Synthesis, Characterization and Electrochemisty of the Mixed Metal Species $(RNC)_4Mo(\mu\text{-}t\text{-}BuS)_2FeX_2$ (R = cyclohexyl, t-butyl; X = Cl, Br)

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Received March 16, 1984

The discovery (*via* various spectroscopic techniques) that the proposed catalytic entity of the nitrogenase enzyme is an iron–molybdenum–sulfur cluster unit has prompted the chemical synthesis of a variety of complexes of this type over the past few years [1]. Most of these synthetic species have been prepared using high-valent molybdenum (usually $MoS_4{}^{2-}$) as a starting material and two distinct classes of complexes have been made in this way: (a) those containing Fe_3MoS_4 cubane units, *e.g.* $[Fe_6Mo_2S_8\text{-}(SPh)_9]^{3-}$, [2] and (b) those containing a linear arrangement of Fe and Mo atoms bridged by sulfide *e.g.* $[Fe(MoS_4)_2]^{3-}$ [3]. Our general interest in chemistry of this type has prompted us to begin examining complexes formed between lower-valent molybdenum species and various iron reagents. Previously, Dias and Green [4] prepared the mixed metal complexes $(C_5H_5)_2Mo(SR)_2FeCl_2$ (R = Me, t-Bu) using the Mo(IV) compounds [5] $(C_5H_5)_2Mo(SR)_2$ as starting materials and it occurred to us that the Mo(IV) complex $Mo(t\text{-}BuS)_4$, whose general chemistry has been extensively explored by Otsuka and coworkers [6], might also bind ferrous halides. In addition, the known [7] Mo(II) species, $Mo(RNC)_4(t\text{-}BuS)_2$ seemed to offer an opportunity to explore the binding of FeX_2 to still lower valent molybdenum. In fact, we have so far been unable to isolate any characterizable products from reactions of $Mo(t\text{-}BuS)_4$ with FeX_2 (X = Cl, Br), but have been able to obtain several new mixed metal complexes from $Mo(RNC)_4(t\text{-}BuS)_2$ and herein we describe their preparation, characterization, and preliminary studies of their electrochemistry.

Recently, $Mo(t\text{-}BuNC)_4(t\text{-}BuS)_2$ has been shown to react smoothly with $CuBr(t\text{-}BuNC)_3$ yielding $(t\text{-}BuNC)_4Mo(\mu\text{-}t\text{-}BuS)_2CuBr$ which was structurally characterized and shown to exist in two conformational isomers with respect to the $Mo(SR)_2\text{-}Cu$ bridge [8]. We have found similar reactivity between this Mo(II) species and ferrous halides. Thus,

TABLE I. Spectral Data for Complexes.

Complex	IR[a]	UV/VIS[b]
$Mo(t\text{-}BuNC)_4(t\text{-}BuS)_2$	1995(vs) 2110(vs)	435(5910) 680(410)
$Mo(t\text{-}BuNC)_4(t\text{-}BuS)_2FeCl_2$	2040(vs) 2090(vs) 2130(vs)	452(3610) 650(690)sh 755(870)
$Mo(t\text{-}BuNC)_4(t\text{-}BuS)_2FeBr_2$	2040(vs) 2085(vs) 2130(vs)	453(4160) 665(650) 800(990)
$Mo(CyNC)_4(t\text{-}BuS)_2$	2010(vs) 2110(vs)	423(5400) 680(340)
$Mo(CyNC)_4(t\text{-}BuS)_2FeCl_2$	2050(vs) 2090(vs) 2130(vs)	455(3730) 660(740) 765(940)
$Mo(CyNC)_4(t\text{-}BuS)_2FeBr_2$	2070(vs) 2130(vs)	455(4240) 655(640) 800(1090)

[a]Positions for N≡C bands in cm^{-1}; spectra recorded as KBr pellets. [b]Wavelength in nm with molar absorptivities in parentheses; toluene solution.

$Mo(RNC)_4(t\text{-}BuS)_2$ (R = cyclohexyl, t-butyl) (0.70 mmol) in MeCN (50 ml) was treated with FeX_2 (X = Cl, Br) (0.70 mmol) for 1–2 hr at ambient temperature [9]. The reaction mixture was evaporated to dryness under vacuum and the product extracted into CH_2Cl_2 or toluene from which it was precipitated with hexane. In general, toluene extraction gave products of higher purity and typical yields were in the range 60–80%. Elemental analytical data for all four complexes were consistent with the formulation $(RNC)_4Mo(t\text{-}BuS)_2FeX_2$ [10]. Infrared spectral data, while not particularly diagnostic, are consistent with the above stoichiometry, containing strong bands due to coordinated RNC and various fingerprint bands assignable to the cyclohexyl and/or t-butyl moieties. Accurate i.r. spectral data for all species are presented in Table I. Although no structural data are availabe as yet for these complexes, the most likely atomic arrangement would involve octahedral molybdenum and tetrahedral iron units bridged by two mercaptides as shown below:
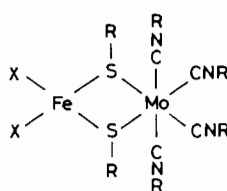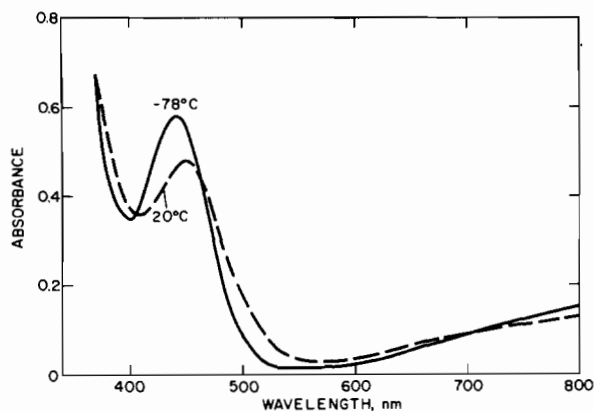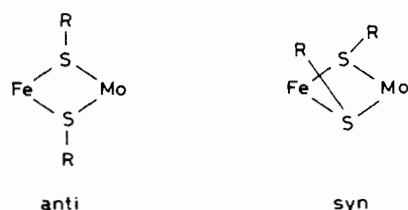
Fig. 1. Electronic spectra of $Cl_2Fe(S-t-Bu)_2Mo(CyNC)_4$ $(2.72 \times 10^{-5}$ *M*) in PrCN at 20 °C (----) and -78 °C (——). Pathlength = 5.7 cm.

Fig. 2. Cyclic voltammograms of $Br_2Fe(S-t-Bu)_2Mo(t-BuNC)_4$ in CH_2Cl_2 $(1.38 \times 10^{-3}$ *M*), PrCN $(1.30 \times 10^{-3}$ *M*), and DMF $(1.53 \times 10^{-3}$ *M*). The scan rate was 50 mv/sec. Temperature was 20 °C for CH_2Cl_2 and PrCN; 0 °C for DMF.

The visible spectra of the heterometallic dinuclear species are very similar to those of the mononuclear Mo(II) starting materials, implying that the bands are due to the same basic charge transfer transitions postulated for the latter species [7]. Figure 1 shows a typical spectrum, while precise wavelength positions and molar absorptivities are given in Table I for all four new complexes as an aid to future characterization of these species. On cooling CH_2Cl_2 or butyronitrile (PrCN) solutions of these complexes from 25 °C to -78 °C, a marked reversible color change from green-yellow to green is evident, with the resulting spectral change shown in Fig. 1. The slight shift in the absorption maximum and the band sharpening, which also occurs for $Mo(RNC)_4(t-BuS)_2$, is most likely due to a stereochemical change involving the ligands, an effect which has been established for other metal complexes [11]. Based on the presumed structure, a possible source of this phenomenon is a change in the relative amounts of *syn* and *anti* conformers with respect to the thiolate bridges. That such differences can affect electronic spectra has precedent in the $Fe(CO)_6(SMe)_2$ system

[12], and in fact although no visible spectral data were given, the related compound $(t-BuNC)_4Mo(t-BuS)_2CuBr$ is reported [8] to have separable *syn* and *anti* conformational isomers which can be identified in solution by NMR. Unfortunately, the paramagnetism of our Mo–Fe complexes prevented the use of this method to investigate this potential conformational change.
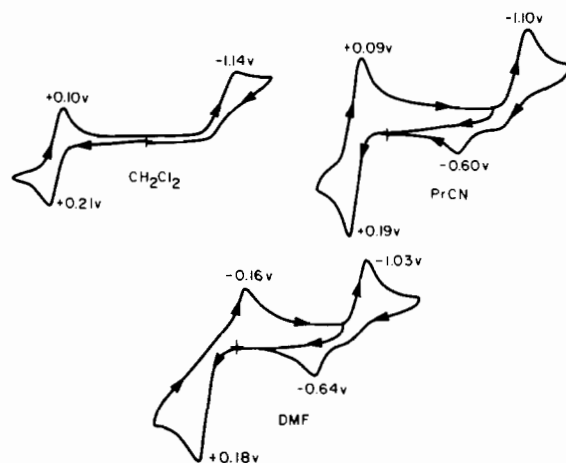
The electrochemical properties of these new heterometallic complexes are exemplified by the cyclic voltammograms [13] of $(t-BuNC)_4Mo(t-BuS)_2FeBr_2$ as a function of solvent (Fig. 2). In CH_2Cl_2 and PrCN, the complex exhibits a reversible oxidation at ~+0.1 V and an irreversible reduction at ~-1.12 V. In PrCN, but not in CH_2Cl_2, an irreversible wave is also observed at -0.60 V. This latter wave is absent when the scan is reversed prior to the irreversible reduction wave and therefore must be due to oxidation of whatever product is formed thermally following reduction of $(t-BuNC_4)Mo(t-BuS)_2FeBr_2$. The absence of this behavior in CH_2Cl_2 may be due to differences in ability to solvate. In DMF, quite a different voltammetric trace is observed for this complex, with the oxidation wave exhibiting irreversible behavior ($E_{pa} - E_{pc} = 340$ mv). This effect also may be due to solvation but, in this case, of the oxidation product of the dinuclear complex, with the DMF-containing species being reduced at a more negative potential.

The current parameters for the reversible oxidations of both $X_2Fe(t-BuS)_2Mo(RNC)_4$ and the precursor $Mo(RNC)_4(t-BuS)_2$ indicate that these redox events are one-electron in nature. The wave for the mononuclear Mo(II) species must be assigned as an oxidation to Mo(III) [14] and the positive shift of ~0.25 V for the mixed metal dinuclear species is in the correct direction if this oxidation is also primarily molybdenum-centered. The reduction wave for $Mo(RNC)_4(t-BuS)_2$ occurs ~0.8 V more negative than for its ferrous halide adducts, again consistent with a molybdenum-centered reduction in $X_2Fe(t-BuS)_2-Mo(RNC)_4$. Preliminary experiments indicate that the positions of the redox events in the Mo(II) starting materials and the Mo–Fe complexes are relatively insensitive to changes in either halide or isonitrile

substituents. Finally, cyclic voltammetry experiments were carried out at $-78\,^{\circ}C$ in both CH_2Cl_2 and PrCN in an effort to confirm the presence of the two conformers proposed above and to explain the thermochromic behavior of these dinuclear species. However, no significant change in the overall appearance was observed in either solvent at the lower temperature, and the small shifts in the half-wave potential of the reversible oxidation (38 mv in PrCN; 37 mv in CH_2Cl_2) are as likely to be due to simple changes in junction potential as to a different ratio of conformers. Thus, the explanation proposed herein for the temperature-dependence of the visible spectrum remains speculative.

More detailed electrochemical investigation of this system is in progress. Of particular interest, in light of the reversibility of the oxidation of these dinuclear complexes, is the possibility that the one-electron oxidized species $[X_2Fe(t\text{-}BuS)_2Mo(RNC)_4]^+$ can be generated on a preparative scale by controlled potential electrolysis (or perhaps chemically). If formed, this cation would be expected to contain formally Mo(III) and Fe(II), which may be antiferromagnetically coupled via the bis thiolate bridge, to yield a net $S = \frac{1}{2}$ system whose EPR properties would be of interest.

Acknowledgements

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9 $Mo(CyNC)_4(t\text{-}BuS)_2$ was prepared similarly to its t-BuNC analog following the method of Otsuka *et al.* [7]. The product crystallizes in pure form from hexane and satisfactory elemental analytical data were obtained for this new complex.
10 $Cl_2Fe(S\text{-}t\text{-}Bu)_2Mo(t\text{-}BuNC)_4$. Calcd for $C_{28}H_{54}N_4S_2Cl_2FeMo$: C, 45.83; H, 7.43; N, 7.63. Found: C, 45.00; H, 7.38; N, 7.42. $Br_2Fe(S\text{-}t\text{-}Bu)_2Mo(t\text{-}BuNC)_4$. Calcd for $C_{28}H_{54}N_4S_2Br_2FeMo$: C, 40.88; H, 6.63; N, 6.81. Found: C, 41.23; H, 6.73; N, 6.54. $Cl_2Fe(S\text{-}t\text{-}Bu)_2Mo(CyNC)_4$. Calcd for $C_{36}H_{62}N_4S_2Cl_2FeMo$: C, 51.60; H, 7.47; N, 6.68. Found: C, 51.15; H, 7.51; N, 6.66. $Br_2Fe(S\text{-}t\text{-}Bu)_2Mo(CyNC)_4$. Calcd for $C_{36}H_{62}N_4S_2Br_2FeMo$: C, 46.65; H, 6.75; N, 6.04. Found: C, 46.30; H, 6.87; N, 6.07.
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13 Cyclic voltammetry studies were done using a BAS CV-1A potentiostat from Bioanalytical Systems and a Hewlett-Packard X–Y recorder. The glassy carbon working electrode was also from BAS and potentials were measured relative to SCE. $[Bu_4N]BF_4$ (0.1 *M*) (Eastman) was used as the supporting electrolyte.
14 Previously [7], a reversible redox event at -0.17 V for $Mo(t\text{-}BuNC)_4(t\text{-}BuS)_2DMF$ was assigned to a *reduction* of the complex. In fact, we find that the rest potential of a 0.002 *M* solution of this complex in MeCN is *more negative* than the redox potential, indicating that this couple corresponds to a reversible *oxidation*. The electrochemistry of these species is not simple, with the shape of the oxidation wave being scan rate dependent. Details of our studies on this complex will be reported subsequently.