Crystal Structure of Iodobis-(*NN*-diethyldithiocarbamato)iron(III)

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The crystal and molecular structure of the title compound has been determined by single-crystal *X*-ray diffraction methods. Solution of the structure by conventional heavy-atom Patterson and Fourier methods followed by block-diagonal least-squares refinement has resulted in a final conventional R value of 0·11 for 567 visually estimated independent observed reflections. The compound crystallizes in the monoclinic system, space group $P2_1/n$ with $Z = 4$, $a = 11{\cdot}65 \pm 0{\cdot}02$, $b = 17{\cdot}38 \pm 0{\cdot}03$, $c = 9{\cdot}34 \pm 0{\cdot}02$ Å, and $\beta = 104{\cdot}2 \pm 0{\cdot}2°$. The structure is similar to that of the chloro-analogue, [FeCl(CS$_2$·NEt$_2$)$_2$], the co-ordination about the iron atom being an approximate square pyramid consistent with the observed spin state of S $\frac{3}{2}$. The iodine atom is at the apex of the pyramid, and the iron atom at its centre lies 0·6 Å above the basal plane of the four S atoms of the dithiocarbamate ligands, the iron atom being substantially coplanar with each of these. The four Fe–S distances [2·28(2) Å] are comparable with those of the chloro-analogue [2·30(1) Å] and the intraligand dimensions are normal for a bidentate dithiocarbamate [S–Fe–S 76(1), S–C–S 108(2)°; C–S 1·73(4), and C–N 1·37(8) Å]. The Fe–I bond [2·59(1) Å] is an unusual example of an iron(III)–iodine(–I) linkage.

THE halogenobis-(*NN*-dialkyldithiocarbamato)iron(III) complexes, [FeX(CS$_2$·NR$_2$)$_2$], have been shown[1] to exemplify iron(III) in the unusual ground-state of intermediate spin, $S = \frac{3}{2}$. This has provoked a number of recent studies on the structure and bonding in these complexes, both in the solid state and solution.[2-9] An *X*-ray crystal structure determination on the derivative [FeCl(CS$_2$·NEt)$_2$], has established the molecular configuration as being that of an approximately square (rectangular) pyramidal co-ordination about the central iron atom,[10,11] the halogen atom being at the apex of the pyramid and the iron atom at the centre, some 0·62 Å above the basal plane of the four sulphur atoms from the dithiocarbamate ligands. The iron atom is, however, coplanar with each ligand, with the exception of the terminal carbon atoms. It is likely that the iodine analogue of this complex, which has been shown to possess the same quartet ground-state may also display this configuration; if so, it provides an unusual example of an iodine atom bonded to iron(III). We have undertaken a crystal structure determination to confirm this possibility and determine the Fe–I bond length.

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EXPERIMENTAL

The complex was prepared as described in ref. 1 as black crystals and recrystallized from chloroform which had been carefully purified from all traces of phosgene, hydrogen chloride, *etc.*, to avoid formation of the chloro-analogue. A few crystals were obtained as small black plates up to 0·2 mm in length (along *c*) and 0·03 mm in thickness (along *a*).

X-Ray Data.—These were obtained by use of a non-integrating Nonius Weissenberg camera at room temperature on a section of a single crystal 0·03 × 0·08 × 0·10 mm, the axes coinciding with the crystal edges. All data were obtained as rapidly as possible as previous work with the complex suggested that it deteriorated in the atmosphere more rapidly than the chloro- or bromo-derivatives, possibly owing to an iron(III)–iodine(−I) oxidation–reduction process by atmospheric moisture. However, although the accuracy of the structure was affected to a serious extent by the limited data accessible [$\sin^2\theta/\lambda^2$(max.) = 0·206], there was no evidence from deterioration in reflection quality or later agreement analyses to suggest that decomposition was appreciable during the data collection. Nickel-filtered copper radiation was used throughout. Data were obtained with the one single-crystal section respectively mounted with the spindle axes parallel to *b* and *c*.

Unit-cell dimensions were obtained from zero-layer Weissenberg photographs about *b* and *c*, calibrated with aluminium powder [*a* (25 °C) = 4·0494 Å].[12] The accuracy of the unit-cell calibrations is not high because of the unavailability of high-angle reflections.

Crystal Data.—$C_{10}H_{20}FeIN_4S_4$, $M = 479$, Monoclinic, $a = 11{\cdot}65 \pm 0{\cdot}02$, $b = 17{\cdot}38 \pm 0{\cdot}03$, $c = 9{\cdot}34 \pm 0{\cdot}02$ Å, $\beta = 104{\cdot}2 \pm 0{\cdot}2°$, $U = 1833$ Å^3, D_m, 1·70(5) (by flotation), $Z = 4$, $D_c = 1{\cdot}75$, $F(000) = 1004$. Space group $P2_1/n$ (C_{2h}^5, No. 14) from systematic absences: $0k0$ $k = 2n + 1$, $h0l$ $h + l = 2n + 1$.[13] Cu-K_α radiation, $\lambda(\text{Cu-}K_{\alpha1}) = 1{\cdot}5444$, $\lambda(\text{Cu-}K_{\alpha2}) = 1{\cdot}5406$, $\lambda(\text{Cu-}K_\beta) = 1{\cdot}3922$; $\mu(\text{Cu-}K_\alpha) = 244$ cm^{-1}.[14]

Intensity data were collected by use of the multiple-film equi-inclination Weissenberg technique for the layers *h*0—5*l* and *hk*0—4. The intensities of 567 independent observed reflections were obtained by visual estimation using an intensity strip calibrated with a Joyce–Loebl microdensitometer, Mark IIIB. Only these non-zero reflections were used in the subsequent structure determination. The data were corrected for absorption by use of a local program based on the algorithm of ABSCOR, the range of transmission coefficients being 0·128—0·501. After correction for Lorentz and polarization factors using a local program (SCALI) the data were internally correlated and scaled by means of a local modification of the Hamilton, Rollett, and Sparks algorithm,[15] giving an arbitrarily scaled set of $|F_o|$, all reflections being assigned unit weights. No corrections were applied for extinction.

Structure Determination.—An unmodified three-dimensional Patterson synthesis computed on all data gave the positions of the iodine and iron atoms. The sulphur and lighter atoms were located in subsequent three-dimensional electron-density distributions. All atoms are located on general positions (x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$) in the unit cell. All atoms were allocated isotropic thermal parameters and all thermal and positional parameters refined to a conventional R of 0·15 using block-diagonal (3 × 3, 6 × 6) least-squares techniques. A weighting scheme[16] of the form $w = (a + |F_o| + b|F_o|^2)^{-1}$ was applied in the latter stages, the function $\Sigma w(|F_o| - |F_c|)^2$ being minimized. Further refinement with the iodine atom permitted to vibrate anisotropically was continued, using thermal parameters of the form $\exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{23}kl + \beta_{13}hl)$, resulting in convergence to a final R of 0·118, the R' being 0·147 {$R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$}. Final weighting scheme constants were $a = 57{\cdot}0$, $b = 0{\cdot}0045$. Parameter shifts for the light atoms at the cessation of refinement were generally $<0{\cdot}1\sigma$ for positional parameters and $<0{\cdot}25\sigma$ for thermal parameters. Introduction of anisotropic thermal parameters for the iodine atom was considered significant.[17] Scattering factors employed were from ref. 18 for neutral iodine, iron, sulphur, carbon, and nitrogen. It was not considered that the overall accuracy of the structure justified an anomalous dispersion correction. There was no evidence for disorder in the structure. A difference map computed at the end of refinement revealed rather heavy ripples in the neighbourhood of the iron–iodine axis, of the order of a carbon atom in peak height. This may be the result of a number of factors, the most likely being series termination effects due to the inaccessibility of high-angle data. Refinement programs were the local 'SFLS1,2'

TABLE 1

(*a*) Atomic positional and isotropic thermal parameters

Atom	*x*	*y*	*z*	B/Å^2
I	0·0949(5)	0·1221(3)	0·2122(7)	
Fe	0·3012(7)	0·1241(6)	0·1542(9)	3·9(2)
S(*a*1)	0·402(2)	0·034(1)	0·308(2)	4·2(4)
S(*a*2)	0·317(1)	0·024(1)	0·002(2)	3·9(4)
S(*b*1)	0·402(2)	0·228(1)	0·271(2)	3·3(4)
S(*b*2)	0·269(1)	0·219(1)	0·978(2)	3·5(4)
N(*a*1)	0·415(4)	0·897(3)	0·159(5)	4·0(1·2)
C(*a*1)	0·384(5)	0·974(4)	0·160(6)	4·8(1·6)
C(*a*2)	0·470(5)	0·860(3)	0·314(6)	4·0(1·5)
C(*a*3)	0·395(7)	0·845(5)	0·009(9)	9·5(2·5)
C(*a*4)	0·596(6)	0·862(4)	0·349(7)	6·1(1·8)
C(*a*5)	0·282(7)	0·806(5)	0·982(8)	8·7(2·3)
N(*b*1)	0·372(5)	0·354(3)	0·082(5)	7·0(1·6)
C(*b*1)	0·358(4)	0·280(2)	0·111(5)	1·1(1·0)
C(*b*2)	0·442(6)	0·400(4)	0·221(7)	5·3(1·7)
C(*b*3)	0·343(6)	0·386(4)	0·917(7)	7·1(1·8)
C(*b*4)	0·573(7)	0·399(4)	0·209(8)	8·6(2·3)
C(*b*5)	0·234(8)	0·421(5)	0·932(9)	10·1(2·4)

(*b*) Anisotropic thermal parameters for iodine

β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
0·0126(6)	0·0036(2)	0·0485(14)	0·0004(8)	0·0256(15)	0·0038(11)

(*c*) Thermal ellipsoid of iodine (Å) and direction cosines of axes *

		l	*m*	*n*
U_{11}	0·254	0·948	−0·306	−0·086
U_{22}	0·228	0·294	0·947	−0·131
U_{33}	0·453	0·121	0·099	0·988

* Relative to orthogonal axes X, Y, Z where $X = ax + cz \operatorname{Cos} \beta$, $Y = by$, and $Z = cz \operatorname{Sin} \beta$.

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Table 2

(*a*) Intramolecular bond lengths (Å)

I–Fe	2·59(1)	N(*a*1)–C(*a*3)	1·63(9)
Fe–S(*a*1)	2·26(2)	C(*a*2)–C(*a*4)	1·43(9)
Fe–S(*a*2)	2·28(2)	C(*a*3)–C(*a*5)	1·45(12)
Fe–S(*b*1)	2·27(2)	S(*b*1)–C(*b*1)	1·71(4)
Fe–S(*b*2)	2·29(2)	S(*b*2)–C(*b*1)	1·76(4)
S(*a*1)–S(*a*2)	2·79(3)	C(*b*1)–N(*b*1)	1·35(7)
S(*b*1)–S(*b*2)	2·79(2)	N(*b*1)–C(*b*2)	1·56(8)
S(*a*1)–C(*a*1)	1·70(6)	N(*b*1)–C(*b*3)	1·59(9)
S(*a*2)–C(*a*1)	1·73(6)	C(*b*2)–C(*b*4)	1·56(11)
C(*a*1)–N(*a*1)	1·39(8)	C(*b*3)–C(*b*5)	1·44(12)
N(*a*1)–C(*a*2)	1·57(7)		

(*b*) Angles (°)

I–Fe–S(*a*1)	103·1(6)	S(*a*1)–C(*a*1)–S(*a*2)	109(3)
I–Fe–S(*a*2)	109·9(6)	S(*a*1)–C(*a*1)–N(*a*1)	129(4)
I–Fe–S(*b*1)	107·8(6)	S(*a*2)–C(*a*1)–N(*a*1)	122(4)
I–Fe–S(*b*2)	99·4(5)	C(*a*1)–N(*a*1)–C(*a*2)	115(4)
S(*a*1)–Fe–S(*a*2)	75·8(7)	C(*a*1)–N(*a*1)–C(*a*3)	124(5)
S(*a*1)–Fe–S(*b*1)	96·8(7)	C(*a*2)–N(*a*1)–C(*a*3)	121(5)
S(*a*1)–Fe–S(*b*2)	157·6(7)	N(*a*1)–C(*a*2)–C(*a*4)	111(5)
S(*a*2)–Fe–S(*b*1)	142·3(7)	N(*a*1)–C(*a*3)–C(*a*5)	110(6)
S(*a*2)–Fe–S(*b*2)	97·3(7)	S(*b*1)–C(*b*1)–S(*b*2)	107(2)
S(*b*1)–Fe–S(*b*2)	75·4(6)	S(*b*1)–C(*b*1)–N(*b*1)	131(4)
Fe–S(*a*1)–C(*a*1)	88(2)	S(*b*1)–C(*b*2)–N(*b*1)	121(4)
Fe–S(*a*2)–C(*a*1)	87(2)	C(*b*1)–N(*b*1)–C(*b*2)	113(5)
Fe–S(*b*1)–C(*b*1)	90(2)	C(*b*1)–N(*b*1)–C(*b*3)	121(5)
Fe–S(*b*2)–C(*b*1)	88(2)	C(*b*2)–N(*b*1)–C(*b*3)	125(5)
		N(*b*1)–C(*b*2)–C(*b*4)	105(5)
		N(*b*1)–C(*b*3)–C(*b*5)	92(6)

(*c*) Intermolecular contacts <4·0 Å

C(*a*4) ··· S(*a*1$^{\mathrm{III}}$)	3·68(7)	C(*b*3) ··· S(*b*1$^{\mathrm{III}}$)	3·87(6)
S(*a*1) ··· S(*a*1$^{\mathrm{IV}}$)	3·92(2)	C(*a*5) ··· S(*b*1$^{\mathrm{VI}}$)	3·77(8)
C(*b*5) ··· S(*a*1$^{\mathrm{V}}$)	3·82(9)	C(*b*4) ··· S(*b*2$^{\mathrm{VIII}}$)	3·60(7)
C(*b*4) ··· S(*a*2$^{\mathrm{VI}}$)	3·68(8)	C(*a*5) ··· C(*a*4$^{\mathrm{IX}}$)	3·65(10)

Roman numerals as superscripts refer to atoms in the following equivalent positions relative to the reference molecule at x, y, z:

III $1 - x, 1 - y, 1 - z$
IV $1 - x, \bar{y}, 1 - z$
V $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$
VI $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
VII $\frac{1}{2} - x, \frac{1}{2} + y, 1\frac{1}{2} - z$
VIII $\frac{1}{2} + x, \frac{1}{2} - y, z - \frac{1}{2}$
IX $x - \frac{1}{2}, 1\frac{1}{2} - y, \frac{1}{2} + z$

(A. I. M. Rae) and 'FCURV' (B. J. Ong). The final set of observed and calculated structure-factors is given in Supplementary Publication No. SUP 20371 (3 pp., 1 microfiche).*

Final atomic positional and thermal parameters of the atoms are given in Table 1. For the iodine atom, root-mean-square vibrational amplitudes are given along the three principal axes of the thermal ellipsoid, together with the orientations of the latter relative to orthogonal axes. Estimated standard deviations, given in parentheses, are derived by a block-diagonal least-squares procedure and are therefore likely to be underestimates.

Table 3

Equations of best least-squares planes in the form $lX + mY + nZ = p$ (where X, Y, and Z are defined in Table 1). Deviations (Å) of atoms from the planes are given in square brackets

	l	m	n	p
Plane (1): Ligand (*a*)	0·960	0·260	−0·102	5·060
[Fe$^{\mathrm{I}}$ − 0·23, *S(a1$^{\mathrm{I}}$) 0·02, S(a2$^{\mathrm{I}}$) − 0·03, N(a1$^{\mathrm{II}}$) 0·01, C(a1$^{\mathrm{II}}$) 0·00, C(a2$^{\mathrm{II}}$) − 0·02, C(a3$^{\mathrm{II}}$) 0·02,* C(*a*4$^{\mathrm{II}}$) 1·28, C(*a*5) − 1·34]				
Plane (2): Ligand (*b*)	0·936	−0·282	−0·210	−1·984
[Fe$^{\mathrm{II}}$ 0·00, *S(b1$^{\mathrm{II}}$) 0·11, S(b2) − 0·11, N(b1$^{\mathrm{II}}$) − 0·06, C(b1$^{\mathrm{II}}$) 0·02, C(b2$^{\mathrm{II}}$) − 0·09, C(b3) 0·13,* C(*b*4$^{\mathrm{II}}$) 1·39, C(*b*5) − 1·29]				
Plane (3): Four sulphur atoms	0·9758	0·0452	−0·2138	−0·704
[Fe$^{\mathrm{II}}$ − 0·59, *S(a1$^{\mathrm{II}}$) − 0·15, S(a2$^{\mathrm{II}}$) 0·15, S(b1$^{\mathrm{II}}$) 0·15, S(b2) − 0·15*]				

Atoms forming the plane are italicized. The mean σ values of these atoms from their planes are: (1) 0·02, (2) 0·10, and (3) 0·15 Å.

Roman numerals as superscripts refer to the equivalent positions:
I $x, 1 + y, z$ II $x, y, 1 + z$

Table 2 lists interatomic distances and angles, computed by the BONDSCAN program.[19] Planes of best fit, together, with atomic deviations (in Å) determined for the two dithiocarbamate ligands and for the four sulphur atoms, are tabulated in Table 3.

Computation was carried out on the DEC PDP 10 computer at the University of Western Australia.

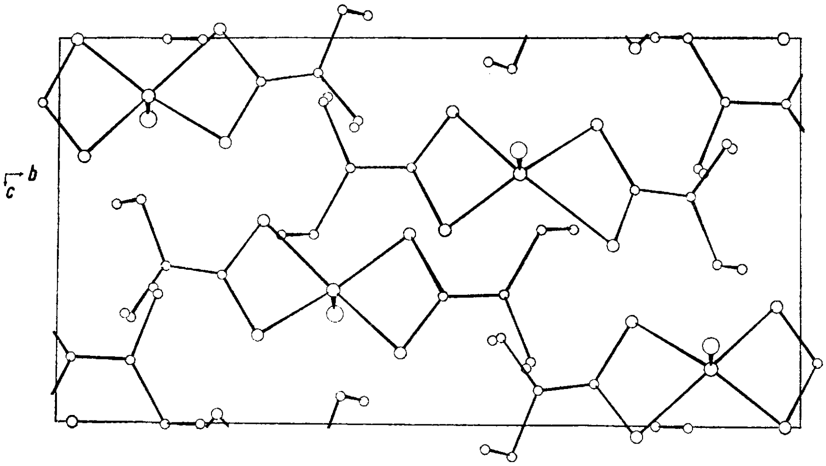

Figure 1 Unit-cell contents viewed normal to the *bc* cell face

DISCUSSION

The crystals are composed of discrete five-covalent square pyramidal molecules, as expected. The unit cell

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

[19] Program NRC-12, M. E. Pippy and F. R. Ahmed, Div. Pure and Applied Physics, NRC, Ottawa, Canada.

contents are shown in Figure 1. The molecular geometry is shown in Figure 2 which also gives the atomic numbering system used. The molecules are separated from each other at distances of the order expected for van der Waals contacts [Table 2(*c*)], the closest observed distances (*ca.* 3·60 Å) being carbon–sulphur contacts whose origin is clearly seen in Figure 1.

The iron atom is covalently bonded to four sulphur atoms and an iodine atom to give a distorted square pyramid, similar to that already found for the chloro-derivative.[11] The four sulphur atoms are not as rigorously coplanar in the iodo-compound as is the case in the chloro-derivative (Table 3); nevertheless, the deviation of the iron atom of 0·59 Å above the mean plane is comparable with the value of 0·62 Å found for the chloro-derivative. The mean iron–sulphur bond length [2·28(2) Å] is comparable with that found for the chloro-derivative [2·30(1) Å]; here again in the iodo-complex there is a greater spread of values which probably reflects the lower accuracy of this structure determination.

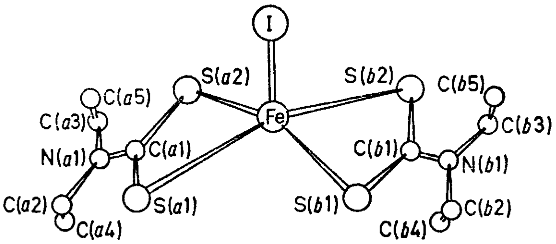

FIGURE 2 Molecular geometry and atom numbering system

However, in both of these five-covalent square pyramidal complexes, and also in the complex bis-(*NN*-dimethyldithiocarbamato)(nitrosyl)iron(III),[20–22] the iron–sulphur bond lengths reported as 2·28—2·30 Å are all less than the values of 2·30—2·33 Å found in the 'low-spin' trigonal six-co-ordinate tris-(*N*-methyl-*N*-phenyldithiocarbamato)iron(III)[23] and tris-(*O*-ethyl dithiocarbonato)iron(III),[24] and also less than the value of 2·41—2·42 Å found in the 'high-spin' tris-(*N*-tetramethylenedithiocarbamato)iron(III), $[Fe\{CS_2 \cdot N(CH_2)_4\}_3]$,[23] and tris-(*NN*-di-n-butyldithiocarbamato)-iron(III).[25] The iodine–iron distance is 2·59 Å and is of the order expected for a covalent iron(III)–iodine(—I) bond;[26] although no other such system appears to have been reported for the solid state,[27] the increase found here in the iron–halogen distance by comparison with that found in $[FeCl(CS_2 \cdot NEt_2)_2]$ of 2·26 Å is in good agreement with the expected increase in the covalent radius of the halogen (Cl 0·99, I 1·33 Å).[28] This structure determination represents the first measurement of the iron(III)–iodide covalent distance.

As with the derivative $[FeCl(CS_2 \cdot NEt_2)_2]$, the overall geometry of the metal atom is consistent with the observed magnetic moment of 3·9 μ_B.[1]

There are no significant differences between the dimensions of the two ligand entities, these being approximately planar apart from the terminal methyl groups (Table 3). The iron atom is almost coplanar with each of the ligands. The terminal methyl groups are not equivalent, those on each ligand being directed out of the ligand plane but on opposite sides, the two ligands being approximately related by a mirror plane through the Fe–I axis and bisecting the angle S(*b*1)–Fe–S(*a*1).

The mean carbon–nitrogen distance C(*i*1)–N(*i*1) is 1·37(7) Å, considerably shorter than the single-bond distance of 1·472 Å;[26] it is in good agreement with values reported for other transition-metal dithiocarbamates (*e.g.* ref. 11 and refs. therein).

The mean bond length for the bonds N(*i*1)–C(*i*2,3) is 1·5 Å; the estimated standard deviations are high but are in substantial agreement with the single carbon–nitrogen bond value already quoted.

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