An Unusual Bonding Mode for a Dithiocarboxylate Ligand: a Tetradentate Interaction; *X*-Ray Crystal Structure of the Product of the Reaction of Nonacarbonyldi-iron with 1,2-Benzodithiole-3-thione

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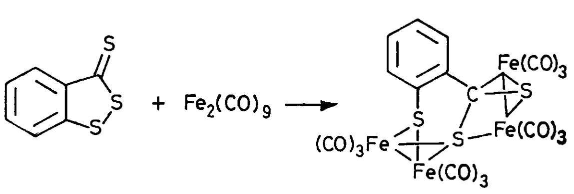
Summary The compound 1,2-benzodithiole-3-thione (**1**), on reaction with $Fe_2(CO)_9$, incorporates two $Fe_2(CO)_6$ units giving complex (**2**), the structure of which has been determined by *X*-ray crystallography; it contains a novel tetradentate RCS_2 ligand possessing an iron–carbon bond.

THIOKETONES and disulphides abstract the $Fe_2(CO)_6$ unit from $Fe_2(CO)_9$ to give complexes in which organosulphur ligands bridge the iron–iron bond.[1] As part of synthetic investigations directed towards the development of catenated polysulphur ligands,[2] compound (**1**), which contains both a thioketone group and a disulphide linkage, was treated with $Fe_2(CO)_9$. It gave complex (**2**) with a tetradentate RCS_2 ligand possessing an iron–carbon bond.



(1) (2)

The thione (**1**)[3] was treated with 2 equiv. of $Fe_2(CO)_9$ in tetrahydrofuran (THF) under N_2. After stirring for 18 h the solvent and other volatile materials were removed. The residue was washed with hexanes, chloroform, and toluene–heptane (1 : 1) and extracted in a Soxhlet apparatus with boiling hexane to give 40% of analytically pure deep red crystals of (**2**) (decomp. 175 °C); i.r. (hexane) (CO): 2088m, 2065s, 2051vs, 2037s, 2017m, 2005m, 1990w, 1982w, and 1967w cm^{-1}; *m/e* 744 (M^+), followed by stepwise loss of 12 CO groups. Crystals suitable for *X*-ray studies were obtained from benzene solution.

Crystal Data: $C_{19}H_4Fe_4O_{12}S_3$, $M = 743{\cdot}82$, triclinic, space group $P\bar{1}$, $a = 16{\cdot}04(2)$, $b = 10{\cdot}71(1)$, $c = 9{\cdot}05(1)$ Å, $\alpha = 59{\cdot}57(9)$, $\beta = 85{\cdot}2(1)$, $\gamma = 105{\cdot}6(1)°$, $U = 1245{\cdot}5$ Å^3, $Z = 2$, $D_m = 1{\cdot}96(3)$, $D_c = 1{\cdot}982$ g cm^{-3}, $F(000) = 732$. Intensity data were collected on a Picker FACS-1 diffractometer. Direct methods were used to determine the positions of the four iron atoms, and the remaining non-hydrogen atoms were found on an electon density Fourier map. The structure has been refined to $R = 0{\cdot}050$ for 2292 reflections in the range $2\theta \leqslant 45°$ (Mo-K_α, $\lambda = 0{\cdot}7107$ Å) with $I > 3\sigma(I)$.†

The complex (Figure 1) consists of discrete molecules containing two $Fe_2(CO)_6$ subunits connected together by one sulphur atom, S(2). Thus, the thioketone group and the disulphide linkage in (**1**) incorporated one $Fe_2(CO)_6$ unit each as if they were unrelated. The carbonyl geometries are normal with small variations in the metal–carbon distances reflecting the asymmetry of the co-ordination sphere about each iron atom. The two sulphur atoms S(1)

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

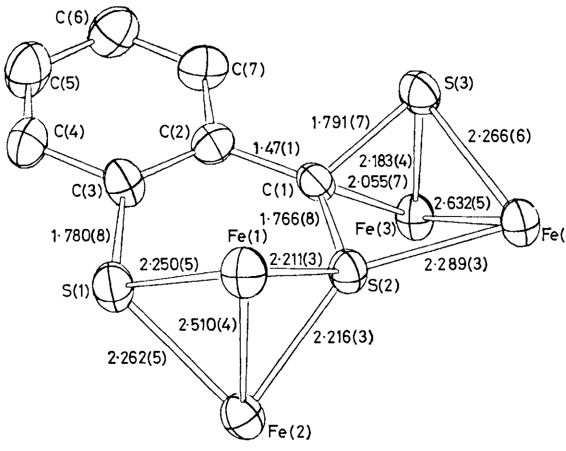


Figure 1. An ORTEP representation of complex (**2**) giving bond distances for the ligand and the metal atoms. The carbonyl ligands have been removed for clarity.

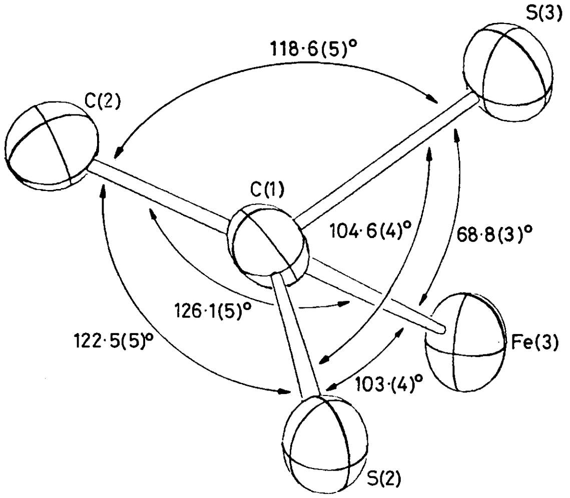


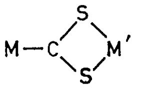
Figure 2. An ORTEP representation of the dithiocarboxylate ligand showing the bond angles.

and S(3) behave as bridges for two sets of iron atoms Fe(1),Fe(2) and Fe(3),Fe(4), respectively. The Fe(1)–S(1), Fe(2)–S(1), and Fe(4)–S(3) distances are within normal limits[2a] for this type of complex; however, the Fe(3)–S(3) distance is a little shorter than usual probably owing to the bonding associated with C(1) discussed below.

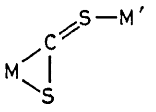
The C(1)–S bond distances for S(2) and S(3) are somewhat shorter than expected for single bonds[4] yet longer than those measured for conventional dithiocarboxylate complexes[5] where a delocalized π-system over the three atoms has been proposed. The ligand is not planar, with S(3) and S(2) being displaced by 0·91 and 0·27 Å respectively from the plane formed by the phenyl ring. Atoms C(1) and S(1) are effectively in this plane. The four iron atoms form a distorted tetrahedral array with S(2) bonded to three atoms, Fe(1), Fe(2), and Fe(4), with unremarkable bond distances. The Fe(3)–S(2) bond distance of *ca.* 3 Å is essentially non-bonding.

Perhaps the most interesting aspect of the structure is the attachment of C(1) to Fe(3) (Figure 2). The Fe(3)–C(1) distance is in the range expected for a single bond.[6] The Fe(4)–C(1) distance, 2·76(2) Å, is non-bonding. Carbon atom C(1) can be regarded as an alkyl group with respect to Fe(3) thus completing its co-ordination sphere. The complex is diamagnetic; therefore, a formal triple negative charge may be assigned to the PhC(1)S(2)S(3) ligand. The ligand is attached to four metal atoms whereas dithiocarboxylate groups are normally bidentate.[5] This novel form of bonding affects the Fe(3)–Fe(4) bond distance which is considerably longer than normal owing to the involvement of C(1). The Fe(1)–Fe(2) distance is within the normal range for this class of complex.[2b] The mechanism whereby the ligand causes these deviations from normality is not readily apparent. The vibrational spectra of this complex are being studied as a possible model to test the correlation of the Fe–Fe stretching frequency with bond distance.

The structure and bonding of the PhC(1)S(2)S(3) unit is to our knowledge unprecedented for a dithiocarboxylate ligand. The closest formal analogy appears to be complexes containing a tridentate bridging CS_2 ligand of the types (A)[5b,7] and (B).[8]



(A)



(B)

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