Two Quadruply-bonded Dimolybdenum Tetra(dithiocarboxylato) Compounds

F. A. COTTON, P. E. FANWICK, R. H. NISWANDER and J. C. SEKUTOWSKI

Department of Chemistry, Texas A&M University, College Station, Texas 77843, U.S.A.

Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

Structural data for compounds of the type $\text{Mo}_2(\text{S}_2\text{CR})_4\text{L}_2$ are reported for the first time. The compounds studied are those with $\text{R}=\text{CH}_3$ and C_6H_5 ; in both cases $\text{L}=\text{tetrahydrofuran}$. The dithioacetate is a new compound and a superior method of preparation is given for the benzoate. They are found to be fairly stable toward air when in crystalline form, and, unlike the xanthato compound, they do not give stable addition products with Br_2 or I_2 . The acetate forms triclinic crystals in space group $\text{P}\bar{1}$ with $Z=2$ and unit cell dimensions $a=10.937(2)$ Å, $b=14.358(3)$ Å, $c=9.132(1)$ Å, $\alpha=93.43(1)^\circ$, $\beta=111.33(1)^\circ$, $\gamma=88.98(1)^\circ$. Each molecule lies on an inversion center. The benzoate forms monoclinic crystals in space group $\text{P}2_1/\text{c}$ with $Z=2$ and $a=9.192(3)$ Å, $b=19.701(6)$ Å, $c=11.658(3)$ Å, $\beta=110.95(1)^\circ$, and the molecules are equivalent and reside on inversion centers. In both compounds there are tetrahydrofuran molecules loosely coordinated in the axial positions. The dimensions of the central $\text{Mo}_2\text{S}_8\text{O}_2$ units are very similar in all three crystallographically independent molecules and have the following values: $\text{Mo}-\text{Mo}=2.138(4)$ Å; $\text{Mo}-\text{S}=2.465(8)$ Å; $\text{Mo}-\text{O}=2.70(3)$ Å; $\angle \text{Mo}-\text{Mo}-\text{S}=99.4(2)^\circ$.

Carboxylato-bridged species, $\text{M}_2(\text{O}_2\text{CR})_4$, have played a prominent role in the developing chemistry of compounds with quadruple bonds between metal atoms,¹ especially Cr_2 and Mo_2 species, and many have been studied structurally.^{2,3} It is therefore surprising that only one dithiocarboxylate, $\text{Mo}_2(\text{S}_2\text{CR})_4$, has ever been reported, namely, the dithiobenzoate,^{4,5} and only two monothiocarboxylates,⁵ and no structure has previously been reported. In order to see what effect the replacement of RCO_2 by RCS_2 might have on the metal-to-metal bonding, we have begun an investigation of

several $\text{Mo}_2(\text{S}_2\text{CR})_4$ compounds. The first step has been to develop convenient, general and minimally odoriferous preparative methods. The second has been to obtain accurate structural information on representative compounds. For this second purpose we have chosen a compound with the simplest aliphatic R group, *viz.*, $\text{Mo}_2(\text{S}_2\text{CCH}_3)_4$, and a compound with the simplest aromatic R group, $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4$. The results of x-ray crystallographic studies of both these compounds, each in the form of its tetrahydrofuran adduct, are reported here. We have also conducted some exploratory studies of the chemical reactivity of the $\text{Mo}_2(\text{S}_2\text{CR})_4$ compounds to see whether they might resemble chemically the xanthato compound, $\text{Mo}_2(\text{S}_2\text{COEt})_4$.^{6,7}

EXPERIMENTAL

Materials and analyses. $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ was prepared by reaction of $\text{Mo}(\text{CO})_6$ with acetic acid in refluxing diglyme. $\text{C}_6\text{H}_5\text{MgBr}$ and CH_3MgBr were purchased from Aldrich Chemical Company, Inc. Carbon disulfide was obtained from Fischer Scientific Company and dried over molecular sieves prior to use. All other compounds and solvents were of reagent grade or better from commercial sources. Tetrahydrofuran, THF, was always distilled shortly before use. Carbon and hydrogen analyses were performed at the Center for Trace Characterization, Texas A&M University.

Preparation of $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4 \cdot 2\text{THF}$. Under nitrogen, 5 ml of a 3 M solution of $\text{C}_6\text{H}_5\text{MgBr}$ were added to 50 ml of THF. To this stirred solution, 2 ml of CS_2 were added very slowly at room temperature. The mixture was then allowed to react for one hour. $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, 1.67 g, was added and the mixture stirred for an additional hour.

Deoxygenated methanol, 100 ml, was added slowly producing a burgundy-red crystalline precipitate. The product was stirred for 15 min, filtered, and washed with 50 ml of deoxygenated methanol. After it had been dried under vacuum at room temperature, the compound appeared to be quite air stable. Elemental analysis indicated the compound was solvated with THF. *Anal.* Calc. for $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4 \cdot 2\text{C}_4\text{H}_8\text{O}$: C 45.57; H 3.80. Found: C 45.6; H 3.76.

THF appears to be easily replaced by other donor molecules such as glyme, diglyme, and pyridine. When the compound is placed in these solvents, slight color and physical changes are apparent. Products, however, were not isolated or characterized.

Attempted preparation of $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4\text{I}_2$. In 100 ml of deoxygenated chloroform $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4 \cdot 2\text{THF}$, 0.80 g (1.25 mmol), and 0.32 g (1.25 mmol) of I_2 were mixed. The mixture was stirred for 6 h at room temperature without conspicuous change. The product was filtered, washed with 50 ml of deoxygenated hexane and dried under vacuum at room temperature for 3 h. Elemental analysis indicated that the product had the composition $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4\text{I}_2$. *Anal.* Calc. C 31.76; H 1.89. Found: C 31.2; H 1.86. This compound was then dissolved (under nitrogen) in THF, the solution filtered and a layer of deoxygenated hexane placed gently over the filtrate. After three days, small crystals had formed at the interface of the two liquids. These crystals were collected by filtration and dried by passing nitrogen through the filter. One of these crystals was chosen for X-ray analysis. However, this was found to be the unreacted dithiobenzoate and no iodide (or iodine) was found. This identification was later substantiated by elemental analysis of the crystals.

Preparation of $\text{Mo}_2(\text{S}_2\text{CCH}_3)_4 \cdot 2\text{THF}$. In a procedure similar to that used for benzoate, 10 ml of a 2.8 M solution of CH_3MgBr was added to 50 ml of THF. To this stirred solution 4 ml of CS_2 was added very slowly and the reaction was cooled by means of an ice bath. The mixture was stirred for 2 h while the flask was allowed to warm to room temperature. $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, 3.11 g, was added, whereupon an orange-red product precipitated. After addition of 100 ml of deoxygenated methanol, stirring was continued for 30 min. The compound was then collected by filtration, washed with 50 ml of deoxygenated methanol, and dried under vacuum at room temperature for 3 h. The dry product appeared to be quite air stable. Elemental analysis indicated the product obtained as above was not solvated. *Anal.* Calc. for $\text{Mo}_2(\text{S}_2\text{CCH}_3)_4$: C 17.27; H 2.16. Found: C 17.7; H 2.18.

Crystals suitable for X-ray analysis were grown by gently placing a layer of hexane over a saturated THF solution of the compound. The crystals which

formed were solvated with THF. *Anal.* Calc. for $\text{Mo}_2(\text{S}_2\text{CCH}_3)_4 \cdot 2\text{C}_4\text{H}_8\text{O}$: C 24.43; H 4.00. Found: C 24.8; H 3.68.

X-Ray crystallography of $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4 \cdot 2\text{THF}$. A crystal measuring approximately $0.3 \times 0.2 \times 0.2$ mm was mounted on a glass fiber and coated with epoxy resin. The crystal was examined on a Syntex P1 four-circle automated diffractometer.⁸ Both rotation photographs and ω -scans were used to determine the quality of the crystal. Preliminary examination indicated that the crystal was monoclinic. Cell constants, determined by a least-squares fit of 15 reflections having $18^\circ < 2\theta(\text{MoK}\alpha) < 30^\circ$, were: $a = 9.192(3)$ Å, $b = 19.701(6)$ Å, $c = 11.658(3)$ Å, $\beta = 110.95(1)^\circ$, and $V = 1972(1)$ Å³. The observed volume is consistent with $Z = 2$.

Data were collected at $22 \pm 2^\circ\text{C}$ using the Syntex P1 autodiffractometer, with graphite-monochromated $\text{MoK}\alpha$ radiation and the $\theta - 2\theta$ scan technique. Variable scan rates from 4° to $24^\circ/\text{min}$ were used, depending on the intensity. The scan range was from $K\alpha_1 - 0.9^\circ$ to $K\alpha_2 + 1.0^\circ$. The systematic absences, k odd for $0k0$ and l odd for $h0l$, indicated the space group to be $P2_1/c$ (No. 14). A total of 2866 reflections having $0^\circ < 2\theta(\text{MoK}\alpha) < 45^\circ$ were collected. Of these, 1499 unique reflections with $I > 3\sigma(I)$ were used to solve and refine the structure. Three standard reflections were checked after every 97 measurements and were found to remain effectively constant. Lorentz and polarization corrections were applied but absorption was neglected.

The presence of only two formula units in the unit cell requires each one to reside on an inversion center. The position of one crystallographically unique Mo atom was determined from a three-dimensional Patterson function. The positions of the other atoms were obtained from subsequent difference Fourier maps. The function minimized in least squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ and the parameter ρ in the expression⁸ for the weights was assigned a value of 0.07. The discrepancy indices used are defined as follows:

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$$

The structure was refined to convergence with all temperature parameters anisotropic. The final discrepancy indices were $R_1 = 0.046$ and $R_2 = 0.057$. The estimated standard deviation of an observation of unit weight was 1.18. A final difference Fourier revealed no features of structural significance.

X-Ray crystallography of $\text{Mo}_2(\text{S}_2\text{CCH}_3)_4 \cdot 2\text{THF}$. An approximately equidimensional crystal with a mean thickness of about 0.25 mm was wedged in a

soft glass capillary, immersed in mineral oil and mounted on a Syntex P1 autodiffractometer. Procedures for preliminary examination and data collection were essentially the same as those just described for the benzoate. In this case there was an overall decline of about 10 % in the standards and a linear correction was made for this before the 2558 unique data having $I > 3\sigma(I)$ were used to solve and refine the structure.

The preliminary examination showed that the crystal belonged to the triclinic system with the following unit cell dimensions: $a = 10.937(2)$ Å, $b = 14.358(3)$ Å, $c = 9.132(1)$ Å, $\alpha = 93.43(1)^\circ$, $\beta = 111.33(1)^\circ$, $\gamma = 88.98(1)^\circ$, and $V = 1333(1)$ Å³. This volume is consistent with $Z = 2$, and a formula unit of $\text{Mo}_2(\text{S}_2\text{CCH}_3)_4 \cdot 2\text{C}_4\text{H}_8\text{O}$.

The structure was solved by conventional heavy atom methods and successfully refined in the space group $P\bar{1}$ using anisotropic thermal parameters for the Mo and S atoms and isotropic ones for the C and O atoms. Each molecule in the unit cell resides on one of the inversion centers at the origin and $1/2, 1/2, 1/2$ so that the asymmetric unit consists of half of each molecule. The final values of the residuals, defined above, were $R_1 = 0.050$ and

Fig. 1. An ORTEP drawing of the $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4 \cdot 2\text{THF}$ molecule in which each atom is represented by its ellipsoid of thermal vibration scaled to enclose 50 % of its electron density.

Table 1. Positional and thermal parameters and their estimated standard deviations for $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4 \cdot 2\text{THF}$.^a

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	0.1080(1)	0.01751(5)	0.06531(7)	0.0140(1)	0.00304(2)	0.00576(5)	-0.0018(1)	0.0060(1)	0.00005(8)
S(1)	0.2036(3)	0.0838(1)	-0.0724(2)	0.0165(4)	0.00395(9)	0.0074(2)	-0.0045(3)	0.0075(4)	0.0012(2)
S(2)	-0.0912(3)	0.0332(1)	-0.2526(2)	0.0162(4)	0.00361(9)	0.0068(2)	-0.0030(3)	0.0064(4)	0.0009(2)
S(3)	-0.0250(3)	-0.1254(1)	-0.1266(2)	0.0176(4)	0.00336(9)	0.0082(2)	-0.0012(3)	0.0070(4)	-0.0010(2)
S(4)	0.2741(3)	-0.0776(1)	0.0520(2)	0.0157(4)	0.00365(9)	0.0088(2)	-0.0006(3)	0.0078(4)	-0.0007(2)
O(1)	0.3958(8)	0.0558(5)	0.2216(6)	0.016(1)	0.0068(3)	0.0108(7)	-0.003(1)	0.006(1)	0.0029(8)
C(1)	0.072(1)	0.0787(5)	-0.2161(8)	0.015(1)	0.0031(3)	0.0076(7)	0.000(1)	0.009(1)	0.0009(8)
C(2)	0.100(1)	0.1184(5)	-0.3149(8)	0.018(1)	0.0034(3)	0.0086(8)	-0.000(1)	0.011(2)	0.0017(9)
C(3)	0.033(1)	0.0954(7)	-0.4374(8)	0.018(2)	0.0079(5)	0.0071(7)	-0.003(2)	0.006(2)	0.0051(11)
C(4)	0.060(1)	0.1324(8)	-0.5274(9)	0.023(2)	0.0114(6)	0.0085(9)	-0.012(2)	0.005(2)	0.0068(13)
C(5)	0.151(1)	0.1913(8)	-0.4988(11)	0.019(2)	0.0096(6)	0.0162(12)	-0.001(2)	0.010(3)	0.0135(13)
C(6)	0.223(1)	0.2133(7)	-0.3781(10)	0.030(2)	0.0060(5)	0.0145(10)	0.001(2)	0.022(2)	0.0066(12)
C(7)	0.199(1)	0.1754(6)	-0.2868(9)	0.023(2)	0.0038(4)	0.0138(9)	-0.002(1)	0.023(2)	0.0019(10)
C(11)	0.165(1)	-0.1348(5)	-0.0479(7)	0.018(1)	0.0035(3)	0.0076(7)	-0.001(1)	0.015(1)	0.0016(8)
C(12)	0.246(1)	-0.1986(5)	-0.0709(9)	0.024(2)	0.0029(3)	0.0127(9)	-0.000(1)	0.021(2)	0.0006(9)
C(13)	0.390(1)	-0.2177(6)	0.0169(11)	0.023(2)	0.0050(4)	0.0171(14)	0.008(1)	0.012(3)	0.0001(13)
C(14)	0.458(1)	-0.2756(7)	-0.0058(14)	0.024(2)	0.0055(5)	0.0342(21)	0.005(2)	0.023(3)	-0.0058(17)
C(15)	0.392(1)	-0.3123(6)	-0.1162(13)	0.031(2)	0.0039(4)	0.0318(15)	0.001(2)	0.042(2)	-0.0044(14)
C(16)	0.253(1)	-0.2924(6)	-0.2008(11)	0.031(2)	0.0038(4)	0.0243(13)	-0.002(2)	0.034(2)	-0.0053(12)
C(17)	0.178(1)	-0.2354(6)	-0.1819(9)	0.033(2)	0.0039(4)	0.0130(10)	-0.003(2)	0.022(2)	-0.0023(11)
C(31)	0.517(2)	0.0781(11)	0.1843(14)	0.021(2)	0.0161(11)	0.0180(15)	-0.014(2)	0.013(3)	0.0064(21)
C(32)	0.664(1)	0.0668(9)	0.2877(12)	0.017(2)	0.0119(9)	0.0147(14)	-0.005(2)	0.006(3)	0.0046(19)
C(33)	0.620(2)	0.0342(12)	0.3757(15)	0.025(3)	0.0181(12)	0.0199(16)	-0.008(3)	0.009(3)	0.0184(22)
C(34)	0.453(2)	0.0369(13)	0.3428(13)	0.020(2)	0.0186(12)	0.0133(14)	-0.016(3)	0.007(3)	-0.0005(24)

^a The form of the anisotropic thermal parameter is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

$R_2 = 0.074$, and the esd for an observation of unit weight was 1.61.

Structure factor tables. A complete list of the observed and final calculated structure factors for each compound may be obtained, on request, from FAC.

RESULTS

Structural. Tables 1 and 2 list the atomic positional and thermal vibration parameters for the benzoate and acetate, respectively. The $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4 \cdot 2\text{THF}$ molecule is shown in Fig. 1, where the atom numbering scheme used in all tables pertaining to this molecule is defined. The molecule resides on a crystallographic inversion

center; all unlabelled atoms may be identified, when necessary, by primed labels corresponding to those given for atoms related by the inversion operation. Fig. 2 shows one of the two independent molecules of $\text{Mo}_2(\text{S}_2\text{CCH}_3)_4 \cdot 2\text{THF}$, and its numbering scheme. In the other molecule a related set of numbers, Mo(2), Mo(2)', S(5), S(6), *etc.* is used. The relationship will be quite clear from the tables of bond lengths and angles in the dithioacetate, where corresponding dimensions of the two molecules are listed side by side.

The two molecules of $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4 \cdot 2\text{THF}$ in the unit cell are equivalent and there is a crystallographically rigorous center of symmetry at the midpoint of the Mo—Mo bond. The bond lengths and angles are listed in Tables 3 and 4 and it may

Table 2. Positional and thermal parameters and their estimated standard deviations for $\text{Mo}_2(\text{S}_2\text{CCH}_3)_4 \cdot 2\text{THF}$.^a

Atom	x	y	z	β_{11}^b	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	0.39747(8)	0.48341(6)	0.45406(9)	0.00681(7)	0.00427(4)	0.0103(1)	0.0000(1)	0.0071(1)	0.0012(1)
Mo(2)	0.09856(8)	-0.02419(6)	0.04901(9)	0.00765(8)	0.00448(5)	0.0110(1)	-0.0010(1)	0.0080(1)	-0.0000(1)
S(1)	0.4070(3)	0.3261(2)	0.3340(3)	0.0114(3)	0.0048(1)	0.0153(4)	-0.0017(4)	0.0113(5)	-0.0026(4)
S(2)	0.3109(3)	0.6291(2)	0.5366(3)	0.0095(3)	0.0055(2)	0.0192(4)	0.0025(3)	0.0139(5)	0.0014(4)
S(3)	0.3378(3)	0.5438(2)	0.1906(3)	0.0104(3)	0.0071(2)	0.0117(3)	-0.0008(4)	0.0064(5)	0.0043(4)
S(4)	0.6200(3)	0.5894(2)	0.3157(3)	0.0103(3)	0.0061(2)	0.0134(3)	-0.0017(3)	0.0118(4)	0.0029(4)
S(5)	0.1521(3)	0.0351(2)	0.3239(3)	0.0115(3)	0.0072(2)	0.0117(4)	-0.0023(4)	0.0054(5)	-0.0015(4)
S(6)	-0.1205(3)	0.1000(2)	0.1898(3)	0.0125(3)	0.0061(2)	0.0151(4)	0.0011(4)	0.0152(5)	-0.0016(4)
S(7)	0.2157(3)	0.1127(2)	0.0124(3)	0.0090(3)	0.0055(2)	0.0196(4)	-0.0027(3)	0.0113(5)	0.0015(4)
S(8)	-0.0557(3)	0.1804(2)	-0.1228(3)	0.0104(3)	0.0050(1)	0.0169(4)	-0.0004(4)	0.0099(5)	0.0028(4)
O(1)	0.1440(8)	0.4363(6)	0.3320(9)	6.4(2)					
O(2)	0.3444(9)	-0.0945(7)	0.1731(10)	7.2(2)					
C(10)	0.0893(14)	0.3459(11)	0.330(2)	8.0(4)					
C(11)	-0.0575(15)	0.3615(11)	0.244(2)	8.2(4)					
C(12)	-0.0859(14)	0.4641(11)	0.238(2)	7.6(4)					
C(13)	0.0428(15)	0.5066(12)	0.261(2)	8.7(4)					
C(14)	0.4518(15)	-0.0654(11)	0.128(2)	8.5(4)					
C(15)	0.5711(15)	-0.0836(11)	0.261(2)	8.5(4)					
C(16)	0.5335(17)	-0.1370(13)	0.369(2)	9.8(5)					
C(17)	0.3893(14)	-0.1545(11)	0.300(2)	7.6(4)					
C(20)	0.5629(9)	0.2996(7)	0.365(1)	3.7(2)					
C(21)	0.5964(12)	0.2046(9)	0.302(1)	5.9(3)					
C(30)	0.4725(10)	0.5874(7)	0.175(1)	4.1(2)					
C(31)	0.4596(12)	0.6293(9)	0.018(1)	5.9(3)					
C(40)	0.0226(10)	0.0910(7)	0.344(1)	4.1(2)					
C(41)	0.0317(13)	0.1336(9)	0.502(1)	6.2(3)					
C(50)	0.1068(10)	0.1952(7)	-0.075(1)	4.0(2)					
C(51)	0.1580(12)	0.2868(9)	-0.104(1)	5.8(3)					

^a The form of the anisotropic thermal parameter is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

^b For atoms refined isotropically this column gives B_{iso} in $\text{\AA}^2$.

Fig. 2. An ORTEP drawing of Molecule I of $\text{Mo}_2(\text{S}_2\text{CCH}_3)_4 \cdot 2\text{THF}$. Atoms are represented by ellipsoids or spheres of thermal vibration scaled to enclose 50 % of the electron density.

be seen that the central portion of the molecule, that is, the $\text{Mo}_2(\text{S}_2\text{CC})_4\text{O}_2$ part, has essentially D_{4h} symmetry. The THF molecules violate this and so also do the phenyl rings. As shown in Table 5 these rings are twisted out of coplanarity with their respective CS_2 planes by 21.1° and 25.0° . This may be only a result of intermolecular packing.

Table 3. Bond distances (Å) for $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4 \cdot 2\text{THF}$.^{a,b}

$\text{Mo}(1) - \text{Mo}(1)'$	2.139(2)	$\text{S}(3) - \text{C}(11)$	1.67(1)
$\text{Mo}(1) - \text{S}(1)$	2.462(2)	$\text{S}(4) - \text{C}(11)$	1.67(1)
$\text{Mo}(1) - \text{S}(2)'$	2.455(2)	$\text{C}(11) - \text{C}(12)$	1.53(1)
$\text{Mo}(1) - \text{S}(3)'$	2.449(3)	$\text{C}(12) - \text{C}(13)$	1.40(2)
$\text{Mo}(1) - \text{S}(4)$	2.456(3)	$\text{C}(13) - \text{C}(14)$	1.37(2)
$\text{Mo}(1) - \text{O}(1)$	2.727(7)	$\text{C}(14) - \text{C}(15)$	1.41(2)
$\text{S}(1) - \text{C}(1)$	1.683(9)	$\text{C}(15) - \text{C}(16)$	1.37(2)
$\text{S}(2) - \text{C}(1)$	1.666(9)	$\text{C}(16) - \text{C}(17)$	1.38(2)
$\text{C}(1) - \text{C}(2)$	1.49(1)	$\text{C}(17) - \text{C}(12)$	1.42(1)
$\text{C}(2) - \text{C}(3)$	1.41(1)	$\text{O}(1) - \text{C}(31)$	1.40(1)
$\text{C}(3) - \text{C}(4)$	1.37(2)	$\text{O}(1) - \text{C}(34)$	1.37(2)
$\text{C}(4) - \text{C}(5)$	1.40(2)	$\text{C}(31) - \text{C}(32)$	1.47(2)
$\text{C}(5) - \text{C}(6)$	1.39(2)	$\text{C}(32) - \text{C}(33)$	1.39(2)
$\text{C}(6) - \text{C}(7)$	1.38(1)	$\text{C}(33) - \text{C}(34)$	1.44(2)
$\text{C}(7) - \text{C}(2)$	1.41(1)		

^a The esd in the least significant digit is given in parentheses. ^b Atoms with primed symbols are related by the inversion center to those with the same unprimed symbol.

Table 4. Bond angles (deg.) for $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4 \cdot 2\text{THF}$.^{a,b}

$\text{Mo}(1)' - \text{Mo}(1) - \text{S}(1)$	99.43(7)
$\quad - \text{S}(2)'$	99.45(7)
$\quad - \text{S}(3)'$	100.41(8)
$\quad - \text{S}(4)$	98.55(8)
$\quad - \text{O}(1)$	175.2(2)
$\text{S}(1) - \text{Mo}(1) - \text{S}(2)'$	161.08(9)
$\quad - \text{S}(3)'$	87.18(9)
$\quad - \text{S}(4)$	89.36(9)
$\text{S}(2)' - \text{Mo}(1) - \text{S}(3)'$	88.18(9)
$\quad - \text{S}(4)$	89.09(9)
$\text{S}(3)' - \text{Mo}(1) - \text{S}(4)$	161.04(9)
$\text{O}(1) - \text{Mo}(1) - \text{S}(1)$	78.6(2)
$\quad - \text{S}(2)'$	82.7(2)
$\quad - \text{S}(3)'$	83.9(2)
$\quad - \text{S}(4)$	77.1(2)
$\text{Mo}(1) - \text{S}(1) - \text{C}(1)$	108.6(3)
$\text{Mo}(1)' - \text{S}(2) - \text{C}(1)$	109.2(3)
$\text{S}(1) - \text{C}(1) - \text{S}(2)$	123.2(5)
$\quad - \text{C}(2)$	118.5(7)
$\text{S}(2) - \text{C}(1) - \text{C}(2)$	118.3(7)
$\text{C}(1) - \text{C}(2) - \text{C}(3)$	118.7(9)
$\quad - \text{C}(7)$	120.9(9)
$\text{C}(3) - \text{C}(2) - \text{C}(7)$	120.2(9)
$\text{C}(2) - \text{C}(3) - \text{C}(4)$	118(1)
$\text{C}(3) - \text{C}(4) - \text{C}(5)$	121(1)
$\text{C}(4) - \text{C}(5) - \text{C}(6)$	122(2)
$\text{C}(5) - \text{C}(6) - \text{C}(7)$	117(1)
$\text{C}(6) - \text{C}(7) - \text{C}(2)$	121(1)
$\text{Mo}(1)' - \text{S}(3) - \text{C}(11)$	108.1(4)
$\text{Mo}(1) - \text{S}(4) - \text{C}(11)$	109.2(4)
$\text{S}(3) - \text{C}(11) - \text{S}(4)$	123.7(6)
$\quad - \text{C}(12)$	118.2(8)
$\text{S}(4) - \text{C}(11) - \text{C}(12)$	118.0(8)
$\text{C}(11) - \text{C}(12) - \text{C}(13)$	118(1)
$\quad - \text{C}(17)$	120(1)
$\text{C}(13) - \text{C}(12) - \text{C}(17)$	122(1)
$\text{C}(12) - \text{C}(13) - \text{C}(14)$	117(1)
$\text{C}(13) - \text{C}(14) - \text{C}(15)$	122(1)
$\text{C}(14) - \text{C}(15) - \text{C}(16)$	120(1)
$\text{C}(15) - \text{C}(16) - \text{C}(17)$	121(1)
$\text{C}(16) - \text{C}(17) - \text{C}(12)$	118(1)
$\text{Mo}(1) - \text{O}(1) - \text{C}(31)$	124.5(8)
$\quad - \text{C}(34)$	122.6(8)
$\text{C}(31) - \text{O}(1) - \text{C}(34)$	110(1)
$\text{O}(1) - \text{C}(31) - \text{C}(32)$	107(1)
$\text{C}(31) - \text{C}(32) - \text{C}(33)$	105(1)
$\text{C}(32) - \text{C}(33) - \text{C}(34)$	110(1)
$\text{C}(33) - \text{C}(34) - \text{O}(1)$	106(1)

^a The esd in the least significant digit is given in parentheses. ^b Atoms with primed symbols are related by the inversion center to those with the same unprimed symbol.

Table 5. Planes and dihedral angles for $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4 \cdot 2\text{THF}$.^a

Plane	Atom	Distance from Plane
1	C(2)	0.023(11)
	C(3)	-0.013(13)
	C(4)	-0.014(14)
	C(5)	0.022(14)
	C(6)	0.002(13)
	C(7)	-0.022(11)
2	C(12)	-0.008(11)
	C(13)	0.016(12)
	C(14)	-0.018(14)
	C(15)	0.009(14)
	C(16)	0.003(13)
	C(17)	0.005(12)
3	S(1)	0.000(3)
	S(2)	0.000(3)
	C(1)	0.000(10)
4	S(3)	0.000(3)
	S(4)	0.000(3)
	C(11)	0.000(10)
Dihedral Angles		
	Plane	Angle
1	3	-25.0
2	4	21.1

^aThe esd in the least significant digit is given in parentheses.

The unit cell of $\text{Mo}_2(\text{S}_2\text{CCH}_3)_4 \cdot 2\text{THF}$ contains two molecules. Each one has a crystallographically rigorous center of inversion at the midpoint of the Mo—Mo bond. Neglecting the orientations of the THF rings and the hydrogen atoms of the methyl groups (which were not included in the refinement) the $\text{Mo}_2(\text{S}_2\text{CC}_4)\text{O}_2$ core of the molecule has symmetry approximating very closely to D_{4h} . Thus, the various distances and angles that ought to be equal on the basis of that symmetry are equal within a few times their esd's. These internal dimensions are recorded in Tables 6 and 7.

Chemical. The preparation of $\text{Mo}_2(\text{S}_2\text{CR})_4$ compounds has been shown to be relatively simple and odor-free if the RCS_2^- ion is generated by reaction of the Grignard reagent, RMgBr , with CS_2 and reacted *in situ* with $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. The solid $\text{Mo}_2(\text{S}_2\text{CR})_4$ compounds are stable toward ordinary laboratory air for periods of at least several days. It has also been shown that, in contrast to the

Table 6. Bond distances (Å) for $\text{Mo}_2(\text{S}_2\text{CCH}_3)_4 \cdot 2\text{THF}$.^{a,b}

Molecule I		Molecule II	
Mo(1)—Mo(1)'	2.141(1)	Mo(2)—Mo(2)'	2.133(1)
Mo(1)—S(1)	2.469(2)	Mo(2)—S(5)	2.462(2)
Mo(1)—S(2)	2.470(2)	Mo(2)—S(6)	2.467(2)
Mo(1)—S(3)	2.461(2)	Mo(2)—S(7)	2.469(2)
Mo(1)—S(4)	2.472(2)	Mo(2)—S(8)	2.481(2)
Mo(1)—O(1)	2.667(7)	Mo(2)—O(2)	2.712(6)
S(1)—C(20)	1.665(8)	S(5)—C(40)	1.677(9)
S(2)—C(20)	1.673(8)	S(6)—C(40)	1.690(9)
C(20)—C(21)	1.54(1)	C(40)—C(41)	1.51(1)
S(3)—C(30)	1.667(9)	S(7)—C(50)	1.681(9)
S(4)—C(30)	1.657(9)	S(8)—C(50)	1.682(9)
C(30)—C(31)	1.54(1)	C(50)—C(51)	1.51(1)
O(1)—C(10)	1.43(1)	O(2)—C(14)	1.45(1)
O(1)—C(13)	1.48(1)	O(2)—C(17)	1.42(1)
C(10)—C(11)	1.53(2)	C(14)—C(15)	1.46(2)
C(11)—C(12)	1.50(2)	C(15)—C(16)	1.46(2)
C(12)—C(13)	1.48(2)	C(16)—C(17)	1.49(2)

^aThe esd in the least significant digit is given in parentheses. ^bAtoms with primed symbols are related by the inversion center to those with the same unprimed symbol.

behavior of $\text{Mo}_2(\text{S}_2\text{COEt})_4$, the dithiocarboxylato compounds do not react with Br_2 or I_2 to give stable, well-defined addition products. The benzoate gave a product of composition $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4\text{I}_2$ but upon attempted recrystallization, the iodine was lost.

DISCUSSION

Preparative chemistry. As noted at the outset $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4$, $\text{Mo}_2(\text{OSCC}_6\text{H}_5)_4$ and $\text{Mo}_2(\text{OSCCCH}_3)_4$ were the only known thioacid^{4,5} derivatives of quadruply-bonded M_2 units until now. Lack of interest in such compounds may have stemmed in part from the offensive odor generated by acids such as HS_2CR . Although it is the sodium salt that is normally used to prepare the complex, previous methods^{9,10} have called for the intermediate formation of the free acid. In the earlier preparation⁴ of $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4$, the reaction of CS_2 with the Grignard reagent $\text{C}_6\text{H}_5\text{MgBr}$ was followed first by acidification and then by neutralization and reaction with $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$.

We sought a procedure which does not at any point involve the free acid. An attempt to react the Grignard salt, $C_6H_5CS_2MgBr$, directly with $Mo_2(O_2CCH_3)_4$ was successful and suggested that, in general, the acidification step, which was primarily employed to purify the thio acid, could be omitted. The general effectiveness of this simple procedure was then confirmed by preparing for the first time the dithioacetate.

For unknown reasons, attempts to use C_6H_5Li and CH_3Li instead of the respective Grignard reagents were unsuccessful.

It was shown⁷ recently that $Mo_2(S_2COR)_4$ molecules react with I_2 and Br_2 to yield products in which the Mo—Mo bond order is reduced from 4 to 1 because the oxidative addition of X_2 is accompanied (followed?) by an unprecedented rearrangement of the xanthate groups relative to the metal atoms. We have examined the reactions of Br_2 and I_2 with the $Mo_2(S_2CR)_4$ species to see if they would undergo simple oxidative addition to afford triply-bonded products. The stoichiometric reactions of I_2 and Br_2 with $Mo_2(S_2CCH_3)_4$ in $CHCl_3$ or THF did not result in simple oxidative addition

Table 7. Bond angles (deg) for $Mo_2(S_2CCH_3)_4 \cdot 2THF$.^{a,b}

Molecule I		Molecule II	
Mo(1)'—Mo(1)—S(1)	99.18(7)	Mo(2)'—Mo(2)—S(5)	99.22(7)
—S(2)	99.50(7)	—S(6)	99.59(7)
—S(3)	99.31(7)	—S(7)	99.65(7)
—S(4)	99.46(7)	—S(8)	99.16(7)
—O(1)	177.6(2)	Mo(2)'—Mo(2)—O(2)	177.1(2)
S(1)—Mo(1)—S(2)	161.31(9)	S(5)—Mo(2)—S(6)	161.18(9)
—S(3)	88.10(8)	—S(7)	87.65(9)
—S(4)	89.04(8)	—S(4)	89.41(9)
—O(1)	78.5(2)	—O(2)	81.52(2)
S(2)—Mo(1)—S(3)	88.20(9)	S(6)—Mo(2)—S(7)	88.51(8)
—S(4)	88.59(8)	—S(8)	88.31(8)
—O(1)	82.8(2)	—O(2)	79.73(2)
S(3)—Mo(1)—S(4)	161.22(9)	S(7)—Mo(2)—S(8)	161.19(9)
S(3)—Mo(1)—O(1)	80.0(2)	—O(2)	83.16(2)
S(4)—Mo(1)—O(1)	81.2(2)	S(8)—Mo(2)—O(2)	78.03(2)
Mo(1)—S(1)—C(20)	109.0(3)	Mo(2)—S(5)—C(40)	110.1(3)
Mo(1)—S(2)—C(20)	108.6(3)	Mo(2)—S(6)—C(40)	109.4(3)
Mo(1)—S(3)—C(30)	108.4(3)	Mo(2)—S(7)—C(50)	109.7(3)
Mo(1)—S(4)—C(30)	108.0(3)	Mo(2)—S(8)—C(50)	109.5(3)
S(1)—C(20)—S(2)	123.6(5)	S(5)—C(40)—S(6)	121.6(5)
S(1)—C(20)—C(21)	119.6(7)	S(5)—C(40)—C(41)	119.9(7)
S(2)—C(20)—C(21)	116.8(6)	S(6)—C(40)—C(41)	118.5(7)
S(3)—C(30)—S(4)	124.7(5)	S(7)—C(50)—S(8)	120.0(5)
S(3)—C(30)—C(31)	118.0(7)	S(7)—C(50)—C(51)	118.5(7)
S(4)—C(30)—C(31)	117.3(7)	S(8)—C(50)—C(51)	119.4(7)
Mo(1)—O(1)—C(10)	126.6(7)	Mo(2)—O(2)—C(14)	122.7(8)
—C(13)	120.7(7)	—C(17)	125.7(7)
C(10)—O(1)—C(13)	112.7(9)	C(14)—O(2)—C(17)	111.2(9)
O(1)—C(10)—C(11)	103(1)	O(2)—C(14)—C(15)	105(1)
C(10)—C(11)—C(12)	110(1)	C(14)—C(15)—C(16)	107(1)
C(11)—C(12)—C(13)	103(1)	C(15)—C(16)—C(17)	109(1)
C(12)—C(13)—O(1)	107(1)	C(16)—C(17)—O(2)	104(1)

^a The esd in the least significant digit is given in parentheses. ^b Atoms with primed symbols are related by the inversion center to those with the same unprimed symbol.

Table 8. Mean values of distances (Å) and angles (deg) common to all $\text{Mo}_2(\text{S}_2\text{CR})_4 \cdot 2\text{THF}$ molecules.

Distance or angle	R = C_6H_5	R = CH_3 I	R = CH_3 II	Grand average
Mo—Mo	2.139(2)	2.141(1)	2.133(1)	2.138(4)
Mo—S	2.456(5)	2.468(5)	2.470(8)	2.465(8)
Mo—O(THF)	2.727(7)	2.667(7)	2.712(6)	2.70(3)
Mo—Mo'—S	99.46(80)	99.36(15)	99.40(20)	99.4(2)

products. Elemental analyses indicated incomplete reactions, though the products were completely different in appearance from the starting material. They were non-crystalline, insoluble substances which defied attempts at recrystallization. The exact nature of these products is still uncertain, with the possibility that they are polymeric with bridging halide ions being conceivable.

The reaction of Br_2 with $\text{Mo}_2(\text{S}_2\text{CC}_6\text{H}_5)_4$ also resulted in an insoluble substance, but the reaction of I_2 gave a slightly soluble product resembling the starting compound. Elemental analysis of this product suggested complete oxidative addition. However, attempts to recrystallize the material resulted in its decomposition back to the starting compound. Since it seems unlikely that reductive elimination could take place under such mild conditions, it is unlikely that the "reacted" compound was an oxidative addition product. It may possibly be an inclusion compound or even a weak π -complex between I_2 and the benzene rings.

The failure of the $\text{Mo}_2(\text{S}_2\text{CR})_4$ species to react with Br_2 and I_2 in the way that the $\text{Mo}_2(\text{S}_2\text{COR})_4$ molecules do, or in any other simple, definite way suggests that simple oxidative addition is not in itself an important reaction even for the xanthates and that the unusual bonding of two of the xanthato groups in the products is crucial to the occurrence of the reaction.

Structural. The structures are qualitatively as expected, and there are no significant differences between the structures of the two compounds studied here (see Table 8), nor between these structures and that of the xanthato compound.⁶

There are slight but real differences between the bond lengths for the two crystallographically independent molecules of the dithioacetate, and these are in accord with the well-known^{2,3,11} inverse relationship between the strength of M—M and M— L_{ax} bonds. The molecule which has the slightly shorter Mo—Mo bond, 2.133(1) Å has the slightly longer Mo—O axial bond, 2.716(6) Å, while the

longer Mo—Mo distance in the other molecule, 2.141(1) Å, is accompanied by the shorter Mo—O bond, 2.667(7) Å.

In all three compounds with bridging dithio units that have now been studied, the Mo—S distances are practically identical. Those in the structures reported here (see Table 8) average 2.465(8) Å while those in the xanthate have a mean of 2.477(2) Å.

It is clear that the Mo—Mo distances in the compounds bridged by dithiocarboxylates and xanthate are about 0.045 Å longer than those in the carboxylato bridged species,^{1,3} such as $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, 2.093(1) Å, $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$, 2.090(4) Å, and $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4$, 2.096(1) Å. In all of the latter (and other) cases, there are only loose intermolecular axial interactions, with Mo...O distances around 2.85 Å. Even when fairly strong axial donors are brought in as in $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4 \cdot 2\text{py}$,¹² where Mo—N = 2.55 Å and Mo—Mo = 2.129(2) Å and $\text{Mo}_2(\text{O}_2\text{CC}_6\text{H}_5)_4 \cdot 2\text{diglyme}$,¹³ where Mo—O = 2.72 Å and Mo—Mo = 2.100 Å, the Mo—Mo distances increase rather little, *viz.*, 0.039 Å for the very short Mo—N bond but <0.01 Å for the benzoate where the axial Mo—O distance is similar to those in the dithiocarboxylates reported here. We therefore conclude that while a part of the increase in Mo—Mo distances may be attributed to the presence of axial THF molecules in each of the dithio cases, this cannot account fully for the difference. The steric and electronic properties of the XCS_2^- -type ligand must themselves favor a slightly greater Mo—Mo distance.

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