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Preliminary communication

THE REACTION OF μ-DITHIOBIS(TRICARBONYLIRON) WITH DIMANGANESE DECACARBONYL: A NOVEL PRODUCT AND AN INTERESTING STRUCTURAL PROBLEM

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Summary

The photo-induced reaction of $(\mu\text{-}S_2)Fe_2(CO)_6$ and $Mn_2(CO)_{10}$ in tetrahydrofuran solution gave a complex of composition $S_2Fe_2Mn_2(CO)_{14}$. A combination of X-ray crystallography, Mössbauer spectroscopy, mass spectroscopy and elemental analysis established this composition and the structure as $Fe_2Mn(CO)_9(\mu_3\text{-}S)(\mu_4\text{-}S)Mn(CO)_5$, the Fe_2Mn system of which contains one Fe—Fe and one Fe—Mn bond.

Few examples of reactions of μ-dithiobis(tricarbonyliron) (I) with dinuclear metal carbonyls have been reported thus far. In two, the product formed contained one-half of a molecule of I and a dinuclear metal carbonyl fragment which resulted from loss of a CO ligand from each metal atom. Thus reaction with $Co_2(CO)_8$ gave II [1] while $Cp_2Ni_2(CO)_2$ [2] reacted to give III. In contrast, the reaction of I with $Fe_2(CO)_9$ gave $(\mu_3\text{-}S)_2Fe_3(CO)_9$ (IV). We report here the reaction of I with dimanganese decacarbonyl which proceeds in yet another manner.

The reaction was carried out with 2.9 mmol of I and 5.8 mmol of $Mn_2(CO)_{10}$ in 50 ml of THF under nitrogen in a quartz flask under UV (350 nm) irradiation (Rayonet photoreactor) for 20 h*. Chromatography (silicic acid) of the black solid which remained upon removal of THF gave 0.623 g of $Mn_2(CO)_{10}$ (elution with pentane) and 1.91 g (97% yield) of air-stable, gleaming black crystals (elution with dichloromethane), m.p. (sealed capillary) ~ 145°C (dec). Anal.

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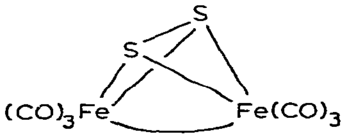
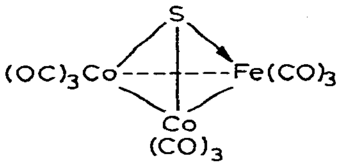
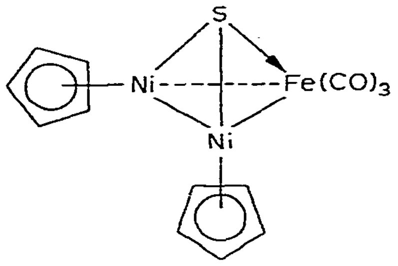
*No reaction occurred in the dark. An attempted thermal reaction (24 h in refluxing THF solution) resulted in decomposition of I and a 94% recovery of $Mn_2(CO)_{10}$.



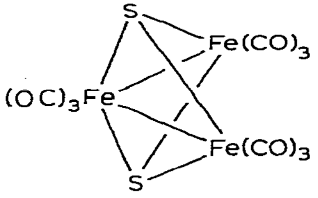
(I)



(II)



(III)



(IV)

Found: C, 24.74. $SFeMn(CO)_7$ calcd.: C, 24.81%. The 70 eV mass spectrum showed the molecular ion at *m/e* 678 (corresponding to $S_2Fe_2Mn_2(CO)_{14}$), followed by fragment ions due to successive loss of 14 CO ligands. Analysis of the isotopic pattern of the molecular ion showed the peak height of the $[M-2]^+$ species was equal to that calculated for a 2Mn/2Fe ratio, in confirmation of the metal analysis. The IR spectrum (CH_2Cl_2) showed bands at 2139w, 2072s, 2059vs, 2032s, 2015s, 1999m, 1994(sh), 1937w and 1916w cm^{-1} in the terminal CO region and none in the bridging CO region.

The data above were not sufficient to allow any firm conclusions concerning the structure of $S_2Fe_2Mn_2(CO)_{14}$ and, for this reason, an X-ray crystal structure determination was undertaken*. Fig. 1 shows the structure thus determined, without metal atom assignments. The largest peaks in the final difference

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*A crystal (0.1 × 0.03 × 0.01 mm) was centered at ambient temperature on a Syntex $P2_1$ diffractometer. The scan rate was varied from 2.0° to 29.3° per min. The background time to scan time ratio was 0.5 and the background scan ranged from 1.0° to 1.2°. Lorentz, polarization and decay factor corrections were applied to measured intensities. The monoclinic space group $P2_1/n$ was indicated by systematic absences ($h0l$: $h + l = 2n$, $0k0$: $k = 2n$). Direct methods (MULTAN) and Patterson syntheses (GENFR) provided the initial metal and sulfur atom positions. The oxygen and carbon atom positions were determined through Fourier syntheses. Computer programs for X-ray crystallography are local programs [3] adapted [4] for the Research Computing Laboratory VAX/VMS computer at Case Western Reserve University.

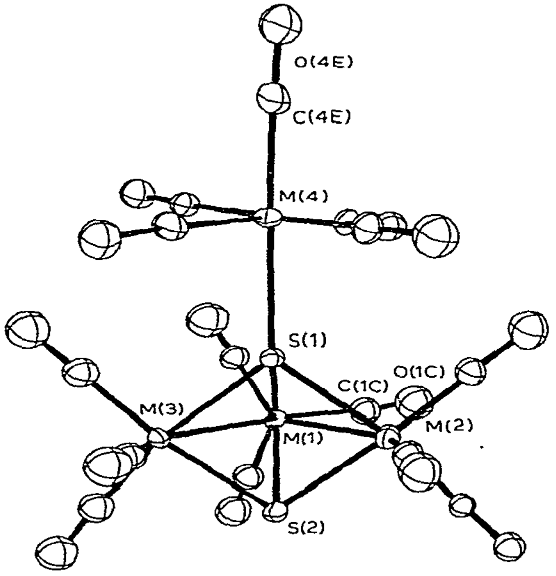


Fig. 1. ORTEP drawing of the molecular structure of $S_2Fe_2Mn_2(CO)_{14}$. The "best" structure places Fe at M(1) and M(3), with Mn at M(2) and M(4).

Fourier were 0.78 $eÅ^{-3}$ and were located at the metal atom positions**. Intramolecular distances and angles are given in Table 1.

While structure VA (M(1), M(3) = Fe) is favored crystallographically from the distances observed, the conclusion did not appear to be unambiguous since

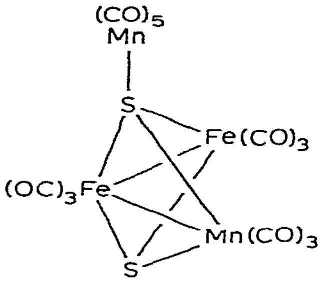
TABLE 1

SELECTED INTRAMOLECULAR DISTANCES AND ANGLES FOR $S_2Fe_2Mn_2(CO)_{14}$

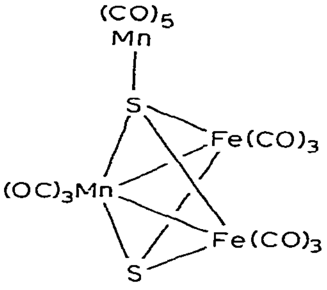
M(1)—M(2)	2.714(3)
M(1)—M(3)	2.580(2)
M(2) . . . . M(3)	3.506(3)
S(1). . . . . S(2)	2.831(4)
M(*n*)—S(*m*) mean[a]	2.265(9)
M(4)—S(1)	2.384(3)
M(n)—C(*n*) mean[a]	1.76(4)
M(4)—C(4)(*p*) mean[a]	1.85(3)
C—O mean	1.15(8)
C(4E)—M(4)—S(1)	175.3(5)
M(3)—M(1)—M(2)	82.90(12)
S(1)—M(1)—S(2)	77.17(16)
M(1)—C(1C)—O(1C)	168.0(12)
M(*n*)—C(*n*)—O(*n*) mean[a]	177.2(10)

[a] $n = 1—3$, m - 1—2, and $p = 1—5$

**Summary of crystal data for $S_2Fe_2Mn_2(CO)_{14}$: a 9.125(1) Å; b 13.402(3) Å; c 18.716(4) Å; α 90.00 (1)°; β 91.672(1)°; γ 90.03(2)°; V 2288.1(8) $Å^3$; space group [5] $P2_1/n$ (no. 14); Z 4; d (calc) 1.97 g cm^{-3}, d (obs) 1.97 g cm^{-3}; μ 26.5 cm^{-1}; λ (Mo - K_α) 0.710 73 Å, F (000) 1320. Summary of final refinement for $S_2Fe_2Mn_2(CO)_{14}$: data collected, 4468, hkl, $\bar{h}kl$, $2° < 2\theta < 50°$; data with $I > 3\sigma(I)$, 2491; final number of variables, 376; number of varied parameters, 167; number of reflections/number of varied parameters, 14.9; error in observation of unit weight, 1.38; final R, 0.079; final R_W, 0.076.



(V A)



(V B)

the scattering factors for Fe and Mn are so similar. Furthermore, refinement gives marginally better statistics with M(1), M(2) = Fe. Mössbauer spectroscopy served to distinguish between VA (in which the iron atoms are not equivalent) and the isomeric VB (in which they are equivalent)*. Although a structure placing one iron atom at M(4) and the other at M(1), M(2) or M(3) cannot be excluded by the Mössbauer data, such a structure produces a 20-electron count Fe atom, an unlikely possibility. The M(4)—C distances are similar to those found [6] (1.79—1.85 Å) for $Mn_2(CO)_{10}$. The preferred structure which places Mn at M(2) (as well as at M(4)) is based primarily upon the interesting "semi-bridging" behavior [7] of one of the CO ligands of M(1). This CO displays a distinctly non-linear M—C—O angle of 168.0° and a shortened non-bonding

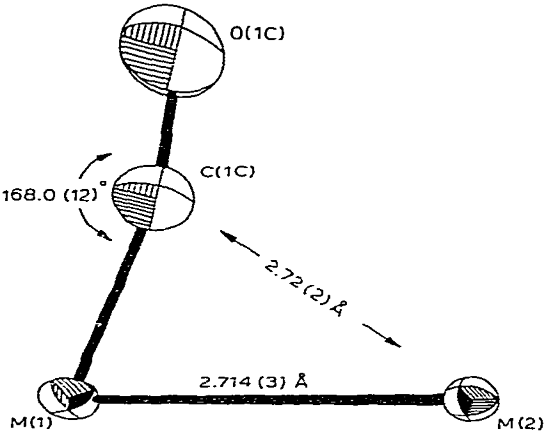


Fig. 2. The semi-bridging nature of the CO ligand between M(1) and M(2).

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*The measurements were made at 4.2 K using a conventional constant acceleration Mössbauer spectrometer with a source of ^{57}Co in rhodium which was maintained at room temperature. The experimental spectra were least-square fitted to theoretical Mössbauer spectra with Lorentzian line shapes in order to yield isomer shifts, quadrupole splittings, line widths and line intensities. Isomer shifts are reported relative to metallic iron at room temperature. For a one-site fit (i.e., two equivalent Fe atoms, as in VB), χ^2 = 1.57, isomer shifts (*IS*) 0.051 mm/sec, width at half-height ($W_{1/2}$) 0.292 mm/sec, quadrupole splittings (*QS*) 0.725 mm/sec. For a two-site fit (i.e., two nonequivalent Fe atoms, as in VA), χ^2 = 1.10, *IS* 0.053 mm/sec, $W_{1/2}$ 0.261 mm/sec, *QS* 0.629 mm/sec for one site and *IS* 0.049 mm/sec, $W_{1/2}$ 0.255 mm/sec, *QS* 0.821 mm/sec for the other site. Contribution of the former to the spectrum is 51%, of the latter, 49%. A "normal" $W_{1/2}$ is 0.25 mm/sec, so on the $W_{1/2}$ basis, as well as on the basis of the value χ^2, the two-site structure VA is favored.

M—C distance of 2.72 Å (Fig. 2). With a slightly electron-deficient Mn in position M2 (compared with the Fe atom in this position), the observed semi-bridging behavior of the nearest CO can be understood.

A brief discussion of complex VA is in order. This structure features both tri- and tetracoordinate sulfur in a configuration which is compatible with "Wade's Rules" [8]. The $X_2Fe_3(CO)_9$ ($X = S, Se, Te$) complexes [9] can be viewed as *nido* structures (i.e., they have n (=5) skeletal atoms and $2n+4$ (= 14) skeletal electrons*).

An additional $M(CO)_n$ fragment might be expected to occupy the open site to complete the *closo* structure, but, as seen from the molecular structure, VA, this does not occur. The hypothetical $S_2Fe_2Mn(CO)_9$ cluster has 13 skeletal electrons. The addition of an electron will produce a *nido* structure according to Wade's scheme; the removal of an electron would create a five-coordinate *closo* framework. The addition of an $(OC)_5Mn\cdot$ radical to the $S_2Fe_2Mn(CO)_9$ cluster gives VA, a structure which is most certainly *nido* and which is consistent with Wade's electron counting procedure.

The parent $S_2Fe_2(CO)_6$ also is a *nido* cluster and the derived dianion species [11] is an *arachno* structure. Although no $S_2Fe_2M_n$ *closo* species have been reported to date, a related S_2M_3 cluster, $S_2Co_3(n^5\text{-}C_5H_5)_3$, has been structurally characterized [12]. Efforts are underway to prepare a *closo* $S_2Fe_2M_n$ species.

We have also prepared and characterized the selenium analog of VA, $Fe_2Mn(CO)_9$ (μ_3-Se) (μ_4-Se)$Mn(CO)_5$. Full details of this and related work will be reported at a later date.

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*For example, the $S_2Fe_3(CO)_9$ *nido* structure [10] has 54 valence shell and ligand electrons. The substraction of 12 electrons for each iron atom and two electrons for each sulfur in the cluster skeleton results in a total of 7 skeletal electron pairs.