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Preliminary communication

SYNTHESIS, STRUCTURE AND CHARACTERIZATION OF $Fe_3(CO)_{10}S$, A NEW IRON CARBONYL SULPHIDE

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Summary

The new complex $Fe_3(CO)_{10}S$ has been prepared by treating $Fe_3(CO)_{12}$ with methanolic NaOH and acidifying the solution in the presence of Na_2SO_3. X-ray analysis has shown the molecule to have an Fe_3S trigonal pyramidal core, one μ_3- and nine terminal CO ligands. The compound shows fluxional behaviour in solution.

Two iron carbonyl sulphides have been previously described, $Fe_3(CO)_9S_2$ and $Fe_2(CO)_6S_2$. They are formed on acidifying solutions containing $Fe(CO)_4^{2-}$ in the presence of sodium sulphite or sodium polysulphide, respectively [1]. Solutions containing the tetracarbonylferrate anion are most easily obtained by treating $Fe(CO)_5$ with methanolic NaOH.

We have now found that by starting from $Fe_3(CO)_{12}$ instead of $Fe(CO)_5$ and by acidifying the solution obtained after treatment with methanolic NaOH in the presence of sodium sulphite a third iron carbonyl sulphide (I) can be obtained, as well as $Fe_3(CO)_9S_2$ (II), $Fe_2(CO)_6S_2$ and the recently isolated $Fe_3(CO)_9S(SO)$ (III) [2].

I can be separated from the hexane-soluble reaction products by chromatography on silica gel and has the composition $Fe_3(CO)_{10}S$ as proved by elementary analysis and mass spectroscopy. Its structure has been determined by X-ray analysis, and is shown in Fig. 1.

The molecules of I contain closed triangles of iron atoms triply bridged by a CO group and an S atom. The bond lengths in the molecular core (Fe—Fe 261 ± 1 pm, Fe—S 221 ± 1 pm, Fe—C 206 ± 2 pm) almost ideally conform to threefold symmetry which is not preserved in the twisted $Fe(CO)_3$ units. Thus

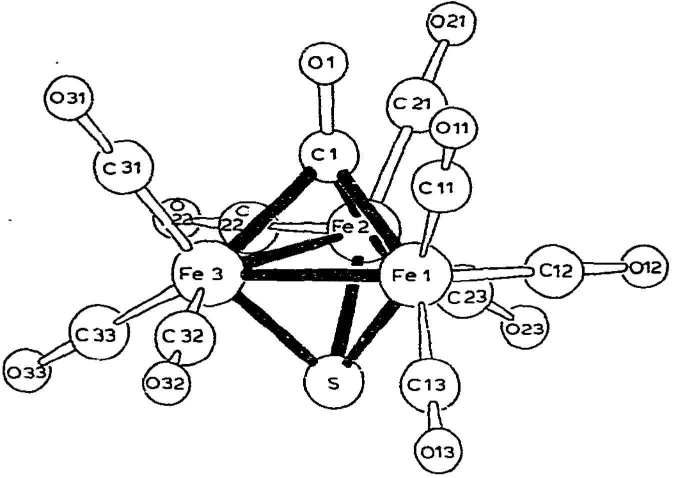


Fig. 1. Structure of I.

I obeys the 18-electron rule and is similar to $Fe_3(CO)_9As_2$ [3] and $Fe_3(CO)_{10}(NSiMe_3)$ [4].

The iron—iron and iron—sulfur bond lengths in I are very close to those in II [5] and III [2]. However because of the presence of two more electrons, II and III contain open triangles of metal atoms with only two metal—metal bonds. The drastic structural difference is obvious from Fig. 2.

The bonding situation in I and II/III differs noticeably from that in the isoelectronic complexes $Cp_3Co_3(S)(CO)$ (IV) and $Cp_3Co_3S_2$ (V) [6]. The latter both contain closed triangles of metal atoms with individual metal—metal bond orders of 1 in IV and $\frac{2}{3}$ in V, implying delocalized metal—metal bonding in contrast to the localized situation in II, respectively III. Whether this results from the different π-bonding capacity of three CO ligands compared with one C_5H_5 unit or from the different seric strain caused by these two ligand groupings will have to be elucidated by further studies.

Compared with the symmetrical structure of I determined in the crystal the

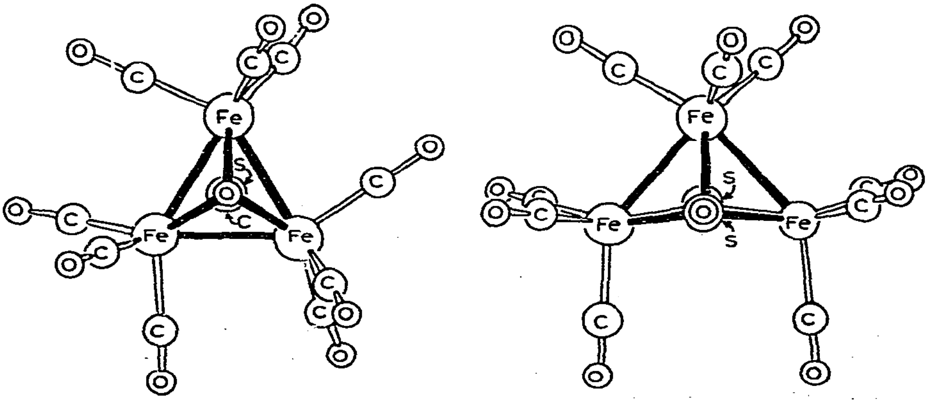


Fig. 2. Top view of the structures of I (left) and II, respectively (right).

compound has a rather complex IR spectrum in n-hexane solution: 2099vw, 2095.5vw, 2056.5vs, 2036(sh), 2030.5s, 2014vw, 1977w, 1896.5w(br), 1730.5m(br) cm^{-1}. Furthermore, the absorption around 1730 cm^{-1} characteristic for the μ_3-CO ligand is a composite band having several shoulders and the relative intensities of these shoulders change significantly on cooling, as shown in Fig. 3. This latter observation suggests fluxional behaviour, which is further supported by the ^{13}C NMR spectrum of I in $CDCl_3$: only one single sharp signal, at 211.3 ppm (reference TMS), was observed.

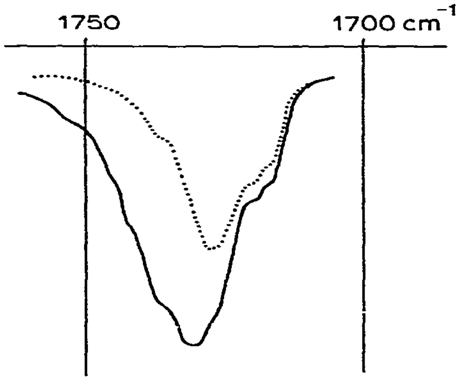
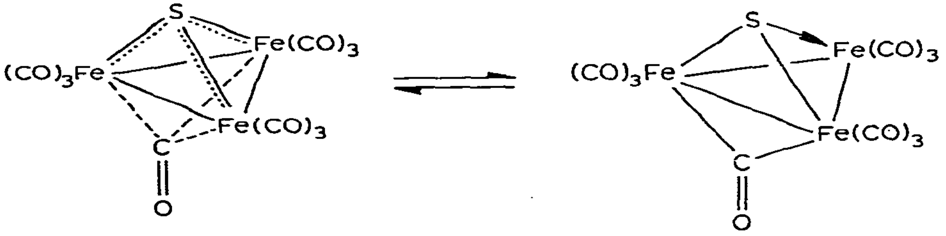


Fig. 3. Infrared spectrum of I in the 1760—1700 cm^{-1} region in hexane. —— at +23°C; ---- at −21°C.

The IR spectrum of I merits two further comments. First, the band at 1896.5 cm^{-1} in hexane can not be observed in a KBr pellet and accordingly belongs to a structure present only in solution. The absorption frequency indicates an isomer with a μ_2-CO (bridging) ligand. Second, the two very weak bands at 2099 and 2095.5 cm^{-1} in hexane presumably belong to the totally symmetric in-phase A_1 vibrations of two different species and suggest therefore also at least two isomers to be present in solution. In accordance with the above observations we suggest that I exists in solution in the two valence isomeric forms (Ia) and (Ib) as shown.



(Ia) (Ib) (1)

The equilibrium 1 is shifted towards isomer Ia on lowering the temperature. This conclusion is based on the observed increase of the relative intensity of the band at 1730.5 with respect to that at 1896.5 cm^{-1}, assumed to be caracteristic for Ia and Ib, respectively. It should be mentioned here that in solution Ia is apparently a complex mixture of several conformers with very similar structures, as suggested by the shape of the μ_3-CO band.

The complexity of the infrared spectrum of I in solution thus proves a multistage mechanism for the rapid interchange of the CO ligands, which accordingly takes place over several conformers of Ia and their valence isomer Ib as intermediates.

Experimental

1.28 g (2.5 mmol) $Fe_3(CO)_{12}$, 2.5 ml of a 50% solution of NaOH in water and 10 ml MeOH are allowed to react under CO for one hour. 2.48 g (10 mmol) $Na_2SO_3 \cdot 7H_2O$ dissolved in 25 ml water are added and the mixture is acidified after 10 min with excess hydrochloric acid. The product is extracted with 50 ml hexane and the dark coloured hexane solution chromatographed on a silicagel column. With hexane as eluent, I appears as a dark brown band following $Fe_2(CO)_6S_2$ (II) and $Fe_3(CO)_{12}$. Complex III remains on the column. Crystalline I is obtained after concentrating the appropriate fraction in vacuo and chilling to −78°C. Yield 67 mg, 0.14 mmol (5.6%). The compound decomposes at 80°C without melting.

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