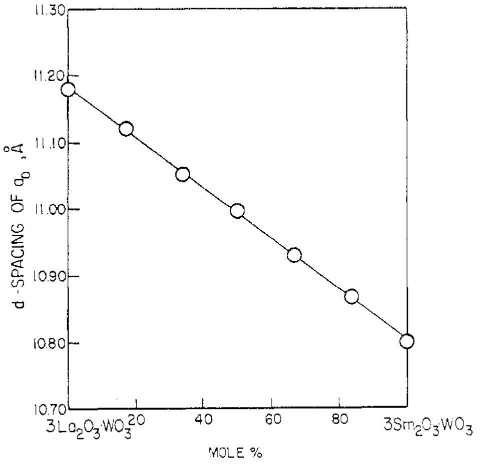

Fig. 2.—Diagram illustrating values of $a_0$ for compositions in the $3(La_xSm_{2-x}O_3) \cdot WO_3$ series.

are simple and can be indexed easily as those of a face-centered cubic unit cell. By comparison with several common known structural types of mixed oxides, both compounds have a similar structure and can be classed as disordered pyrochlore (or ordered defect fluorite[4]) with $a_0 = 10.80$ Å. for $3Sm_2O_3 \cdot WO_3$ and $a_0 = 11.18$ Å. for $3La_2O_3 \cdot WO_3$. The X-ray powder data of and the composition–structure relations among the two compounds, an ordered pyrochlore and fluorite, are presented in Table I and Fig. 1.[5] The presence of specific reflections in the patterns of the tungstates, *e.g.*, the 200 and 422 in $3La_2O_3 \cdot WO_3$, requires the use of pyrochlore cell sizes. Reducing the *hkl* values to correspond to a fluorite cell results in odd–even combinations which are prohibited in face-centered cubic lattices.

The disordering of both $3Sm_2O_3 \cdot WO_3$ and $3La_2O_3 \cdot WO_3$ is shown by the absence of the three distinct ordering reflections (111), (331), and (531) which exist for ordered pyrochlore. The intensity of the reflection (200) of a disordered pyrochlore is found to be a function of composition in the $3(La_xSm_{2-x}O_3) \cdot WO_3$ series. The more samarium contained, the lower is the intensity of the reflection (200), and it can be barely detected in the $3Sm_2O_3 \cdot WO_3$ phase, indicating a decrease in order with an increase in samarium content. Attempts to develop ordering of the type that exists in an ordered pyrochlore by heat treatment at 800 and 1000° for 4 days were unsuccessful.

Plotting the nominal values of $a_0$ calculated from the last seven diffraction lines of the disordered pyrochlore structure against composition in the $3(La_xSm_{2-x}O_3) \cdot WO_3$ series shows a close correlation with Vegard's law (Fig. 2). This could be expected in view of the similarity of lanthanum and samarium.

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[5] It deserves mention that by coincidence the *d*-spacing values and relative intensities of the $3Sm_2O_3 \cdot WO_3$ end member prepared in this study are similar to those reported for the zinc blende form of ZnS. The mixed oxide, cannot, of course, be of the zinc blende type, but the similarity is deceiving and therefore noteworthy.

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## Tricarbonyl(condensed aromatic)iron(0) Complexes

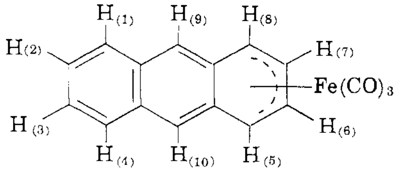
BY T. A. MANUEL

*Received June 22, 1964*

Benzene and its simple substitution products have not been reported to form isolable iron carbonyl complexes. However, extended conjugation appears to permit the π-electrons of a benzene ring to participate in bonding to iron carbonyl groups, as has been demonstrated in the cases of hexacarbonyl(*m*- or *p*-divinylbenzene)diiron[1] and hexacarbonyl(acenaphthalene)diiron.[2] The compounds tricarbonyl(naphthalene)iron and tricarbonyl(anthracene)iron have been briefly described,[3] the former being identified only by infrared analysis. Seeking to learn more about these two compounds and about the extent of conjugation needed to permit complex formation between aromatics and iron tricarbonyl groups, we have investigated the reactions between iron carbonyls and naphthalene, anthracene, 1-vinylnaphthalene, and 9-acetylanthracene.

Among the products of the treatment of naphthalene with pentacarbonyliron or dodecacarbonyltriiron we have found evidence of only one iron carbonyl complex, isolated only in trace amounts, and in less than analytical purity. This material has been shown to contain appreciable amounts of sulfur, and its infrared and n.m.r. spectra identify it as hexacarbonyl(thianaphthene)diiron.[4] This compound may well be identical with Harper's "naphthalene-iron tricarbonyl."[3]

We have also obtained the tricarbonyl(anthracene)-iron reported by Harper.[3] The n.m.r. spectrum (Table I) of the slightly soluble compound is consistent with structure I, in which the iron atom is bonded to a terminal ring. For comparison we include the n.m.r.



I

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[1] T. A. Manuel, S. L. Stafford, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3597 (1961).

[2] R. B. King and F. G. A. Stone, *ibid.*, **82**, 4557 (1960).

[3] R. J. Harper, U. S. Patent 3,073,855 (Jan. 15, 1963) (assigned to the Ethyl Corporation).

[4] R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).

TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRA

| Compound | Resonance, $\tau$ | Relative intensity | Structure[a] | H assignment |
|---|---|---|---|---|
| Anthracene[5,b,c] | 1.62 | 2 | s | 9, 10 |
| | 2.05 | 4 | q | 1, 4, 5, 8 |
| | 2.58 | 4 | q | 2, 3, 6, 7 |
| $Fe(CO)_3(C_{14}H_{10})$[c] | 2.78 | 4 | d, c | 1, 2, 3, 4 |
| (I) | 3.10 | 2 | s | 9, 10 |
| | 3.80 | 2 | d, c | 6, 7 |
| | 6.30 | 2 | d, c | 5, 8 |
| $Cr(CO)_3(C_{14}H_{10})$[6,b,d] | 2.85 | 2 | s | 9, 10 |
| | 2.95 | 2 | c | 1, 4 |
| | 3.35 | 2 | c | 2, 3 |
| | 4.97 | 2 | c | 5, 8 |
| | 5.43 | 2 | c | 6, 7 |
| $Fe(CO)_3(C_{12}H_{10})$[c] | 1.88 | 1 | d | 3, 5, 6, 7, 8, 9, 10 |
| (II) | 2.65 | 3 | d | |
| | 2.90–3.90 | 3 | c | |
| | 7.52 | 1 | d, $J$ = 7 c.p.s. | 4 |
| | 8.23 | 1 | dd, $J$ = 7, 3 c.p.s. | 1 |
| | 9.80 | 1 | dd, $J$ = 7, 3 c.p.s. | 2 |

[a] s, singlet; d, doublet; q, quartet; c, complex; dd, double doublet. [b] Numbered as in I. [c] Deuteriochloroform solution. [d] Hexadeuteriobenzene solution.

spectra of anthracene[5] and tricarbonyl(anthracene)-chromium,[6] which also involves a terminal ring–metal bond. The spectra of the chromium and iron complexes resemble one another only in the general respect that complex formation causes shifts to higher fields.

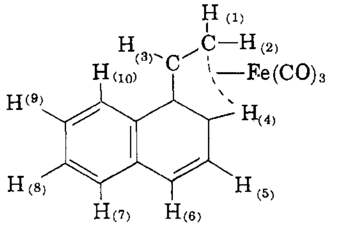
The assignments of the absorption at $\tau$ 3.80 to the center protons (6 and 7) on the complexed diene system and of the absorption at $\tau$ 6.30 to the terminal protons (5 and 8) on the complexed diene system are consistent with earlier data.[7] The spectrum of the entire ligand has undergone a significant shift to a higher field upon complex formation.

Structure I leaves a more stable "free" aromatic system than would the alternative having the iron atom attached to the center ring.

Treatment of 9-acetylanthracene with dodecacarbonyltriiron has yielded tricarbonyl(9-acetylanthracene)-iron, the n.m.r. spectrum of which (new bands at $\tau$ 3.17, 3.83, and 6.42, shift of methyl protons from $\tau$ 7.32 to 7.53) indicates a structure similar to that of tricarbonyl(anthracene)iron.

Although substitution of a single vinyl group on benzene did not activate the ring sufficiently to permit the preparation of tricarbonyl(styrene)iron,[1] 1-vinylnaphthalene has been found to react readily with dodecacarbonyltriiron to give tricarbonyl(1-vinylnaphthalene)iron. The n.m.r. spectrum (Table I) of the compound clearly shows that the vinyl group is involved in the bonding to iron (structure II) as in the case of the divinylbenzene–iron complexes.[1]

The bands at $\tau$ 8.23 and 9.80, assigned to protons 1 and 2, are very similar to those at $\tau$ 8.32 and 9.78, assigned to the terminal protons in tricarbonyl(butadiene)iron.[7,8] The positions of the bands due to protons 3 and 4 are likewise expected.[7] Tricarbonyl(1-vinylnaphthalene)iron did not absorb hydrogen under mild conditions, showing that both rings of the complexed naphthalene system retain some aromaticity.



II

Apparently, then, one may anticipate the formation of iron carbonyl complexes of aromatic compounds with a more extended $\pi$-electron system than that of naphthalene. These compounds appear to be fully as stable as ordinary tricarbonyl(conjugated diene)-iron complexes; the difficulty lies simply in obtaining sufficient activation of the ligand to permit complex formation.

## Experimental

**General.**—Naphthalene (Matheson Coleman and Bell), anthracene (Eastman, "blue-violet fluorescence"), 9-acetylanthracene (Aldrich Chemical Co.), and 1-vinylnaphthalene (Monomer-Polymer Laboratories) were used without further purification. Reactions and chromatography on alumina were carried out under nitrogen.

Microanalyses and molecular weight determinations (osmometric, in chloroform) were performed by Galbraith laboratories, Inc., Knoxville, Tenn., and the Analytical Research Division of this company. The 2200–1600 cm.$^{-1}$ region of the infrared spectrum was studied in cyclohexane solution on a Perkin-Elmer Model 421 instrument, with a resolution of 1 cm.$^{-1}$, except as otherwise noted. Nuclear magnetic resonance spectra were recorded on a Varian A-60 instrument with tetramethylsilane as internal standard[9]; line positions are reported as p.p.m. on the $\tau$ scale.

**The Treatment of Naphthalene with Pentacarbonyliron.**—A mixture of 5.0 g. (39 mmoles) of naphthalene and 29 g. (150

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(5) R. H. Martin, N. Defay, F. Geerts-Evrard, and S. Delavarenne, *Tetrahedron*, **20**, 1073 (1964).

(6) B. R. Willeford and E. O. Fisher, *Naturwissenschaften*, **51**, 38 (1964).

(7) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 594 (1961).

(8) M. L. H. Green, L. Pratt, and G. Wilkinson, *ibid.*, 3753 (1960).

(9) We acknowledge the help of Dr. J. J. Elliott in obtaining infrared spectra, of Mr. J. J. Waters in obtaining n.m.r. spectra,and of Dr. J. M. Kelliher in obtaining mass spectrometric data.

mmoles) of pentacarbonyliron in 20 ml. of ethylcyclohexane was heated in a bath at 130° for 64 hr. The cooled mixture was filtered, and the filtrate was chromatographed. The orange solution eluted by pentane was evaporated, and the residue was dissolved in 20 ml. of pentane. The solution was cooled to $-78°$ and filtered. Evaporation of the filtrate followed by fractional sublimation (product taken at 90° (0.1 mm.)) gave 10 mg. of red-orange solid, m.p. 88°, dec. 145°. Combination of the products from a number of such runs gave sufficient material for analysis and spectroscopic studies. Duplication of the procedure in the literature[3] employing dodecacarbonyltriiron gave the same product.

The infrared spectrum of the material showed carbonyl stretching bands (carbon disulfide solution, NaCl optics) at approximately 2079, 2045, and 2008 cm.$^{-1}$ (lit.[4] 2076, 2044, 2004, and 1992 cm.$^{-1}$). Its n.m.r. spectrum showed bands at $\tau$ 0.97, 2.93, and 4.50 (*vs.* external tetramethylsilane), with the relative intensities and coupling constants reported for the bands of hexacarbonyl(thianaphthene)diiron at $\tau$ 1.10, 3.05, and 4.60 (*vs.* internal tetramethylsilane).[4]

*Anal.* Calcd. for $C_{14}H_6O_6SFe_2$: C, 40.61; H, 1.46; S, 7.74; mol. wt., 414. Found: C, 41.64; H, 2.32; S, 7.20; mol. wt , 424.

**The Reaction between Anthracene and Dodecacarbonyltriiron.**—A mixture of 1.8 g. (10 mmoles) of anthracene with 8.0 g. (16 mmoles) of dodecacarbonyltriiron in 100 ml. of cyclohexane was heated in a bath at 90° for 48 hr. The cooled mixture was filtered, and the filtrate was chromatographed. The orange solution eluted with a 4:1 pentane–dichloromethane mixture was evaporated. After sublimation of the solid product at 90° (0.1 mm.) for 12 hr., the unsublimed portion was crystallized several times from a chloroform–cyclohexane mixture to give 100 mg. (3% yield) of fine orange needles of the complex, dec. 140°. The actual conversion to product was much higher, but freeing the complex from traces of excess anthracene was exceedingly difficult. The infrared spectrum of the compound showed carbonyl stretching bands at 2054 (s), 1993 (s), and 1975 (s) cm.$^{-1}$. Mass spectrometric analysis showed the hydrocarbon moiety of the complex to be anthracene.

*Anal.* Calcd. for $C_{17}H_{10}O_3Fe$: C, 64.18; H, 3.16; S, 0.0; mol. wt., 318. Found: C, 64.29; H, 3.21; S, 0.05; mol. wt., 357.

**The Reaction between 9-Acetylanthracene and Dodecacarbonyltriiron.**—A mixture of 2.0 g. (9 mmoles) of 9-acetylanthracene and 5.0 g. (10 mmoles) of dodecacarbonyltriiron in 100 ml. of cyclohexane was heated in a bath at 90° for 21 hr. The cooled mixture was filtered, and the filtrate was chromatographed. The orange solution eluted with a 3:2 pentane–dichloromethane mixture was evaporated. Three crystallizations (pentane–dichloromethane) of the residue gave 100 mg. (3% yield) of orange solid, m.p. 135° dec. Again the complex was formed in more substantial amounts, but freeing it from excess ligand was difficult. The infrared spectrum of the compound showed carbonyl stretching bands at 2061 (s), 2056 (s), 2003 (s), 1995 (s), 1982 (s), and 1698 (w) cm.$^{-1}$.

*Anal.* Calcd. for $C_{19}H_{12}O_4Fe$: C, 63.36; H, 3.35; mol. wt., 360. Found: C, 63.19; H, 3.28; mol. wt., 354.

**The Reaction between 1-Vinylnaphthalene and Dodecacarbonyltriiron.**—A mixture of 1.8 g. (14 mmoles) of 1-vinylnaphthalene and 5.0 g. (10 mmoles) of dodecacarbonyltriiron in 100 ml. of cyclohexane was heated in a bath at 90° for 16 hr. The cooled mixture was filtered, and the filtrate was chromatographed. The orange solution eluted by a 4:1 pentane–dichloromethane mixture was evaporated, and two crystallizations (pentane–dichloromethane) of the residue gave 1.25 g. (31% yield) of orange crystals, m.p. 92–95°. A portion was recrystallized to an analytical sample, m.p. 94–96°. The infrared spectrum of the compound showed carbonyl stretching bands at 2048 (s), 1983 (s), and 1973 (s) cm.$^{-1}$.

*Anal.* Calcd. for $C_{15}H_{10}O_3Fe$: C, 61.25; H, 3.42; mol. wt., 294. Found: C, 61.48; H, 3.56; mol. wt., 278.

The compound did not absorb hydrogen at atmospheric pressure over palladium-on-charcoal catalyst in ethanol. It reacted with triphenylphosphine at room temperature in acetone solution to give tricarbonylbis(triphenylphosphine)iron and tetracarbonyl(triphenylphosphine)iron, identified by their infrared spectra.[10]

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(10) F. A. Cotton and R. V. Parish, *J. Chem. Soc.*, 1440 (1960).

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## Study of the Relative Solubilities of Diastereoisomers of Cobalt(III) Complexes Containing Optically Active Amino Acids[1]

BY CHONG TAN LIU AND BODIE E. DOUGLAS

*Received July 13, 1964*

The most generally used method for the resolution of optically active complex ions involves the fractional crystallization or precipitation of diastereoisomers. A solubility rule has been used[2,3] for relating the configurations of octahedral complexes based on the expectation that, for similar complexes resolved with the same resolving agent, the configurations will be the same for all of the complexes with the same relative solubilities of their diastereoisomers. Jaeger[4] at first criticized the solubility rule and later used it in his own work.[5]

The complexes for which the solubility rule has been applied differ in the chirality of the spiral arrangement of the chelate rings formed by the bidentate ligands AA in complexes of the type $[M(AA)_3]^{n+}$ or *cis*-$[M(AA)_2X_2]^{n+}$. The present study was concerned with complexes of the type $[Co(en)_2aa]^{2+}$ (aa = bidentate amino acid anion) using L- and D-alanine (alan), L- and D-leucine (leuc), L- and D-phenylalanine (palan), glycine (gly), and picolinic acid (pic). L and D refer to the absolute configurations of the amino acids.

The preparations of the complexes have been described.[6] The unresolved complexes as the iodide salts (in solution) were converted to the diastereoisomers by adding equivalent amounts of the silver salt of the resolving agent to remove all of the iodide ions as AgI. The diastereoisomers were fractionally separated by either: (1) slow crystallization from aqueous solution by cooling or by evaporation at room temperature, or (2) adding at least an equal volume of an organic solvent followed by slow crystallization. The first method was used for the diastereoisomers which

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(1) This work was supported by a research grant (GM10829-06S1) from the Division of General Medical Studies, Public Health Service.

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