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Reactions of small molecules at transition metal sites: studies relevant to nitrogenase, an organometallic enzyme [1]

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Contents

Abstract

This article outlines some coordination chemistry of Mo, V and Fe relevant to the function of the active centre of nitrogenase, FeMoco. The focus is on work which has been carried out in the Nitrogen Fixation Laboratory, whose founding Director was Joseph Chatt, and the article is dedicated to him. The introduction sketches the properties of nitrogenase and its reductions of isocyanides, cyanide and alkynes, and interaction with carbon monoxide, which established the organometallic nature of this enzyme. A brief description of the chemistry of isolated FeMoco is given, particularly its reactions with thiols, selenols and cyanide. These reactions are discussed with respect to the structure of FeMoco. The reduction of dinitrogen (and alternative nitrogenase substrates such as isocyanides and alkynes) at metal centres is then described, leading from reactions of these substrates at metal centres with phosphine co-ligands to those metal centres with mainly sulphur ligation. The current state of knowledge of this chemistry is then discussed with respect to the likely site or sites of interaction of dinitrogen on FeMoco.

Keywords: FeMoco; Nitrogenase; Transition metal site

[1] Dedicated to the memory of Joseph Chatt.

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1. Introduction

I began study of nitrogenase when I joined Joseph Chatt at the then newly formed Unit of Nitrogen Fixation at the University of Sussex, beginning a working relationship which spanned some 16 years. To me, Joseph Chatt was at that time an awe-inspiring figure who demanded from his colleagues the same high standards that he always applied to his own activities. I quickly learned also of his fairness and loyalty to his co-workers. He was an inspirational Director of the Unit, who guided us with intuitive foresight and clarity, yet always gave us the freedom and support to follow our own ideas, provided that good science would follow. Joseph Chatt's name will be remembered with admiration for his scientific achievements. I will remember Joseph for his scientific rigour and brilliance and with deep warmth and affection for his kindness and humanity.

This article will describe some chemistry which has developed from the early, rather dim knowledge of the structure of nitrogenase and is targeted towards understanding the function of this enzyme. I will make brief mention of those early studies, which helped, together with the work of other groups, to define the organometallic nature of nitrogenase, but I will concentrate on more recent work which has received a closer focus with the determination of the X-ray structure of the nitrogenase proteins from *Azotobacter vinelandii* by Rees and co-workers [1] and from *Clostridium pasteurianum* by Bolin and colleagues [2].

2. The nitrogenase enzyme and FeMoco

Regardless of the bacterial origin, the nitrogenase enzyme consists of two component proteins, the Fe protein and the FeMo protein. When supplied in vitro with the magnesium salt of ATP and a reducing agent such as $Na_2S_2O_4$ (sodium dithionite) to supply electrons, they carry out the reduction of N_2 to NH_3 as shown in Eq. (1), where it should be noted that one H_2 molecule is evolved for every N_2 reduced to $2NH_3$, and two molecules of ATP are consumed for every electron transferred to the N_2 molecule:

$$N_2 + 8H^+ + 8e^- + 16ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16Pi \quad (1)$$

Nitrogenase also reduces a number of other unsaturated molecules, such as CH_3NC (to CH_4 and NH_3) [3], cyanide ion (to CH_4 and NH_3) [4], and C_2H_2 (to C_2H_4) [4]. These reactions, and the observation that carbon monoxide inhibits the reduction of all substrates except the proton, established the organometallic nature of the enzyme. In the absence of any other substrate, protons are reduced to H_2; there is a corresponding reduction in the molecular yield of H_2 in presence of substrate.

The two component proteins of nitrogenase differ in size and, as mentioned above, have been structurally characterized by X-ray crystallography for the organism *Azotobacter vinelandii*. In particular, the larger FeMo protein contains a cluster unit, the iron–molybdenum cofactor, FeMoco, which is considered to be the active site at which dinitrogen and other substrates are reduced. Its structure, deduced from the X-ray analysis at 2.2 Å resolution [1], is shown in Fig. 1.

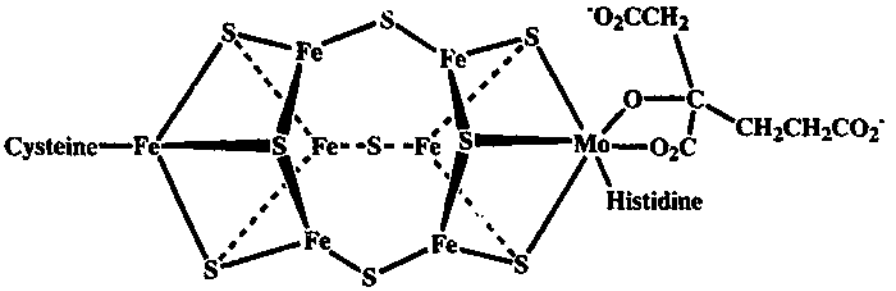


Fig. 1. Model fitting the electron density profile of FeMoco from the MoFe protein, showing ligation by cysteine and histidine residues. The nature of one of the central bridging atoms is poorly defined, but it is probably sulphur. (Adapted from Ref. [1].)

FeMoco can be extracted from the FeMo protein, and its chemistry has been studied in the hope of obtaining crystals to allow a high-resolution X-ray structure determination and to deduce where on the cluster the binding and activation of dinitrogen and the alternative substrates occur. FeMoco can only be extracted in small quantity, and this limitation, together with its extreme sensitivity to dioxygen, has so far precluded crystallization. Normally, FeMoco is extracted in the so-called semi-reduced form, the oxidation level achieved with sodium dithionite which is used to protect FeMoco from oxidative damage. The properties in solution of the semi-reduced form have been examined by spectroscopic means, particularly using its characteristic $S=3/2$ electron paramagnetic resonance (EPR) spectroscopy and by X-ray absorption spectroscopy (XAS) [6]. These studies were of course begun before knowledge of the X-ray crystallographic conclusions, and indeed bond distances within the cluster deduced from XAS investigation of FeMoco were used in deriving the structure shown in Fig. 1 [1].

When removed from the protein, FeMoco contains no amino acids, and it is therefore reasonable to propose that its cysteine–Fe and histidine–Mo bonds to the protein are severed in the extraction process, and replaced by solvent such as *N*-methyl formamide, or possibly its anion, as shown in Fig. 2. FeMoco when isolated is anionic, with a probable 2^- charge, and it could be dimeric or oligomeric [7]. Some progress has been made in understanding its chemical reactivity. As might be expected from its extraction with loss of a cysteine–Fe link to the protein, FeMoco reacts with thiols and selenols. A combination of EPR titration data and Fe- and Se-XAS studies have shown that this interaction is of one thiolate or selenate at an Fe atom, presumed to be the Fe atom originally bound to cysteine as indicated in Fig. 2. In this condition the characteristic broad EPR resonance of FeMoco sharpens, appearing more like the resonance seen for FeMoco within the protein [6,8,9].

Similar studies of FeMoco treated with cyanide ion show that the $S=3/2$ resonance becomes more axial and that cyanide binds to two sites on FeMoco; one is Mo, and the other is presumed to be Fe, the latter interaction giving rise to the EPR spectral change. When cyanide and thiolate are in competition for the FeMoco sites, it appears that thiolate displaces cyanide from Fe but not from Mo, as indicated in Fig. 2 (a monomeric unit is shown, but this has not yet been established, and cyanide

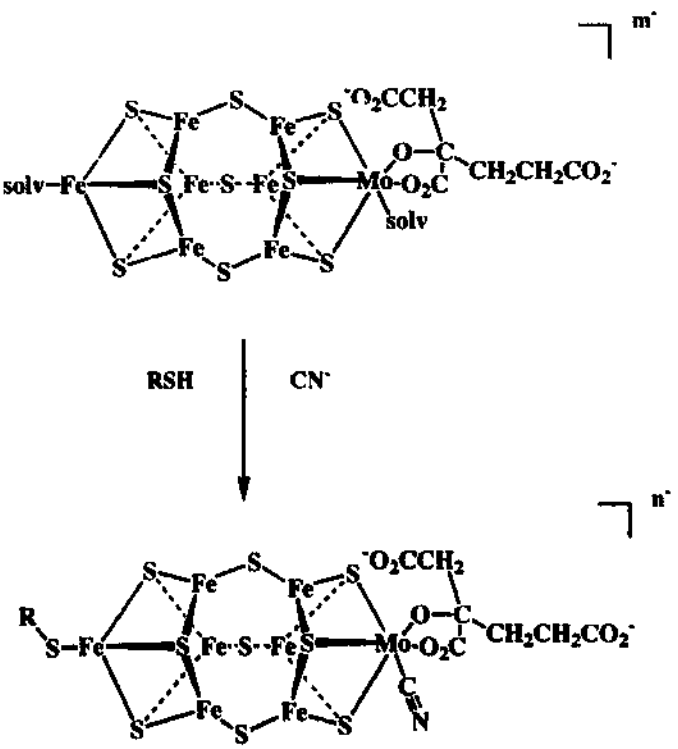


Fig. 2. Representation of the reactions of FeMoco with thiol and cyanide ion. The values of m and n are uncertain. Solv = solvent such as *N*-methylformamide, or its anion.

could be acting in the terminal or bridging mode) [10,11]. MeNC also interacts with semi-reduced FeMoco, but di- and tri-thiols disrupt the cluster structure, giving as yet uncharacterized products [12,13].

The dithionite-reduced oxidation level of FeMoco, when extracted and as also seen in the X-ray study of the FeMo protein, is not that of the active state during turnover, and although electrochemical studies have shown that semi-reduced FeMoco can lose or gain an electron, no interaction with N_2 has yet been observed at any oxidation level [6,8–13].

The X-ray structural model of FeMoco has therefore not given a clear lead as to the site of binding and reduction of N_2 and the alternative substrates of nitrogenase. The interaction could be at Mo or Fe, possibly with proton transfer from sulphur, or perhaps, in the case of alternative substrates, direct interaction with sulphur could occur, as has been observed between alkynes and sulphur ligands bridging Mo atoms, e.g. in the complex $[\{Mo(C_5H_5)_2\}_2(\mu\text{-}S_2)_2]$ [14]. At this stage it is also important to note that, at least in *Azotobacter*, two alternative nitrogenases exist; in the first, molybdenum is replaced by vanadium, and in the second it appears to have been replaced by iron [15].

In order to consider further a likely mechanism for the binding and reduction of N_2 and alternative substrates on nitrogenase, it is necessary to turn to the established chemistry of these ligands at metal centres.

3. Reduction of nitrogenase substrates at metal centres

3.1. Phosphine-ligated metals

The development of inorganic/organometallic chemistry in modern times owes a great debt to Joseph Chatt for his many contributions. Of particular note is his pioneering work in establishing the coordination chemistry of the now ubiquitous diphosphine ligands (e.g. $Ph_2PCH_2CH_2PPh_2$ and $Me_2PCH_2CH_2Me_2$), which are crucial to this field of study [16], and most important in the current context is his contribution to the development of the coordination chemistry of dinitrogen [17].

The interaction of N_2 and the other nitrogenase substrates with metal centres has been studied in considerable depth, and it has been shown that N_2 can be bound and reduced to NH_3 at Mo, V or Fe centres, particularly where these metals are in a low oxidation state and have a tertiary phosphine ligand environment [17–19]. The most thoroughly studied of these metals is Mo, and the mechanism of reduction of N_2 at such a centre is shown in Fig. 3 [20,21]. Using this chemistry, an electrochemical cycle has been developed for the production of ammonia [22]. Alternative substrates such as isocyanides (Fig. 4) and alkynes (Fig. 5) are bound and reduced at the Mo centres to give similar products to those from nitrogenase [23]. A similar chemistry is being developed for the related V and Fe systems [18,19].

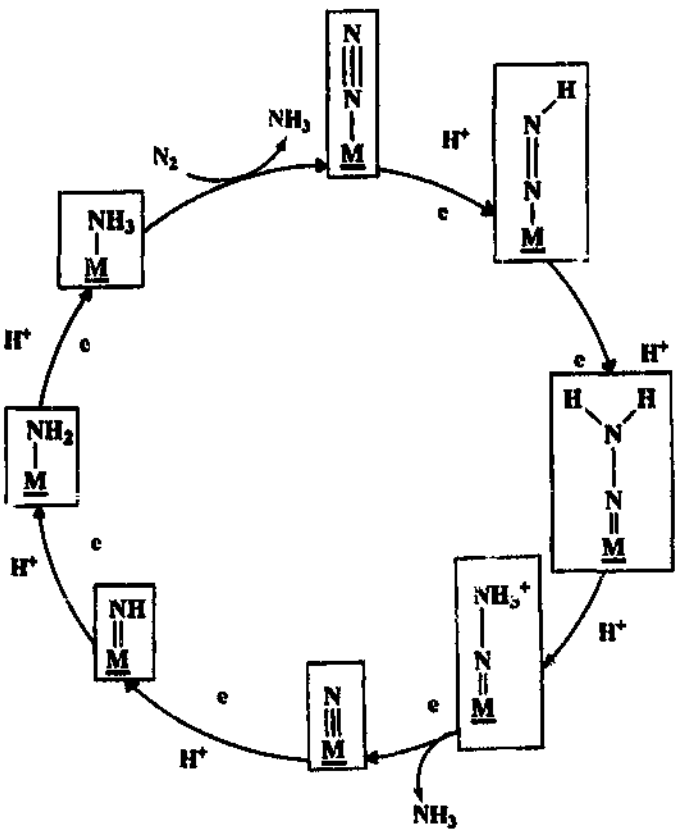
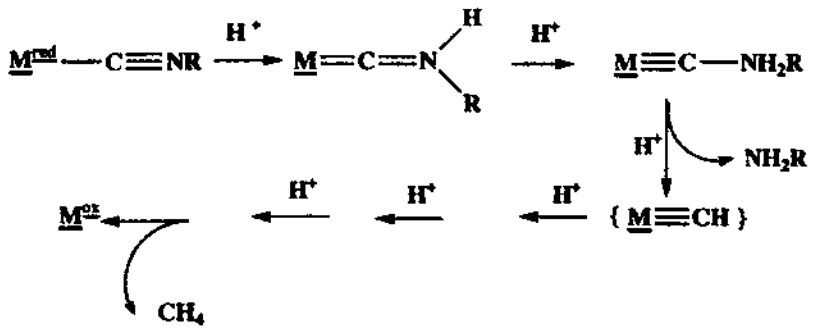
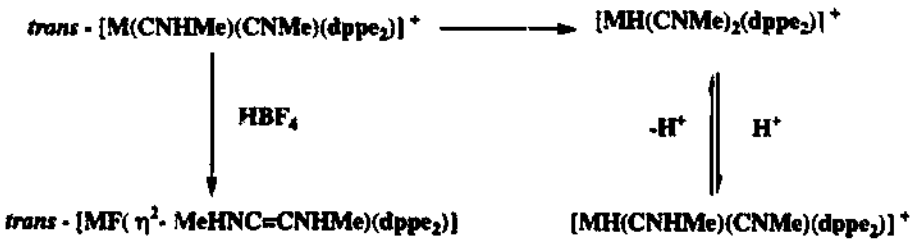


Fig. 3. Reduction of N_2 at tertiary phosphine sites. $\underline{M} = M(diphosphine)_2$, where M = Mo, W, V or Fe.



(A)



(B)

Fig. 4. (A) General scheme of reduction of isocyanides at phosphine-ligated metals, M. (B) Reductive coupling of isocyanides at these centres (see Ref. [56]). dppe = $Ph_2PCH_2CH_2PPh_2$.

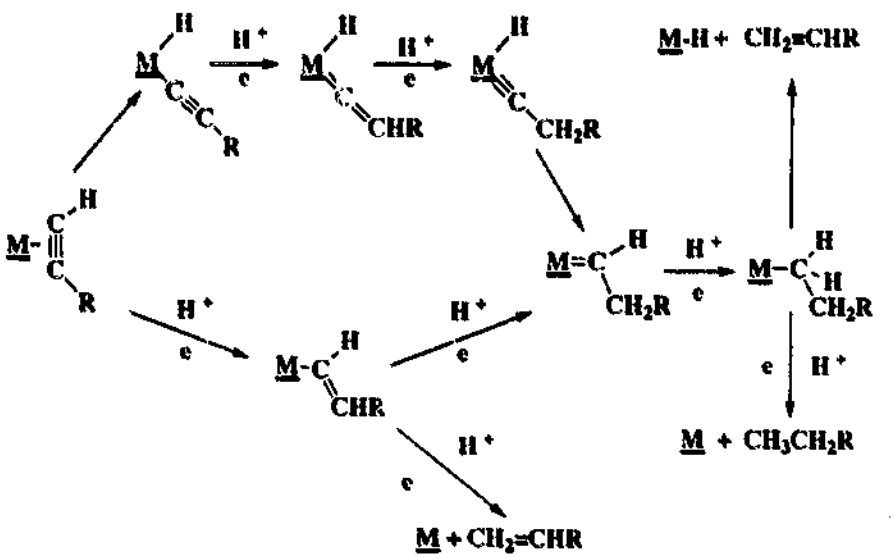


Fig. 5. General scheme of reduction of alkynes at phosphine-ligated metals, M (for details, see Refs. [17,20]).

The {M(diphosphine)$_2$} centres (M = Mo or Fe) also bind H_2, which can be displaced by N_2. This type of reaction might well relate to the reduction of protons by nitrogenase and the release of H_2 when N_2 is bound and reduced, and has been discussed in detail elsewhere [17–19,24].

The above chemistry has primarily involved mononuclear metal sites, but dinitrogen has a well-documented chemistry in the bridging mode [17,25]. Although reduction of bridging dinitrogen usually gives hydrazine, ammonia can be produced, e.g. from acid treatment of [V{($C_6H_4CH_2NMe_2$)$_2$(C_5H_5N)}$_2$(μ-N_2)] [26].

Thus, on the basis of this well-established chemistry, Fe and Mo in FeMoco (Fe and V or Fe only in the alternative nitrogenases) are equal candidates for the substrate binding centre. However, the ligand environment in the phosphine complexes is clearly not that of FeMoco, and we will postpone further discussion until after consideration of sulphur-ligated metal systems in the next section.

3.2. Sulphur-ligated metals

Because it has been clear for many years that the metals in nitrogenase have a sulphur-ligand environment, efforts have been made to prepare complexes of dinitrogen or its derivatives such as hydrazine and diazene, and of other nitrogenase substrates, at metal centres where the co-ligands have sulphur-donor atoms. The nature of the sulphur donor has varied between thioether, thiolate and sulphide or mixtures of these.

The most successful system in terms of binding N_2 has been pioneered by Yoshida [27] and utilizes a four-sulphur macrocyclic thioether, Me_8[16]aneS_4 (see Fig. 6) to form the core ligation to Mo or W, thus resembling the four-phosphorus core of the complexes of Fig. 3. The thioether compounds are prepared by displacement of CO from halide–carbonyl precursors [27,28], followed by reduction of the resulting halide complex under N_2 (or an analogue such as CO) to give the zero-valent complexes as shown in Fig. 6. The reducing agent can be chemical or an electrode [29]. Other nitrogenase substrates such as isocyanides also bind these centres [30]. The dinitrogen ligands can be reduced, but the yields of ammonia are low relative to the phosphine system [31] and the greater susceptibility of the thioether ligand to degradation makes an electrochemically driven cycle for ammonia analogous to the phosphine system unlikely at present.

Unlike the {M(diphosphine)$_2$} (M = Mo or W) centres, the {M(Me_8[16]aneS_4)} centres do not appear to interact with H_2. It is not clear why this should be the case, and this is a weakness of this centre in terms of modelling nitrogenase function.

As yet no analogues of *trans*-[Mo(N_2)$_2$(Me_8[16]aneS_4)] in which V or Fe replace Mo have been obtained.

These observations, together with knowledge of the S_3NO_2 coordination environment of the Mo in FeMoco provided by the X-ray structure, has prompted an extension of the above studies to the use of macrocycles with mixed thioether–alkoxide ligation (S_3O_2 donor system), such as is shown in Fig. 7 [32]; this chemistry is at an early stage of development. It should be noted in this context that the ligation of Mo in FeMoco is mimicked closely in the cluster complexes shown in Fig. 8 [33,34], where the coordination environment of the Mo can be S_3O_2N (e.g.

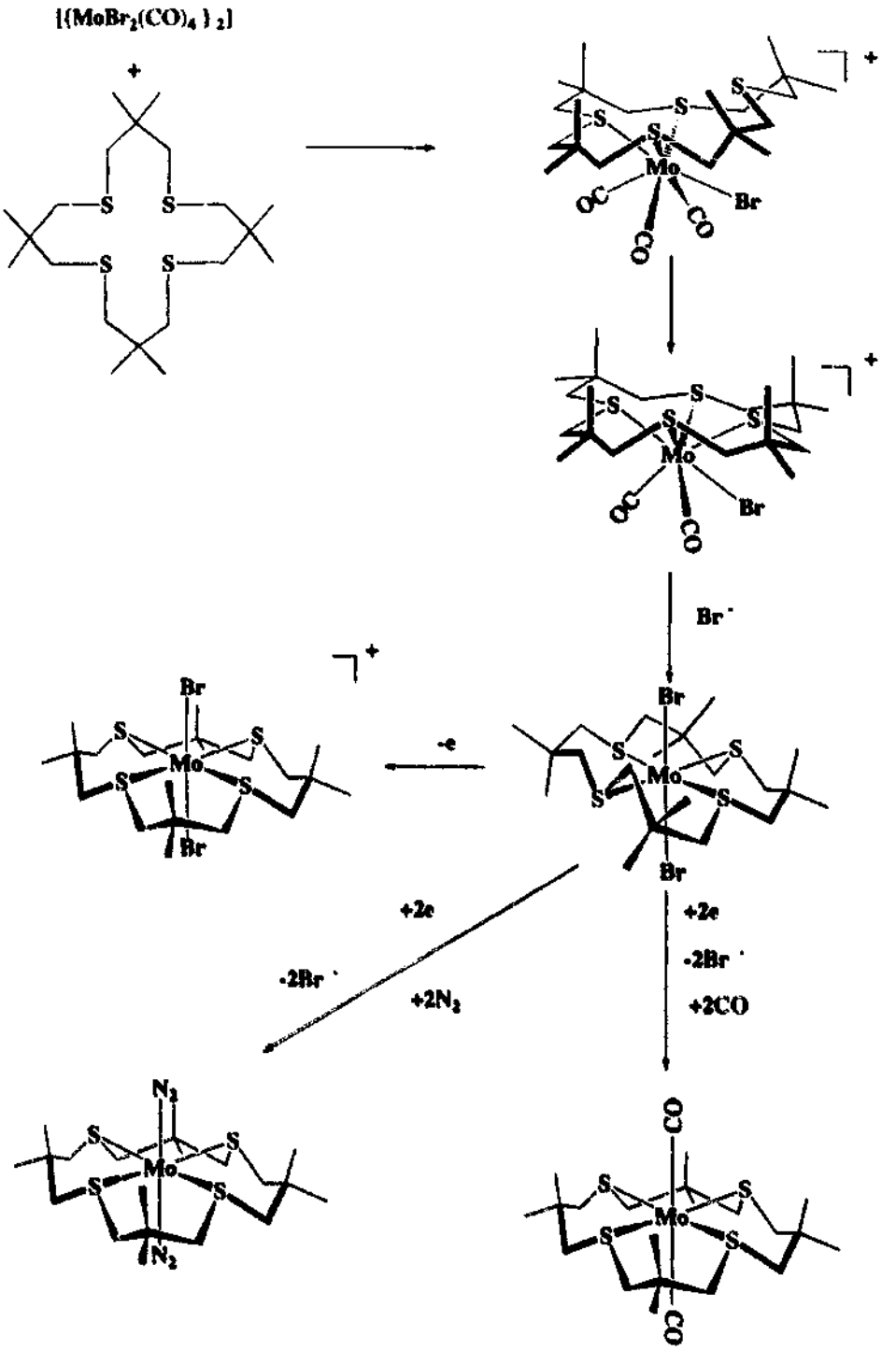


Fig. 6. General scheme of preparation of complexes of $Me_8$16[ane]S_4. Parts of the macrocyclic ligand are omitted for clarity.

S_3 from μ-sulphides, O_2 from catecholate or citrate, N from MeCN [33,34] or imidazole [35]). Indeed, structural parameters from such compounds were used in the formulation of the crystallographic model of FeMoco [1].

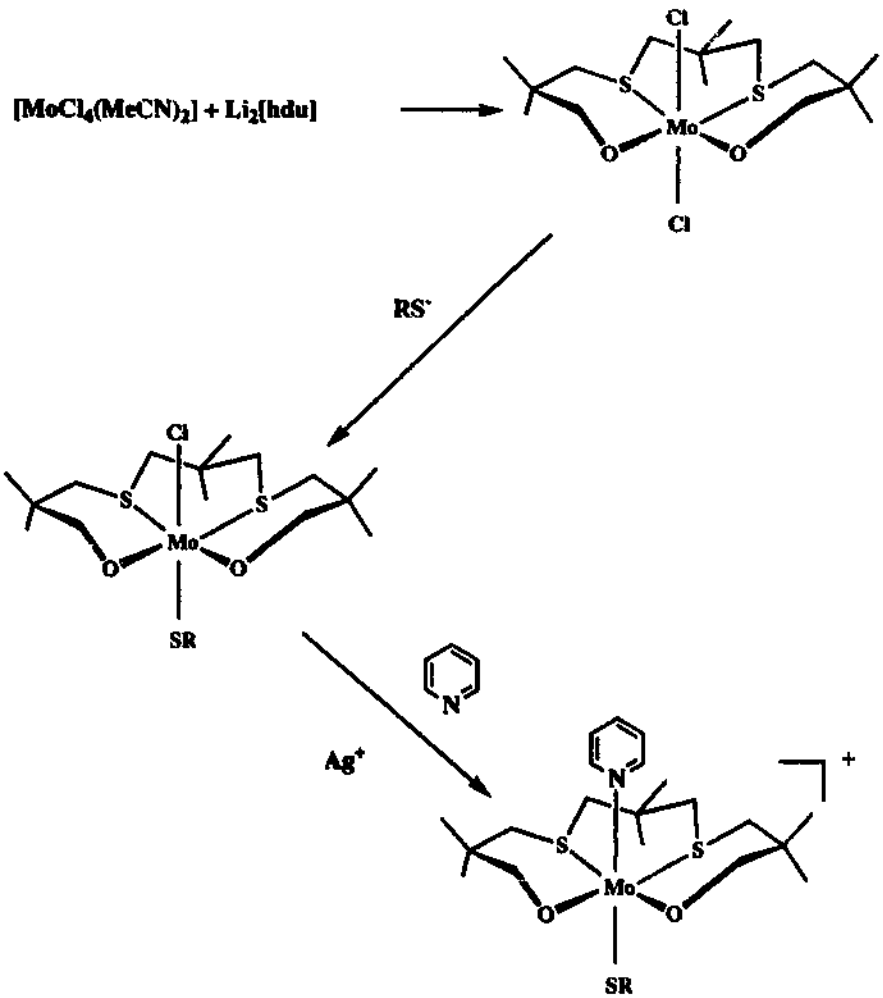


Fig. 7. General scheme of preparation of complexes of 4,8-dithio-2,2,6,6,10,10-hexamethylundecane-1,11-diol (hdu). R = $C_6H_2Me_3$-2,4,6 or $C_6H_2Pr^i_3$-2,4,6.

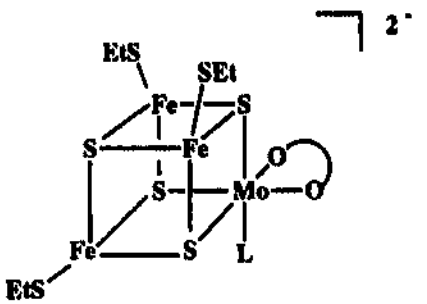


Fig. 8. Cluster anions which model the coordination environment of Mo in FeMoco (L = MeCN, imidazole, etc.; O–O = $C_6Cl_4O_2^{2-}$)

As yet none of the complexes shown in Figs. 7 and 8 have been induced to react with N_2, but cluster anions such as $[MoFe_3S_4Cl_3(C_6Cl_4O_2)MeCN)]^{2-}$ catalyse the disproportionation and reduction of hydrazine. The site of binding of N_2H_4 appears

to be Mo, since $PhNHNH_2$ has been shown to bind at Mo in the above cluster [34]. These observations have relevance to the possible function of nitrogenase in that bound hydrazine, and derivatives of it such as N_2H_2, NNH_2^-, or NNH_3^- (see Fig. 3), are likely intermediates in the reduction of N_2, whether at a mononuclear or a multinuclear site.

Molybdenum–thiolate complexes have also been used to model aspects of nitrogenase chemistry, in particular the reduction of hydrazine, and also the binding of hydrogen to sulphur-ligated metal centres. In one such demonstration of the catalytic disproportionation and reduction of hydrazine, the catalyst precursor is the binuclear complex $[Mo_2Cl_4(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2(\mu\text{-}S_2)(\mu\text{-}2\text{-}SC_5H_3NH\text{-}3\text{-}SiMe_3)]$ [36], and the catalyst itself may be binuclear also, but this has not been established.

A second study involves the use of the unsaturated thiolate–hydride complexes $[MoH(SR)_3(PR^1Ph_2)]$ ($R = C_6H_2Me_3$-2,4,6 or $C_6H_2Pr^i_3$-2,4,6; R^1 = Me or Et) [37]. These complexes were prepared to examine the behaviour of hydride ligands at a metal which also carries sulphur-donor groups. This has relevance to the possible involvement of metal hydride(s) in the metal–μ-sulphide environment of FeMoco when N_2 is reduced and H_2 is evolved. The stability of the $[MoH(SR)_3(PR^1Ph_2)]$ complexes with respect to elimination of thiol is kinetic and rests upon the bulk of the substituent groups on the ligands. If the thiolate substituent in such compounds is small, then dihydrogen and the dithiol are eliminated [38]. As might be expected from their unsaturation, these complexes are very reactive and, as shown in Fig. 9 [39–42], undergo, inter alia, exchange of hydride for deuteride under deuterium [40] and cleavage of S–aryl bonds of the thiolate ligands with elimination of arene. The last reaction relates to hydrodesulphurization chemistry [41].

As observed for the cluster and the binuclear compounds above, disproportionation and reduction of hydrazine are catalysed by these compounds. The adducts $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)(PhNHNH_2)]$ (from reaction of $PhNHNH_2$) and $[MoH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMePh_2)(NH_2NH_2)]$ (from reaction of NH_2NH_2) have been structurally characterized, indicating that, at least in outline, the reduction reaction occurs at a single Mo and follows the pathway shown in Fig. 10 [42]. Although binding of N_2 at this type of site has not yet been demonstrated, isolation of such a compound may be a matter of time, since the complex $[Re(SC_6H_2Pr^i_3\text{-}2,4,6)_3(N_2)(PPh_3)]$ is known [43].

Chemistry of vanadium in this area is less well developed, but similar patterns of reaction are emerging. Reactions of hydrazines with simple vanadium precursors have been studied with the aim of developing a chemistry related to that above. Hydrazine adducts such as $[VCl_3(Me_2NNH_2)_2]$ [44] and $[V(OC_6H_2Pr^i_3\text{-}2,6)_3(Me_2NNH_2)_2]$ [45], and hydrazide complexes such as $[VCl_2(NNMePh)(NH_2NMePh)]Cl$ [46] and $[NH_2Me_2]_2[(VCl_3)_2(\mu\text{-}NNMe_2)_3]$ [47], and its thiolate derivative $[NH_2Me_2]_2[\{V(SC_6H_2Pr^i_3\text{-}2,4,6)_3\}_2(\mu\text{-}NNMe_2)_2]$ [45], have been obtained and structurally characterized in some cases (see Fig. 11 for examples). Further reactions of the hydrazide ligands in these compounds await investigation.

Some elegant iron–sulphur ligand chemistry has been carried out in two areas; in the first are sought analogues of the apparently trigonally coordinated central iron

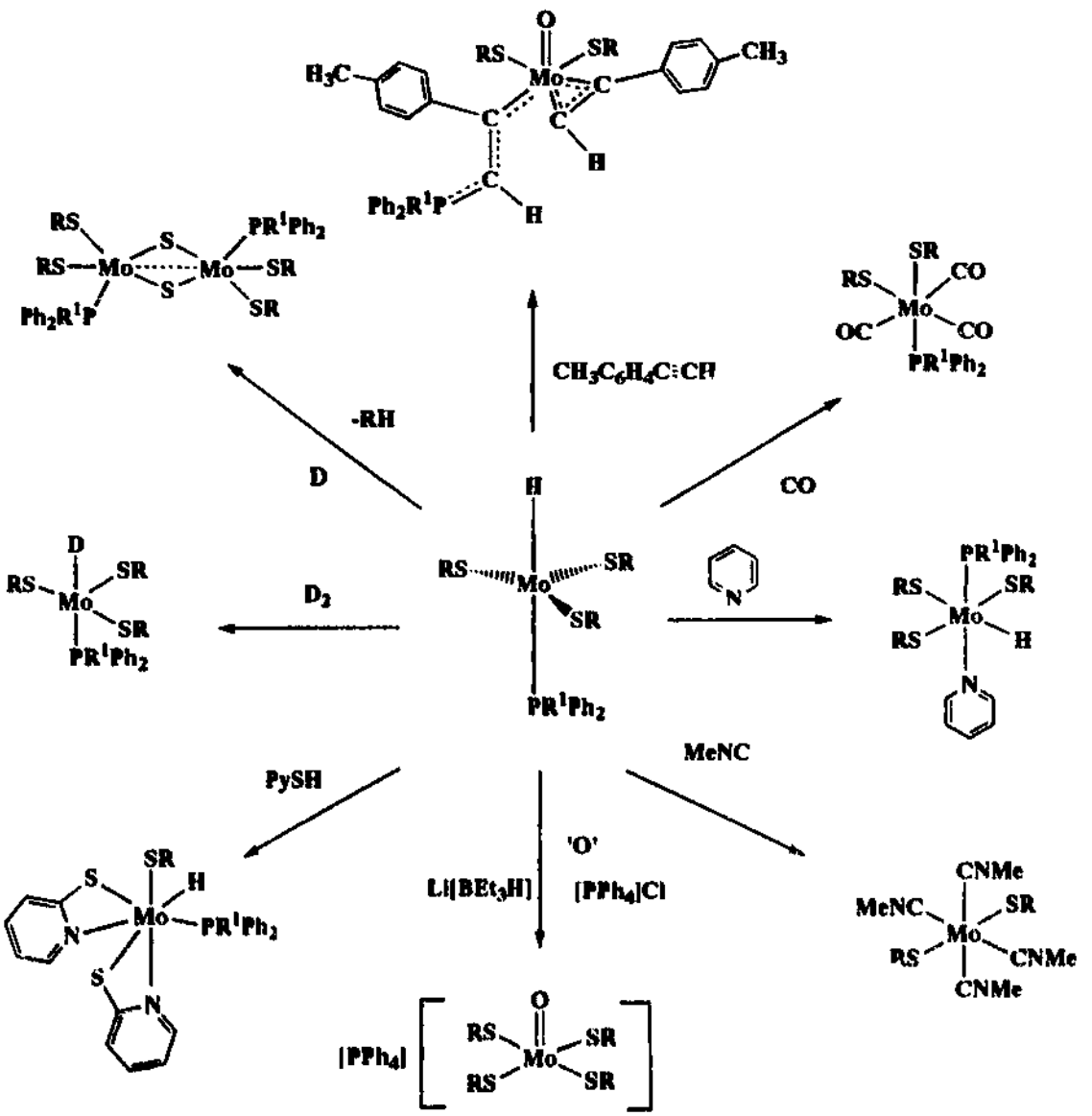


Fig. 9. General scheme of reactions of the complexes $[MoH(SR)_3(PR^1Ph_2)]$ (R = $C_6H_2Me_3$-2,4,6 or $C_6H_2Pr^i_3$-2,4,6; R^1 = Me or Et).

atoms of FeMoco, and in the second are sought intermediates on pathways of reduction of N_2, should it occur at these metals.

In the first area, the only compounds to date which approach the low coordination number and geometry of the central trigonal Fe atoms are the thiolato-complexes $[\{Fe(SAr)\}_2(\mu\text{-}SAr)_2]$ ($SAr = SC_6H_2Bu^t_3$-2,4,6) [48].

In the second area, diazene (formed from hydrazine) has been stabilized between two iron atoms in the complex $[\{Fe(N_HS_4)\}_2(\mu\text{-}NHNH)]$ [N_HS_4 = 2,2′-bis(2-mercaptophenylthio)diethylamine] [49]. Hydrogen-bonding between the (μ-NHNH) ligand and the sulphur atoms appears to aid the stability of this complex.

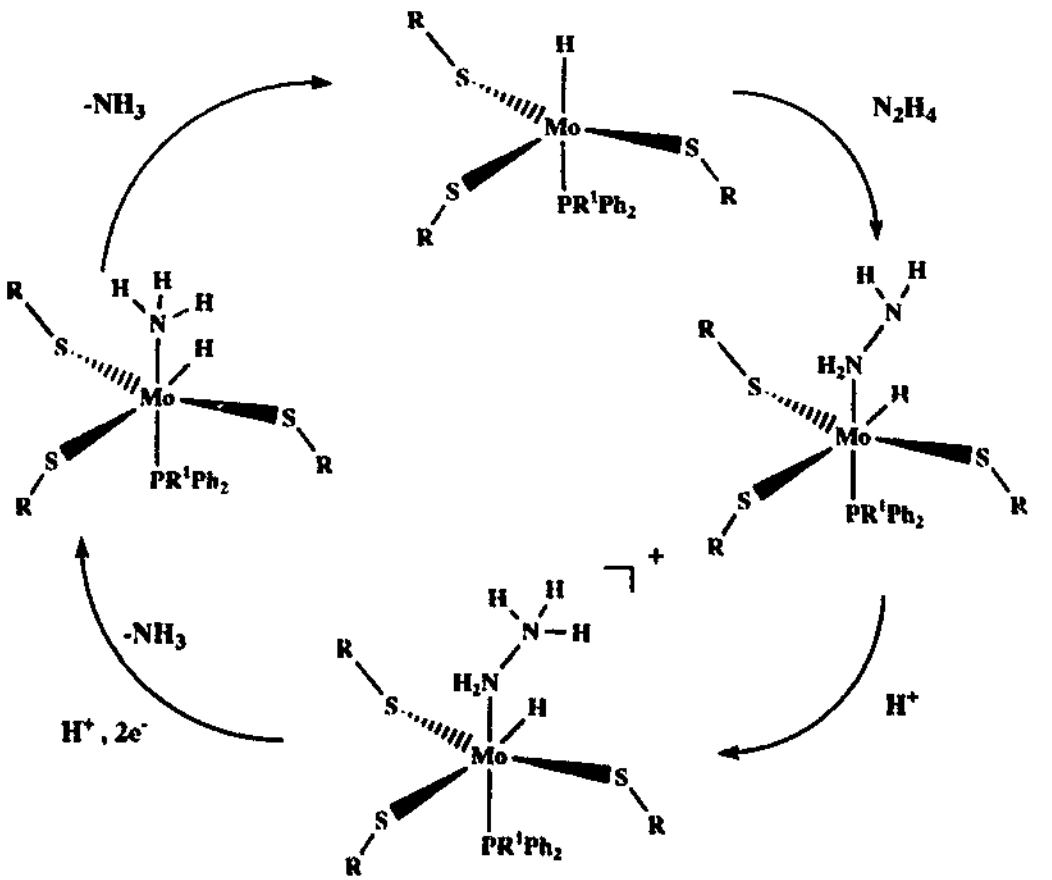


Fig. 10. Scheme of reduction of hydrazine by the complexes [MoH(SR)$_3$(PR^{1}Ph$_2$)] (R = $C_6H_2Me_3$-2,4,6 or $C_6H_2Pr^i_3$-2,4,6; R^1 = Me or Et).

4. Conclusions

Where do these observations leave us with regard to the mechanism of reduction of N_2 by FeMoco? Although the necessity of binding N_2 to a metal to allow its reduction has been established, any of the metals present in FeMoco and its analogues could be the candidate for such binding, with some caveats.

For example, if Mo is the binding site in FeMoco, since it is six-coordinated, it must either lose a ligand in order to bind substrate, or increase its coordination number. Although cyanide ion appears to bind in place of histidine at Mo in isolated FeMoco [10,11], if six-coordinate Mo is retained during substrate binding in the intact protein, it seems likely that, rather than displacement of histidine, partial displacement of the chelating homocitrate ligand should occur, perhaps as a result of a protonation of ligating oxygen [50]. Such a process could allow substrate binding to Mo (or V or Fe in the alternative nitrogenases). Although an increase of coordination number of Mo in FeMoco cannot be ruled out and seven-coordination of Mo with sulphur-donor ligands is known (e.g. in the complexes [$MoI_2(CO)_2$\{$MeS(CH_2)_2S(CH_2)_2SMe$-S,S′,S″\}] [51] and [MoI(SPh)$(CO)_3$\{Fe_4-

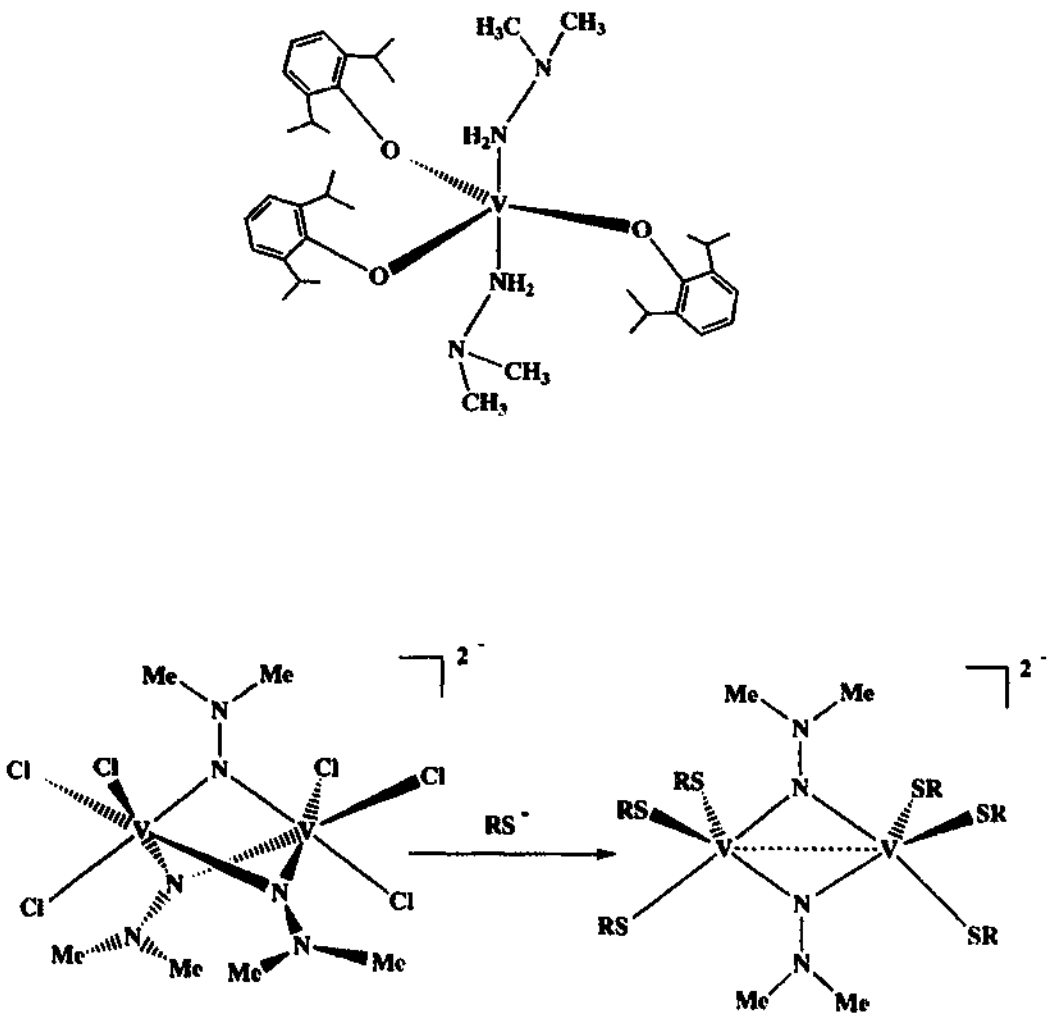


Fig. 11. Hydrazine and hydrazide complexes of vanadium.

$(C_5H_5)_4S_2(\mu\text{-}S_2)_2\}$] [52]), as yet no compounds of this type have been prepared with N_2 as a ligand.

Whilst binding of N_2 end-on to a single metal is firmly established as leading to a reduction of N_2 to NH_3, binding between two or more metals is also well established, and can lead to formation of NH_3 [17,18,53]. It could be that the apparently unsaturated trigonal Fe atoms at the relatively open centre of FeMoco provide the site for N_2 reduction. It has been suggested that N_2 could occupy the central cavity in FeMoco in the active state of the enzyme [11], although it is difficult to see how this site could accommodate the larger, partially reduced states of N_2. Theoretical studies have been made of the likely binding sites of N_2 on FeMoco [54,55], and currently favour binding between two irons, either on an edge of the central cavity or across a face. As is apparent from the foregoing discussion, there are no iron complexes of N_2 from which one can draw support for these conclusions.

Further study of metal complexes of N_2 and other substrates, particularly where the metal environments are close to those seen in FeMoco, is clearly necessary before

definitive mechanisms can be established for the function of nitrogenase at the atomic level.

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