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The Isoelectronic Iron Carbonyl Sulphide Clusters $H_{2-n}Fe_3S(CO)_9^{n-}$ (n = 0,1,2)

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The acidification of carbonylferrate solutions in the presence of sulphite or sulphide leads – depending on the conditions – to $Fe_3S_2(CO)_9$ [1], $Fe_2S_2(CO)_6$ [1], $Fe_3S(SO)(CO)_9$ [2] or $Fe_3S(CO)_{10}$ [3]. We have now found that by adjusting the Fe:S ratio to 3:1 a fifth iron carbonyl sulphide $H_2Fe_3S(CO)_9$ can be prepared from $HFe(CO)_4^-$ and H^+.

To a methanolic solution of $NaHFe(CO)_4$ prepared from 7.0 ml (50 mmol) $Fe(CO)_5$, 40 ml MeOH and 16 ml 50% NaOH in water were added 4.0 g (16.5 mmol) $Na_2S\cdot 9H_2O$ dissolved in 100 ml water, the reaction mixture acidified with diluted HCl and extracted five times with 60–60 ml hexane. The combined dark brown hexane solution was washed with water, dried over Na_2SO_4 and chilled to –78 °C. 1.47 g (3.2 mmol, 19% yield) of black crystalline $H_2Fe_3S(CO)_9$ could be separated. The formula of the diamagnetic complex was determined by elementary analysis and mass spectrum. It decomposes at 98 °C without melting.

$H_2Fe_3S(CO)_9$ behaves in polar solvents as a dibasic acid: in ethanol solution one proton and in pyridine solution two protons can be determined by potentiometric titration with $(Bu_4N)OH$. The two acidic dissociation steps are also indicated by the changes in the infrared spectra (Table I). Accordingly in polar (but not basic) solvents like ethanol or acetonitrile the complex is present in the form of its monoanion $HFe_3S(CO)_9^-$ (eqn. 1) and in basic solvents like pyridine or butylamine as the dianion $Fe_3S(CO)_9^{2-}$ (eqn. 2).

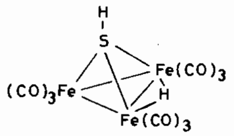
$$H_2Fe_3S(CO)_9 \xrightarrow{\text{polar solvent (solv)}} HFe_3S(CO)_9^- + \text{solv}\cdot H^+ \qquad (1)$$

$$H_2Fe_3S(CO)_9 \xrightarrow{\text{basic solvent (B)}} Fe_3S(CO)_9^{2-} + 2BH^+ \qquad (2)$$

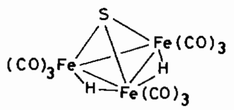
The dianion could be separated in crystalline form as its tetraethyl ammonium salt by dissolving $H_2Fe_3S(CO)_9$ in pyridine, adding a concentrated water solution of $(Et_4N)OH$ in small excess, evaporating to dryness and recrystallizing from CH_2Cl_2. $(Et_4N)_2[Fe_3S(CO)_9]$ forms red plates soluble in polar aprotic solvents like acetone or acetonitrile.

Experiments to separate the monoanion as a crystalline salt were not successful till now.

Two alternative structures I and II may be considered for $H_2Fe_3S(CO)_9$. Structure I would be the SH analogue of the thiol complexes $HFe_3(SR)(CO)_9$ [4, 5] and structure II would correspond to the ruthenium [6, 7] and osmium [8–10] complexes $H_2M_3S(CO)_9$.



I



II

We prefer structure II and base this conclusion on the following observations:

a) The ^1H NMR spectrum of $H_2Fe_3S(CO)_9$ shows no signal which could be attributed to an SH group, the signal at δ = –24.6 ppm (s) being consistent with bridging hydrido atoms. The Ru and Os complexes show this absorbance at –18.98 [6] and –20.70 ppm [8], respectively. The fact that the two hydrogens have only one signal is explained by the fluxional character of the molecule (*vide infra*).

b) The infrared spectra of $H_2Fe_3S(CO)_9$, its monoanion and its dianion suggest an increasing symmetry of these species in this order: the number of ν_{CO} bands is 9, 6 and 4. Such an effect can only be explained if both protons were coordinated to the cluster since the presence or absence of a hydrogen atom on the sulphur atom would have no influence on the symmetry of the molecule.

c) Experiments to transform the monoanion (which according to ^1H NMR contains its single hydrogen on the cluster, (see Table I)) by alkylation to a thiolato complex of type $HFe_3(SR)(CO)_9$ failed. A reasonable explanation of this result is that in $HFe_3S(CO)_9^-$ the HOMO orbital is not the lone pair on the sulphur atom but rather a cluster orbital. Therefore also the second hydrogen will be located on the cluster if this anion is being protonated to form $H_2Fe_3S(CO)_9$.

d) The Mössbauer spectrum of $H_2Fe_3S(CO)_9$ at 77 K shows two types of iron atoms to be present. The signal with lower intensity has an isomer shift of –0.49 (relative to the ^{57}Co–Pt source) and a quadrupole splitting of 0.76 mm sec^{-1}, the values for the

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TABLE I. Spectroscopic Properties of the $H_{2-n}Fe_3S(CO)_9^{n-}$ Clusters.

	n = 0	n = 1[a]	n = 2[b]
IR, cm^{-1}	2106 m 2069.5 vs 2050 vs 2040 s 2034.5 m 2013.5 s 2001 m 1992.5 w 1985.5 w (in hexane)	2052 w 2009 vs 1982 vs 1965 s 1950 m,sh 1914 w (in EtOH)[c]	1996.5 w 1927.5 vs 1901 m 1870 w (in acetone)
^1H NMR δ, ppm	−24.6 (in $CDCl_3$)	−23.1 (in CH_3OD)[d]	
^{13}C NMR δ, ppm (reference TMS)	203.5 (in $CDCl_3$)	213.2 (in C_2D_5OD)	221.9 (in CD_3CN)

[a] $H_2Fe_3S(CO)_9$ dissolved in the given solvent, anion formed by dissociation (eqn. 1).
[b] In the form of $(Et_4N)_2[Fe_3S(CO)_9]$.
[c] Spectrum does not change on adding 1 mol $(Et_4N)OH$ per mol complex.
[d] 1 mol CH_3ONa added per mol $H_2Fe_3S(CO)_9$.

more intensive signal are −0.40 and 0.95 mm sec^{-1}, respectively. As expected, $(Et_4N)_2[Fe_3S(CO)_9]$ contains only one type of iron atoms which have a −0.48 mm sec^{-1} isomer shift and 0.35 mm sec^{-1} quadrupole splitting.

All three complexes are fluxional at room temperature as shown by the single lines observed in their ^{13}C NMR spectra (Table I). The gradual shift of this signal towards lower field positions on increasing the negative charge is in accordance with earlier observations [11].

It should be mentioned finally that $H_2Fe_3S(CO)_9$ is decomposed by acids (including some silica gels) to $Fe_3S_2(CO)_9$ and $Fe_3(CO)_{12}$.

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