CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
COLUMBIA UNIVERSITY, NEW YORK, NEW YORK 10027

The Crystal and Molecular Structure of Bis(ethyl thioxanthato)-μ-bis(ethyl thioxanthato)-μ'-bis(ethylthio)-diiron(III)

BY D. COUCOUVANIS, S. J. LIPPARD,*[1a] AND J. A. ZUBIETA[1b]

Received May 18, 1970

The molecular structure of bis(ethyl thioxanthato)-μ-bis(ethyl thioxanthato)-μ'-bis(ethylthio)-diiron(III), $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$, has been determined in a single-crystal X-ray diffraction study. The complex crystallizes in the monoclinic system, space group $P2_1/c$, with $a = 12.193$ (5) Å, $b = 8.469$ (4) Å, $c = 19.82$ (1) Å, and $\beta = 130.11$ (5)°. The density of 1.657 (1) g/cm³ calculated on the basis of two dimeric formulas per unit cell is in agreement with the measured density of 1.64 ± 0.01 g/cm³. The structure was solved using ~1350 independent, statistically significant reflections collected on a full-circle automated diffractometer. Refinement of all atoms including several of the hydrogen atoms led to a final value of the discrepancy index, R_1, of 0.048. The molecular structure consists of centrosymmetric dimers in which two ethyl mercaptide and two ethylthioxanthate groups function as bridging ligands and two more nonbridging ethylthioxanthate ligands complete the distorted octahedral coordination polyhedra around the two iron atoms. The iron–iron distance of 2.618 (2) Å is 0.39 Å shorter than the S···S bite of the bridging thioxanthate ligand. This result, together with the small Fe–S–Fe angle of 72.35 (7)° at the bridging sulfur atoms, provides direct structural proof for metal–metal bonding. Average values for the three chemically distinct types of iron–sulfur bonds in the molecule are 2.218 (2) Å for the bridging mercaptide ligands, 2.287 (2) Å for the bridging thioxanthate ligands, and 2.338 (4) Å for the terminal thioxanthate ligands. From the observed carbon–sulfur distances it is concluded that resonance form VII (see text) contributes significantly (~20%) to the electronic structure of the coordinated thioxanthate groups.

Introduction

The coordination chemistry of iron–sulfur complexes has been a subject of recent study in our laboratory[2–4] and elsewhere,[5] inspired by the biochemical characterization of certain nonheme iron protein systems.[6,7] As reported briefly before,[3] an iron(III) dimer containing two ethyl mercaptide and two ethyl thioxanthate groups as bridging ligands has been prepared and its structure determined. A number of related molecules have also been made and extensively investigated.[4] Here are described the details of the X-ray crystallographic analysis of bis(ethyl thioxanthato)-μ-bis(ethylthio)-μ'-bis(ethyl thioxanthato)-diiron(III).

Experimental Procedure and Results

Collection and Reduction of X-Ray Data.—The compound, prepared as described elsewhere,[4a] formed small black prismatic crystals, several of which were mounted along the longest dimension (cell b axis) for study. Space group and approximate unit cell dimensions were determined by film methods on precession and Weissenberg cameras using Ni-filtered Cu Kα radiation (λ 1.5418 Å). The observed extinctions, $h0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$, suggested $P2_1/c$ as the probable space group,[8] a choice later confirmed by the successful refinement of the structure. The unit cell parameters obtained from the film data were refined by a least-squares technique to give the best fit between calculated and observed settings χ, ϕ, and 2θ for 17 independent reflections, carefully centered in the counter window of a Picker full-circle automated X-ray diffractometer.[9] The results are $a = 12.193 \pm 0.005$ Å, $b = 8.469 \pm 0.004$ Å, $c = 19.82 \pm 0.01$ Å, and $\beta = 130.11 \pm 0.05$°, where the estimated precision errors are derived from the inverse least-squares matrix. The density of 1.657 ± 0.001 g/cm³ calculated from these parameters on the basis of four formula units of $C_8H_{15}S_7Fe$ per unit cell is in satisfactory agreement with the value, 1.64 ± 0.01 g/cm³, measured by flotation in aqueous KI solutions.

Intensity measurements were taken at 21–23° on the Picker diffractometer using a crystal of approximate dimensions 0.17 mm along a^*, 0.36 mm along b^*, and 0.08 mm along c^*, with b^* as the mounting axis. Experimental details are as reported previously[10] with the following exceptions and notations: the wavelength was Cu Kα (λ 1.5418 Å), the takeoff angle was 2.5°, and the scan range was 1.25° in 2θ plus the Kα_1–Kα_2 allowance. The $\bar{1}34$ reflection was used to monitor crystal and instrument stability. Its integrated intensity varied by no more than $\pm 1.8\%$ of the mean value for the entire run. Data were collected with the indices of the shortest reciprocal cell edges varying fastest ($l > h > k$), resulting in an overall efficiency of ~70%. A total of 1500 independent reflections within the sphere defined by $\theta \leq 43°$ were obtained in 3 days.

Observed intensities were corrected for background, use of attenuators, Lorentz, polarization, and absorption effects ($\mu = 164$ cm^{-1}) using the program ACAC-3.[9,10] The resultant transmission factors ranged from 0.08 to 0.36. As a check on the absorption correction, the variation with ϕ of the intensity of axial reflections measured at $\chi = 90°$ was found to correlate well with the variation of the calculated transmission factors. Scaling of the corrected data was accomplished by XDATA,[9] which produced values of $|F_o|$ and $|F_o|^2$ for the subsequent solution of the structure (see below). Scattering factors for the zerovalent Fe,

---

* To whom correspondence should be addressed.

(1) (a) Alfred P. Sloan Research Fellow, 1968–1970. (b) Woodrow Wilson Fellow, 1966–1967; National Institutes of Health Predoctoral Fellow, 1967–present.

(2) D. Coucouvanis and S. J. Lippard, *J. Amer. Chem. Soc.*, **90**, 3281 (1968); D. Coucouvanis and S. J. Lippard, *ibid.*, **91**, 307 (1969).

(3) D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *ibid.*, **91**, 761 (1969).

(4) (a) D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *ibid.*, **92**, 3342 (1970); (b) S. J. Lippard and J. A. Zubieta, to be submitted for publication.

(5) *Cf.* A. L. Balch, *J. Amer. Chem. Soc.*, **91**, 6962 (1969), and references cited therein.

(6) R. Malkin and J. C. Rabinowitz, *Annu. Rev. Biochem.*, **36**, 113 (1967).

(7) T. Kimura, *Struct. Bonding (Berlin)*, **5**, 1 (1968).

(8) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1962, p 99.

(9) Programs for the IBM 360-91 computer used in this work include local versions of MODE-1, the Brookhaven diffractometer setting and cell constant and orientation refinement program, GSET, the Prewitt diffractometer setting program, ACAC-3, a revised version of the Prewitt absorption correction and data reduction program, XDATA, the Brookhaven Wilson plot and scaling program, FORDAP, the Zalkin Fourier program, CULS, a local version of the Busing–Martin–Levy structure factor calculation and least-squares refinement program (ORFLS), ORFFE, the Busing–Martin–Levy molecular geometry and error function program, and ORTEP, the Johnson thermal ellipsoid plotting program.

(10) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **6**, 2223 (1967).

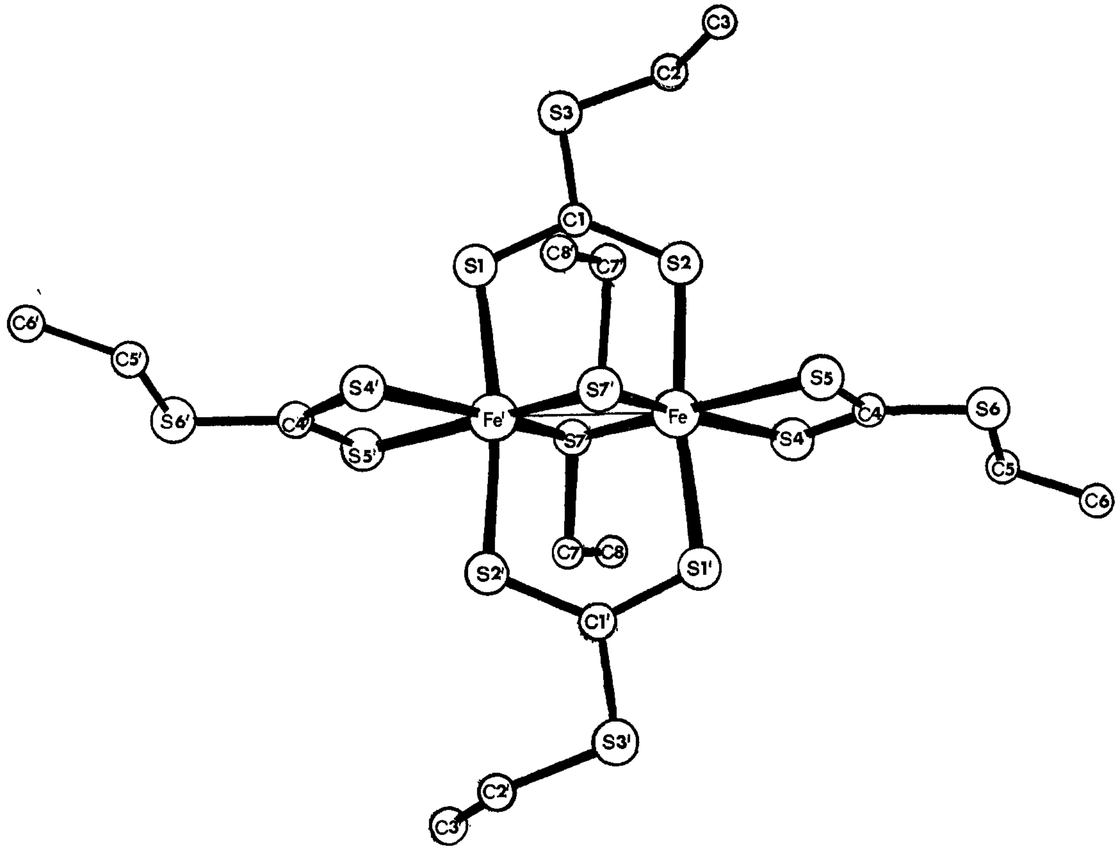


Figure 1.—The molecular structure showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

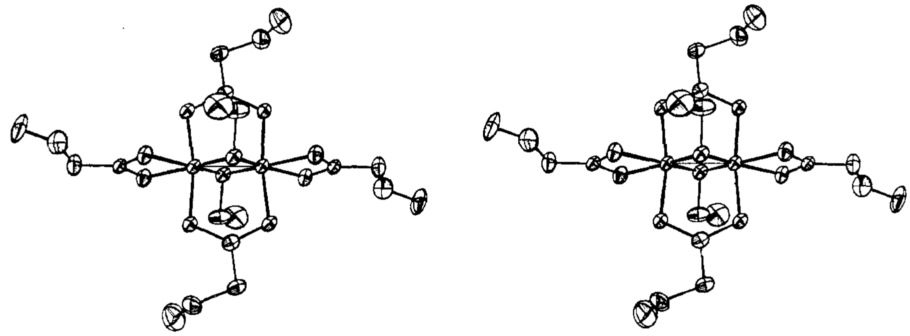
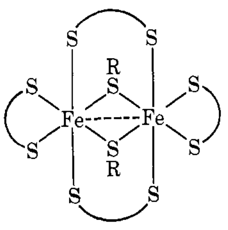
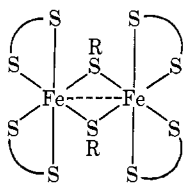


Figure 2.—A stereoscopic view of the structure. The 50% probability ellipsoids are shown.

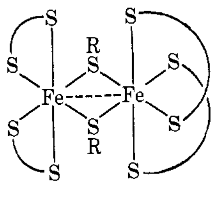
S, and C atoms were obtained from ref 11. The calculated structure factors were corrected for the effects of anomalous dispersion of the iron and sulfur atoms.[12] The hydrogen atom scattering factors were those of Stewart, *et al.*[13] Weights, w, were set equal to $4F^2/\sigma^2(F^2)$, where $\sigma(F^2)$ is the standard deviation of F^2 obtained from $\sigma(I)$ after absorption, Lorentz, and polarization corrections were applied. I is the integrated intensity corrected for background and attenuators. The standard deviation in I, $\sigma(I)$, was obtained from the expression[14,15] $\sigma(I) = [E + (T_E/2T_B)^2(B_1 + B_2) + (\epsilon I)^2]^{1/2}$, in which E is the total counts in the peak plus background observed for a time T_E, B_1 and B_2 are the background counts observed for a time T_B at each extreme of the scan, and ϵ is the "ignorance" factor,[15] set equal to 0.03, to prevent excessively high weight being given to the strong reflections. Reflections for which $I \leq 3\sigma(I)$ were excluded from



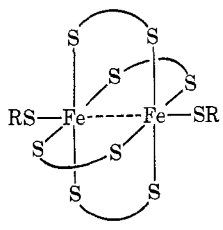
I



II



III



IV

---

[11] See ref 8, Vol. III, pp 202, 204.

[12] See ref 8, Vol. III, p 213 ff.

[13] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[14] (a) G. M. Brown and H. A. Levy, *J. Phys.* (*Paris*), **25**, 497 (1964); (b) R. D. Ellison and H. A. Levy, *Acta Crystallogr.*, **19**, 260 (1965).

[15] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (IN ELECTRONS × 10) FOR $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$[a]

H	L	OBS	CAL
***** K= 0*****			
-11	14	328	324
-11	12	519	498
-11	10	107	112
-11	8	496	506
-11	6	622	709
-10	6	104	128
-10	10	402	394
-10	12	131	127
-10	14	468	466
-10	16	528	504
-10	18	674	680
-9	18	490	468
-9	16	122	145
-9	14	208	185
-9	12	433	432
-9	10	237	232
-9	8	325	308
-9	4	251	287
-9	2	301	317
-8	2	439	448
-8	6	117	94
-8	8	611	596
-8	10	38	76
-8	12	277	263
-8	14	294	289
-8	16	262	269
-8	18	492	526
-7	18	439	443
-7	16	448	458
-7	14	666	674
-7	12	1524	1580
-7	10	1095	1085
-7	8	295	274
-7	6	646	632
-7	4	962	1018
-7	2	457	482
-6	2	859	922
-6	4	1475	1511
-6	6	815	773
-6	8	749	744
-6	10	616	618
-6	12	907	928
-6	14	579	531
-6	16	118	121
-6	18	131	136
-5	18	425	439
-5	14	1213	1290
-5	12	237	249
-5	10	200	186
-5	8	353	341
-5	6	450	434
-5	4	1950	2069
-5	2	1567	1586
-4	2	435	443
-4	4	1525	1584
-4	6	280	269
-4	8	535	567
-4	10	427	417
-4	12	94	87
-4	14	402	409
-4	16	246	249
-4	18	518	505
-3	16	339	344
-3	14	197	203
-3	12	563	576
-3	8	182	183
-3	6	611	579
-3	4	265	207
-3	2	702	688
-2	2	462	353
-2	4	80	102
-2	6	792	755
-2	8	987	1061
-2	10	80	80
-2	12	338	360
-2	14	423	420
-1	14	274	270
-1	12	218	216
-1	10	409	382
-1	8	1284	1399
-1	6	279	256
-1	4	543	571
-1	2	1053	1173
0	4	861	993
0	6	958	1004
0	8	824	839
0	10	276	263
0	12	196	202
0	14	302	271
1	12	88	84
1	10	159	169
1	8	104	111
1	6	81	31
1	4	91	70
1	2	248	237
2	0	586	430
2	2	237	227
2	4	145	117
2	6	725	748
2	8	130	125
2	10	76	54
2	12	72	59
3	10	317	307
3	8	233	226
3	6	939	888
3	4	469	452
3	2	870	777
3	0	652	591
4	0	818	794
4	2	83	84
4	4	226	225
4	6	135	119
4	8	64	73
5	8	273	274
5	6	71	59
5	4	334	336
5	2	200	197
5	0	824	863
6	0	108	139
6	2	432	428
6	6	69	77
7	4	522	521
7	2	520	535
8	0	234	231
8	2	669	673
9	0	163	166
***** K= 1*****			
9	0	250	252
8	2	192	213
8	1	63	45
8	0	101	77
7	1	389	393
7	2	355	357
7	3	97	94
6	6	109	103
6	5	440	442
6	4	64	66
6	3	270	277
6	2	456	452
6	1	139	144
5	0	302	311
5	1	49	45
5	2	515	508
5	3	353	335
5	4	323	317
5	5	229	229
5	6	164	177
5	8	393	385
4	9	127	127
4	6	529	509
4	5	202	186
4	4	962	906
4	3	352	346
4	2	989	945
4	1	50	15
4	0	819	814
3	0	1209	1116
3	1	276	254
3	2	260	246
3	3	512	501
3	4	586	555
3	5	548	516
3	6	782	722
3	8	364	358
3	9	110	65
3	10	81	52
3	11	66	56
2	12	300	290
2	9	592	560
2	8	501	496
2	7	637	632
2	6	187	177
2	5	112	103
2	4	443	443
2	3	154	125
2	2	1077	1060
2	1	171	146
2	0	1322	1205
1	0	1377	1363
1	1	679	673
1	2	314	263
1	3	371	406
1	4	166	153
1	5	109	122
1	6	522	507
1	7	542	568
1	8	491	483
1	9	304	305
1	10	137	165
1	11	281	280
1	12	193	180
1	13	222	220
0	14	187	169
0	13	93	106
0	12	197	213
0	11	160	200
0	9	73	73
0	7	532	562
0	6	951	1022
0	5	102	107
0	4	314	275
0	3	534	565
0	1	717	796
-1	1	1306	1575
-1	2	253	277
-1	3	1051	1098
-1	4	1373	1514
-1	5	1162	1300
-1	6	1056	1177
-1	7	1397	1538
-1	8	704	732
-1	9	903	978
-1	10	65	67
-1	11	240	241
-1	12	358	345
-1	13	198	199
-1	14	105	93
-1	15	293	288
-2	16	260	256
-2	15	153	163
-2	14	74	76
-2	13	186	160
-2	12	77	97
-2	11	94	109
-2	10	552	606
-2	9	843	893
-2	8	1037	1091
-2	7	1102	1248
-2	6	93	116
-2	5	447	429
-2	4	1132	1160
-2	3	340	321
-2	2	86	114
-2	1	1106	1041
-3	1	105	74
-3	2	504	452
-3	3	986	995
-3	4	507	487
-3	5	148	156
-3	6	947	929
-3	7	431	437
-3	8	702	702
-3	9	36	36
-3	10	90	94
-3	11	413	420
-3	12	640	650
-3	13	78	91
-3	14	75	63
-3	16	644	658
-3	17	215	215
-4	17	193	210
-4	16	502	505
-4	14	223	205
-4	13	65	70
-4	12	433	445
-4	11	310	287
-4	10	385	381
-4	9	503	456
-4	8	310	278
-4	7	844	658
-4	6	741	744
-4	5	455	476
-4	4	814	732
-4	3	306	307
-4	2	1240	1242
-4	1	202	183
-5	1	346	358
-5	2	986	960
-5	3	728	675
-5	4	887	891
-5	5	551	546
-5	6	384	363
-5	7	105	89
-5	8	373	332
-5	9	281	275
-5	10	74	76
-5	11	861	875
-5	12	256	255
-5	13	142	141
-5	14	190	196
-5	15	82	93
-5	16	153	140
-5	17	281	270
-5	18	107	117
-6	18	80	68
-6	17	164	164
-6	15	69	57
-6	14	433	431
-6	13	537	525
-6	12	181	175
-6	11	1236	1266
-6	10	70	85
-6	9	1162	1138
-6	8	242	231
-6	7	733	705
-6	6	641	631
-6	5	977	936
-6	4	168	171
-6	3	595	593
-6	2	162	193
-6	1	394	410
-7	1	356	385
-7	2	101	79
-7	3	152	142
-7	4	493	439
-7	5	101	82
-7	7	119	107
-7	8	353	346
-7	9	596	592
-7	10	476	454
-7	11	774	747
-7	12	617	619
-7	13	540	541
-7	14	462	466
-7	15	57	54
-7	16	112	107
-7	17	201	172
-7	18	60	56
-7	19	122	122
-8	19	311	310
-8	18	271	271
-8	17	503	510
-8	16	235	232
-8	15	236	217
-8	14	122	124
-8	13	636	627
-8	12	658	630
-8	11	684	653
-8	10	70	76
-8	9	499	492
-8	8	62	35
-8	5	166	177
-8	4	459	479
-8	3	260	274
-8	2	84	95
-8	1	64	55
-9	1	262	290
-9	2	381	413
-9	3	399	431
-9	4	496	513
-9	5	238	251
-9	6	407	428
-9	7	272	264
-9	8	192	200
-9	9	406	384
-9	10	633	627
-9	11	507	481
-9	12	115	93
-9	13	265	247
-9	14	123	125
-9	15	86	70
-9	16	72	77
-9	17	219	226
-9	18	57	41
-10	18	191	178
-10	17	128	107
-10	16	182	181
-10	15	395	374
-10	14	88	67
-10	13	403	394
-10	8	222	215
-10	7	227	232
-10	6	756	830
-10	5	235	248
-10	4	385	404
-11	7	123	130
-11	8	287	320
-11	10	347	370
-11	11	69	54
-11	12	101	73
-11	13	460	441
-11	14	409	337
-11	15	273	259
-11	16	158	140
***** K= 2*****			
-11	13	213	190
-11	14	273	263
-11	13	533	533
-11	12	72	49
-11	11	551	559
-11	10	63	59
-11	9	433	475
-11	8	73	82
-10	4	379	378
-10	5	576	626
-10	7	650	731
-10	9	565	545
-10	10	137	112
-10	11	369	355
-10	12	458	443
-10	13	451	456
-10	14	286	291
-10	17	81	72
-9	18	192	192
-9	17	423	433
-9	15	229	230
-9	14	515	497
-9	13	629	603
-9	12	344	344
-9	11	141	138
-9	10	132	156
-9	9	169	173
-9	8	244	230
-9	7	175	180
-9	6	540	568
-9	5	346	373
-9	4	182	188
-9	3	293	309
-9	1	435	451
-8	2	140	141
-8	3	358	377
-8	4	329	349
-8	5	96	96
-8	6	326	313
-8	7	640	637
-8	8	273	254
-8	12	141	131
-8	13	714	705
-8	14	449	439
-8	15	481	451
-8	16	68	60
-8	17	439	427
-8	18	242	257
-7	18	491	512
-7	17	165	153
-7	16	138	144
-7	15	415	425
-7	14	77	76
-7	13	324	303
-7	12	62	48
-7	11	396	379
-7	10	627	613
-7	9	282	275
-7	8	459	447
-7	7	458	430
-7	5	55	34
-7	4	345	326
-7	3	307	320
-7	2	519	533
-7	1	59	75
-6	1	51	41
-6	2	152	154
-6	3	63	70
-6	4	412	405
-6	5	486	483
-6	6	323	293
-6	7	370	357
-6	8	617	539
-6	9	508	496
-6	10	136	141
-6	11	74	56
-6	12	316	310
-6	13	186	173
-6	14	127	134
-6	15	314	322
-6	16	80	75
-6	17	167	150
-6	18	228	240
-5	17	77	97
-5	16	221	213
-5	15	91	89
-5	14	399	426
-5	13	164	174
-5	12	104	113
-5	11	195	198
-5	10	307	305
-5	9	709	744
-5	8	348	334
-5	7	541	527
-5	6	527	499
-5	5	1065	1048
-5	4	101	42
-5	3	822	806
-5	2	90	62
-5	1	800	636
-4	1	1002	1024
-4	2	705	673
-4	3	333	333
-4	4	691	693
-4	5	374	337
-4	6	850	817
-4	7	179	171
-4	8	204	194
-4	9	357	338
-4	10	492	407
-4	11	410	427
-4	12	532	545
-4	13	355	373
-4	14	136	146
-4	15	336	353
-4	16	126	133
-4	17	485	475
-3	16	135	182
-3	15	646	670
-3	14	445	457
-3	13	800	823
-3	12	340	344
-3	11	1036	1099
-3	10	49	22
-3	9	935	974
-3	8	1084	1135
-3	7	619	599
-3	6	604	763
-3	5	405	360
-3	4	109	105
-3	3	610	576
-3	2	41	17
-3	1	206	163
-2	1	485	437
-2	2	371	343
-2	3	83	93
-2	4	703	655
-2	5	356	350
-2	6	968	1019
-2	7	1018	1082
-2	8	202	209
-2	9	1244	1355
-2	10	241	255
-2	11	1254	1321
-2	12	435	444
-2	13	516	536
-2	14	431	423
-2	15	504	485
-1	15	224	211
-1	14	352	344
-1	13	72	70
-1	12	254	261
-1	11	433	439
-1	10	144	152
-1	9	253	264
-1	8	423	438
-1	7	310	334
-1	6	296	314
-1	5	64	53
-1	4	726	801
-1	3	222	172
-1	2	404	421
-1	1	63	51
0	1	634	660
0	2	652	735
0	3	142	138
0	4	168	167
0	5	588	630
0	6	655	671
0	7	182	185
0	8	278	254
0	9	193	169
0	10	430	432
0	11	54	37
0	12	248	241
0	14	282	270
1	10	140	142
1	9	144	149
1	8	250	241
1	7	177	179
1	6	85	134
1	5	62	52
1	4	330	323
1	3	430	453
1	2	449	514
1	1	563	563
1	0	156	102
2	0	917	833
2	1	143	157
2	2	447	406
2	3	102	100
2	4	478	471
2	5	434	471
2	6	501	516
2	7	961	953
2	8	332	323
2	9	450	425
2	10	67	59
2	11	569	524
3	9	494	463
3	8	735	683
3	7	1330	1292
3	5	1233	1164
3	4	125	110
3	3	635	636
3	2	184	187
3	1	85	74
3	0	1067	1046
4	0	543	527
4	1	202	188
4	2	573	568
4	3	821	813
4	4	337	316
4	5	734	714
4	7	506	474
4	8	339	297
4	9	207	200
5	7	67	49
5	6	96	93
5	5	100	49
5	4	200	201
5	3	168	153
5	2	387	377
5	1	106	120
5	0	427	426
6	0	161	140
6	1	65	64
6	2	53	56
6	3	302	315
6	5	81	68
7	4	163	163
7	3	212	207
7	2	61	40
7	1	119	120
7	0	397	337
8	1	232	236
***** K= 3*****			
8	1	315	313
8	0	388	404
7	0	65	24
7	1	95	89
7	2	240	245
7	3	164	151
6	5	162	186
6	4	166	165
6	3	357	341
6	2	152	159
6	1	523	504
6	0	589	590
5	0	863	959
5	1	501	457
5	2	201	201
5	3	313	303
5	4	214	202
5	5	135	138
5	7	266	264
4	8	343	377
4	7	584	579
4	6	329	312
4	5	127	112
4	4	575	547
4	3	431	413
4	2	832	799
4	1	879	841
4	0	1151	1125
3	0	438	497
3	1	189	193
3	2	826	785
3	3	624	573
3	4	448	427
3	5	281	268
3	6	429	408
3	8	174	158
3	9	116	106
3	10	246	225
2	11	510	470
2	10	230	216
2	9	101	94
2	8	158	140
2	6	418	409
2	5	102	87
2	4	118	124
2	3	48	45
2	2	382	391
2	1	1283	1268
2	0	370	356
1	0	83	28
1	1	861	917
1	2	54	43
1	3	471	456
1	4	204	198
1	5	365	359
1	6	541	561
1	7	111	118
1	8	162	153
1	9	292	252
1	10	196	190
1	11	510	475
1	12	297	277
0	12	264	266
0	10	308	313
0	9	179	172
0	8	437	420
0	7	438	463
0	6	121	129
0	5	648	633
0	4	364	392
0	3	745	814
0	2	642	671
0	1	774	865
-1	1	300	295
-1	2	977	1016
-1	3	877	909
-1	4	902	936
-1	5	886	924
-1	6	477	494
-1	7	351	352
-1	8	362	303
-1	9	443	450
-1	10	667	655
-1	11	301	273
-1	12	142	161
-1	13	231	224
-1	14	237	219
-2	15	176	167
-2	14	175	163
-2	13	231	225
-2	12	293	301
-2	11	587	612
-2	10	419	422
-2	9	753	771
-2	8	101	97
-2	7	194	204
-2	6	605	533
-2	5	570	525
-2	4	650	653
-2	3	321	313
-2	2	420	437
-2	1	205	156
-3	1	295	293
-3	2	374	425
-3	3	652	583
-3	4	412	341
-3	5	996	1008
-3	6	757	759
-3	7	40	11
-3	8	113	127
-3	9	322	333
-3	10	384	406
-3	11	347	344
-3	12	392	377
-3	13	263	259
-3	14	637	639
-3	15	442	443
-3	16	247	241
-4	16	340	351
-4	15	735	764
-4	14	493	474
-4	13	167	165
-4	12	67	75
-4	11	190	185
-4	10	303	263
-4	8	331	335
-4	7	644	642
-4	6	531	524
-4	5	389	391
-4	4	137	119
-4	3	102	100
-4	2	933	895
-4	1	543	552
-5	1	624	661
-5	2	420	407
-5	3	128	121
-5	4	212	183
-5	5	419	392
-5	6	75	63
-5	7	277	255
-5	8	371	352
-5	10	59	55
-5	11	67	75
-5	12	475	474
-5	13	146	136
-5	14	118	119
-5	15	105	101
-5	16	392	404
-5	17	74	62
-6	17	354	360
-6	16	358	354
-6	15	65	88
-6	14	77	53
-6	13	255	249
-6	12	188	189
-6	11	275	281
-6	10	109	121
-6	9	597	587
-6	8	457	436
-6	7	555	520
-6	6	242	210
-6	5	388	383
-6	4	313	291
-6	3	549	555
-6	2	457	457
-6	1	63	67
-7	1	251	206
-7	2	232	266
-7	3	478	493
-7	4	178	155
-7	5	333	326
-7	6	581	561
-7	7	603	562
-7	8	94	88
-7	9	838	870
-7	11	582	554
-7	12	48	26
-7	13	1133	1147
-7	14	438	433
-7	15	559	557
-7	17	160	164
-8	17	137	172
-8	16	171	154
-8	15	346	342
-8	14	425	433
-8	13	674	677
-8	12	102	98
-8	11	130	170
-8	10	156	148
-8	9	135	127
-8	8	225	215
-8	7	131	148
-8	6	622	626
-8	5	91	84
-8	4	250	256
-8	3	241	247
-8	2	244	252
-9	2	366	370
-9	3	135	140
-9	4	323	333
-9	6	204	206
-9	7	420	436
-9	8	185	185
-9	10	49	90
-9	11	258	250
-9	12	150	139
-9	13	201	191
-9	14	70	65
-9	17	145	144
-10	15	230	225
-10	14	76	83
-10	13	121	97
-10	12	243	230
-10	11	87	70
-10	10	265	249
-10	9	236	242
-10	8	250	275
-10	7	407	430
-10	6	207	235
-11	5	52	18
-11	11	366	342
-11	12	497	494
***** K= 4*****			
-10	9	345	380
-10	9	194	165
-10	10	480	463
-10	11	271	277
-10	13	75	57
-9	15	243	250
-9	14	225	230
-9	13	169	147
-9	12	245	232
-9	11	534	515
-9	10	226	223
-9	9	196	194
-9	7	339	344
-9	5	144	150
-9	4	165	163
-8	1	57	51
-8	2	183	180
-8	3	199	200
-8	4	81	80
-8	5	84	73
-8	6	135	148
-8	7	363	359
-8	8	172	155
-8	9	73	71
-8	10	51	57
-8	11	133	135
-8	12	156	143
-8	13	144	155
-8	14	333	319
-8	15	87	80
-8	16	453	473
-7	16	323	332
-7	14	500	476
-7	13	267	268
-7	12	117	90
-7	11	165	154
-7	10	295	284
-7	9	206	191
-7	8	523	515
-7	7	160	153
-7	6	191	198
-7	5	178	170
-7	4	159	140
-7	3	102	112
-7	2	97	79
-6	1	407	426
-6	2	647	660
-6	3	271	254
-6	4	517	530
-6	5	508	479
-6	6	1411	1415
-6	7	79	96
-6	8	1015	1009
-6	10	435	421
-6	12	141	134
-6	13	630	647
-6	14	554	554
-6	15	95	97
-6	16	175	176
-5	16	74	61
-5	15	540	559
-5	14	122	111
-5	12	257	257
-5	11	441	453
-5	10	302	291
-5	9	240	231
-5	8	329	317
-5	7	341	329
-5	6	1447	1452
-5	5	351	334
-5	4	654	635
-5	3	303	314
-5	2	462	467
-5	1	392	395
-4	1	271	262
-4	2	67	40
-4	3	228	212
-4	4	229	227
-4	5	221	214
-4	6	561	557
-4	7	560	568
-4	8	131	124
-4	9	283	286
-4	10	435	422
-4	11	186	134
-4	12	350	364
-4	13	76	54
-4	14	119	137
-4	15	247	258
-4	16	170	153
-3	15	177	180
-3	13	191	187
-3	11	261	265
-3	10	174	169
-3	9	43	33
-3	8	218	218
-3	7	250	239
-3	6	176	184
-3	5	241	235
-3	4	474	449
-3	3	645	584
-3	2	397	366
-3	1	239	236
-2	1	807	770
-2	2	236	216
-2	3	551	543
-2	4	285	290
-2	5	337	326
-2	6	423	441
-2	7	222	226
-2	8	193	195
-2	9	302	305
-2	10	117	116
-2	12	159	147
-2	13	194	214
-2	14	252	242
-1	13	191	188
-1	12	262	297
-1	11	98	86
-1	10	206	210
-1	9	462	486
-1	8	139	82
-1	7	405	428
-1	6	836	890
-1	4	1152	1220
-1	3	77	83
-1	2	1096	1104
-1	1	154	151
0	0	896	1000
0	1	653	712
0	2	1016	1121
0	3	57	74
0	4	843	911
0	5	212	214
0	6	345	338
0	7	145	135
0	8	738	748
0	9	311	303
0	10	115	119
0	12	160	143
1	11	68	52
1	10	247	233
1	9	160	156
1	8	416	407
1	7	114	120
1	5	249	236
1	4	716	745
1	3	53	25
1	2	989	1035
1	1	749	837
1	0	767	671
2	1	583	547
2	2	569	598
2	3	372	381
2	4	497	464
2	5	684	679
2	6	75	73
2	8	233	229
2	9	79	75
2	10	323	289
3	9	85	60
3	8	160	153
3	7	345	313
3	4	172	156
3	3	71	60
3	2	135	134
3	1	410	368
3	0	113	101
4	1	115	107
4	2	383	362
4	3	433	424
4	4	365	357
4	5	83	64
4	6	238	220
5	6	247	247
5	5	416	400
5	4	335	314
5	3	90	76
5	2	356	328
5	1	448	432
5	0	567	547
6	0	748	756
6	1	60	12
6	2	177	195
6	4	148	140
7	2	126	120
7	1	289	277
7	0	405	408
***** K= 5*****			
7	0	94	110
6	1	426	417
6	0	134	131
5	0	739	746
5	1	462	460
5	2	558	544
5	3	63	51
5	4	174	165
4	6	194	183
4	4	263	250
4	3	110	111
4	2	766	755
4	1	394	402
4	0	561	533
3	2	481	453
3	3	199	206
3	4	259	246
3	5	122	93
3	6	80	80
3	7	97	64
2	9	167	153
2	7	225	222
2	4	93	80
2	3	131	132
2	2	297	231
2	1	364	346
2	0	84	80
1	0	145	112
1	1	393	407
1	3	341	352
1	4	316	330
1	5	457	467
1	6	414	432
1	7	185	180
1	8	313	302
1	9	374	365
0	11	482	464
0	10	103	89
0	9	436	510
0	7	165	171
0	6	149	147
0	5	896	988
0	4	138	136
0	3	607	642
0	2	196	198
0	1	340	379
-1	1	111	106
-1	2	175	158
-1	3	604	617
-1	4	707	737
-1	5	516	533
-1	6	465	487
-1	7	247	244
-1	8	62	54
-1	9	80	66
-1	11	185	181
-2	13	113	100
-2	12	407	421
-2	11	140	200
-2	10	284	294
-2	8	144	124
-2	7	510	525
-2	6	886	915
-2	5	321	322
-2	4	853	864
-2	3	767	769
-2	2	77	41
-2	1	211	199
-3	2	445	425
-3	3	352	348
-3	4	352	343
-3	5	55	52
-3	6	93	105
-3	7	723	735
-3	8	496	495
-3	9	301	312
-3	10	493	504
-3	11	481	510
-3	12	282	255
-3	13	131	143
-3	14	401	424
-4	14	288	287
-4	13	403	413
-4	12	93	103
-4	11	141	127
-4	10	674	632
-4	9	114	113
-4	8	527	519
-4	7	71	57
-4	5	541	533
-4	4	194	177
-4	1	203	196
-5	1	124	111
-5	2	456	464
-5	3	34	65
-5	4	431	422
-5	5	267	261
-5	6	502	500
-5	7	703	705
-5	8	167	177
-5	9	300	303
-5	10	93	71
-5	11	181	160
-5	13	451	452
-5	14	143	147
-5	15	231	236
-6	15	470	493
-6	13	274	277
-6	12	56	23
-6	11	186	177
-6	10	251	258
-6	9	267	252
-6	8	175	153
-6	7	727	724
-6	6	97	103
-6	5	61	67
-6	4	87	92
-6	3	108	103
-6	1	78	63
-7	1	209	235
-7	3	279	292
-7	5	247	248
-7	6	374	385
-7	7	829	806
-7	8	333	336
-7	9	486	459
-7	10	257	254
-7	11	481	483
-7	12	65	87
-7	13	256	249
-7	15	582	593
-8	13	204	195
-8	12	392	380
-8	11	505	511
-8	10	174	173
-8	9	290	287
-8	7	413	410
-8	6	86	92
-8	4	263	267
-8	3	140	133
-9	6	87	69
-9	8	172	164
-9	10	115	111
-9	11	159	147
-9	12	490	467
***** K= 6*****			
-8	7	140	149
-8	8	343	323
-8	9	182	181
-8	10	150	136
-7	11	61	46
-7	10	111	122
-7	9	37	106
-7	7	267	265
-7	6	232	239
-7	5	381	394
-7	4	243	271
-7	3	259	279
-6	1	215	232
-6	3	374	374
-6	4	57	67
-6	5	289	279
-6	6	95	72
-6	7	494	486
-6	8	100	99
-6	9	173	180
-6	10	170	163
-6	11	287	277
-6	12	220	206
-6	13	71	59
-5	12	231	233
-5	11	132	130
-5	10	360	367
-5	9	220	210
-5	8	295	280
-5	7	313	306
-5	4	196	179
-5	3	152	128
-5	2	76	70
-4	1	73	54
-4	2	195	183
-4	3	201	193
-4	4	119	109
-4	5	323	318
-4	6	171	167
-4	7	730	713
-4	8	364	351
-4	9	93	95
-4	10	84	77
-4	11	240	245
-3	11	454	452
-3	10	147	156
-3	9	179	171
-3	8	90	102
-3	7	617	624
-3	5	374	370
-3	4	296	300
-3	3	204	200
-3	1	395	377
-2	1	637	658
-2	2	559	535
-2	3	474	469
-2	4	525	509
-2	5	351	332
-2	6	207	212
-2	7	87	101
-2	9	240	238
-2	10	184	175
-2	11	401	390
-1	11	345	337
-1	10	270	237
-1	9	362	370
-1	8	78	82
-1	7	77	57
-1	6	68	91
-1	5	616	623
-1	3	50	35
-1	2	171	135
0	0	385	399
0	1	241	252
0	2	175	186
0	3	172	183
0	4	104	101
0	5	259	276
0	7	36	78
0	8	337	342
0	10	314	306
1	8	345	335
1	7	277	272
1	6	490	503
1	5	240	246
1	4	372	370
1	3	416	449
1	2	226	233
1	1	65	23
1	0	214	130
2	0	254	236
2	1	114	108
2	2	183	178
2	4	302	313
2	5	234	246
2	6	215	201
2	7	101	95
3	5	419	398
3	3	449	432
3	2	293	281
3	1	471	462
3	0	431	429
4	0	151	166
4	1	674	656
4	3	430	397
4	4	144	134
5	1	222	224
5	0	105	98
6	0	203	185
***** K= 7*****			
4	1	160	157
4	0	131	130
3	0	395	390
3	2	466	449
3	3	393	374
2	5	211	202
2	4	267	264
2	3	348	338
2	2	642	632
2	0	486	465
1	0	186	169
1	2	72	35
1	3	236	233
1	4	239	238
1	5	160	167
1	6	112	140
0	7	122	139
0	6	393	410
0	5	182	195
0	4	265	279
0	3	61	33
0	2	171	196
-1	1	150	137
-1	2	365	380
-1	3	238	242
-1	5	462	478
-1	6	382	390
-1	7	456	473
-1	8	179	177
-2	9	139	147
-2	8	258	270
-2	7	619	650
-2	6	485	494
-2	5	195	197
-2	4	329	332
-2	3	145	123
-2	2	349	356
-2	1	257	241
-3	2	435	430
-3	3	95	87
-3	4	404	404
-3	5	86	110
-3	6	364	373
-3	7	515	522
-3	8	103	110
-4	10	230	255
-4	9	203	213
-4	8	87	67
-4	7	420	417
-4	6	312	301
-4	4	174	178
-4	2	96	105
-5	2	148	141
-5	3	79	56
-5	4	378	361
-5	5	115	99
-5	6	275	276
-5	7	94	108
-5	8	83	76
-5	9	105	103
-6	8	235	240
-6	7	510	516
-6	6	88	114
***** K= 8*****			
-2	1	216	196
-2	2	282	283
-2	4	135	126
-1	4	106	96
-1	2	414	419
0	0	465	501
0	1	212	231
0	2	429	451
0	3	84	53
1	2	304	336
1	1	455	472
1	0	515	447
2	0	177	174

[a] The calculated value (×10) of $F(000)$ is 7846.

the refinement (~150 reflections). No *systematic* attempt was made to correct the observed data for extinction effects. The (002) and (100) reflections were excluded from the final refinement cycles, however, since these appeared to be seriously affected by secondary extinction.

Determination of the Structure.—Using the corrected data, an origin-removed, sharpened Patterson map was computed[9] and solved for the coordinates (x, y, z in the general position of the space group $P2_1/c$) of the iron and two sulfur atoms. From the position of the iron atom it was immediately obvious that the complex was a dimer with a center of symmetry as required by the space group. Structures consistent with this finding are I, II, and IV; III could be ruled out, barring disorder. The positional coordinates of the iron and sulfur atoms were then used in a calculation to produce a set of phased structure factors for a difference Fourier synthesis. The difference map readily revealed the remaining five sulfur atom coordinates and those of three carbon atoms. Phasing on these atoms was sufficient for the location of the remaining atoms in the asymmetric unit. Refinement of the positional parameters and isotropic temperature factors for these 16 atoms converged at values of 0.068 and 0.106 for the discrepancy indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, respectively. At this stage a difference Fourier map showed anisotropic thermal motion for most of the atoms. Refinement was therefore continued in which anisotropic temperature factors were assigned to all atoms. After several cycles R_1 was reduced to 0.055 and R_2 to 0.071. A difference Fourier map at this point revealed the location of several peaks of electron density ~0.6 e$^-$/Å^3 (on a scale where the average value for a carbon atom is 4.0 e$^-$/Å^3), three of which were at chemically reasonable positions for hydrogen atoms. These were introduced into the structure with isotropic thermal parameters, and refinement continued to produce values of R_1, 0.048, and R_2, 0.061. A final Fourier map failed to show the remaining hydrogen atoms and had no region of electron density greater than 0.5 e$^-$/Å^3.

TABLE II

FINAL POSITIONAL AND THERMAL PARAMETERS OF THE ATOMS[a,b]

Atom	x	y	z	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0.0739 (1)	0.1103 (1)	−0.00128 (7)	7.1 (2)	8.5 (2)	2.59 (6)	0.0 (1)	3.08 (9)	0.46 (9)
S1	−0.0125 (2)	−0.0289 (2)	0.1318 (1)	10.8 (3)	11.6 (4)	3.1 (1)	−1.8 (3)	4.5 (1)	−0.3 (1)
S2	0.1547 (2)	0.2262 (2)	0.1277 (1)	10.2 (3)	10.3 (4)	3.1 (1)	−2.1 (3)	4.2 (1)	−0.6 (1)
S3	0.1234 (2)	0.2053 (3)	0.2650 (1)	14.2 (3)	14.5 (4)	3.4 (1)	−2.7 (3)	5.4 (2)	−1.5 (2)
S4	0.0636 (2)	0.3653 (2)	−0.0510 (1)	8.1 (3)	9.9 (4)	3.8 (1)	0.7 (2)	4.0 (1)	1.1 (1)
S5	0.3011 (2)	0.1641 (2)	0.0452 (1)	7.7 (3)	11.3 (4)	3.8 (1)	0.8 (2)	3.6 (2)	1.3 (2)
S6	0.3422 (2)	0.4708 (3)	−0.0064 (1)	9.1 (3)	12.1 (4)	4.9 (1)	−1.5 (3)	4.5 (2)	1.2 (2)
S7	−0.1468 (2)	p.1342 (2)	−0.0485 (1)	7.5 (3)	9.9 (4)	2.9 (1)	1.1 (2)	3.3 (1)	0.9 (1)
C1	0.0878 (8)	0.1360 (9)	0.1698 (5)	8 (1)	10 (1)	2.9 (4)	1.8 (9)	3.3 (6)	0.5 (6)
C2	0.237 (1)	0.375 (1)	0.2995 (7)	19 (2)	16 (2)	6.0 (6)	−8 (1)	8.6 (9)	−5.7 (9)
C3	0.392 (1)	0.337 (2)	0.3549 (7)	14 (2)	34 (3)	7.8 (8)	−6 (2)	5.4 (9)	−1 (1)
C4	0.2362 (8)	0.3398 (9)	−0.0047 (4)	7 (1)	9 (1)	2.6 (4)	−0.1 (9)	3.1 (5)	0.5 (6)
C5	0.219 (1)	0.620 (1)	−0.0841 (8)	14 (2)	8 (2)	5.9 (7)	3 (1)	6 (1)	1.3 (9)
C6	0.283 (1)	0.711 (1)	−0.1164 (7)	18 (2)	20 (2)	7.8 (7)	0 (2)	8.7 (9)	5.9 (9)
C7	−0.291 (1)	0.145 (1)	−0.1684 (6)	11 (1)	18 (2)	2.8 (5)	4 (1)	2.7 (7)	0.8 (8)
C8	−0.346 (1)	0.315 (1)	−0.1936 (7)	17 (2)	19 (2)	5.9 (6)	7 (2)	3.2 (9)	5.6 (9)
H2A	0.227 (9)	0.42 (1)	0.329 (5)	4 (2)[d]					
H5A	0.139 (8)	0.581 (8)	−0.133 (5)	2 (2)					
H7B	−0.278 (8)	0.091 (9)	−0.198 (5)	3 (2)					

[a] Atoms are labeled as indicated in Figure 1. Hydrogen atoms are labeled to correspond to the carbon atoms to which they are attached. [b] Standard deviations, in parentheses, occur in the last significant figure for each parameter. [c] The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Values reported are $\times 10^3$. [d] $\beta_{11} = B$ Å^2, since hydrogen atoms were assigned isotropic thermal parameters.

Table I contains the final list of calculated and observed structure factors. The atomic positional and thermal parameters, along with their standard deviations as derived from the inverse matrix of the last least-squares refinement cycle, are given in Table II. The root-mean-square amplitudes of vibration derived from the atomic anisotropic thermal parameters are summarized in Table III. The atom-labeling scheme is shown in Figure 1, and the orientation of the thermal ellipsoids, in Figure 2. Intramolecular bond distances and interbond angles appear in Tables IV and V.

TABLE III

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (IN Å)[a,b]

Atom	Min	Intermed	Max
Fe	0.151 (2)	0.176 (3)	0.183 (2)
S1	0.153 (4)	0.197 (3)	0.229 (3)
S2	0.161 (3)	0.181 (3)	0.225 (3)
S3	0.159 (4)	0.216 (4)	0.263 (3)
S4	0.165 (3)	0.182 (4)	0.221 (3)
S5	0.179 (4)	0.184 (4)	0.229 (3)
S6	0.163 (4)	0.216 (3)	0.257 (3)
S7	0.167 (3)	0.173 (3)	0.203 (3)
C1	0.16 (1)	0.18 (1)	0.21 (1)
C2	0.16 (2)	0.22 (1)	0.34 (1)
C3	0.23 (2)	0.33 (1)	0.37 (2)
C4	0.15 (1)	0.18 (1)	0.19 (1)
C5	0.16 (2)	0.25 (1)	0.27 (2)
C6	0.15 (2)	0.28 (1)	0.35 (1)
C7	0.18 (1)	0.23 (2)	0.29 (1)
C8	0.16 (2)	0.31 (1)	0.37 (1)

[a] Taken along the principal axes of the thermal ellipsoids. The orientation of these axes may be seen from Figure 2. [b] See footnotes *a* and *b*, Table II.

Discussion

General Description of the Structure.—The crystal structure consists of centrosymmetric iron dimers in which two ethyl mercaptide and two ethyl thioxanthate groups function as bridging ligands. The remaining coordination sites at the two iron atoms are occupied by the sulfur atoms of two more, terminal thioxanthate ligands (Figures 1 and 2). From a comparison of the appropriate bond distances (Table IV) and angles (Table V), it is apparent that, ignoring the ethyl groups, the approximate point group sym-

TABLE IV

INTRAMOLECULAR BOND DISTANCES (Å)[a,b]

Fe–Fe′	2.618 (2)	C2–C3	1.48 (2)
Fe′–S1	2.287 (2)	S1···S2(bite)	3.007 (3)
Fe–S2	2.286 (2)	S4–C4	1.682 (7)
Fe–S4	2.343 (2)	S5–C4	1.676 (8)
Fe–S5	2.333 (2)	S6–C4	1.720 (7)
Fe–S7	2.217 (2)	S6–C5	1.80 (1)
Fe′–S7	2.219 (2)	C5–C6	1.50 (1)
S1–C1	1.681 (8)	S4···S5(bite)	2.795 (3)
S2–C1	1.679 (8)	S7–C7	1.835 (9)
S3–C1	1.743 (7)	C7–C8	1.53 (1)
S3–C2	1.80 (1)		

[a] See footnotes *a* and *b*, Table II. [b] Reported values have not been corrected for thermal motion.

TABLE V

SELECTED INTRAMOLECULAR BOND ANGLES (DEG)[a]

S1′–Fe–S2	170.20 (9)	S1–C1–S2	126.9 (4)
S1′–Fe–S4	84.95 (8)	S1–C1–S3	111.5 (4)
S1′–Fe–S5	86.89 (8)	S2–C1–S3	121.5 (5)
S1′–Fe–S7	97.27 (8)	C1–S3–C2	105.8 (4)
S1′–Fe–S7′	88.10 (8)	S3–C2–C3	114.1 (8)
S2–Fe–S4	86.69 (8)	Fe–S4–C4	86.7 (3)
S2–Fe–S5	85.83 (8)	Fe–S5–C4	87.2 (2)
S2–Fe–S7	87.95 (8)	S4–C4–S5	112.6 (4)
S2–Fe–S7′	98.24 (8)	S4–C4–S6	126.7 (5)
S4–Fe–S5	73.40 (7)	S5–C4–S6	120.6 (4)
S4-Fe-S7	90.96 (8)	C4–S6–C5	104.1 (4)
S4–Fe–S7′	160.83 (9)	S6–C5–C6	110.1 (8)
S5–Fe–S7	163.46 (9)	Fe–S7–Fe′	72.35 (7)
S5–Fe–S7′	88.42 (8)	Fe–S7–C7	116.3 (3)
S7–Fe–S7′	107.65 (7)	Fe′–S7–C7	113.6 (3)
Fe′–S1–C1	111.7 (3)	S7–C7–C8	108.9 (7)
Fe–S2–C1	111.3 (3)		

[a] See footnotes *a* and *b*, Table II.

metry is D_{2h}. Since the dimer is required by the space group symmetry to be centrosymmetric, the Fe,S7,Fe′,S7′ rhombus is strictly planar with the ethyl groups in the anti[16] configuration. Distortions from idealized octahedral symmetry at each iron atom result in part from metal–metal bonding and partly from the geometrical constraints of the four-membered terminal thioxanthate chelate rings, both of which are discussed in detail below.

The function of thioxanthate groups as bridging ligands in $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ is similar to that of simple carboxylate anions in a number of transition metal complexes.[17] Other compounds in which YCS_2^{m-} groups bridge two metal atoms include a copper tetramer ($Y = (C_2H_5)_2N$, $m = 1$),[18] a copper octamer ($Y = (NC)_2C$, $m = 2$),[19] and a nickel dimer ($Y = C_6H_5CH_2$, $m = 1$).[20] It is interesting that in the iron, copper, and nickel complexes with bridging YCS_2^{m-} groups, metal–metal bonding is thought to be an important feature of the structure. In each case, the S···S bite distance of the bridging ligand is 3.0–3.1 Å and the metal–metal distances range from 2.56 to 2.87 Å. In the absence of metal–metal bonding, it might be difficult for ligands containing the YCS_2^{m-} broup to bridge two metal atoms, expecially if the M–M distance becomes significantly greater than 3.1 Å.

Structural Evidence for and Discussion of Metal–Metal Bonding.—The observed iron–iron distance of 2.618 Å is well within the range (2.37–3.05 Å) of crystallographically determined values[21–23] for which metal–metal bonding has been postulated. By contrast, the $[FeS_4C_4(CN)_4]_2^{2-}$ dimer,[24] in which metal–metal bonding is apparently unimportant, has a nonbonded iron–iron distance of 3.08 Å. Two additional structural features strongly suggest the presence of an iron–iron bond in $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$. In many other compounds containing M_2X_2 rings, where X is the donor atom of a bridging ligand, "sharply acute" M–X–M angles are postulated to be characteristic of metal–metal bonding.[23] In the present structure, the Fe–S–Fe angle has a value of 72.35(7)°. It is, moreover, noteworthy that the iron–iron bond length in $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ is significantly shorter than the bite distance, 3.007 (3) Å, of the bridging thioxanthate ligands. This fact is also taken as evidence[25] for the presence of a direct iron–iron bond.

As briefly discussed before,[3] the iron–iron bonding may be described in terms of a qualitative molecular orbital scheme involving direct overlap of iron d orbitals. At each iron atom a coordinate system is chosen with the x and y axes situated approximately along the iron–sulfur bonds in the plane of the Fe_2S_2 rhombus. Each iron atom then uses a set of $d_{x^2-y^2}d_{z^2}sp^3$ hybrid orbitals for σ bonding with the sulfur atoms. The 12 bonding σ MO's which result are populated with electrons formally donated by the sulfur atoms. Of the remaining six metal d orbitals, three on each metal atom, the two d_{xy} orbitals have the correct symmetry to form $\sigma(xy)$ bonding and $\sigma^*(xy)$ antibonding molecular orbitals to the adjacent iron atom. The remaining d_{xz} and d_{yz} orbitals are of appropriate symmetry for iron–sulfur π bonding.[26,27] The ten valence electrons of the two formally Fe(III) atoms occupy all but the $\sigma^*(xy)$ orbital, requiring an Fe–Fe σ bond order of 1. The molecule $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ and its *n*-propyl, *n*-butyl, and benzyl analogs[4a] thus appear to belong to the recently delineated[23] class of seven-coordinated M_2X_2 bridged systems with metal–metal interactions.

Metal–Ligand Geometry.—In $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$, there are three chemically distinct types of iron–sulfur bonds, which are reflected in the average values of 2.218 (2) Å for the bridging mercaptide ligands, 2.287 (2) Å for the bridging thioxanthate ligands, and 2.338 (4) Å for the terminal thioxanthate ligands. The Fe–S bond lengths in the Fe_2S_2 rhombus are comparable to the distances found in $[Ni(SC_2H_5)_2]_6$ (2.20 Å)[28] and $[Ni(SCH_2CH_2SCH_2CH_2S)]_2$ (2.18 and 2.22 Å)[29] for the Ni–S bridge bonds but are significantly shorter than the Fe–S distances in $[Fe(NO)_2(SC_2H_5)]_2$ (2.26 (2) Å),[30] $[Fe(CO)_3(SC_2H_5)]_2$ (2.259 (7) Å),[31] and $[Fe_2(CO)_6(SCH_3)]_2S$ (2.274 (8) Å).[32] Apparently the presence of strong π-acceptor ligands such as carbonyl or nitrosyl can weaken to some extent the metal–sulfur bonds in the same molecule.

As was the case for (thio-*p*-toluoyl disulfido)bis(dithio-*p*-toluato)iron(III), Fe(TTD)(DTT)$_2$,[2] the presence of both four- and five-membered rings in $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ offers an excellent opportunity to explore the effects of ring constraints on geometry. Here the results for these two molecules will be discussed. The basic principles can easily be extended to the geometries of other 1,1- and 1,2-dithiolato complexes[33] and to other ligand systems.[34]

When a bidentate ligand participates in the formation of a four- or a five-membered ring with one or more

---

(16) M. Dekker, G. R. Knox, and C. G. Robertson, *J. Organometal. Chem.*, **18**, 161 (1969), and references contained therein.

(17) C. Oldham, *Progr. Inorg. Chem.*, **10**, 223 (1968).

(18) R. Hesse, *Ark. Kemi*, **20**, 481 (1963).

(19) L. E. McCandlish, E. C. Bissel, D. Coucouvanis, J. P. Fackler, and K. Knox, *J. Amer. Chem. Soc.*, **90**, 7357 (1968).

(20) M. Bonamico, G. Dessy, and V. Fares, *Chem. Commun.*, 1106 (1969).

(21) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1 (1965).

(22) M. R. Churchill, *ibid.*, **6**, 190 (1967).

(23) L. F. Dahl, E. R. deGil, and R. D. Feltham, *J. Amer. Chem. Soc.*, **91**, 1653 (1969).

(24) W. C. Hamilton and I. Bernal, *Inorg. Chem.*, **6**, 2003 (1967).

(25) *Cf.* the discussion by F. A. Cotton, *Rev. Pure Appl. Chem.*, **17**, 25 (1967).

(26) It may be noted that iron–sulfur π bonding involving the iron d_{xz} and d_{yz} orbitals would not affect the conclusions about metal–metal bond formation or the general electron bookkeeping scheme which accounts for the observed diamagnetism[4a] of the compound. In fact, strong π bonding would require the highest filled molecular orbital to be $\sigma(xy)$, a result which can be used to explain the irreversibility of the one-electron oxidation of the dimer.[4]

(27) An equivalent molecular orbital description can be derived by combining the local sets of iron orbitals to transform according to the irreducible representations of the idealized molecular point group D_{2h}.

(28) P. Woodward, L. F. Dahl, E. W. Abel, and B. C. Crosse, *J. Amer. Chem. Soc.*, **87**, 5253 (1965).

(29) G. A. Barclay, E. M. McPartlin, and N. C. Stephenson, *Acta Crystallogr., Sect. B*, **25**, 1262 (1969).

(30) J. T. Thomas, J. H. Robertson, and E. G. Cox, *ibid.*, **11**, 599 (1958).

(31) L. F. Dahl and C. H. Wei, *Inorg. Chem.*, **2**, 328 (1963).

(32) J. M. Coleman, A. Wojcicki, P. J. Pollick, and L. F. Dahl, *ibid.*, **6**, 1236 (1967).

(33) R. Eisenberg, *Progr. Inorg. Chem.*, in press.

(34) See, for example, S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **8**, 2755 (1969).

TABLE VI

SUMMARY OF AVERAGE STRUCTURAL FEATURES OF FOUR- AND FIVE-MEMBERED RINGS IN $Fe(TTD)(DTT)_2$[a] AND $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$[b]

Compound	Ring	Fe–S distance, Å	S–Fe–S angle, deg	S···S bite distance, Å
$Fe(TTD)(DTT)_2$	Fe—S=C=S	2.32 (2)	73.8 (2)	2.783 (6)
$Fe(TTD)(DTT)_2$	Fe—S—S—C=S	2.21 (2)	92.6 (2)	3.199 (8)
$[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$	Fe—S=C=S	2.338 (4)	73.40 (7)	2.795 (3)
$[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$	Fe—S=C=S—Fe	2.287 (1)	94.9 (7)[c]	3.007 (3)

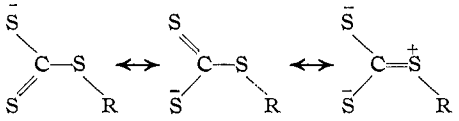
[a] TTD = thio-*p*-toluoyl disulfide, $CH_3C_6H_4CS_3^-$; DTT = dithio-*p*-toluate, $CH_3C_6H_4CS_2^-$; data from ref 2. [b] Numbers in parentheses are root-mean-square errors or estimated standard deviations, whichever are larger. [c] S–Fe–Fe′ angle (see Figure 1).

metal atoms having similar idealized coordination geometries and oxidation states, several stereochemical effects may be noted (Table VI). The angle at the metal atom is usually $\sim$15–25% smaller and the metal–ligand bond lengths $\sim$5% longer in the four-atom ring than in the five-atom ring. Reduction of the internal angles occurs at every atom in the smaller ring and is the geometrical consequence of requiring atoms with normal valence angles greater than 90° to form a four-membered ring. Although 90° may be the usual valence angle at the metal atom, it too will generally be reduced in order to relieve steric strain in the smaller ring. As a result of the decreased angle at the metal atom, metal–ligand overlap is poorer, the bond lengths are greater, and, for chelating ligands, the "bite" distance is commonly smaller in the four-membered ring. These effects are illustrated for $Fe(TTD)(DTT)_2$ and $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ in Table VI and are also evident in more extensive tabulations[33] of structural patterns in metal–sulfur chelate complexes.

The S4–Fe–S5 angle of 73.43 (7)° in the four-membered ring may be contrasted with the more normal "octahedral" S–Fe–S angles involving Fe, S1, S1′, and S2 (Table V). As expected from the foregoing considerations, the S···S bite distance of the terminal thioxanthate ligand is smaller than in the bridging ligand (Table VI). Similarly, the internal angles at the sulfur and carbon atoms are smaller in the four-atom ring than in the five-atom ring. Noteworthy, however, is the fact that although the S–C–S angle is only 11% less in the terminal than in the bridging thioxanthate ligand, the average Fe–S–C angle has decreased by $\sim$22% in the smaller ring. The larger, more polarizable, sulfur atom apparently can relieve steric strain better than an sp^2-hybridized carbon atom.

Intraligand Geometry and Intramolecular Steric Effects.—The average of the four crystallographically independent C=S bond lengths is 1.680 Å with a standard deviation from the mean of 0.002 Å. This value is similar to the average C=S bond distances obtained in $Fe(TTD)(DTT)_2$ (1.69 (2) Å)[2], $(C_6H_5CH_2CS_2)_4Ni_2$ (1.69 (6) Å),[20] $(C_6H_5CS_2)_6Ni_3$ (1.70 (2) Å),[35] $(C_6H_5CS_2)_2Pd$ (1.70 (1) Å),[36] $(C_2H_5OCS_2)_2Ni$ (1.7 Å),[37] $(NCNCS_2)_2Ni^{2-}$ (1.72 (3) Å),[38] $(C_2H_5OCS_2)_3Fe$ (1.684 (8) Å),[39] $(C_2H_5OCS_2)_3Co$ (1.67 (1) Å),[40] and other related compounds.[41] The C–S and C–C bond lengths and Fe–S–C and S–C–C bond angles in the bridging ethyl mercaptide ligand as well as in the S–C–C unit of both ethyl thioxanthate ligands (Tables II, III) are all in agreement with the values expected on the basis of crystallographic results[28–31] for analogous molecules.

Examination of the C1–S3 and C4–S6 bond distances (Table IV) reveals them to be significantly shorter than the value of 1.79 Å calculated by correcting the average of the S3–C2, S6–C5, and S7–C7 bond lengths for the difference (0.02 Å) between single-bond radii[42] of sp^3- and sp^2-hybridized carbon atoms. It therefore appears that resonance form VII participates to an appreciable extent, along with V and VI, in the overall electronic structure of coordinated thioxanathate ligands. This result is consistent with the conclusion that substantial double-bond character exists in the exocyclic C–S bond of the closely related trithiocarbonate ligand, as previously inferred from a structural study of the $Ni(CS_3)_2^{2-}$ ion.[43,44]



V VI VII

In a recent X-ray crystallographic study of $Co(S_2COC_2H_5)_3$,[40] the resonance form corresponding to VII was calculated to contribute 13% to the electronic structure of the ethyl xanthate ligand, compared to 43.5% each for resonance hybrids V and VI. An identical calculation for $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$, using the data of Table IV and the method of ref 40, indicates that the bridging thioxanthate group consists of 41% V, 41% VI, and 18% VII and that the terminal thioxanthate group has 39% V, 39% VI, and 22%

---

(35) M. Bonamico, G. Dessy, and V. Fares, *Chem. Commun.*, 324 (1969).

(36) M. Bonamico and G. Dessy, *ibid.*, 483 (1968).

(37) M. Franzini, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **118**, 393 (1963).

(38) F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **7**, 2141 (1968).

(39) B. F. Hoskins and B. P. Kelly, *Chem. Commun.*, 45 (1970).

(40) S. Merlino, *Acta Crystallogr., Sect. B*, **25**, 2270 (1969).

(41) T. Brennan and I. Bernal, *J. Phys. Chem.*, **73**, 443 (1969), and references cited therein.

(42) Z. B. Maksic and M. Randic, *J. Amer. Chem. Soc.*, **92**, 424 (1970), and references therein.

(43) J. S. McKechnie, S. L. Miesel, and I. C. Paul, *Chem. Commun.*, 152 (1967).

(44) Reference 33 contains a general discussion of resonance in a number of other YCS_2^- ligand systems.

VII. As discussed previously,[4a] the fact that canonical form VII contributes more to the resonance stabilization of the terminal thioxanthate ligand than to the bridging one facilitates the assignment of the molecule's pmr spectrum. Since the terminal thioxanthate is involved in the formation of a four-membered ring with the iron atom (Fe–S–C angle, 86.9°), it is reasonable that resonance form VII would contribute more to its electronic structure than to that of the bridging thioxanthate group (Fe–S–C angle, 111.5°).

A final point worthy of mention is that, although the CS_3 atom groupings are calculated to be strictly coplanar, the two $S{=}C{=}S$ angles within each ethyl thioxanthate are unexpectedly nonequivalent (Table V). One possible explanation is that intramolecular packing forces distort the angles at C1 and C4 in order to accommodate the stereochemical requirements of the ethyl groups. Consistent with this suggestion is the fact that, for both thioxanthate ligands, the larger $S{=}C{=}S$ angle occurs on the side of the ligand occupied by the ethyl group (Table V and Figure 1). Similar results have been obtained for the $S{=}C{=}O$ angles of the ethyl xanthate ligands in their $M(S_2COC_2H_5)_3$ complexes, where M is iron[39] and cobalt.[44]

Acknowledgments.—We are grateful to the National Institutes of Health for its generous support of this research under Grant No. GM 16449 and to Dr. S. J. LaPlaca for assistance in preparing the figures for this paper.

Notes

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
JADAVPUR UNIVERSITY, CALCUTTA-32, INDIA

Specific Interaction between Tetraalkylammonium and Hexacyanoferrate(III) Ions

BY MUKUL KUMAR BASU AND MIHIR NATH DAS*

Received January 14, 1970

In a previous communication,[1] it has been reported that tetramethylammonium chloride exerts a negative salt effect on the equilibrium

$$2Fe(CN)_6^{3-} + 3I^- \rightleftharpoons 2Fe(CN)_6^{4-} + I_3^- \qquad (1)$$

whereas alkali metal salts exhibit the normal positive effect. To obtain detailed information about such an abnormal salt effect exerted by tetraalkylammonium salts, investigations have been carried out on the specific cation effects on the activity coefficients of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ ions by emf and solubility measurements.

Experimental Section

Materials.—$K_3Fe(CN)_6$ (E. Merck, *pro analysi*) was dried in an electric oven at 110° and standard solutions were prepared by accurate weighing. $K_4Fe(CN)_6$ (E. Merck, *pro analysi*) was recrystallized and dried. Standard solutions were prepared by weighing and used on the same day.

The halide salts used were of reagent quality (Merck) and solutions were standardized against silver nitrate solution. Potassium nitrate, lithium nitrate, and tetramethylammonium nitrate were prepared by mixing equivalent amounts of the corresponding hydroxides and nitric acid.

Potassium barium hexacyanoferrate(II), $K_2BaFe(CN)_6$, was prepared by adding $BaCl_2$ solution to a saturated solution of $K_4Fe(CN)_6$. The pale yellow precipitate was kept overnight and then filtered under suction, with thorough washing with water and alcohol. The purity of the sample was checked by estimating the barium content as sulfate.

$Tl_4Fe(CN)_6$ was prepared by mixing equivalent amounts of $TlNO_3$ and $K_4Fe(CN)_6$ and keeping the precipitate overnight, filtering under suction, and thoroughly washing with water and alcohol.

Hexaamminecobalt(III) hexacyanoferrate(III) was prepared by mixing equivalent amounts of $K_3Fe(CN)_6$ and $Co(NH_3)_6Cl_3$ which was prepared and purified by the usual method.[2] All the samples were stored in a vacuum desiccator.

Twice distilled water was used for solubility measurements, and triple distilled de-oxygenated water for electrometric measurements.

Electrometric Measurements.—Emf measurements at 35° were carried out on the concentration cell

$$\mathrm{Pt}|\underset{(0.05\,M)}{Fe(CN)_6^{4-}},\ \underset{(0.05\,M)}{Fe(CN)_6^{3-}}\,||\,\underset{(0.05\,M)}{Fe(CN)_6^{4-}},\ \underset{(0.05\,M)}{Fe(CN)_6^{3-}},\ \underset{(1\,M)}{\text{salt solution}}|\mathrm{Pt} \qquad (A)$$

Potassium chloride (saturated) in agar was used in the salt bridge.

The measurements were carried out with a specially designed cell, made of Pyrex glass, having two compartments 7 cm high and 2.5 cm in diameter, and each of them was fitted with two standard joints (B7). Through the two extreme joints the platinum electrodes were fitted, and the joints at the inner side were used for inserting the salt bridge. The electrodes and the salt bridge were also provided with standard joints (B7).

After placing the solutions in the cell compartments, pure and dry nitrogen gas was passed through the extreme joints of both the compartments for about 10 min. Then the platinum electrodes (after cleaning with aqua regia and washing thoroughly with distilled water and burning over alcohol flame) were quickly inserted through the extreme joints of both the compartments. The salt bridge (agar + KCl) was then introduced through the inner joints. The nitrogen atmosphere was maintained within the cell compartments. The cell was placed in a thermostat (35 ± 0.01°). The asymmetry potentials of the electrodes were tested before use and the best pairs were selected for experimental observations. Readings were taken at intervals of 10 min and found to remain constant for 1 hr or more. The emf measurements were made with a potentiometer (Rubicon Co., Philadelphia, Pa.) and a moving coil galvanometer until the values were constant within ±0.1 mV.

---

* To whom correspondence should be addressed.

(1) M. K. Basu and M. N. Das, *Indian J. Chem.*, **7**, 356 (1969).

(2) J. Bjerrum and J. P. McReynolds, *Inorg. Syn.*, **2**, 217 (1963).