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Preliminary communication

Trinuclear π-cyclopentadienyl bridging sulphido derivatives of iron

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SUMMARY

The reaction of $[Fe(\pi\text{-}C_5H_5)(CO)_2]_2$ with the dialkyl disulphides R_2S_2 ($R = CH_3$, C_2H_5, $t\text{-}C_4H_9$ or $CH_2C_6H_5$) affords, as well as dinuclear derivatives of the type $[Fe(\pi\text{-}C_5H_5)(CO)SR]_2$, trinuclear species of formula $[Fe_3(\pi\text{-}C_5H_5)_3(CO)_2(S)SR]$.

Previous studies have revealed that, whereas alkanethiols RSH and dialkyl disulphides R_2S_2 react with $[Fe(\pi\text{-}C_5H_5)(CO)_2]_2$ to give dinuclear derivatives of the type $[Fe(\pi\text{-}C_5H_5)(CO)SR]_2$ [1-3], elemental sulphur reacts with $[Fe(\pi\text{-}C_5H_5)(CO)_2]_2$ to afford a tetranuclear product characterised as $[Fe(\pi\text{-}C_5H_5)S]_4$ [4]. Both types of compound have received considerable attention of late in view of their possible relevance to plant and bacterial ferredoxins[5-8]. We now wish to report the isolation of a trinuclear bridging sulphido species, derived hypothetically from $[Fe(\pi\text{-}C_5H_5)(CO)_2]_2$, a dialkyl disulphide, and elemental sulphur.

The reaction of $[Fe(\pi\text{-}C_5H_5)(CO)_2]_2$ with the dialkyl disulphides R_2S_2 ($R = CH_3$, C_2H_5, $t\text{-}C_4H_9$ or $CH_2C_6H_5$) in benzene under reflux conditions affords, as well as the dinuclear derivatives $[Fe(\pi\text{-}C_5H_5)(CO)SR]_2$, low yields of trinuclear compounds characterised by elemental analysis (C, H, Fe, S and O), molecular weight determinations, and mass spectrometry as $[Fe_3(\pi\text{-}C_5H_5)_3(CO)_2(S)SR]$. Two peaks assigned to bridging carbonyl groups are observed in the C–O stretching region of the infrared spectra of these compounds [ca. 1800(s) and 1765(w) cm^{-1}, measured in cyclohexane] and two resonances, of relative intensity 2/1, corresponding to C_5H_5 protons are found in their NMR spectra. On

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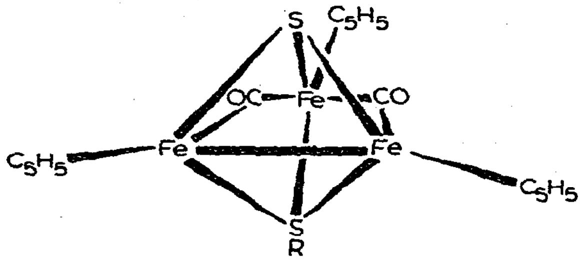

Fig. 1.

the basis of this spectroscopic evidence and the 18 electron rule the structure illustrated in the Figure is proposed.

The iron-57 Mössbauer spectra contain only two asymmetric resonance lines, the peak at lower velocity being both slightly broader and less intense than the other component. The expected inequivalence of the iron environments is therefore indicated, but there is not sufficient resolution to confirm the postulated 2/1 intensity ratio. The benzyl derivative was studied at 195, 77 and 4.2 K, and gives essentially the same pattern at each temperature, whereas the butyl derivative was studied only at 77 K. At this temperature the chemical isomer shifts*, δ, for these two compounds are respectively +0.28 and 0.27 mm s^{-1} and the quadrupole splittings, Δ, 1.67 and 1.70 mm s^{-1}; the linewidths, Γ, are typically 0.28 and 0.26 mm s^{-1} for the low-velocity and high-velocity peaks. The related trinuclear species $Fe_3(CO)_9S_2$, which has been shown by X-ray crystallography to contain one iron atom in a different environment from the other two [9], also gives only a sharp Mössbauer doublet over a wide range of temperature. The parameters at 85 K are δ +0.04, Δ 0.56, and Γ_1, Γ_2 0.27 mm s^{-1}, in good agreement with data of Crow and Cullen who recorded the spectrum at 80 K only [10]. The much lower value of δ for this compound compared with the values for the compounds discussed earlier reflects the superior π-accepting capacity of the terminal carbonyl groups compared with that of the π-C_5H_5 group.

Cyclic voltammograms of $[Fe_3(\pi\text{-}C_5H_5)_3(CO)_2(S)SR]$ ($R = t\text{-}C_4H_9$ or $CH_2C_6H_5$) in 1,2-dimethoxyethane have been measured and shown to exhibit waves corresponding to two reversible redox processes. These are assigned to:

$$[Fe_3(\pi\text{-}C_5H_5)_3(CO)_2(S)SR] - e \rightleftharpoons [Fe_3(\pi\text{-}C_5H_5)_3(CO)_2(S)SR]^+ \text{ and}$$
$$[Fe_3(\pi\text{-}C_5H_5)_3(CO)_2(S)SR]^+ - e \rightleftharpoons [Fe_3(\pi\text{-}C_5H_5)_3(CO)_2(S)SR]^{2+}$$

on the basis of the potentials involved. Consistent with these assignments, treatment of $[Fe_3(\pi\text{-}C_5H_5)_3(CO)_2(S)SR]$ ($R = t\text{-}C_4H_9$ or $CH_2C_6H_5$) with iodine gives a product with a C—O stretching frequency of ca. 1835 cm^{-1}, measured in CH_2Cl_2. This species, presumably $[Fe_3(\pi\text{-}C_5H_5)_3(CO)_2(S)SR]^+$, decomposes fairly rapidly to a dinuclear cation of the

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* These results are based on two-line fits to the spectra and the chemical isomer shifts, δ, are quoted relative to iron metal as zero. The spectra were obtained using a ^{57}Co/Rh source at the same temperature as the absorber. To compare the chemical isomer shift data with results obtained using a room-temperature source, a correction factor of $+0.12_5$ mm·s^{-1} must be added.

type $[Fe(\pi\text{-}C_5H_5)(CO)SR]_2^+$, however, and could not be isolated. In contrast to those for $[Fe_3(\pi\text{-}C_5H_5)_3(CO)_2(S)SR]$ ($R = t\text{-}C_4H_9$ and $CH_2C_6H_5$), the cyclic voltammogram of $[Fe_3(CO)_9S_2]$ exhibits a wave corresponding to a single redox process, the potentials of this wave being considerably more cathodic than the potentials associated with the oxidation of the π-cyclopentadienyl compounds. A one- or two-electron reduction of $[Fe_3(CO)_9S_2]$ is thus presumably involved.

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