

NEW CHEMICAL REACTIVITY IN AROMATIC DITHIOCARBAMATE AND MONOTHIOCARBAMATE LIGANDS: SYNTHESSES OF $\text{Mo}_2\text{L}_4 \cdot 2\text{THF}$ (L = PYRROLE OR INDOLE MONOTHIOCARBAMATE OR PYRROLE DITHIOCARBAMATE) AND $\text{Mo}_2\text{L}'_2$ (L' = INDOLINE MONOTHIOCARBAMATE)¹

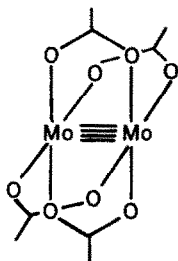
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Abstract—The reactions between $\text{Mo}_2(\text{C}_2\text{H}_3\text{O}_2)_4$ and several new dithio- and monothiocarbamates have been studied. The first example of a dimolybdenum compound of a dithiocarbamate with the “molybdenum acetate” structure is reported ($\text{Mo}_2\text{L}_4 \cdot 2\text{THF}$; L = pyrrole dithiocarbamate). In addition, the synthesis of $\text{Mo}_2\text{L}'_2 \cdot 2\text{THF}$ (L' = pyrrole monothiocarbamate, indole monothiocarbamate, indole dithiocarbamate) and $\text{Mo}_2\text{L}'_2$ (L' = indoline monothiocarbamate) are reported. A discussion of the unique stabilization of the dithiocarbamate bridge by “aromatic” dithio- and monothiocarbamates is presented.

INTRODUCTION

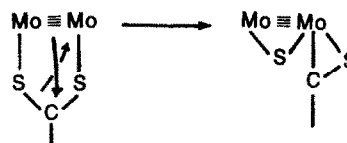
The chemistry of compounds containing metal-metal bonds constitutes one of the major topics of inorganic chemistry currently attracting vigorous and diverse research efforts.² This realm of metal-metal bonds was largely unknown prior to 1970 and is an exciting area of study. A large array of ligands have been coordinated to the dimolybdenum unit (Mo_2^{4+}) including halides, amines and carboxylates.³⁻⁵ Perhaps the most well studied of these systems are the carboxylates which have the structural features indicated below as shown by an X-ray diffraction study performed by Cotton.⁶



One of the most glaring absences in this array of ligands is the lack of dithiocarbamate (dtc) and monothiocarbamate (mtc) complexes of the dimolybdenum unit. The paucity of dithiocarbamate compounds is because of the unusual metal insertion into the C-S bond

of the dithiocarbamate, resulting in a thiocarbene linkage and a Mo=Mo double bond (Scheme 1).⁷

We choose to view this reaction as a “nucleophilic” attack of one of the Mo-Mo bonds on the CS_2 carbon (Scheme 2). If indeed this model were valid, we felt that



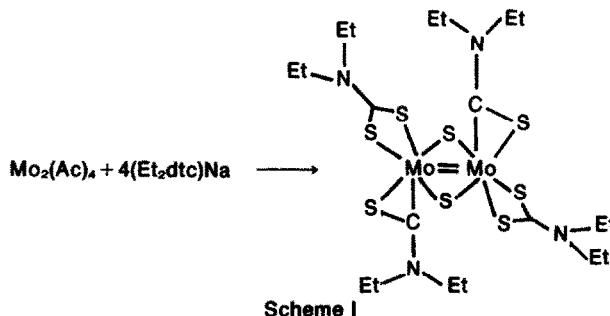
Scheme II

we could exploit the unique resonance properties of new aromatic mono- and dithiocarbamates recently prepared in these laboratories to synthesize the first examples of mono- or dithiocarbamate dimolybdenum complexes that adopted the dimolybdenum acetate structure. That is, we have recently show that “aromatic” dithiocarbamates such as those derived from pyrrole have only a minor contribution from the resonance form IIIB often used to describe dithiocarbamates⁸ and it is this resonance form which would favor the “nucleophilic” attack for one of the Mo-Mo bonds on the CS_2 carbon.

EXPERIMENTAL

Syntheses of ligands

Potassium salts of pyrrole-N-carbodithioate (pdc), pyrrole-N-carbothioate (ptc),⁹ indole-N-carbodithioate (ildc),⁹ indole-N-



Scheme I

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carbothioate (iltc),¹ and indoline-N-carbothioate (intc)¹ were prepared as reported previously.

Mo₂(pdc)₄·2THF

Excess (1.7 eq.) of potassium pyrrole-N-carbodithioate dissolved in 50 ml dry THF was added slowly to a mixture of 1 g Mo₂(OAc)₄ (OAc = acetate) in dry THF. The yellow color of the Mo₂(OAc)₄ was immediately replaced by a deep purple color. After all the Kpdc was added, the solution was filtered to remove any insoluble materials. The volume of the solution was reduced to about 50 ml, and 10 ml hexane was added. Refrigeration for several days produced purple crystals of Mo₂(pdc)₄·2THF. This compound was recrystallized by dissolution in THF and addition of an equal volume of hexane. Several elemental analyses were attempted; however, in each case some THF was lost so that analyses usually indicated somewhere between one and two THF molecules per Mo₂ unit. NMR spectra of freshly prepared samples integrated in such a way as to indicate two THF molecules per four pyrrole groups. NMR(*d*₆-DMSO) δ 2.0 (4H, m), 3.82 (4H, m), 6.57 (4H, m), 8.03 (4H, m). Found: C, 35.67; H, 3.31; S, 28.75; Calc. for C₂₈H₃₂N₄O₂S₈Mo₂: C, 37.14; H, 3.56; S, 28.35. This corresponds to the loss of approx. 20% of the THF.

Mo₂(iltc)₄·2THF

This compound was prepared by the same method as that above used for Mo₂(ptc)₄·2THF. This compound is dark purple and can be recrystallized from THF and hexane. Elemental analyses corresponded to approx. Mo₂(iltc)₄·1.6 THF. NMR again however integrated to give 2THF/4 indole groups.

Mo₂(ptc)₄·2THF and Mo₂(ptc)₄

A solution of 1.5 g Kptc in 50 ml THF was added slowly through a Schlenk frit to a mixture of 0.97 g Mo₂(OAc)₄ in 100 ml dry THF. During this period an orange solution formed and KOAc precipitated from solution. After an additional 1 hr of stirring the solution was filtered. The volume of solution was reduced by half by vacuum evaporation and an equal volume of hexane was added. Refrigeration for several days afforded an orange powder which was shown to be Mo₂(ptc)₄·2THF by NMR. However, when recrystallized from CH₂Cl₂, the THF molecules were lost. Found: C, 34.35; H, 2.39; S, 18.33; Calc. for C₂₀H₁₆N₄O₄S₄Mo₂: C, 34.50; H, 2.32; S, 18.41.

Mo₂(iltc)₄·2THF

A solution of 2 g Kiltc in 100 ml dry THF was added through a Schlenk frit to mixture of 0.98 g Mo₂(Ac)₄ in 50 ml dry THF. During this period an orange solution and a colorless precipitate formed (KAc). The solution was filtered to remove KAc. The volume of the solution was reduced to half and an equal volume of hexane was added. Refrigeration produced an orange powder which was collected by filtration.

Mo₂(Intc)₄

Since Kintc shows only very limited solubility in dry THF, this reaction was attempted in very dry ethanol. 1 g Kintc was added directly to 0.5 g Mo₂(Ac)₄ in 100 ml ethanol. After stirring for 2 hr an orange-red precipitate formed. This precipitate was collected on a Schlenk frit and dried under vacuum. This compound is extremely air sensitive. Exposure to air for even the briefest period transforms the compound to a brown and then black powder.

Spectral data collection

IR spectra were determined as before.¹ Optical data were obtained on either a Cary 14 or a Hitachi 110 spectrophotometer.

NMR

The ¹H and ¹³C NMR spectra were obtained on a Bruker WM-250 spectrometer operating in the pulsed-FT mode. The ¹H NMR spectra were run at 250 MHz and the ¹³C NMR spectra at 62.5 MHz.

RESULTS AND DISCUSSION

The reaction of the aromatic dithiocarbamates, pyrrole-N-carbodithioate and indole-N-carbodithioate, with Mo₂(OAc)₄ in dry THF, leads to dark purple compounds

which we formulate as Mo₂L₄·2THF based on spectral analyses. IR and electronic spectra and ¹H and ¹³C spectral results suggest that a slow decomposition occurs wherein THF is lost with the possible concomitant formation of a thiocarbene linkage. All aromatic dithio- and monothio- ligands behaved in an identical fashion. Therefore, only data for Mo₂(pdc)₄·2THF and Mo₂(ptc)₄·2THF are presented.

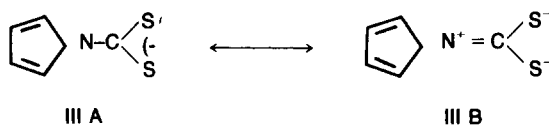
IR studies

A report by Steele and Stephenson¹⁰ of the attempted synthesis of a diethyldithiocarbamate complex of dimolybdenum suggested that in the presence of air the green reaction product immediately formed the violet Mo₂O₃(Et₂dtc)₄ compound. These Mo(V) dimers have been studied extensively by Newton¹¹ and the $\nu(\text{Mo}=\text{O})$ vibration frequencies for Mo₂O₃(R₂dtc)₄ occur close to 938 cm⁻¹ as a strong band in the IR spectra. Since the molybdenum pyrroledithiocarbamate compound was also violet, the IR spectrum was recorded in order to rule out the presence of the Mo₂O₃ core. The spectrum of this compound exhibited bands at 1250 cm⁻¹, $\nu(\text{C}=\text{N})$, as well as bands at 1100 and 850 cm⁻¹ that are characteristic of the presence of pdc. However, no bands appeared between 900 and 1000 cm⁻¹ that were strong enough to be assigned to $\nu(\text{Mo}=\text{O})$. The only band in this region was a medium intensity band at 980 cm⁻¹ which also appears in the IR spectra of all pdc complexes as well as in the spectrum of the ligand itself.^{8,9} Therefore, this band is assumed to arise from the ligand, not from a Mo-O bond.

The IR spectrum of the analogous monothiocarbamate complex was also recorded. No Mo=O bands occurred in this spectrum either. The $\nu(\text{C}=\text{O})$ frequency was located near 1580 cm⁻¹ in Mo₂(ptc)₄ which is fairly high; however, we feel that the oxygen is indeed coordinated to Mo in this orange compound.¹

ELECTRONIC SPECTRA

The electronic spectra of both the dithiocarbamate and monothiocarbamate were recorded in CH₂Cl₂ solution between 900 and 350 nm. The lowest energy band was found at 510 nm for the dithiocarbamate and at 405 nm for the monothiocarbamate. This band is believed to correspond to the $\delta \rightarrow \delta^*$ transition, if indeed, the molybdenum acetate structure is preserved in these compounds. While the $\delta \rightarrow \delta^*$ band occurs between 500 and 700 nm ($\epsilon = 200\text{--}3000$) for most Mo₂⁴⁺ species,¹² it occurs at a much higher energy (340 nm) for tetrakis-carboxylates.¹³ However, San Filippo and Sniadoch¹⁴ have found that values for the $\delta \rightarrow \delta^*$ transition in aryl-carboxylates appear as a broad intense band centered between 350 and 480 nm. If our argument which eliminates resonance form IIIB (Scheme 3) were correct, we could then describe the aromatic mono- and dithiocarbamate as a COS or CS₂ group attached to an aromatic ring similar to monothio- or dithiobenzoate. As a result we can suggest that the position of the band in the spectra of our complexes agrees nicely with position and



Scheme III

shape of the same band in arylocarboxylates of dimolybdenum. In other words, the spectra can be interpreted as indicating the presence of a Mo-Mo quadruple bond in these compounds. The spectra of both the monothio- and dithio-derivatives are very similar. Thus we believe, on the basis of this and the NMR data (see below), that the structures of the compounds are similar. Finally, the shift of the $\delta \rightarrow \delta^*$ band in the monothiocarbamate to higher energy is as expected for replacing a sulfur donor with an oxygen donor.

¹H NMR

The proton NMR spectrum of both the pdc complex and the ptc complex of Mo_2^{4+} exhibit resonance lines characteristic of the pyrrole ring; a pair of multiplets suggestive of an A A'B B' system. The pyrrole resonances are centered about δ 8.03 and δ 6.56 for the dithiocarbamate complex and δ 7.57 and δ 6.56 for the monothiocarbamate. Both spectra also exhibit resonances characteristic of THF. Integration of the spectra give pyrrole/THF as 2:1 as would be expected for a molybdenum acetate structure with two axially coordinated THF molecules. It is very important to note that THF molecules would not be expected to be associated with the thiocarbene complexes as the reported examples do not have solvent molecules associated.^{15,16} On the other hand, Mo_2^{4+} does not have a strong affinity to bond donor molecules on the axial position except when the ligand is a dithio ligand.^{17,18}

In order to be sure that the THF was coordinated, additional THF was added to the NMR sample of the monothiocarbamate complex. Exchange between coordinated and uncoordinated THF molecules is apparently slow on the NMR time scale since two sets of resonances were observed. Resonances at δ 3.72 and δ 1.86 associated with uncoordinated THF and resonances at δ 3.12 and δ 1.24 associated with coordinated THF were observed. The assignments were made based on the integration for ptc/THF using the upfield resonances, while the positions of the downfield resonances correlate closely with the reported value for uncoordinated THF (δ 1.79 and δ 3.60).¹⁹

¹³C NMR

A recent study by van der Linden *et al.* reported the position of the CS_2 carbon in the ¹³C spectra of 71 dithiocarbamates.²⁰ The carbon of the CS_2 group was found between 185 and 220 p.p.m. for every example. We felt that the ¹³C spectrum of the dithiocarbamate complex here could help distinguish whether the molybdenum acetate structure of the thiocarbene structure was present in this compound. The spectrum of a dithiocarbamate with the acetate structure should exhibit only a single resonance line in the CS_2 region, while a dithiocarbamate with the thiocarbene structure should exhibit a pair of resonances in this region corresponding to the thiocarbene carbon and the normal dithiocarbamate carbon respectively. Unfortunately, the intensity of this resonance is very weak since there are no hydrogens

attached to the carbon. The lack of hydrogens coupled with limited solubility of the complex in available NMR solvents made detection of the desired signal very difficult. However, a spectrum of the complex (dissolved in d_6 -THF) obtained by scanning 32000 times at 63.5 MHz did display resonance lines in the CS_2 carbon region. Unfortunately, there were three lines which were barely detectable and might correspond to the CS_2 carbon. The time frame of the experiment was sufficiently long that it appeared that a decomposition was occurring during the experiment. The most intense resonance line was at 209.8 p.p.m. and is suggested to result from $\text{Mo}_2(\text{pdc})_4 \cdot 2\text{THF}$ which has the molybdenum acetate structure. This suggested assignment is made based on the proximity of this line to the CS_2 resonance in Kpdc which was found at 217 p.p.m.

In summary, it appears that the products of the reaction between $\text{Mo}_2(\text{Ac})_4$ and Kpdc or Kptc have the molybdenum acetate structure, based on ¹H NMR and electronic spectra, at least for the length of time it takes to perform those measurements. However, the ¹³C spectra as well as the loss of THF during mailing time for elemental analysis point to slow decomposition to thiocarbene or a dithiocarbamate-thiocarbene equilibrium.

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REFERENCES

- ¹This paper is number 24 in the series, Coordination Chemistry of New Sulfur Containing Ligands. Paper number 23: R.D. Bereman, D. M. Baird, J. Bordner and J. R. Dorfman, *Polyhedron*, in press.
- ²J. L. Templeton, *Prog. Inorg. Chem.* 1970, 26, 211.
- ³J. V. Brencic and F. A. Cotton, *Inorg. Chem.* 1970, 9, 351.
- ⁴A. R. Bowen and H. Taube, *Inorg. Chem.* 1974, 13, 2245.
- ⁵A. B. Brignole and F. A. Cotton, *Inorg. Synth.* 1973, 13, 81.
- ⁶F. A. Cotton, Z. C. Mester and T. R. Webb, *Acta Crystallogr.* 1974, B30, 5698.
- ⁷L. Ricard, J. Estienne and R. Weiss, *Inorg. Chem.* 1973, 9, 2182.
- ⁸R. D. Bereman, M. R. Churchill and D. Nalewajek, *Inorg. Chem.* 1979, 18, 3112.
- ⁹R. D. Bereman and D. Nalewajek, *Inorg. Chem.* 1978, 17, 1085.
- ¹⁰D. F. Steele and T. A. Stephenson, *Inorg. Nucl. Chem. Lett.* 1973, 9, 777.
- ¹¹W. E. Newton, J. L. Corbin, D. C. Bravard, J. E. Searles and J. W. McDonald, *Inorg. Chem.* 1974, 13, 1100.
- ¹²F. A. Cotton, *Chem. Soc. Rev.* 1975, 4, 27.
- ¹³L. Dubicki and R. L. Martin, *Aust. J. Chem.* 1969, 22, 1571.
- ¹⁴J. San Filippo and H. J. Sniadoch, *Inorg. Chem.* 1975, 15, 2209.
- ¹⁵L. R. Ricard, J. Estienne and R. Weiss, *Inorg. Chem.* 1973, 12, 2182.
- ¹⁶D. F. Steele and T. A. Stephenson, *Inorg. Nucl. Chem. Lett.* 1973, 9, 777.
- ¹⁷F. A. Cotton, P. E. Fanwick, R. H. Niswander and J. L. Sekutowski, *Acta Chem. Scand., Ser. A.* 1978, A32, 663.
- ¹⁸L. R. Ricard, K. Karagiannidis and R. Weiss, *Inorg. Chem.* 1973, 12, 2179.
- ¹⁹"N.M.R. of Common Solvents", Sadler Research Laboratories, In. p. 10.
- ²⁰H. L. M. Van Goal, J. W. Diesveld, F. W. Pijpers and J. G. W. van der Linden, *Inorg. Chem.* 1979, 18, 3251.