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The Characterization of $CdFe(CO)_4$ and $HgFe(CO)_4$ by Infrared and Mössbauer Spectroscopy and X-Ray Diffractometry

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Two compounds, $MFe(CO)_4$ (M=Cd or Hg), were investigated by the use of infrared and Mössbauer spectroscopy and X-ray diffractometry. The infrared data suggested that the M atoms link $Fe(CO)_4$ units to form infinite zig-zag chains; these metal atoms are attached to the iron atom at *cis*-positions and form an octahedron with four carbonyl groups. The Mössbauer spectra and infrared data indicate that the Cd–Fe and Hg–Fe bonds are not ionic but covalent, that they are as strong as C–Fe bonds in iron carbonyls. The isomorphism of the two compounds was confirmed by the X-ray diffractometry.

Among the compounds with metal-metal bonds, those with the simplest composition, $MFe(CO)_4$ (M= Cd, Hg), are interesting for their structures. They have been thought to have a polymeric structure formed by means of direct Cd–Fe or Hg–Fe bonds. Wells[1] proposed an endless structure of $HgFe(CO)_4$ in which the iron and mercury atoms are alternatively bonded to form a straight, linear chain. Adams *et al.*[2] and Beck and Noak[3] suggested that two cadmium or two mercury atoms and four carbonyl groups form an octahedral *cis*-configuration around the central iron atom of $CdFe(CO)_4$ or $HgFe(CO)_4$. However, so far no attempts have been made to provide precise structural information about these compounds. In this paper, their electronic states and structures will be discussed on the basis of infrared and Mössbauer spectroscopy and X-ray diffraction data.

Experimental

The sample of $HgFe(CO)_4$ was prepared by treating iron carbonyl with mercuric sulphate.[4] The corresponding cadmium compound was synthesized by the method of Feigl and Krumholtz,[5] yellow needle-like crystals of $CeFe(CO)_4$ being obtained after heating voluminous precipitates of $Cd(NH_3)_2Fe(CO)_4$ in an aqueous solution at 50°C for three days. The results of elemental analyses were satisfactory with regard to the above compositions. Thermal decomposition was carried out in a nitrogen stream over the temperature range of 15—300°C, using a Shimadzu Thermal Balance and a Rigaku Denki DTA apparatus. The infrared spectra were recorded with Nihon-Bunko DS402G (4000—700 cm^{-1}), Hitachi EPI-L02 (700—200 cm^{-1}), and Hitachi FIS-1 (300—60 cm^{-1}) spectrometers as Nujol mulls and as dispersion in fused polyethylene, at room temperature and at the temperature of

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[1] A. F. Wells, "Structural Inorganic Chemistry," 3rd ed. Oxford University Press, London (1962), p. 723.

[2] D. M. Adams, D. J. Cook, and R. D. W. Kemmit, *Nature*, **205**, 589 (1965).

[3] W. Beck and K. Noak, *J. Organometal. Chem.*, **10**, 307 (1967).

[4] H. Stuhlman and H. Hock, *Ber.*, **62**, 431 (1929).

[5] F. Feigl and P. Krumholtz, *Z. Anorg. Allg. Chem.*, **215**, 242 (1933).

liquid nitrogen. The Mössbauer spectra were measured with a constant-velocity drive-type spectrometer with a source of ^{57}Co diffused onto a Pt-foil. The powder X-ray diffraction patterns were recorded with Rigaku-Denki and Norelco X-ray diffractometers. Filtered Cu$K\alpha$ and Fe$K\alpha$ radiations were used. Weissenberg cameras were used to obtain oscillation photographs of single crystals.

Results and Discussion

IR Spectra. The observed infrared absorption frequencies (measured as Nujol mulls at room temperature) are listed in Table 1a. The use of polyethylene as the dispersion media gave essestially the same results. In the far-infrared region, there appeared to be some discrepancies between our results and those of previous workers.[2,3] In the carbonyl region, four prominent stretching bands were observed for both compounds. This characteristic is just like that found for *cis*-$M(CO)_4L_2$ molecules of the C_{2v} symmetry with regard to the central metal atom, M. The four carbonyl stretching modes, assigned as is shown in Table 1a, and their force constants, calculated according to the Cotton-Kraihanzel model,[6] are listed in Table 1b, where K_1 is the stretching force constant of C–O *trans* to Hg or Cd, and where K_2 is the stretching force constant of C–O *cis* to Hg or Cd. The agreement between these values and the calculated frequencies of the A_1^1 mode support the present assignments. The fact that the frequency of each CO stretching band for $CdFe(CO)_4$ is lower than that of the corresponding band of $HgFe(CO)_4$ is consistent with the observations for $M[Co(CO)_4]_2$, where M refers to Cd or Hg.[7] In both cases, the order of frequencies may be associated with the difference in electronagativity and in atomic size between Cd and Hg.

TABLE 1a. INFRARED FREQUENCIES (cm^{-1})

$CdFe(CO)_4$	$HgFe(CO)_4$	Assignments	
2031 m	2047 m	A_1^1	(C–O) str.
2010 w sh	2012 w sh		
1960 s	1979 s	A_1^2	
1941 w sh			
1921 s	1952 s	B_1	
1871 s	1917 s	B_2	
1829 w sh			
632 vw			
604 vs br[a)]	596 vs br[a)]		(MCO) bend. or (M–C) str.
550 m	550 m		
524 m	533 m		
500 w	516 w		
454 s	443 s		
432 s	427 m		
412 w	419 w		
408 vw	413 vw		
217 s	196 s	B_1^1	(M–M) str.
88 w			(CMC) bend.

a) The splitting of both bands could not be detected at the temperature of liquid nitrogen.

vs very strong, s strong, m medium, w weak, vw very weak, br broad, sh shoulder,str str. stretching, bend. bending.

TABLE 1b. FORCE CONSTANTS FOR CARBONYL STRETCHING FREQUENCIES

	K_1	K_2	K_i md/Å	Calcd. freq. of A_1^1 mode cm^{-1}
$CdFe(CO)_4$	14.17	15.84	0.53	2025
$HgFe(CO)_4$	15.26	16.22	0.42	2044

Thus, it may be concluded that Cd is poorer π-electron acceptor than Hg in these molecules; in other words, the *p* orbitals of cadmium are less facile than those of mercury in forming $d\pi$–$p\pi$ bonds with the *d*-orbitals of iron.

The bands due to metal-metal vibrations are expected to appear in the region of the far-infrared spectra, where no band due to the M–CO group except those due to CMC bending vibrations is likely to appear.[8,9] Accordingly, the bands clearly observed at 217 cm^{-1} and 196 cm^{-1} can most reasonably be assigned to the Cd–Fe and Hg–Fe stretching modes; the other mode, A_1^1, could not be detected, presumably because this skeletal vibration frequency is lowered when molecules are polymeric,[10] as in the present cases. By assuming that a cadmium or mercury atom links $Fe(CO)_4$ groups to form a zig-zag chain, the force constants are calculated to be 2.1 and 1.9 md/Å for $HgFe(CO)_4$ and $CdFe(Co)_4$ respectively. These values, although rather rough, are still acceptable.[11] As for the above-mentioned cobalt carbonyl compounds, $M[Co(CO)_4]_2$ (M=Cd, Hg), the *K*(Cd–Co) and *K*(Hg–Co) values were reported to be 2.33 and 2.61 md/Å respectively by Stammreich, Kawai, and Sala.[7] These four bonds seem to be stronger than the Sn–Mn bonds in $Cl_3SnMn(CO)_5$ or $(CH_3)_3SnMn(CO)_5$, for which the values of 1.00 and 0.67 md/Å were obtained.[12]

The strength of the metal-metal bond in the compounds in question may be estimates to be comparable with those covalent metal-carbon bonds in neutral metal carbonyls. By comparing the K_1, K_2, and K_i values with those of iron carbonyl derivatives containing various ligands and Fe(0), the oxidation number of the iron atom in the present compounds was estimated to be nearly zero.

Mössbauer Spectra. The Mössbauer spectra data are given in Table 2 and in Fig. 1, along with those for the related compounds containing metal-metal bonds between different elements (these later values being taken from the literature).[13,14] In $HgFe(CO)_4$ the

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6) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **84**, 4432 (1962).

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8) P. N. Brier, A. A. Chalmers, and S. B. Wild, *J. Chem. Soc. A*, **1967**, 1889.

9) N. A. D. Carey and H. C. Clark, *Chem. Commun.*, **1967**, 293.

10) S. Mizushima and T. Shimanouchi, *J. Amer. Chem. Soc.*, **71**, 1320 (1947).

11) H. M. Gager, J. Lewis, and M. J. Ware, *Chem. Commun.*, **1966**, 616.

12) S. Onaka, private communication.

13) N. E. Erickson and A. W. Fairfall, *Inorg. Chem.*, **4**, 1320 (1965).

14) M. T. Jones, *Inorg. Chem.*, **6**, 1249 (1967).

Table 2. Mössbauer effect data

Absorber	Temp. °K	I.S. (mm/sec)	Q.S. (mm/sec)	Ref.
$CdFe(CO)_4$	79	0.190±0.03	0.20±0.05	
	123	0.140±0.03	0.10±0.05	
	292	0.136±0.03	0.10±0.05	
$Na_2Fe(CO)_4$	298	0.110	0	12
$Me_4SnFe_4(CO)_{16}$	298	0.16	0.30	14
$Me_4SnFe_2(CO)_8$	298	0.15	0.16	14
n-$Bu_4Sn_2Fe_2(CO)_8$	78	0.24	0.12	14

I.S. Isomer shift measured relative to the midpoint of the spectrum of $[Na_2Fe(CN)_5NO]\cdot 2H_2O$.
Q.R. Quadrupole splitting.

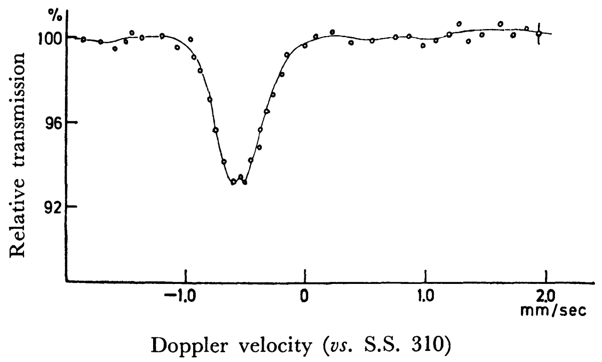

Fig. 1. Mössbauer spectrum of $CdFe(CO)_4$ at 292°K.

Mössbauer effect could not be measured because of the large non-resonant absorption of mercury nuclides. The spectra of $Cd(NH_3)_2Fe(CO)_4$ which is the starting material for preparing $CdFe(CO)_4$ were too weak to be registered even at the temperature of liquid nitrogen. The large, negative isomer shift of $CdFe(CO)_4$ indicates that the charge on the iron atom is only slightly negative or is almost neutral.

The observed absorption, which is intense even at room temperature, suggests a rigid poymeric structure. Consequently, the polymeric structure containing the Cd(0)–Fe(0) covalent bond seems to be preferable to the ionic form, Cd^{2+}–$Fe(CO)_4{}^{2-}$, in the present complex.

It can be seen from the data that the compounds with the Sn–Fe–Sn bond, which also have a *cis*-configuration around the iron atoms,[14] closely resemble $CdFe(CO)_4$ in the valence state of the iron atom.

Two remarkable features of the Mössbauer spectra of $CdFe(CO)_4$ are the small value of the quadrupole splitting and its small temperature dependence. This fact may reflect a high-electric-field gradient symmetry around the iron atom, which can be interpreted in terms of the hybrid orbitals of the iron.

In six octahedral hybrid orbitals of these carbonyl compounds of iron in the low-valency state, the d-orbitals are so occupied as to complete the inert gas structure. The resulting electronic configuration reduces the angular dependency of the expanded d-electron clouds to some degree,[15] so that the field gradient at the iron nucleus becomes smaller, even in the present case, where a *cis*-configuration of the C_{2v} symmetry is suggested by the infrared data.

Considering the nature of the metal-metal bonds in terms of force constants, the results of our infrared and Mössbauer spectroscopy are compatible with regard to the electronic environment of the central iron atom.

Thermal Decomposition. On heating under nitrogen, $CdFe(CO)_4$ suddenly began to decompose at 245°C, while releasing just four CO per chemical unit. The residue burned violently on exposure to air. On its DTA curve, a sharp and huge endothermic-peak corresponding to the sudden decomposition appeared at 260°C. The stability of $CdFe(CO)_4$ against thermal decomposition up to 245°C seems unique among the metal carbonyl compounds of this type. On the other hand, $HgFe(CO)_4$ began to decompose gradually, releasing both carbon monoxide and mercury vapor.

Crystal Structure. The polarizing microscopic observations of the crystals of these compounds supported the idea that they belong to either a triclinic or a monoclinic system. The twenty-two diffraction lines observed for each compound were examined by Ito's method,[16] and it could be concluded that both compounds are triclinic and isomorphous, with the following lattice parameters:

$CdFe(CO)_4$ $a=11.8$, $b=9.4$, $c=9.3$ Å,
$\alpha=111.5$, $\beta=124.5$, $\gamma=106.0°$
Vol. $=748.2$ Å^3, $D_{\text{calcd.}}=2.48$ g/cm^3,
$HgFe(CO)_4$ $a=12.9$, $b=10.8$, $c=10.3$ Å,
$\alpha=108.5$, $\beta=121.5$, $\gamma=106.0°$
Vol. $=782.6$ Å^3, $D_{\text{calcd.}}=3.03$ g/cm^3.

Their densities, measured pycnometrically in benzene, gave the values of 2.5 and 3.1 g/cm^3, values which agreed with $Z=4$, for $CdFe(CO)_4$ and $HgFe(CO)_4$ respectively.

Although we have not been able to determine their precise structures from these results, there should be no significant differences in the crystal and molecular structures between the cadmium and mercury compounds. From the site symmetry about the iron atoms of C_{2v}, as estimated from the infrared data, one of the most probable structures is given in Fig. 2.

The weakness of the Mössbauer spectra of $Cd(NH_3)_2$-$Fe(CO)_4$ suggests that the metal-metal links are absent in this compound and that they formed on the heat decomposition of this complex to yield $CdFe(CO)_4$.

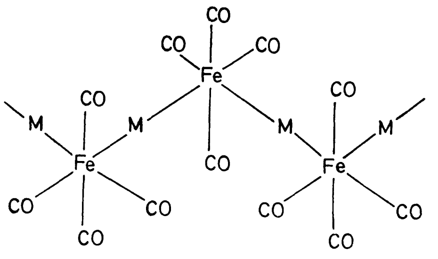

Fig. 2. Probable structure for $MFe(CO)_4$ (M=Cd, Hg).

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16) T. Ito, *Nature*, **164**, 755 (1947).