Discussion

Crystallographic characterization of some of these complexes reveals an approximate capped octahedral geometry with the newly formed tungsten–carbon bond as the cap. Unlike many seven-coordinate complexes (8), these are not fluxional, probably due to the rigid geometry imposed by the chelating ligand. Students should be able to use the 18-electron rule (9) in rationalizing the structures of the starting materials and products. The suppression of the oxidative addition process in nitrite solvents should lead students to propose a two-step mechanism, with a pre-equilibrium involving nitrite dissociation, for the overall reaction. The role of the ligand in promoting the insertion chemistry is quite apparent when compared with the behavior of free chlorobenzene. This provides students with insight into the importance of ligand design in controlling the reaction chemistry of a metal center. Two three-hour laboratory periods should prove adequate for isolation and characterization of ligand 1, substitution product 2, and oxidative addition product 3.

Acknowledgment

We thank the donors of the American Chemical Society’s Project Supporting Research and Education in Chemistry (Project SERC) for financial assistance. Special thanks are due to Dr. William A. Goddard III, who generously provided the 6-31G* level quantum mechanics calculations used in this study.

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The Synthesis of Some Diazenido and Hydrazido Complexes of Molybdenum

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Transition metal complexes with metal–nitrogen multiple bonds are currently of considerable interest in the inorganic chemistry of nitrogen fixation (1). Protonation of coordinated dinitrogen in certain molybdenum tertiary phosphine dinitrogen complexes proceeds stepwise. The first identifiable intermediate is a diazenido complex containing the M=N–NH3 group. The initial product of protonation is believed to be a diazenido complex containing the M=N=NH moiety, but this species cannot be isolated directly (2). Analogous species with nitrogen–carbon bonds can be obtained by the reaction of certain dinitrogen complexes with alkyl and activated aryl halides (3). In this series of experiments we report the syntheses of some complexes containing these types of nitrogenous ligands with the readily available sulfur donor, dithiocarbamate. The reactions are all carried out in air, water, or reagent solvents. They generally proceed reliably and in good yield. The syntheses are thus relatively easy to perform and involve inexpensive chemicals. They are appropriate for use in undergraduate teaching laboratories. The complexes are all air-stable and provide useful examples of using IR spectroscopy to monitor the course of a reaction.

The dithiocarbamate anion generally functions as a bidentate monocationic ligand, binding to the metal at two sulfur atoms. Significant contributions from a canonical form for the ligand involving a positive charge on the nitrogen atom (Fig. 1) mean that the ligand can stabilize high oxidation states. The chelating nature of the ligand confers high stabilities on the complexes, and the delocalization of charge density renders the sulfur atoms reasonably inert to electrophilic attack. Increase in the C=S bond order on coordination can be seen in the infrared spectra from the appearance of the strong band at about 1500 cm⁻¹ in the spectra of the complexes.

Discussion

Syntheses and Structures of Complexes

The starting material, [MoO2(S2CNEt2)2], is synthesised by a slightly modified version of a standard literature procedure (4) by addition of aqueous dithiocarbamate to excess ammonium molybdate. It is essential to avoid excess

![Figure 1. Canonical forms of the dithiocarbamate anion.](image1)

![Figure 2. IR spectrum of [MoO2(S2CNEt2)2].](image2)
dithiocarbamate, which causes formation of a purple oxo-
bridged Mo(V) dimer. The reported synthesis uses
diethylthiocarbamate, but works equally well with other
dithiocarbamates, which are readily prepared from the
appropriate amine, carbon disulfide, and base in water. The
two terminal oxo groups are cis to minimize competition for
appropriate acceptor orbitals on the molybdenum. They
give rise to characteristic, very strong IR bands at about
880 and 910 cm\(^{-1}\) (Fig. 2). IR bands due to mineral oil in this
and other IR spectra have been subtracted. The IR spec-
trum of sodium diethylthiocarbamate is shown for com-
parison (Fig. 3).

Despite their functioning as strong \(\pi\) donors there is
sufficient electron density on the terminal oxo groups to
render one of them susceptible to electrophilic attack. Thus,
reaction of \([\text{MoO}_2(S_2\text{CNEt}_2)_2]\) with concentrated aqueous
acid in acetone gives the monooxo complex,
\([\text{MoOCl}_2(S_2\text{CNEt}_2)_2]\), in good yield (5). This seven-coor-
dinate complex has a distorted pentagonal bipyramidal geo-
metry with oxo and chloro ligands in apical sites. The
removal of one of the oxo groups by protonation is shown in
the IR spectrum by the disappearance of one of the two
bands assigned to the cisdioxo unit (Fig. 4).

In some respects these are parallels between the reactiv-
ity of Mo=O groups and the carbonyl functional group in
organic chemistry. Thus, reaction of the dioxo complex with
N,N-dimethyldihydrazine to give an oxahydridazido deriva-
tive (reaction 1) is an inorganic analog of the formation of a
Schiff’s base (6).

\[
[\text{MoO}_2(S_2\text{CNEt}_2)_2] + \text{H}_2\text{NNMe}_2 \\
\rightarrow [\text{MoO} (=\text{NNMe}_2)(S_2\text{CNEt}_2)_2]
\]  

The complex \([\text{MoO} (=\text{NNMe}_2)(S_2\text{CNEt}_2)_2]\) has a structure
analogous to the parent dioxo complex with the oxo and
hydradizido (2-) groups in cis positions. The IR spectrum has
a strong band at about 885 cm\(^{-1}\) assigned to the single oxo
group (Fig. 5). The \(^1\)H NMR spectrum of \([\text{MoO}(\text{NNMe}_2)(S_2\text{CNEt}_2)_2]\)
in CDC\(_3\) at room temperature shows singlets
at 3.78 and 3.39 ppm due to the hydradizido and dithio-
carbamato methyl groups, respectively. The equivalence of
the dithiocarbamate methyl groups, indicates that the com-
plex may be fluxional at room temperature.

The number of hydradizido (2-) groups introduced is a func-
tion of the basicity of the hydrazine used. Thus, PhMe-
NNH\(_2\) is less basic than Me\(_2\)NNH\(_2\) and reacts with the dioxo
complex to give the yellow bis-hydradizido complex \([\text{Mo}(
\text{NNMePh}_2)(S_2\text{CNEt}_2)_2]\) in good yield (7). The hydradizido
ligand can formally donate 2 or 4 electrons to the metal,
depending on whether or not the lone pair of electrons on
the nitrogen adjacent to the metal is used in the metal-
nitrogen multiple bond. Somewhat surprisingly, the struc-
ture of \([\text{Mo}(\text{NNMePh}_2)(S_2\text{CNEt}_2)_2]\) shows that both
hydradizido ligands are linear, giving a formal 20-valence
electron count on the metal (7). One of the hydradizido
ligands in the bis-hydradizido (2-) complex can readily be protonated
or alkylated to give a hydradizido (2-) hydradizido (1-) complex
in which the hydradizido (1-) ligand is bound “side-on” to the
molybdenum (8).

The phenyldiazenido complex \([\text{Mo} (\text{NNPh})(S_2\text{CNEt}_2)_2]\)
can readily be prepared by reaction of the dioxo complex with
phenyldihydrazine in the presence of excess dithio-
carbamate. Without additional dithiocarbamate the bis-
(diazenido-) complex \([\text{Mo} (\text{NNPh})(S_2\text{CNEt}_2)_2]\) is formed,
this reaction proceeding by the hydradizido (1-) diazenido
complex \([\text{Mo} (\text{NNPh})(\text{NHNNPh})(S_2\text{CNEt}_2)_2]\) (9). The latter
complex is relatively oxygen-sensitive and oxidizes in solu-
tion in air to give the bis-diazenido complex. The complex
\([\text{Mo} (\text{NNPh})(S_2\text{CNEt}_2)_2]\) was shown by X-ray crystallogra-
phy to have a pentagonal bipyramidal structure with the
diazenido ligand in the apical site. The M–N–N system is
essentially linear, confirming that the diazenido ligand
is formally functioning as a three-electron donor, analogous
to N0 in its linear bonding mode. The IR spectrum of
the monodiazenido complex shows no bands assignable to
Mo=O in the 800–900 cm\(^{-1}\) region, but medium intensity
bands at about 1600 cm\(^{-1}\) are associated with the
phenyldiazenido ligand (Fig. 6). The \(^1\)H NMR spectrum of
\([\text{Mo} (\text{NNPh})(S_2\text{CNEt}_2)_2]\) in nitrobenzene solution shows
two doublets in the ratio 2:1 in the dithiocarbamate alkyl
region, consistent with the observed solid-state geometry.
At higher temperatures a singlet is observed, and analysis
of the temperature dependence of the spectra suggests a
first-order exchange process with a free energy of activation of about 80 kJ mol\(^{-1}\).

**Experimental**

**Synthesis of [MoO\(_2\)(S\(_2\)CNEt\(_2\)]\(_2\)**

A solution of ammonium molybdate (10 g) in distilled water (100 mL) is stirred vigorously, mechanically or by hand. (Magnetic stirring is not sufficient.) A solution of sodium diethylenebiscarbamate trihydrate (10 g) in water (50 mL) is added dropwise. Filtration of the dialcetylated solution is needed if cloudy. Stirring is continued for 15 min after the addition is complete, and the orange-yellow dioxo complex is filtered off in air. The precipitate may be very fine, and some patience may be needed with the filtration. Finally the precipitate is washed with water (50 mL) and 3-10 mL portions of reagent-grade methanol. The product is allowed to dry overnight at ambient temperature, spread out on a filter paper.

**Synthesis of [MoOCl\(_2\)(S\(_2\)CNEt\(_2\)]\(_2\)**

[MoO\(_2\)(S\(_2\)CNEt\(_2\)]\(_2\) (1.0 g) is suspended in reagent-grade acetone (30 mL), and concentrated hydrochloric acid (5 mL) is added with magnetic stirring over 15 min. The resulting bright-yellow solid is filtered off and dried in air.

**Synthesis of [MoO\(_2\)(NNMe\(_2\))\(_2\)(S\(_2\)CNEt\(_2\)]\(_2\)**

[MoO\(_2\)(S\(_2\)CNEt\(_2\)]\(_2\) (2.0 g) and N,N-dimethylhydrazine (1 mL) are heated under reflux in reagent-grade methanol for 1 h in a fume hood. The solution is allowed to cool to room temperature, and the colored product is filtered off. The solid may be deep-orange to pink, depending on the particular impurities present in the hydrazine. It may be necessary to use a rotary evaporator to reduce the solution volume to maximize the yield of solid product. The complex can be recrystallized from dichloromethane–diethyl ether as pinkish crystals. (Use the minimum volume of dichloromethane to dissolve the complex, and then add the ether slowly.)

**Safety Note:** Dimethylhydrazine is a carcinogen and should be used in a fume hood at all times. Appropriate gloves should be worn.

**Synthesis of [MoO\(_2\)(NNPh\(_2\))\(_2\)(S\(_2\)CNEt\(_2\)]\(_2\)**

[MoO\(_2\)(S\(_2\)CNEt\(_2\)]\(_2\) (2.0 g), sodium diethylenebiscarbamate (1.0 g), and phenylhydrazine (1 mL) are heated under reflux in methanol (30 mL) for 1 h. On cooling, the product appears as a dark-brown microcrystalline precipitate which can be filtered off in air.

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**A Pressure Source for Flash Chromatography**

The major problem associated with incorporating flash column chromatography into the undergraduate laboratory is often the lack of a suitable pressure source. Balloons and aquarium air pumps have been suggested to fill this need. Neither of these pressure sources provides enough pressure, by Jacobson’s admission, to expel air from the adsorbent during column packing. Therefore, slurry packing must be used, and that detracts from the technique. We would like to suggest the use of a 50-mL plastic syringe (Aldrich Z11, 840-0, less than $1 \text{ ea.}$) as an alternative simple source of pressure for flash chromatography. We insert a plastic Y-tube into a one-hole rubber stopper which is fitted to the top of a 20 × 400-mm column (Corning 38450-20) for up to 1-g sample sizes. The syringe tip conveniently fits snugly into one opening of the Y-tube, and a single thickness of Parafilm is molded over the other and held in place by slipping a short piece of tubing over it. The Parafilm acts as a pressure release valve and ruptures at about 10 p.s.i. This method generates solvent drop rates up to 20 cm/min as opposed to less than 4 cm/min by the other methods. This high flow rate does allow the standard packing procedure to be used. Since solvent changeover can be done so quickly at these flow rates, we have discovered the added benefit of being able to use the same silica gel bed several times for certain separations by eluting with one column volume of ethyl acetate followed by one column volume of the eluting solvent. We can supply upon request complete experimental details for the ferrocene—acytlyferrocene and fluorene—fluorone separations.

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790 Journal of Chemical Education