Correlation between Structure- and Temperature-Dependent Magnetic Behavior of Iron Dithiocarbamate Complexes.   Crystal Structure of Tris(*N,N*-diethyldithiocarbamato)iron(III) at 297 and 79°K

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The crystal structure of tris(*N,N*-diethyldithiocarbamato)iron(III), $Fe(S_2CNEt_2)_3$, has been determined from three-dimensional counter data at 297 and at 79°K to correlate the temperature dependence of its magnetic moment (4.3 and 2.2 BM at the two temperatures, respectively) with structural changes. The space group of the crystals changes on cooling from $P2_1/c$ to $C2/n$. Lattice constants are $a = 14.29$ (1), $b = 10.37$ (1), $c = 17.87$ (1) A, $\beta = 116.6$ (1)° at 297°K and $a = 13.96$ (1), $b = 10.24$ (1), $c = 17.71$ (1) A, $\beta = 116.5$ (1)° at 79°K. $Z = 4$ at both temperatures. The data have been refined by least-squares to $R(F) = 5.4\%$ (297°K) and 6.8% (79°K). At room temperature the iron atoms are located on a pseudo-twofold axis, which becomes a true twofold axis in the low-temperature structure. The change in space group is accompanied by a contraction of the Fe–S distances of 0.05 A and a small but significant decrease in distortion from octahedral symmetry of the FeS_6 group. When the average Fe–S distances in all known iron dithiocarbamato complexes are plotted against their magnetic moments, a smooth curve is obtained indicating strong correlation between geometry and magnetic behavior. Differences of 0.018–0.028 A between the averages over the two sets of Fe–S distances related by the pseudothreefold axis observed in earlier studies of low-spin complexes are not present in the structure at 79°K. Thus, these differences are probably not due to Jahn–Teller and spin–orbit interactions in the low-spin state as proposed earlier. Slight differences in the geometry of the ligand at the two temperatures are compatible with a mechanism by which the effect of the substituent on the crystal field is transmitted through the conjugated system of the ligand. Analysis of the temperature parameters at room temperature indicates that the present diffraction data cannot distinguish between a mixed-spin state and the existence of a mixture of two different spin states as an explanation for the variability of the magnetic moment.

Introduction

Earlier studies have shown that the tris(*N,N*-dialkyldithiocarbamato)iron(III) complexes with general formulas Fe-$(S_2CNR_2)_3$ have a distorted octahedral geometry with a temperature-dependent magnetic moment.[1,2] The temperature dependence has been explained through the existence of two nearly equienergetic ground states of symmetry ^6A and ^2T, but Mossbauer[3] and proton nmr studies failed to show evidence for the simultaneous population of two electronic levels. Though it is possible to explain the spectroscopic results by a rapid crossover between the levels ($>10^7$ sec^{-1}), there is an alternative explanation based on crystal field calculations by Harris,[4,5] according to which the ground state may be a mixed-spin state, the variable magnetic moment being due to a change in character of the ground state with temperature. The calculations by Harris served to explain the difference in magnetic moments of the ferric ion in hemoglobin derivatives and in different heme proteins. Thus, the iron dialkyldithiocarbamates may be magnetic analogs of heme iron proteins and an elucidation of their magnetic behavior is of considerable importance.

Whether the compound is high spin or low spin at a given temperature depends on the substituent R^2 although R is on the periphery of the molecule. It has been proposed that R affects the crystal field due to the sulfur atoms through the conjugated system of the ligands.[2]

If the complexes change from the high-spin state to the low-spin state, one would expect a contraction of the FeS_6 core. Evidence for this contraction is obtained (i) from pressure-dependent studies[1] and (ii) from structural data available for different complexes.[6–8]

(i) It was calculated from pressure-dependent studies (in solution) that the Fe–S distance decreases by about 0.07 Å on going from the high-spin to the low-spin state if the entire volume change is due to the change in the radius of the FeS_6 molecular core. This assumption is supported by the absence of a volume change with increasing pressure for the isomorphous cobalt dithiocarbamates.

(ii) Crystallographic evidence for this contraction can be obtained from the available structural data of tris(*N,N*-di-*n*-butyldithiocarbamato)iron(III) (A),[6] tris(*o*-ethyl xanthato)-iron(III) (B),[7] tris(1-pyrrolidinedithiocarbamato)iron(III) (C),[5] and tris(*N*-methyl-*N*-phenyldithiocarbamato)iron(III) (D).[8] The mean Fe–S distance is 2.41 Å for compounds A and C which are predominantly in the high-spin state, with magnetic moments respectively 5.3 and 5.9 BM, while the mean Fe–S distance is 2.315 Å for compounds B and D which are predominantly in the low-spin state, with magnetic moments 2.7 and 2.9 BM, respectively. Thus, there appears to be a contraction of about 0.08 Å in the Fe–S distances on going from the high-spin to the low-spin state. The structural data for compounds A–D also show that there is a significant change in the geometry of the FeS_6 polyhedron.

The structural information as summarized above is from room-temperature (film) data on four different compounds. Because the geometry of the FeS_6 polyhedron could be affected by the variation of R, we decided to collect diffractometer data for one compound at both room temperature and 79°K. Tris(*N,N*-diethyldithiocarbamato)iron(III) was selected; it is predominantly in the high-spin state at room temperature with a magnetic moment of 4.3 BM and predominantly in the low-spin state at 79°K with a magnetic moment of 2.2 BM.[2]

By studying one compound at different temperatures the geometric change accompanying the variation in magnetic moment can be measured, and information can be obtained

(1) A. H. Ewald, R. L. Martin, I. G. Ross, and A. H. White, *Proc. Roy. Soc., Ser. A*, **280**, 235 (1964).

(2) A. H. Ewald, R. L. Martin, E. Sinn, and A. H. White, *Inorg. Chem.*, **8**, 1837 (1969).

(3) P. B. Merrithew and P. G. Rasmussen, *Inorg. Chem.*, **11**, 325 (1972).

(4) G. Harris, *Theor. Chim. Acta*, **5**, 379 (1966).

(5) G. Harris, *Theor. Chim. Acta*, **10**, 119 (1968).

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

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

(8) P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1163 (1972).

that is not accessible through studies confined to room temperatures.

Experimental Section

The compound was prepared by adding 100 ml of a concentrated solution of the sodium salt of the ligand (0.03 mol) to 100 ml of a concentrated aqueous solution of ferric chloride (0.01 mol). The precipitate was filtered and extracted with chloroform. Small black crystals precipitated on slow addition of ethanol to the separated chloroform layer. They can be recrystallized from benzene. The crystals are not air sensitive and can be stored for prolonged periods.

The same crystal (with dimensions 0.17 × 0.17 × 0.26 mm^3, elongated parallel to c) was used for both the high- and low-temperature data collection. The three-dimensional diffraction data were collected on an automated Picker diffractometer. The c axis was approximately parallel to the ϕ axis of the diffractometer. For low-temperature data collection, cooling was achieved with the self-regulating X-ray cryostat CT 38.[9] The crystal is mounted on a copper block which is continuously cooled by cryogen supplied through a flexible transfer line. Calibration of the cryostat with a sample of TbVO$_4$ showed that at the phase-transition temperature of 32°K the sample is not more than 2° above the temperature of the copper block. In the present experiment the copper block was kept at 78°K, so the sample temperature will be described as 79 ± 1°K. To prevent thermal shock damage to the crystal special care was taken to keep the temperature constant during refill of the intermediate supply dewar.

The systematic absences as obtained from room-temperature Weissenberg film data are $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$. The cell dimensions at room temperature and at 79°K are given in Table I.

The reflections of the type $h + k = 2n + 1$ were very weak, indicating that the lattice is pseudo-C-centered. Precession photographs at about −140° showed that all reflections of the type $h + k = 2n + 1$ disappeared to give the space group $C2/c$. It follows that the molecule has pseudo-twofold symmetry at room temperature and a true twofold symmetry axis at low temperature. This phase change is reversible as shown by subsequent precession photographs of the same crystal at room temperature.

In the room-temperature data collection (Mo Kα radiation) the intensities were measured by the moving-crystal, moving-counter technique using a 2(1.5 + 0.692 tan θ) scan in 2θ at a rate of 1°/min, with $2\theta_{max} = 45°$. The background intensities were estimated by the counting for 10 sec at the beginning and end of each scan. A set of symmetry-equivalent reflections up to $2\theta = 20°$ was also collected. Three standard reflections were measured after every 25 reflections to monitor long-range changes in the beam intensity or the crystal reflectivity. No such changes were observed during data collection.

The low-temperature data were obtained in the same way except that the step-scan method was used with a step size of 0.06°. The background intensities were determined from the first five and last five steps. The data were collected up to $2\theta = 60°$. Symmetry-equivalent reflections were collected up to $2\theta = 35°$.

The intensity data were corrected for Lorentz and polarization effects and for absorption ($\mu = 11.6$ cm^{-1}) using the program DATAPP. A grid size of 6 × 6 × 8 was used for the absorption correction.

After averaging the reflections the agreement factors R and R_w were 1.9 and 2.0% for the room-temperature data and 4.6 and 2.7% for the low-temperature data, where $R = \Sigma |F - \langle F \rangle|/\Sigma F$ and $R_w = \Sigma w|F - \langle F_w \rangle|/\Sigma wF$.

The room-temperature structure was solved by the usual heavy-atom method. The iron and sulfur atoms were located from a three-dimensional Patterson map. The carbon and nitrogen atoms were subsequently found in a three-dimensional Fourier map, phased by the iron and sulfur atoms.

After three cycles of full-matrix least-squares refinement (with isotropic thermal parameters for all the atoms), it was clear that the structure did not refine correctly. The R value ($R = \Sigma |F_o| - |F_c||/\Sigma F_o$) for all reflections was 18%, while R was equal to 11% for the reflections of the type $h + k = 2n$ and 37% for the $h + k = 2n + 1$ reflections. It appeared that the preponderance of the first group of reflections in the refinement effectively blocked the convergence of the weaker reflections with $h + k = 2n + 1$, which represent the deviation from twofold symmetry of the molecule. To test this hypothesis, all the reflections of the type $h + k = 2n + 1$ and approximately the same number of high-order reflections of the

(9) P. Coppens, F. K. Ross, R. H. Blessing, W. F. Cooper, F. K. Larsen, J. G. Leipoldt, B. Rees, and R. Leonard, to be submitted for publication.

Table I. Crystal Data for Fe(S$_2$CNEt$_2$)$_3$ at 297 and 79°K

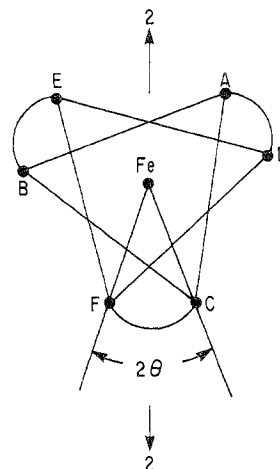|	297°K	79°K
a, Å	14.29 (1)	13.96 (1)
b, Å	10.37 (1)	10.24 (1)
c, Å	17.87 (1)	17.71 (1)
β, deg	116.6 (1)	116.5 (1)
Z	4	4
d_x, g cm^{-3}	1.404	1.467
Space group	$P2_1/c$	$C2/n$

Figure 1. Schematic drawing of the FeS$_6$ polyhedron.

type $h + k = 2n$ were used in the next two cycles. The R value for these data was reduced to 2% with little difference between the two groups of reflections, indicating satisfactory convergence.

The structure was then further refined with all data using anisotropic thermal parameters for all the atoms. The final R value was 5.4% ($R_w = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]^{1/2} = 6.1\%$).

To use the same atom parameters for the refinement of the low-temperature data, $^1/_2$, $^1/_2$, 0 was added to the equivalent positions of the room-temperature space group $P2_1/c$. This means that the low-temperature space group was $C2/n$, rather than the conventionally listed space group $C2/c$. The final R value for the low-temperature structure was 6.8% ($R_w = 8.3\%$).

In both refinements the weights $w(F)$ were obtained with the expressions $\sigma^2(F^2) = \sigma^2$(counting) + $(0.03F^2)^2$ and $\sigma(F) = \sigma(F^2)/2F$. The estimate of the proportionality constant (0.03) is based on the comparison of the intensities of symmetry-related reflections. Reflections with $F < 3\sigma$ were considered to be unobserved and eliminated from the refinement. The numbers of observations and variables are respectively 1752 and 223 for the room temperature, and 2521 and 121 for the low temperature refinement.

The final atomic coordinates with their standard deviations for the structure at 297 and at 79°K are given in Table II. The final anisotropic temperature coefficients at 297 and at 79°K are given in Tables III and IV, respectively.

Discussion

Fe–S Distances. The system of numbering for the FeS$_6$ polyhedron is shown in Figure 1, while the interatomic distances and angles within the polyhedron are summarized in Tables V and VI.

The mean Fe–S distance is 2.357 Å at 297°K and 2.306 Å at 79°K. This corresponds to a contraction of 0.051 Å on cooling from the predominantly high-spin room-temperature structure to the low-spin state at liquid nitrogen temperature.

Structural parameters and the magnetic moments for some structures containing the FeS$_6$ core are summarized in Table VII, while Figure 2 shows the variation of magnetic moment with the mean observed Fe–S distance. The points for six of the compounds in the table lie on one curve, while the point for the butyl compound is far off the curve. This could be possibly due either (or both) to inaccuracy of the data or (and) to the discontinuous magnetic behavior of this compound at about 150°K.

Table II. Positional Parameters in Fractional Coordinates and, in Parentheses, the Standard Deviations for the Structure at 297 and 79°K

	297°K			79°K		
	x	*y*	*z*	*x*	*y*	*z*
Fe	−0.2485 (1)	0.2487 (1)	0.2509 (1)	−0.25000	0.24654 (8)	0.25000
			Ligand 1			
S(1)	−0.1346 (2)	0.0786 (2)	0.2586 (2)	−0.14669 (9)	0.06860 (11)	0.25295 (7)
S(2)	−0.3380 (2)	0.0568 (3)	0.2491 (2)			
C(1)	−0.2312 (7)	−0.0232 (8)	0.2530 (6)	−0.25000	−0.02606 (64)	0.25000
N	−0.2243 (6)	−0.1530 (7)	0.2534 (5)	−0.25000	−0.15654 (57)	0.25000
C(2)	−0.1266 (10)	0.2160 (10)	0.2549 (8)	−0.16045 (55)	−0.23150 (52)	0.24817 (37)
C(3)	−0.0545 (11)	−0.2667 (12)	0.3444 (8)	−0.07446 (66)	−0.27105 (65)	0.33668 (42)
C(4)	−0.3104 (10)	−0.2340 (9)	0.2490 (8)			
C(5)	−0.3752 (11)	−0.2809 (12)	0.1592 (10)			
			Ligand 2			
S(1)	−0.1541 (2)	0.4058 (2)	0.2169 (2)	−0.14394 (9)	0.39275 (12)	0.22201 (7)
S(2)	−0.3403 (2)	0.2771 (2)	0.1052 (2)	−0.34021 (8)	0.27956 (11)	0.10665 (7)
C(1)	−0.2453 (7)	0.3851 (8)	0.1144 (6)	−0.23726 (35)	0.38230 (43)	0.11793 (28)
N	−0.2417 (6)	0.4444 (8)	0.0504 (6)	−0.23121 (31)	0.44492 (40)	0.05445 (24)
C(2)	−0.1631 (9)	0.5512 (12)	0.0651 (7)	−0.14644 (46)	0.54840 (56)	0.07318 (34)
C(3)	−0.1194 (10)	0.5488 (15)	0.0035 (9)	−0.11855 (50)	0.57075 (59)	0.00134 (39)
C(4)	−0.3274 (8)	0.0764 (10)	0.4633 (6)	−0.31948 (38)	0.06267 (48)	0.46910 (27)
C(5)	−0.4053 (9)	−0.0340 (11)	0.4362 (7)	−0.39438 (43)	−0.05699 (59)	0.55127 (34)
			Ligand 3			
S(1)	−0.3628 (2)	0.3801 (3)	0.2797 (2)			
S(2)	−0.1594 (2)	0.2953 (2)	0.3949 (2)			
C(1)	−0.2668 (4)	0.3826 (8)	0.3804 (6)			
N	−0.2756 (6)	0.4461 (8)	0.4424 (5)			
C(2)	−0.3743 (10)	0.5141 (16)	0.4249 (8)			
C(3)	−0.3919 (12)	0.5942 (20)	0.4471 (11)			
C(4)	−0.1879 (8)	0.0557 (10)	0.0285 (6)			
C(5)	−0.1152 (9)	−0.0587 (12)	0.0445 (7)			

Table III. Thermal Parameters with Their Standard Deviations (All ×10⁴) for the Structure at 297°K

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	429 (7)	373 (6)	395 (7)	25 (9)	162 (5)	3 (8)
			Ligand 1			
S(1)	571 (16)	440 (14)	580 (19)	29 (13)	266 (13)	−7 (13)
S(2)	534 (17)	552 (16)	552 (19)	−54 (14)	258 (14)	25 (14)
C(1)	522 (69)	414 (51)	281 (47)	0 (48)	143 (47)	57 (50)
N	939 (78)	445 (48)	455 (50)	22 (46)	236 (55)	37 (44)
C(2)	1065 (101)	576 (74)	652 (89)	431 (67)	436 (76)	36 (59)
C(3)	1456 (128)	976 (99)	669 (96)	526 (89)	303 (90)	239 (75)
C(4)	1066 (101)	404 (58)	1004 (105)	−373 (64)	394 (856)	120 (60)
C(5)	1129 (120)	882 (95)	1166 (133)	−373 (81)	−90 (98)	−103 (87)
			Ligand 2			
S(1)	552 (17)	511 (16)	427 (18)	−103 (13)	116 (13)	5 (13)
S(2)	436 (16)	498 (16)	427 (19)	−89 (12)	180 (13)	44 (13)
C(1)	481 (61)	350 (57)	329 (77)	2 (44)	129 (52)	2 (4)
N	589 (54)	528 (53)	507 (68)	−37 (45)	212 (49)	−3 (50)
C(2)	744 (79)	1008 (99)	502 (76)	−419 (78)	232 (61)	−40 (72)
C(3)	1083 (107)	1613 (135)	1021 (114)	−409 (98)	770 (93)	−229 (103)
C(4)	650 (68)	737 (75)	307 (68)	−40 (64)	156 (51)	−70 (58)
C(5)	793 (84)	900 (81)	781 (90)	−392 (70)	178 (69)	−43 (71)
			Ligand 3			
S(1)	498 (16)	682 (17)	422 (19)	186 (14)	86 (13)	−15 (14)
S(2)	404 (16)	541 (16)	431 (19)	80 (12)	110 (13)	21 (14)
C(1)	418 (57)	456 (61)	411 (80)	27 (45)	163 (51)	9 (50)
N	595 (61)	778 (63)	395 (58)	210 (52)	191 (47)	−26 (51)
C(2)	1122 (109)	2270 (189)	1022 (112)	1251 (115)	201 (87)	−551 (115)
C(3)	2100 (66)	4362 (101)	2991 (103)	2418 (110)	159 (86)	−2170 (97)
C(4)	553 (70)	779 (71)	381 (76)	2 (61)	5 (55)	17 (58)
C(5)	757 (84)	760 (87)	786 (89)	174 (73)	197 (67)	82 (74)

The difference between the two averages over Fe–S distances related by the (pseudo) threefold axis is 0.018 Å for the compound Fe(S₂COEt)₃ and 0.028 Å for the compound Fe(S₂CNMePh)₃. Healy and White[8] tentatively interpreted the distortion in the low-spin complexes as electronic in origin and due to Jahn-Teller and spin-orbit interactions. However, there is no distortion of this kind in the FeS₆ polyhedron of the compound Fe(S₂CNEt₂)₃ at 79°K which is also in the low-spin state at this temperature.

S–S Distances and Neighbor S–Fe–S Angles. The nearest sulfur-sulfur distances can be divided into three types (Figure 1). (i) Type A–D, the "bite" distance, has an average value of 2.846 Å (range 2.843–2.849 Å) at 297°K and 2.836 Å at 79°K. The difference of 0.010 Å in the mean distance is very small and not of a high significance level. (ii) Type A–B, the sulfur-sulfur distance within the same triangle, has a mean of 3.440 Å at 297°K and 3.357 Å at 79°K. The difference (0.083 Å) is correlated with the contraction of the
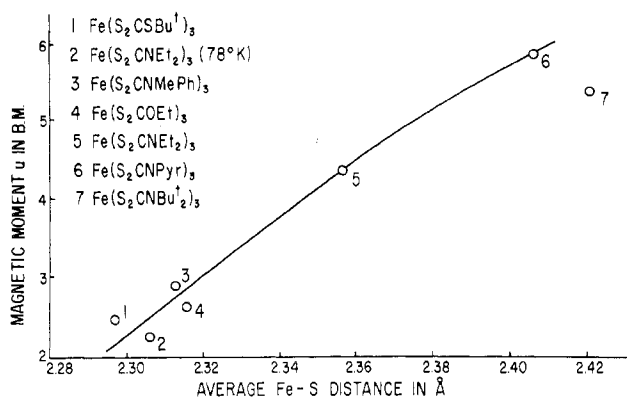
Figure 2. Variation of magnetic moment with mean observed Fe–S distance for some known structures.

Table IV. Thermal Parameters with Their Standard Deviations (All $\times 10^4$) of the Structure at 79°K

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	165 (4)	134 (4)	100 (4)		50 (3)	
			Ligand 1			
S(1)	212 (6)	192 (5)	142 (5)	47 (4)	80 (4)	13 (5)
C(1)	294 (34)	230 (31)	54 (28)		80 (25)	
N	467 (37)	176 (27)	145 (29)		178 (26)	
C(2)	584 (39)	198 (26)	233 (28)	163 (25)	149 (27)	21 (21)
C(3)	866 (52)	441 (39)	264 (33)	325 (36)	250 (34)	140 (28)
			Ligand 2			
S(1)	228 (6)	280 (6)	110 (5)	−86 (5)	30 (4)	17 (4)
S(2)	162 (5)	178 (5)	107 (5)	12 (4)	50 (4)	−4 (4)
C(1)	199 (21)	150 (20)	130 (21)	−14 (16)	55 (17)	5 (16)
N	231 (20)	287 (21)	102 (18)	−72 (16)	57 (15)	−3 (16)
C(2)	431 (31)	453 (30)	240 (27)	−226 (24)	111 (23)	43 (23)
C(3)	524 (35)	487 (33)	427 (32)	−1141 (27)	324 (28)	−82 (27)
C(4)	249 (23)	293 (24)	70 (19)	17 (19)	22 (17)	−5 (18)
C(5)	293 (27)	419 (33)	253 (25)	−106 (24)	94 (21)	−11 (24)

Table V. Interatomic Distances within the FeS$_6$ Polyhedron (Å)[a]

	297°K	79°K		297°K	79°K
Fe–S(1)	2.364 (3)	2.309 (1)	S(1)–S(6)	3.417 (4)	3.346 (2)
Fe–S(2)	2.362 (3)	2.308 (1)	S(2)–S(6)	3.446 (4)	3.359 (2)
Fe–S(3)	2.351 (3)	2.301 (1)	S(1)–S(2)	3.468 (4)	3.365 (2)
Fe–S(4)	2.356 (3)		S(3)–S(4)	3.444 (4)	
Fe–S(5)	2.361 (3)		S(4)–S(5)	3.433 (4)	
Fe–S(6)	2.352 (3)		S(5)–S(3)	3.429 (4)	
S(1)–S(3)	2.843 (4)	2.834 (2)	S(1)–S(4)	3.641 (4)	3.518 (2)
S(4)–S(6)	2.849 (4)	2.839 (2)	S(2)–S(3)	3.630 (4)	3.526 (2)
S(2)–S(5)	2.847 (4)		S(5)–S(6)	3.669 (4)	

[a] For numbering of sulfur atoms see Figure 4.

FeS$_6$ core. (iii) Type A–E, the "nonbite" sulfur–sulfur distance between the two triangles, averages to 3.647 Å at 297°K and 3.522 Å at 79°K. The difference (0.125 Å) is due to both the contraction of the FeS$_6$ polyhedron and the change in the geometry of the polyhedron.

The change in the geometry of the polyhedron can best be seen in the change of the various types of S–Fe–S angles.

The S–Fe–S angles can be divided into four groups. (i) Type A–Fe–D, the "bite" angle, has an average value of 74.3° at 297°K and 75.9° at 79°K. The change is 1.6°. (ii) Type A–Fe–B is the angle between iron and two sulfur atoms of the same triangle. The mean angle of this type is 93.8° at 297°K and 93.4° at 79°K. (iii) Type A–Fe–E, the "nonbite" angle between iron and two sulfur atoms of two different triangles of the polyhedron, has an average of 101.3° at 297°K and 99.6° at 79°K. All three types of angles are equal to 90° for an octahedron. (iv) Type A–Fe–F has the two sulfur atoms on opposite sides of the distorted octahedron. The average values are 161.2° at 297°K and 163.6°

Table VI. Interatomic Angles within the FeS$_6$ Polyhedron (deg)[a]

	297°K	79°K
S(1)–Fe–S(3)	74.2 (1)	75.9 (1)
S(2)–Fe–S(5)	74.2 (1)	75.9 (1)
S(4)–Fe–S(6)	74.5 (1)	75.9 (1)
S(3)–Fe–S(4)	94.0 (1)	93.1 (1)
S(3)–Fe–S(5)	93.4 (1)	93.5 (1)
S(1)–Fe–S(6)	92.9 (1)	93.1 (1)
S(2)–Fe–S(6)	94.0 (2)	93.5 (1)
S(4)–Fe–S(5)	93.8 (1)	93.5 (1)
S(1)–Fe–S(2)	94.4 (1)	93.5 (1)
S(2)–Fe–S(3)	100.8 (1)	99.8 (1)
S(5)–Fe–S(6)	102.2 (1)	99.8 (1)
S(1)–Fe–S(4)	101.0 (1)	99.2 (1)
S(3)–Fe–S(6)	161.0 (1)	163.1 (1)
S(2)–Fe–S(4)	161.1 (1)	163.8 (1)
S(1)–Fe–S(5)	161.5 (1)	163.8 (1)

[a] For numbering of sulfur atoms see Figure 4.

**Table VII.** Structural Parameters and Magnetic Moments for Some Known Structures Containing the FeS$_6$ Core

	μ, BM	⟨Fe–S⟩, Å	2θ, deg	α,[a] deg	β,[b] deg	Ref
Fe(S$_2$CN(t-Bu)$_2$)$_3$	5.3	2.42	33.2	93.5	72.8	c
Fe(S$_2$CNPyr)$_3$	5.9	2.406	38.6	93.5	74.5	d
Fe(S$_2$CNMePh)$_3$	2.9	2.312	40.4	94.1	75.1	d
Fe(S$_2$COEt)$_3$	2.7	2.316	41.2	94.3	75.5	e
Fe(S$_2$CS(t-Bu)$_2$)$_3$	2.5	2.297	42	94.8	75.2	f
Fe(S$_2$CNEt$_2$)$_3$ (297°K)	4.3	2.357	37.6	93.8	74.3	
Fe(S$_2$CNEt$_2$)$_3$ (79°K)	2.2	2.306	40.5	93.4	75.9	

[a] Angle of type A–Fe–B; see Figure 1. [b] The "bite" angle, type A–Fe–D. [c] Reference 6. [d] Reference 8. [e] Reference 7. [f] D. F. Lewis, S. J. Lippard, and J. A. Zubieta, *Inorg. Chem.*, 11, 823 (1972).

at 80°K. These angles are equal to 180° for an octahedron, again indicating an appreciable distortion from octahedral geometry.

The degree of trigonal distortion of the FeS$_6$ polyhedron can be described also by the angle 2θ (Figure 2) which is the angle of twist relative to the threefold axis between the upper and lower triangles. 2θ is equal to 60° for an octahedron and equal to 0° for a trigonal prism. The mean 2θ angle is 37.6° at 297°K and 40.5° at 79°K. The change (2.9°) is further evidence for the decrease in the distortion of the octahedron on transition from the high- to the low-spin state.

Geometry of the Ligands. The system of numbering of the atoms in the ligands is shown in Figure 3 while the ORTEP drawing of the Fe(S$_2$CNEt$_2$)$_3$ molecule is shown in Figure 4. The interatomic distances and angles within the ligands are summarized in Tables VIII and IX. The interatomic distances and angles are similar to those in related structures. Ewald, *et al.*,[2] have proposed that the electronic structures of the ligand in the high-spin and low-spin complexes differ, with the larger negative charge on the sulfur creating a stronger field

weak field   strong field
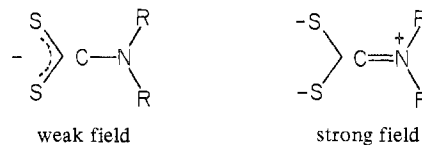
Since the present results are somewhat more precise than earlier information, a comparison of S–C and C–N bond lengths may support the hypothesis. The values averaged over chemically equivalent bonds are for S–C 1.708 (4) and 1.721 (2) Å and for C–N 1.337 (6) and 1.323 (4) Å at room and low temperature, respectively. The difference in S–C
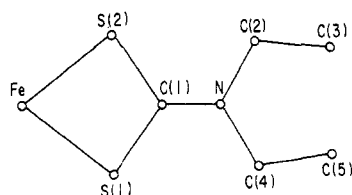
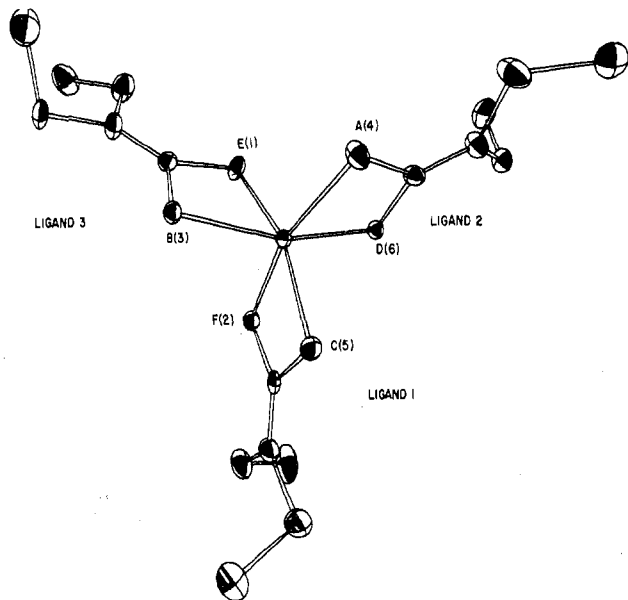**Figure 3.** The numbering of the ligand atoms.

Figure 4. ORTEP drawing of the molecule at room temperature. Ellipsoids are 50% probability surfaces.

Table VIII. Interatomic Distances within the Ligands (Å)

	297°K	79°K
	Ligand 1	
S(1)-C(1)	1.704 (9)	1.720 (4)
S(2)-C(1)	1.711 (10)	
C(1)-N	1.349 (10)	1.326 (6)
N-C(2)	1.532 (13)	1.480 (7)
N-C(4)	1.462 (13)	
C(2)-C(3)	1.555 (16)	1.537 (9)
C(4)-C(5)	1.528 (17)	
	Ligand 2	
S(1)-C(1)	1.720 (10)	1.720 (4)
S(2)-C(1)	1.710 (10)	1.723 (4)
C(1)-N	1.320 (10)	1.320 (6)
N-C(2)	1.514 (11)	1.466 (7)
N-C(4)	1.503 (12)	1.493 (8)
C(2)-C(3)	1.489 (16)	1.544 (9)
C(4)-C(5)	1.517 (16)	1.505 (9)
	Ligand 3	
S(1)-C(1)	1.705 (10)	
S(2)-C(1)	1.700 (9)	
C(1)-N	1.343 (10)	
N-C(2)	1.485 (11)	
N-C(4)	1.481 (12)	
C(2)-C(3)	1.516 (16)	
C(4)-C(5)	(0.999 (17))	

bond length is about 3σ and perhaps significant, while the C-N difference is only 2σ. Nevertheless, both changes are in agreement with the hypothesis of Ewald, *et al.*

None of the bond lengths have been corrected for apparent shortening due to thermal motion, because the nature of the molecular modes is unknown. Inspection of the thermal parameters shows that the molecule does not behave as a rigid body. For example, the carbon atoms of the dithiocarbamate group have a smaller rms displacement than the

Table IX. Interatomic Angles (deg)

	297°K	79°K
	Ligand 1	
Fe-S(1)-C(1)	86.6 (3)	86.4 (1)
Fe-S(2)-C(1)	86.6 (3)	
S(1)-C(1)-S(2)	112.7 (4)	111.3 (2)
S(1)-C(1)-N	123.1 (4)	124.4 (2)
S(2)-C(1)-N	124.2 (5)	
C(2)-N-C(4)	119.6 (8)	117.4 (4)
N-C(2)-C(3)	109.0 (10)	112.5 (4)
N-C(4)-C(5)	109.8 (10)	
	Ligand 2	
Fe-S(1)-C(1)	86.6 (3)	86.5 (1)
Fe-S(2)-C(1)	87.2 (4)	86.8 (1)
S(1)-C(1)-S(2)	112.0 (5)	110.9 (2)
S(1)-C(1)-N	124.0 (5)	124.3 (2)
S(2)-C(1)-N	124.0 (5)	124.9 (2)
C(2)-N-C(4)	118.7 (9)	118.8 (5)
N-C(2)-C(3)	112.7 (11)	111.6 (5)
N-C(4)-C(5)	111.3 (11)	110.2 (5)
	Ligand 3	
Fe-S(1)-C(1)	86.0 (3)	
Fe-S(2)-C(1)	86.2 (3)	
S(1)-C(1)-S(2)	113.4 (4)	
S(1)-C(1)-N	123.1 (5)	
S(2)-C(1)-N	123.4 (5)	
C(2)-N-C(4)	120.4 (9)	
N-C(2)-C(3)	111.9 (12)	
N-C(4)-C(5)	112.6 (11)	

sulfur atoms which are closer to the center of the complex. As the correction always lengthens the bonds, it would tend to decrease the difference between S-C bonds at the two temperatures but increase the change in the C-N bond lengths.

The carbon atoms of some of the ethyl groups, especially C(5) in ligand 3, show anomalously large thermal parameters at room temperatures, probably indicating the presence of disorder of the ethyl groups. Even at liquid nitrogen temperature some of the ethyl carbon atoms have suspiciously large thermal parameters: U_{11} for C(3) in ligand 1 is 0.087 Å^2, for example (corresponding to an isotropic thermal parameter of about 7 Å^2). The behavior could be investigated further by constrained least-squares methods, but no such study has been undertaken.

Nature of the Magnetic Transition. In much of the earlier work on the iron dithiocarbamates it was assumed that the variable magnetic moment is due to the existence of two almost equienergetic ground states, the variation being a result of the change in relative population of the two levels with temperature.

Mossbauer and proton nmr studies have consistently failed to show evidence for the simultaneous existence of two electronic species in samples with intermediate magnetic moments.[3] This means that if a thermal equilibrium exists, the crossover must be more rapid than the lifetime of the excited state of ^{57}Fe or the time scale of the nmr experiment.

It has been pointed out by Merrithew and Rasmussen[3] that such a rapid transition ($>10^{-7}$ sec) is not characteristic for complexes with different spin states and that two doublets are observed in the Mossbauer spectra of iron(II) compounds with temperature-dependent magnetic moments. An alternative explanation, compatible with the spectroscopic data, is given by theoretical crystal field calculations by Harris,[4,5] which provide support for the existence of a mixed-spin state of variable character.

In principle, the diffraction data are capable of distinguishing between the two models, because the thermal equilibrium hypothesis would imply a disorder in the crystal, as the

sextet A and doublet T states have different Fe–S bond lengths. The time-averaged structure observed in the diffraction experiment would be a superposition of two molecular geometries for a complex with intermediate magnetic moment.

The room-temperature magnetic moment of tris(N,N-diethyldithiocarbamato)iron is 4.2 BM and such a disorder might, therefore, be detectable in the present room-temperature study.

Average U_{ii} values for the Fe, S, and C atoms are summarized in Table X. Though the sulfur atoms have the largest U_{ii} values at room temperature of the three atom types listed, the ratio of $(U_{ii})_{279°}/(U_{ii})_{79°}$ is not anomalous and smaller than the ratio of the temperatures.

It may be shown that the superposition of two gaussian distributions of equal occupancy at distance $2x_0$ gives a (nongaussian) distribution with root-mean-square displacement, *i.e.*

$$(U_{ij})_{new} = (U_{ij})_{old} + x_0^2$$

This expression can be easily extended to the case of nonequal occupancy. But since the room-temperature magnetic moment of 4.2 BM is not too different from the average of the pure high-spin and low-spin values (5.9 and 2.2 BM neglecting spin-orbit coupling), we may use the expression as given above.

It follows that with $x_0 = 0.05$ Å the apparent increase in the corresponding thermal motion parameter would be 0.0025 Å^2, or only 5% of the observed value of U_{ij}. Clearly, no conclusion can be drawn from the present temperature factors as to the nature of the magnetic transition.

Difference maps obtained after refinement was completed did not show any evidence of the existence of disorder. It

Table X. Average U_{ii} Values at 279 and 79°K (Å^2)

	279°K	79°K	Ratio col 2/ col 3
Fe	0.0399	0.0133	3.0
S	0.0500	0.0179	2.8
C (of SCS group)	0.0407	0.0176	2.3

is possible that such disorder would be observable in the difference maps of a sample in which the relative populations of the two states differ considerably. The resulting distribution would be asymmetric and, therefore, less well approximated by a harmonic vibration. Further information may also be obtained by accurate studies of a complex with intermediate magnetic moment at liquid nitrogen temperature.

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Crystallographic Elucidation of the Molecular Geometry of Bis(pentalenyl)iron, Including the Location and Refinement of Hydrogen Atoms

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Bis(pentalenyl)iron, (C$_8$H$_6$)$_2$Fe, crystallizes in the noncentrosymmetric orthorhombic space group $P2_12_12_1$ (D_2^4; No. 19) with $a = 13.809$ (3), $b = 10.828$ (2), $c = 7.339$ (2) Å and $Z = 4$. Observed and calculated densities are 1.582 (10) and 1.574 g cm^{-3}, respectively. A single-crystal X-ray structural analysis of this species has been completed. Diffraction data to $2\theta = 55°$ (Mo Kα radiation) were collected with a Picker FACS-1 automated diffractometer, and the structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogens, have been located, the final discrepancy indices being $R_F = 6.65\%$ and $R_{wF} = 3.74\%$ for 1475 independent reflections. The completed analysis shows the molecule to be [4,5,6,7,8,4',5',6',7',8'-*decahapto*-1,1'-dihydro-1,1'-bipentalenyl] iron, *i.e.*, a highly substituted ferrocene derivative with a bridge of only two carbon atoms between the two five-membered π-cyclopentadienyl systems. The molecule has C_2 symmetry within the limits of experimental error. The "ferrocene" moiety is distorted such that iron-carbon distances are in the range 1.985 (5)–2.077 (5) Å in ring A and 1.974 (4)–2.088 (5) Å in ring B. The angle CpA–Fe–CpB (where CpA and CpB are the centroids of the two delocalized five-membered rings) is 161.7 (3)°, and the interplanar angle is 23.6°.

Introduction

Although highly substituted pentalenes, such as dibenzopentalene[1] and hexaphenylpentalene,[2] have been prepared, and evidence has been presented for the existence of 1-meth-

ylpentalene (albeit, at −196°),[3] the parent hydrocarbon, pentalene (I), has successfully eluded synthesis.[4] (We may note

(1) C. T. Blood and R. P. Linstead, *J. Chem. Soc.*, 2263 (1952).
(2) E. LeGoff, *J. Amer. Chem. Soc.*, **84**, 3975 (1962).

(3) R. Bloch, R. A. Marty, and P. de Mayo, *J. Amer. Chem. Soc.*, **93**, 3071 (1971).
(4) (a) See, *inter alia*, E. D. Bergmann in "Non-benzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience, New York, N. Y., 1959; (b) G. M. Badger in "Aromatic Character and Aromaticity," Cambridge University Press, New York, N. Y., 1969.