

# Reactions of CS<sub>2</sub> with Metal Cluster Carbonyls of the Iron Triad: Synthesis and X-Ray Crystal Structure of [Fe<sub>4</sub>(CO)<sub>12</sub>(C<sub>2</sub>S<sub>4</sub>)]

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Dodecacarbonyltri-iron, [Fe<sub>3</sub>(CO)<sub>12</sub>], reacts with an excess of CS<sub>2</sub> in hexane at 80 °C under a CO–Ar atmosphere (1 : 1, pressure *ca.* 10 atm) to give a number of products including, in low yield, [Fe<sub>4</sub>(CO)<sub>12</sub>(C<sub>2</sub>S<sub>4</sub>)] which, on the basis of a single-crystal X-ray analysis, has been shown to contain two Fe<sub>2</sub>(CO)<sub>6</sub> units bridged by a C<sub>2</sub>S<sub>4</sub> unit which may be regarded as a derivative of ethenetetrathiol.

In its reactions with transition metal centres, CS<sub>2</sub> has been observed to undergo a wide variety of cleavage and rearrangement reactions to produce, for example, carbide,<sup>1</sup> sulphide,<sup>†</sup> CS,<sup>2–5</sup> C<sub>2</sub>S<sub>2</sub>,<sup>1,6,7</sup> CS<sub>3</sub>,<sup>8–11</sup> and C<sub>2</sub>S<sub>4</sub><sup>12,13</sup> groups in varying co-ordination modes.

The coupling of two CS<sub>2</sub> molecules to give *formally* a C<sub>2</sub>S<sub>4</sub> unit has been shown to occur in one instance.<sup>12,13</sup> In this case, however, coupling occurs *via* C–S bond formation to produce an MC(:S)SC(:S)S ring (Figure 1). Carbon–carbon bond formation to produce a C<sub>2</sub>S<sub>2</sub> unit has been noted in one case.<sup>7</sup>

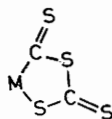
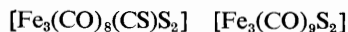


Figure 1

Previously we have reported<sup>4,5</sup> the isolation and characterisation of a number of thiocarbonyl (CS) containing products from the reaction of [Fe<sub>3</sub>(CO)<sub>12</sub>] with CS<sub>2</sub>. We now report the preparation and X-ray crystallographic study of an additional product of this reaction, [Fe<sub>4</sub>(CO)<sub>12</sub>(C<sub>2</sub>S<sub>4</sub>)], in which the coupling of two CS<sub>2</sub> molecules has occurred *via* C–C bond formation.

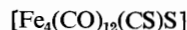
The product was obtained from the reaction of [Fe<sub>3</sub>(CO)<sub>12</sub>] and an excess of CS<sub>2</sub> in hexane at 80 °C under a CO–Ar atmosphere (1 : 1, pressure *ca.* 10 atm): the yield is low, in the range between 1 and 2% for reaction times between 2 and 18 h. After removal of the solvent and separation by t.l.c. four or five major products were obtained depending on the reaction time involved. For times less than 7 h, five products were observed. These were identified as (1) (dark red), (2) (dark red),<sup>14</sup> (3) (yellow), (4) (grey-brown),<sup>4</sup> and (5) (orange-brown).<sup>5</sup>



(1) (2)



(3) (4)



(5)

The complex (3) showed †  $\nu(\text{CO})/\text{cm}^{-1}$  at 2073ms, 2071(sh), 2052s, 2040w, 2013s, 2007ms, 2004(sh), 1998(sh), 1994w, and 1986vw; mass spectrum: §  $m/e$  680 ( $M - 32$ ); m.p. *ca.* 145 °C (decomp.); microanalytical data for C and H were satisfactory for the formula C<sub>14</sub>O<sub>12</sub>S<sub>4</sub>Fe<sub>4</sub>. Orange-red blocks of (3) were deposited by the slow cooling of a benzene–hexane

solution and were suitable for single-crystal X-ray diffraction data to be collected.

*Crystal data:* C<sub>14</sub>O<sub>12</sub>S<sub>4</sub>Fe<sub>4</sub>,  $M = 711.74$ , triclinic, space group  $P\bar{1}$ ,  $a = 6.541(3)$ ,  $b = 7.744(5)$ ,  $c = 12.619(6)$  Å,  $\alpha = 102.17(2)$ ,  $\beta = 100.07(2)$ ,  $\gamma = 103.20(2)^\circ$ ,  $U = 591.4$  Å<sup>3</sup>,  $Z = 1$ ,  $D_m = 2.00$  g cm<sup>-3</sup>,  $F(000) = 348$ , graphite monochromated Mo- $K_\alpha$  radiation,  $\lambda = 0.71069$  Å,  $\mu(\text{Mo-}K_\alpha) = 27.65$  cm<sup>-1</sup>. The diffracted intensities were measured to  $2\theta_{\text{max}} = 55.0^\circ$  on a Stoe four-circle diffractometer and were corrected for absorption. 1135 reflections [ $F > 4\sigma(F)$ ] were used to solve (direct methods and Fourier difference techniques) the structure which was refined by full-matrix least squares (all atoms anisotropic) to  $R = 0.047$  and  $R_w = 0.037$ . ¶

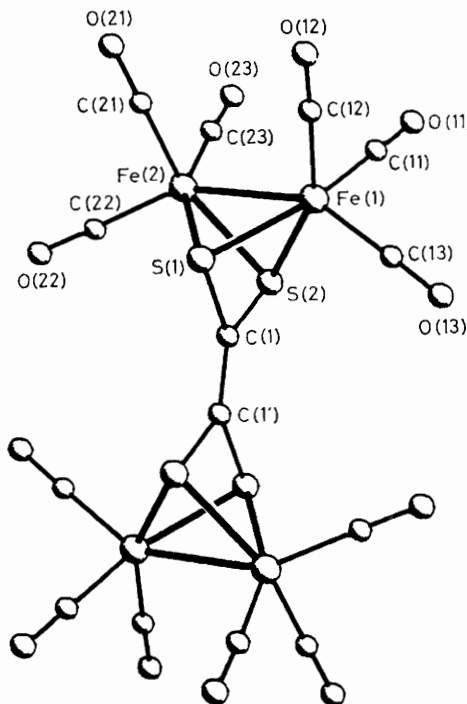


Figure 2. The molecular structure of [Fe<sub>4</sub>(CO)<sub>12</sub>(C<sub>2</sub>S<sub>4</sub>)] (3). Bond lengths: Fe(1)–Fe(2), 2.486(2); Fe(1)–S(1), 2.296(2); Fe(1)–S(2), 2.288(2); Fe(2)–S(1), 2.292(2); Fe(2)–S(2), 2.295(2); S(1)–C(1), 1.778(8); S(2)–C(1), 1.773(8); C(1)–C(1'), 1.332(13) Å. Bond angles: Fe(2)–Fe(1)–S(1), 57.1(1); Fe(2)–Fe(1)–S(2), 57.3(1); S(1)–Fe(1)–S(2), 73.5(1); Fe(1)–Fe(2)–S(1), 57.3(1); Fe(1)–Fe(2)–S(2), 2.295(2); S(1)–Fe(2)–S(2), 73.4(1); Fe(1)–S(1)–Fe(2), 65.6(1); Fe(1)–S(2)–Fe(2), 65.7(1); Fe(1)–S(1)–C(1), 84.5(6); Fe(2)–S(1)–C(1), 85.3(6); Fe(1)–S(2)–C(1), 84.9(6); Fe(2)–S(2)–C(1), 85.3(6); S(1)–C(1)–C(1'), 128.9(8); S(2)–C(1)–C(1'), 129.9(7); S(1)–C(1)–S(2), 101.2(9)°.

† See for example references 1–8.

‡ Recorded on a Perkin-Elmer 257 instrument, using the 2143 cm<sup>-1</sup> band of CO as reference in cyclohexane solution.

§ Recorded on an A.E.I. MS12 instrument at *ca.* 50 eV and 90 °C.

¶ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

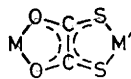


Figure 3

In Figure 2 is shown the structure of (3) and some of the important molecular parameters are given. The molecule sits on a crystallographic centre of symmetry at the mid-point of the C(1)–C(1') bond. Two Fe<sub>2</sub>(CO)<sub>6</sub> units are linked by a C<sub>2</sub>S<sub>4</sub> unit presumably derived by the linkage of two CS<sub>2</sub> molecules. This is unlike the previously observed C<sub>2</sub>S<sub>4</sub> groups and is formally a derivative of ethenetetrathiol, rather than a tetrathio-oxalate group. The carbon–carbon distance of 1.33 Å is typical for a double bond and the carbon–sulphur distances of ca. 1.77 Å are only slightly shorter than a typical single bond value. These can be compared with the longer carbon–carbon and shorter carbon–sulphur distances in the bridging, side-on bonded dithio-oxalate complexes [M{(C<sub>2</sub>O<sub>2</sub>S<sub>2</sub>)Ag-(PPh<sub>3</sub>)<sub>2</sub>}]<sub>3</sub> (M = Fe, Al)<sup>15</sup> and [Ni{(C<sub>2</sub>O<sub>2</sub>S<sub>2</sub>)SnCl<sub>4</sub>}]<sub>2</sub><sup>16</sup> (see Figure 3). The planarity of the C<sub>2</sub>S<sub>4</sub> unit is consistent with its assignment as an ethene derivative, although the bond angles around the carbon atoms indicate a rather strained sp<sup>2</sup> state. The structure is related to that of [Fe<sub>2</sub>(CO)<sub>6</sub>(μ<sub>2</sub>-SEt)<sub>2</sub>]<sup>17</sup> in which two thiolate groups bridge the iron–iron bond in a similar puckered Fe<sub>2</sub>S<sub>2</sub> ring conformation.

Each iron atom has three terminal carbonyl groups and the two iron–iron bonds are of a length typical for single character. Thus, each sulphur must donate three electrons to an Fe<sub>2</sub>(CO)<sub>6</sub> unit for an electron precise cluster, as do the sulphur atoms in [Fe<sub>2</sub>(CO)<sub>6</sub>(μ<sub>2</sub>-SEt)<sub>2</sub>].<sup>17</sup>

Apart from demonstrating a novel rearrangement of CS<sub>2</sub> to a C<sub>2</sub>S<sub>4</sub> unit, this compound also demonstrates the formation of a carbon–carbon double bond, a key factor in the synthesis

of C<sub>2</sub> or larger organic molecules from single carbon starting materials in homo- or hetero-geneously catalysed reactions.

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