is appreciably changed from that of pure sodium perchlorate solution. This is especially true in the case of heptafluorobutyrate where the plots exhibited a good deal of curvature. Extrapolation of large scale plots of $F_1(X)$ to zero perfluorocarboxylate concentration yielded the values for β_1. Extrapolation of $F_2(X)$ yielded values for β_2 which agreed quite well with the limiting slope of $F_1(X)$.

The results of the potentiometric method are summarized in Tables IV–VI. Plots of $F(X)$ *vs.* the concentration of perfluorocarboxylate were found to be essentially linear functions with a positive slope, indicating a two-step equilibrium for the complex. The values of β_1 and β_2 were obtained from the intercepts and slopes of the plots.

The formation (stability) constants for lead with all three perfluorinated anions (Table VII) indicate that the complexes are very weak and are of about the same degree of stability. The extreme curvature in the $F_2(X)$ polarographic plot for heptafluorobutyrate suggested that a higher complex might be present at high ligand concentration. A similar curvature was obtained in the $F(X)$ potentiometric plot for heptafluorobutyrate.

TABLE VII

FORMATION CONSTANTS FOR LEAD PERFLUOROCARBOXYLATE COMPLEXES AT 25°

Ligand	β_1	β_2	Method
CF_3COO^-	1.04	0.73	Polarography
CF_3COO^-	0.93	0.33	Potentiometry
$CF_3CF_2COO^-$	0.93	0.98	Polarography
$CF_3CF_2COO^-$	0.61	0.46	Potentiometry
$CF_3CF_2CF_2COO^-$	0.62	1.00	Polarography
$CF_3CF_2CF_2COO^-$	0.44	0.45	Potentiometry

Evaluation of experimental uncertainty resulted in a limit of ±0.35 for the formation constants from both methods of measurement.

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CONTRIBUTION FROM THE
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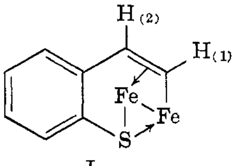
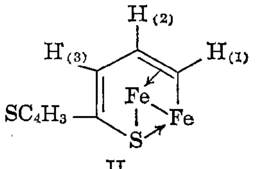
Iron Carbonyl Derivatives of 2,2′-Dithienyl and *o*-Aminobenzenethiol

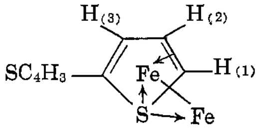
BY T. A. MANUEL AND T. J. MEYER

Received December 31, 1963

The treatment of thiophene with triiron dodecacarbonyl was found to yield the sulfur-free ferrole, $C_4H_4Fe_2(CO)_6$, as well as sulfur-containing complexes which were not isolated.[1] In a study suggested by the results of the thiophene–iron carbonyl experiments a series of hexacarbonyl(alkylvinyl sulfide)diiron complexes was prepared.[2] These complexes were shown to be similar in structure to hexacarbonyl(thianaphthene)diiron,[3] for which structure I was proposed.[2,4]

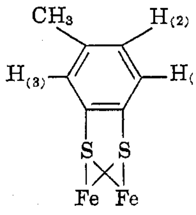

I

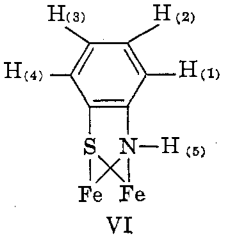

II

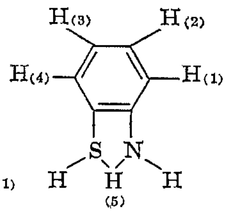

III

In the hope of isolating iron carbonyl complexes of a thiophene ring by utilizing the stabilizing influence of a potentially chelating ligand, we have treated 2,2′-dithienyl[5] with iron carbonyl. From this reaction we have obtained hexacarbonyl(2,2′-dithienyl)diiron. The n.m.r. spectrum of this complex (Table I) shows clearly that only one thiophene ring is involved in the bonding to iron; the data may be explained by a structure II, analogous to I.[6] However, on the basis of the available evidence one may not exclude structures of type III, in which the carbon–sulfur bond has not been broken, for the diiron hexacarbonyl complexes of 2,2′-dithienyl, thianaphthene, and alkylvinyl sulfides.[2]

The carbonyl stretching bands of the dithienyl complex, at 2079 (s), 2046 (vs), 2011 (vs), 2006 (vs), 1996 (m), and 1963 (vw) cm.$^{-1}$, may be compared to those of the oils obtained from treatment of thiophene with iron carbonyl, at 2072 (s), 2035 (vs), 2000 (vs), 1989 (vs), and 1956 (vw) cm.$^{-1}$,[1] those of the thianaphthene complex at 2076 (m), 2044 (vs), 2004 (s), and 1992 (m) cm.$^{-1}$,[2] and those of the complex prepared from 3,4-toluenedithiol, for which structure IV was proposed, at 2080 (s), 2045 (vs), 2030 (vs), 2000 (vs), and 1990 (s) cm.$^{-1}$.[7]


IV


VI


V

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[1] H. D. Kaesz, R. B. King, T. A. Manuel, L. D. Nichols, and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 4749 (1960).

[2] R. B. King, P. M. Treichel, and F. G. A. Stone, *ibid.*, **83**, 3600 (1961).

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TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRA

Compound or structure	Line position (τ)	Relative intensity	Structure	Assignment
2,2′-Dithienyl	3.03	1	Complex multiplet	
II or III	1.15	1	Doublet, $J = 9$ c.p.s.	$H_{(1)}$
	3.07	3	Identical with that from 2,2′-dithienyl	Uncomplexed thiophene ring
	3.66	1	Doublet, $J = 5$ c.p.s.	$H_{(3)}$
	4.98	1	Double doublet, $J_{21} = 9$ c.p.s. $J_{23} = 5$ c.p.s.	$H_{(2)}$
I[2]	1.10	1	Doublet, $J = 9$ c.p.s.	$H_{(1)}$
	3.05	4	...	Aromatic protons
	4.60	1	Doublet, $J = 9$ c.p.s.	$H_{(2)}$
IV[7]	3.11	2	...	$H_{(1)}$ and $H_{(3)}$
	3.61	1	Doublet, $J = 8$ c.p.s.	$H_{(2)}$
	7.93	3	...	Methyl group
V	2.80	1	Doublet, $J = 7$ c.p.s.	$H_{(1)}$ or $H_{(4)}$
	3.09	1	Doublet, $J = 7$ c.p.s.	
	3.47	2	Triplet, $J = 7$ c.p.s.	$H_{(2)}$ and $H_{(3)}$
	6.42	3	Singlet	$H_{(5)}$
VI	3.12	1	Doublet, $J = 7$ c.p.s.	$H_{(4)}$
	3.65	3	Complex multiplet	$H_{(1)}$, $H_{(2)}$, and $H_{(3)}$
	7.5	1	Very broad	$H_{(5)}$

Treatment of chromium hexacarbonyl in ethylcyclohexane with 2,2′-dithienyl gave traces of a red material, not isolated in the pure state, having carbonyl stretching bands at 1978 (s), 1913 (m), and 1898 (m) cm.$^{-1}$. The compound tricarbonyl(thiophene)chromium[8] has carbonyl stretching bands at 1977, 1907, and 1889 cm.$^{-1}$.[9] In contrast to its behavior with iron carbonyl, in this case 2,2′-dithienyl functions as an aromatic ligand, as does thiophene itself.

While organosulfur compounds give iron carbonyl derivatives of the type mentioned above, only by indirect methods have compounds been obtained having NH or NH_3 groups and CO groups bonded to the same metal atom, *e.g.*, $[Fe(CO)_3NH]_2$.[10] Treatment of primary amines with iron carbonyls normally involves disproportionation to products containing complex iron–amine cations and iron carbonyl anions.[11]

Thus, NH_2 and SH groups in a single ligand molecule might promote the formation of different types of iron carbonyl complex. Indeed, the reaction between *o*-aminobenzenethiol (V) and iron carbonyl yields, in addition to insoluble, pyrophoric materials, a red, volatile, crystalline complex, $Fe_2(CO)_6C_6H_4SNH$, presumably having bridging RS and RNH groups. Its infrared spectrum, having bands at 2077 (s), 2042 (vs), 2002 (vs), and 1996 (vs) cm.$^{-1}$, supports a structure (VI) analogous to that (IV) of the complex from toluenedithiol. A similar band pattern was found for a material formed in trace amounts in the reaction between 2-aminoethanethiol hydrochloride and triiron dodecacarbonyl. The n.m.r. spectra of *o*-aminobenzenethiol and the complexes from *o*-aminobenzenethiol and 2,4-toluenedithiol may be assigned on the basis of structures V, VI, and IV (Table I).

Experimental

General.—Practical grade *o*-aminobenzenethiol (Matheson Coleman and Bell) was used without further purification; 2,2′-dithienyl was prepared as described in the literature.[5] Reactions and chromatography were carried out under nitrogen.

Microanalyses and molecular weight determinations (osmometric, in benzene) were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, and the Analytical Research Division of this company. The 2200–1800 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.$^{-1}$.[12] Nuclear magnetic resonance spectra[11] were recorded on a Varian A-60 instrument for carbon disulfide solutions with tetramethylsilane as internal standard.

Reaction between 2,2′-Dithienyl and Triiron Dodecacarbonyl.—A mixture of 1.7 g. (10 mmoles) of 2,2′-dithienyl and 1.7 g. (3.3 mmoles) of triiron dodecacarbonyl in 50 ml. of cyclohexane was stirred and heated in a 95° bath for 21 hr. The cooled mixture was chromatographed on alumina. The eluates obtained with pentane were evaporated to 1.5 g. of oily red solid. This material was heated to 55° (0.1 mm.) under a probe cooled to −78°; the orange-tinted sublimate (unreacted ligand) was discarded. The unsublimed portion was twice crystallized (pentane) to give 120 mg. of fine red needles, m.p. 133–134° (5.6% yield). Thermal decomposition of an acetone solution of this material in the inlet to a Bendix time-of-flight mass spectrometer gave one part of 2,2′-dithienyl and six parts of carbon monoxide.

Anal. Calcd. for $C_{14}H_6O_6S_2Fe_2$: C, 37.69; H, 1.35; S, 14.37; mol. wt., 446. Found: C, 38.30, 37.60; H, 1.62, 1.47; S, 14.10; mol. wt., 464.

A second product, which could not be entirely freed from the main one, could be obtained in low yield by fractional sublimation of the reaction mixtures. This substance, more volatile than the main product, of m.p. 82–83°, with carbonyl stretching

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[8] E. O. Fischer and K. Öfele, *Ber.*, **91**, 2395 (1958).

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[10] W. Hieber and H. Beutner, *Z. anorg. allgem. Chem.*, **317**, 63 (1962).

[11] W. Hieber, W. Beck, and G. Braun, *Angew. Chem.*, **72**, 795 (1960).

[12] We gratefully 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 Mr. E. S. McBride and Dr. P. E. Butler in obtaining and interpreting mass spectrometric data.

bands at 2073, 2040, 2006, 1998, and 1957 cm.$^{-1}$, might be a partially desulfurized complex analogous to the $C_4H_4Fe_2(CO)_6$ formed from thiophene itself.[1]

Anal. Calcd. for $C_{14}H_6O_6SFe_2$: C, 40.61; H, 1.46; S, 7.74; mol. wt., 414. Found: C, 39.80; H, 1.58; S, 6.21; mol. wt., 458.

Reaction between *o*-Aminobenzenethiol and Triiron Dodecacarbonyl.—A mixture of 2.50 g. (20 mmoles) of *o*-aminobenzenethiol and 6.0 g. (12 mmoles) of triiron dodecarbonyl in 60 ml. of cyclohexane was stirred for 45 min. in a bath at 80°. The cooled mixture was chromatographed on alumina. (Filtration of other runs yielded quantities of intractable, insoluble, pyrophoric, red solids.) The eluates obtained with pentane were discarded; a 1:1 pentane-dichloromethane mixture eluted a deep red solution, which was evaporated to a sticky orange solid. Impurities were sublimed away (70° (0.1 mm.)) and the residue was crystallized (pentane) to 200 mg. of brick-red solid, m.p. 106–108° (2.5% yield).

Anal. Calcd. for $C_{12}H_5O_6NSF_2$: C, 35.76; H, 1.25; N, 3.47; S, 7.95; mol. wt., 403. Found: C, 35.58; H, 1.60; N, 3.55; S, 7.86; mol. wt., 420.

In addition to the carbonyl stretching bands the infrared spectrum (CS_2 solution, NaCl optics) showed bands at 3330 (N–H stretching), 3067, 2959 (C–H stretching), and 746, 725 (C–H deformation) cm.$^{-1}$. Thermal decomposition of an acetone solution of the complex gave primarily aniline, identified by mass spectrometric techniques.[12]

CONTRIBUTION FROM THE CHEMISTRY DIVISION,
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Hydrolysis of Tantalum(V): Equilibrium Ultracentrifugation and Raman Spectra of Potassium Tantalate[1]

BY J. AVESTON[2] AND JAMES S. JOHNSON

Received January 23, 1964

The comparative dearth of information on the solution chemistry of tantalum is in marked contrast to the abundance of data in the literature on the hydrolytic behavior of the elements in adjacent groups. This stems from the fact that the oxide is soluble only in complexing media such as hydrofluoric acid, or in strongly basic solution, where the degree of hydrolysis of the tantalate species appears to be essentially constant. The more popular methods which have been used to establish both the stoichiometry and degree of aggregation of such species in solution, such as potentiometric and conductometric titrations, are therefore inapplicable, and the use of some direct method for the determination of ionic weight is especially indicated.

Jander and Ertel,[3] on the basis of measurements by the much criticized diffusion method, reported that in alkaline solutions of Ta(V), the $Ta_5O_{16}{}^{7-}$ ion predominates. More recently, Nelson and Tobias[4] (who review the literature more extensively than we do here), using light-scattering techniques, obtained evidence for the hexatantalate ion ($Ta_6O_{19}{}^{8-}$) in the pH range 10–13. This species is consistent with the formulation $K_8(Ta_6O_{19})\cdot 16H_2O$ for crystalline potassium tantalate advanced by Lindqvist and Aronsson[5] from a single-crystal X-ray diffraction study. Very recently, Nelson and Tobias[6] have also centrifuged tantalate in KCl supporting electrolyte.

We present here further evidence, obtained by equilibrium ultracentrifugation, for a hexatantalate ion, together with the Raman spectra of crystalline $K_8(Ta_6O_{19})\cdot 16H_2O$ and the corresponding solution; the latter indicate a similar structure for the species in the crystal and in the solution. Although the ultracentrifugation study duplicates to some extent that of Nelson and Tobias,[6] we shall report it briefly. Our results, which encompass some conditions not investigated by them (KOH supporting electrolyte), confirm theirs.

Experimental

(1) **Ultracentrifugation.**—Details of the centrifugation technique and of the computational procedure used in the interpretation of results have been presented elsewhere.[7] For the tantalate centrifugations, the temperature was 25°, the speed was 17,250 r.p.m., and interference optics was used. The cells were 30 mm. for 0.008 *M* Ta(V) and 12 mm. for the other concentrations; centerpieces were of epoxy resin (not metal filled). The stoichiometric potassium concentration was *ca.* 1 *M* in all solutions; the free K^+ concentration will be slightly less if there is any counterion binding. Approximate constancy of this concentration is important in the estimation of charge by comparison of results obtained with different solutions.

(2) **Density and Refractive Index Measurements.**—Apparent molal volumes of the tantalate solute were computed from density data obtained with a *ca.* 24-ml. pycnometer. Refractive index increments of the tantalate in the appropriate supporting electrolyte and also of KOH were measured with a Brice-Phoenix differential refractometer. The apparent molal volume of the tantalate was found to be, within experimental uncertainty, independent of concentration; a mean volume of 216 ml./mole of $K_8Ta_6O_{19}$ was used to compute the partial specific volume, $\bar{v}$, necessary for interpretation of the centrifugation results. Similarly, the refractive index increment of the tantalate species showed no significant concentration dependence and a mean value of $\Delta n/c$ of 0.0295 l./mole at 546 mμ was used in both supporting electrolytes. Both volumes and refractive index increments are corrected for the small amount of excess base in the solid (see section 4). The corresponding constants for KCl were obtained from literature density and refractive index data.[8] The values used were as follows: KCl, $dn/dc = 0.009322$ l./mole, $\bar{v} = 0.403$; for KOH, $dn/dc = 0.00999$ l./mole, and $\bar{v} = 0.164$, for 1 *M* KOH.

(3) **Raman and Infrared Spectra.**—Raman spectra were obtained with a Cary Model 81 spectrophotometer, with 436 mμ exciting radiation. The cell used for the crystalline spectrum was developed by Keller.[9] A standard Cary 7-mm. cell was used for the solution. The scan speed was 0.25 cm.$^{-1}$/sec. for the solid

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[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory, operated by Union Carbide Corporation.

[2] Guest Scientist, Oak Ridge National Laboratory, during 1963.

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