

Fig. 2.—(i) Proposed structure of  $\text{CF}_3\text{OSF}_4\text{NF}_2$ , spin coupling constant, and chemical shifts. (ii) Experimental spectrum at high scan rate. (iii)  $>\text{SF}_4$  and  $\text{CF}_3$  portions of the spectrum at low scan rates.

perfectly with that observed. Agreement is very good for the part of the spectrum caused by the fluorine in position C.

The  $\text{N}^{14}$  to  $\text{NF}$  coupling constant was 110 c.p.s.

The single resonance line on the low-field side of the  $\text{NF}_2$  resonance was believed to be due to an impurity, since its relative intensity varied in different samples. The chemical shift of the  $\text{CF}_3$  group was measured relative to  $\text{CFCl}_3$  (internal) and was found to be  $\delta$  55.8 p.p.m. The variation of this quantity with concentration was not examined. A comparison of the  $\text{CF-SF}$  and  $\text{NF-SF}$  coupling constants with those of related compounds supports a structure with a  $\text{F}_3\text{CO}$  and an  $\text{NF}_2$  group attached to the sulfur atom of the  $\text{SF}_4$  group.

TABLE III  
COMPARISON OF  $\text{F}^{19}$  COUPLING CONSTANTS OF  $\text{CF}_3\text{OSF}_4\text{NF}_2$  AND RELATED S-F COMPOUNDS

Compound	"Type" fluorine coupling ( $\text{SF}_6$ is $\text{A}_4\text{B}$ system)	J, c.p.s.
$\text{CF}_3\text{SiF}_5^a$	$\text{CF}_3-\text{SF}_{\text{A}_4}$	22.4
( <i>trans</i> ) $\text{CF}_3\text{SF}_4\text{NF}_2^b$	$\text{CF}_3-\text{SF}_{\text{A}_4}$	22
$\text{CF}_3\text{OSF}_5^a$	$\text{CF}_3-\text{SF}_{\text{A}_4}$	9.9
( <i>cis</i> ) $(\text{CF}_3\text{O})_2\text{SF}_4^c$	$\text{CF}_3-\text{SF}_{\text{A}_2}$	9.0
$\text{CF}_3\text{OSF}_4\text{NF}_2$	$\text{CF}_3-\text{SF}_{\text{A}_2}$	12.8
	$\text{CF}_3-\text{SF}_{\text{C}}$	12.8
$\text{CF}_3\text{SF}_5^a$	$\text{CF}_3-\text{SF}_{\text{B}}$	6.4
$\text{CF}_3\text{OSF}_5^a$	$\text{CF}_3-\text{SF}_{\text{B}}$	1.5
$\text{CF}_3\text{OSF}_4\text{NF}_2$	$\text{CF}_3-\text{SF}_{\text{B}}$	1
$\text{SF}_5\text{NF}_2^d$	$\text{NF}_2-\text{SF}_{\text{A}_4}$	19.1
( <i>trans</i> ) $\text{CF}_3\text{SF}_4\text{NF}_2^b$	$\text{NF}_2-\text{SF}_{\text{A}_4}$	20
$\text{CF}_3\text{OSF}_4\text{NF}_2$	$\text{NF}_2-\text{SF}_{\text{A}_2}$	21.8
	$\text{NF}_2-\text{SF}_{\text{B}}$	22.3
$\text{SF}_5\text{NF}_2^d$	$\text{NF}_2-\text{SF}_{\text{B}}$	4.1
$\text{CF}_3\text{OSF}_4\text{NF}_2$	$\text{NF}_2-\text{SF}_{\text{C}}$	2.4
$\text{FSO}_3\text{NF}_2^e$	$\text{NF}_2-\text{SF}$	4.6

<sup>a</sup> C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, Jr., *Inorg. Chem.*, **1**, 215 (1962). <sup>b</sup> A. L. Logothetis, G. N. Sausen, and R. J. Shozda, *ibid.*, **2**, 173 (1963). <sup>c</sup> Ref. 2. <sup>d</sup> These values were obtained from the spectrum of this compound reported by G. H. Cady, D. F. Eggers, Jr., and B. Tittle, *Proc. Chem. Soc.*, 65 (1963). <sup>e</sup> M. Lustig and G. H. Cady, *Inorg. Chem.*, **2**, 388 (1963).

The respective  $\text{CF}_3-\text{SF}$  coupling constants in  $\text{CF}_3\text{OSF}_4\text{NF}_2$  are of a magnitude that might be expected for a  $\text{CF}_3$  group bound through oxygen, interacting with sulfur fluorines at 90 and 180°. The observed  $\text{NF-SF}$  coupling constants are also within the range that might be expected for a  $\text{NF}_2$  group bound directly to sulfur. The *cis* structure of the compound is in accord with the reported structures of other derivatives of  $\text{SF}_6$  formed by direct oxidation of  $\text{SF}_4$ , *cis*-( $\text{FSO}_3$ ) $_2\text{SF}_4$ ,<sup>4</sup> *cis*-( $\text{F}_6\text{SO}_2$ )- $\text{SF}_4$ ,<sup>5</sup> and *cis*-( $\text{CF}_3\text{O}$ ) $_2\text{SF}_4$ .<sup>2</sup>

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(4) J. M. Shreeve and G. H. Cady, *J. Am. Chem. Soc.*, **83**, 4521 (1961).  
(5) C. I. Merrill and G. H. Cady, *ibid.*, **85**, 909 (1963).

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## The Formation Constants of Lead Perfluorocarboxylate Complexes

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Hershenson, Smith, and Hume<sup>1</sup> found evidence for weak complex formation between nitrate ions and lead ions in aqueous solution. The relative acid strengths of the perfluorocarboxylic acids  $\text{CF}_3\text{COOH}$  and  $\text{C}_2\text{F}_7\text{COOH}$  are comparable to that of nitric acid, and the existence of weak complexes between lead and the anions of these acids might be expected. The only evidence

(1) H. M. Hershenson, M. E. Smith, and D. N. Hume, *J. Am. Chem. Soc.*, **75**, 507 (1953).

TABLE I

ANALYSIS OF  $E_{1/2}$  DATA FOR LEAD IN TRIFLUOROACETATE MEDIUM

(CF <sub>3</sub> COO <sup>-</sup> ), <i>M</i>	$\Delta E_{1/2}$ , mv.	$I_3/I_0$	$F_0(X)$	$F_1(X)$	$F_2(X)$
0	...	1.000	(1.000)	...	...
0.30	3.6	1.020	1.350	1.17	0.43
0.60	7.3	1.073	1.898	1.50	0.77
0.90	10.4	1.124	2.530	1.70	0.73
1.20	14.5	1.165	3.616	2.18	0.95
1.50	18.0	1.209	4.920	2.61	1.05
1.80	21.8	1.254	6.870	3.26	1.25
2.00	24.6	1.274	8.700	3.85	1.41

TABLE II

ANALYSIS OF  $E_{1/2}$  DATA FOR LEAD IN PENTAFLUOROPROPIONATE MEDIUM

(CF <sub>3</sub> CF <sub>2</sub> COO <sup>-</sup> ), <i>M</i>	$\Delta E_{1/2}$ , mv.	$I_3/I_0$	$F_0(X)$	$F_1(X)$	$F_2(X)$
0	...	1.000	(1.000)	...	...
0.30	3.0	1.088	1.372	1.24	1.03
0.60	6.3	1.165	1.900	1.50	0.95
0.90	9.6	1.218	2.578	1.75	0.91
1.20	13.1	1.275	3.541	2.12	0.99
1.50	16.6	1.338	4.770	2.47	1.03
1.80	20.3	1.407	6.860	3.26	1.29
2.00	23.3	1.458	8.980	3.99	1.53

TABLE III

ANALYSIS OF  $E_{1/2}$  DATA FOR LEAD IN HEPTAFLUOROBUTYRATE MEDIUM

(CF <sub>3</sub> CF <sub>2</sub> - CF <sub>2</sub> COO <sup>-</sup> ), <i>M</i>	$\Delta E_{1/2}$ , mv.	$I_3/I_0$	$F_0(X)$	$F_1(X)$	$F_2(X)$
0	...	1.000	(1.000)	...	...
0.30	1.7	1.107	1.276	0.92	1.00
0.60	4.6	1.218	1.743	1.24	1.03
0.90	9.2	1.326	2.720	1.91	1.40
1.20	14.3	1.457	4.450	2.88	1.88
1.50	20.0	1.568	7.470	4.31	2.46
1.80	26.6	1.699	13.57	6.98	3.53
2.00	29.8	1.772	18.11	8.56	3.97

reported to date for a weak complex was for trifluoroacetic acid and lead ions in anhydrous hydrogen fluoride.<sup>2</sup> The potentiometric and polarographic methods described by Hershenson, Smith, and Hume<sup>1</sup> were used to determine the stability constants in this study of the lead-trifluoroacetate, -pentafluoropropionate and -heptafluorobutyrate systems.

### Experimental

**Polarography.**—The general technique utilized has been described elsewhere.<sup>1</sup> The particular modifications of the reference electrode necessary for obviating nonreproducible potentials due to contamination from chloride ions and to precipitation of potassium perchlorate were introduced. Polarographic current-voltage curves were obtained with a Leeds and Northrup Electrochemograph, equipped with a voltage expander. The capillary had an  $m^2/s^{1/6}$  value of 2.09 mg.<sup>2/3</sup> sec.<sup>1/6</sup> at zero applied potential. Measurements were carried out at a constant ionic strength of 2.0 *M* in mixtures of sodium perchlorate and sodium perfluorocarboxylate. The pH was maintained at 2.0 and the temperature at 25 ± 0.1°. The reduction waves of lead in both sodium perchlorate and sodium perchlorate-sodium perfluorocarboxylate solutions were well defined, and the plot of  $\log i/(i_d - i)$  against  $E_{de}$  showed good linearity with a slope of 30 ± 0.1 mv. Triton X-100 was used as a maximum suppressor.

(2) H. J. Emel us, R. N. Haszeldine, and R. C. Paul, *J. Chem. Soc.*, 569 (1955).

TABLE IV

LEAD TRIFLUOROACETATE SYSTEM

(CF <sub>3</sub> COO <sup>-</sup> ), <i>M</i>	$E$ (cor.), mv.	$F_0(X)$	$F_1(X)$
0	0.00	1.00	...
0.1165	1.39	1.114	0.980
0.220	2.54	1.218	0.993
0.313	3.54	1.316	1.010
0.396	4.53	1.421	1.062
0.554	6.14	1.611	1.103
0.696	7.45	1.782	1.121
0.823	8.73	1.968	1.172
0.938	9.92	2.163	1.235
1.041	11.08	2.366	1.307
1.136	11.67	2.477	1.299

TABLE V

LEAD PENTAFLUOROPROPIONATE SYSTEM

(CF <sub>3</sub> CF <sub>2</sub> COO <sup>-</sup> ), <i>M</i>	$E$ (cor.), mv.	$F_0(X)$	$F_1(X)$
0.000	0.00	1.000	...
0.1165	0.94	1.076	0.652
0.220	1.88	1.157	0.715
0.313	2.78	1.241	0.770
0.396	3.64	1.327	0.826
0.554	5.14	1.490	0.885
0.696	6.40	1.644	0.923
0.823	7.63	1.811	0.987
0.938	8.77	1.977	1.040
1.041	9.76	2.138	1.090
1.136	10.66	2.291	1.136

TABLE VI

LEAD HEPTAFLUOROBUTYRATE SYSTEM<sup>a</sup>

(CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> COO <sup>-</sup> ), <i>M</i>	$E$ (cor.), mv.	$F_0(X)$	$F_1(X)$
0.00	0.00	1.000	...
0.1165	0.71	1.057	0.496
0.220	1.46	1.120	0.546
0.313	2.16	1.183	0.585
0.396	2.92	1.254	0.641
0.554	4.38	1.406	0.734
0.696	5.88	1.579	0.830
0.823	7.50	1.791	0.960
0.938	9.06	2.023	1.091
1.041	10.58	2.275	1.219

<sup>a</sup> Lead concentration is 5 *mM*.

**Potentiometry.**—The general technique was that used in previous investigations.<sup>1,3</sup> Potential measurements were made with a Leeds and Northrup K-3 potentiometer sensitive to 0.02 mv.; solid lead stick electrodes were used. Measurements were carried out under the same conditions of ionic strength, pH, and temperature as the polarographic measurements. Potential differences were measured among four electrodes and were corrected for liquid junction potentials.

### Results

The polarographic results are summarized in Tables I–III. The conventional plot of  $F_0(X)$  in each case was a curve while  $F_1(X)$  and  $F_2(X)$  were straight lines in the region of lower perfluorocarboxylate concentration. The linearity of the  $F_1(X)$  plots indicated the presence of the simple aquolead ion and the mono- and the diperfluorocarboxylate complexes. It is not necessary to rely on data taken at higher concentration of the ligand where ionic environment

(3) I. Leden, *Z. physik. Chem.*, **A188**, 160 (1941).

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  $\beta_1$ . Extrapolation of  $F_2(X)$  yielded values for  $\beta_2$  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  $\beta_1$  and  $\beta_2$  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

TABLE VII  
FORMATION CONSTANTS FOR LEAD PERFLUOROCARBOXYLATE  
COMPLEXES AT 25°

Ligand	$\beta_1$	$\beta_2$	Method
$\text{CF}_3\text{COO}^-$	1.04	0.73	Polarography
$\text{CF}_3\text{COO}^-$	0.93	0.33	Potentiometry
$\text{CF}_3\text{CF}_2\text{COO}^-$	0.93	0.98	Polarography
$\text{CF}_3\text{CF}_2\text{COO}^-$	0.61	0.46	Potentiometry
$\text{CF}_3\text{CF}_2\text{CF}_2\text{COO}^-$	0.62	1.00	Polarography
$\text{CF}_3\text{CF}_2\text{CF}_2\text{COO}^-$	0.44	0.45	Potentiometry

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.

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

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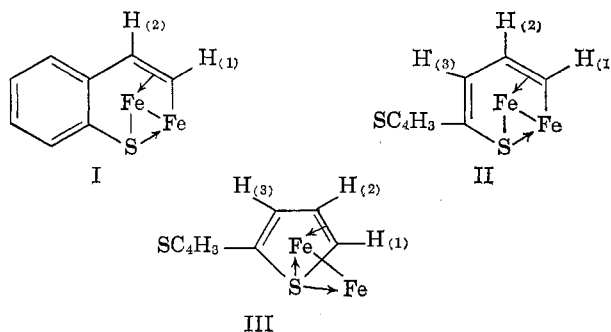
### Iron Carbonyl Derivatives of 2,2'-Dithienyl and *o*-Aminobenzenethiol

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

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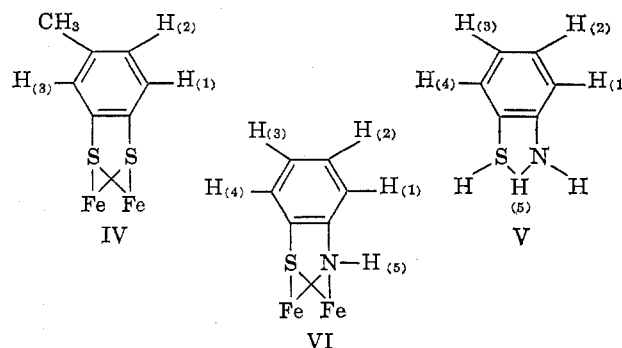
The treatment of thiophene with triiron dodecacarbonyl was found to yield the sulfur-free ferrole,  $\text{C}_4\text{H}_4\text{Fe}_2(\text{CO})_6$ , as well as sulfur-containing complexes

which were not isolated.<sup>1</sup> In a study suggested by the results of the thiophene-iron carbonyl experiments a series of hexacarbonyl(alkylvinyl sulfide)diiron complexes was prepared.<sup>2</sup> These complexes were shown to be similar in structure to hexacarbonyl(thianaphthene)diiron,<sup>3</sup> for which structure I was proposed.<sup>2,4</sup>



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<sup>5</sup> 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.<sup>6</sup> 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.<sup>2</sup>

The carbonyl stretching bands of the dithienyl complex, at 2079 (s), 2046 (vs), 2011 (vs), 2006 (vs), 1996 (m), and 1963 (vw)  $\text{cm}^{-1}$ , 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)  $\text{cm}^{-1}$ ,<sup>1</sup> those of the thianaphthene complex at 2076 (m), 2044 (vs), 2004 (s), and 1992 (m)  $\text{cm}^{-1}$ ,<sup>2</sup> 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)  $\text{cm}^{-1}$ .<sup>7</sup>



- (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).
- (3) R. B. King and F. G. A. Stone, *ibid.*, **82**, 4537 (1960).
- (4) The three carbonyl groups on each iron atom in these structures are omitted in the interest of simplicity.
- (5) W. Steinkopf and J. Roch, *Ann.*, **482**, 251 (1930).
- (6) The suggestion of a referee resulted in recognition of this similarity.
- (7) R. B. King, *J. Am. Chem. Soc.*, **85**, 1584 (1963).