [51]. Evidently, the bulk of the DIPP$^-$ ligands in compound **4** prevent close intermolecular approach.

2.2. Reactivity of vanadium diisopropylphenolates toward N_2-intermediates

Reduction of N_2 to NH_3 by nitrogenases might involve intermediate species N_2H_m and NH_n (m = 0–4; n = 0–3) bound at active sites. The isolation of complexes with these species bound to aryloxido vanadium centers is of current interest in dinitrogen coordination chemistry.

Compounds **1**–**4** did not fix N_2. However, **3** [46] and **4** [48] participate in generation of a variety of fixed nitrogenous intermediates. As is shown in Scheme 3 compound **3** reacts with hydrazine and its organic derivatives to form hydrazine adducts **5a** [52], **5b** and **5c** [53].

Compounds **5a**–**c** have bipyramidal geometry around the vanadium with the aryloxo ligands in the girdle and the axial hydrazine ligands coordinated end-on by the NH_2 groups. Selected average bond dimensions are shown in Table 1. The *trans*-hydrazine groups have N–N distances in the range normally associated with N–N single bonds and the V–N–N angles as expected for sp^3-hybridized orbitals at nitrogen atoms in hydrazines. The average V–N and N–N distances for **5a**–**c** vary from 2.161(4) to 2.211(8) Å and from 1.467(6) to 1.392(10) Å, respectively and reflect the relationship of decreasing basicity of substituted hydrazine in the order $NH_2NH_2 > NH_2NMe_2 \sim NH_2NMePh$.

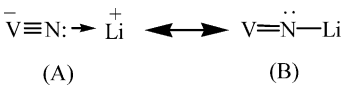
Deprotonation of **5a**–**c** with KO*t*Bu or [Pb(CH$_3$COO)$_2$] does not lead to desired hydrazido derivatives. These intermediates can be achieved by the reaction of dianion [{VCl$_3$}$_2$(μ-NNMe$_2$)$_3$]$^{2-}$ [53] with Li(DIPP) or in the condensation reaction of compound **4** with dimethyl hydrazine [54]. The last

Table 1
Selected bond lengths (Å) and angles (°) for **5a**–**c**

	5a	5b	5c
V–N(av.)	2.161(4)	2.194(6)	2.211(8)
N–N(av.)	1.467(6)	1.457(9)	1.392(10)
V–N–N(av.)	112.3(3)	121.8(5)	130.5(6)

route is reversible and a mixture of **4** and **6** exists in the equilibrium (Scheme 3). Compound **6** has tetrahedral geometry at the vanadium with linear V–N–N [angle 175.8(3)°]. The V–N and N–N distances of 1.654(3) and 1.311(4) Å, respectively are in the range typical for hydrazido(2-) ligands in early transition-metal complexes.

The formation of nitrido ligands as end products of N_2 reduction is an important area to understand nitrogenase, especially in the light, recently of Rees' discovery of a central ligand in the FeMo-cofactor. A common route to nitride complexes of transition-metals generally, and vanadium in particular, is by the reaction of $SiMe_3N_3$ with a suitable low-valent precursor to give a complex of the $NSiMe_3$, ligand via loss of N_2 from an intermediate azide complex. In some cases, the $NSiMe_3$ ligand can be hydrolysed to the =NH group and then converted to the nitride ligand by deprotonation [55]. This route appears convenient to reach the diamagnetic compound **7** from the precursor **3** [54]. Although, the detailed mechanism of this reaction is not established, no doubt a driving force of the reaction is the formation of $Me_3Si(DIPP)$. Compound **7** has tetrahedrally coordinated vanadium with the V–N distance, 1.565(5) Å in the range typically observed for vanadium(V)-nitrido complexes. Therefore, compound **7** is best regarded as a $[Li(THF)_3]^+$ adduct of the nitride anion $[V(DIPP)_3N]^-$ in which the V–N group has a high degree of triple-bond character. Thus, structure (A) is a better representation of the bonding in **7** than is the imide structure (B).



(A) (B)

The Li–N–V angle is 164.0(5)° and the deviation of the VNLi system from strict linearity could be a consequence of some involvement of the (B) form in the structure, although crystal-packing factors should not be discounted. Controlled protonation of **7** with water led to evolution of stoichiometric amounts of ammonia and a novel metallocyclic compound **8** was formed [54].

3. Thiolato vanadium complexes

Intense interest in discrete vanadium thiolate complexes is prompted by the relevance not only to biological systems but also to certain processes in the petroleum industry [56] as well as the novel structure of such complexes and the potential of applications in organosulfur chemistry. The chemistry of vanadium thiolates has been discussed in previous reviews [33,57]. Our interest in vanadium thiolates was focused on the synthesis, structural characterization and reactivity of vanadium complexes with 2,2′-oxydiethanethiolato (OS_2^{2-}) ligand as chemical models the vanadium centre in the FeVco.

3.1. Synthesis of 2,2′-oxydiethane thiolato vanadium complexes

The substitution of diisopropylphenolates in **1** by the OS_2^{2-} ligand leads to the formation of two products: an olive non-crystalline complex **9** and red-violet crystalline **10** (Scheme 4) [58].

The solid-state EPR spectrum of **9** exhibits a broad line ($\Delta H = 86$ G, $g = 1.974$) with eight principal lines (^{51}V, I = 7/2). Compound **9** shows a temperature-dependent magnetic moment with μ_{eff} per V atom varying from 2.22 μ_B at 297 K to 1.78 μ_B at 77 K. This suggests weak antiferromagnetic coupling between the vanadium(IV) atoms and indicates a non-monomeric structure, so that, a dimeric structure is proposed for **9**. The crystals of **10** consist of a cation $[V^{II}(CH_3CN)_6]^{2+}$ and an anion $[V^{III}Cl_2(OS_2)]^-$ in a 1:2 molar ratio with six-coordinate V(II) in the cation and a pentacoordinate V(III) center adopting a slightly distorted trigonal bipyramidal geometry in the ion. The temperature-independent magnetic moment of **10** (2.99 μ_B) per vanadium atom is consistent with non-interacting two d^2 and one d^3 vanadium centers.

Because of the insolubility of the lithium salt of 2,2′-oxydiethanethiol in organic solvents its using to synthesis of V(III) dithiolates from $[VCl_3(THF)_3]$ appeared unsuccessful. The desired compound **11** was derived from the reaction of diisopropylphenolato precursor **3** and 2,2′-oxydiethanethiol (Scheme 5) [59].

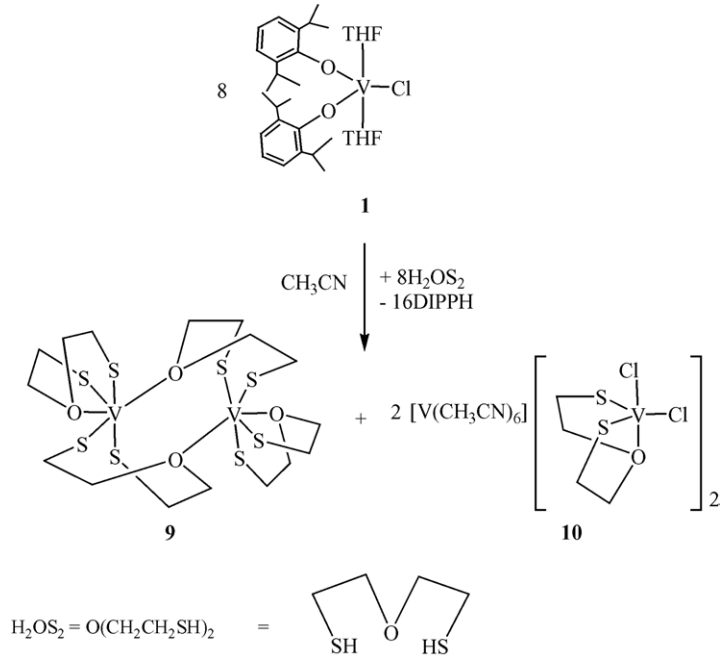
The crystal structure determination of **11** showed it to contain a five-coordinate V(III) center adopting a slightly distorted trigonal bipyramidal geometry. In the heterobimetallic compound **11** both aryloxo oxygen atoms are engaged in the bridging interaction to tetrahedral Li, inducing distortion from the ideal bipyramidal structure. Addition of pyridine breaks up the heterodinuclear structure of **11** forming a monomeric compound **12** with unchanged geometry around the vanadium centre.

Vanadium(V) complexes of OS_2^{2-} ligand, **13** and **14** were created by simple substitution of isopropoxide groups in the oxo-precursor $[VO(OiPr)_3]$ (Scheme 6) [60].

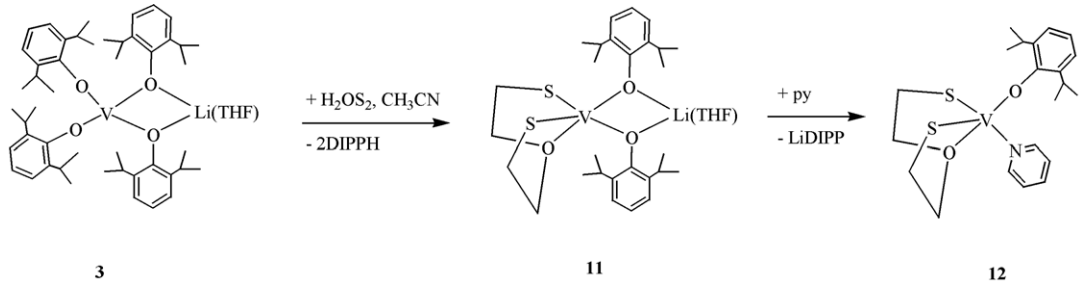
Compound **13** is not soluble in organic solvents so that its structure can only be postulated as polymeric on the basis of elemental analysis and IR spectroscopy. The presence of a sterically hindered group such as diisopropylphenolato at the VO-coordination sphere significantly increases solubility and prevents the formation of polymeric aggregates. In this manner, **14** was obtained. Compound **14** has ν(V=O) at 982 cm^{-1} and its X-ray structure showed it to have trigonal bipyramidal geometry.

3.2. Reactivity of vanadium dithiolates toward N_2-intermediates

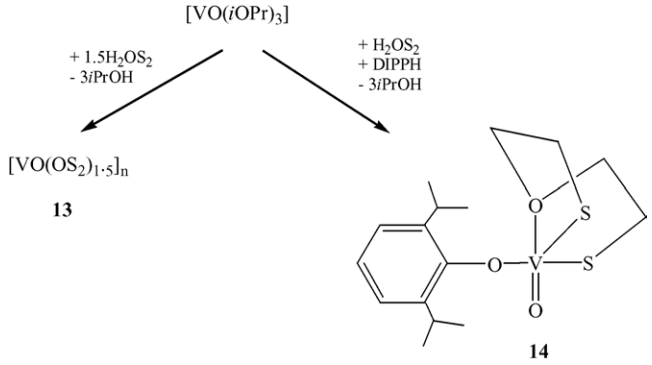
The investigation of the ability of vanadium carrying sulfur atoms to interact with nitrogenous species is of great importance to understand the mode of action of the nitrogenase



Scheme 4.



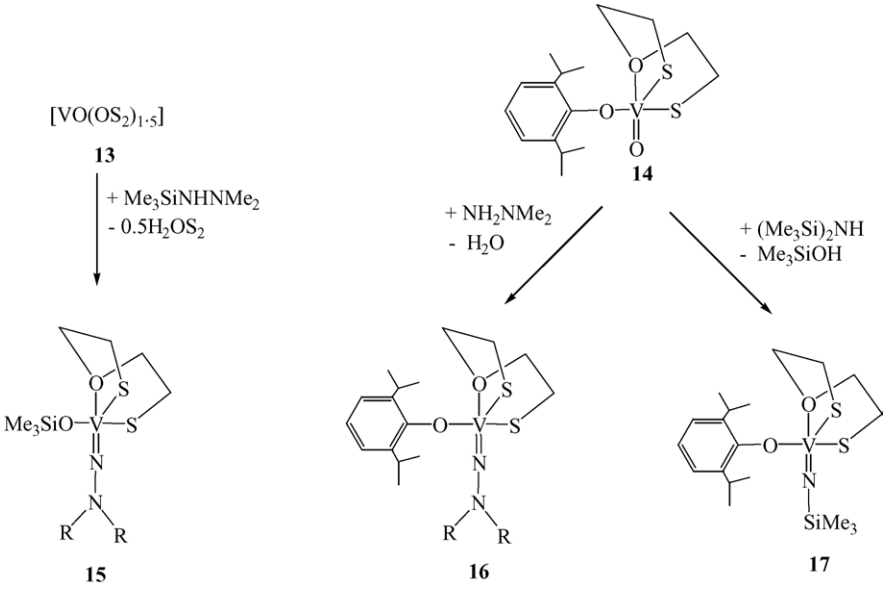
Scheme 5.



Scheme 6.

enzyme. So far, there is no crystallographically documented sulfur-ligated vanadium species with a coordinated dinitrogen molecule. Our studies have also established that none of compounds **9**–**14** fixed dinitrogen under appropriate conditions. Among them only oxo-precursors **13** and **14** are able to participate in generation of hydrazido(2-) derivatives **15**, **16** and imido **17** (Scheme 7) [60].

The X-ray structures of **15**, **16**, and **17** are very similar to that of **14** and all have the expected trigonal bipyramidal structure with two sulfur atoms of the $[OS_2]^{2-}$ ligand and one oxygen atom of the $OSiMe_3$ (**15**) or DIPP (**16** and **17**) ligand defining the trigonal plane. The axial positions in **14**–**17** consist of a trans influence system, of the O–V–X group, where O is the central oxygen of the $[OS_2]^{2-}$ ligand and X = O, $NNMe_2$ or $NSiMe_3$, which gives trans influence order, O > $NSiMe_3$ > $NNMe_2$. As a consequence, the V–S distances in **14**–**17** increase as the axial V–O(OS_2) distance decreases. The equatorial V–O distances in **14**–**17**, which span the range 1.785(2)–1.808(3) Å, are shorter than the corresponding axial V–O distances, no doubt a consequence of the proximity of neighboring ligands in the five coordinate complexes and the anionic nature and stronger binding of the equatorial phenoxide or alkoxide oxygen compared to the ether-type oxygen of the axial linkage.



Scheme 7.

3.3. Reactivity of vanadium trithiolates toward N_2-intermediates

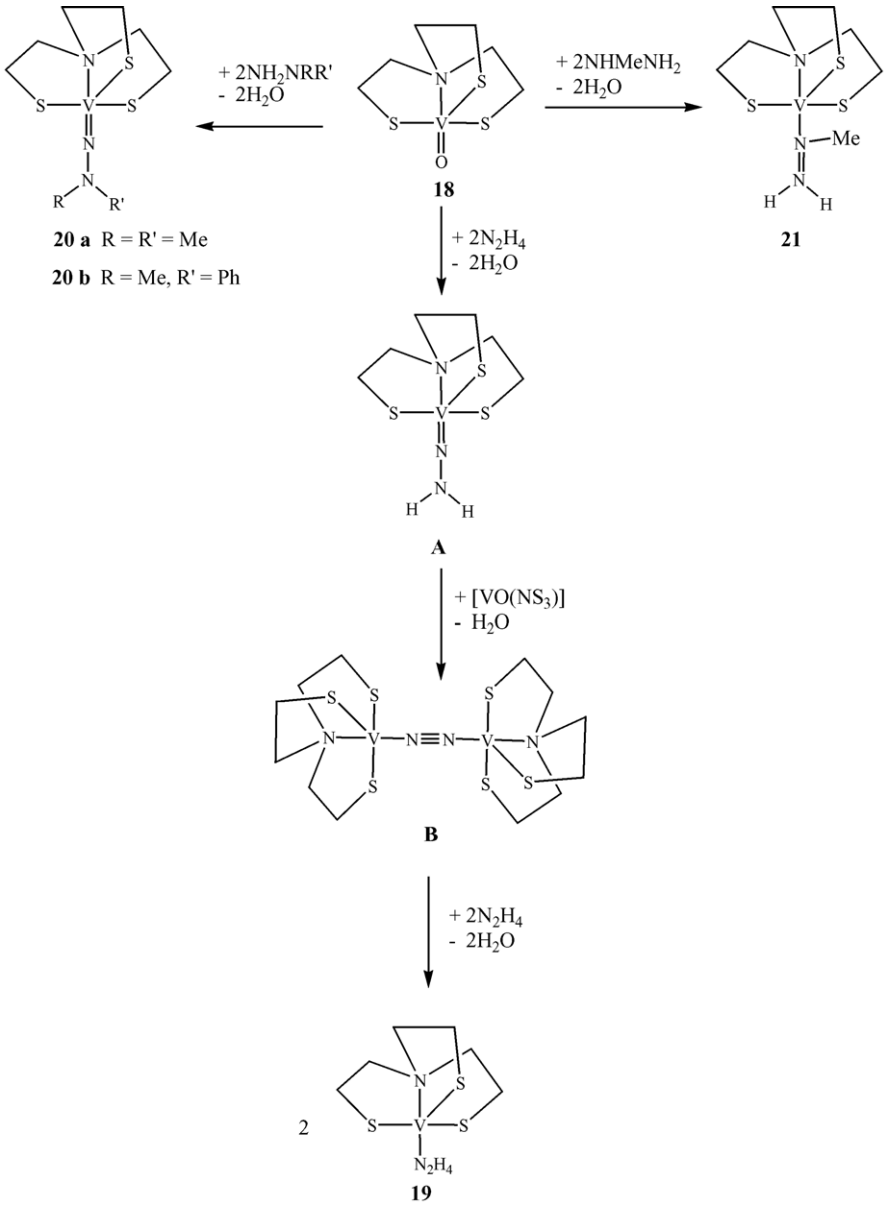
The chemistry of the vanadium center, which carries three sulfur atoms from the tris(2-thiolatoethyl)amine ligand (NS_3^{3-}) has been intensively studied by Richards et al. [59–61]. Key reactions to generate a range of complexes of N_2H_m and NH_n are shown in Schemes 8 and 9.

Complex **18** [62] appeared to be a useful precursor to generate a rich family of nitrogenous derivatives. Treatment of **18** with an excess of anhydrous hydrazine removes the oxide ligand and reduces V(V) to give the V(III) hydrazine adduct **19** (Scheme 8) [60]. The geometry about the vanadium in **19** is trigonal bipyramid with the S atoms of the NS_3^{3-} in the equatorial positions and nitrogen atoms of NS_3^{3-} and N_2H_4 ligands in apical sites. In contrast, the "PS_3" ligand [$PS_3 = \{P(C_6H_3\text{-}3\text{-}Me_3Si\text{-}2\text{-}S)_3\}^{3-}$] creates a capped octahedral compound [$V(PS_3)(N_2H_4)_3$] [63]. The hydrazine ligand in **19** is end-on bound to the vanadium and bent at the ligating nitrogen with V–N–N angle of 111.7(8)°, which is in the range of those seen in related hydrazine complexes of vanadium(III) (see Section 2.2). The V–N and N–N distances are both of single bonds. It has been suggested that the formation of **19** might involve an intermediate dinitrogen complex [$\{V(NS_3)\}_2(\mu\text{-}N_2)$] (**A**) formed via a hydrazide species [$V(NS_3)(NNH_2)$] (**B**). Although the intermediate **A** has not been isolated in a characterizable form, but its formation appears reasonable in view of the products quantitatively derived from it and the fact that stable, linear vanadium(III) dinitrogen-bridged complexes are well-known [64]. The proposal of the hydrazide intermediate precursor **B** follows because treatment of **1** with substituted hydrazines gives the diamagnetic hydrazido(2-) complexes [$V(NS_3)(NNRR')$] (**20a–b**), which can be regarded as stabilized analogues of **B**. In view of the isolation of the hydrazido(1-) complex of vanadium(IV) **21** [61], it seems most likely that the formation of **19** might involve more stages than are shown in Scheme 8.

The stoichiometric disproportionation reaction of **19** results in the formation of the ammonia complex **22** (Scheme 9). Displacement of NH_3 from **22** by MeCN gives the adduct **23.** The CN stretching frequencies in **23** as well as in aryloxide complex **2** are slightly increased compared to those in the free ligand, whereas these frequencies generally decrease when this ligand coordinates to a site capable of binding CO or N_2 [65]. The reaction of complex **19** with Me_3SiN_3 leads to the imido species **24**. The imido $NSiMe_3$ in **24** can be smoothly hydrolyzed to the NH^{2-} derivative to create complex **25**. The X-ray structures of **20–25** showed them to have the same form as complex **19**. They all have trigonal bipyramidal geometry with variations in the fifth apical ligand site. The V–N(nitrogenous species) bond lengths in **20–25** and N–N distances in **20** and **21** are in the usual range (Table 2). However, the V–N(NS_3) distances in these both series of [$V^{III}(NS_3)X$] (X = N_2H_4, NH_3, MeCN) and [$V^{V}(NS_3)Y$] (Y = O, $NNMe_2$, NNMePh, $NSiMe_3$, NH) complexes vary because of trans interaction and give orders of trans influences for X of $NH_3 \sim N_2H_4 >$ MeCN and for Y of O > $NSiMe_3$ > NH > $NNMe_2 \sim$ NNMePh.

Table 2
Selected bond lengths (Å) in [$V^{III}(NS_3)X$] and [$V^{V}(NS_3)Y$] complexes

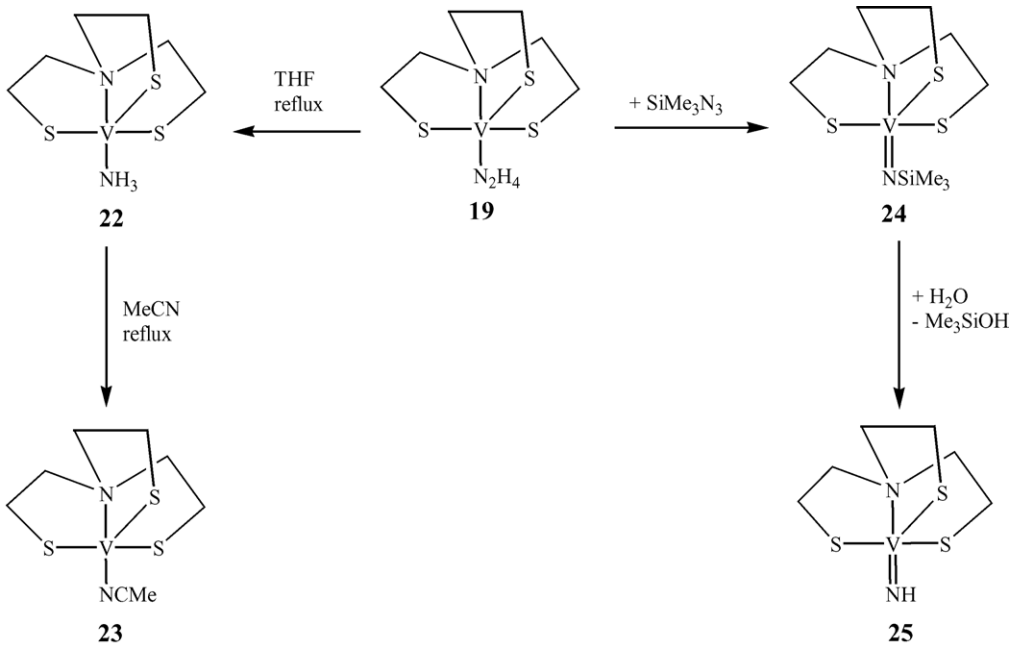
Compound	V–N(NS_3)	V–X or Y	N–N
[$V(NS_3)(N_2H_4)$] (**19**)	2.180(9)	2.135(10)	1.48(2)
[$V(NS_3)(NH_3)$] (**22**)	2.155(8)	2.154(7)	–
[$V(NS_3)$(NCMe)] (**23**)	2.147(2)	2.097(2)	–
[$V(NS_3)$O] (**18**)	2.291(6)	1.578(6)	–
[$V(NS_3)(NNMe_2)$] (**20a**)	2.214(3)	1.681(3)	1.305(5)
[$V(NS_3)$(NNMePh)] (**20b**)	2.218(2)	1.682(2)	1.310(3)
[$V(NS_3)(NSiMe_3)$](**24**)	2.271(6)	1.647(6)	–
[$V(NS_3)$(NH)] (**25**)	2.234(2)	1.638(3)	–



Scheme 8.

4. ^{51}V NMR spectroscopy of diisopropylphenalato, di- and tri-thiolato vanadium compounds

^{51}V NMR spectroscopy is a convenient and powerful tool to probe the electronic manifold of vanadium complexes. The vanadium chemical shift was shown [66] in general to move to low field (relative to a chosen standard, $VOCl_3$) as the electronegativity of non-polarizable ligands at vanadium decreased, thus decreasing the mean HOMO-LUMO gap, ΔE, and increasing the paramagnetic shielding term σ. Ligands that participate in low-energy ligand-to-metal charge transfer cause a reduction of ΔE and hence additional deshielding [66]. As might be expected on this basis, because of the presence of the highly polarizable sulfur ligands, all the compounds $[V(NS_3)Y]$ (Y = O, NR, or NNR_2) of this study show shifts downfield of $VOCl_3$ and the resonances of the NS_3 complex series (VNS_3L ligation) are to the low field of the corresponding members of the OS_2 series (VO_2S_2L ligation) (Table 3). Illustrative of this general trend are the ^{51}V shifts (ppm) of the analogous pairs of compounds: $[V(NS_3)O]$ 557; $[V(OS_2)O(DIPP)]$ 191; $[VO(DIPP)_3]$ −531 and $[V(NS_3)(NNMe_2)]$ 416; $[V(OS_2)(DIPP)_3(NNMe_2)]$ 269; $[V(DIPP)_3(NNMe_2)]$ −527. Within the $[V(NS_3)Y]$ series, the order of the Y ligands in terms of ^{51}V chemical shift (greatest deshielding) is O (557) > $NNMe_2$ (420) > NR (349). For the series $[V(OS_2)(DIPP)Y]$, the corresponding order is $NNMe_2$ (269) > O (191) > NR(61) and for the series $[V(DIPP)_3Y]$ the order is NR [R = $Li(THF)_2$] (39) > $NNMe_2$ (−527) ∼ O (−531). Here, we note that the order for both series does not follow that expected simply from electroneg-



Scheme 9.

Table 3
^{51}V NMR chemical shifts for vanadium(V) aryloxides and thiolates

Compound	^{51}V (ppm)
[VO(DIPP)$_3$] (**4**)	−531
[V(DIPP)$_3$(NNMe$_2$)] (**6**)	−527
[V(DIPP)$_3$NLi(THF)$_2$] (**7**)	39
[VO(OS$_2$)(DIPP)] (**14**)	191
[V(OS$_2$)(DIPP)(NNMe$_2$)] (**16**)	269
[V(OS$_2$)(DIPP)(NSiMe$_3$] (**17**)	61
[VO(NS$_3$)] (**18**)	557
[V(NS$_3$)(NNMe$_2$)] (**20a**)	416
[V(NS$_3$)(NSiMe$_3$)] (**22**)	349

ativities, where the position for Y = O would be expected to be to the high field of the nitrogen ligands, as is seen for the series [V{N(CH$_2$CH$_2$NSiMe$_3$)$_3$}Y] (Z = O or NR) [67].

Although the variation of ^{51}V shift with electronic transitions and thus ΔE appears to be internally consistent within the [V(NS$_3$)Y] series, the relative position of the oxides [VO(NS$_3$)], [VO(OS$_2$)(DIPP)] and [VO(DIPP)$_3$] are unexpectedly to low field with respect to complexes of nitrogen donors, which have lower electronegativity than oxide. In the absence of detailed theoretical studies, it is not clear what factors influence ΔE to give rise to this apparent anomaly, but clearly, it is a consequence of the presence of the NS$_3$ ligand, since the analogous [V{N(CH$_2$CH$_2$NSiMe$_3$)$_3$}Y] [67] follow the expected order of electronegativities.

5. Conclusions

In this review, we have tried to present our recent observations in the ability of oxygen-and/or sulfur-ligated vanadium centers to bind coligands relevant to the nitrogenase. The reaction of the V=O unit in **4**, **13**, **14** and **18**, particularly with hydrazines but also with other reagents, has allowed access to a range of vanadium complexes with various NR (NR = N$_2$H$_4$, NH$_3$, NH, etc.) ligands at VO$_3$, VOS$_2$ and VNS$_3$ sites. However, although these vanadium sites are adept at binding nitrogenous species that could be involved in the latter stages of fixation of N$_2$ at the vanadium site of the nitrogenase, they are incapable of binding N$_2$ or other substrates or inhibitors of nitrogenase such as CO or H$_2$. Similar behavior is seen for their NN$_3$-analogues [66]. This might be due to the inability of the VO$_3$, VOS$_2$, VNS$_3$ and VNN$_3$ sites to match the π-acceptor requirement of a terminal N$_2$ group. An indication of this is that although the d^2 VO$_3$ and VNS$_3$ sites are able to bind MeCN in **2** and **23** the CN stretching frequencies in these compounds are slightly increased compared to those in the free ligands, whereas these frequencies generally decrease when these ligands coordinate sites capable of binding CO or N$_2$.

The geometry of the vanadium sites described here, mostly trigonal bipyramidal, would also accommodate the bridging mode of N$_2$ binding. Some evidence that this does occur weakly has been presented for the VNS$_3$ site, but it might be necessary to lower the oxidation state of the vanadium to make VNS$_3$, or a related site VO$_3$ and VOS$_2$, sufficiently electron-releasing to accomplish stable N$_2$ binding in either the terminal or the bridging mode. Ligands other than N$_2$ bind strongly in the bridging mode in for example the dinuclear compounds [NBu$_4$][(NS$_3$)V(μ-CN)V(NS$_3$)] and [NEt$_4$][(NS$_3$)V(μ-N)V(NS$_3$)] [60a]. Examination of the X-ray structures of the family of aryloxo and thiolato complexes presented here, allowed us to notice that either O- or S-ligated vanadium centers are able to bind the same N$_2$-intermediates, having similar V–N, N–N and V–N–N bond lengths and an-

gles, respectively. This means that both O- and S-ligands can create good simple models for the vanadium site in the FeV-cofactor. However, since, so far there is no strong evidence for N_2 binding at the S-rich ligation environment of vanadium sites, we can only suggest that the vanadium center in the FeV-cofactor could participate at binding of reduced and protonated dinitrogen intermediates.

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