Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stonv Brook, New York 11973 and Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973, U.S.A.

The Crystal Structure of Bis-(Cyclopentamethylenedithiocarbamato) Fe^{II} Dicarbonyl*

J.S. Ricci, Jr.,[1] C.A. Eggers,[2] and I. Bernal[3]

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The crystal structure of bis(cyclopentamethylenedithiocarbamato)Fe^{II}dicarbonyl, $(Cpdtc)_2Fe(CO)_2$, has been determined from three-dimensional x-ray data collected by Weissenberg techniques. The compound crystallizes in the space group D_{2h}^{15}–Pbca of the orthorhombic system with eight molecules in a cell of dimensions $a = 9.67(2)$, $b = 11.65(2)$, and $c = 33.74(8)$ Å; $V = 3802.2$ Å^3. The observed and calculated densities are 1.52(2) and 1.51 gm/cm^{-3}. The molecules contain six-fold coordinated Fe^{II} in which the carbonyl groups are cis *to each other and the polyhedron around the central atom is an octahedron distorted by the limited ligand «bite». The two dithiocarbamate ligands consists of nearly planar S_2CNC_2 fragments which make an angle of 88.8° to each other while the piperidine rings are in the chair conformation and contain normal C–N and C–C bonds. The Fe–S bonds occur in pairs (av. Fe–S lengths being 2.338(6) and 2.306(5) Å, respectively and the longer pair is associated with sulfurs located* trans *to the carbonyl ligands. The Fe–C–O fragments are essentially linear and the average value of the Fe–C, C–O, and Fe–C–O parameters are: 1.78(3) Å, 1.12(3) Å, and 177(1)°, respectively.*

Introduction

For the sake of simplicity, we have used the following abbreviations in naming the ligands mentioned in this manuscript:

(Cyclopentamethylenedithiocarbamato) = Cpdtc

(N,N-dimethyldithiocarbamato) = Me$_2$dtc

(N,N-diethyldithiocarbamato) = Et$_2$dtc, etc...

1,2-dicyano-1,2-ethylenedithiolato = MNT

1,2-bisperfluoromethyl-1,2-ethylenedithiolato = PFD

In 1933 Cambi and Szego[4] reported that compounds of the type (dtc)$_3$Fe^{II}, with dtc = any dithiocarbamate, have abnormal magnetic moments. Ewald, *et al.*[5] carried out an extensive set of measurements on tris-dithiocarbamato Fe^{III} compounds which agreed with and enlarged the original findings of Cambi and Szego.[4] Since then the subject has been studied extensively by White, Martin and their associates.[6] Nonetheless, the reason for the unusual behavior of these substances is not fully understood since some of these species behave as simple paramagnets while others sugegst the presence of spin states in thermal equilibrium.[5,6] Among the interesting structural observations that can be made about the tris-dithiocarbamates of Fe^{III} is the following: the bulk of the alkyl group seems to affect the magnitude of the magnetic moment. Bulky groups such as isopropyl and cyclohexyl produce derivatives with low magnetic moments[6] (2.34 and 2.62 B.M., respectively, for the di-isopropyl and di-cyclohexyl derivatives) while small alkyl groups produce species with high magnetic moments:[6] the diethyl and piperidyl compounds have magnetic moments of 4.41 and 4.16 B.M. It is natural, therefore, to turn to structural studies to explain the differences in the magnetic properties of the various alkyl dithiocarbamates.

Our attempts to collect single crystal x-ray data on crystals of several tris-dithiocarbamates of Fe^{III} met

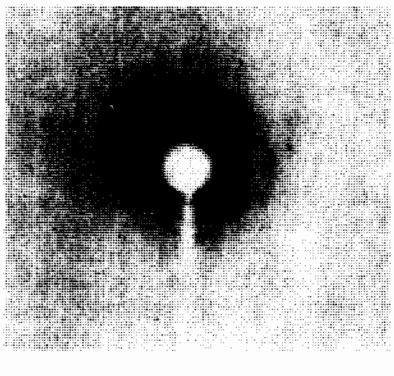

Figure 1. This is a precession photograph of (Cpdtc)$_3$Fe taken approximately 3 hours after withdrawing the crystal from the mother liquor. The earlier alignment photographs showed discrete spots which allowed us to determie that this substance was initially highly crystalline.

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(1) Present Address: Department of Chemistry, Windham College, Putney, Vermont 05346.

(2) Present Address: Shell Development Laboratories, Emeryville, California 94608.

(3) Present Address: Department of Chemistry, Brookhaven National Laboratory, Upton, L.I., New York 11973.

(4) L. Cambi and L. Szego, *Ber.*, *66*, 656 (1933).

(5) A.H. Ewald, R.L. Martin, I.G. Ross, and A.H. White, *Proc. Roy. Soc.* (London) *A280*, 235 (1964).

(6) For the most recent paper of this series see: A.H. Ewald, R.L. Martin, E. Sinn, and A.H. White, *Inorg. Chem.*, *8*, 1837 (1969) and references to their previous work.

with little success since the crystals either decompose or undergo extensive crystalline or molecular changes which destroy the lattices shortly after withdrawing the samples from the mother liquor (benzene solutions). Figure 1, for example, is a reproduction of a precession photograph taken two to three hours after a crystal of $(Cpdtc)_3Fe^{III}$ was withdrawn from the solution from which it was grown. These changes are not due to loss of solvent of crystallization since elemental analyses show that these substances crystallize from benzene without solvent of crystallization. In view of the fact that the $Cpdtc^-$ anion is biologically interesting[7] and that magnetically iron dithiocarbamates are an important class of compounds, we decided to examine the structure of the stable $(Cpdtc)_2Fe(CO)_2$ derivative with the hope of shedding some light on the relationship between structure and the anomaly in the magnetic behavior of the Fe^{III} derivatives.

A brief report has appeared in which Hoskins and Kelly[8] presented some of the structural characteristics of $(n\text{–}but_2dtc)_3Fe$. We have included in our Discussion a comparison of the structural parameters for the Fe–S and $R_2N\text{–}CS_2$ fragments found for the Fe^{II} $(3d^6)$ dicarbonyl and the Fe^{III} $(3d^5)$ *tris* complex since the differences may provide useful clues in a future understanding of the unusual magnetic behavior of the trisdithiocarbamates of Fe^{III}.

Experimental Section

Synthesis. $(Cpdtc)_2Fe(CO)_2$ was prepared as follows: A three-to-one excess of cyclopentamethylenethiuramdisulfide to $Fe(CO)_5$ was refluxed under a nitrogen atmosphere in freshly distilled tetrahydrofuran. The reaction proceeds quickly to a stage where the solution is orange and the product isolated at this point was later found to be $(Cpdtc)_2Fe(CO)_2$. Elemental analysis of the orange, diamond-shaped crystals (m.p. 162°C, decomp) gave: $C=39.00\%$; $H=4.64\%$; $N=6.44\%$. Calculated for $C_{14}H_{20}N_2O_2FeS_4$: $C=38.88\%$; $H=4.66\%$; $N=6.48\%$. Formation of the *tris* derivative is difficult probably because of steric crowding at the two remaining bonding sites; however, on prolonged refluxing with excess thiuramdisulfide the *tris derivative* can be obtained as a deep green solid.

Crystal Data. Precession, oscillation and Weissenberg photographs showed the compound to crystallize in the orthorhombic system with a cell of dimensions $a=9.67(2)$, $b=11.65(2)$, and $c=33.74(8)$ Å; $V=3803$ Å^3. A density of 1.51 gm/cm^{-3}, calculated for eight molecules in the unit cell, is satisfactory agreement with that of 1.52 gm/cm^{-3} measured by flotation in aqueous $ZnCl_2$ solution. The systematic extinctions observed in photographs of the $h0\ell$, $hl\ell$, $hk0$ and $hk1$ zones are $0k\ell$, $k\neq 2n$; $h0\ell$, $\ell\neq 2n$ and $hk0$, $h\neq 2n$, which uniquely define the space group as Pbca. Thus, no crystallographic symmetry conditions are impossed on the molecules.

The crystal chosen for intensity measurements was a diamond-shaped plate bound by the (110), $(\bar{1}10)$, $(1\bar{1}0)$, $(\bar{1}\bar{1}0)$, (001) and $(00\bar{1})$ faces and having dimensions of 0.10, 0.11 and 0.04 mm along the $[110]$, $[\bar{1}10]$ and $[001]$ directions, respectively. The crystal was mounted with the spindle axis along the *b* direction and a complete set of equi-inclination data was recorded with an Enraf-Nonius integrating Weissenberg camera. X-rays were generated with a Picker 809 unit using a high intensity Cu target tube whose beam was filtered with Ni foil. Intensities were collected at room temperature using an oscillating range of 206°. The levels $h0\ell$ to $h9\ell$, $0k\ell$ and $1k\ell$ were recorded and read out to $\theta\leqslant 60°$. Since Fe compounds fluoresce when exposed to Cu radiation, we placed a thin sheet of brass (0.05 mm thick) in front of the film package. In this mannes fairly uniform, clean backgrounds were obtained for all five layers of film exposed. The intensities of the reflections were estimated visually using a calibrated film strip whose spot shapes and sizes were the same as those in the integrated films. Of the 2460 independent reflections allowed in the angular range of $\theta\leqslant 60°$, 983 were recorded as being significantly above background. These data were corrected for Lorentz and polarization effects and also for absorption (using Prewitt's program[9]). The data were brought to a common scale using program INTERSCALE[10] and a Wilson plot[11] was calculated in order to place the values of the F_o^2's on an absolute scale and to estimate the overall effect of thermal motion. The atomic scattering factors used[12a] included corrections for the anomalous dispersion[12b] of iron and sulfur.

Solution and Refinement of the Structure. The approximate positions of the iron and the four sulfur atoms were determined from a sharpened, origin-removed, three-dimensional Patterson synthesis. Ten of the light atoms were located at chemically sensible positions in a Fourier map which was calculated using all the observed data and phased by the iron and four sulphur atoms. A second Fourier synthesis using the Fe, 4S and the 10 light atoms revealed the positions of the 8 remaining non-hydrogen atoms. Two cycles of refinement in which the positional and isotropic thermal parameters of all the non-hydrogen atoms were varied gave an $R(F^2)$ value of 0.26. The Fe and 4S atoms were further refined using anisotropic thermal motion while the lighter atoms were constrained to isotropic motion, resulting in a reduction of the conventional residual of $R(F)=0.128$. A difference Fourier synthesis computed at this stage revealed a number of peaks whose heights were approximately 0.60 e/(Å)^3, or about 40% of the height of the peaks for a carbon atom. Since the peaks in the difference map were at chemically reasonable posi-

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(7) J.A. Cohen, O. Vos, and D.W. von Bekkum, « Advances in Radiobiology », Ed. by G.C. Hevesy, Oliver and Boyd, Edinburgh, 1957 pp. 134-144.

(8) B.F. Hoskins and B.P. Kelly, *Chem. Commun.*, 1517 (1968).

(9) The absorption coefficient, as estimated from the sum of the atomic contributions (see ref. 12c) is 104.8 cm^{-1}. A local CDC 6600 version of Prewitt's ABN absorption program was used to carry out the correction. Transmission coefficients ranged from 0.61 to 0.75.

(10) INTERSCALE is our version of the program initially written by W.C. Hamilton, J.S. Rollett and R.A. Sparks, *Acta Cryst.*, *18*, 129 (1965).

(11) X-DATA is our program to calculate scale factors and overall temperature factors using the procedure of A.J.C. Wilson, *Nature*, *150*, 151 (1942).

(12) « International Tables for X-Ray Crystallography », Kynoch Press, Birmingham, England, 1968. (a) Vol. III, pp. 202-212; (b) Vol. III, pp. 215; (c) Vol. III, p. 162-169.

Table I. Atoms were labelled as shown in Fig. 2. Hydrogen atom labels correspond to those of the carbon atoms to which they are attached. Standard deviations, in parentheses, occur in the last significant figure for each parameter. All hydrogen atoms were assigned arbitrary, isotropic, thermal parameters of 5.0 Å^2.

Atom	X/A	Y/B	C/Z	B11	B22	B33	B12	B13	B23
FE	.1607(3)	.0385(2)	.3779(1)	105(4)	66(2)	8(0)	7(2)	1(1)	0(1)
S1	.1389(6)	—.1222(4)	.3384(1)	161(10)	41(4)	7(1)	6(4)	—1(4)	0(1)
S2	.1502(5)	.1080(3)	.3130(1)	99(8)	32(4)	7(0)	0(4)	3(1)	0(1)
S3	—.0796(5)	.0556(4)	.3835(1)	54(7)	59(4)	9(1)	—24(4)	1(2)	2(1)
S4	.1232(5)	.2165(4)	.4060(1)	59(7)	58(4)	8(0)	—11(4)	0(2)	—4(1)
O1	.1671(16)	—.0753(13)	.4533(4)	149(23)	130(15)	7(1)	29(16)	3(5)	3(4)
O2	.4598(17)	.0624(16)	.3762(6)	58(23)	162(19)	25(3)	4(19)	3(8)	0(6)
N1	.0860(18)	—.0649(13)	.2639(3)	147(26)	86(13)	3(1)	—46(16)	1(5)	—4(3)
N2	—.1478(19)	.2552(12)	.4161(4)	217(32)	22(11)	9(2)	39(16)	—4(6)	—3(3)
C1	.1636(24)	—.0332(23)	.4224(7)	128(35)	171(27)	8(2)	91(26)	—21(9)	—24(7)
C2	.3492(25)	.0515(25)	.3769(7)	38(29)	205(34)	11(3)	—20(30)	—1(9)	0(8)
C3	.1204(16)	—.0337(14)	.2986(6)	26(25)	70(14)	12(2)	—7(14)	—11(9)	—11(8)
C4	.0701(25)	—.1851(13)	.2508(6)	195(45)	45(19)	10(4)	45(26)	—10(10)	—4(6)
C5	.1681(20)	—.2216(15)	.2222(6)	48(32)	77(22)	13(3)	3(20)	—1(9)	—12(7)
C6	.1604(23)	—.1404(20)	.1858(7)	86(40)	116(27)	13(3)	—9(27)	16(9)	—20(8)
C7	.1797(27)	—.0167(17)	.1990(7)	171(50)	52(21)	11(3)	—42(24)	5(10)	—10(6)
C8	.0779(19)	.0162(15)	.2296(6)	37(30)	84(20)	10(3)	—16(20)	6(8)	—3(6)
C9	—.0472(25)	.1829(14)	.4040(5)	205(46)	29(18)	5(2)	—22(25)	—6(9)	—12(5)
C10	—.1169(20)	.3633(15)	.4382(6)	82(36)	63(19)	11(3)	—49(20)	—4(8)	—7(6)
C11	—.1758(24)	.3615(20)	.4787(6)	124(46)	84(22)	12(3)	9(24)	3(10)	10(7)
C12	—.3221(29)	.3326(23)	.4791(6)	285(70)	190(39)	8(3)	—168(46)	18(12)	—23(9)
C13	—.3579(24)	.2222(16)	.4559(5)	112(42)	107(25)	9(3)	—26(26)	—1(9)	—1(6)
C14	—.2991(23)	.2290(14)	.4143(6)	28(35)	88(21)	12(3)	19(21)	—5(7)	—7(7)
		H4-1		.0747	—.2367		.2738		
		H4-2		—.0239	—.1918		.2377		
		H5-1		.2610	—.2172		.2355		
		H5-2		.1467	—.3030		.2158		
		H6-1		.0639	—.1466		.1730		
		H6-2		.2299	—.1600		.1656		
		H7-1		.2740	—.0077		.2101		
		H7-2		.1678	.0364		.1757		
		H8-1		.0999	.0966		.2385		
		H8-2		—.0165	.0149		.2177		
		H10-1		—.0114	.3729		.4394		
		H10-2		—.1537	.4311		.4228		
		H11-1		—.1247	.3001		.4943		
		H11-2		—.1631	.4364		.4915		
		H12-1		—.3493	.3211		.5076		
		H12-2		—.3731	.3978		.4677		
		H13-1		—.3159	.1541		.4697		
		H13-2		—.4596	.2130		.4545		
		H14-1		—.3118	.1537		.4005		
		H14-2		—.3482	.2905		.3990		

tions for hydrogen atoms of the methylene groups, we decided to compute the idealized positions of the twenty hydrogens on the assumption that C–H = 0.97 Å. One cycle of refinement which included these fixed hydrogen atom contributions with $B(H) = 5.0$ Å^2 gave a discrepancy index of $R(F) = 0.108$. Subsequent refinement was carried out, with hydrogens at recalculated idealized positions following each cycle resulting in convergence with values of the unweighted andand weighted R factors of 0.093 and 0.113, respectively, and a goodness of fit of 0.995. These three quantities are defined as follows:

$$\text{Unweighted } R = \Sigma \| |F_o| - |F_c| \| / \Sigma |F_o|$$

$$\text{Weighted } R = \{\Sigma\omega(|F_o| - |F_c|)^2 / \Sigma F_o^2\}^{1/2}$$

$$\text{Goodness of fit } = [\Sigma\omega(|F_o| - |F_c|)^2/(\text{NO-NV})]^{1/2}$$

where $\omega = \sigma(F_o)^{-2}$ and NO and NV are the number of observations and the number of variables, respectively. During the refinement the quantity minimized was $\Sigma\omega(|F_o| - |F_c|)^2$ and the weighting scheme, derived from an analysis of variance[13] was:

$$\text{For } F_o \leqslant 10.0,\ \sigma(F_o) = 1.0$$

$$\text{For } F_o > 10.0,\ \sigma(F_o) = 1.0 + 0.095\ F_o$$

The positional and thermal parameters thus obtained are listed in Table I. Table II gives a comparison of the observed and calculated structure amplitudes.

Description of the Structure. The structure of the $(Cpdtc)_2Fe(CO)_2$ molecule is depicted in Figure 2, which is a stereo pair. The molecules are monomeric and the configuration of the 4S and two carbonyl carbons around the Fe is that of an distorted octahedron, whose principal source of distortion is the limited bite of the dithiocarbamate ligands. The degree of distortion can be estimated from the fact that within the four-membered CS_2Fe ring the S–Fe–S angle is only about 75°. The two carbonyl groups ocupy *cis* positions, making the sulfur ligands equivalent in pairs (experimentally we find that the two sulfur atoms *trans* to the carbonyl groups have longer Fe–S langths,

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(13) The analsis of variance was carried out using our program HANOVA, available on request.

Table II. Observed structure factors, their estimated standard deviations and structure factors calculated using the refined structural parameters listed in Table I. The form of the anisotropic ellipsoid is exp $[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. All value reported are x 10.

K	L	FO	SIG	FC
***	H=	0	***	
0	12	396	44	464
0	14	970	102	1047
0	16	615	64	567
0	20	506	54	511
0	24	518	56	484
0	26	461	54	447
0	28	494	45	249
0	30	377	46	336
0	32	517	54	467
0	34	214	31	190
0	42	243	33	246
2	0	1177	129	970
2	1	158	25	146
2	2	1078	112	969
2	3	924	94	971
2	4	819	84	845
2	5	874	93	1040
2	6	567	64	674
2	7	1236	127	1225
2	8	962	96	1025
2	9	489	56	603
2	11	1125	117	1413
2	12	1402	145	1713
2	13	228	32	272
2	14	127	22	138
2	15	643	75	838
2	16	1220	124	1497
2	17	390	47	407
2	18	436	51	505
2	20	693	76	756
2	21	521	66	520
2	22	603	67	615
2	23	188	28	215
2	24	316	46	217
2	26	744	81	677
2	27	174	27	153
2	28	242	33	223
2	31	395	48	386
2	34	194	29	198
2	35	358	44	305
4	1	915	97	811
4	2	224	31	185
4	3	137	23	141
4	4	475	55	534
4	5	954	101	1161
4	6	1317	135	1618
4	7	640	71	739
4	8	816	84	891
4	9	914	97	965
4	10	688	75	735
4	11	960	101	974
4	12	592	66	574
4	13	445	52	426
4	14	319	46	309
4	15	913	97	992
4	17	571	64	649
4	19	958	101	1031
4	22	222	31	221
4	23	568	64	545
4	24	409	49	443
4	25	186	28	211
4	27	323	41	259
4	29	196	29	209
4	31	506	54	475
4	34	346	43	322
4	38	284	37	296
4	40	205	30	248
6	0	448	53	443
6	1	842	96	749
6	3	1734	175	1650
6	4	431	51	396
6	6	562	63	542
6	11	403	44	405
6	14	158	25	178
6	15	207	30	219
6	16	520	56	593
6	22	223	31	239
6	25	300	34	308
6	28	327	41	350
6	31	220	31	247
6	35	247	33	217
6	39	156	28	149
8	2	226	31	223
8	3	156	25	158
8	4	163	26	190
8	5	283	27	327
8	6	510	55	588
8	7	451	53	560
8	8	711	78	868
8	9	665	73	725
8	12	478	55	554
8	13	445	52	436
8	14	139	23	163
8	19	555	61	629
8	23	390	47	425
10	0	184	27	182
10	4	341	42	361
10	7	339	42	321
10	8	408	56	518
10	11	236	32	251
10	12	404	49	383
10	16	212	30	208
10	18	172	26	210
10	20	242	33	307
10	22	278	36	306
10	23	191	28	242
12	0	566	64	595
12	4	411	50	424
***	H=	1	***	
0	8	222	31	206
0	14	559	63	650
0	16	461	54	479
0	18	239	33	255
0	22	226	31	217
0	24	190	24	136
0	26	505	58	462
0	30	405	49	387
0	34	455	53	366
1	1	873	93	916
1	2	911	97	895
1	3	874	93	859
1	4	317	40	342
1	5	442	52	465
1	6	239	32	258
1	7	217	31	235
1	8	840	90	1016
1	9	246	33	287
1	10	234	33	281
1	11	128	23	143
1	12	571	64	655
1	13	482	56	518
1	15	137	23	139
1	16	139	23	138
1	17	333	42	350
1	20	205	29	212
1	21	231	32	210
1	24	298	38	272
1	25	514	59	461
1	29	293	39	276
1	30	209	30	191
2	1	418	49	516
2	2	1303	134	1131
2	3	212	30	174
2	4	444	52	405
2	5	340	42	327
2	9	465	55	550
2	10	463	52	515
2	11	433	51	463
2	12	114	21	139
2	13	592	66	693
2	14	447	52	449
2	15	504	59	543
2	17	143	24	169
2	18	538	61	522
2	19	671	74	644
2	22	521	60	484
2	24	155	25	137
2	25	397	49	384
2	26	332	42	318
2	28	283	35	302
2	29	245	33	230
2	33	336	42	276
3	1	155	25	149
3	2	77	10	72
3	3	292	34	206
3	4	148	24	122
3	5	290	38	262
3	6	213	30	193
3	8	259	35	245
3	9	145	24	161
3	10	234	33	237
3	11	432	51	464
3	12	453	53	463
3	13	424	50	440
3	14	891	95	922
3	15	433	51	460
3	17	387	47	420
3	18	544	62	526
3	20	199	29	162
3	21	393	47	350
3	24	226	31	169
3	25	212	30	233
3	26	260	35	184
3	28	413	49	381
3	31	313	40	256
3	32	260	35	213
4	2	114	21	121
4	3	545	62	454
4	4	819	84	750
4	6	654	73	624
4	7	554	63	498
4	8	143	24	157
4	10	641	71	634
4	11	158	25	171
4	12	202	29	184
4	13	643	72	675
4	14	275	36	289
4	15	455	53	443
4	17	305	39	293
4	18	250	34	234
4	19	251	34	246
4	21	268	35	234
4	25	215	30	179
4	28	262	35	216
4	36	257	34	205
4	38	258	34	188
5	2	550	62	479
5	5	825	89	775
5	6	916	97	885
5	9	382	46	450
5	10	245	33	294
5	11	212	30	195
5	12	290	38	300
5	16	142	24	152
5	17	234	32	209
5	20	413	49	390
5	22	252	38	337
5	24	184	28	178
5	26	176	27	189
5	27	236	32	214
5	30	185	29	169
6	2	124	22	128
6	3	528	60	475
6	4	317	40	291
6	5	729	79	626
6	6	430	51	427
6	7	621	68	555
6	8	207	30	218
6	9	417	50	447
6	11	240	33	221
6	12	192	28	191
6	13	136	23	137
6	20	183	27	146
6	21	381	46	383
6	22	301	39	304
6	23	260	35	248
6	25	302	39	285
6	27	392	47	404
6	31	272	36	270
7	1	384	46	284
7	2	354	47	342
7	4	148	24	159
7	5	342	42	274
7	6	412	49	614
7	7	241	33	237
7	8	110	20	116
7	9	370	45	356
7	10	348	43	354
7	13	145	24	169
7	16	254	34	257
7	20	357	44	394
7	22	217	31	250
7	24	331	41	257
8	1	159	25	164
8	4	421	50	399
8	5	173	26	190
8	7	436	51	384
8	8	215	30	249
8	10	253	34	220
8	11	464	54	481
8	12	131	22	147
8	13	177	27	204
8	15	145	24	181
8	16	150	24	149
8	17	198	29	235
8	20	180	27	193
8	21	330	41	367
8	25	294	39	204
9	3	111	21	120
9	4	143	24	165
9	6	103	20	84
9	9	340	42	385
9	10	180	27	194
9	11	329	41	360
9	13	127	22	138
9	14	263	34	257
9	17	211	30	224
9	18	207	30	234
9	21	181	27	212
9	25	186	29	183
10	1	232	32	239
10	10	356	44	342
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0	18	217	31	235
0	20	213	30	229
1	0	485	54	416
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1	2	553	63	562
1	3	205	29	194
1	4	280	37	263
1	5	210	31	212
1	6	145	24	150
1	7	652	74	710
1	9	315	40	312
1	10	624	70	681
1	11	216	31	206
1	12	206	30	202
1	14	369	44	356
1	15	307	39	340
1	17	253	34	278
1	18	344	43	388
1	20	180	27	136
1	22	503	58	503
1	24	205	29	194
1	27	458	53	441
1	29	227	32	223
1	33	247	33	223
2	0	133	24	127
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2	3	445	52	400
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2	6	171	26	152
2	7	119	22	113
2	8	144	24	144
2	9	107	23	105
2	11	243	33	241
2	15	182	27	201
2	16	237	34	250
2	17	215	30	230
2	24	190	28	161
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3	6	354	44	301
3	7	492	57	484
3	9	281	37	264
3	10	351	43	323
3	11	530	65	516
3	12	254	34	286
3	13	541	61	589
3	14	164	26	124
3	16	539	61	567
3	17	291	38	293
3	18	335	42	357
3	20	432	51	426
3	23	225	31	215
3	30	253	34	249
3	32	249	34	192
4	2	113	21	112
4	4	248	34	257
4	5	162	25	151
4	6	411	49	376
4	11	155	25	147
4	14	175	27	198
5	0	241	33	260
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5	3	456	53	414
5	4	526	60	477
5	5	416	50	341
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5	8	174	27	201
5	10	219	31	214
5	11	397	48	434
5	12	129	22	108
5	13	161	25	167
5	14	138	23	129
5	15	158	25	171
5	18	211	30	185
5	19	166	26	146
5	23	182	27	145
5	24	205	29	199
5	25	320	40	304
5	26	231	32	214
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5	32	359	44	336
5	33	198	29	171
6	4	109	20	87
6	6	185	28	161
6	8	195	29	181
6	9	293	38	244
6	12	210	30	191
7	0	122	22	117
7	1	146	24	110
7	2	323	41	262
7	3	138	23	140
7	4	484	56	415
7	5	570	65	484
7	7	348	43	278
7	8	448	53	473
7	9	153	25	165
7	10	434	52	402
7	13	160	25	137
7	14	217	31	257
7	15	205	29	199
7	16	252	34	216
7	18	344	43	374
7	19	386	47	416
7	20	359	44	374
7	21	258	35	240
7	22	216	31	216
7	23	327	41	301
7	24	434	51	402
7	25	224	31	205
7	28	356	44	297
8	0	407	49	348
8	2	139	23	120
8	4	117	21	118
8	5	110	20	90
8	7	155	25	137
8	9	166	26	205
9	0	96	10	92
9	1	615	68	564
9	3	289	37	257
9	5	243	33	213
9	6	156	25	168
9	7	161	25	158
9	8	466	54	526
9	9	363	44	434
9	12	361	44	410
9	16	223	31	276
9	17	173	26	207
9	20	148	24	137
9	23	177	27	169
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0	16	257	34	252
0	18	132	23	154
0	20	294	38	280
0	26	261	35	235
0	28	245	33	237
0	30	170	26	175
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1	9	118	21	138
1	11	239	33	255
1	12	371	45	406
1	13	420	50	478
1	14	201	29	197
1	16	181	27	176
1	17	387	47	435
1	18	305	39	341
1	19	182	27	188
1	20	273	36	315
1	21	293	38	289
1	25	409	49	413
1	29	394	47	385
2	2	278	36	267
2	3	254	38	247
2	4	339	42	329
2	6	388	47	338
2	7	187	29	175
2	9	229	32	208
2	11	244	33	226
2	12	182	28	195
2	13	138	23	131
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2	19	169	26	173
2	21	198	29	211
2	25	264	35	280
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3	4	405	48	334
3	5	593	64	533
3	6	242	38	290
3	9	549	62	500
3	10	429	51	380
3	11	533	61	496
3	12	503	58	498
3	13	270	36	319
3	14	774	84	839
3	15	335	42	332
3	17	282	37	285
3	18	634	70	722
3	19	208	30	189
3	21	292	38	280
3	28	276	36	236
4	1	386	47	292
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4	5	319	40	266
4	7	241	33	257
4	8	392	47	330
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5	3	438	52	387
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5	6	405	46	838
5	8	560	63	540
5	10	451	53	471
5	20	253	34	228
5	21	197	29	150
5	22	323	41	339
5	26	373	45	312
5	27	193	28	206
5	30	299	38	281
6	5	241	35	234
6	6	136	23	139
6	8	188	28	160
6	9	231	32	209
6	10	150	24	135
6	11	244	33	223
6	13	333	42	328
6	14	241	33	227
6	15	208	30	195
6	17	338	42	344
6	20	193	28	211
6	22	220	31	185
6	23	264	33	294
7	1	224	31	193
7	2	282	37	272
7	5	232	32	184
7	6	738	80	603
7	7	135	23	110
7	8	257	34	220
7	9	155	25	165
7	10	561	63	514
7	12	311	40	294
7	13	225	31	240
7	14	160	24	125
7	16	202	29	219
7	20	403	48	388
7	22	359	44	348
7	26	516	59	402
8	1	239	33	207
8	2	362	44	288
8	3	199	29	175
8	4	127	22	96
8	6	275	36	262
8	7	211	30	193
8	9	184	27	194
8	11	278	36	295
8	12	275	32	245
8	20	203	29	217
9	2	204	29	185
9	3	303	39	246
9	4	189	28	180
9	5	235	32	149
9	9	276	36	269
9	10	308	38	200
9	11	394	47	455
9	14	263	35	272
9	18	178	27	229
9	21	213	30	250
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0	16	222	31	236
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0	28	426	50	442
0	32	334	42	324
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1	6	236	32	217
1	7	201	29	166
1	8	296	38	313
1	11	721	78	816
1	12	196	29	222
1	14	290	34	288
1	15	599	66	666
1	17	183	27	215
1	19	306	39	339
1	23	356	44	387
1	27	392	47	376
1	31	288	35	293
2	0	366	45	326
2	2	405	48	345
2	3	124	22	105
2	4	216	30	202
2	5	209	30	209
2	6	252	38	295
2	7	430	51	411
2	8	401	44	373
2	9	259	35	217
2	11	604	67	632
2	12	532	61	559
2	15	366	45	404
2	16	594	67	668
2	17	284	38	320
2	20	319	40	373
2	23	217	31	205
2	26	327	41	316
2	31	294	38	222
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3	1	171	26	140
3	2	358	44	347
3	3	486	56	497
3	4	706	77	636
3	5	250	34	252
3	7	496	57	490
3	8	626	69	596
3	9	326	41	314
3	10	366	45	358
3	11	327	41	333
3	12	540	61	485
3	13	319	40	289
3	14	212	30	222
3	15	417	50	386
3	16	539	61	539
3	17	230	32	248
3	19	266	35	263
3	20	326	41	372
4	1	202	29	158
4	4	282	34	269
4	6	852	91	720
4	8	541	61	494
4	9	302	39	242
4	10	387	47	373
4	11	361	44	350
4	12	307	39	318
4	13	199	29	209
4	15	391	46	449
4	17	262	33	256
4	19	401	48	418
4	23	249	34	209
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5	1	134	23	121
5	3	242	33	204
5	4	776	84	725
5	7	394	44	339
5	8	740	80	723
5	10	148	24	133
5	12	479	55	459
5	13	173	26	177
5	14	262	35	277
5	16	357	44	406
5	18	233	32	249
5	20	289	37	303
5	22	272	36	282
5	24	232	32	185
5	26	211	30	204
5	28	189	28	184
6	0	431	51	336
6	1	491	57	376
6	3	940	99	706
6	7	510	59	373
6	9	350	43	328
6	14	180	27	171
6	17	340	42	350
6	19	216	31	239
7	0	629	70	550
7	1	148	24	114
7	2	147	24	155
7	3	347	43	253
7	4	612	68	469
7	6	218	31	210
7	7	284	35	238
7	8	721	78	650
7	11	214	30	190
7	12	260	35	193
7	13	202	29	197
7	14	206	30	184
7	18	238	33	224
7	19	182	27	167
7	20	201	29	161
7	22	266	35	258
7	24	290	38	264
7	28	207	30	172
8	0	230	32	247
8	2	145	24	143
8	5	161	25	168
8	6	341	42	316
8	7	236	32	193
8	8	400	48	366
8	9	463	54	437
8	12	251	34	286
8	13	254	34	287
8	14	324	41	369
8	23	318	40	303
9	3	413	49	368
9	4	214	30	214
9	5	136	23	140
9	7	349	45	424
9	8	139	23	153
9	9	188	28	192
9	11	277	36	283
9	12	279	37	274
9	13	145	24	186
9	15	147	24	150
9	16	148	24	158
9	19	142	25	189
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0	14	344	43	394
0	16	363	44	362
0	18	183	27	222
0	24	188	24	173
0	26	295	38	331
0	28	243	33	247
0	30	412	45	393
0	34	258	35	247
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1	2	343	41	339
1	3	302	39	307
1	4	505	58	519
1	6	225	31	231
1	8	322	41	307
1	9	237	33	223
1	10	153	25	174
1	12	253	34	240
1	13	164	26	157
2	1	474	55	391
2	2	746	81	697
2	3	289	37	297
2	6	162	25	175
2	7	149	24	114
2	9	556	63	560
2	10	550	62	597
2	11	304	39	292
2	13	551	62	570
2	14	563	64	617
2	16	179	27	173
2	17	303	39	288
2	18	466	54	497
2	19	435	51	509
2	22	349	43	426
2	24	298	38	286
2	28	391	47	384
2	29	224	31	242
3	8	207	30	184
3	10	195	28	188
3	13	206	30	184
3	14	369	45	390
4	3	441	52	373
4	4	531	60	486
4	6	538	61	465
4	7	496	57	416
4	8	349	43	336
4	9	294	38	304
4	10	587	64	578
4	11	385	45	320
4	13	490	55	486
4	15	226	32	235
4	17	588	66	580
4	21	330	42	333
4	25	308	39	287
5	2	297	38	227
5	4	222	31	214
5	6	279	36	276
5	7	278	36	272
5	11	230	33	219
5	12	266	35	273
5	17	220	31	261
5	18	185	28	168
6	3	512	59	441
6	5	885	94	737
6	7	436	51	381
6	9	636	70	569
6	11	267	35	233
6	12	226	32	236
6	14	193	28	184
6	15	281	37	294
6	19	203	29	239
6	21	364	45	369
7	1	286	37	251
7	4	393	47	377
7	9	306	39	317
8	1	178	27	150
8	4	490	57	427
8	5	297	38	241
8	7	432	51	366
8	8	283	37	248
8	9	181	27	193
8	10	306	39	250
8	11	480	54	445
8	13	222	31	188
8	17	293	38	292
8	21	331	41	336
9	2	147	24	179
9	11	149	24	136
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0	2	144	24	143
0	4	331	41	348
0	6	446	52	430
0	8	288	37	287
0	10	142	23	132
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0	20	239	33	285
0	24	187	28	197
0	28	214	30	181
0	32	157	26	209
1	0	259	34	231
1	1	522	60	509
1	3	249	34	213
1	5	277	36	255
1	6	214	30	236
1	10	356	44	346
1	14	284	39	276
1	20	201	29	180
1	22	225	31	279
2	0	184	27	166
2	3	163	26	152
2	4	373	45	407
2	12	198	25	185
2	15	251	34	267
2	16	304	39	325
2	17	282	37	318
3	11	240	33	215
3	12	222	32	241
3	13	247	34	275
3	16	334	42	354
4	1	220	31	164
4	4	240	33	211
4	5	219	31	240
4	6	348	43	353
4	8	270	36	299
4	11	230	32	188
4	12	233	32	221
5	0	309	39	270
5	3	346	45	309
5	4	334	42	270
5	7	405	49	350
5	11	238	33	257
5	18	190	28	228
6	3	193	28	145
6	8	258	34	255
6	9	420	50	366
7	3	263	35	216
7	7	200	29	231
7	10	183	27	146
7	18	183	27	169
7	19	182	27	188
7	24	184	27	183
8	0	335	42	341
8	2	173	26	157
9	0	158	25	164
9	1	205	30	200
9	4	152	24	169
9	9	151	24	158
9	12	163	26	177
9	13	162	25	199
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0	4	255	34	243
0	6	429	51	487
0	10	311	40	352
0	14	591	66	612
0	18	420	50	490
0	20	186	28	167
0	22	269	36	287
0	24	166	26	178
0	28	235	32	254
1	1	194	28	169
1	2	194	28	192
1	3	293	38	299
1	8	365	45	370
2	2	602	67	642
2	4	303	39	325
2	6	384	46	432
2	7	246	33	251
2	9	208	30	248
3	2	251	34	240
3	4	274	36	269
3	11	258	35	284
3	14	292	38	296
4	1	423	50	399
4	3	401	48	378
4	5	458	53	439
4	9	389	47	303
4	13	245	34	237
5	5	346	43	403
5	9	332	42	358
6	14	224	31	194
7	6	189	28	166
7	8	188	28	192
7	10	226	31	182
7	12	249	33	262
8	1	196	29	219
8	9	171	26	172
8	10	170	26	169
9	1	169	26	214
***	H=	8	***	
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0	12	290	38	289
0	16	204	29	230
1	1	335	42	352
1	3	319	40	332
1	5	279	37	302
1	15	322	41	356
1	16	224	31	263
1	19	222	31	225
2	0	322	41	360
2	5	198	29	175
3	0	396	48	304
3	3	323	41	322
4	7	253	34	279
5	0	201	29	201
5	16	185	28	190
6	13	240	33	186
6	17	228	32	203
7	0	234	32	216
8	0	191	28	238
9	12	138	23	164
***	H=	9	***	
0	12	240	33	205
2	1	227	32	220
5	10	182	27	186
6	12	202	29	156

see Table III). The Fe–C–O fragments are linear within the standard deviations for these quantities. Each dithiocarbamate, excluding the outer $-CH_2-CH_2-CH_2-$ fragments of the pentamethylene chain, is nearly planar (see Table III) and the two planes intersect at right angles (88.7°) at the iron atom. Selected values of the dihedral angles are also listed in Table III.

A stereoscopic view of the unit cell and its contents is given in Figure 3. The longest dimensions is c (=33.74 Å) whose positive direction points towards the top of the Figure; i.e., the view is approximately perpendicular to the (110) plane. The iron atoms are well separated with Fe–Fe nearest-neighbor distances of over 6 Å. There are no unusually close intermolecular contacts, the shortest being O(2) to C(7) which is 3.44 Å. The hydrogen atoms, which were placed at idealized positions (see the section on Refinement), come close to the carbonyl oxygens in two instances indicating the possible presence of weak C–H ... O bonds. The two close contacts are between H(12-1) and O)1) and between H(10-1) and O(2) which are 2.87 and 2.93 Å in length, respectively. Such contacts between C–H hydrogens and carbonyl oxygens have been noted by other workers in structural studies of organic compounds.[14,15] It has also been noted by Brennan and Bernal[16] that in $(Et_2dtc)_3Co$ there are short contacts between the hydrogens of the alkyl groups and the $-CS_2$ sulfurs. However, the reader should be reminded of the fact that there are serious objections to classing these contacts as hydrogen bonds.[17]

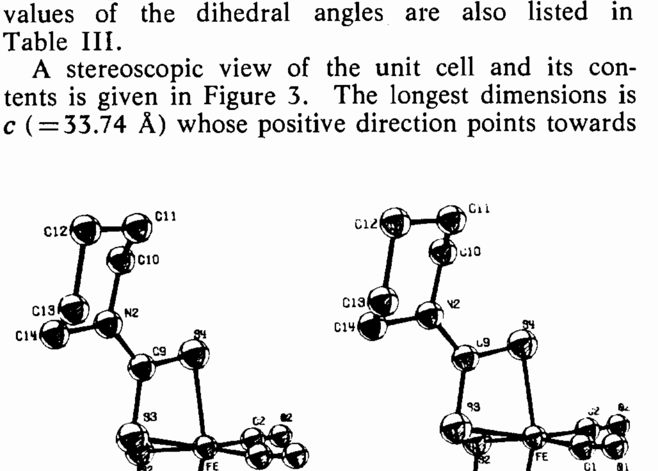

Figure 2. The Molecular Structure of Bis(cyclopentamethylenedithiocarbamato)Fe^{II} Dicarbonyl. This is a stereoscopic pair showing the approximate two-fold axis of the molecule.

$(Cpdtc)_2Fe(CO)_2$ has almost precisely a molecular two-fold symmetry axis even though there is no crystallographic requirement for this symmetry element to be present in the molecule. The result is that the two piperidine rings, both of which are in the

[14] D.J. Sutor, *Nature, 195,* 68 (1962).
[15] G. Palenik, *Acta Cryst., 19,* 47 (1965).
[16] T. F. Brennan and I. Bernal, *J. Phys. Chem., 73,* 443 (1969).
[17] J. Donohue in « Structural Chemistry and Molecular Biology », A. Rich and N. Davison, Eds, San Francisco, W.H. Freeman and Co., 1968, p. 443.

Table III. Bond Lengths (in Å) and Angles (in °) with their estimated standard deviations in parentheses. The e.s.d. affect the last significant digit.

A. Bond Lengths

Fe-S(1)	2.308(5)	C(4)-C(5)	1.42(3)	C(2)-O(2)	1.08(2)
Fe-S(2)	2.337(6)	C(5)-C(6)	1.55(3)	C(2)-N(9)	1.35(3)
Fe-S(3)	2.340(6)	C(6)-C(7)	1.52(3)	N(2)-C(10)	1.49(2)
Fe-S(4)	2.309(5)	C(7)-C(8)	1.48(3)	N(2)-C(14)	1.50(2)
Fe-C(1)	1.72(3)	S(1)-C(3)	1.70(2)	C(10)-C(11)	1.48(3)
Fe-C(2)	1.83(2)	S(2)-C(3)	1.75(2)	C(11)-C(12)	1.46(3)
C(3)-N(1)	1.27(2)	S(3)-C(9)	1.67(2)	C(12)-C(13)	1.54(3)
N(1)-C(4)	1.48(2)	S(4)-C(9)	1.70(2)	C(13)-C(14)	1.52(3)
N(1)-C(8)	1.50(2)	C(1)-O(1)	1.15(3)		

B. Angles

S(1)-Fe-S(2)	74.7(2)	C(3)-N(1)-C(8)	123(2)	C(1)-Fe-C(2)	92.2(12)
S(3)-Fe-S(4)	74.6(2)	N(1)-C(4)-C(5)	115(2)	Fe-S(3)-C(9)	85.6(9)
S(1)-Fe-S(3)	91.5(2)	C(4)-C(5)-C(6)	109(2)	Fe-S(4)-C(9)	85.9(7)
S(2)-Fe-S(4)	93.9(2)	C(5)-C(6)-C(7)	110(2)	S(3)-C(9)-S(4)	114(1)
S(1)-Fe-S(4)	162.1(3)	C(6)-C(7)-C(8)	112(2)	S(3)-C(9)-N(2)	123(2)
S(2)-Fe-S(3)	90.2(2)	C(7)-C(8)-N(1)	110(2)	S(4)-C(9)-N(2)	123(1)
S(2)-Fe-S(4)	93.9(2)	C(4)-N(1)-C(8)	111(1)	C(9)-N(2)-C(10)	122(2)
S(1)-Fe-C(1)	96.4(8)	S(1)-Fe-C(2)	98.5(9)	C(9)-N(2)-C(14)	124(1)
Fe-S(1)-C(3)	88.5(7)	S(2)-Fe-C(1)	171.1(8)	N(2)-C(10)-C(11)	112(2)
Fe-S(2)-C(3)	86.6(7)	S(2)-Fe-C(2)	89.9(8)	C(10)-C(11)-C(12)	113(2)
S(1)-C(3)-S(2)	110(1)	S(3)-Fe-C(1)	89.2(9)	C(11)-C(12)-C(13)	114(2)
S(1)-C(3)-N(1)	126(2)	S(3)-Fe-C(2)	169.7(10)	C(12)-C(13)-C(14)	110(1)
S(2)-C(3)-N(1)	125(2)	S(4)-Fe-C(1)	94.6(8)	C(13)-C(14)-N(2)	109(1)
C(3)-N(1)-C(4)	125(2)	S(4)-Fe-C(2)	95.1(10)	C(10)-N(2)-C(14)	113(1)

C. Least-Squares Planes and Deviations of Selected Atoms from These Planes

(1) Plane through Fe, S1, S2, C3, N1, C4 and C8
$0.9913x-.0777y-0.1060z=0.1750$

Fe	−0.020	S2	0.046	N1	−0.235
S1	0.058	C3	0.055	C4	−0.220
				C8	−0.269

(2) Plane through Fe, S3, S4, C9, N2, C10 and C14
$-0.0434x+0.4146y-0.9089z=-11.4668$

Fe	−0.004	S4	0.011	N2	−0.006
S3	0.006	C9	−0.021	C10	−0.163
				C14	−0.018

(3) Plane through Fe, S2, S3, C1, C2, O1, O2
$-0.087x-0.9352y-0.3565z=-5.1012$

Fe	0.003	S3	−0.047	C2	−0.277
S2	0.038	C1	0.233	O1	0.318
				O2	−0.497

(4) Plane through Fe, S1, S2, S4, C1, O1, C3, N1
$0.9984x+0.0455y-0.0331z=1.0560$

Fe	0.096	S2	0.101	O1	0.026
S1	−0.156	S4	−0.205	C3	−0.243
		C1	0.047	N2	−0.554

(5) Plane trough Fe, S1, S3, S4, C2, O2, C9, N2
$-0.0391x+0.493y-0.869z=-10.8421$

Fe	−0.079	S3	−0.056	O2	−0.011
S1	0.163	S4	0.135	C9	0.062
		C2	0.046	N2	0.168

D. Angles Between Normals to Planes A and B

Plane A	Plane B	Angle (°)
1	2	88.79
1	3	88.65
1	5	89.14
2	3	93.32
2	4	89.68
3	4	96.75
3	5	98.36
4	5	89.31

chair conformation (see Figure 2), are correctly oriented for the molecule to have point symmetry 2(C2). However, if one of them were to be rotated by 180° about the vector defined by one of the dithiocarbamate nitrogens and the iron atom, (without changing the chair conformation of the piperidine rings), a new isomer would result. These two conformational isomers have been labelled A and B in Figure 4. It is clear that electronically there should be a negligible, if any, energy difference between these two conformational isomers. Therefore, it is interesting that in the crystals studied here only one (that with the 2-fld axis) is present. A difference electron density map computed at the end of the refinement shows peaks which are randomly distributed and with intensities no higher than those expected from noise (*i.e.*, they are lower than the H peaks discussed in the section on Refinement).

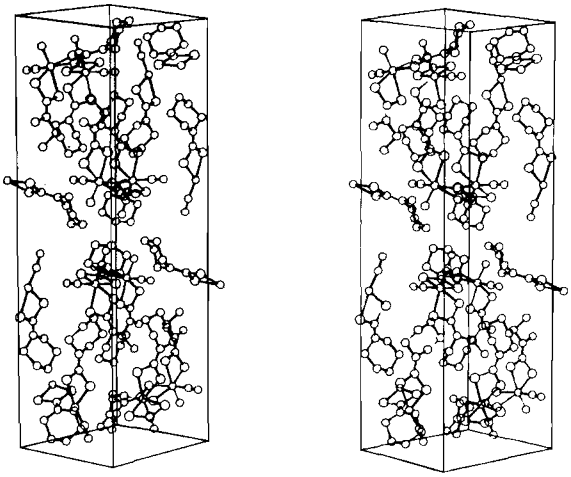

Figure 3. The Molecular Packing of Bis(cyclopentamethylenedithiocarbamato)Fe^{II} Dicarbonyl. A stereo view of the unit cell and its contents. The longest dimension, *c*, coincides with the z-axis and has its positive direction towards the top (binding) of the page. The view is approximately perpendicular to the (110) plane.

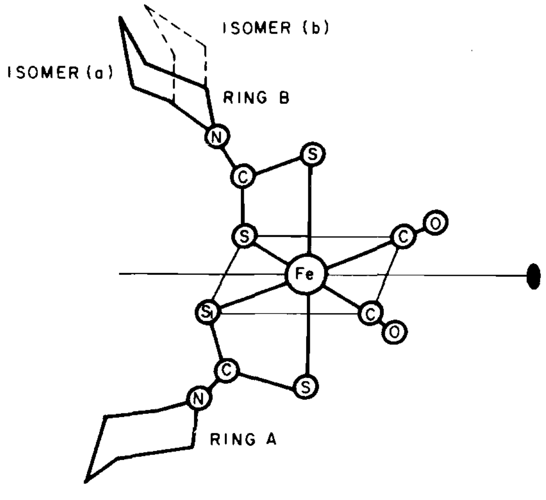

Figure 4. The two structural isomers which may exist in a bis-(cyclopentamethylenedithiocarbamato)Fe(CO)$_2$. Note that in both isomers the two piperidine rings remain in the chair conformation.

Discussion

Of the many structural studies of metal dithiocarbamates only four reports[8,16,18,19] deal with metal *tris*-dithiocarbamates. Of these, only one substance has been studied and reported in full detail, (Et$_2$dtc)$_3$-Co.[16,18] Other reports[8,19] on metal tris-dithiocarbamates have, so far, been restricted to limited descriptions of the structural details based on partially refined sets of data. For convenience, we have summarized in Table IV structural data on metal dithiocarbamates which are pertinent to our Discussion. In (Cpdtc)$_2$-Fe(CO)$_2$ the mean Fe–C and C– distances of 1.78(3) and 1.12(3) Å compare well with those reported for (OC)$_3$Fe(C$_8$H$_8$)Fe(CO)$_3$[20] (1.76 and 1.15 Å), [(C$_6$H$_5$)-CSFe(CO)$_3$]$_2$[21] (1.77 and 1.16 Å), and Fe(CO)$_5$[22] (1.79 and 1.12 Å). The deviation from linearity in the two Fe–C–O fragments is not statistically significant and the mean value (177°) is very nearly that found for this type of metal carbonyl (see for example, [C$_2$H$_5$SFe–(CO)$_3$]$_2$[23] with a mean Fe–C–O angle of 173±4°).

In metal dithiocarbamates the strongly distorted (from 90°) S–C–S angles are part of the interesting four membered rings formed by small chelating groups such as xanthates and 1,1–ethylenedithiolates. Valency angles (110 and 114°) about the sp^2 hybridized carbon atom are not greatly different from those found in (Et$_2$dtc)$_3$Co[16,18] where these angles are 108 and 111°. Other structural studies on the tris-dithiocarbamates[8,19] do not report values for these angles; however, in a large number of *bis*-dithiocarbamates[24-35] (see Table IV) the average value for the S–C–S angle is approximately 110° irrespective of the central metal ion, its charge, the fact that the complex is *bis* or *tris* or that it is a monomeric or dimeric *bis* complex. In Table IV we also list the value of the angle at the sulfurs, *i.e.*, the M–S–C angle. The average value of this angle for our compound is 86.7(7) which is in excellent agreement with the results found by a variety of workers for many dithiocarbamates;[24-35] however, the amount of distortion of this angle depends on what one considers the value for a normal sulfur angle. The following series[35] of compounds serves to illustrate the decrease in the sulfur bond angle as one passes to smaller and smaller rings: Rhombic sulfur, S$_8$ (105°); 1,4–dithiin, C$_4$H$_4$S$_2$ (100°); thiophene, C$_4$H$_4$S (91°); and in the four-membered ring in tetramethylcyclodisilthiane the Si–S–Si angle is reported as 75°. Thus

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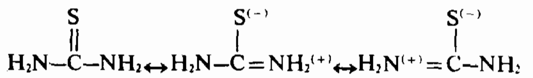
Table IV. The distances are in Å and the angles in degrees; standard deviations are given in parentheses and either modify the least significant digit(s) quoted, or are quoted as given by author (see ref. 35). Entries not appearing in this Table are either not relevant for the molecule in question or were not supplied by the authors.

Compound	S—C	C=N	N—C	S—C—S	M—S—C	C=N—C	C—N—C	Ref.
$(Cpdtc)_2Fe(CO)_2$	1.71(2)	1.31(3)	1.49(2)	112(1)	86.7(7)	124(2)	112(1)	this work
$(n\text{-}but_2dtc)_3Fe$	1.71(2)	1.41(3)	—	—	—	—	—	8
$(Et_2dtc)_3Co$	1.704(5)	1.319(9)	1.496(8)	109.5(4)	87.4(3)	120.8(8)	118.2(8)	16,18
$(n\text{-}prop_2dtc)_2Ni$	1.708(6)	1.330(9)	1.470(7)	110.5(4)	85.0(3)	120.9(7)	118.0(6)	24
$(Me_2dtc)_2Zn\,.\,C_5H_5N$	1.718(5)	1.338(9)	1.472(12)	118.3(—)	84.3(—)	121.7(—)	116.5(—)	25
$(Et_2dtc)_2Cu$	1.717(4)	1.333(10)	1.470(5)	113.7(7)	84.6(5)	121.4(9)	117.2(9)	27
$(Et_2dtc)_2Zn$	1.727(5)	1.325(9)	1.473(7)	117.7(8)	84.7(6)	122.1(10)	116.0(10)	28
$(Et_2dtc)_2Se$	1.71(2)	1.35(2)	1.51(2)		85.4(5)	121.6(15)	115.8(15)	29
$(H_2dtc)_2Ni$	1.69(3)	1.38(3)	—	111.7(1.2)	84.9(7)	—	—	30
$(Et_2dtc)_2As\phi$	1.670(14)	1.345(21)	1.483(15)	118.5(1.1)	93.5(7)	121(1)	116(1)	31
$(Et_2dtc)_2$	1.648(9) 1.816(9)	1.348(12)	1.473(8)	—	—	122(1)	116(1)	32
$\alpha\text{-}(Et_2dtc)_2Ni$	1.706(7)	1.330(10)	1.485(15)	110.6(6)	85.1(4)	121.3(10)	116.9(12)	33
$[(Et_2NCOS)Cu]_6$[a]	1.802(16)	1.338(17)	1.462(20)	—	—	119(1)	115(1)	34
$(Me_2dtc)_2Zn$	1.722(10)	1.347(18)	1.472(15)	118.73(1.13)	87.46(66)	121.11(1.70)	116.88(1.77)	35

[a] This substance is a *mono*thiocarbamate.

a mean value of 87° is quite reasonable for the FeS_2C ring.

Some relevant C–S bond distances from various dialkyldithiocarbamates are presented in Table IV for comparison with those in the current study. The average C–S bond length, 1.71 Å, compares well with values found for thiourea,



$$H_2N{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}NH_2 \leftrightarrow H_2N{-}\overset{\overset{\displaystyle S^{(-)}}{|}}{C}{=}NH_2^{(+)} \leftrightarrow H_2N^{(+)}{=}\overset{\overset{\displaystyle S^{(-)}}{|}}{C}{-}NH_2$$

several of its derivatives, and in coordinated thiourea[36] and seems to be normal for a S–(sp^2) distance. This result is fairly common for metal dithiocarbamates (see Table IV) regardless of the metal and the number of ligands around it. In $(Cpdtc)_2Fe(CO)_2$ the S–C distances occur in pairs with values of 1.70(2), 1.67(2), 1.75(2), and 1.70(2) Å, respectively, for C(3)–S(1), C(9)–S(3), C(3)–S(2), and C(9)–S(4). These values are similar to those found in other dithiocarbamates where the two C–S bonds within a dithiocarbamate are somewhat asymmetric; for example Peyronel and Pignedoli[24] found C–S distances of 1.702(8) and 1.726 (8) Å in $(n\text{–}prop_2dtc)_2Ni$; Frazer and Harding[25] found values of 1.707(10), 1.707(10), 1.727(10) Å and 1.732(10) Å in $(Me_2dtc)_2Zn(pyridine)$. Finally, Klug[35] found that in $(Me_2dtc)_2Zn$ the C–S distances for the non-bridging dithiocarbamate ligands are 1.701(19) and 1.748(19) Å, while those in the bridging dithiocarbamates are 1.699 and 1.739 Å, which are in excellent agreement with our results. Also, Klug's results[35] emphasize the fact that in most cases the dithiocarbamate ligands have structural features which are largely invariant to considerations such as whether the ligand has both sulfurs attached to the same metal or is acting as a bridge. In this regard it is worthwhile considering the results of Colapietro, *et al.*[26] on the structure of $(Et_2dtc)Na\,.\,3H_2O$ where only one of the sulfurs of each dtc ligand is attached to a sodium ion. In this salt the C–S distances are equal within the standard deviations and the average C–S distance is 1.720(9) Å.

In $(Cpdtc)_2Fe(CO)_2$ the piperidine rings have the chair conformation. The bond lengths are those of normal single bonds with the average value of 1.49 Å for the (alkyl)–N distance and 1.50 Å for the C–C distance. These values are in good agreement with those found in the piperidine ring of pseudotropine[37] (1.45 and 1.52 Å, respectively). There is also good agreement between the valency angles of the piperidine rings in the present study and those in pseudotropine. The angles at the nitrogen are significantly dissimilar because of the deformation due to the ethylene bridge in the bicyclic compound. The average carbon valency angle in $(Cpdtc)_2Fe(CO)_2$ is 111(2), which is the sp^3 tetrahedral angle within one standard deviation.

The average bond length of 1.32 Å for C–N shows high double bond character, as it does in all dithiocarbamates thus far reported, except perhaps in $(n\text{–}bu_2dtc)_3Fe$ which Hoskins and Kelly[8] report to have a C–N bond of 1.42 Å. The report of Nardelli, *et al.*[30] (see Table IV) that C=N in $(H_2NCS_2)_2Ni$ is 1.38 (3) Å is no exception since this value is only one standard deviation away from the general result of 1.33-1.34 Å found in all other studies.[16,18,24-35] Table IV sumarizes the data available for this bond for a wide variety of metal dithiocarbamates and it seems clear that the result of Hoskins and Kelly implies an unusually low degree of conjugation between the R_2N– and the $-CS_2$ fragments. In the LCAO–MO approximation the double bond order calculated from Coulson's[38] C–C formula as modified by Liquori and Vaciago[39] for the C–N bond is:

$$B = S - \frac{S-D}{1+0.6625(1-p)/p}$$

where

B = observed C = N bond distance, 1.31 Å,
S = single bond distance, 1,472 Å
D = double bond distance, 1.287 Å
(Pauling[40])

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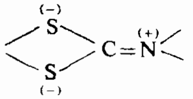
Table V. All bond distances are in Å and bond angles in degrees. The quantities in parentheses are e.s.d. in the least significant digit(s). Where e.s.d. are not quoted, the source reference did not provide the information.

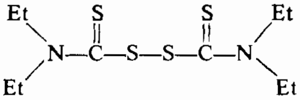
Name of compound	Av(Fe—S)	Formal Charge on Fe	Ref.
$(Cpdtc)_2Fe(CO)_2$	2.322(6)	2	this work
$((n\text{-}but)_2dtc)_3Fe$	2.418(6)	3	8
$(CH_3\Phi CS_3)(CH_3\Phi CS_2)Fe$ [a]	2.32(2)	3	48
$(CH_3\Phi CS_3)(CH_3\Phi CS_2)Fe$ [b]	2.21(2)	3	48
$[(SC_2H_5)(S_2CSC_2H_5)_2Fe]_2$[a]	2.338(4)	3	52
$[(SC_2H_5)(S_2CSC_2H_5)_2Fe]$[c]	2.287(1)	3	52
$(Et_2dtc)_2FeNO$	2.29(1)	1 [d]	41
$(Me_2dtc)_2FeNO$	2.294(2)	1 [d]	42
$(Et_2dtc)_2FeCl$	2.32(2)	3	43
$[(MNT)_2Fe]_2^{2-}$	2.23(2)	3	44
$[(MNT)_2FeNO]^{2-}$	2.27(1)	1 [d]	45
$[(MNT)_3Fe]^{2-}$	2.265(3)	4	46
$(PFD)_2Fe(As\Phi_3)$	2.135(3)	4	47
$[(OC)_3FeS]_2$	2.228	0 [e]	49
$(OC)_9Fe_3S_2$	2.231	0 [e]	50
$CuFe_2S_3$	2.26(6)	2,3	51
$KFeS_2$	2.24(—)	3	52

[a] For an FeSCS four-membered fragment of the molecule. [b] For an Fe-S-S-C-S five-membered fragment of the molecule. [c] For an Fe-S-C-S-Fe five-membered fragment of the molecule. [d] The nitrosyl ligand is assumed to be NO^+; for those who prefer NO^-, the charge on Fe would be +3. [e] As preferred by the authors.

is p = 0.76. This indicates a high contribution of the form:



to the structure of the ligand. By the same criterion, the results of Hoskins and Kelly[8] imply that p=0.21; i.e., practically no conjugation between the R_2N— and the $-CS_2$ fragments of the dithiocarbamates ligands. The dithiocarbamate groups of the present study can also be compared to similar groups contained in tetraethylthiouramdisulfide:[32]



In both cases the dithiocarbamate fragments are essentially planar and the C—N bond adjacent to the S atoms is quite short, 1.32-1.33 Å, while the single N—C(alkyl) bonds are in the range-1.48 Å.

In $(Cpdtc)_2Fe(CO)_2$ the Fe—S bond lengths are: Fe—S(1)=2.308(5), Fe—S(4)=2.303(5), Fe—S(2)=2.338(5), and Fe—S(3)=2.338(6) Å and can be described as occurring in pairs, with average Fe—S distances of 2.306(5) and 2.338(6). Note that the difference is statistically significant since the difference.

$$\Delta = 0.032 = n(5^2+6^2)^{1/2}x10^{-3}$$

or, n=32/7.8=4, approximately. Figure 2 shows that the longer pair of Fe—S bonds is that associated with those sulfurs *trans* to the carbonyl ligands, which suggests that the difference in bond lengths is caused by the *trans* effect of the latter fragments. If the four values for the Fe—S bonds are averaged, one obtains an overall average (Fe—S) bond of 2.322(6) Å, which is in good agreement with a large body of data in the literature (see Table V). For example, $(Et_2dtc)_2Fe(NO)$,[41] $(Me_2dtc)_2Fe(NO)$[42] and $(Et_2dtc)_2FeCl$[43] are particularly appropriate examples to compare with our results. The average value of the Fe—S bonds lengths in these substances is 2.29(1), 2.294(2), and 2.32(2) Å, respectively. In $(Et_2dtc)_3Co$[16,18] the average Co—S distances is 2.237(3) Å, which is in excellent agreement with all the above values. The results of four studies of iron derivatives of MNT and PFD are also available for comparison: Hamilton and Bernal[44] reported the structure of the $[(MNT)_2\text{—}Fe\text{—}Fe(MNT)_2]^{2-}$ where the four independent Fe—S bond distance average to 2.23(2) Å. Rae[45] reported the results of a crystallographic study of the anion $[(MNT)_2Fe(NO)]^{2-}$ for which he found an average Fe—S bond length of 2.27 Å.

Bernal and Sequeira[46] found an average Fe—S distance of 2.265(3) Å for the six-fold coordinated $(MNT)_3Fe^{2-}$ anion which contians Fe^{IV}. Epstein and Bernal[47] found an Fe—S distance of 2.135(3) Å as the average length for the four independent bonds in $(PFD)_2Fe(As\Phi 3)$, wich also contains Fe^{IV} but in a square pyramidal arrangement. A interesting new compound, bis(dithio-*p*-toluato)Fe^{III} thio-p-toluyldisulfide, was reported by Coucouvanis and Lippard[48] to have three types of Fe—S bonds whose average length is 2.28 Å, the longest being 2.32 Å. Finally, a few randomly chosen compounds containing simple inorganic sulfur give the following results: Wei and Dahl[49,50] studied $[(CO)_3FeS]_2$ and $(CO)_9Fe_3S_2$ where they found avera-

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ge values of 2.228(2) and 2.231(9) Å for the Fe–S distances. The mineral cubanite, $CuFe_2S_3$, was studiev by Azaroff and Buerger[51] who found an average Fe–S distance of 2.26(6)Å, while Boon and McGillavry[52] reported a value of 2.24 Å for the Fe–S bonds in $KFeS_2$. Consequently, given the broad range of compounds examined, the fact that they contain different size chelate rings, different charges of the metal and the ligands and that some contain simple inorganic sulfur as the Fe ligand, the abnormally large value of the average Fe–S bond length 2.418(6)Å (the largest value being 2.426(6)Å) reported by Hoskins and Kelly[8] is very important. It appears that the anomalous magnetic moment for $((n\text{–}but)_2dtc)_3Fe^{III}$ is associated with the following structural features which are quite different from those of most other Fe–S compounds thus far studied: (a) Fe–S distance are abnormally high; (b) this is coupled with an abnormally large value of the $C = N$ bond, which is almost a single bond as shown by the value of p of 0.21 (vide supra). Thus the normal conjugation between the dialkylamine and the $-CS_2$ fragments is practically nil (this effect should be observable in the IR spectra of such substances); and (c) a distortion from the normal trigonal antiprismatic coordination of the six sulfurs around the Fe towards the trigonal prismatic configuration of the six sulfurs around the Fe towards the trigonal prismatic configuration.[8] We feel that the study of $(Cpdtc)_2Fe(CO)_2$ has been rewanding since it forced us to compare the differences in structural behavior between the magnetically anomalous tris–dithieocarbamates with those of better behaved species.

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