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The Structure of the Anion $[Fe_2(CO)_8H]^-$

By K. FARMERY and M. KILNER

(Chemistry Department, University of Durham)

and R. GREATREX and N. N. GREENWOOD*

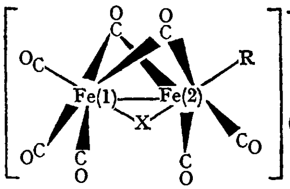
(Department of Inorganic Chemistry, The University, Newcastle upon Tyne, NE1 7RU)

IN view of recent speculation regarding the bonding of hydrogen in metal carbonyl hydrides, we report the results of an infrared and Mössbauer study of the anion $[Fe_2(CO)_8H]^-$. The preparation was reported by Hieber and Brendel[1] and certain aspects of its chemistry have been studied, but no physical data on this anion have been reported; its structure is, therefore, unknown. The three most likely structures in which the hydrogen is bound directly to iron are those derived from $Fe_2(CO)_9$ [(I) and (II)] or from $[Fe_2(CO)_8]^{2-}$ [*e.g.* (III)].

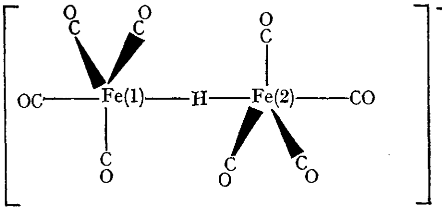
The relevant data for $[Et_4N][Fe_2(CO)_8H]$ are presented in the Table, which includes our data for $Fe_2(CO)_9$ for comparison.

Structure (III), which is analogous to $[M_2(CO)_{10}H]$ (where M = Cr, Mo, and W),[2,3] can be discounted, because (i) the spectrum of the anion shows bands in the bridging carbonyl region, and (ii) the low value of the quadrupole splitting is inconsistent with a five-co-ordinate iron atom.[4]

In structure (II), iron atom (1) would be in an identical environment to that of the iron atoms in $Fe_2(CO)_9$, and different from that of Fe(2). Thus the Mössbauer spectrum should consist of four peaks, two of which would be similar to those observed for $Fe_2(CO)_9$. The observed spectrum consisted of only two unbroadened peaks in positions different from those observed for $Fe_2(CO)_9$. The two iron atoms are therefore equally affected by the presence of the hydrogen, which must be in a bridging position, as in structure (I). The fact that the spectrum is not very different from that of $Fe_2(CO)_9$ indicates the similarity of their structures. The changes which are observed in the Mössbauer parameters on going from $Fe_2(CO)_9$ to $[Fe_2(CO)_8H]^-$ parallel those observed in the analogous trinuclear system.[5] Thus, using data obtained at 80°K, we find that substitution of one of the bridging carbonyl groups in $Fe_3(CO)_{12}$ to give $[Fe_3(CO)_{11}H]^-$ reduces the isomer shift from 0·37 to 0·29 mm./sec. and increases the quadrupole splitting from 1·13 to 1·41 mm./sec.



(I) X=H,R=CO
(II) X=CO,R=H



(III)

TABLE

Species	Infrared† ν(C–O) stretch (cm.$^{-1}$)		Mössbauer‡ Isomer shift δ(mm./sec.)	Line width at half height Γ(mm./sec.)	Quadrupole splitting Δ(mm./sec.)
$[Fe_2(CO)_8H]^-$	2068w 2045w 1997s 1923vs 1860s	terminal	0·325 ± 0·010	0·33	0·504 ± 0·010
	1778m 1750s	bridging			
$Fe_2(CO)_9$	2082s 2026s	terminal	0·420 ± 0·010	0·32	0·425 ± 0·010
	1845s 1833s 1825sh	bridging			

† Nujol mull.
‡ Spectra recorded at 80°K with respect to sodium nitroprusside.

The i.r. spectrum of the anion is consistent with structure (I) (C_{2v} symmetry), for which five terminal modes, $2A_1 + 2B_1 + B_2$ (A_1 modes will be of weak intensity and the B modes strong) and two strong bridging modes, $A_1 + B_2$ are predicted (*cf.* Noack's results for the isostructural and soelectronic $Co_2(CO)_8$).[6]

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[5] N. E. Erickson and A. W. Fairhall, *Inorg. Chem.*, 1965, **4**, 1320; and our own results.
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