Reactions of Metal Carbonyl Derivatives. Part 20.[1] Synthesis, Redox Behaviour, and Crystal and Molecular Structure of μ-Ethylthio-bis[dicarbonyl(η-methylcyclopentadienyl)manganese](*Mn–Mn*) Perchlorate: An Unusual Monothio-bridged Derivative of Manganese

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Treatment of $[Mn(MeC_5H_4)(CO)_2(SEt)]^-$, prepared *in situ* from $[Mn(MeC_5H_4)(CO)_2(thf)]$ and $[SEt]^-$, with perchloric acid in aqueous tetrahydrofuran leads to the formation of the unusual monothio-bridged derivative $[\{Mn(MeC_5H_4)(CO)_2\}_2(SEt)][ClO_4]$, in which the manganese atoms are joined by a metal–metal bond (MeC_5H_4 = η-methylcyclopentadienyl). A crystal structure determination by the heavy-atom method from diffractometer data of this complex reveals the cyclopentadienyl groups to be *trans*, and Mn–Mn 2.930(1) Å. Crystals are monoclinic, space group $P2_1/n$, $Z = 4$, $a = 8.676(5)$, $b = 16.062(5)$, $c = 15.872(5)$ Å, $\beta = 104.45(20)°$, and the structure was refined to R 0.51 for 1 785 observed reflections. The compound undergoes two reversible one-electron reductions as established by cyclic voltammetry and polarography.

PREVIOUS studies have revealed that the dibridged binuclear compounds $[\{Fe(C_5H_5)(CO)(SR)\}_2]$ and $[\{Fe(C_5H_5)(CO)(PR_2)\}_2]$ (R = alkyl or aryl groups; C_5H_5 = η-cyclopentadienyl) exhibit reversible redox properties [2-6] and that their one- and two-electron oxidations are accompanied by a decrease in the metal–metal distance.[7-9] Further, the iron–iron distances for the neutral parent compounds have been shown to be consistent with a bond order of zero while those for the one- and two-electron oxidation products have been suggested to correspond to formal one- and two-electron metal–metal bonds respectively. Thus, the iron–iron distance for $[\{Fe(C_5H_5)(CO)(PPh_2)\}_2]$ is 3.498 Å while those for $[\{Fe(C_5H_5)(CO)(PPh_2)\}_2]^+$ and $[\{Fe(C_5H_5)(CO)(PPh_2)\}_2]^{2+}$ are 3.14 and 2.764 Å respectively.[9] On the basis of these results it has been suggested that the oxidation involves an orbital which is anti-bonding with respect to the two metal atoms. Two separate bonding schemes to account for the foregoing trend have been suggested: one that the orbital is of σ-symmetry,[10] the other that it is of π-symmetry.[11]

In contrast to these observations, one-electron oxidation of the metal–metal bonded species, $[\{Fe(C_5H_5)(CO)\}_2(Ph_2P{\cdot}CH_2{\cdot}PPh_2)]$,[12] to $[\{Fe(C_5H_5)(CO)\}_2(Ph_2P{\cdot}CH_2{\cdot}PPh_2)]^+$,[13] is accompanied by a slight increase in the metal–metal distance, from 2.513 to 2.527 Å.[14] A similar small increase is observed on oxidation of $[\{Mo(C_5H_5)(SMe)_2\}_2]$ to $[\{Mo(C_5H_5)(SMe)_2\}_2]^+$.[15] The essential invariance of the metal–metal distance in these

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examples may, however, result from steric constraints due to the other bridging ligands and would not reflect the nature of the electron involved.

With a view to establishing a general pattern for the oxidation of dibridged binuclear compounds with a formal metal–metal bond, attempts were made to synthesise $[\{Mn(C_5H_5)(CO)(SEt)\}_2]$ for subsequent redox studies. This proved unsuccessful. However, an unusual binuclear monothio-bridged derivative, $[\{Mn(MeC_5H_4)(CO)_2\}_2(SEt)]ClO_4$, was isolated from one of the syntheses. Because little is known about the redox properties of dinuclear monobridged compounds, a study was initiated to investigate the influence of the removal or addition of valence electrons on the structural parameters of species of this type.

RESULTS AND DISCUSSION

Synthetic Studies.—A recognised synthesis of thio-bridged metal carbonyl derivatives involves the reaction of the parent carbonyl with dialkyl or diaryl disulphides or alkane- or arene-thiols.[16] A thf solution of $[Mn(MeC_5H_4)(CO)_3]$ and dibenzyl disulphide was thus irradiated with u.v. light and a product whose $\nu(CO)$ corresponded to those expected for $[Mn(MeC_5H_4)(CO)_2\{(PhCH_2)_2S_2\}]$ was observed to have been formed. Attempts to convert this compound into $[\{Mn(MeC_5H_4)(CO)(HSC_2Ph)\}_2]$ proved unsuccessful, however, and always led to the decomposition of the mononuclear species to carbonyl-free products. Use of ethanethiol as the source of the bridging ligand also met with little success. Thus although a second product [ν(C–O) 1 981 and 1 918 cm^{-1}], as well as $[Mn(MeC_5H_4)(CO)_2(HSEt)]$ [ν(C–O) 1 934 and 1 860 cm^{-1}], was formed on u.v. irradiation of a solution of $[Mn(MeC_5H_4)(CO)_3]$ and EtSH in thf, it decomposed readily on heating. The inability to synthesise $[\{Mn(MeC_5H_4)(CO)(SEt)\}_2]$ by the methods employed is attributed to the difficulty in removing carbonyl groups from derivatives of the type $[Mn(MeC_5H_4)(CO)_2L]$ (L = ligand).

A previous study [2] has shown that the electrochemical oxidation of $[Fe(C_5H_5)(CO)_2(SMe)]$ results in the formation of $[\{Fe(C_5H_5)(CO)(SMe)\}_2]^+$. Attempts were thus made to oxidise $[Mn(MeC_5H_4)(CO)_2(SEt)]^-$, prepared *in situ* from $[Mn(MeC_5H_4)(CO)_2(thf)]$ and $[SEt]^-$, by addition of 35% $HClO_4$ to a tetrahydrofuran (thf) solution of this species under aerobic conditions. This resulted in a colour change from orange-brown through red to green. The green product was isolated and characterised by elemental analysis and conductivity measurements as being the monothio-bridged derivative $[\{Mn(MeC_5H_4)(CO)_2\}_2(SEt)][ClO_4]$. Apart from an extra peak at 1 937 cm^{-1} in the former, resulting possibly from a site-symmetry effect, the solid-state and dichloromethane-solution i.r. spectra are similar in the C–O stretching region [ν(C–O) (Nujol mull): 2 015sh, 1 994s, 1 964s, and 1 937m; (CH_2Cl_2) 2 019sh, 1 994s, and 1 969ms cm^{-1}] suggesting that the solid-state structure is retained in solution. As discussed later the structure illustrated in Figure 1 has been established by means of *X*-ray crystallography for this compound in the crystalline state. Although the cyclopentadienyl groups are non-equivalent for this molecular geometry, the room-temperature ^1H n.m.r. spectrum revealed a single resonance for the methyl groups of the cyclopentadienyl rings and single resonances for the protons bonded to the β- and γ-carbons of the cyclopentadienyl rings respectively. However the same spectrum measured at −60 °C contained two sets of resonances associated with the cyclopentadienyl protons, two peaks assigned to the cyclopentadienyl methyl groups, but a single triplet corresponding to the methyl group of the ethylthio-group. The temperature dependence of the cyclopentadienyl resonances is interpreted in terms of the presence of two enantiomers of $[\{Mn(MeC_5H_4)(CO)_2\}_2(SEt)][ClO_4]$ in solution with rapid interconversion of the two at room temperature. The low-temperature spectrum affords two quadruplets associated with the methylene of the ethylthio-group but this is readily explained in terms of the magnetic non-equivalence of the two methylene protons.

The mechanism for the formation of this ionic species is not immediately clear. However it has been established previously that H_2S reacts with $[Mn(MeC_5H_4)(CO)_2(thf)]$ to afford the adduct $[Mn(MeC_5H_4)(CO)_2(H_2S)]$ [17] while our more recent studies have revealed that this compound decomposes, in solution at room temperature, to the bridging sulphide derivative $[\{Mn(MeC_5H_4)(CO)_2\}_2S]$. Treatment of $[\{Co(CO)_4\}_2]$, $[Au(PPh_3)Cl]$, or sodium molybdate with H_2S also leads to the formation of bridging sulphide products.[18-20] On this basis it is suggested that $[Mn(MeC_5H_4)(CO)_2(SEt)]^-$ is protonated to give $[Mn(MeC_5H_4)(CO)_2(H_2SEt)]^+$, and that the latter reverts to $[\{Mn(MeC_5H_4)(CO)_2\}_2(SEt)]^+$ by loss of dihydrogen, by a mechanism analogous to that for the formation of $[\{Mn(MeC_5H_4)(CO)_2\}_2S]$. Significantly $[Ru(NH_3)_5(H_2S)][BF_4]_2$ has very recently been shown to decompose in the solid state by loss of dihydrogen even when dioxygen and water are rigorously excluded from it.[21]

X-*Ray Crystallographic Studies*.—The molecular geometry of $[\{Mn(MeC_5H_4)(CO)_2\}_2(SEt)]ClO_4$ and the atom numbering system used in the analysis are shown in Figure 1, and bond distances and angles in Table 1. The compound consists of two $Mn(\eta\text{-}MeC_5H_4)(CO)_2$ moieties bridged symmetrically by an ethanethiol group. The methylcyclopentadienyl rings are *trans* with respect to the Mn · · · Mn vector but not quite parallel to each other, the angle between the normals to the planes being 21.98°. The rings are essentially planar and symmetrically disposed with respect to the manganese atoms, the variation in the angles subtended at

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the latter by adjacent cyclopentadienyl carbon atoms being < 3.5%. The distance of each cyclopentadienyl carbon from the mean plane of its ring is listed in Table 2.

The pairs of carbonyl groups are also roughly *trans* to each other, as revealed by the torsion angles C(1)–Mn(1)–Mn(2)–C(4) (150.26°) and C(2)–Mn(1)–Mn(2)–C(3) (152.33°). In common with that found for numerous other metal carbonyl derivatives the Mn–C–O bond angles show a slight deviation from linearity while the C–O bond distances are typical of those for terminally bonded carbonyl groups.

The environment of the sulphur is distorted tetrahedral with Mn–S distances (2.24 and 2.27 Å) intermediate between those for $[\overline{\mathrm{Mn(CO)_3\{\mu\text{-}SC(SMe)N}}\mathrm{Me\}}]_2$ (2.41—2.43 Å)[22] and that for $[\mathrm{Mn(C_5H_5)(CO)_2(SO_2)}]$ (2.04 Å).[23] The Mn–S–Mn bond angle (81°) as well as the Mn–Mn distance (2.930 Å) is consistent with the presence of a metal–metal bond. This distance is comparable with those found for $[\{\mathrm{Mn(CO)_4}\}_2\mathrm{(H)(PPh_2)}]$ [2.937(5) Å] [24] and the non-bridged species $[\{\mathrm{Mn(CO)_5}\}_2]$ [2.923(3) Å) [25] and $[\{\mathrm{Mn(CO)_4(PEt_3)}\}_2]$ [2.913(6) Å],[26] but longer than those for the dibridged derivatives $[\{\mathrm{Mn(CO)_4(SiPh_2)}\}_2]$ [2.871(2) Å],[27] $[\{\mathrm{Mn(CO)_4}\}_2\mathrm{(CO)(GeMe_2)}]$ [2.854(2) Å],[28] and $[\{\mathrm{Mn(C_5H_5)(CO)(NO)}\}_2]$ [2.571(1) Å].[29] The shorter Mn–Mn distances for the latter have been rationalised in terms of the bridging groups functioning as bridging carbenoids.[28] When a molecular orbital scheme based on that of Teo *et al.*[10] for $[\{\mathrm{Mn(CO)_4(PH_2)}\}_2]^{n+}$ ($n = 0$—2) was employed, results suggested [28] that the bridging 'carbenoid' groups effect a strengthening of the manganese–manganese bond by delocalising the Mn–Mn bonding orbitals of a_g and b_{1u} symmetry and by providing some bonding character to the b_{2g} and $1b_{3u}$ orbitals which are antibonding with respect to the two manganese atoms.

TABLE 1

Selected bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances			
Mn(1)–Mn(2)	2.930(1)	Mn(2)–S(1)	2.270(2)
Mn(1)–S(1)	2.242(2)	Mn(2)–C(3)	1.829(11)
Mn(1)–C(1)	1.800(7)	Mn(2)–C(4)	1.821(7)
Mn(1)–C(2)	1.809(9)	Mn(2)–C(13)	2.155(6)
Mn(1)–C(7)	2.239(8)	Mn(2)–C(14)	2.146(6)
Mn(1)–C(8)	2.159(6)	Mn(2)–C(15)	2.156(7)
Mn(1)–C(9)	2.128(6)	Mn(2)–C(16)	2.169(7)
Mn(1)–C(10)	2.122(6)	Mn(2)–C(17)	2.149(7)
Mn(1)–C(11)	2.170(7)	C(5)–C(6)	1.529(12)
S(1)–C(5)	1.848(6)	C(3)–O(3)	1.133(16)
C(1)–O(1)	1.148(10)	C(4)–O(4)	1.135(11)
C(2)–O(2)	1.144(13)	C(13)–C(14)	1.389(14)
C(7)–C(8)	1.419(17)	C(14)–C(15)	1.412(14)
C(8)–C(9)	1.411(14)	C(15)–C(16)	1.408(19)
C(9)–C(10)	1.413(14)	C(16)–C(17)	1.400(12)
C(10)–C(11)	1.409(20)	C(17)–C(13)	1.425(15)
C(11)–C(7)	1.420(14)	C(13)–C(18)	1.495(13)
C(7)–C(12)	1.499(18)	Cl(1)–O(6)	1.258(19)
Cl(1)–O(5)	1.327(20)	Cl(1)–O(8)	1.402(16)
Cl(1)–O(7)	1.280(21)		
(*b*) Angles			
S(1)–Mn(1)–Mn(2)	49.9(0)	S(1)–Mn(2)–Mn(1)	49.1(0)
Mn(1)–S(1)–Mn(2)	81.0(1)	O(1)–C(1)–Mn(1)	175.5(5)
O(2)–C(2)–Mn(1)	174.1(7)	C(1)–Mn(1)–C(2)	84.0(3)
C(1)–Mn(1)–S(1)	89.6(2)	C(2)–Mn(1)–S(1)	117.2(2)
C(1)–Mn(1)–Mn(2)	113.2(2)	C(2)–Mn(1)–Mn(2)	76.1(2)
O(3)–C(3)–Mn(2)	177.7(6)	O(4)–C(4)–Mn(2)	171.5(6)
C(3)–Mn(2)–C(4)	84.9(3)	C(3)–Mn(2)–S(1)	82.8(2)
C(4)–Mn(2)–S(1)	113.6(2)	C(3)–Mn(2)–Mn(1)	108.6(2)
C(4)–Mn(2)–Mn(1)	74.9(2)	C(13)–C(14)–C(15)	108.5(1.0)
C(7)–C(8)–C(9)	109.5(1.0)	C(14)–C(15)–C(16)	108.5(1.0)
C(8)–C(9)–C(10)	107.5(1.0)	C(15)–C(16)–C(17)	107.0(1.0)
C(9)–C(10)–C(11)	108.0(1.0)	C(16)–C(17)–C(13)	108.5(1.0)
C(10)–C(11)–C(7)	109.5(1.0)	C(17)–C(13)–C(14)	107.5(1.0)
C(11)–C(7)–C(8)	106.0(1.0)	C(17)–C(13)–C(18)	126.5(1.0)
C(11)–C(7)–C(12)	128.5(1.0)	C(14)–C(13)–C(18)	126.0(1.0)
C(8)–C(7)–C(12)	125.5(1.0)		

TABLE 2

Least-squares planes: equations of planes are expressed in direct space as $PX + QY + RZ = S$. Deviations (Å) of atoms from planes are noted in square brackets

Plane (1): C(7)—(12)

$$-7.827\,3X + 3.538\,0Y + 9.275\,8Z = 2.903\,9$$

[C(7) −0.030, C(8) −0.034, C(9) 0.030, C(10) 0.020, C(11) −0.026, C(12) 0.040, Mn(1) −1.801, C(1) −2.634, O(1) −3.091, C(2) −2.549, O(2) −2.946]

Plane (2): C(13)—(18)

$$-5.873\,9X + 6.802\,2Y + 11.934\,0Z = -1.126\,0$$

[C(13) 0.026, C(14) 0.017, C(15) −0.016, C(16) −0.016, C(17) 0.017, C(18) −0.028, Mn(2) 1.798, C(3) 2.704, O(3) 3.234, C(4) 2.654, O(4) 3.060]

Angle between the normals to planes (1) and (2) 21.98°. Angle between the normal to plane (1) and the Mn(1) ··· Mn(2) vector 128.86°. Angle between the normal to plane (2) and the Mn(1) ··· Mn(2) vector 130.45°.

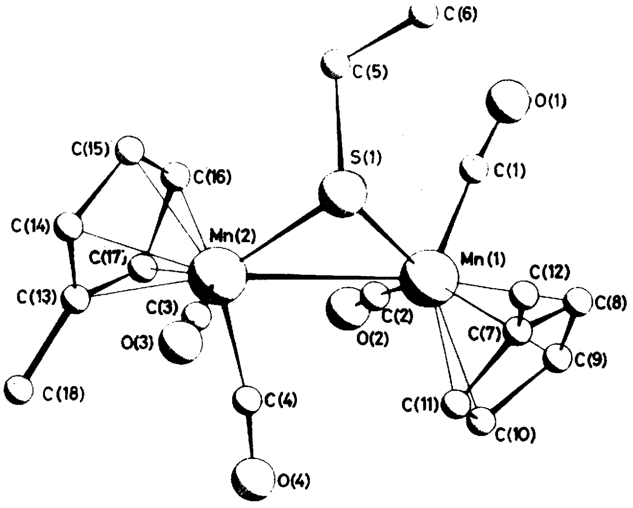

FIGURE 1 The molecular geometry of $[\{\mathrm{Mn(MeC_5H_4)(CO)_2}\}_2\mathrm{(SEt)}]$-$[\mathrm{ClO_4}]$ showing the atom numbering scheme used in the analysis

The longer Mn–Mn bond for $[\{\mathrm{Mn(CO)_4}\}_2\mathrm{(H)(PPh_2)}]$ was ascribed to the fact that this compound contains only one bridging group capable of behaving as a carbenoid,[28]

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and that the inability of the bridging hydride to function as such was due to its lack of *p* orbitals. By analogy, $[\{Mn(MeC_5H_4)(CO)_2\}_2(SEt)][ClO_4]$, which also contains only one bridging ' carbenoid ' group, would be expected to have a longer Mn–Mn bond. A similar explanation would account for the Mn–Mn distance of 2.912 Å for $[Mn_2(C_5H_5)(CO)_6(AsMe_2)]$, also a monobridged species.[30]

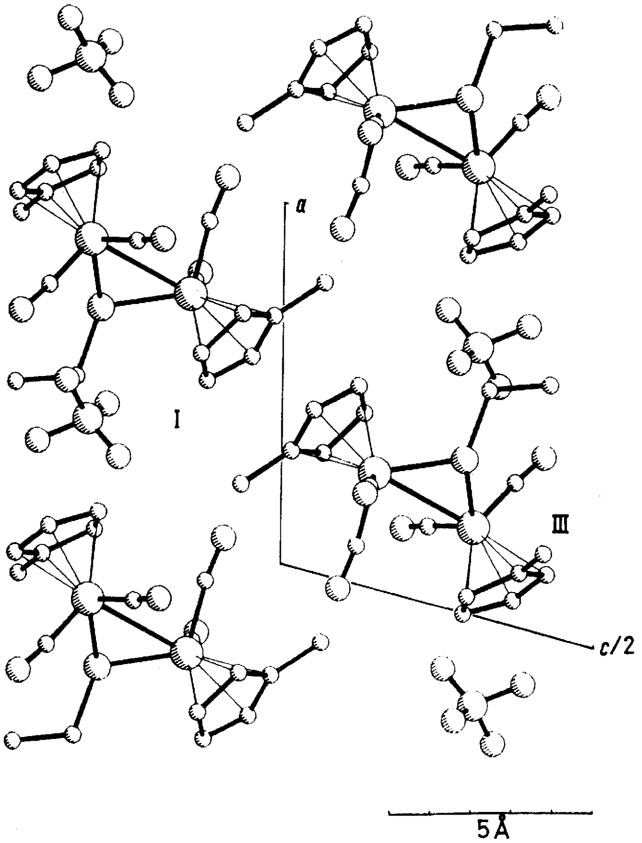


FIGURE 2 The molecular packing along the *x* axis of the unit cell as projected on the (010) plane. Molecule II is at $1-x, -y, -z$ and molecule III at x, y, z

Figure 2 illustrates the molecular packing along the *x* axis of the unit cell, as projected onto the (010) plane. There are no close intermolecular contacts other than that (3.75 Å) between the two methylcyclopentadienyl groups in molecules (I) and (III).

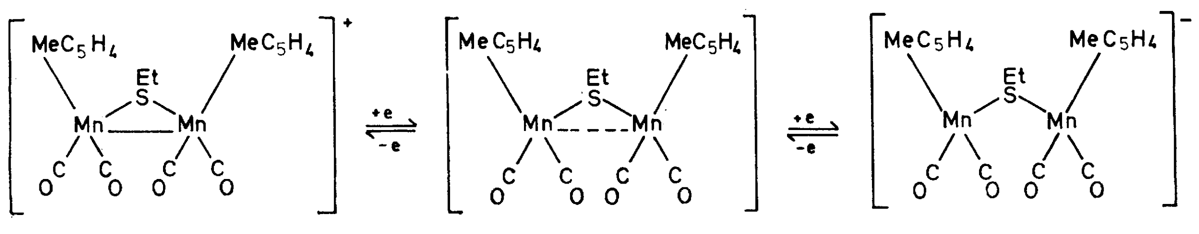
Electrochemical Studies.—$[\{Mn(MeC_5H_4)(CO)_2\}_2(SEt)]^+$ is the two-electron oxidation product of the dinuclear anionic species * $[\{Mn(MeC_5H_4)(CO)_2\}_2(SEt)]^-$ in which the Mn–Mn distance is expected to be non-bonding by analogy with known ' isoelectronic ' iron derivatives of the type $[\{Fe(C_5H_5)(CO)_2\}_2(SR)]^+$ (ref. 31) (R = alkyl group) and with $[\{Fe(C_5H_5)(CO)_2\}_2(SO_2)]$.[32] Electrochemical studies were carried out on $[\{Mn(MeC_5H_4)(CO)_2\}_2(SEt)][ClO_4]$ with a view to establishing whether the two species show electrochemical reversibility and are in fact interconvertible according to the Scheme. A.C. and D.C. polarography and cyclic voltammetry established that the complex does in fact undergo two well-behaved one-electron reductions, and that these meet all the criteria of electrode reversibility at both mercury and platinum electrodes.[33] At the dropping-mercury electrode in acetone–0.1M-$[NEt_4][ClO_4]$ the successive reductions occur at $E_{\frac{1}{2}}$ (D.C. polarography) +0.172 and −0.222 V *vs*. Ag/AgCl. It has also been found that the first reduction product has an indefinite life-time in cold acetone–0.5M-$[NBu_4][ClO_4]$ and attempts are now in progress to isolate and characterise this species.

EXPERIMENTAL

Synthesis of $[\{Mn(MeC_5H_4)(CO)_2\}_2(SEt)][ClO_4]$.—A solution of $[Mn(MeC_5H_4)(CO)_3]$ (2 g, 9.2 mmol) and NaSEt (5 g, 59.5 mmol) in tetrahydrofuran (100 ml) was irradiated with u.v. light until reaction was near complete as shown by i.r. spectroscopy (*ca*. 12 h). An aqueous solution of 35% perchloric acid (100 ml) was then added with stirring under aerobic conditions, whereupon the solution changed from orange-brown through red to green over 5 min. A large volume of water was added (*ca*. 250 ml), the product extracted with dichloromethane, dried, and solvent removed under reduced pressure. The residue was crystallised from dichloromethane–light petroleum (30%) (Found: C, 39.8; H, 3.6; S, 5.8. $C_{18}H_{19}ClMn_2O_8S$ requires C, 40.0; H, 3.6; S, 5.9). ν(C–O) (CH_2Cl_2): 2 019sh, 1 994s, and 1 969s cm^{-1}; ^1H n.m.r. (CD_2Cl_2, 35 °C): τ 4.78 (s, 4 H), 5.00 (s, 4 H), 6.62 (q, 2 H, *J* 7.5 Hz), 8.00 (t, 3 H, *J* 7.5 Hz), and 7.87 (s, 6 H). Conductivity: Λ = 138 S cm^2 mol^{-1}.

Crystal Data.—$C_{18}H_{19}O_8SClMn_2$, *M* = 540.76, Monoclinic, *a* = 8.676(5), *b* = 16.062(5), *c* = 15.872(5) Å, β = 104.45(20)°, *U* = 2 141.76 $Å^3$, D_m = 1.64 g cm^{-3} (by flotation), *Z* = 4, D_c = 1.68 g cm^{-3}. Mo-K_α radiation, λ = 0.710 7 Å; μ(Mo-K_α) = 15.01 cm^{-1}. Space group $P2_1/n$.

Collection and Reduction of Data.—Preliminary cell dimensions and space-group symmetry were determined



SCHEME

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* Although unknown $[\{Mn(MeC_5H_4)(CO)_2\}_2(SEt)]^-$ should be readily synthesised by reaction of $[Mn(MeC_5H_4)(CO)_2(SEt)]^-$ with $[Mn(MeC_5H_4)(CO)_2(thf)]$.

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from rotation and Weissenberg photographs. Accurate cell parameters were obtained from a least-squares analysis of the settings of 25 reflections measured on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo-K_α radiation. Three-dimensional intensity data were collected by the ω—2θ scan technique (scan width 1.1°θ, scan speed 0.04° θ s^{-1}) in the range $6° \leqslant 2\theta \leqslant 50°$ from a crystal of dimensions $0.12 \times 0.22 \times 0.38$ mm. Three reference reflections, monitored every 62 reflections measured, had intensities which remained constant to within $\simeq 6\%$. Of 2 237 reflections collected, 108 were systematically absent, while of the remaining 2 129 reflections, 1 785 had $I > 2.0\sigma(I)$ and were considered observed. Lorentz-polarisation corrections were applied. No absorption corrections were made but anomalous dispersion corrections were applied to the heavy-atom scattering curves.[34]

TABLE 3

Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Mn(1)	2 455(1)	546(1)	3 053(1)
Mn(2)	3 221(1)	1 181(1)	1 475(1)
S(1)	4 275(2)	1 486(1)	2 899(1)
Cl(1)	2 541(4)	1 707(2)	−3 087(2)
O(5)	3 461(22)	2 201(11)	−3 422(10)
O(6)	3 099(22)	1 015(12)	−2 785(10)
O(7)	1 722(25)	2 026(10)	−2 600(10)
O(8)	1 570(22)	1 444(13)	−3 887(10)
C(1)	4 017(9)	−83(6)	3 712(5)
O(1)	4 940(7)	−504(4)	4 159(4)
C(2)	2 152(10)	−342(7)	2 329(6)
O(2)	1 909(8)	−938(5)	1 923(5)
C(3)	2 823(10)	2 300(8)	1 400(5)
O(3)	2 566(9)	2 991(6)	1 325(4)
C(4)	1 064(11)	1 073(6)	1 192(5)
O(4)	−269(7)	1 011(5)	912(4)
C(7)	1 515(11)	1 528(8)	3 793(7)
C(13)	3 195(11)	882(7)	148(5)
C(8)	1 682(9)	749(7)	4 228(6)
C(9)	701(10)	154(7)	3 696(6)
C(10)	−44(9)	551(9)	2 905(7)
C(11)	464(12)	1 387(9)	2 964(7)
C(12)	2 242(16)	2 333(8)	4 175(9)
C(14)	4 502(12)	1 384(7)	498(6)
C(15)	5 500(11)	957(9)	1 205(7)
C(16)	4 798(12)	184(8)	1 300(6)
C(17)	3 371(11)	138(7)	652(6)
C(18)	1 896(15)	1 071(9)	−644(6)
C(5)	6 364(8)	1 137(6)	3 276(5)
C(6)	6 970(11)	1 351(7)	4 241(6)
H(8) *	2 446(9)	628(7)	4 866(6)
H(9)	543(10)	−486(7)	3 865(6)
H(10)	−847(9)	259(9)	2 354(7)
H(11)	99(12)	1 852(9)	2 462(7)
H(121)	2 226(16)	2 827(8)	3 711(9)
H(122)	3 459(16)	2 178(8)	4 494(9)
H(123)	1 631(16)	2 536(8)	4 654(9)
H(14)	4 728(12)	1 993(7)	267(6)
H(15)	6 611(11)	1 187(9)	1 607(7)
H(16)	5 275(12)	−283(8)	1 784(6)
H(17)	2 548(11)	−379(7)	551(6)
H(181)	1 103(15)	542(9)	−772(6)
H(182)	2 290(15)	1 216(9)	−1 221(6)
H(183)	1 277(15)	1 600(9)	−467(6)
H(51)	7 086(8)	1 453(6)	2 911(5)
H(52)	6 428(8)	473(6)	3 182(5)
H(61)	8 210(11)	1 199(7)	4 504(6)
H(62)	6 245(11)	962(7)	4 543(6)
H(63)	6 772(11)	1 997(7)	4 371(6)

* U refined to 0.154 for Me and Et hydrogen atoms, and 0.084 Å^2 for those of the cyclopentadienyl groups.

Structure Determination and Refinement.—Analysis of a three-dimensional Patterson map[35] yielded the positions of the two manganese atoms. They were separated by *ca.* 3 Å, which seemed a reasonable approximate value for a metal–metal bond {*cf.* Mn–Mn for [$\{Mn(CO)_5\}_2$] 2.923(3) Å (ref. 25)}. A subsequent electron-density map revealed the positions of the sulphur and carbon atoms of the ethylthio-group. Six other light atom positions were also apparent, and from interatomic distances and bonding angles were assumed to be three carbonyl ligands. A further two cycles of refinement on the co-ordinates of these 11 atoms resulted in an electron-density map which yielded the positions of all non-hydrogen atoms. After six cycles of full-matrix least-squares refinement[35] all atoms had been located and R had fallen to 0.08. During the final four cycles of refinement, with anisotropic temperature factors, hydrogen atoms were constrained to ride on their parent carbon atoms with C–H distances set at 1.08 Å. Their isotropic temperature factors were refined as one common parameter. Refinement converged to R 0.051 and R' [$= \Sigma w^{\frac{1}{2}}|F_o - F_c|/\Sigma w^{\frac{1}{2}}|F_o|$] 0.056, with a weighting scheme of the form: $w = 1/(\sigma^2 F + gF^2)$. The final value of g (0.000 660) was chosen to give the smallest systematic variation of $w\Delta^2$ with the magnitude of F. An analysis of variance computed after the final cycle, observed and calculated structure factors, and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21948 (15 pp., 1 microfiche).* Final atomic positional and thermal parameters are presented in Table 3.

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1976, Index issue.

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