Crystal Structure of Tris(*NN*-diethyldithiocarbamato)iron(IV) Pentaiodide

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The crystal structure of the title compound, $[Fe(S_2CNEt_2)_3][I_5]$, has been determined by *X*-ray diffraction at 295(1) K, being refined to a residual of 0.049 for 3 328 ' observed ' reflections. Crystals are triclinic, space group $P\bar{1}$, a = 17.41(1), b = 10.197(9), c = 10.184(8) Å, α = 74.71(6), β = 73.29(6), γ = 89.19(7)°, and Z = 2. The structure comprises $[Fe(S_2CNEt_2)_3]^+$ cations and I_5^- anions. Within the cation the symmetry is approximately D_3 with the six Fe–S distances ranging between 2.292(4) and 2.314(4) Å.

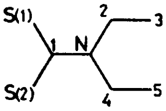
REACTION of complexes of the type $[Fe(S_2CNR_2)_3]$ with iodine in benzene solution has been shown to yield products of the type $Fe(S_2CNR_2)_3I_3$.[1] We have found that reaction of $[Fe(S_2CNEt_2)_3]$ with a further excess of iodine in benzene leads to another iodine-rich product $[Fe(S_2CNEt_2)_3][I_5]$. Mössbauer measurements between 4.2 and 300 K provide evidence that the latter contains tetravalent iron, the isomer shift relative to iron at 300 K being 0.16 mm s^{-1}.[2] Further values of the quadrupole splitting, 2.26 mm s^{-1} (300 K), 2.50 mm s^{-1} (77 K), and 2.55 mm s^{-1} (4.2 K), are very similar to those reported previously for the iron(IV) compound $[Fe(S_2CNEt_2)_3][BF_4]$.[2] *X*-Ray structure determination has confirmed the formulation as $[Fe(S_2CNEt_2)_3][I_5]$ and is reported in this paper.

EXPERIMENTAL

The compound $[Fe(S_2CNEt_2)_3][I_5]$ was prepared by treating $[Fe(S_2CNEt_2)_3]$ (0.5 g, 1 mmol) in CH_2Cl_2 (50 cm^3) with iodine (0.64 g, 2.52 mmol) in C_6H_6 (100 cm^3). Slow evaporation of the resulting solution at room temperature gave large shining black crystals which were collected, washed with n-hexane, and dried at 50 °C for 2 h (Found: C, 15.8; H, 2.7; N, 3.7; S, 16.9. $C_{15}H_{30}FeI_5N_3S_6$ requires C, 15.9; H, 2.7; N, 3.7; S, 16.9%).

Crystal Data.—$C_{15}H_{30}FeI_5N_3S_6$, M = 1 135, Triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 17.41(1), b = 10.197(9), c = 10.184(8), α = 74.71(6), β = 73.29(6), γ = 89.19(7)°, U = 1 667(2) Å^3, D_m = 2.27(1), Z = 2, D_c = 2.26 g cm^{-3}, $F(000)$ = 1 056, specimen size 0.16 × 0.18 × 0.30 mm, monochromatic Mo-K_α radiation, λ = 0.710 6$_9$ Å, μ = 51.5 cm^{-1}, T = 295(1) K.

Structure Determination.—A unique data set to $2\theta_{max.}$ = 50°, measured on a Syntex $P\bar{1}$ four-circle diffractometer, yielded 5 775 independent reflections, 3 328 of which were considered ' observed ' and used in the refinement after absorption correction and solution of the structure by direct methods. Refinement was basically by 9 × 9 block-diagonal least squares but with the parameters of the FeS_6 and I_5 groups refined jointly as single blocks. Hydrogen-atom parameters were included as invariant estimates, U_H (isotropic) being set at 1.25 U_{ii} < (parent C) > (CH_2), 1.5 U_{ii} < (parent C) > (CH_3). The atoms C(34) and C(35), lying close to an adjoining iodine atom, could not be refined meaningfully anisotropically (neither could meaningful hydrogen atoms be located) so their thermal parameters were refined isotropically. Other non-hydrogen-atom thermal parameters were refined anisotropically. The values of the residuals (R and R') were 0.049 and 0.060 respectively with reflection weights $[\sigma^2(F_o) + 0.000\,2\,(F_o)^2]^{-1}$. Scattering factors for the neutral atoms were employed, those of the non-hydrogen atoms being corrected for anomalous dispersion (f', f'').[3-5] Computations were carried out using the ' *X*-RAY '76 ' program system[6] on a CYBER 73 computer. Structure factor amplitudes, thermal parameters, and hydrogen-atom parameters are deposited as Supplementary Publication No. SUP 22796 (26 pp).[*] Table 1 lists the non-hydrogen-atom fractional cell co-ordinates and Table 2 the cation geometry.



Within the dithiocarbamate ligand, non-hydrogen atoms are labelled as shown above; hydrogen atoms are labelled A, B, C for distinguishing purposes.

RESULTS AND DISCUSSION

The structure comprises $[Fe(S_2CNR_2)_3]^+$ cations, accompanied by I_5^- anions (Figure). The latter adopt the usual arrangement of two pseudo I_2 molecules weakly co-ordinated to an I^- ion, and subtending a right angle. In the chain I(1—5), the distances are 2.799(3), 3.148(3), 3.015(3), and 2.837(3) Å, while the angles are 176.19(4), 88.18(6), and 176.92(5)° respectively. Deviations of the atoms from a least-squares plane calculated through them are −0.022, 0.042, −0.023, 0.005, and −0.002 Å.

The cation comprises three bidentate *NN*-diethyldithiocarbamate ligands symmetrically co-ordinated to the iron atom. As usual, the S_2CNC_2 ligand fragments are reasonably planar (Table 3) and ' coplanar ' with the iron atom, with the more common disposition of the terminal methyl groups on either side of the ligand plane. A curious feature in an otherwise well behaved structure is the thermal parameter abnormality observed for one of the ethyl substituents, C(34, 35) in close proximity

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[†] For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

TABLE 1

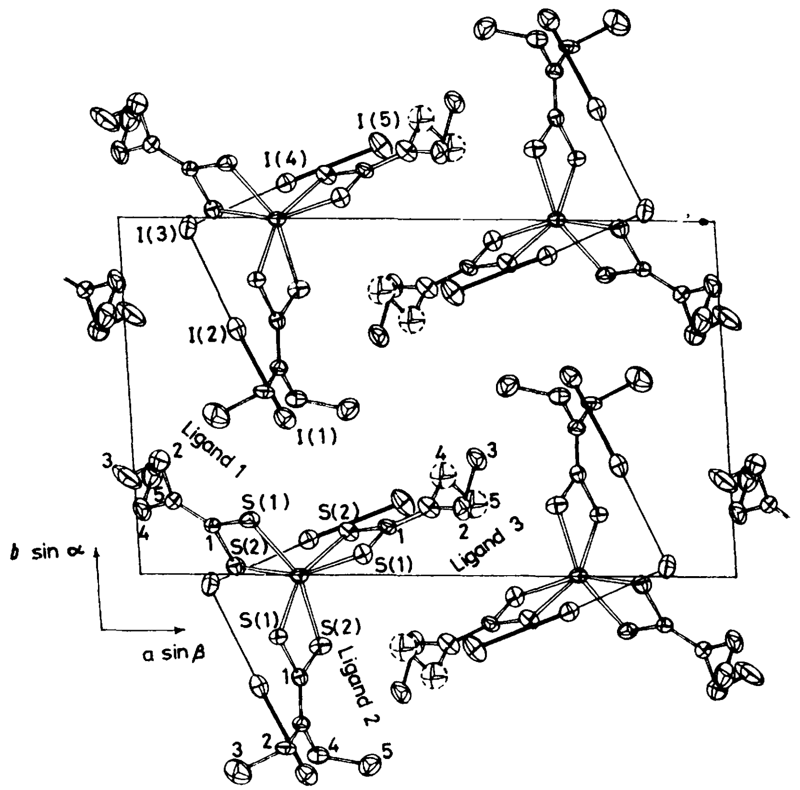
Non-hydrogen-atom fractional cell co-ordinates with estimated standard deviations in parentheses

	Ligand 1			Ligand 2			Ligand 3		
Atom	10^4x	10^4y	10^4z	10^4x	10^4y	10^4z	10^4x	10^4y	10^4z
S(1)	1 885(2)	1 532(2)	9 910(4)	2 245(2)	−1 737(3)	11 040(3)	3 746(2)	593(3)	9 518(3)
S(2)	1 602(2)	223(3)	7 977(4)	2 942(2)	−1 999(3)	8 277(3)	3 531(2)	1 224(3)	6 814(3)
N	629(6)	2 052(10)	8 890(11)	2 533(6)	−4 184(9)	10 534(10)	4 908(7)	1 922(11)	7 192(11)
C(1)	1 256(7)	1 369(11)	8 956(12)	2 556(7)	−2 876(12)	10 039(12)	4 187(7)	1 358(11)	7 720(13)
C(2)	442(9)	3 190(16)	9 588(19)	2 256(8)	−4 863(11)	12 055(14)	5 462(8)	1 882(15)	8 094(15)
C(3)	−123(13)	2 724(19)	11 107(27)	1 429(12)	−5 541(19)	12 501(19)	5 759(9)	3 287(15)	8 053(17)
C(4)	97(8)	1 811(15)	8 090(17)	2 786(9)	−5 063(13)	9 554(17)	5 169(12)	2 905(21)	5 557(22)
C(5)	303(10)	2 783(18)	6 642(19)	3 648(10)	−5 339(16)	9 273(17)	5 640(13)	2 025(21)	5 110(23)
Fe	2 656(1)	−20(2)	8 932(2)						

Anion co-ordinates (10^5x, 10^5y, 10^5z)

I(1)	25 761(6), 43 944(11), 59 658(11)
I(2)	18 644(6), 68 728(10), 53 517(10)
I(3)	11 564(6), 97 191(11), 44 691(12)
I(4)	28 508(6), 109 941(9), 33 959(10)
I(5)	44 751(7), 120 512(13), 23 968(12)

to the anion, possibly indicative of some disordering; U_C (isotropic) are much higher than for the rest of the structure (0.14 Å^2) and I(5) $\cdots$ C(35) is 3.86(3) Å. In this context it is of interest that in the structure determination of [FeI{$S_2CN(CH_2)_4$}$_2$]·0.5I$_2$, the proximity of the iodine ' molecule ' to one of the ligand pyrrolidine rings is found to be accompanied by an unusual conformation in the latter, together with higher local thermal motion.[7] Further, we find that although the FeS_6 core geometry exhibits no gross individual distortions in bond lengths and angles and ⟨Fe–S⟩, 2.29$_9$ Å, agrees well with the value previously reported for the similar [Fe{$S_2CNN(CH_2)_4$}$_3$]$^+$ species (2.30$_0$ Å),[8] the twist angle of the co-ordination sphere about the pseudo-three-fold axis of the FeS_6 core is $2\theta = 33.0°$, a value much lower than that observed in [Fe{$S_2CN(CH_2)_4$}$_3$]$^+$ (38°); the latter value is in much better agreement with the norm for a compound of this type.[9] As other cation core parameters between the two structures are in good agreement (*e.g.* intraligand S $\cdots$ S, S–C distances), it seems likely that the origin of the distortion lies in packing forces, rather than being electronic in nature;



Unit-cell contents projected down *c* showing non-hydrogen-atom 20% thermal ellipsoids and labelling for ligands of small bite (1.22 in the present case) such distortions are not unexpected.[10] Although the presence of the I_5^- species does not help the precision of the light-atom geometry, it is of interest to note that all three conjugated C–N distances are less than 1.30 Å, the mean being 1.29 Å. In the very many *NN*-diethyldithiocarbamate structures which have been determined precisely, the usual C–N distance is *ca.* 1.33 Å.

TABLE 2

Cation geometry (non-hydrogen atoms)

	Ligand 1	Ligand 2	Ligand 3	Mean
Distances (Å)				
Fe–S(1)	2.302(4)	2.314(4)	2.287(5)	2.29_9
Fe–S(2)	2.294(5)	2.292(4)	2.303(4)	
S(1)–C(1)	1.696(15)	1.723(13)	1.734(11)	1.71_4
S(2)–C(1)	1.724(13)	1.717(11)	1.689(15)	
C(1)–N(1)	1.295(15)	1.292(14)	1.291(16)	1.29_3
N(1)–C(2)	1.50(2)	1.46(2)	1.50(2)	1.4_8
N(1)–C(4)	1.46(2)	1.48(2)	1.64(2) *	
C(2)–C(3)	1.53(3)	1.50(2)	1.52(2)	1.5_0
C(4)–C(5)	1.49(2)	1.48(2)	1.29(3) *	
S(1) · · · S(2)	2.804(6)	2.808(5)	2.791(5)	2.80_1
(*b*) Angles (°)				
S(1)–Fe–S(2)	75.2(2)	75.1(1)	74.9(1)	$75._1$
Fe–S(1)–C(1)	87.5(4)	87.3(4)	87.6(5)	$87._6$
Fe–S(2)–C(1)	87.1(5)	88.2(5)	88.1(4)	
S(1)–C(1)–N(1)	125.9(11)	125.6(9)	123.9(11)	$125._2$
S(2)–C(1)–N(1)	123.8(11)	124.9(10)	126.8(10)	
S(1)–C(1)–S(2)	110.2(7)	109.4(6)	109.3(6)	$109._6$
C(1)–N(1)–C(2)	120.6(13)	122.4(11)	122.0(10)	$121._6$
C(1)–N(1)–C(4)	122.6(12)	120.5(10)	118.1(14) *	
N(1)–C(2)–C(3)	112.9(13)	112.2(13)	113.1(12)	$112._5$
N(1)–C(4)–C(5)	111.7(12)	112.8(14)	91.6(15) *	
C(2)–N(1)–C(4)	116.7(11)	117.1(9)	119.2(12) *	$116._9$

Other core angles

S(11)–Fe–S(21), 92.7(1); S(11)–Fe–S(31), 92.3(2); S(21)–Fe–S(31), 91.1(1); S(12)–Fe–S(22), 90.2(2); S(12)–Fe–S(32), 91.8(1); S(22)–Fe–S(32), 90.8(1); $91._5$
S(12)–Fe–S(21), 106.5(1); S(22)–Fe–S(31), 106.3(2); S(11)–Fe–S(32), 106.1(1); $106._3$
S(11)–Fe–S(22), 157.7(1); S(12)–Fe–S(31), 158.6(1); S(21)–Fe–S(32), 156.7(1); $157._7$

* Omitted from calculation of average.

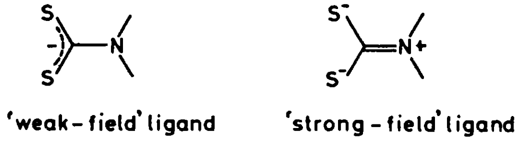
TABLE 3

Least-squares planes, defined by the S_2CNC_2 fragment of each ligand in the form $pX + qY + rZ = s$, relative to the orthogonal right-hand angström frame defined with X parallel to a, Z in the ac plane. Atom deviations, δ and σ (defining atoms), are in Å

	Ligand 1	Ligand 2	Ligand 3
10^4p	3 469	9 922	−2 962
10^4q	6 973	642	8 791
10^4r	−6 272	1 069	3 734
s	−3.072	8.087	1.274
δS(1)	−0.06	−0.04	0.01
δS(2)	0.08	0.05	−0.03
δC(1)	−0.03	−0.02	0.02
δN(1)	−0.03	0.00	0.04
δC(2)	0.09	0.05	−0.03
δC(3)	−1.26	−1.28	1.15
δC(4)	−0.06	−0.04	0.40 *
δC(5)	1.30	1.31	−0.82
δFe	0.11	0.03	−0.18
σ	0.07	0.04	0.03

* Aberrant atom; omitted from plane definition.

In particular, in [$Fe(S_2CNEt_2)_3$], room-temperature and low-temperature structure determinations [11] yield values of 1.337(6) and 1.323(4) Å, corresponding to greater proportions of high- and low-spin ground states respectively in that compound; although these results were handled with some caution, the trend was similar to that predicted earlier for the weak and strong crystal-field forms of the dithiocarbamate ligand (see below).[12] In the present case, the C–N distance as determined is shorter than either of the above, and if, as seems reasonable, the difference is taken to be a real one, then the contribution of the ' strong-field ' ligand form has been considerably enhanced, a not unexpected result in view of the fact that the present compound is totally low-spin. However, in the present case also, we have the added influence of enhanced metal-atom oxidation state and in this regard the ' strong-field ' ligand form is appropriate to a situation in which delocalization of a high intrinsic metal-ion charge must be one of the preconditions of stability of the system.



Worthy of comment among the interspecies interactions are a number of close cation–anion contacts between the anion and the cation sulphur atoms, those less than 4.0 Å being I(1) · · · S(32), 3.628(5); I(4) · · · S(31) (x, $y + 1$, $z - 1$), 3.936(5) Å, presumably indicative of charge-transfer interactions.

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