# Molecular and Polymeric Compounds Resulting from Lewis Acid Interactions with $[CpMo(\mu\text{-}S)N\text{-}t\text{-}Bu]_2$

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There has been an interest in the use of molecular coordination compounds either as intact building blocks or as thermally labile precursors for polymeric materials.[1] The ability to tune the electronic properties of the molecular compounds provides the potential for controlling properties of the resulting polymers. We report here the preparation of a one-dimensional polymeric material based on Lewis acid interactions with a molybdenum sulfide dimer.

The structural characterization of the $\mu$-sulfido complex with terminal imido ligands *trans*-$[CpMo(\mu\text{-}S)(N\text{-}t\text{-}Bu)]_2$ (**1**) was reported several years ago.[2] A comparison of the redox properties of **1** with those of structurally analogous dimers with terminal oxo or sulfido ligands suggests that the imido derivative **1** is more electron-rich than the oxo or sulfido complex. For example, *trans*-$[MeCpMo(\mu\text{-}S)(O)]_2$ underwent a reversible reduction at a platinum electrode at −1.56 V vs SCE,[3] and *trans*-$[Cp^*Mo(\mu\text{-}S)(S)]_2$ showed two reduction waves at −0.70 (irr) and −1.35 V.[4] In contrast, no reduction waves were observed in the cyclic voltammagram of **1** out to ∼−2.0 V vs SCE. Complex **1** did show a quasi-reversible oxidation wave ($\Delta E$ = 93 mV) at 0.37 V vs Fc in acetonitrile. In order to probe the site(s) of high electron density in **1**, we reacted the complex with a Lewis acid.

The reaction of **1** with iodine in toluene led to the formation of a new product, **2**.[5] In the $^1$H NMR spectrum of the isolated complex, two singlet resonances for Cp and *t*-Bu groups were shifted downfield relative to **1**.[5] The UV–visible spectrum of **1** in toluene has a strong absorbance at 322 nm ($\epsilon = 10^4$) with shoulders at 400 and 450 nm. When 2 equiv of $I_2$ is incrementally added to this solution, all of the absorbances increase in intensity and the shoulder at 400 nm developes into a better resolved band with a maximum at 406 nm. The latter band may be due to the $I_2$ $\pi^* \rightarrow \sigma^*$ transition which is observed at 490 nm in this solvent (toluene) in the absence of the molybdenum dimer. The shift of the iodine transition to higher energy is consistent with a significant donor interaction with $I_2$.[6]

Single crystals of **2** were grown from a toluene solution at room temperature, and an X-ray diffraction study was carried out.[7] The structure is made up of discrete dinuclear units of **1** in which each of the bridging sulfide ligands forms an adduct with an $I_2$ molecule, $[CpMo(N\text{-}t\text{-}Bu)(\mu\text{-}S)\cdot I_2]_2$. A perspective drawing is shown in Figure 1. The Cp ligands are rotationally disordered in this room-temperature structure, and only the major ligand orientation (60% occupancy) is shown in the figure. The iodine–sulfur bond distance is 2.720(1) Å while the iodine–iodine distance is lengthened to 2.854(1) Å relative to 2.68 Å in free iodine. The S–I–I-angle is 175.2°. The structural parameters of the dinuclear molybdenum unit are not significantly altered. For example, the Mo–N bond length of 1.728 Å is identical to that in the parent complex **1**. The average Mo–S bond length of 2.363 Å is only slightly longer than that of 2.34 Å for **1**. The structure shows an intermolecular alignment of the iodine adducts with a short intermolecular I--I distance of 3.630 Å, compared to a van der Waals distance between iodine atoms of 3.9–4.0 Å.

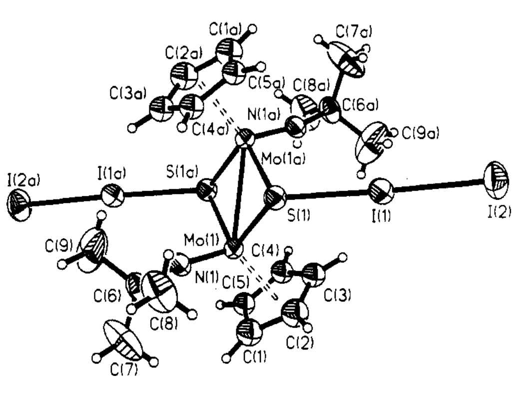

**Figure 1.** Perspective drawing and numbering scheme for $[CpMo(N\text{-}t\text{-}Bu)(\mu\text{-}S)\cdot I_2]_2$ (**2**). See discussion and supplementary material for information on bond distances and angles.

Iodine charge-transfer complexes with organic thiones have been identified,[8–10] and S–I and I–I bonding distances in these adducts were in the ranges 2.58–2.73 and 2.84–2.98 Å, respectively. We are unaware of previous examples of an iodine adduct with a metallosulfur complex. The halogen oxidation of a $\mu$-$\eta^1$-$S_2$ ligand in a dinuclear CpCr complex to form a $\mu$-$\eta^1$-SX ligand has been proposed previously.[11] Oxidative additions of halogens to the sulfur sites in $P_2N_4S_2$ rings have also been characterized.[12] The structure reported here presumably represents an intermediate in a halogen oxidation process.

Reaction of **1** with a potential two-coordinate Lewis acid was investigated in order to obtain a polymer chain of dinuclear units. Addition of excess silver triflate to **1** in toluene led to the precipitation of a new product which was isolated as a crystalline yellow material, **3**.[13] The NMR spectrum for **3** in $CD_3CN$ showed two singlets for Cp and N-*t*-Bu ligands at 5.87 and 0.94 ppm,

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(5) A solution of iodine (0.014 g, $5.7 \times 10^{-5}$ mol) in dry, degassed toluene (10 mL) was added via cannula to a solution of **1** (0.030 g, $5.7 \times 10^{-5}$ mol) in toluene (10 mL). The solution was allowed to sit without stirring at room temperature for 1 week. The solvent was removed by cannula, leaving orange-brown crystals. The following data are tentatively assigned to **2**: $^1$H NMR ($CD_3CN$) $\delta$ 5.93 (s, Cp), 0.96 (s, *t*-Bu). A second unidentified product (25%) was also observed: $^1$H NMR ($CD_3CN$) $\delta$ 6.8 (s, Cp), 1.57 (s, *t*-Bu).

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(7) Crystal data for **2** ($C_{18}H_{28}N_2S_2Mo_2I_4$): triclinic, $P\bar{1}$, $a$ = 9.0320(10) Å, $b$ = 9.814(2) Å, $c$ = 9.957(2) Å, $\alpha$ = 117.570(10)°, $\beta$ = 99.170(10)°, $\gamma$ = 102.120(10)°, $V$ = 730.6(2) Å$^3$, $Z$ = 1, $d$(calc) = 2.355 g/cm$^3$, $\mu$ = 5.168 mm$^{-1}$, $\lambda$(Mo K$\alpha$) = 0.710 73 Å, $T$ = 22–24 °C. Of 3360 unique reflections, 3350 with $F > 4.0\sigma(F)$ were used in the refinement. $R$(obs data) = 0.0390 and $R_w$ = 0.0470. Details of the structure solution are given in the supplementary material.

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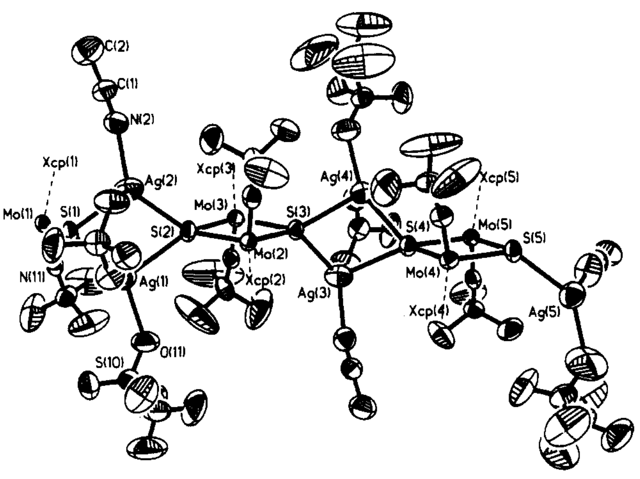

**Figure 2.** Perspective drawing and numbering scheme for the repeating unit of **3**, $[CpMo(N\text{-}t\text{-}Bu)S]_5[Ag(CH_3CN)OTf]_3[AgOTf]_2$. The atoms of the cyclopentadienyl rings and of the $CF_3$ group on the triflate anion of Ag2 have been omitted for clarity. See text for discussion of bond distances and supplementary material for complete listings of distances and angles.

respectively. These shifts are similar to those assigned to the iodine adduct. There was no change in this spectrum down to -45 °C.

Single crystals of **3** were obtained by evaporation of an acetonitrile/dichloromethane solution. The results of a crystallographic study[14] are shown in Figure 2. The crystalline product consists of infinite chains in which the dinuclear molybdenum units are joined by sulfur–silver bonding interactions. Each sulfido ligand is now coordinated to two molybdenum ions and two silver triflate units in a distorted tetrahedron. Sixty percent of the silver ions are also coordinated by an acetonitrile molecule. Crystallographic inversion centers are found in the middle of the Mol–Mol′–S1–S1′ ring and in the middle of the Ag5–Ag5′–S5–S5′ ring, and these generate the polymeric repeating unit which has the formula $[CpMo(N\text{-}t\text{-}Bu)S]_5[Ag(CH_3CN)OTf]_3[AgOTf]_2$; see Figure 2.

The Ag–S bonds within each $Ag_2S_2$ ring are asymmetric. For example, the two opposite longer bonds within the ring average 2.72 Å and the shorter bonds average 2.54 Å when the silver ion is also coordinated to an acetonitrile molecule. The Ag–S bonds tend to be shorter when acetonitrile is not included in the coordination sphere. The asymmetric Ag–S bonds in this case average 2.65 and 2.46 Å. The Ag–S–Ag and Mo–S–Mo angles along the chain are acute with average values of 72.8 and 76.8°, respectively, while the average Mo–S–Ag angle is 129.1°. An interesting feature of the $Ag_2S_2$ rings is the relatively short Ag–Ag distances,[15] which vary from 3.075 Å for Agl–Ag2 to 3.347 Å for Ag5–Ag5a.

The bond distances within the $[CpMo(\mu\text{-}S)(N\text{-}t\text{-}Bu)]_2$ units of **3** are again not perturbed very significantly by the Lewis acid–base interaction. For example, the average molybdenum–sulfur distance of 2.371(1) Å in **3** is slightly longer than that of the parent compound (2.34 Å). The average molybdenum–nitrogen distance is 1.709 Å, compared to the value of 1.73 Å for the Mo–N bond in **1**.[2]

Previous examples of molecular Mo–S–Ag complexes have been reported. In $\{[Mo(S(CH_2)_2S(CH_2)_2S)]_2Ag\}PF_6$, Mo-coordinated thiolate sulfurs interact with a silver ion in a distorted tetrahedral geometry.[16] There are also several examples of chelates of $MoS_4^{2-}$ with one or two silver ions, e.g., $[Ag(\mu\text{-}S)_2MoS_2]^-$.[17-20] Under different conditions, the reaction of $MoS_4^{2-}$ with silver ion and triphenylphosphine led to the formation of $[Mo_2S_8Ag_4](PPh_3)_4$, a cage structure with two six-membered $SAg_2S_2Mo$ rings connected by metal–sulfur bonds.[21] In addition, a polymeric $[Mo(\mu\text{-}S)_2Ag(\mu\text{-}S)_2]_x$ structure with edge-sharing $MS_4$ tetrahedra has been proposed on the basis of powder diffraction and resonance Raman studies.[22] The present structure differs from the previous examples in the incorporation of the $S\text{-}(\mu\text{-}Ag)_2\text{-}S$ repeating unit.[23]

The facile synthesis of **3** suggests that the procedure might be readily adapted to provide a systematic variation of Lewis acid and dinuclear complex components. Electronic effects appear to be important in promoting the Lewis acid–base interactions; for example, no interaction was observed between the Ag ion and the oxo derivative $[CpMo(\mu\text{-}S)(O)]_2$. Further studies of the solid and solution characteristics of **3** and related derivatives are planned.

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**Supplementary Material Available:** Tables describing details of the data collection and refinement for the crystal structures of **2** and **3** and listings of atomic coordinates and isotropic displacement parameters, bond lengths, bond angles, anisotropic displacement coefficients, and H atom coordinates for **2** and **3** (35 pages). Ordering information is given on any current masthead page.

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[13] To a solution of silver triflate (0.13 g, 3.7 × $10^{-3}$ mol) in dry, degassed toluene (20 mL) was added by cannula a toluene solution of **1** (0.10 g, 1.9 × $10^{-4}$ mol). The reaction solution was stirred at room temperature for 2 days. A yellow solid precipitated and was isolated by decantation of solvent. Yield: 80%.

[14] Crystal data for **3** ($C_{56}H_{79}N_8O_{15}S_{10}Mo_5Ag_5$): triclinic, $P\bar{1}$, $a = 10.032(2)$ Å, $b = 17.076(3)$ Å, $c = 27.356(5)$ Å, $\alpha = 105.403(14)°$, $\beta = 92.089(15)°$, $\gamma = 98.409(14)°$, $V = 4455.3(14)$ Å$^3$, $Z = 2$, $d$(calc) = 2.034 g/cm$^3$, $\mu = 2.08$ mm$^{-1}$, λ(Mo K$\alpha$) = 0.710 73 Å, $T$ = 18–22 °C. Of the 11204 unique measured reflections, 7271 with $F > 4.0\sigma(F)$ were used in the refinement. $R$(obs data) = 0.049 and $R_w$ = 0.051. Details of the data collection and refinement are given in the supplementary material.

[15] Ag···Ag interactions have been associated with distances of ca. 3.02 Å: Dietrich, H.; Storck, W.; Manecke, G. *J. Chem. Soc., Chem. Commun.* **1982**, 1036. Birker, P. J. M.; Verschoor, G. C. *J. Chem. Soc., Chem. Commun.* **1981**, 322.

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[23] Similar $S\text{-}(\mu\text{-}Ag)_2\text{-}S$ rings have been observed in homonuclear polymers, e.g.: Anacker-Eickhoff, H.; Hesse, R.; Jennische, P.; Wahlberg, A. *Acta Chem. Scand.* **1982**, *A36*, 251.