

group. The presence of this band in the copper(II) compound at 1724 cm^{-1} reveals that the keto group is not involved in bonding to the metal. A sharp strong band at 1600 cm^{-1} in the copper(II) complex is due to the antisymmetric COO stretching vibration. In the copper(II) alkanoates where there is a dimeric (or polymeric) structure involving a bridging of two copper atoms by four carboxylate groups, the antisymmetric COO stretching mode occurs as a sharp band at 1600 cm^{-1} , while in the monomeric copper(II) alkanoates, only a broad band in the region $1560\text{--}1600\text{ cm}^{-1}$ is observed.^{11,12} The presence of a sharp band at 1600 cm^{-1} in copper(II) levulinate supports the dimeric structure of the compound. The CH_2 rocking vibration, which is considered to be very sensitive to any deformations in the organic molecular chain,⁹ occurs around 770 cm^{-1} both in the sodium salt and in the copper(II) compound. This suggests that the levulinate ion does not undergo any structural deformation on complex formation.

TABLE II
INFRARED SPECTRAL FREQUENCIES OF LEVULINATES
IN KBr PELLET AND THEIR ASSIGNMENT

Sodium levulinate <i>n</i> -hydrate	Copper(II) levulinate monohydrate	Probable assignment
1724 vs	1724 vs	C=O str
1560 vs	1600 vs	Antisym COO str +
1580		H ₂ O bend
1455 vs	1450 vs	Symmetric COO str
1420 vs	1420 s	CH ₂ bend
1375 s	1378 s	
1280 m	1320 m	CH ₂ twist and wag
1255 m	1240 m	
1175 s	1175 s	
1060 m	1068 w	
988 w	1030 w	CC str
938 w	995 w	
925 m	950 w	
825 m	830 w	H ₂ O rock
765 m	770 m	CH ₂ rock
	760 w	...
	725 w	...
700	685 m	COO def

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Octacarbonyldiiododiiron(I): Preparation and Properties¹

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The structure of dimanganese decacarbonyl is well established² as dinuclear with two square-pyramidal

$\text{Mn}(\text{CO})_5$ units joined solely by a manganese-manganese bond to give a staggered structure with D_{4d} symmetry. In this way, each valence shell orbital of each manganese atom participates in the formation of a doubly occupied bonding molecular orbital or else constitutes a filled, more or less nonbonding orbital. The effective utilization of all valence shell orbitals of the metal atoms which this structure permits affords a satisfactory basis for explaining the stability and diamagnetism of the molecule.

The ions $[\text{Cr}_2(\text{CO})_{10}]^{2-}$ and $[\text{Co}_2(\text{CNCH}_3)_{10}]^{4+}$ are isoelectronic with $\text{Mn}_2(\text{CO})_{10}$ and are known to have similar structures. In the case of $\text{Co}_2(\text{CNCH}_3)_{10}^{4+}$ this structural similarity has been proved conclusively by a single-crystal X-ray study³ while for $\text{Cr}_2(\text{CO})_{10}^{2-}$ the infrared spectrum suggests that this is the case.⁴ Finally, the compound $\text{Mn}_2(\text{CO})_8(\text{P}(\text{C}_2\text{H}_5)_3)_2$ has been shown⁵ by X-ray methods to have a structure derived from that of $\text{Mn}_2(\text{CO})_{10}$ by replacing the two axial CO groups by the phosphines. In all cases D_{4d} symmetry is proved or reliably indicated by the evidence at hand. Observations such as these, suggesting the stability of such a structure over a wide range of charges and metal atomic numbers, led us to consider the possibility of preparing an isoelectronic and isostructural compound of iron.

Results

Preparation and Properties of Diiododiiron Octacarbonyl.—The new compound, $\text{Fe}_2(\text{CO})_8\text{I}_2$, has been prepared by the reaction of iodine with triiron dodecacarbonyl. It is a white crystalline solid, melting at *ca.* -5° to a red liquid and it dissolves in a variety of organic solvents to give pale red solutions. Solutions in alkanes or ethers are moderately stable but solutions in chlorinated solvents such as chloroform decompose rapidly. The compound is air sensitive and must be stored under oxygen-free nitrogen or under vacuum. The compound in solution appears, from the observation of proton spectra of the solvents, to be diamagnetic. No esr signal was detected in any solution.

The infrared spectrum (see Table I and Figure 1a and b) of the compound, in pentane or THF solution, throughout the range $750\text{--}3600\text{ cm}^{-1}$, consists of only two strong bands, of nearly equal intensities, at 1980 and 2000 cm^{-1} . This strongly suggests that the structure of the molecule is as shown in Figure 2. This structure had D_{4d} symmetry, and, applying the usual symmetry analysis, it is found that just two infrared-active CO stretching modes, corresponding to the representations e_1 and b_2 , are expected. Of course, the rotationally eclipsed structure, with symmetry D_{4h} , would also have just two infrared-active CO stretching frequencies and is thus equally compatible with the

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TABLE I
CARBONYL STRETCHING FREQUENCIES OF
 $\text{Fe}_2(\text{CO})_8\text{I}_2$ AND $[\text{Fe}(\text{CO})_2\text{I}]_n$

Compound	Medium	Freq., ^a cm^{-1}
$\text{Fe}_2(\text{CO})_8\text{I}_2$	Pentane	2000 s, 1980 s
$\text{Fe}_2(\text{CO})_8\text{I}_2$	Tetrahydrofuran	2000 s, 1980 s
$\text{Fe}(\text{CO})_2\text{I}_2$	Pentane	2100 m, 2060 ms
$\text{Fe}(\text{CO})_2\text{I}_2$	Nujol ^b	2100 m, 2060 ms
$\text{Fe}(\text{CO})_2\text{I}_2$	Nujol ^c	2100 m, 2060 ms

^a s, strong; m, medium. ^b Prepared by the method reported here. ^c Prepared by the method of W. Hieber and H. Legally, *Z. Anorg. Allgem. Chem.*, **204**, 174 (1932).

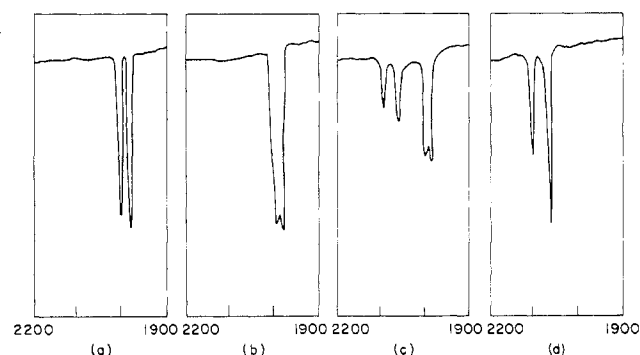


Figure 1.—Spectrophotometric titrations of $\text{Fe}_2(\text{CO})_8\text{I}_2$ with iodine: (a) spectrum of $\text{Fe}_2(\text{CO})_8\text{I}_2$ in pentane; (b) spectrum of $\text{Fe}_2(\text{CO})_8\text{I}_2$ in tetrahydrofuran; (c) $\text{Fe}_2(\text{CO})_8\text{I}_2$ plus 1 equiv of iodine (in tetrahydrofuran, after 4 min); (d) $\text{Fe}_2(\text{CO})_8\text{I}_2$ plus 2 equiv of iodine (in tetrahydrofuran, after 60 min).

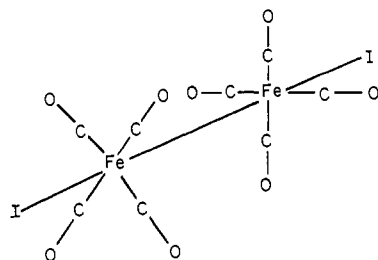


Figure 2.—The structure proposed for $\text{Fe}_2(\text{CO})_8\text{I}_2$.

available evidence. We cannot, however, conceive of any other structure which would, as a matter of principle, have such a simple spectrum.

The D_{4d} , or staggered, structure is preferred to the eclipsed one by direct analogy to the structures of iso-electronic molecules alluded to earlier.^{2,3,5}

An explanation of the red color which the compound possesses in the liquid phase and in solution is clearly required. We attribute this coloration to minute amounts of the mononuclear species $\text{Fe}(\text{CO})_4\text{I}$, produced by reversible dissociation of $\text{Fe}_2(\text{CO})_8\text{I}_2$.

The compound is moderately volatile, having a vapor pressure of ~ 45 torr at 25° . Vapor density measurements at room temperature show that in the gas phase dissociation is virtually complete at room temperature and pressures of a few torr. The vapor shows an extremely intense absorption rising into the ultraviolet region.

The tendency of $\text{Fe}_2(\text{CO})_8\text{I}_2$ to dissociate may be compared to that of other dinuclear species of the same type. $\text{Mn}_2(\text{CO})_{10}$ dissociates into $\text{Mn}(\text{CO})_5$ units at

high temperatures⁶ and $[\text{Co}_2(\text{CNCH}_3)_{10}]^{4+}$ is reported to form the mononuclear complex,⁷ $[\text{Co}(\text{CNCH}_3)_5]^{2+}$. There is also some evidence to suggest that $\text{Mn}_2(\text{CO})_8(\text{P}(\text{C}_6\text{H}_5)_3)_2$ exists under some conditions as the paramagnetic monomer,⁸ $\text{Mn}(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3$.

Reaction of $\text{Fe}_2(\text{CO})_8\text{I}_2$ with Iodine.—Spectrophotometric observation (Figure 1c and d) of the reaction of $\text{Fe}_2(\text{CO})_8\text{I}_2$ with iodine shows that 1 mole of iodine can be consumed per mole of $\text{Fe}_2(\text{CO})_8\text{I}_2$. On a preparative scale, the known compound⁹ $\text{Fe}(\text{CO})_2\text{I}_2$ has been isolated and identified.

The infrared spectrum of this compound has two CO stretching bands (Table I, Figure 1) consistent with a *cis* arrangement of the CO groups. On this basis we suggest that this compound is structurally analogous to $[\text{Ru}(\text{CO})_2\text{I}_2]_n$ and $[\text{Mo}(\text{NO})_2\text{Cl}_2]_n$ which are believed to have a kinked-chain structure (Figure 3).¹⁰ It is of interest that, when the compound is prepared in tetrahydrofuran by oxidation of $\text{Fe}_2(\text{CO})_8\text{I}_2$, it remains in solution and allows determination of the infrared spectrum (Table I, Figure 1) whereas, once isolated or prepared by Hieber's method,⁸ it is insoluble. This suggests to us that the compound present in solution in tetrahydrofuran (THF) is possibly a solvated octahedral species, such as $\text{Fe}(\text{CO})_2\text{I}_2(\text{THF})_2$, in which the two CO groups must be in *cis* positions in order to account for the appearance of two strong CO stretching modes in the infrared spectrum.

Experimental Section

All solvents were purified and degassed before use. All manipulations were carried out under nitrogen or under vacuum. The infrared spectra were recorded with a Perkin-Elmer Model 237 spectrophotometer.

Preparation of $\text{Fe}_2(\text{CO})_8\text{I}_2$.—A three-necked flask fitted with condenser, stirrer, and gas inlet was flushed with nitrogen, and triiron dodecacarbonyl (10 g) and tetrahydrofuran (200 ml) were introduced. Iodine (7 g) in tetrahydrofuran (50 ml) was added dropwise with stirring over a period of 3 hr. The reaction mixture was allowed to stand overnight and then water (250 ml) and pentane (three 10-ml portions) were added. The mixture was shaken vigorously and the pentane layer was separated and dried over calcium chloride. In order to isolate the product, the material was distilled into a vacuum line through a series of U traps maintained at 0° (containing CaCl_2), -55° , and -196° . The product was collected in the -55° trap. It was refractionated and collected at -40° . Yields were typically about 0.3 g ($\sim 2\%$).

Anal. Calcd for $\text{Fe}_2(\text{CO})_8\text{I}_2$: Fe, 18.95; I, 43.14; CO, 38.01. Found: Fe, 19.2; I, 41.6; CO, 38.5.

The analyses for CO were carried out by one or both of two methods for samples obtained in different preparations. (1) The compound was treated with excess of a hot pyridine-iodine mixture on a vacuum line and the volume of CO evolved was measured. (2) The compound was treated with an excess of a 30% H_2O_2 - CH_3COCH_3 mixture and the evolved CO_2 was dissolved in standard base, the excess of which was back-titrated with standard acid.

The molecular weight of the vapor was determined by measuring the vapor density at $\sim 25^\circ$ using a simple vacuum line apparatus. In a typical experiment the following conditions ob-

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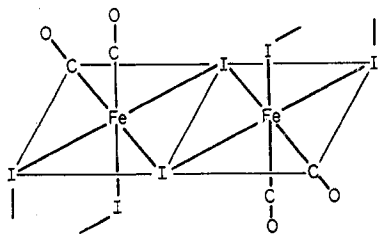


Figure 3.—The structure proposed for $[\text{Fe}(\text{CO})_2\text{I}_2]_n$.

tained: 27°, 11.4 ml, 35 torr, weight of sample 6.6 mg. From these data a molecular weight of 305 ± 10 was obtained. Other similar measurements gave values of 290, 270, and 300, all ± 10 . The average, 290, may be compared with the theoretical value of 295 for $\text{Fe}(\text{CO})_4\text{I}$. The approximate equilibrium vapor pressure over the liquid at 25° is 45 torr.

The diamagnetism of the compound in xylene solution at 25° was demonstrated by the nmr method of Evans.¹¹

Preparation of $\text{Fe}(\text{CO})_2\text{I}_2$.— $\text{Fe}_2(\text{CO})_9\text{I}_2$ in tetrahydrofuran was treated with 2 equiv of iodine in the same solvent. After shaking for 1 hr the solvent was removed under vacuum. A dark brown powder was obtained. This product was insoluble in a wide range of solvents and decomposed instantaneously on contact with air.

$\text{Fe}(\text{CO})_2\text{I}_2$ was also obtained by the method of Hieber and Legally.⁹

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Studies Involving Some Nonmetal Oxy- and Thiofluoride Salts

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Some recent publications describe the reactions of carbonyl fluoride, perfluoroalkylacyl fluorides, and ketones with alkali metal fluorides.¹⁻³ It was of interest to extend this study to other compounds. For example, in the case of thionyl tetrafluoride, SF_4O , the reaction with cesium fluoride led to the formation of the complex pentafluorosulfoxide anion, SF_5O^- . This ion has been considered to be an intermediate when thionyl fluoride, SF_2O , or SF_4O is fluorinated in the presence of cesium fluoride to form pentafluoro-sulfur hypofluoride, SF_5OF ,⁴ but the intermediate has always been prepared *in situ* and no details have been reported regarding its preparation or properties. No attempt was made to isolate the pure CsOSF_5 salt because it slowly decomposes to SF_4O and cesium fluoride, and only a partial characterization of the complex salt is presented below.

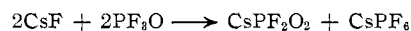
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When phosphoryl fluoride, PF_3O , was used as a substrate toward cesium fluoride, there was no evidence for the formation of the PF_4O^- ion. Instead, an oxygen for fluorine-exchange reaction occurred and equimolar quantities of two products—cesium difluorodioxophosphate, CsPO_2F_2 ,⁵ and cesium hexafluorophosphate, CsPF_6 —were formed according to the equation



The corresponding thio derivative, PF_3S , behaved in a similar manner toward attack by cesium fluoride and quantitatively produced the new difluorodithiophosphate ion,⁶ PF_2S_2^- , as well as the PF_6^- ion. This same reaction now has also been found to take place nearly quantitatively when potassium fluoride is employed. Similarly, reaction between thiophosphoryl chloride, PSCl_3 , and potassium fluoride also yields the fluorophosphates, KPS_2F_2 and KPF_6 , by the route



The alkali metal difluorodithiophosphate salts have been converted to the corresponding tetraphenylarsonium and bis(triphenylphosphine)immonium derivatives. The infrared and ¹⁹F nmr spectra of the pentafluorosulfoxide and the difluorodithiophosphate ions have been examined.

Experimental Section

Reagents.—Thiophosphoryl trichloride and the potassium and cesium fluorides were procured from Alfa Inorganics, Inc. The alkali metal fluorides were heated to 300° while pumping and then ground to fine powders before using. The trichloride was converted to the trifluoride by the method of Tullock and Coffman⁷ and it was purified by gas partition chromatography using a 15-ft perfluorotri-*t*-butylamine on Chromosorb P column at -30°. All solvents were dried by storage over 5A molecular sieves.

Apparatus and General Procedure.—A standard Pyrex vacuum apparatus was used for transfer and purification of gaseous materials. All chemicals were handled with the strict exclusion of moisture. The reactors were 50-ml thick-walled Pyrex bulbs with Fisher-Porter Teflon valves unless otherwise stated. Infrared spectra of the solids were taken as Nujol mulls using a Perkin-Elmer 521 spectrometer in the 4000-200- cm^{-1} region. Cesium bromide plates were employed. Salts containing the known PO_2F_2^- and PF_6^- ions were identified by the infrared bands near 1140 and 1310 cm^{-1} in the spectra of the former and near 840 cm^{-1} in those containing the latter. The ¹⁹F nmr spectra were obtained with a Varian Model V4310 spectrometer operating at 40 Mc using dimethyl sulfoxide, DMSO, as a solvent for the samples and fluorotrichloromethane as an internal standard. Samples were placed in 5-mm o.d. Pyrex tubes.

Reaction between CsF and PF_3O . **A. Neat.**—Cesium fluoride, 0.817 g (5.36 mmoles), was charged into the reactor. While holding the vessel at -196°, PF_3O (5.50 mmoles) was added. The bulb was then heated to 100° for 1 hr. A small pressure decrease was observed, and then the temperature of the reactor was raised to 135° for a 24-hr interval. A small amount of PF_3O remained in the gas phase. After pumping to constant weight the increase in weight of the solid phase corresponded to the absorption of 5.35 mmoles of PF_3O or 99.5% yield based on a 1:1 PF_3O to CsF mole ratio. The PF_2O_2^- and PF_6^- ions were identified by comparing their infrared and nmr spectra with the

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