

ELECTROREDUCTION OF METHYL ISOCYANIDE AT
THIOMOLYBDATO-DERIVED CENTRES: EVIDENCE
FOR AN ACTIVE ROLE OF SULPHUR

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ABSTRACT

Reaction of $[\text{MoS}_4][\text{PPh}_4]_2$ with methyl isocyanide (CNMe) affords species formulated as $[\text{Mo}_2\text{S}_6(\text{SCNMe})_2][\text{PPh}_4]$ or $[\text{Mo}_2\text{S}_6(\text{CNMe})(\text{CNH})(\text{SCN})][\text{PPh}_4]$ in which the isocyanide or the derived ligands undergo cathodic CN bond cleavage to give ammonia, methane and ethylene, in processes involving sulphur as a reductant of the substrate.

INTRODUCTION

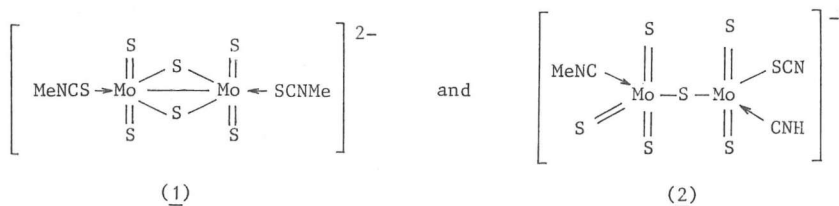
Although molybdenum has been considered [1] as a component of the active centre (formed by Mo, Fe and S atoms possibly arranged in a cluster) of nitrogenase, the N_2 -reducing enzyme, and the activation of its substrates thought to occur via coordination at the metal (whereas iron would be involved in the electron transfer process), alternative forms of this enzyme (without molybdenum but still with sulphur and iron) have been recently discovered [2], raising new questions as to the mechanisms involved in its reactions.

As part of our study on the activation of nitrogenase-substrates by molybdenum or related metal centres [3], we now report our preliminary

investigation of the reactions of methyl isocyanide with a thiomolybdate centre which suggests that the sulfido ligand plays an active role on the binding and reduction of that substrate.

RESULTS AND DISCUSSION

[MoS₄][PPh₄]₂ reacts with CNMe (in a 1:3 molar ratio), in CH₂Cl₂, at room temperature and under dinitrogen, to give a variety of ill-defined products. However, on the basis of microanalytical, ¹H n.m.r. spectroscopic and electrochemical data, the attempted formulations [Mo₂S₆(SCNMe)₂][PPh₄]₂ (1) and [Mo₂S₆(CNMe)(CNH)(SCN)][PPh₄] (2) are proposed for species which precipitated off the solution, in low yields, on addition of diethyl ether; possible structures of these compounds, consistent with the available data, are the following:



The formation of complex (1) involves the addition of isocyanide to sulfido ligands to form ligating methylisothiocyanates, rather than the direct coordination of the isocyanide to the metal. Such a type of reaction relates to the known [4] addition of alkynes to sulfido ligands and to the recently reported [5] addition of the hydrosulfido (SH) ligand to acetonitrile to form ligating >S-C(Me)=NH, e.g. in the reaction of NCMe with [(η-C₅H₅)Mo]₂(μ-S₂CH₂)(μ-S)(μ-SH)⁺; moreover, addition reactions of the S-H bond have been suggested [5] to be involved in the homogeneous catalytic hydrogenation of a variety of unsaturated substrates by some molybdenum complexes with μ-sulfido and μ-hydrosulfido ligands.

The synthesis of compound (2) may be explained by considering the dealkylation of SCNMe or CNMe by sulfido ligands (with possible formation of SMe⁻) to generate the SCN⁻ and the CNH species, the latter being formed in the presence of moisture.

Complexes (1) and (2) are diamagnetic and undergo cathodic reductions at values of potential which are close to that observed for the reduction of

the parent [MoS₄]²⁻ compound (see below). These observations suggest that, in all these complexes, molybdenum has the oxidation state VI.

The i.r. spectra of compounds (1) and (2) exhibit, besides the characteristic bands associated with the tetraphenylphosphonium ion, a band at ca. 465-470 cm⁻¹ which is assigned to ν(Mo=S). Furthermore, in complex (1), strong bands observed at 2220 and 2160(sh) cm⁻¹ are attributed to ν(CN) of the methylisothiocyanato ligands, whereas, for (2), the corresponding bands for the bonded isocyanides are detected at 2190(s) and 2140(w,m) cm⁻¹.

In the ¹H n.m.r. spectra (25°C) of these complexes, the resonances of the methyl group are observed as singlets, with the expected intensities, at δ ca. 1.7 p.p.m. (SCNMe) and 1.6 p.p.m. (CNMe), for (1) (in CDCl₃) and (2) (in CD₂Cl₂), respectively. In the latter compound, the CNH resonance occurs at δ ca. 0.8 p.p.m. and, as expected, integrates for a single proton, is broad and is almost lost on addition for D₂O; no appreciable change in the spectrum is observed when the temperature is lowered to ca. -40°C.

By cyclic voltammetry, at a Pt electrode and in 0.2M[Bu₄N][BF₄]/tetrahydrofuran or CH₂Cl₂, complexes (1) and (2) undergo irreversible cathodic reductions at E_p^{red} ca. -1.8 V vs. SCE [e.g., -1.77 or -1.81 V for (2) in tetrahydrofuran or CH₂Cl₂, respectively], * a value which is close to that observed for [MoS₄][PPh₄]₂ under identical experimental conditions (-1.80 or -1.87 V, in tetrahydrofuran or CH₂Cl₂, respectively), * in agreement with the hypothesis of a common oxidation state of the metal.

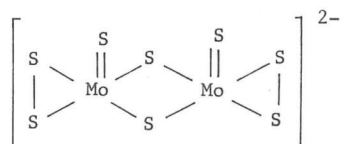
By controlled potential electrolysis at this cathodic wave, carried out at 25°C, under argon in a closed electrochemical cell, reductive cleavage of the unsaturated CN bond of the isocyanide or derived ligands occurs to give ammonia (analysed by the indophenol test) and hydrocarbons (methane and ethylene detected by glc).

The mechanism of this reductive cleavage, however, is not straightforward. For instance, after a measured charge corresponding to 2.3 electrons/molecule of complex (2), ammonia was detected in a yield of 2.4 mol NH₃/mol complex. This yield corresponds to a minimum consumption of 5.2 electrons/molecule of

* Values measured by using the ferrocene/ferricinium redox couple as an internal standard with E_{1/2}^{OX} = 0.54(5)V vs. S.C.E.

complex, * a value which is well above that measured during the electrolysis.

The higher yield of ammonia suggests that the coordinated sulphur may behave as a source of electrons (reductant) to the reducible substrate (oxidant), conceivably through an internal redox process known to occur in other systems. For instance, an internal electron transfer from S to Mo induced by an external oxidant (RSSR) was demonstrated [6] to occur in the reaction of RSSR with $[\text{MoS}_4]^{2-}$ to give RS^- and the following complex of Mo(V) with disulfido ligands (S_2^{2-} , derived from the oxidation of bonded sulfido, S^{2-}):

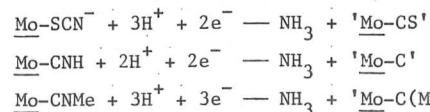


A chemical reductive cleavage of isocyanides to ammonia, amines and hydrocarbons was previously achieved by treating electron-rich isocyanide complexes, e.g., *trans*- $[\text{Mo}(\text{CNMe})_2\text{L}_4]$ [7], *mer*- $[\text{W}(\text{CNMe})_3\text{L}_3]$ [7] ($\text{L} = \text{PMe}_2\text{Ph}$) or *mer*- $[\text{ReCl}(\text{N}_2)(\text{CNR})\{\text{P}(\text{OMe})_3\}_3]$ ($\text{R} = \text{Me}, \text{Bu}^t$ or $\text{C}_6\text{H}_4\text{Me}-4$) [8], with a mineral acid. However, in contrast to these systems where the d^6 metal behaves as the reducing agent, those studied in the present work have the metal in its highest oxidation state, hence the reduction of the substrate requires an external electron source (cathodic reduction) and, apparently, the involvement of sulfido ligands as internal reducing agents.

CONCLUSIONS

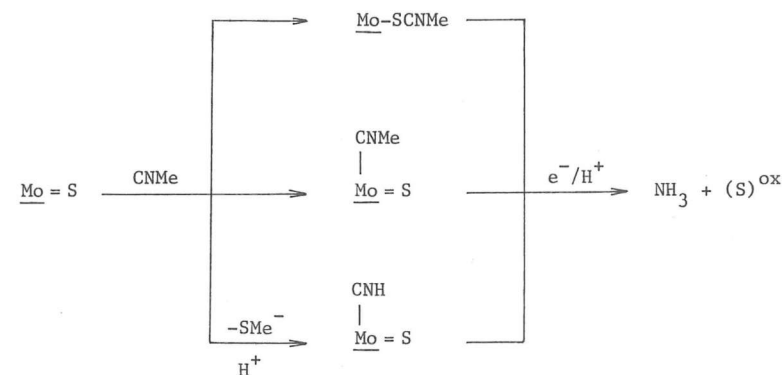
The results of the present work suggest a novel type of isocyanide reduction at a metal-sulphur site, requiring an active role of the sulfido ligand, not only by adding to the substrate (formation of isothiocyanato) or

* This may be evaluated by considering the following partial ligand reductions:



The formation of a total of 2.4 mol NH_3 requires a minimum of 4e^- (2 mol NH_3 from SCN^- and CNH) + $0.4 \times 3\text{e}^-$ (0.4 mol NH_3 from CNMe) = 5.2e^- .

behaving as a dealkylating agent (formation of SCN^- or CNH), but also by acting as an electron source (reducing agent). These reactions of isocyanide, summarized in the scheme below, may have some biological significance since the participation of sulphur (at the active site of nitrogenase) in the enzymatic reduction of isocyanides and related substrates is now conceivable.



Scheme - Reactions of methyl isocyanide at thiomolybdate-derived centres. [(S)^{ox} represents a product of sulfido oxidation, e.g., S_2^{2-}].

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