Reactions of CS_2 with Metal Cluster Carbonyls of the Iron Triad; Synthesis and *X*-Ray Structure of $[Fe_4(CO)_{12}(CS)S]$

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Summary Reaction of $[Fe_3(CO)_{12}]$ with CS_2 in hexane, at 80 °C, under moderate CO/Ar pressure gives, as one of the main products, $[Fe_4(CO)_{12}(CS)S]$, which has been shown by a single crystal *X*-ray analysis to contain a thiocarbonyl ligand co-ordinated to the cluster in a novel bonding mode.

ALTHOUGH the chemistry of transition metal cluster carbonyls has been extensively studied there have been few reports of clusters containing the closely related thiocarbonyl ligand. μ_1 and μ_2 Bonding modes have been established for the CS ligand in mono- and di-nuclear species.[1,2] There have been three recent examples of the thiocarbonyl ligand in cluster compounds, two with a terminal CS group[3,4] and one with a μ_3-CS capping a metal triangle.[5] The CS ligand may also link two metal centres by co-ordinating to one through carbon and the other through the sulphur atom,[6,7] or link four metal atoms by co-ordination of three to carbon and an independent fourth atom to the sulphur.[5]

In this communication we report the synthesis of $[Fe_4(CO)_{12}(CS)S]$ in which there is a novel mode of bonding for the thiocarbonyl ligand. It is also the first thiocarbonyl linked to a core of four metal atoms which themselves exhibit an uncommon skeletal arrangement.

$[Fe_4(CO)_{12}(CS)S]$ was obtained as one of the products from the reaction of $[Fe_3(CO)_{12}]$ with excess of CS_2 in hexane solution at 80 °C under a 10 atm CO/Ar (1 : 1) pressure after 7·5 h. Following the removal of solvent and dissolution of the resulting solid in minimal CH_2Cl_2, separation was achieved by t.l.c., with hexane as eluant. This gave four major bands: red, yellow, grey-brown, and orange-brown (**1**)—(**4**) in order of decreasing R_f. Complex (**1**) was shown to be $[Fe_3(CO)_9S_2]$[8] by spectroscopy and microanalysis. Complexes (**2**) and (**3**) are as yet uncharacterised, while the spectroscopic data for $[Fe_4(CO)_{12}(CS)S]$ (**4**) are as follows: i.r.† ν(CO) 2101w, 2070vs, 2052vs, 2041m, 2024vs, 2012m, 1985w, and 1964w cm^{-1}, ν(CS)/cm^{-1} 963 cm^{-1}, ^1H n.m.r. blank, mass spectrum‡ *m/e* 636, m.p. *ca.* 120 °C (decomp.), microanalytic data were satisfactory. The products (**1**)—(**4**) were each obtained in *ca.* 4% yield.

Black platelets of (**4**) were deposited by slow cooling from hexane solution.

Crystal data $C_{13}Fe_4O_{12}S_2$, $M = 635·65$, monoclinic, space group $P2_1/c$, $a = 9·150(3)$, $b = 13·880(3)$, $c = 15·846(4)$ Å, $\beta = 97·60(2)°$, $U = 1\,994·79$ Å, $Z = 4$, $D_c = 2·12$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 30·8$ cm^{-1}. 2 530 Intensities were recorded ($2\theta_{max} = 55·0°$) on a Stoe 4-circle diffractometer using graphite-monochromated Mo-K_α radiation. These were merged to give 1 762 unique observed intensities $[F > 3\sigma(F)]$. The structure was solved by a combination of direct methods and Fourier difference techniques, and refined by blocked-cascade least-squares to $R = 0·029$ and $R_w = [\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|] = 0·027$.§

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† I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer, using the 2143 cm^{-1} band of CO as reference, and a cyclohexane solution for CO vibrations, and a Perkin-Elmer 557 spectrometer, using the 1603 cm^{-1} band of polystyrene as reference, and a Nujol mull between CsBr plates for CS vibrations.

‡ Recorded on an AEI MS12 instrument at 50 eV and 90 °C.

§ The atomic co-ordinates for this work are available on request from Prof. Dr. G. Bergerhoff, Institut fur Anorganische Chemie, Universitat, Gerhard-Domagk-Str. 1, D-5300 Bonn 1, West Germany. Any request should be accompanied by the full literature citation for this communication.

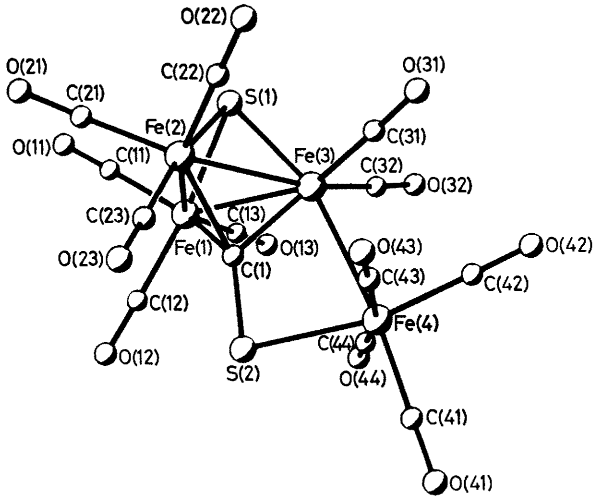

FIGURE. The molecular structure of $[Fe_4(CO)_{12}(CS)S]$, including the atom numbering scheme. Bond lengths: Fe(1)–Fe(2), 2·558(2); Fe(1)–Fe(3), 2·573(2); Fe(2)–Fe(3), 2·561(2); Fe(3)–Fe(4), 2·710(2); Fe(1)–S(1), 2·224(4); Fe(2)–S(1), 2·229(4); Fe(3)–S(1), 2·163(2); Fe(4)–S(2), 2·311(2); Fe(1)–C(1), 2·010(5); Fe(2)–C(1), 2·029(5); Fe(3)–C(1), 1·875(6); C(1)–S(2), 1·695(5) Å, bond angle: Fe(4)–S(2)–C(1), 83·5(2)°.

The structure of (**4**) is shown in the Figure which includes some important bond parameters. Three of the Fe atoms define an equilateral triangle while the fourth metal atom is terminally bound to the triangle. A sulphur caps, in a μ_3 mode, one face of the Fe_3 triangle, lying 1·63 Å below it. The most novel feature of the structure is the co-ordination of the thiocarbonyl ligand. It is terminally bound to the Fe(4) atom *via* sulphur, while the C atom caps, in a μ_3 mode, the other side of the Fe_3 triangle to S(1). The C(1)–S(2) distance does not indicate the presence of appreciable multiple bonding, and the Fe–C and Fe–S bonds are also single. The twelve carbonyl ligands are terminal, three co-ordinated to each of Fe(1) and Fe(2), two to Fe(3), and four to the terminal Fe(4) atom, giving it a distorted octahedral co-ordination geometry.

The structure may also be considered as a 'butterfly' arrangement of iron atoms with one edge broken. Then the CS ligand co-ordinates in a manner similar to that of the four-electron donor carbonyl group in $[Fe_4H(CO)_{13}]^-$.[9]

A possible mechanism for the formation of (**4**) may involve the production *in situ* of a compound $Fe_3(CO)_9(\mu_3\text{-}S)(\mu_3\text{-}CS)$, similar to $[\{(\eta_5\text{-}C_5H_5)Co\}_3(\mu_3\text{-}S)(\mu_3\text{-}CS)]$.[5] $Fe(CO)_4$ fragments are likely to be present in the reaction mixture, and a donation from the μ_3-CS sulphur to such a fragment may occur, which with CO elimination may rearrange to give the observed product. The fact that $[\{(\eta^5\text{-}C_5H_5)Co\}_3(\mu_3\text{-}S)(\mu_3\text{-}CS)]$ forms an adduct with a $Cr(CO)_5$ unit[5] is in agreement with our proposal.

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