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Article

Reactions of Thioethers with $Mn_2(CO)_7(\mu\text{-}S_2)$ Proceed with CO Displacement and Insertion of the Sulfur Atom into the Mn–Mn Bond

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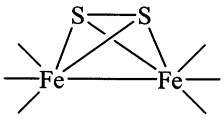
The reaction of $Mn_2(CO)_7(\mu\text{-}S_2)$ (**2**) with SMe_2 yielded the new complexes $Mn_2(CO)_6(\mu\text{-}S_2)(\mu\text{-}SMe_2)$ (**3**) and $Mn_4(CO)_{14}(SMe_2)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$ (**4**) in 18 and 41% yields, respectively. The reaction of **2** with the cyclic thioether thietane $SCH_2CH_2CH_2$ yielded the new complexes $Mn_2(CO)_6(\mu\text{-}S_2)(\mu\text{-}SCH_2CH_2CH_2)$ (**5**) and $Mn_4(CO)_{14}(SCH_2CH_2CH_2)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$ (**6**) in 12 and 52% yields, respectively, and the reaction of **2** with 1,4,9-trithiacyclododecane (12S3) yielded $Mn_2(CO)_6(\mu\text{-}12S3)(\mu\text{-}S_2)$ (**7**) and $Mn_4(CO)_{14}(12S3)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$ (**8**) in 8 and 24% yields, respectively. Compounds **3** and **5**–**7** were characterized crystallographically. Compounds **3**, **5**, and **7** have similar structures in which the thioether ligand has replaced the bridging carbonyl ligand of **2** and its sulfur atom has been inserted into the manganese–manganese bond. The two manganese atoms are not mutually bonded, and two $Mn(CO)_3$ groups are held together through the bridging disulfido ligand and the bridging sulfur atom of the thioether ligand. Compound **6** contains a $Mn_4(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$ moiety without metal–metal bonds. On the basis of spectroscopic data, compounds **4** and **8** are believed to have similar structures.

Introduction

The simplest disulfide of iron carbonyl, $Fe_2(CO)_6(\mu\text{-}S_2)$ (**1**), was first reported by Hieber in 1958[1] and has been extensively investigated in the years since.[2−4] We have recently prepared the related disulfide of manganese carbonyl, $Mn_2(CO)_7(\mu\text{-}S_2)$ (**2**), from the reaction of $Mn_2(CO)_9(NCMe)$ with thiirane.[5a,6]



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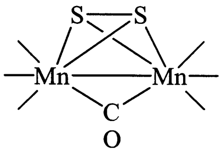
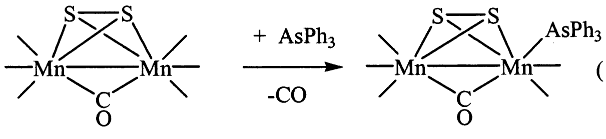
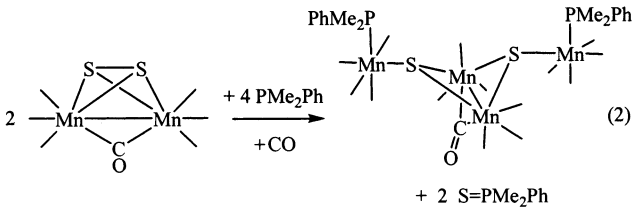


2

Compound **2** reacts with $AsPh_3$ by CO substitution (eq 1),[6] but PMe_2Ph reacts with **2** by attack at the disulfido ligand to yield the bis(sulfido)tetramanganese complex $Mn_4(CO)_{15}(PMe_2Ph)_2(\mu_3\text{-}S)_2$[5a] and $S{=}PMe_2Ph$[5b] (eq 2).



(1)



(2)

More interestingly, we have found that donors also induce an aggregation reaction that leads to tetranuclear metal complexes containing two bridging disulfido ligands (eq 3).[5a]

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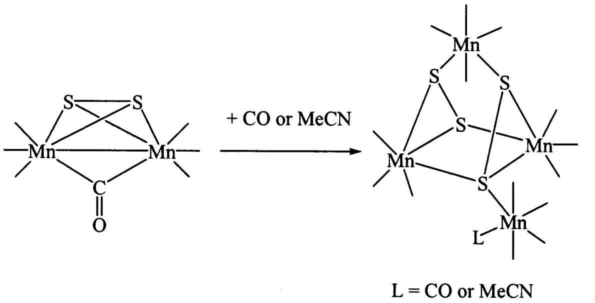
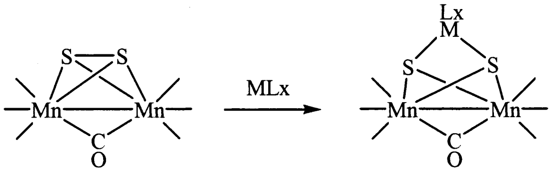


(3)

Compound **2** reacts with electron-deficient metal groupings by insertion of the metal atom into the S−S bond (eq 4).[7,8]



(4)

We have now found that electron-rich donors such as thioethers react with **2** at the metal atoms by replacement of the bridging CO ligand and insertion of the thioether sulfur atom into the manganese−manganese bond. Four new products have been characterized crystallographically. The results of these studies are reported here.

Results and Discussion

The reactions of **2** with the thioethers SMe_2, thietane, and 1,5,9-trithiacyclododecane (12S3) have yielded the new dimanganese complexes $Mn_2(CO)_6(\mu\text{-}SMe_2)(\mu\text{-}S_2)$ (**3**), $Mn_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2)(\mu\text{-}S_2)$ (**5**), and $Mn_2(CO)_6(\mu\text{-}12S3)(\mu\text{-}S_2)$ (**7**) in 18, 12, and 8% yields, respectively. For each reaction, there was also a second product containing four manganese atoms $Mn_4(CO)_{14}(SMe_2)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$ (**4**), $Mn_4(CO)_{14}(SCH_2CH_2CH_2)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$ (**6**), and $Mn_4(CO)_{14}(12S3)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$ (**8**) that was obtained in even better yields of 41, 52, and 24%, respectively.

All three dimanganese complexes **3**, **5**, and **7** were characterized by IR and ^1H NMR spectroscopies and by single-crystal X-ray diffraction analyses. The infrared spectra of **3**, **5**, and **7** show absorptions consistent with terminal carbonyl ligands only. The ^1H NMR spectrum of **3** exhibits a singlet at $\delta = 2.49$, indicating that the two methyl groups are equivalent. The ^1H NMR spectrum of **5** exhibits two resonances as expected at $\delta = 3.40$ and $\delta = 2.75$ for the thietane ligand. The ^1H NMR spectrum of **7** exhibits multiplets in the range of $\delta = 1.6-3.0$ for the methylene groups on the 1,5,9-trithiacyclododecane.

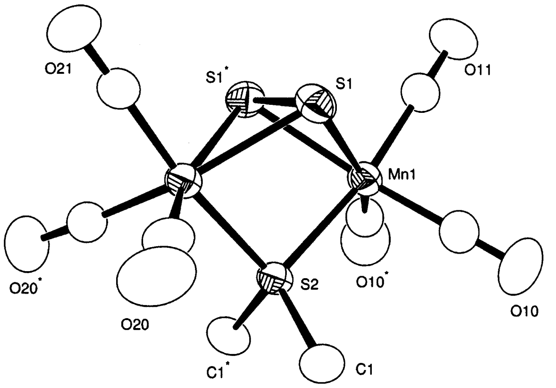


Figure 1. ORTEP diagram of $Mn_2(CO)_6(\mu\text{-}SMe_2)(\mu\text{-}S_2)$ (**3**) showing 50% probability thermal ellipsoids.

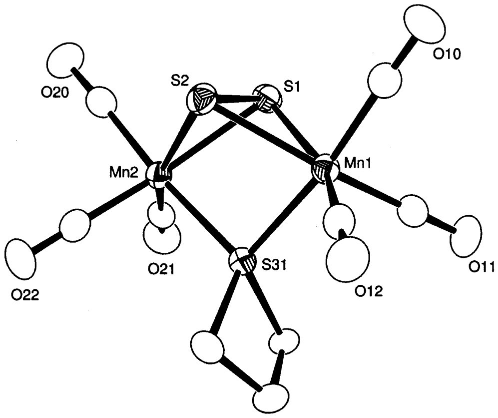


Figure 2. ORTEP diagram of $Mn_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2)(\mu\text{-}S_2)$ (**5**) showing 50% probability thermal ellipsoids.

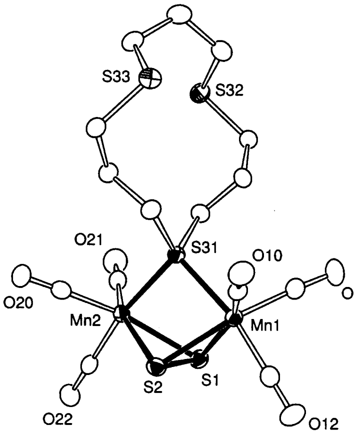


Figure 3. ORTEP diagram of $Mn_2(CO)_6(\mu\text{-}12S3)(\mu\text{-}S_2)$ (**7**) showing 50% probability thermal ellipsoids.

The molecular structures of **3**, **5**, and **7** are shown in Figures 1−3, respectively. Selected bond distances are listed in Table 1. Each compound consists of two manganese tricarbonyl groups held together by a bridging disulfido ligand and a bridging thioether ligand. The bridging sulfur atom of the thioether ligand donates two electrons to each metal atom. Compound **3** contains a crystallographic reflection plane that includes the two metal atoms and lies perpendicular to the direction of the S−S bond. In each compound, each metal atom has an 18 electron configuration. There is no metal−metal bond. The nonbonding manganese−manganese distances are 3.4311(4), 3.4338(7), and 3.4477(5) Å for **3**, **5**, and **7**, respectively. These distances are significantly longer than the Mn−Mn distance in **2** [2.6745-

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Table 1. Selected Bond Distances (in Å) for Compounds **3** and **5**−**7**

compound	Mn−Mn	Mn−S	S−S
3	Mn(1)···Mn(1′) = 3.4311(4)	Mn(1)−S(1) = 2.3582(4)	S(1)−S(1′) = 2.0471(7)
		Mn(2)−S(1) = 2.3543(4)	
		Mn(1)−S(2) = 2.3380(5)	
		Mn(2)−S(2) = 2.3430(5)	
5	Mn(1)···Mn(2) = 3.4338(7)	Mn(1)−S(1) = 2.3632(9)	S(1)−S(2) = 2.0459(11)
		Mn(1)−S(2) = 2.3715(10)	
		Mn(2)−S(1) = 2.3679(9)	
		Mn(2)−S(2) = 2.3676(9)	
		Mn(1)−S(31) = 2.3153(9)	
		Mn(2)−S(31) = 2.3038(9)	
6	Mn(1)···Mn(2) =3.5017(10)	Mn(1)−S(1) = 2.3487(13)	S(1)−S(3) = 2.0859(16)
		Mn(1)−S(2) = 2.3661(14)	S(2)−S(4) = 2.0725(14)
		Mn(1)−S(3) = 2.3276(14)	
		Mn(2)−S(1) = 2.3826(13)	
		Mn(2)−S(2) = 2.3481(14)	
		Mn(2)−S(4) = 2.3089(14)	
		Mn(3)−S(3) = 2.3384(14)	
		Mn(3)−S(4) = 2.3421(14)	
		Mn(4)−S(1) = 2.3835(14)	
		Mn(4)−S(51) = 2.3387(15)	
7	Mn(1)···Mn(2) = 3.4477(5)	Mn(1)−S(1) = 2.3627(7)	S(1)−S(2) = 2.0448(9)
		Mn(1)−S(2) = 2.3503(7)	
		Mn(2)−S(1) = 2.3750(7)	
		Mn(2)−S(2) = 2.3418(7)	
		Mn(1)−S(31) = 2.3499(6)	
		Mn(2)−S(31) = 2.3469(6)	

(5) Å], which contains a manganese−manganese single bond with a bridging disulfido ligand, and the Mn−Mn distance in $Mn_2(CO)_8(\mu\text{-}3,3\text{-DMT})$[9] (3,3-DMT = 3,3-dimethylthietane) [2.8243(9) Å], which has a manganese−manganese single bond with a bridging thietane ligand but no disulfido ligand. The S−S distances in the disulfido ligands in **3**, **5**, and **7** are all very similar [2.0471(7), 2.0459(11), and 2.0448(9) Å, respectively] and not significantly different from the S−S distance found in **2** [2.0474(11) Å].[5a] The Mn−S distances to the disulfido ligand are very similar in **3**, **5**, and **7**, see Table 1, but all are significantly longer than those found in **2**, where Mn−S = 2.2890(8), 2.2877(7), 2.2855(8), and 2.2842(8) Å. The shorter distances in **2** might be due to the presence of the Mn−Mn bond that brings the metal and sulfur atoms closer together. The Mn−S distances to the bridging thioether ligand in **3**, **5**, and **7** are also very similar (see Table 1), but all are longer than those involving the bridging thioether ligands in $[Mn(Cp\text{-}Me)(CO)_2]_2SMe_2$ (2.286 Å)[10] and $Mn_2(CO)_8(3,3\text{-DMT})$ [2.207(1) and 2.211(1) Å].[9]

Compound **7** contains a bridging 12S3 ligand. There have been a few previous examples of bridging coordination of 12S3 in polynuclear metal complexes, such as $Ru_5(CO)_{11}(12S3)(\mu_5\text{-}C)$[11] and $Os_4(CO)_{13}(12S3)$,[12] but this is the first example in a first row transition metal complex.

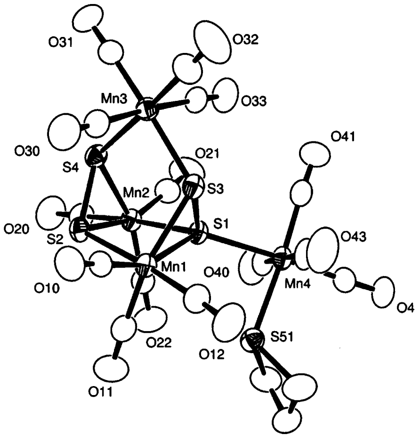
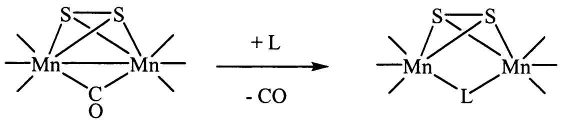


Figure 4. ORTEP diagram of $Mn_4(CO)_{14}(SCH_2CH_2CH_2)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$ (**6**) showing 50% probability thermal ellipsoids.

In our previous studies, we showed that the electron-deficient metal grouping inserts into the sulfur−sulfur bond of **2** (eq 4).[7,8] These studies now show that the thioether serves as four-electron donor, adds to **2** at the metal atoms by displacing the bridging CO ligand, and inserts into the metal−metal bond (see eq 5).



(5)

2

3, L = SMe_2
5, L = Thietane
7, L = 12S3

The spectroscopic properties of **4**, **6**, and **8** are similar, and all three of these products are believed to be structurally similar. Only one of them, **6**, was characterized crystallographically. An ORTEP diagram of the molecular structure of **6** is shown in Figure 4. Selected bond distances for **6** are listed in Table 1. Compound **6** contains four manganese atoms with two bridging disulfido ligands; one is a triple bridge, and the other is a quadruple bridge. There are no

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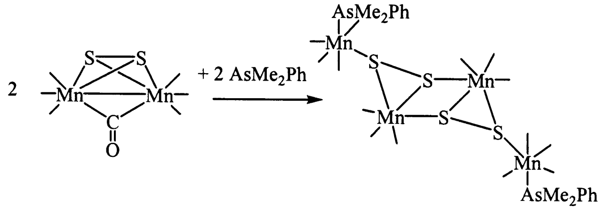
(9) Adams, R. D.; Belinski, J. A.; Chen, L. *Organometallics* **1992**, *11*, 4104.

(10) Belforte, A.; Calderazzo, F.; Vitali, D.; Zanazzi, P. F. *Gazz. Chim. Ital.* **1985**, *115*, 125.

(11) Adams, R. D.; Falloon, S. B.; McBride, K. T. *Organometallics* **1994**, *13*, 4870.

(12) Edwards, A. J.; Johnson, B. F. G.; Khan, F. K.; Lewis, J.; Raithby, P. R. *J. Organomet. Chem.* **1992**, *426*, C44.

metal−metal bonds in compound **6**. The structure of **6** is very similar to those of $Mn_4(CO)_{15}(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$ and $Mn_4(CO)_{14}(NCMe)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$.[5a] The thietane ligand in **6** is terminally coordinated to the manganese atom Mn(4) that lies outside the cluster. The Mn−S distance to the thietane ligand, 2.3387(15) Å, is similar to that found in other manganese complexes that have terminally coordinated thietane ligands.[9] The mechanism of the formation of the tetramanganese compounds has been shown to proceed by a ligand-induced dimerization involving formation of bridging disulfido ligands. This is a two-step process involving a ligand elimination that leads to formation of the trimanganese cluster (eqs 6 and 7). A similar process can be imagined for the formation of the clusters of **4**, **6**, and **8**.[6]



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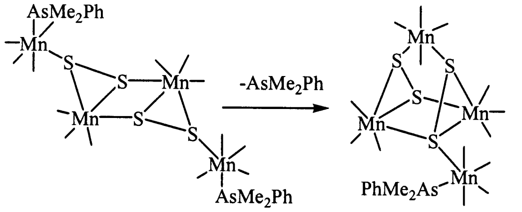

(7)

Experimental Section

General Data. All reactions were performed under a nitrogen atmosphere. Reagent-grade solvents were dried by the standard procedures and were freshly distilled prior to use. Infrared spectra were recorded on a Nicolet 5DXBO FTIR spectrophotometer. ^{1}H NMR spectra were recorded on a Varian Inova 300 spectrometer operating at 300 MHz. Elemental analyses were performed by Desert Analytics (Tucson, AZ). SMe_2 and thietane ($SCH_2CH_2CH_2$) were purchased from Aldrich. 1,4,9-Trithiacyclododecane[13] (12S3) and $Mn_2(CO)_7(\mu\text{-}S_2)$[5a] were prepared by our previously reported procedures. Product separations were performed by TLC in air on Analtech 0.25- and 0.5-mm silica gel 60-Å F_{254} glass plates.

Reaction of 2 with SMe$_2$. A 25.0-mg (0.068-mmol) sample of **2** was dissolved in 15 mL of hexane in a 25-mL three-neck round-bottomed flask equipped with a stir bar and a nitrogen inlet and outlet. To this solution was added 50 μL of SMe_2 via syringe. The resulting solution was stirred at room temperature for 2 h. The volatiles were removed in vacuo, and the product was separated by TLC plate using a hexane/CH_2Cl_2 (2/1, v/v) solvent mixture as the eluant. In order of elution, this yielded 6.0 mg of unreacted **2**, 4.9 mg (18%) of $Mn_2(CO)_6(\mu\text{-}SMe_2)(\mu\text{-}S_2)$ (**3**), and 11.2 mg (41%) of $Mn_4(CO)_{14}(SMe_2)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$ (**4**). Spectral data for **3**: IR ν_{CO} (cm^{-1} in CH_2Cl_2) 2018 (vs), 1950 (s), 1928 (s). ^{1}H NMR (δ in $CDCl_3$) 2.49 (s, 6H). Anal. Calcd (%) C 23.77, H 1.50; found (%) C 24.13, H 1.67. Spectral data for **4**: IR ν_{CO} (cm^{-1} in hexane) 2104 (w), 2089 (m), 2038 (vs), 2032 (vs), 2021 (s), 2009 (s), 1986 (s), 1979 (s), 1949 (s), 1934 (w), 1920 (w), 1911 (w). ^{1}H NMR (δ in $CDCl_3$) 2.64 (s, 6H). Anal. Calcd (%) C 23.95, H 0.75; found (%) C 23.89, H 0.89.

Reaction of 2 with Thietane. A 20.0-mg (0.054-mmol) sample of **2** was dissolved in 10 mL of methylene chloride in a 25-mL three-neck round-bottomed flask equipped with a stir bar and a nitrogen inlet and outlet. To this solution was added 4.0 mg of thietane via syringe. This solution was stirred at room temperature for 1 h. The volatiles were removed in vacuo, and the products were separated by TLC using a hexane/CH_2Cl_2 (3/2, v/v) solvent mixture as the eluant. In order of elution**,** 2.6 mg (12%) of $Mn_2(CO)_6(\mu\text{-}SCH_2CH_2CH_2)(\mu\text{-}S_2)$ (**5**) and 11.5 mg (52%) of $Mn_4(CO)_{14}(SCH_2CH_2CH_2)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$ (**6**) were yielded. Spectral data for **5**: IR ν_{CO} (cm^{-1} in hexane) 2042 (vw), 2022 (vs), 2010 (vw), 1960 (vs), 1932 (vs), 1999 (vw). ^{1}H NMR (δ in CD_2Cl_2) 3.41 (t, $J_{H-H} = 7.8$ Hz, 4H), 2.75 (q, $J_{H-H} = 8.1$ Hz, 2H). Anal. Calcd (%) C 25.97, H 1.45; found (%) C 25.53, H 1.36. Spectral data for **6**: IR ν_{CO} (cm^{-1} in hexane) 2105 (w), 2090 (m), 2039 (vs), 2033 (vs), 2020 (vs), 2009 (vs), 1984 (s), 1978 (s), 1949 (s), 1944 (m), 1933 (w), 1921 (w), 1912 (w). ^{1}H NMR (δ in CD_2Cl_2) 3.74 (t, $J_{H-H} = 7.5$ Hz, 4H), 3.13 (m, 2H). Anal. Calcd (%) C 25.07, H 0.74; found (%) C 25.08, H 0.83.

Reaction of 2 with 1,5,9-Trithiacyclododecane (12S3). A 22.0-mg (0.059-mmol) sample of **2** and 14.0 mg (0.059 mmol) of 1,5,9-trithiacyclododecane (12S3) were dissolved in 15 mL of CH_2Cl_2 in a 25-mL three-neck round-bottomed flask equipped with a stir bar and a nitrogen inlet. This solution was stirred at room temperature overnight. The volatiles were removed in vacuo, and the product was separated by TLC plate using a hexane/CH_2Cl_2 (1/1, v/v) solvent mixture as the eluant. In order of elution, 2.7 mg (8%) of $Mn_2(CO)_6(\mu\text{-}12S3)(\mu\text{-}S_2)$ (**7**) and 6.9 mg (24%) of $Mn_4(CO)_{14}(12S3)(\mu_3\text{-}S_2)(\mu_4\text{-}S_2)$ (**8**) were yielded. Spectral data for **7**: IR ν_{CO} (cm^{-1} in hexane) 2038 (vw), 2016 (vs), 1948 (s), 1925 (s). ^{1}H NMR (δ in $CDCl_3$) 2.88 (m, 4H), 2.78 (m, 4H), 2.68 (m, 4H), 2.02 (m, 4H), 1.78 (m, 2H). Anal. Calcd (%) C 31.91, H 3.21; found (%) C 31.85, H 3.29. Spectral data for **8**: IR ν_{CO} (cm^{-1} in hexane) 2102 (w), 2089 (m), 2036 (vs), 2029 (vs), 2020 (s), 2009 (s), 1986 (s), 1979 (s), 1954 (w), 1948 (s), 1944 (m), 1933 (w), 1918 (w), 1910 (w). ^{1}H NMR (δ in CD_2Cl_2) 3.24 (m, 2H), 3.12 (m, 2H), 2,84 (m, 4H), 2.68 (m, 4H), 2.17 (m, 4H), 1.87 (m, 2H). Anal. Calcd (%) C 28.70, H 1.88; found (%) C 28.79, H 1.79.

Crystallographic Analyses. Orange crystals of **3** and **5**, red crystals of **6**, and yellow crystals of **7** were grown from solutions in hexane/CH_2Cl_2 solvent mixtures by slow evaporation of the solvent at −17 °C. The crystals used for the data collections were glued onto the ends of thin glass fibers. X-ray intensity data for each structural analysis was measured on a Bruker SMART APEX CCD-based diffractometer using Mo Kα radiation ($\lambda = 0.710\,73$ Å). The unit cells were determined on the basis of reflections obtained from sets of three orthogonal scans. Crystal data, data collection parameters, and results of the analyses are listed in Table 2. The raw intensity data frames were integrated with SAINT+,[14] which also applied corrections for Lorentz and polarization effects. Final unit cell parameters are based on the least-squares refinement of all reflections with $I > 5(\sigma)I$ from the data sets. For each analysis, an empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using SADABS.[14]

Compound **3** crystallized in the monoclinic system. Systematic absences in the intensity data were consistent with the space groups $P2_1/m$ and $P2_1$. The space group $P2_1/m$ was assumed and confirmed by successful solution and refinement of the structure. Compound **5** crystallized in the monoclinic system. The space group $P2_1/c$ was identified by the pattern of systematic absences in the intensity data. Compound **6** crystallized in the monoclinic crystal system. Sys-

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(13) Adams, R. D.; Falloon, S. B. *J. Am. Chem. Soc.* **1994**, *116*, 10540.

(14) *SAINT+*, version 6.02a; Bruker Analytical X-ray System, Inc.: Madison, Wisconsin, 1998.

Table 2. Crystallographic Data for Compounds **3** and **5**−**7**

	3	**5**	**6**	**7**
empirical formula	$Mn_2S_2O_6C_8H_6$	$Mn_2S_3O_6C_{19}H_{16}\cdot 0.5C_6H_{14}$	$Mn_4S_5O_{14}C_{17}H_6$	$Mn_2S_5O_6C_{15}H_{18}$
formula weight	404.19	459.28	814.28	564.47
crystal system	monoclinic	monoclinic	monoclinic	triclinic
lattice parameters				
a (Å)	8.4615(5)	10.0080(16)	31.584(4)	10.2793(10)
b (Å)	10.5978(6)	10.8920(17)	9.2130(11)	10.4560(10)
c (Å)	9.0285(5)	16.375(3)	19.710(2)	11.1034(11)
α (deg)	90	90	90	106.943(2)
β (deg)	114.1920(10)	97.467(3)	101.521(3)	91.098(2)
γ (deg)	90	90	90	106.817(2)
V (Å^3)	738.51(7)	1769.9(5)	5619.7(12)	1085.78(18)
space group	$P2_1/m$ (No. 14)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
Z value	2	4	8	2
ρ_{calc} (g/cm^3)	1.82	1.72	1.93	1.73
m (Mo Kα) (mm^{-1})	2.15	1.80	2.19	1.67
temperature (K)	190	190	296	190
$2\Theta_{max}$ (°)	56.58	52.80	50.06	52.80
no. obs [$I > 2\sigma(I)$]	1800	3810	2922	3633
no. variables	98	209	361	253
GOF	1.083	0.981	1.055	0.996
max shift in final cycle	0.000	0.001	0.000	0.000
residuals: R1, wR2[a]	0.0220, 0.0602	0.0380, 0.0828	0.0470, 0.1115	0.0288, 0.0639
transmission coeff, max/min	1/0.788	0.894/0.785	1.000/0.548	0.862/0.685
largest peak in final diff four (e$^-$/Å^3)	0.266	0.527	0.919	0.463

[a] $R = \Sigma_{hkl}(||F_{obs}| - |F_{calc}||)/\Sigma_{hkl}|F_{obs}|$, $R_w = [\Sigma_{hkl}w(|F_{obs}| - |F_{calc}|)^2/\Sigma_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$, GOF $= \{\Sigma_{hkl}[w(|F_{obs}| - |F_{calc}|)]^2/(n_{data} - n_{vari})\}^{1/2}$. R1 $= \Sigma(||F_{obs}| - |F_{calc}||)/\Sigma|F_{obs}|$, wR2 $= \{\Sigma[w(F_{obs}^2 - F_{calc}^2)^2/\Sigma[w(F_{obs}^2)^2]\}^{1/2}$, $w = 1/\sigma^2(F_{obs}^2)$, GOF $= \{\Sigma_{hkl}[w(|F_{obs}^2| - |F_{calc}^2|)]^2/(n_{data} - n_{vari})\}^{1/2}$.

tematic absences indicated the space groups $C2/c$ or Cc. Intensity statistics indicated the centric space group $C2/c$, which was subsequently confirmed by the successful solution and refinement of the structure. Compound **7** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. For each structure, all non-hydrogen atoms were refined with anisotropic displacement parameters. The structure was solved by a combination of direct methods and difference Fourier syntheses and refined by full-matrix least-squares on F^2 using SHELXTL.[15] The positions of the hydrogen atoms were calculated by assuming idealized geometries and included as riding atoms.

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Supporting Information Available: CIF tables for the structural analyses of **3** and **5**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Sheldrick, G. M. *SHELXTL*, version 5.1; Bruker Analytical X-ray Systems, Inc.: Madison, Wisconsin, 1997.