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Oxidation of Molybdenum Dithiocarbamate Complexes with Elemental Sulfur

JOHN W. McDONALD AND WILLIAM E. NEWTON

Charles F. Kettering Research Laboratory, Yellow Springs, Ohio 45387, U.S.A.

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Introduction

The reactions of elemental sulfur with the molybdenum(IV) and molybdenum(II) dithiocarbamate complexes $OMo(S_2CNR_2)_2$ and $Mo(CO)_2(S_2CNEt_2)_2$ were described several years ago by Weiss and coworkers [1]. In both systems, the initial motivation for the experiments was a better synthetic procedure for the blue disulfur adduct $OMo(S_2CNR_2)_2(S_2)$ which could be prepared in low yield via reaction of $MoO_2(S_2CNR_2)_2$ with H_2S in air followed by chromatography of the reaction mixture on silica gel [2]. For the reaction of the Mo(IV) species with S_8, they reported the formation of an uncharacterized orange solid when the reaction was carried out anaerobically and the generation of some (but apparently little) $OMo(S_2CNR_2)(S_2)$ under aerobic conditions with very long reaction times. Thus, little success was realized in improving the method for synthesis of the disulfur adduct by this route even though it seemed a very reasonable one since $OMo(S_2CNR_2)_2$ is known [3–6] to react with a variety of oxidative addition type substrates.

For the $Mo(CO)_2(S_2CNEt_2)_2$-S_8 system, the reported [1] procedure involved reaction of the Mo(II) species and sulfur in a 1:2 ratio followed by aerial oxidation of the reaction mixture. Here, the hope was that a species of general form $Mo(S_2CNEt_2)_2(S_2)$ would be generated and that subsequent reaction with O_2 would produce $OMo(S_2CNEt_2)_2(S_2)$. In this case, only a small amount of the disulfur species was produced, although the interesting compound $[Mo(S_2CNEt_2)_2(S_2O)]_2$ was isolated and shown by X-ray crystallography to contain two bridging S_2O moieties. Again, however, the development of a better synthetic procedure for $OMo(S_2CNR_2)_2(S_2)$ was not attained.

Because of our interest both in the chemistry of molybdenum in a sulfur environment and in the ability of Mo(IV) [3–6] and Mo(II) [7, 8] dithiocarbamates to bind and activate small molecules, we have reinvestigated the reactions of these complexes with elemental sulfur. In addition, like the Weiss group, we were motivated to develop a high yield synthesis of $OMo(S_2CNR_2)_2(S_2)$ in order to obtain sufficient quantities for studies of its reactivity and, in particular, its propensity for sulfur atom transfers. Herein, we report our further studies on these systems.

Reaction of Sulfur with $OMo(S_2CNR_2)_2$

We find that $OMo(S_2CNR_2)_2$ reacts smoothly with two equivalents of elemental sulfur in refluxing acetone to form the disulfur adduct $OMo(S_2CNR_2)_2(S_2)$. In a typical preparation, $OMo(S_2CNEt_2)_2$ (0.50 g; 1.23 mmol) and S_8 (0.09 g; 2.81 mg. atom of S) were dissolved in acetone (50 ml) and the solution heated under reflux for 3 hr during which time it became dark blue. After filtration, the reaction mixture was evaporated to dryness under vacuum and the residue triturated with diethylether to give the product (0.47 g; 1.03 mmol; 84% yield). *Anal.* Calcd for $C_{10}H_{20}N_2MoOS_6$: C, 25.4; H, 4.23; N, 5.93. Found: C, 25.3; H, 4.46; N, 5.80. Similar synthetic procedures gave $OMo(S_2CNMe_2)_2(S_2)$ (81% yield. *Anal.* Calcd for $C_6H_{12}N_2MoOS_6$: C, 17.3; H, 2.88; N, 6.73. Found: C, 17.8; H, 3.11; N, 6.55) and $OMo[S_2CN(n\text{-}Pr)_2]_2(S_2)$ (65% yield. *Anal.* Calcd for $C_{14}H_{28}N_2MoOS_6$: C, 31.8; H, 5.30; N, 5.30. Found: C, 31.5; H, 5.61; N, 5.12). Infrared and visible spectral data for the three complexes are collected in Table I and are consistent with those previously reported [1] for $OMo[S_2CN(n\text{-}Pr)_2]_2(S_2)$ by Weiss and coworkers. Thus we find that, under the proper conditions, the coordinatively unsaturated Mo(IV) species do in fact undergo the expected oxidative addition reaction with sulfur. The choice of solvent in this system is critical and no doubt explains the lack of success of the previous attempts [1]. We were unable to obtain pure $OMo(S_2CNR_2)_2(S_2)$ from 1:2 mixtures $OMo(S_2CNR_2)_2$ and sulfur either after long reaction times in CH_2Cl_2 at room temperature or after refluxing for several hours in 1,2-dichloroethane. The successful syntheses in acetone were carried out anaerobically, indicating that the previous postulation [1] of an O_2 requirement for the formation of the disulfur adducts is incorrect. The method of preparation of $OMo(S_2CNR_2)_2(S_2)$ described herein would thus seem to be superior to the previously reported [1, 2] procedure as the yield is much higher and chromatography of the crude product is not required. In a recent brief report [9], DuBois and coworkers described the synthesis of the disulfur adducts via reaction of $Mo_2O_3(S_2CNR_2)_4$ with Na_2S_4. Although the actual reactive species in this system would seem to be in doubt ($Mo_2O_3L_4$ is known [10] to be in equilibrium with MoO_2L_2 and $OMoL_2$), the synthesis is described as high yield and would seem to provide another good preparative method for $OMo(S_2CNR_2)_2(S_2)$.

TABLE I. Spectral Data for the Complexes $OMo(S_2CNR_2)_2(S_2)$.

Complex	Infrared[a]		Visible[b]
	ν_{S-S}	$\nu_{Mo=O}$	
$OMo(S_2CNMe_2)_2(S_2)$	555 m	916 s	582(1240), 390(3370)
$OMo(S_2CNEt_2)_2(S_2)$	560 m	908 s, 922 s	580(1340), 394(3810)
$OMo[S_2CN(n\text{-}Pr)_2]_2(S_2)$	555 m	917 s	580(1110), 394(3230)

[a] Spectra recorded as KBr disks. Values in cm^{-1}. [b] Peak positions in nm with molar absorbtivity in parentheses.

Reaction of Sulfur with $Mo(CO)_2(S_2CNEt_2)_2$

As described in the previous report [1], the Mo(II) species (2.00 g; 4.46 mmol) reacts smoothly with S_8 (0.36 g; 11.25 mg atom of S) in CH_2Cl_2 (75 ml) over a 2 hr period at room temperature to form a yellow-brown solution. Instead of exposing the reaction mixture to air [1], we evaporated it to dryness under vacuum and triturated the residue with diethylether to give the product as a brown solid (1.95 g). The elemental analytical data (C, 25.3; H, 4.37; N, 5.90; S, 40.3) is reasonably consistent with the formulation $Mo(S_2CNEt_2)_2(S_2)$ (Calcd for $C_{10}H_{20}N_2MoS_6$: C, 26.3; H, 4.39; N, 6.14; S, 42.1) and fits very well if the product is formulated [11] as $Mo(S_2CNEt_2)_2(S_2)\cdot 1/4CH_2Cl_2$ (Calcd for $C_{10.25}H_{20.5}N_2Cl_{0.5}MoS_6$: C, 25.8; H, 4.29; N, 5.87; S, 40.2). Unlike the complexes $OMo(S_2CNR_2)_2(S_2)$, the infrared spectrum of this solid contains no band assignable to an S–S stretch in the 500–600 cm^{-1} region.

A reasonable description of the product might be a Mo(IV) species, probably diamagnetic, containing the S_2^{2-} moiety and we were therefore surprised to find that the epr spectrum of the complex (Fig. 1) contained a strong signal (g = 1.976; $A(^{95,97}Mo)$ = 38.1 gauss) characteristic of monomeric Mo(V) [13]. Titration of this signal with PPh_2Et (a reagent known [9] to remove coordinated S_2 groups as phosphine sulfide) showed that 2.0 (±0.2) equivalents of phosphine were required to quench the epr signal if the formulation $Mo(S_2CNEt_2)_2(S_2)\cdot 1/4CH_2Cl_2$ is assumed. While this experiment, taken together with the elemental analytical data, appears to confirm the formation of a species of empirical stoichiometry $Mo(S_2CNEt_2)_2(S_2)$, the nature of the product is still open to question. If Mo(II) has been oxidized to Mo(V), then the sulfur ligand of the product must be formally S_2^{3-} and this moiety should exhibit an epr signal. Fig. 1 shows that at least three very weak signals are observed in the g = 1.98–2.01 region of the spectrum of the product but assignment of any of these to an S_2^{3-} moiety is questionable. The product might be formulated as a dinuclear species in which the $Mo(S_2CNEt_2)_2$ groups are bridged by two S_2^{3-} moieties with sulfur electrons paired under these conditions and this hypothesis is consistent with the fact that reaction of the complex with O_2 [1] yields some $(Et_2NCS_2)_2Mo(S_2O)_2Mo(S_2CNEt_2)_2$. Perhaps inconsistent with this formulation, however, is the fact that the molybdenum electrons remain unpaired, since no epr signals are observed for the analogously bridged species $(NH_4)_2[Mo_2(S_2)_6]\cdot 2H_2O$ [14] or for any other dinuclear Mo(V) complex prepared previously [13] except those containing a linear O=Mo–O–Mo=O moiety [15].

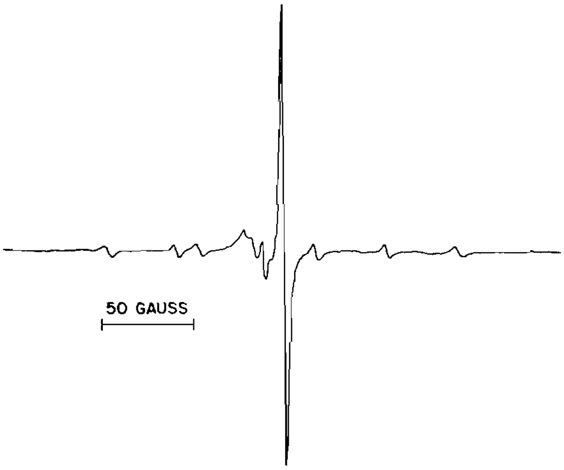

Fig. 1. EPR spectrum of '$Mo(S_2CNEt_2)_2(S_2)$' in CH_2Cl_2 at ambient temperature.

In summary, our experiments have implicated a product of empirical stoichiometry $Mo(S_2CNEt_2)_2(S_2)$ from reaction of $Mo(CO)_2(S_2CNEt_2)_2$ with sulfur. The product has conclusively been shown to contain Mo(V), but the spectral data is not definitive in determining whether this species is mono-, di-, or even polynuclear in nature. It would seem that an X-ray structural study will be required to establish the exact nature of the bonding in this complex.

Conclusions

The reactions of elemental sulfur with the Mo(IV) and Mo(II) dithiocarbamate complexes OMo-

$(S_2CNR_2)_2$ and $Mo(CO)_2(S_2CNEt_2)_2$ have been reinvestigated. The Mo(IV) complexes react smoothly in refluxing acetone to give the disulfur adducts $OMo(S_2CNR_2)_2(S_2)$ in high yield. The choice of solvent is critical for this reaction. A species of empirical formulation $Mo(S_2CNEt_2)_2(S_2)$ is implicated as the product of the reaction between $Mo(CO)_2(S_2CNEt_2)_2$ and sulfur although its structure and/or degree of aggregation is unknown. Surprisingly, the oxidation state of the molybdenum in this species has been shown to be V by epr studies.

The ability of $OMo(S_2CNR_2)_2(S_2)$ to undergo sulfur atom transfer reactions with PPh_3 (to give $SPPh_3$), MeNC (to give MeNCS) CN^- (to give SCN^-), and SO_3^{2-} (to give $S_2O_3^{2-}$) has been reported [9]. In all cases, the molybdenum-containing product is $OMo(S_2CNR_2)_2$. We have had previous success [16, 17] in utilizing intermetal oxygen and halogen atom transfer reactions as synthetic tools (*e.g.*, eq. 1–2) and plan to explore the potential of the

$$MoO_2(acac)_2 + MoCl_2(acac)_2 \rightarrow 2OMoCl(acac)_2 \quad (1)$$

$$2Mo_2O_3[S_2P(OEt)_2]_4 + W(CO)_2(PPh_3)(S_2CNR_2)_2 \rightarrow 4OMo[S_2P(OEt)_2]_2 + WO_2(S_2CNR_2)_2 + 2CO + PPh_3 \quad (2)$$

this kind of chemistry in hopes of preparing molybdenum and tungsten species containing M=S linkages. A preliminary experiment has shown that $OMo(S_2CNEt_2)_2(S_2)$ does in fact react with $Mo(CO)_2(S_2CNEt_2)_2$ and characterization of the products is currently in progress.

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11 Solvent molecules of crystallization have been observed in X-ray studies of many molybdenum dithiocarbamate complexes, *e.g.* $OMo(S_2CNEt_2)_2(TolCOC_2COTol)$ [6] and $Mo_2O_3(SPh)_2(S_2CNEt_2)_2$ [12]. This formulation therefore does not seem unreasonable.

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