$[MnFe_2(CO)_{12}]^-$, A New Anion Isoelectronic with $Fe_3(CO)_{12}$

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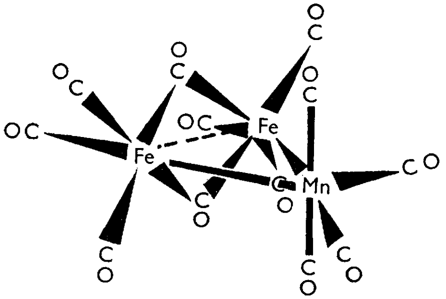
THE structure of tri-iron dodecacarbonyl in the solid state has finally been established,[1] and the results confirm the earlier suggestion based on the structure of the $[HFe_3(CO)_{11}]^-$ ion.[2] The interest in this structural type prompts us to communicate our discovery of a new carbonylmetallate anion, $[MnFe_2(CO)_{12}]^-$, which is isoelectronic with $Fe_3(CO)_{12}$ and for which we propose a similar structure (I).



(I)

The new anion is prepared in diglyme by reaction of pentacarbonylmanganese anion with iron pentacarbonyl, and is isolated as the tetraethylammonium salt, purified by recrystallization from ethanol. The intensely blue–black salt (λ_{max} 580 mμ, $\epsilon_{molar} = 3100$; ethanol solution) was characterized by complete elemental analysis.

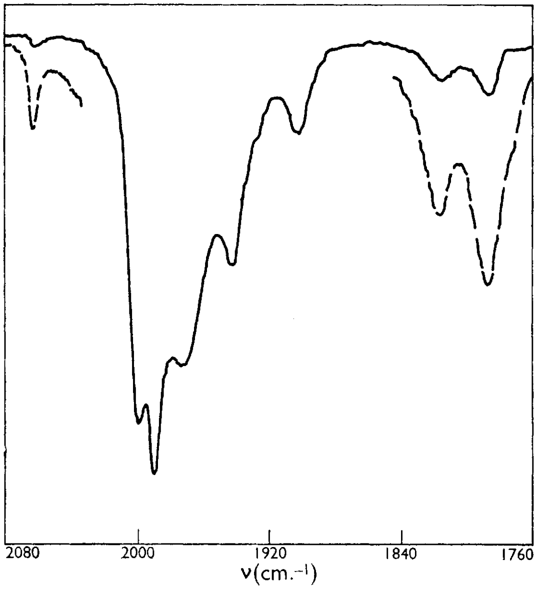


FIGURE 1. *Infrared spectrum of* $[Et_4N]^+[MnFe_2(CO)_{12}]^-$ *in tetrahydrofuran. Upper curve,* 0·46 *mg./ml.; lower dashed curve,* 4·6 *mg./ml.*

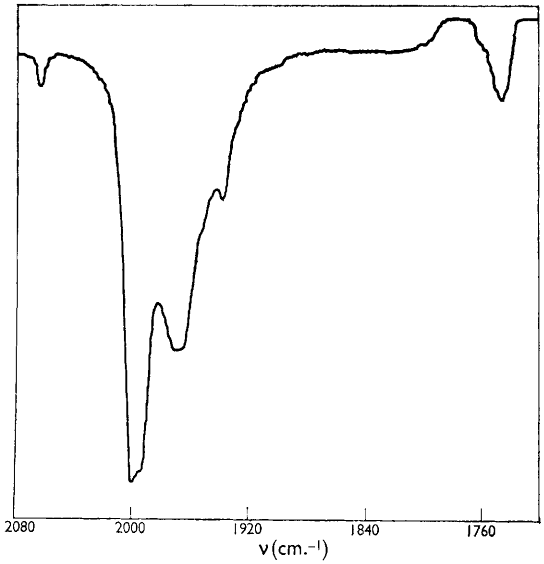


FIGURE 2. *Infrared spectrum of* $[Et_3NH]^+[HFe_3(CO)_{11}]^-$ *in tetrahydrofuran;* 0·46 *mg./ml.*

The carbonyl stretching region of the infrared spectrum of $[MnFe_2(CO)_{12}]^-$ is shown in Figure 1. The spectrum was determined on a freshly prepared solution in dry tetrahydrofuran to achieve sufficient solubility. The proposed structure had C_{2v} symmetry, for which one expects nine infrared-active terminal carbonyl stretching modes ($3A_1 + 3B_1 + 3B_2$) and two bridging carbonyl bands ($A_1 + B_2$). Despite solvent broadening, six terminal bands are visible at 2063, 1999, 1990, 1972, 1944, and 1903 cm.$^{-1}$, and the expected bridging carbonyl modes at 1827 and 1785 cm.$^{-1}$ As found for $Fe_3(CO)_{12}$ in solution,[3] the bridging absorption is of unexpectedly low intensity. For $Fe_3(CO)_{12}$, however, only *two* terminal CO bands can be resolved, making it appear likely that the structure in solution differs from that in the solid state; the infrared evidence supports a linear structure in solution.[3] It would appear that the $[MnFe_2(CO)_{12}]^-$ anion, in contrast, retains its triangular structure in solution.

For comparison, we show in Figure 2 the infrared spectrum of the $[HFe_3(CO)_{11}]^-$ ion. In this case, with a single bridging carbonyl group,[2] only the expected single band is observed at 1734 cm.$^{-1}$ The terminal region resembles that of $[MnFe_2(CO)_{12}]^-$ rather closely, with bands at 2064, 2000, 1995, 1970, 1953 (shoulder), and 1941 cm.$^{-1}$, thus providing further support for the proposed $[MnFe_2(CO)_{12}]^-$ structure.

The stability of this species implies that a number of related structures should exist, and suitable synthetic routes to such compounds are currently being explored.

(*Received, April* 13*th,* 1966; *Com.* 237.)

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[3] G. R. Dobson and R. K. Sheline, *Inorg. Chem.*, **1963**, **2**, 1313.