772. *Alkyl- and Aryl-thio-iron Tricarbonyls.*

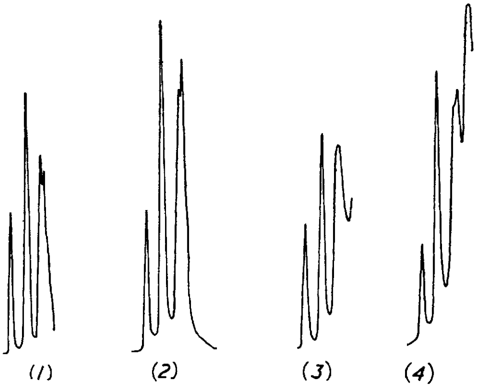
By S. F. A. KETTLE and L. E. ORGEL.

It is shown that the compound $Fe(CO)_3 \cdot SPh$, previously reported to be a monomer, is dimeric. The nature of the bridging group is briefly discussed.

THE report that cryoscopic determination of the molecular weight in benzene indicates that the compound $[Fe(CO)_3 \cdot SPh]_n$ is a monomer [1] is remarkable in view of the unusual stability, for that implies the presence of an unpaired electron. Re-examining the substance by modern physical methods, we found that: (1) The substance is diamagnetic in acetone. (2) The proton resonance spectrum consists of a single broad peak displaced 1·95 p.p.m. to low field of the water resonance. This is characteristic of a variety of diamagnetic phenyl compounds. If an unpaired electron were present, large chemical shifts of the proton resonance frequencies would be expected. (3) The ebullioscopic molecular weight in chloroform is 476 (calc. for the dimer: 498). (4) The infrared spectrum in the carbonyl region of a solution in carbon tetrachloride or chloroform is very similar to that of the ethylthio-compound (Table), which is known to be a dimer,[2] $[Fe(CO)_3 \cdot SEt]_2$. (5) The infrared spectrum is almost the same in benzene, carbon tetrachloride, and chloroform (Table).

Infrared spectra in the carbonyl region (numbers in parentheses refer to the Figure).

	CCl_4 soln.	C_6H_6 soln.
$[Fe(CO)_3 \cdot SPh]_2$	(1) 2078, 2041, 2009, 2001	(3) 2077, 2041, 2003
$[Fe(CO)_3 \cdot SEt]_2$	(2) 2073, 2037, 2000, 1991	(4) 2073, 2036, 2000, 1990



Infrared spectra in the carbonyl region of $[Fe(CO)_3 \cdot SPh]_2$ (nos. 1 and 3) and $[Fe(CO)_3 \cdot SEt]_2$ (nos. 2 and 4). *For details see the Table. [The right-hand peak in* (4) *is due to solvent.]*

We conclude that the correct formula, in solution in carbon tetrachloride, chloroform, and benzene, is $[Fe(CO)_3 \cdot SPh]_2$. The absence of absorption in the bridging carbonyl region indicates that the structure is (I), which is similar to that of the isoelectronic nitrosyl sulphide [3] $[Fe(NO)_2 \cdot SEt]_2$. The details of the carbonyl absorption are not sufficient to establish the structure unambiguously. The slight splitting of one of the $C\equiv O$ stretching frequencies is yet another indication that safe conclusions about structure cannot be drawn from the number of frequencies observed in low-dispersion infrared studies; we observed three rather than four when using a rock-salt prism. If the number of carbonyl frequencies is taken at its face value, we may deduce that the molecule does not have a centre of symmetry, but again such deductions are unreliable.

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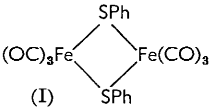
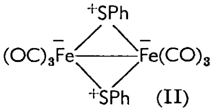
[1] Hieber and Spacu, *Z. anorg. Chem.*, 1937, **233**, 353.
[2] Reihlen, Friedolsheim, and Oswald, *Annalen*, 1928, **465**, 72.
[3] Hofmann and Wiede, *Z. anorg. Chem.*, 1895, **9**, 300.

The electronic structure of the molecule is not particularly clear. If we apply the usual " inert-gas structure " rules we deduce either that each phenylthio-group contributes four electrons or, more plausibly, that there is a metal–metal bond and that each phenylthio-group contributes three electrons. The best " classical " structure is (II), but should not be considered as a satisfactory representation of the electronic structure. It should be noted that neither the infrared spectrum nor theoretical considerations about the electronic structure require the iron and sulphur atoms to be co-planar.



(I)



(II)

Dr. L. E. Sutton has kindly measured the dipole moment of this compound and finds a value of 2·1 ± 0·1 D. He informs us that this evidence is inconclusive but that there may be some departure from planarity.

EXPERIMENTAL

(*a*) $[Fe(CO)_3{\cdot}SPh]_2$.—Thiophenol (5 ml.) was refluxed with iron tetracarbonyl (4 g.) under nitrogen on a water-bath. When the green colour was discharged, the flask was cooled, and acetone (40 ml.) added. The solution was filtered and poured into dilute aqueous sodium hydroxide (100 ml.). After being boiled and stored for 1 hr. the product was filtered off, dried under high vacuum, and recrystallised from xylene (Found: C, 43·6; H, 2·1. Calc. for $C_{18}H_{10}Fe_2O_6S_2$: C, 43·4; H, 2·0%; it had m. p. 135° (lit.,[1] 140°).

(*b*) $[Fe(CO)_3{\cdot}SEt]_2$.—Ethanethiol (8 ml.) was refluxed with iron tetracarbonyl (4 g.) under nitrogen. Separation of the product was as described above except that much passed through the final filtration. This was recovered by ether-extraction. The product, recrystallised from xylene (Found: C, 30·1; H, 2·75. Calc. for $C_{10}H_{10}Fe_2O_6S_2$: C, 29·9; H, 2·5%), had m. p. 74° (lit.,[2] 67°).

Physical Measurements.—The magnetic susceptibility was determined by the Gouy method at room temperature: 0·949 g. of compound, dissolved in acetone to 20 ml., deflected $-0{\cdot}001 \pm 0{\cdot}002$ gauss in the field; 1·179 g. of "AnalaR " nickel ammonium sulphate, dissolved in water to 20 ml., deflected $-0{\cdot}035 \pm 0{\cdot}002$ gauss in the field. The compound is probably diamagnetic although it may be very weakly paramagnetic.

The compound (0·0882 g.) in chloroform (7·445 g.) ($K \sim 42{\cdot}20°$) gave a b. p. elevation of 0·105°, corresponding to a molecular weight of 476.

The proton magnetic resonance spectrum of a solution in acetone was recorded on a Varian Associates high-resolution nuclear magnetic resonance spectrometer, model no. V-4300 B.

Infrared spectra were recorded with a Perkin–Elmer Model 21 infrared spectrometer, with a 0·1 mm. sodium chloride cell and fluorite prism.

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DEPARTMENT OF THEORETICAL CHEMISTRY, UNIVERSITY CHEMICAL LABORATORY,
LENSFIELD ROAD, CAMBRIDGE.
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