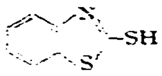
The identity of $CH_2S_2Fe_3(CO)_{10}$ and $S_2Fe_3(CO)_9$

In some of their earliest work on metal carbonyl complexes, Hieber and coworkers[1,2] described the reactions of mercaptans with iron carbonyls. The products were correctly formulated as $[RSFe(CO)_3]_n$, where $n = 2$ to ~ 4, depending upon the nature of the group R. The thiol (I), 2-mercaptobenzothiazole, appeared to behave in



(I)

an anomalous manner, and produced, in very low yield, a complex described as $CH_2S_2Fe_3(CO)_{10}$ (II); this could also be prepared in a much smaller yield from parathioformaldehyde and triiron dodecacarbonyl. The unusual stoichiometry suggested for (II) attracted our attention and prompted us to re-investigate the nature of this product.

Following the excellent experimental detail given by Hieber and Scharfenberg, a purple crystalline material, m.p. 110° (lit. m.p. 110°) was isolated by sublimation and crystallisation. This material, however, still contained traces of nitrogen. Careful chromatography of the crystallised product did not show any indication of decomposition but separated a trace of a white organic by-product (benzothiazole?) and the complex (II), m.p. 114°. This procedure did not affect the IR carbonyl absorption pattern of (II). However, the chromatographed material no longer showed IR absorption in the 2.5–4.0 μ region, whilst PMR spectroscopy indicated that the complex was diamagnetic and devoid of hydrogen nuclei. Analysis suggested an empirical formula $S_2Fe_3(CO)_9$ (III).

Two complexes of empirical formula $S_2Fe_3(CO)_9$ have been claimed[3,4]; contrary to an earlier report[4] we now find that these are one and the same, and furthermore are identical with "$CH_2S_2Fe_3(CO)_{10}$".

The reaction between $Fe_3(CO)_{12}$ and cyclohexene episulphide, described by King[4,*] as a route to (III) was repeated; the product, m.p. 114°, was isolated according to the published procedure, and was identical in all respects with (II). The preparation of Hieber's complex (III)[3] was carried out according to the literature and yielded a product, having an IR spectrum only slightly different in the relative intensities of the CO peaks compared to (II). Chromatography revealed this difference to be due only to a small quantity of a contaminating orange complex (IV). The preparation of Hieber's complex (III) was also repeated, according to the isolation procedure described subsequently by King[4]. The complex was again shown to be identical in all respects with (II), but contaminated by (IV), unless separated chromatographically. Each of the above procedures was repeated using different isolation techniques, but without any changes in the observed results.

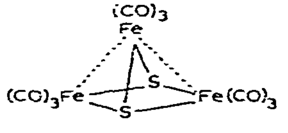
Although (III) is comparatively stable, it does decompose in solution, especially when heated. Solutions of the complex in chlorinated solvents are particularly unstable, and decompose after several hours. Consequently the observations of Hieber,

---

[*] Wei and Dahl[7] find that King's compound is a mixture of $S_2Fe_2(CO)_6$ and a 1:1 adduct of $S_2Fe_2(CO)_6$ with a conformer of $S_2Fe_3(CO)_9$. We find that $S_2Fe(CO)_6$ is a minor product (Experimental).

and of King, can be reconciled with a mixture of products (III) and (IV) which have suffered partial decomposition.

The IR spectrum of (III) in the carbonyl region is shown in the figure (Fig. 1A). It approximates to the values given by Hieber[3]; when taken as a Nujol mull the peaks are less well resolved and more numerous, but only vaguely resemble both sets of figures given by King for a different mull medium. The X-ray work of Dahl and Sutton[5] indicates that the only now known complex $S_2Fe_3(CO)_9$ has the structure



(III)

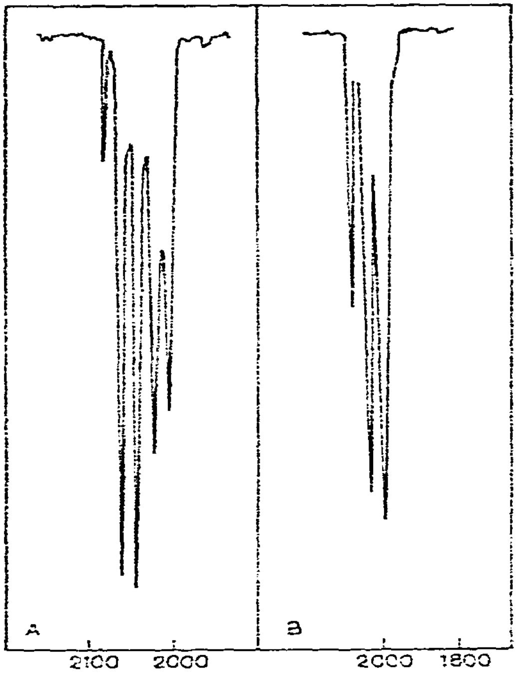


Fig. 1. (A) $S_2Fe_3(CO)_9$ in CCl_4 solution; peak positions at 2086, 2067, 2051, 2032 and 2014 cm^{-1}. (B) $S_2Fe_2(CO)_6$ in CCl_4 solution; peak positions 2083, 2042 and 2005 cm^{-1}. These spectra were obtained on a Perkin Elmer 125 grating I.R. spectrometer and calibrated against CO gas.

Complex (IV), although produced in only small quantities, was identified[3,6] as $S_2Fe_2(CO)_6$. The CO region of the IR spectrum of this complex is shown in Fig. 1B. The complex (IV) may have been produced directly from (III), (a straightforward route can be visualised) but several attempts to effect this conversion by thermal and UV irradiation methods were not successful.

Experimental

All preparations were carried out under an atmosphere of dry, oxygen-free nitrogen. Melting points are uncorrected as measured in sealed, evacuated capillaries.

(*a*) *Reaction of mercaptobenzothiazole (I) with* $Fe_3(CO)_{12}$. This reaction was performed according to the published directions[2] using similar quantities. The product (approx. 0.1 g), m.p. 110°, was isolated by sublimation at 60°/0.1 mm and recrystallisation from 40–60° petrol. Analysis indicated that the sample contained hydrogen, and a sodium fusion gave a positive test for nitrogen. (Found: C, 22.37; H, 0.45; O, 27.61; S, 14.89. $C_{12}H_2Fe_3O_{10}S_2$ calcd.: C, 25.10; H, 0.38; O, 29.75; S, 12.20. Lit.[2]: C, 24.83; H, 0.62; S, 12.3%.)

The material was dissolved in petrol and chromatographed carefully on a column of alumina (activity I, neutral). Petrol–benzene (1:1) eluted a trace quantity of a white solid, closely followed by a purple-red band, which yielded long black-purple needles, m.p. 114°, from petrol. A mixed m.p. with unchromatographed material was 112°, and the IR spectra of both samples (CO stretch region; CCl_4 solution; Perkin Elmer 237) were identical. (Found: C, 22.32; H, 0.00; O, 30.00; S, 13.15. $Fe_3(CO)_9S_2$ calcd.: C, 22.32; H, 0.00; O, 29.85; S, 13.21 %.) The reaction was repeated ,but worked up directly by chromatography on alumina (activity I, Spence's type H). The complex (22 % based on 1 S atom) was isolated from the first coloured band; the subsequent orange and red bands were not investigated.

(*b*) *Reaction of cyclohexene episulphide with* $Fe_3(CO)_{12}$. The experimental details given by King were followed; the product, m.p. 114° (lit. 114°), 35 %, was identical in every respect with that from (*a*).

(*c*) *Preparation of Hieber's compound* $S_2Fe_3(CO)_9$. (*i*) The quantities and experimental conditions given by Hieber and Gruber were duplicated. The crystalline product, m.p. approx. 112°, had a similar IR to both (*a*) and (*b*) except that the intensity of the 2014 cm^{-1} peak was greater than the other three major peaks. Chromatography resolved a small quantity of an orange crystalline solid, (IV), before the major purple-red band; the product isolated from the latter, m.p. 114°, was identical to that from (*a*) and (*b*). Some decomposition was noted at the top of the column.

(*ii*) The preparative details given by King were followed to the point of isolating a crude solid; this was divided into two parts, and each worked up differently. One part was submitted to Soxhlet extraction (lit.) with petrol, and allowed the isolation of a product, m.p. 112°, identical with that from (*a*), (*b*), and (*c-i*), (the black, infusible residue did not show CO absorption in the IR). The other part was chromatographed in benzene on alumina (Activity I, Spence's type H). A small quantity of (IV) was isolated from the first band followed by (III), m.p. 114°, after a single crystallisation.

The complex (IV), purified by sublimation at room temperature at 10^{-2} mm, was isolated as an orange red solid, m.p. 44.5° [mixed m.p. undepressed with an authentic sample of $S_2Fe_2(CO)_6$, m.p. 46°].

Acknowledgements

The authors thank Dr. PETER BLADON and his staff for the spectroscopic measurements; a generous supply of iron carbonyl was made available to us by the International Nickel Co. Ltd. We thank the Gas Council and the Cross Trust for the financial support which made this work possible.

Department of Organic Chemistry,
University of Strathclyde, Glasgow (Scotland)

R. HAVLIN
G. R. KNOX

1 W. HIEBER AND P. SPACU, *Z. Anorg. Allgem. Chem.*, 233 (1937) 353.
2 W. HIEBER AND C. SCHARFENBERG, *Ber.*, 73 (1940) 1012.
3 W. HIEBER AND J. GRUBER, *Z. Anorg. Allgem. Chem.*, 296 (1958) 91.
4 R. B. KING, *Inorg. Chem.*, 2 (1963) 327.
5 L. F. DAHL AND P. W. SUTTON, *Inorg. Chem.*, 2 (1963) 1067.
6 C. H. WEI AND L. F. DAHL, *Inorg. Chem.*, 4 (1965) 1.
7 C. H. WEI AND L. F. DAHL, *Inorg. Chem.*, 4 (1965) 493.

Received April 8th, 1965.