Structural Studies in the Tris(*NN*-dialkyldithiocarbamato)iron(III) 'Cross-over' System

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The crystal and molecular structures of ' high-spin ' tris(1-pyrrolidinecarbodithioato)iron(III) (I) {$[Fe(CS_2{\cdot}N\text{-}[CH_2]_4)_3]$, μ(300 K, solid) 5·9 B.M.}, and the predominantly ' low-spin ' tris(*N*-methyl-*N*-phenyldithiocarbamato)-iron(III) (II) {$[Fe(CS_2{\cdot}NMePh)_3]$, μ(300 K, solid) 3·0 B.M.} have been determined by single-crystal *X*-ray diffraction methods, using conventional Patterson–Fourier heavy-atom methods followed by block-diagonal least-squares refinement. Final conventional *R* values were 0·13 [(I), 1346 reflections] and 0·09 [(II), 1014 reflections]. The compounds both crystallize in the monoclinic system with $Z = 4$ (I): $a = 16{\cdot}23 \pm 0{\cdot}04$, $b = 14{\cdot}53 \pm 0{\cdot}02$, $c = 10{\cdot}22 \pm 0{\cdot}03$ Å, $\beta = 90{\cdot}3 \pm 0{\cdot}4°$, space-group $P2_1/n$; (II): $a = 25{\cdot}31 \pm 0{\cdot}05$, $b = 12{\cdot}90 \pm 0{\cdot}01$, $c = 9{\cdot}48 \pm 0{\cdot}03$ Å, $\beta = 116{\cdot}2 \pm 0{\cdot}2°$, space-group $P2_1/a$.

Both molecules consist of three substantially planar dithiochelate ligands surrounding the central iron atom in an approximately D_3 configuration. The angular FeS_6 geometries are closely comparable but there is a large contraction in the Fe–S distance on passing from the ' high-spin ' to the ' low-spin ' configuration. In (I), the iron–sulphur distance ranges from 2·38(1) to 2·44(1) Å, whereas in (II), the range is 2·28(1)—2·33(1) Å. The remainder of the molecular dimensions are normal within the limits of experimental error.

THE tris(*NN*-dialkyldithiocarbamato)iron(III) complexes, $[Fe(CS_2{\cdot}NR_2)_3]$ provide a well defined example of the ' crossover ' situation which arises when a transition-metal ion possesses two almost equi-energetic ground states.[1-4] If the energy separation between these states, ΔE, is of the order of kT, the relative populations of the two states vary with the temperature of the sample. In the iron(III) case, the alternative ground states in the O_h approximation are ${}^2T_{2g}(t_{2g}{}^5)$ (' low-spin '), and ${}^6A_{1g}(t_{2g}{}^3e_g{}^2)$ (' high-spin '). In this series of complexes, ΔE may be varied by suitable choice of the substituents R; although well removed from the FeS_6 molecular core, these substituents can appreciably affect the electronic parameters of the central iron atom and the surrounding crystal field due to the six sulphur atoms by way of the conjugated system of the ligand. [The relative disposition of the two spin states in any given sample is most easily ascertained by measurement of the magnetic moment, μ,[5-7] μ(300 K) being 5·93 B.M. for a purely high-spin undistorted complex, and *ca.* 2·3 B.M. for a low-spin complex, this latter figure being rather dependent on distortion and spin–orbit coupling effects.[8]]

A selection of possible situations is depicted in Figure 1. Determinations of Mössbauer[9-14] and proton n.m.r. spectra[15-17] have indicated that doublet–sextet exchange is normally at a frequency $>10^7$ s^{-1} so that, the ' long-term ' physical properties of a bulk sample should reflect an average of the contributions of each ground state.

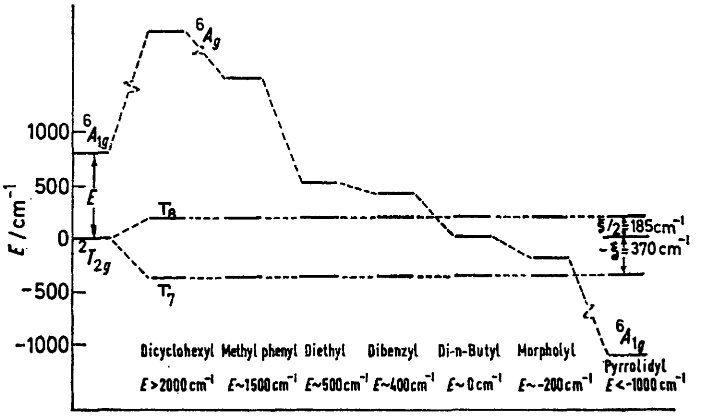

FIGURE 1 The disposition of the ${}^6A_{1g}$ state relative to the spin–orbit components of the ${}^2T_{2g}$ state, using the octahedral approximation, for a variety of tris(*NN*-dialkyldithiocarbamato)iron(III) complexes

If the spin state of the molecule is changed from sextet to doublet we expect that depopulation of the sextet levels should lead to an associated contraction of the iron(III)–sulphur radius,[18] so that the molecular geometry of these complexes, and in particular, the geometry of the FeS_6 core, should be markedly dependent on the ligand substituent R. Evidence in support of this is obtained from studies of the pressure depend-

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ence of the electronic properties in chloroform solution at pressures of up to 5000 atmospheres at room temperature.[2,3] If all molecular-volume contraction, ΔV, arises from contraction of the FeS_6 molecular core [and the insusceptibility of the cobalt(III) analogues to compression strongly suggests that it does], we can describe the behaviour of the system in terms of a sextet–doublet equilibrium constant K, ΔV for the process being given by the relation $\Delta V = -RT(\partial \ln K/\partial P)_T$, and so derive a ΔV of the order of 5 cm^3 mol^{-1} for complexes with a wide variety of ligand substituents R; this can reasonably be accounted for by a change in the iron(III)–sulphur bond length of *ca.* 0·1 Å.

Crystallographic evidence at room temperature substantiating this has been obtained by Hoskins and Kelly, who have shown that in tris(*NN*-di-n-butyldithiocarbamato)iron(III),[19] largely 'high-spin' [μ(300 K, solid) 5·32 B.M.], the mean iron–sulphur distance is 2·42 Å. In the predominantly 'low-spin' related complex tris(*O*-ethyldithiocarbonato)iron(III),[20] [μ(300 K, solid) 2·70 B.M.], it is 2·32 Å. They also report a substantial difference in the angular trigonal distortion about the three-fold axis between the two complexes. In order to better define the nature and origin of the above molecular contraction, we have determined the crystal structure of the only known complex in this series which is believed to be purely 'high-spin' in its behaviour at room temperature [μ(300 K, solid) 5·9 B.M.], tris(1-pyrrolidinecarbodithioato)iron(III), (I), $[Fe(CS_2{\cdot}N[CH_2]_4)_3]$, together with that of the analogue, tris(*N*-methyl-*N*-phenyldithiocarbamato)iron(III), $[Fe(CS_2{\cdot}NMePh)_3]$, (II), in which the room-temperature ground state is predominantly a doublet [μ(300 K, solid) 3·0 B.M.]. (A preliminary report on this work has already appeared.[21])

EXPERIMENTAL AND RESULTS

The two complexes were prepared and purified as described elsewhere.[1] Crystals of (I) were obtained as shining black cuboids, the crystallographic axes being coincident with the cell edges, by the slow evaporation of ethanol–chloroform solutions, the latter solvent being carefully purified to avoid contamination by the formation of the five-covalent complex $[ClFe(CS_2{\cdot}N[CH_2]_4)_2]$.[22] Crystals of (II) were obtained as small, elongated, lenticular crystals from benzene solution, the crystallographic *a* axis being the long axis of the crystal.

Intensity data were collected photographically on a Nonius non-integrating Weissenberg camera using the multiple-film equi-inclination technique. Unit-cell calibration was effected by superimposing aluminium powder lines (a_{298K} 4·0494 Å)[23] on zero-layer Weissenberg photographs about the axes on which data was gathered, an additional photograph being taken about the *b* axis for complex (I). Nickel-filtered Cu-K_α radiation was used throughout [$\lambda(K_{\alpha1}) = 1{\cdot}5406$, $\lambda(K_{\alpha2}) = 1{\cdot}5444$ Å].[24] Densities were determined by flotation in aqueous potassium iodide solution.

Crystal Data.—(i) (I), $C_{15}H_{24}FeN_3S_6$, $M = 494$, Monoclinic, $a = 16{\cdot}23 \pm 0{\cdot}04$, $b = 14{\cdot}53 \pm 0{\cdot}02$, $c = 10{\cdot}22 \pm 0{\cdot}03$ Å, $\beta = 90{\cdot}3 \pm 0{\cdot}4°$, $U = 2410$ Å^3, $D_m = 1{\cdot}37 \pm 0{\cdot}03$, $Z = 4$, $D_c = 1{\cdot}37$, $F(000) = 1028$. Space-group, $P2_1/n$ (C_{2h}^5, No. 14, Ref. 25) from systematic absences: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$. Data collected on two independent crystals of size 0·10 × 0·10 × 0·10 mm about *a* and *c* respectively for the layers 0—8*kl*, *hk*0—6. μ(Cu-K_α) = 98 cm^{-1}, transmission coefficient range 0·236—0·338.

(ii) (II), $C_{24}H_{24}FeN_3S_6$, $M = 602$, Monoclinic, $a = 25{\cdot}31 \pm 0{\cdot}05$, $b = 12{\cdot}90 \pm 0{\cdot}01$, $c = 9{\cdot}48 \pm 0{\cdot}03$ Å, $\beta = 116{\cdot}2 \pm 0{\cdot}2°$, $U = 2779$ Å^3, $D_m = 1{\cdot}42 \pm 0{\cdot}04$, $Z = 4$, $D_c = 1{\cdot}45$, $F(000) = 1244$. Space-group, $P2_1/a$ from systematic absences: $h0l$, $h = 2n + 1$; $0k0$, $k = 2n + 1$. Data collected on two independent crystals of size 0·16 × 0·05 × 0·05 mm about *a* and *b* respectively for the layers 0—12*kl*, *h*0—6*l*. μ(Cu-K_α) = 86 cm^{-1}, transmission coefficient range 0·477—0·682.

[In complex (II), the two crystals on which data was collected appear to have been well matched; this does not appear to have been so for (I) where the reflection quality differed between the two axial sets and scaling was less satisfactory. We think this the most probable reason for the less favourable final R value for (I).]

The data for both complexes and for other tris(*NN*-dialkyldithiocarbamato)iron(III) derivatives we have examined is typically very poor in quality and limited in quantity; *e.g.* in (I) 94% of the reflections observed were found to have a Bragg angle of less than 43° and the available data of (II) is similar. This imposes severe limitations on the accuracy of the structure determinations as well as the unit-cell calibrations. Intensities were estimated visually using an intensity strip calibrated with a Joyce–Loebl Mark IIIB microdensitometer. Both sets of data were corrected for absorption using a local program based on that of ABSCOR,[26] for Lorentz and polarization factors using a local program, SCAL1, and scaled by internal correlation using a program based on the algorithm of Hamilton, Rollett, and Sparks[27] to give a final arbitrarily scaled set of $|F_o|$. All reflections were assigned unit weights in the scaling procedure. For (I) 1346 and for (II) 1014 independent observed reflections, were obtained; at no stages were unobserved reflections included in the subsequent structure determinations.

Structure Determinations.—(*a*) *Complex* (I).—The positions of the iron and two sulphur atoms were correctly located from an unmodified Patterson function computed on all data; the remaining four sulphur atoms and all lighter atoms were successively located in subsequent three-dimensional electron-density distributions. All atoms were located on general positions (x, y, z), $(\bar{x}, \bar{y}, \bar{z})$, $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$, and $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$ in the unit cell. Using arbitrary isotropic thermal parameters of 3·0 for the iron and sulphur atoms and 4·0 for carbon and nitrogen, R 0·40 was obtained. Refinement by block-diagonal

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(3 × 3, 6 × 6) least-squares procedures was introduced using independent isotropic thermal parameters, R converging to 0·15, a weighting scheme [28] of the form $w = (a + |F_o| + b|F_o|^2)^{-1}$ being introduced in the latter stages and the refinement minimizing the function $w(|F_o| - |F_c|)^2$; a and b were adjusted at successive stages during the refinement. The weighted factor, R' was 0·21 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. At this stage in the refinement the iron and sulphur atoms were allocated anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Refinement proceeded until parameter shifts in both atomic positional and thermal parameters were $< 0{\cdot}2\ \sigma$ for the light atoms, those of the heavier atoms being considerably less. The structure converged to a final R of 0·13, R' being 0·18 and the weighting-scheme constants being $a = 11{\cdot}6$ and $b = 0{\cdot}021$. The introduction of anisotropic thermal parameters was found to be statistically significant.[29] (Derivation of the thermal ellipsoids, however, showed the root-mean-square vibrational amplitudes along the principal axes to be almost equal for each atom and this, coupled with the rather small drop in R and R' on the introduction of the thermal anisotropies, suggests that, in spite of the result of the significance test, the additional thermal parameters are little better than 'fudge' factors in this structure. Accordingly, the ellipsoids are not given in detail). A difference map computed after the final round of least-squares refinement revealed no significant or spurious peaks, being flat to $<0{\cdot}5$ carbon atoms. There was no evidence for disorder in the structure.

(*b*) *Compound* (II). The solution and refinement of this structure proceeded similarly. The initial Fourier was phased solely on the iron atom which was located from the Patterson function. All atoms were located on general positions (x, y, z), $(\bar{x}, \bar{y}, \bar{z})$, $(\frac{1}{2} - x, \frac{1}{2} + y, \bar{z})$, and $(\frac{1}{2} + x, \frac{1}{2} - y, z)$ in the unit cell. At convergence with isotropic thermal parameters and a similar weighting scheme R was 0·095, and R' 0·137. Refinement with anisotropic thermal parameters terminated at R 0·087, R' 0·121, the weighting-scheme parameters being $a = 11{\cdot}25$, $b = 0{\cdot}022$. Final parameter shifts were of a similar order to those found for (I) and the flatness of the difference map was rather better. Again, although anisotropic thermal

TABLE 1

(*a*) Compound (I)

(i) Final atomic fractional cell co-ordinates and isotropic thermal parameters (Å^2) with standard deviations in parentheses.

Atom	x	y	z	B
Fe	0·7715(3)	0·3391(2)	0·5193(4)	[4·7(1)] *
S(*a*1)	0·6770(5)	0·4112(4)	0·3685(6)	[4·5(2)] *
S(*a*2)	0·7132(5)	0·4668(4)	0·6353(7)	[5·1(2)] *
S(*b*1)	0·8955(5)	0·3959(4)	0·4116(7)	[4·7(2)] *
S(*b*2)	0·8838(5)	0·3133(5)	0·6697(7)	[5·6(2)] *
S(*c*1)	0·7850(5)	0·2012(4)	0·3959(7)	[4·8(2)] *
S(*c*2)	0·6808(5)	0·2318(4)	0·6247(8)	[5·1(2)] *
C(*a*1)	0·663(1)	0·488(1)	0·490(2)	4·1(5)
C(*b*1)	0·944(2)	0·347(1)	0·546(2)	4·6(5)
C(*c*1)	0·715(2)	0·160(2)	0·505(2)	5·4(6)
N(*a*1)	0·615(1)	0·557(1)	0·473(2)	5·0(4)
N(*b*1)	0·026(2)	0·341(1)	0·543(2)	6·6(5)
N(*c*1)	0·689(1)	0·074(1)	0·502(2)	5·8(5)
C(*a*2)	0·574(2)	0·579(2)	0·353(3)	6·3(6)
C(*a*3)	0·602(2)	0·623(2)	0·581(3)	6·7(6)
C(*a*4)	0·542(2)	0·675(2)	0·378(3)	9·7(9)
C(*a*5)	0·546(2)	0·698(2)	0·514(3)	8·2(8)
C(*b*2)	0·083(2)	0·368(2)	0·433(3)	6·9(7)
C(*b*3)	0·068(2)	0·298(2)	0·664(3)	6·9(7)
C(*b*4)	0·170(3)	0·340(2)	0·497(5)	12·6(1·3)
C(*b*5)	0·157(3)	0·274(2)	0·607(5)	13·3(1·3)
C(*c*2)	0·724(2)	0·010(2)	0·402(3)	6·9(7)
C(*c*3)	0·628(2)	0·040(2)	0·593(3)	7·1(7)
C(*c*4)	0·685(2)	0·920(2)	0·451(3)	8·1(7)
C(*c*5)	0·612(2)	0·943(2)	0·520(3)	9·0(7)

* Isotropic B values at R 0·15 before the introduction of anisotropic thermal parameters.

TABLE 1 (*Continued*)

(ii) Anisotropic thermal parameters (× 10^4) for iron and sulphur atoms

Atom	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Fe	35(3)	17(3)	−9(5)	58(2)	14(5)	150(5)
S(*a*1)	53(5)	17(6)	−24(10)	59(3)	−5(8)	140(8)
S(*a*2)	54(5)	9(7)	−13(10)	75(4)	−15(9)	138(8)
S(*b*1)	55(5)	−9(7)	−9(10)	67(4)	54(10)	151(9)
S(*b*2)	54(5)	30(8)	−1(11)	99(5)	28(11)	131(8)
S(*c*1)	49(5)	10(6)	53(10)	62(3)	14(9)	151(9)
S(*c*2)	45(5)	14(6)	19(10)	65(4)	10(10)	183(10)

(*b*) Compound (II)

(i) Final atomic fractional cell co-ordinates and isotropic temperature factors (Å^2) with standard deviations in parentheses

Atom	x	y	z	B
Fe	0·1211(2)	0·6710(3)	0·9427(4)	[3·1(1)] †
S(*a*1)	0·0973(3)	0·7864(5)	0·0917(8)	[2·5(1)] †
S(*a*2)	0·1895(3)	0·8033(6)	0·0020(9)	[4·2(2)] †
S(*b*1)	0·0469(3)	0·7361(6)	0·7149(7)	[3·3(2)] †
S(*b*2)	0·1362(3)	0·5964(6)	0·7398(8)	[3·6(2)] †
S(*c*1)	0·0629(3)	0·5401(6)	0·9554(8)	[3·2(2)] †
S(*c*2)	0·1855(3)	0·5592(6)	0·1353(8)	[3·6(2)] †
C(*a*1)	0·151(1)	0·859(2)	0·095(3)	4·7(7)
C(*b*1)	0·075(1)	0·664(2)	0·619(3)	3·4(6)
C(*c*1)	0·125(1)	0·484(2)	0·089(3)	4·3(7)
N(*a*1)	0·169(1)	0·950(1)	0·170(2)	3·0(5)
N(*b*1)	0·049(1)	0·656(1)	0·457(2)	2·9(4)
N(*c*1)	0·126(1)	0·389(2)	0·161(2)	3·6(5)
C(*a*2)	0·226(1)	0·003(2)	0·186(3)	6·1(8)
C(*a*3)	0·138(1)	0·997(2)	0·255(3)	4·7(7)
C(*a*4)	0·170(1)	0·000(3)	0·420(3)	3·4(6)
C(*a*5)	0·137(1)	0·042(2)	0·499(4)	4·3(7)
C(*a*6)	0·081(1)	0·083(2)	0·411(3)	6·0(8)
C(*a*7)	0·050(1)	0·074(2)	0·246(3)	6·3(8)
C(*a*8)	0·081(1)	0·033(2)	0·172(3)	5·5(8)
C(*b*2)	0·074(1)	0·582(3)	0·372(4)	6·5(9)
C(*b*3)	0·997(1)	0·707(2)	0·368(3)	4·4(7)
C(*b*4)	0·997(1)	0·814(2)	0·329(3)	5·2(7)
C(*b*5)	0·947(1)	0·864(2)	0·239(4)	6·1(8)
C(*b*6)	0·892(1)	0·818(3)	0·191(4)	6·4(8)
C(*b*7)	0·890(1)	0·722(3)	0·228(3)	6·6(8)
C(*b*8)	0·943(1)	0·659(2)	0·322(3)	4·0(6)
C(*c*2)	0·071(1)	0·331(2)	0·112(3)	5·3(7)
C(*c*3)	0·178(1)	0·343(2)	0·278(3)	3·3(6)
C(*c*4)	0·179(1)	0·318(2)	0·423(3)	5·2(8)
C(*c*5)	0·229(1)	0·265(3)	0·538(4)	6·5(8)
C(*c*6)	0·273(1)	0·248(2)	0·504(3)	4·0(6)
C(*c*7)	0·276(1)	0·274(2)	0·367(3)	5·7(7)
C(*c*8)	0·225(1)	0·321(2)	0·423(3)	4·0(7)

† Isotropic B values at R 0·095 before the introduction of anisotropic thermal parameters.

(ii) Anisotropic temperature factors (× 10^4) for iron and sulphur atoms

Atom	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Fe	14(1)	0(3)	33(4)	41(3)	−9(8)	80(6)
S(*a*1)	12(2)	−15(5)	50(7)	31(5)	−54(12)	114(11)
S(*a*2)	22(2)	−6(6)	92(9)	54(6)	−24(16)	185(14)
S(*b*1)	17(2)	28(6)	40(8)	62(6)	25(14)	86(10)
S(*a*2)	14(2)	5(6)	57(3)	66(7)	−12(15)	147(13)
S(*c*1)	13(2)	0(6)	40(7)	52(6)	35(14)	113(11)
S(*c*2)	14(2)	−5(6)	18(7)	64(6)	−5(15)	116(11)

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parameters may be statistically significant according to a ratio test on both *R* and *R'*, we do not consider the vibrational amplitudes enlightening and omit them.

Scattering factors for both structures were drawn from ref. 30 for neutral iron, sulphur, carbon, and nitrogen atoms, the iron atom being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$) according to ref. 31. The refinement programs were local modifications of SFLS1 and SFLS2 (A. I. M. Rae) and FCURV (B. J. Ong, local). The final sets of observed and calculated structure-factors are listed in Supplementary Publication No. SUP 20355 (3 pp., 1 microfiche).*

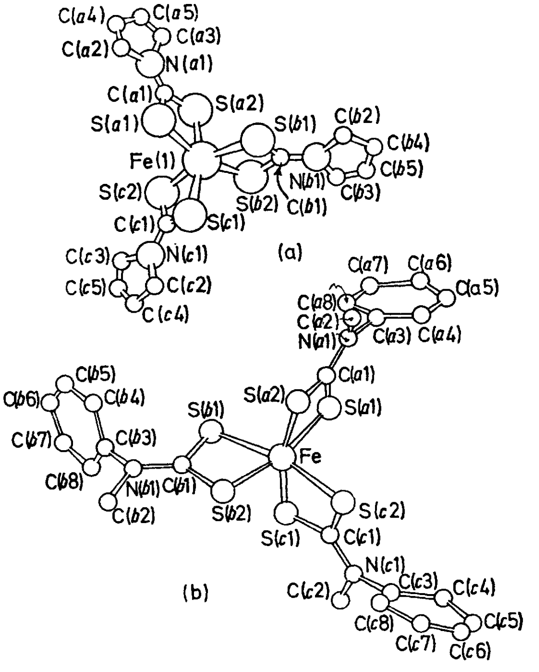

FIGURE 2 Molecular configuration and numbering system of (a) complex (I), and (b) complex (II)

Final atomic positional and thermal parameters are given in Table 1, together with the least-squares estimated standard deviations which are probably underestimated since they are derived from a block-diagonal refinement procedure. The atom-numbering system used is shown in Figure 2 (a) and (b).

Interatomic distances and angles were computed using the BONDSCAN program [32] and are given for bonding distances and angles within the molecules in Table 2, with least-squares estimated standard deviations.

Planes of best fit were calculated through each of the three dithiocarbamate ligands within the molecules, together with atomic deviations. These are given in Table 3.

Computing was carried out on the DEC PDP10 machine at the University of Western Australia.

DISCUSSION

In both (I) and (II) the crystals are composed of discrete molecules of the complex, the molecule in each

TABLE 2

(*a*) Compound (I)

(i) Final intramolecular distances (Å)

Fe–S(*a*1)	2·41(1)	N(*b*1)–C(*b*2)	1·51(4)
Fe–S(*a*2)	2·40(1)	N(*b*1)–C(*b*3)	1·55(4)
S(*a*1)–S(*a*2)	2·90(1)	C(*b*2)–C(*b*4)	1·61(5)
S(*a*1)–C(*a*1)	1·69(2)	C(*b*3)–C(*b*5)	1·60(5)
S(*a*2)–C(*a*1)	1·71(2)	C(*b*4)–C(*b*5)	1·50(6)
C(*a*1)–N(*a*1)	1·29(3)		
N(*a*1)–C(*a*2)	1·41(3)	Fe–S(*c*1)	2·38(1)
N(*a*1)–C(*a*3)	1·48(3)	Fe–S(*c*2)	2·40(1)
C(*a*2)–C(*a*4)	1·52(4)	S(*c*1)–S(*c*2)	2·93(1)
C(*a*3)–C(*a*5)	1·57(5)	S(*c*1)–C(*c*1)	1·71(3)
C(*a*4)–C(*a*5)	1·43(5)	S(*c*2)–C(*c*1)	1·70(3)
		C(*c*1)–N(*c*1)	1·32(3)
Fe–S(*b*1)	2·44(1)	N(*c*1)–C(*c*2)	1·50(3)
Fe–S(*b*2)	2·41(1)	N(*c*1)–C(*c*3)	1·46(4)
S(*b*1)–S(*b*2)	2·90(1)	C(*c*2)–C(*c*4)	1·54(4)
S(*b*1)–C(*b*1)	1·73(2)	C(*c*3)–C(*c*5)	1·61(4)
S(*b*2)–C(*b*1)	1·68(3)	C(*c*4)–C(*c*5)	1·42(5)
C(*b*1)–N(*b*1)	1·32(4)		

(ii) Final intramolecular angles (°)

S(*a*1)–Fe–S(*a*2)	74·3(3)	S(*b*1)–C(*b*1)–N(*b*1)	117(2)
S(*a*1)–Fe–S(*b*1)	95·1(3)	S(*b*2)–C(*b*1)–N(*b*1)	126(2)
S(*a*1)–Fe–S(*b*2)	162·5(3)	S(*c*1)–C(*c*1)–N(*c*1)	122(2)
S(*a*1)–Fe–S(*c*1)	94·9(3)	S(*c*2)–C(*c*1)–N(*c*1)	120(2)
S(*a*1)–Fe–S(*c*2)	100·4(3)	C(*a*1)–N(*a*1)–C(*a*2)	125(2)
S(*a*2)–Fe–S(*b*1)	106·8(3)	C(*a*1)–N(*a*1)–C(*a*3)	120(2)
S(*a*2)–Fe–S(*b*2)	96·0(3)	C(*a*2)–N(*a*1)–C(*a*3)	116(2)
S(*a*2)–Fe–S(*c*1)	162·1(3)	C(*b*1)–N(*b*1)–C(*b*2)	128(2)
S(*a*2)–Fe–S(*c*2)	92·1(3)	C(*b*1)–N(*b*1)–C(*b*3)	117(2)
S(*b*1)–Fe–S(*b*2)	73·5(3)	C(*b*2)–N(*b*1)–C(*b*3)	115(2)
S(*b*1)–Fe–S(*c*1)	88·1(3)	C(*c*1)–N(*c*1)–C(*c*2)	118(2)
S(*b*1)–Fe–S(*c*2)	158·3(3)	C(*c*1)–N(*c*1)–C(*c*3)	122(2)
S(*b*2)–Fe–S(*c*1)	97·8(3)	C(*c*2)–N(*c*1)–C(*c*3)	119(2)
S(*b*2)–Fe–S(*c*2)	94·4(3)	N(*a*1)–C(*a*2)–C(*a*4)	103(2)
S(*c*1)–Fe–S(*c*2)	75·5(3)	C(*a*2)–C(*a*4)–C(*a*5)	112(3)
Fe–S(*a*1)–C(*a*1)	84·4(7)	C(*a*4)–C(*a*5)–C(*a*3)	106(3)
Fe–S(*a*2)–C(*a*1)	84·2(7)	C(*a*5)–C(*a*3)–N(*a*1)	102(2)
Fe–S(*b*1)–C(*b*1)	83·2(8)	N(*b*1)–C(*b*2)–C(*b*4)	100(2)
Fe–S(*b*2)–C(*b*1)	85·4(8)	C(*b*2)–C(*b*4)–C(*b*5)	110(3)
Fe–S(*c*1)–C(*c*1)	83·6(9)	C(*b*4)–C(*b*5)–C(*b*3)	106(3)
Fe–S(*c*2)–C(*c*1)	82·9(9)	C(*b*5)–C(*b*3)–N(*b*1)	101(2)
S(*a*1)–C(*a*1)–S(*a*2)	117(1)	N(*c*1)–C(*c*2)–C(*c*4)	98(2)
S(*a*1)–C(*a*1)–N(*a*1)	120(2)	C(*c*2)–C(*c*4)–C(*c*5)	108(3)
S(*a*2)–C(*a*1)–N(*a*1)	123(2)	C(*c*4)–C(*c*5)–C(*c*3)	108(3)
S(*b*1)–C(*b*1)–S(*b*2)	116(1)	C(*c*5)–C(*c*3)–N(*c*1)	96(2)

(*b*) Compound (II)

(i) Final intramolecular distances (Å)

Fe–S(*a*1)	2·308(9)	N(*b*1)–C(*b*3)	1·37(4)
Fe–S(*a*2)	2·317(9)	C(*b*3)–C(*b*4)	1·43(4)
S(*a*1)–S(*a*2)	2·82(1)	C(*b*4)–C(*b*5)	1·35(5)
S(*a*1)–C(*a*1)	1·66(3)	C(*b*5)–C(*b*6)	1·40(5)
S(*a*2)–C(*a*1)	1·70(3)	C(*b*6)–C(*b*7)	1·30(5)
C(*a*1)–N(*a*1)	1·35(3)	C(*b*7)–C(*b*8)	1·48(5)
N(*a*1)–C(*a*2)	1·53(4)	C(*b*8)–C(*b*3)	1·39(4)
N(*a*1)–C(*a*3)	1·48(4)		
C(*a*3)–C(*a*4)	1·41(4)	Fe–S(*c*1)	2·280(9)
C(*a*4)–C(*a*5)	1·44(5)	Fe–S(*c*2)	2·334(8)
C(*a*5)–C(*a*6)	1·41(5)	S(*c*1)–S(*c*2)	2·82(1)
C(*a*6)–C(*a*7)	1·41(4)	S(*c*1)–C(*c*1)	1·69(3)
C(*a*7)–C(*a*8)	1·35(4)	S(*c*2)–C(*c*1)	1·70(3)
C(*a*8)–C(*a*3)	1·41(4)	C(*c*1)–N(*c*1)	1·40(4)
		N(*c*1)–C(*c*2)	1·47(4)
Fe–S(*b*1)	2·307(8)	N(*c*1)–C(*c*3)	1·43(3)
Fe–S(*b*2)	2·328(9)	C(*c*3)–C(*c*4)	1·41(4)
S(*b*1)–S(*b*2)	2·82(1)	C(*c*4)–C(*c*5)	1·43(4)
S(*b*1)–C(*b*1)	1·67(3)	C(*c*5)–C(*c*6)	1·31(5)
S(*b*2)–C(*b*1)	1·70(3)	C(*c*6)–C(*c*7)	1·37(4)
C(*b*1)–N(*b*1)	1·39(3)	C(*c*7)–C(*c*8)	1·44(4)
N(*b*1)–C(*b*2)	1·55(4)	C(*c*8)–C(*c*3)	1·38(4)

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. supplied as full size copies).

[30] J. A. Ibers, ref. 24, p. 210.

[31] D. H. Templeton, ref. 24, p. 213.

[32] M. E. Pippy and F. R. Ahmed, BONDSCAN program (N.R.C. 12), Div. Pure and Appl. Physics, National Research Council, Ottawa, Canada.

TABLE 2 (*Continued*)

(ii) Final intramolecular angles (°)

S(*a*1)–Fe–S(*a*2)	75·2(3)	C(*a*1)–N(*a*1)–C(*a*2)	120(3)
S(*b*1)–Fe–S(*b*2)	74·9(3)	C(*a*1)–N(*a*1)–C(*a*3)	122(3)
S(*c*1)–Fe–S(*c*2)	75·2(3)	C(*b*1)–N(*b*1)–C(*b*2)	121(2)
S(*a*1)–Fe–S(*b*1)	90·8(3)	C(*b*1)–N(*b*1)–C(*b*3)	121(2)
S(*b*1)–Fe–S(*c*1)	92·3(3)	C(*c*1)–N(*c*1)–C(*c*2)	119(2)
S(*c*1)–Fe–S(*a*1)	95·5(3)	C(*c*1)–N(*c*1)–C(*c*3)	124(2)
S(*a*2)–Fe–S(*b*2)	97·4(3)	C(*a*2)–N(*a*1)–C(*a*3)	117(2)
S(*b*2)–Fe–S(*c*2)	94·6(3)	C(*b*2)–N(*b*1)–C(*b*3)	118(2)
S(*c*2)–Fe–S(*a*2)	94·4(3)	C(*c*2)–N(*c*1)–C(*c*3)	118(2)
S(*b*1)–Fe–S(*c*2)	163·1(3)	C(*a*3)–C(*a*4)–C(*a*5)	114(3)
S(*c*1)–Fe–S(*a*2)	164·7(3)	C(*a*4)–C(*a*5)–C(*a*6)	120(3)
S(*a*1)–Fe–S(*b*2)	162·7(3)	C(*a*5)–C(*a*6)–C(*a*7)	122(3)
S(*a*1)–C(*a*1)–S(*a*2)	114(2)	C(*a*6)–C(*a*7)–C(*a*8)	117(3)
S(*b*1)–C(*b*1)–S(*b*2)	114(1)	C(*a*7)–C(*a*8)–C(*a*3)	112(3)
S(*c*1)–C(*c*1)–S(*c*2)	113(2)	C(*a*8)–C(*a*3)–C(*a*4)	124(3)
Fe–S(*a*1)–C(*a*1)	86(1)	C(*b*3)–C(*b*4)–C(*b*5)	122(3)
Fe–S(*a*2)–C(*a*1)	85(1)	C(*b*4)–C(*b*5)–C(*b*6)	121(3)
Fe–S(*b*1)–C(*b*1)	86(1)	C(*b*5)–C(*b*6)–C(*b*7)	119(3)
Fe–S(*b*2)–C(*b*1)	85(1)	C(*b*6)–C(*b*7)–C(*b*8)	123(3)
Fe–S(*c*1)–C(*c*1)	87(1)	C(*b*7)–C(*b*8)–C(*b*3)	117(3)
Fe–S(*c*2)–C(*c*1)	85(1)	C(*b*8)–C(*b*3)–C(*b*4)	117(3)
N(*a*1)–C(*a*1)–S(*a*1)	124(2)	C(*c*3)–C(*c*4)–C(*c*5)	122(3)
N(*a*1)–C(*a*1)–S(*a*2)	122(2)	C(*c*4)–C(*c*5)–C(*c*6)	117(3)
N(*b*1)–C(*b*1)–S(*b*1)	122(2)	C(*c*5)–C(*c*6)–C(*c*7)	127(3)
N(*b*1)–C(*b*1)–S(*b*2)	124(2)	C(*c*6)–C(*c*7)–C(*c*8)	119(3)
N(*c*1)–C(*c*1)–S(*c*1)	123(2)	C(*c*7)–C(*c*8)–C(*c*3)	116(2)
N(*c*1)–C(*c*1)–S(*c*2)	124(2)	C(*c*8)–C(*c*3)–C(*c*4)	123(3)

TABLE 3

Equations of best least-squares planes in the form $AX + BY + CZ = D$ where X, Y, and Z are orthogonal coordinates in Å related to the crystallographic axes by $X = ax + cz\cos\beta$, $Y = by$, $Z = cz\sin\beta$. Distances (Å) of atoms from the planes are given in square brackets

(*a*) Compound (I)

Ligand (*a*): $0{\cdot}7875X + 0{\cdot}5329Y - 0{\cdot}3096Z = 10{\cdot}67$

[Fe 0·15, *S(a1) −0·02, *S(a2) 0·02, *C(a1) 0·00, *N(a1) −0·01, *C(a2) 0·03, *C(a3) −0·02, C(a4) 0·27, C(a5) 0·06]

σ 0·02 Å.†

Ligand (*b*): $0{\cdot}0813X + 0{\cdot}9075Y + 0{\cdot}4120Z = 8{\cdot}12$

[Fe −0·45, *S(b1) 0·01, *S(b2) −0·01, *C(b1) 0·00, *N(b1) 0·01, *C(b2) −0·01, *C(b2) 0·01, C(b4) −0·01, C(b5) −0·43]

σ 0·00 Å.†

Ligand (*c*): $0{\cdot}7385X - 0{\cdot}2733Y + 0{\cdot}6163Z = 7{\cdot}14$

[Fe 0·04, *S(c1) −0·02, *S(c2) 0·04, *C(c1) −0·02, *N(c1) 0·00, *C(c2) 0·04, *C(c3) −0·03, C(c4) 0·23, C(c5) −0·29]

σ 0·03 Å.†

(*b*) Compound (II)

Ligand (*a*): (i) S_2CNC_2 plane

$0{\cdot}2445X - 0{\cdot}4881Y + 0{\cdot}8378Z = 2{\cdot}25$

[Fe 0·03, *S (a1) 0·06, *S(a2) −0·02, *C(a1) −0·04, *N(a1) −0·04, *C(a2) 0·07, *C(a3) −0·02]

σ 0·04 Å.†

(ii) Phenyl group

$0{\cdot}4230X + 0{\cdot}9043Y - 0{\cdot}0576Z = 12{\cdot}53$

[*C(a3) 0·01, *C(a4) 0·00, *C(a5) −0·02, *C(a6) 0·04, *C(a7) −0·03, *C(a8) 0·01]

σ 0·02 Å.†

Ligand (*b*): (i) S_2CNC_2 plane

$0{\cdot}6438X + 0{\cdot}7633Y - 0{\cdot}0533Z = 22{\cdot}07$

[Fe −0·16, *S(b1) −0·02, *S(b2) −0·02, *C(b1) 0·03, *N(b1) 0·04, *C(b2) −0·02, *C(b3) −0·02]

σ 0·03 Å.†

TABLE 3 (*Continued*)

(ii) Phenyl group

$-0{\cdot}4575X + 0{\cdot}2923Y + 0{\cdot}8398Z = -5{\cdot}52$

[*C(b3) −0·02, *C(b4) 0·03, *C(b5) −0·01, *C(b6) 0·00, *C(b7) 0·01, *C(b8) 0·01]

σ 0·02 Å.†

Ligand (*c*): (i) S_2CNC_2 plane

$-0{\cdot}5254X + 0{\cdot}4532Y + 0{\cdot}7201Z = 10{\cdot}26$

[Fe −0·09, *S(c1) 0·02, *S(c2) 0·00, *C(c1) −0·02, *N(c1) 0·00, *C(c2) −0·01, *C(c3) 0·01]

σ 0·01 Å.†

(ii) Phenyl group

$0{\cdot}2566X + 0{\cdot}8916Y + 0{\cdot}3731Z = 5{\cdot}68$

[*C(c3) 0·00, *C(c4) 0·02, *C(c5) −0·02, *C(c6) −0·01, *C(c7) 0·03, *C(c8) −0·02]

σ 0·02 Å.†

Angles (°) between plane of phenyl group and plane of S_2CNC_2 system for each ligand:

(*a*) 68, (*b*) 83, (*c*) 64.

† σ Is the standard deviation of the distances from the plane of those atoms marked with an asterisk which comprise that plane.

case being the crystallographic asymmetric unit with all atoms occupying general positions. (Both complexes have previously been shown to be monomeric in freezing benzene solution [1]). The unit-cell contents for (I) and (II) are displayed in Figure 3 (a) and (b) and the molecular geometries are in Figure 2 (a) and (b), the symmetry being a good approximation to D_3 in both cases [excluding terminal ligand substituents in (II)]. Since the space-group is centrosymmetric, both of the possible *d* and *l* forms of the molecule exist in equal numbers within the unit cell and the crystals may be regarded as racemates. In (II) all phenyl substituents do not lie on the same side of the $Fe(CN)_3$ plane. There are no contacts of <4·0 Å between metal or sulphur atoms of adjacent molecules in either structure and we do not examine other intermolecular interactions in any great detail because of the poor resolution of the outer atoms.

In both structures, the environment of the iron atom consists of six sulphur atoms, constrained by the four-membered ring systems with the ligand to D_3 symmetry, being intermediate between octahedral and trigonal-prismatic stereochemistries. In (I) the six sulphur atoms are at distances ranging from 2·38(1) to 2·44(1) Å, mean 2·41 Å. Because of the large standard deviations involved, it may well be that this spread is not significant but reflects the poverty of the data. The mean of 2·41 Å agrees well with the value found for the related tris(di-n-butyldithiocarbamato)iron(III), $[\mathrm{Fe(CS_2{\cdot}NBu^n{}_2)_3}]$ [19] in which the mean iron–sulphur distance is 2·42 Å. This is reasonable in view of the fact that the latter complex has a high room-temperature magnetic moment [μ(300 K, solid) 5·3 B.M.[1]] indicative of the presence of a large proportion of the sextet (' high-spin ') component. In (II), the iron–sulphur distances lie between 2·28(1) and 2·33(1) Å, mean 2·31 Å. This value is considerably lower than those found for the other two derivatives we have discussed. In the last-named μ(300 K, solid) is 3·0 B.M.,[1] and it is very likely that the observed contraction in mean iron–sulphur bond length of *ca.* 0·10 Å is a result of the change in the relative ground-state populations from almost pure ' high-spin ' to substantially ' low-spin '. (This value is also of the order of magnitude expected from the studies of the pressure-dependence of the room-temperature magnetic moments of these derivatives in chloroform solution.[2,3]) The inversion of the possible sextet and doublet ground states in these complexes is presumably brought about by subtle modification of the crystal-field parameters of the metal atom by the change of substituent on the conjugated ligand. Complex (II) has an electronic and stereochemical parallel in the complex tris(*O*-ethyldithiocarbonato)-iron(III) which has a room-temperature magnetic moment of *ca.* 2·7 B.M. indicating a dominance of the doublet ground state[3] In this complex Hoskins and Kelly find the mean iron–sulphur distance to be 2·31 Å.[20] Here also, there is a small population of the high-spin component and it might be reasonable to suppose that in a purely ' low-spin ' complex such as tris(*NN*-di-i-propyldithiocarbamato)iron(III) [μ(300 K, solid) *ca.* 2·3 B.M.[1]] that a value of 2·29—2·30 Å might be found for the iron-sulphur distance. The ' low-spin ' value of <2·32 Å for the d^5 metal–sulphur distance found here is similar to that found also in the five-covalent square-pyramidal d^5 complexes, chloro- and iodo-bis-(*NN*-diethyldithiocarbamato)iron(III), $[FeCl(CS_2{\cdot}NEt_2)_2]$ [33] and $[FeI(CS_2{\cdot}NEt_2)_2]$,[34] compounds in which the ground state is typically a quartet [μ(300 K) *ca.* 3·9 B.M., ⟨Fe–S⟩, 2·30, 2·28 Å respectively]. The distance is rather longer than that in the ' low-spin ' d^6 cobalt(III) tris-derivatives of the *O*-ethyldithiocarbonate [35] and *NN*-diethyldithiocarbamate [36,37] ligands (⟨Co–S⟩ *ca.* 2·28, 2·26 Å respectively).

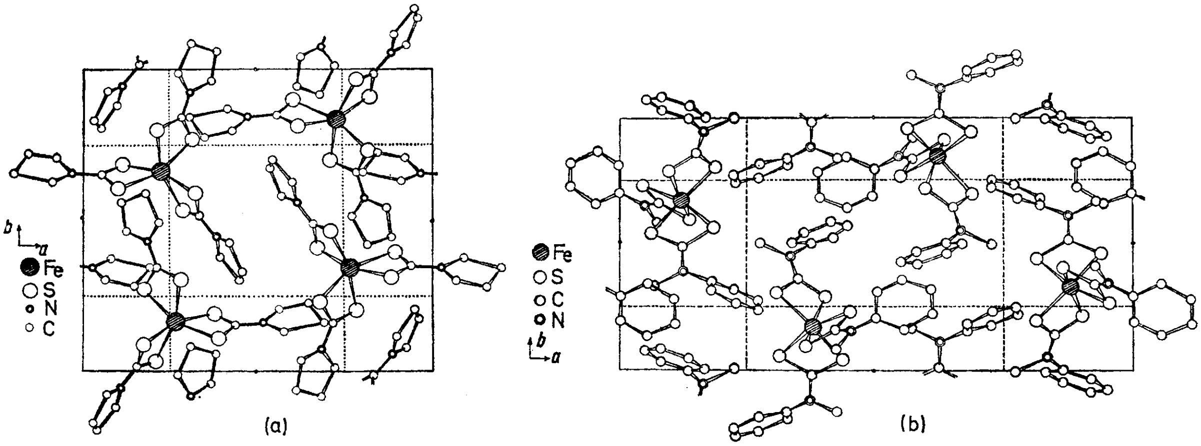
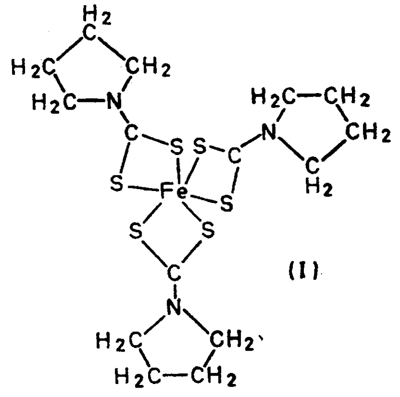
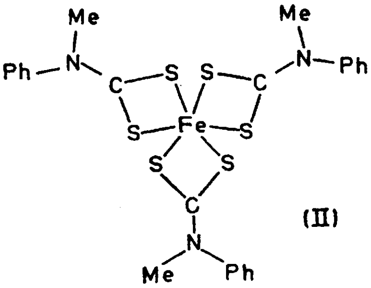


FIGURE 3 View of the unit cell (a) complex (I), and (b) complex (II), both projected on the *ab* plane



(I)



(II)

A warning is in order here. Determination of the cobalt-59 n.m.r. chemical shift in the diamagnetic derivatives of the type $[Co(CS_2{\cdot}NR_2)_3]$ gives σ values {%, all $\pm$0·002, relative to $K_3[Co(CN)_6]$} of $-$0·715 $\pm$ 0·010 for $[Co(CS_2{\cdot}NH_2)_3]$ and $[Co(CS_2{\cdot}N[CH_2]_4)_3]$, 0·668 for $[Co(CS_2{\cdot}NBu^n{}_2)_3]$, 0·658 for $[Co(CS_2{\cdot}NMePh)_3]$, and 0·632 for $[Co\{CS_2{\cdot}N(CHMe_2)_2\}_3]$.[38] A crystal-structure determination on $[Ni(CS_2{\cdot}NH_2)_2]$ [39] yields a mean nickel–sulphur distance of 2·215 $\pm$ 0·01 Å; our recent deter-

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[33] B. F. Hoskins and A. H. White, *J. Chem. Soc.* (*A*), 1970, 1668.

[34] P. C. Healy, B. F. Hoskins, and A. H. White, to be published.

[35] S. Merlino, *Acta Cryst.*, 1968, **B24**, 1441.

[36] S. Merlino, *Acta Cryst.*, 1969, **B25**, 2270.

[37] T. Brennan and I. Bernal, *J. Phys. Chem.*, 1969, **73**, 443.

[38] R. L. Martin and A. H. White, *Nature*, 1969, **223**, 394, and unpublished work.

[39] G. F. Gasparri, M. Nardelli, and A. Villa, *Acta Cryst.*, 1967, **23**, 384.

mination of the structure of $[Ni\{CS_2{\cdot}N(CHMe_2)_2\}_2]$ reveals a nickel–sulphur distance of 2·181 ± 0·003 Å.[40] The implication is that within a series of these complexes of constant ground state, there is a quite substantial difference in metal–sulphur distance between a complex of a ligand of weaker ligand-field strength and one of stronger. Hence in the iron(III) complexes, care should be taken not to attribute the whole of the contraction to the change in spin state; just how much of the 0·10 Å observed is to be attributed to this cause is very debatable: the high-pressure studies will give this result unambiguously but less accurately.

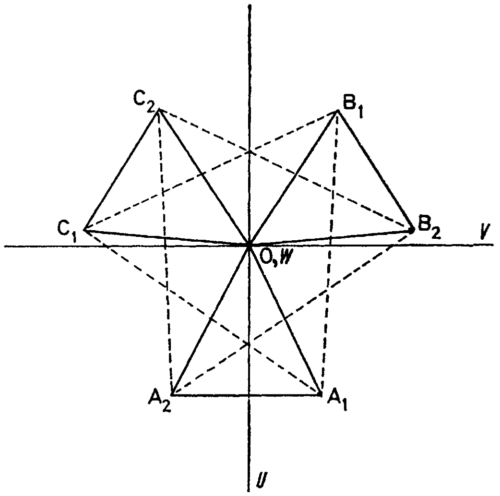

FIGURE 4 Geometric representation of the MS_6 core in a Cartesian frame (*U,V,W*)

To investigate the angular distortion of the MS_6 system in these complexes, we idealize it as the D_3 configuration displayed in Cartesian co-ordinates (*U*, *V*, *W*) in Figure 4, such that *W* is the C_3 symmetry axis and *U* is coincident with a C_2 axis. The FeS_6 core can then be envisaged as two triangles of sulphur atoms A_1, B_1, C_1 and A_2, B_2, C_2 above and below the plane *UV* and parallel to it, with the iron atom at the origin, the two planes being separated by a distance *d*. It is useful to describe this configuration as a three-bladed propeller where δ (the angle A_1–O–A_2) is a measure of the angular width of the blade, *i.e.* the angular-ligand ' bite ' [which might be described in terms of sulphur–sulphur distance *s* (A_1–A_2) or, better, the ratio $b = s/r$] and where ε (the angle between *W* and A_1O projected on the *VW* plane) is a measure of the pitch of the blade. Related to these is θ, the angle between *U* and A_1O projected on plane *UV*; thus 2θ is the projection of the propeller blade on plane *UV*, and the angle between triangles $A_1B_1C_1$ and $A_2B_2C_2$. ϕ Is the azimuthal polar co-ordinate between the *W* axis and the metal–sulphur bond. The most convenient sources of raw data for determining these parameters are the mean iron–sulphur bond lengths (*r*) and the angles δ and ζ (the angle A_1–O–B_1). Using these, *s*, *d*, θ, and ε are easily obtained by the relations: $s = 2r \sin(\delta/2)$, $d = r \cos \varepsilon$, $\cos \theta = \cos(\delta/2) \sin \phi$, and $\cos \varepsilon = \cos \phi / \sin(\delta/2)$ where $\cos \phi = [(1 + 2 \cos \zeta)/3]^{\frac{1}{2}}$. The manner in which these parameters vary among this and the other complexes is given in Table 4 together with those of the limiting cases of the octahedron and trigonal prism.

TABLE 4

Distortion parameters of MS_6 systems in D_3 symmetry

Compound	$\langle r \rangle$/Å	$\langle s \rangle$/Å	*d*/Å	*b*	$\langle \delta \rangle$	$\langle \zeta \rangle$	2θ	ε	ϕ
$[Fe(CS_2{\cdot}NBu^n_2)_3]$ [a]	2·42	2·86	2·56	1·18	72·8°	93·5°	33·2°	26·5°	57·9°
(I) [b]	2·41	2·91	2·57	1·21	74·5	93·5	38·6	27·8	57·9
(II) [b]	2·32	2·82	2·47	1·22	75·1	94·1	40·4	28·8	57·7
$[Fe(CS_2{\cdot}OEt)_3]$ [c]	2·32	2·85	2·48	1·23	75·5	94·1	41·2	29·4	57·7
$[Co(CS_2{\cdot}OEt)_3]$ [d]	2·28	2·80	2·43	1·24	76·2	94·3	42·4	30·1	57·9
$[Co(CS_2{\cdot}NEt_2)_3]$ [e]	2·26	2·81	2·46	1·23	76·1	94·2	43·0	29·8	57·8
Octahedron	1	$\sqrt{2}$	$\sqrt{2/3}$	$\sqrt{2}$	90	90	60	35·3	55·3
Trigonal prism						<120	0	0	

[a] The data given here differ from that given in ref. 19 (B. F. Hoskins, personal communication). [b] This work. [c] Ref. 20. [d] Ref. 35. [e] Refs. 36 and 37.

Although differences between the entries in this Table are not at a high level of significance, we find that a number of interesting general broad trends emerge between entries (1) and (6). There is a contraction in ***r***, which is paralleled by changes in δ, ζ, 2θ, and ε: all increase down the series, while *d* and *s* decrease, *i.e.* as the metal–sulphur distance decreases, the propeller becomes flatter, and although the distance *s* also decreases slightly, the effect of this is more than offset by the decrease in *r* so that the ligand ' bite ', *b*, increases. Kepert, in a recent paper has suggested a simple electrostatic theoretical model which reproduces the ' bite ' *vs.* distortion behaviour observed here.[41] Although inclusion of (1) probably helps our case we are suspicious of the great deviation it exhibits in 2θ, and would prefer not to include it. The magnetic moment *vs.* temperature curve of the di-n-butyl derivative exhibits a large, sharp, and reversible discontinuity at 150 K, indicative of a phase change. The solid-state magnetic moment of 5·33 B.M. at 300 K is atypically high for a complex $[Fe(CS_2{\cdot}NR_2)_3]$ in which R is an n-alkyl substituent; at 300 K, the magnetic moments in the solid state of the *NN*-dimethyl, -diethyl, and -di-n-propyl, derivatives are 4·17, 4·24, and 4·48 B.M. In chloroform solution, μ(300 K) for all these di-n-alkyl derivatives is 4·3 ± 0·2 B.M.[1,3]

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[40] P. W. G. Newman and A. H. White, to be published.

[41] D. L. Kepert, *Inorg. Chem.*, in the press.

The deviation is thus large and suggests the presence of strongly perturbing lattice forces resulting in abnormal magnetic behaviour which is presumably the result of an abnormality in the geometry of the complex. The entries for δ, ε, and 2θ (especially the latter) are at variance with those in the remainder of the Table and it is not unlikely that they may be the result of such lattice forces. A full report of this structure is not yet available to enable examination of this point.

In the low-spin d^5 and d^6 complexes tris(*O*-ethyldithiocarbonato)-iron(III) [20] and -cobalt(III),[35] $[M(CS_2{\cdot}OEt)_3]$, which are isomorphous and isostructural in space-group $R\bar{3}$ with the molecular and crystallographic three-fold axes in coincidence, only two independent metal–sulphur distances are necessary to describe the MS_6 core. In the cobalt derivative these are almost equal (2·276, 2·277, σ 0·004 Å), but not in the iron complex (2·308, 2·326, σ 0·003 Å). In view of the use of full-matrix refinement methods in both cases, it is likely that these may represent significantly different stereochemistries, the MS_6 point-symmetry being D_3 in the cobalt case and C_3 in the iron case. Although our data is not of the quality of Hoskins' diffractometer data, examination of the two triangular sets of sulphur atoms in our compound (II) suggests the possible existence of a parallel discrepancy in spite of our less co-operative space-group which does not exact the necessity of three-fold symmetry [set (1): Fe–S(*a*1) 2·31, Fe–S(*b*1) 2·31, Fe–S(*c*1) 2·28, $\langle$Fe–S(*i*1)$\rangle$ *ca.* 2·30 Å; set (2): Fe–S(*a*2) 2·32, Fe–S(*b*2) 2·33, Fe–S(*c*2) 2·33, $\langle$Fe–S(*i*2)$\rangle$ *ca.* 2·33 Å]. In all three ligands, the iron–sulphur bond in set (1) is shorter than that in set (2). This difference is not found systematically in the ' high-spin ' iron(III) derivatives; in the di-n-butyl derivative it is specifically forbidden by the crystallographic requirement that one of the ligands must contain a two-fold axis.

TABLE 5

Intraligand dimensions in the complexes referred to in the text

Compound	$\langle S_i–C_1\rangle$/Å	$\langle C_1{=}N\rangle$/Å	$\langle N–C_{2,3}\rangle$/Å	$\langle$S–C–S$\rangle$	$\langle$M–S$\rangle$/Å
$[Fe(CS_2{\cdot}NBu^n{}_2)_3]$ [a]	1·70	1·41		115°	2·42
(I) [b]	1·70	1·31	1·50	117	2·41
(II) [b]	1·68	1·37	1·50	113	2·32
$[Co(CS_2{\cdot}NEt_2)_3]$ [c]	1·71	1·31	1·50	110	2·26
$[Fe(CS_2{\cdot}OEt)_3]$ [d]	1·68			115	2·32
$[Co(CS_2{\cdot}OEt)_3]$ [e]	1·67			114	2·28

[a] Ref. 19. [b] This work. [c] Refs. 36 and 37. [d] Ref. 20. [e] Ref. 35.

If, as seems possible on the basis of the available evidence, this distortion in the ' low-spin ' complexes is real and not random, then an explanation must be sought as to why the molecular symmetry is lowered from D_3 to C_3. It is possible that crystal packing forces could superimpose their effect on the metal to such an extent that a distortion of the magnitude produced could be observed (as may well be the case with the di-n-butyl derivative). However, it would seem coincidental that they should cause a dichotomy of the type found between ' high-spin ' and ' low-spin ' iron(III) complexes; if it were coincidence, it is strange that, in the isomorphous iron(III) and cobalt(III) dithiocarbonates which have similar mean metal–sulphur distances, the iron complex is distorted and the cobalt not.

This leaves electronic effects as a possible cause. In the O_h approximation, the $^2T_{2g}$ ground state of the ' low-spin ' complexes differs in behaviour from the $^6A_{1g}$ and $^1A_{1g}$ ground states of the other complexes discussed in this paper, in that it is susceptible to spin–orbit mixing and also to a loss of orbit degeneracy by a tetragonal Jahn–Teller distortion. The latter possibility is not immediately helpful: all the complexes discussed really are D_3 in symmetry at best, the $^2T_{2g}$ octahedral ground state becoming $^2A_1$ and ^2E, neither of which are susceptible of a further loss of degeneracy by a lowering of symmetry to C_3. However, if we include spin–orbit interaction we find that the degeneracy of a ^2E ground state is redefined to give two doublets in double group D_3', the degeneracy of which is lowered on passing to C_3', suggesting that spin–orbit interaction within the doublet ground state could provide a mechanism for distortion of the type observed. If so, it is surprising that the effect is large enough to be observable in this manner; it is also surprising that the communication on the structure of the complex tris-(*NN*-diethyldithiocarbamato)ruthenium(III), $[Ru(CS_2{\cdot}NEt_2)_3]$,[42] (which would be expected to show an enhanced effect of this type by virtue of greater spin–orbit interaction within its doublet ground state) reports no such distortion. The test of this hypothesis must await further data of a better quality than that available here.

The Ligand.—The S_2CN system of the ligand in dialkyldithiocarbamate complexes is generally conjugated. This is reflected in the generally good planarities of the S_2CNC_2 ligand fragments (Table 3). The iron atom is also reasonably coplanar with the ligand although it appears to be less well constrained than the other atoms of the plane, one of the deviations from the plane [complex (I) ligand (*b*)] being as high as 0·45 Å. The phenyl rings in complex (II) are twisted out of the planes of the ligands by at least 65°, and this is probably due to steric interaction with the adjacent methyl group. [This is also the case in *N*-methylacetanilide,[43]

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[42] A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Comm.*, 1966, 476.

[43] B. F. Pedersen, *Acta Chem. Scand.*, 1967, **21**, 1415.

and in a recent determination of bis(*N*-methyl-*N*-phenyldithiocarbamato)-nickel(II) and -copper(II),[40] the phenyl ring in these compounds lying at 80—90° to the remainder of the molecule.] On the whole, intra-ligand dimensions (Table 5) are normal and compare favourably with those found in related structures. In the conjugated system, accuracy is not high enough to permit any firm conclusions to be drawn concerning the C–N or C–S bonds or associated angles, which would be of interest, as it is clearly desirable to know in some detail the way in which substituent changes on the one hand and spin-state changes on the other interact throughout the system.

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