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Structure of a New Modification of Bromobis(*N*,*N*-diethyldithiocarbamato)iron(III), $Fe[S_2CN(C_2H_5)_2]_2Br$

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Abstract. $M_r = 432{\cdot}3$, monoclinic, $P2_1/n$, $a = 15{\cdot}158\ (6)$, $b = 17{\cdot}321\ (13)$, $c = 6{\cdot}876\ (6)$ Å, $\beta = 94{\cdot}52\ (6)^\circ$, $V = 1800\ (2)$ Å^3, $Z = 4$, $F(000) = 876$, $D_m = 1{\cdot}59\ (1)$, $D_x = 1{\cdot}597$ g cm^{-3}, μ(Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å) $= 36{\cdot}0$ cm^{-1}, $T = 295\ (2)$ K, number of unique reflections = 2372, $2\theta < 45^\circ$. Least-squares refinement based on 984 reflections $[I > 2\sigma(I)]$ gave a final $R(F)$ value of 0·082. The title compound also crystallizes in a modification (I) isomorphous with $Fe(S_2CNEt_2)_2Cl$ {described in space group $P2_1/c$ by Chapps, McCann, Wickman & Sherwood [*J. Chem. Phys.* (1974), **60**, 990–997]}. That modification becomes ordered ferromagnetically with $T_c = 1{\cdot}52\ (2)$ K with suitable conditions of crystallization [Decurtins, Wells, Sun & Wickman (1982). *Chem. Phys. Lett.* **89**, 79–83]. Mössbauer spectroscopy shows that the material which crystallizes in the new modification (II) remains paramagnetic to 1·2 K. The Mössbauer parameters at 77 K are $\Delta E_Q = 2{\cdot}87\ (1)$ mm s^{-1}, $\delta E = 0{\cdot}49\ (1)$ mm s^{-1}.

Introduction. Cooperative magnetic transitions are observed in a number of halobis(*N*,*N*-dialkyldithiocarbamato)iron(III) compounds (Chapps, McCann, Wickman & Sherwood, 1974; Grow, Robbins & Wickman, 1976; Yoshikawa, Sorai, Suga & Seki, 1981). The long-range magnetic order arises from intermolecular superexchange between adjacent, nonbonded, paramagnetic molecules in the molecular crystals. This exchange is weak, and magnetic critical temperatures (T_c) are rather low. In all known cases, T_c is below 4 K. The exchange interactions are modulated by poorly understood geometrical factors such as relative orientations of adjacent molecules. Thus, the chemical crystallography of these complexes is of considerable interest (Hoskins & White, 1970; Healy, White & Hoskins, 1972; Raston, Sly & White, 1980).

An earlier structure study of $Fe(dietdtc)_2Br$ showed it to be isomorphous to ferromagnetic ($T_c = 2{\cdot}43$ K) $Fe(dietdtc)_2Cl$ (Chapps *et al.*, 1974). This is referred to as modification I. No long-range order was observed in $Fe(dietdtc)_2Br$ until Yoshikawa *et al.* (1981) prepared the material by precipitation from benzene solution. Previous Mössbauer and susceptibility work had employed materials crystallized by evaporation of chloroform–toluene solutions (Wickman & Trozzolo, 1968; Ganguli, Marathe & Mitra, 1975). In recent work we duplicated the method of Yoshikawa *et al.*, and confirmed a ferromagnetic transition in $Fe(dietdtc)_2Br$ [$T_c = 1{\cdot}52\ (2)$ K]. We found the unit-cell parameters for the benzene precipitate to be nearly identical to those of modification I. It is not known why modification I exhibits variable magnetic properties depending upon crystallization conditions, although superparamagnetic effects have been suggested as being at least partially responsible.

During careful examination of $Fe(dietdtc)_2Br$ crystals, obtained from a chloroform–toluene solution, we observed a small amount of crystal modification II, which is the subject of this report. Since both modifications crystallize under similar conditions, their packing arrangements will energetically be nearly equal and are of interest in the context of their magnetic properties.

Experimental. The material was prepared according to the method of Martin & White (1967) by the reaction of $Fe(dtc)_3$ with HBr in benzene. As suggested by Yoshikawa *et al.* (1981) we used the diluted ethanol solution of aqueous hydrobromic acid in order to make the reaction proceed homogeneously. The compound was recrystallized starting from a saturated 50:50 (by volume) solution of chloroform and toluene. Normally an evaporation within 24 h produced both modifications in the same beaker, but always dominantly modification I. In contrast to that flat rectangular plates of this form the new modification crystallizes as elongated prisms.

D_m by flotation technique ($CCl_4/CHBr_3$). Syntex $P\bar{1}$ diffractometer, graphite monochromator, crystal $0{\cdot}14 \times 0{\cdot}16 \times 0{\cdot}18$ mm. Reflections $0k0$ with $k = 2n + 1$ and $h0l$ with $h + l = 2n + 1$ systematically absent. Lorentz and polarization correction, absorption ignored ($\mu r \simeq 0{\cdot}29$). $2\theta_{\max} = 45^\circ$, h ranged from 0 to +16, k from 0 to +18, l from −7 to +7. Standard reflections 602, 800, 080 measured after every 75 reflections; 2574 reflections measured. Structure solved by three-dimensional Patterson and difference Fourier syntheses and refined by least-squares calculations (based on F) of 984 reflections with $I > 2\sigma(I)$ (133 parameters). Computer programs: Zalkin's *FORDAP*, *LS* (Zalkin, undated, XRAY program system),* *ORTEP*-II (Johnson, 1976). Parameters of the $[Fe(S_2CN)_2Br]$ core and of the C atoms of one ethyl group [C(14), C(15)] refined as thermally anisotropic (see below). H-atom positions: estimated from a difference Fourier; held constant in the last refinement cycle; B (isotropic) set at $1{\cdot}25\,B$[parent C (CH_2)], $1{\cdot}5\,B$[parent C (CH_3)]. Final refinement cycle: ratio of maximum least-squares shift to error of positional parameters was 0·43 for the y parameter of C(24); average ratio of shift to error, 0·09. $wR = 0{\cdot}065$, $S = 1{\cdot}908$, w is based on $\sigma(I_o) = [C + Bt^2 + (0{\cdot}03C)^2]^{1/2}$ (C = integrated count, B = total background count, $t = 2$ is the ratio of scan time over background time), maximum and minimum heights in final difference Fourier map $< |1{\cdot}2|$ eÅ^{-3}. Scattering factors for the neutral atoms from *International Tables for X-ray Crystallography* [(1962) for non-hydrogen atoms, (1974), p. 102, for H atoms] and corrected for the real and imaginary parts of the anomalous dispersion [*International Tables* (1974), p. 149].

Discussion. The refined atomic parameters are presented in Table 1,† and the intramolecular distances and angles are given in Table 2.

The structure (Fig. 1) of the molecule includes the expected iron environment: pentacoordination, with the bromine at the apex of a square pyramid of four basal S atoms and an apical Br atom. The four S atoms deviate at most by ±0·043 (6) Å from their plane of best fit; the Fe atom lies 0·595 (4) Å above it. Displacements of up to 0·10 (3) Å of the defining atoms from the ligand planes defined by the S_2CNC_2 fragments are observed.

Table 2. *Intramolecular distances* (Å) *and bond angles* (°) *with e.s.d.'s*

Fe–Br	2·414 (4)	C(21)–N(21)	1·31 (2)
Fe–S(11)	2·277 (7)	N(11)–C(14)	1·55 (4)
Fe–S(21)	2·285 (6)	N(21)–C(22)	1·50 (3)
Fe–S(12)	2·282 (6)	N(11)–C(12)	1·46 (3)
Fe–S(22)	2·287 (7)	N(21)–C(24)	1·53 (3)
C(11)–S(11)	1·71 (2)	C(14)–C(15)	1·29 (5)
C(21)–S(21)	1·74 (2)	C(22)–C(23)	1·45 (4)
C(11)–S(12)	1·74 (2)	C(12)–C(13)	1·50 (3)
C(21)–S(22)	1·68 (2)	C(24)–C(25)	1·38 (4)
C(11)–N(11)	1·29 (3)		
S(11)–Fe–S(12)	76·1 (0·2)	S(12)–C(11)–N(11)	124·3 (1·7)
S(21)–Fe–S(22)	76·3 (0·2)	S(22)–C(21)–N(21)	126·9 (1·6)
S(11)–Fe–S(21)	95·2 (0·2)	S(11)–C(11)–S(12)	109·2 (1·2)
S(12)–Fe–S(22)	96·7 (0·2)	S(21)–C(21)–S(22)	111·7 (1·1)
Br–Fe–S(11)	102·6 (0·2)	C(11)–N(11)–C(14)	119·4 (2·1)
Br–Fe–S(21)	108·1 (0·2)	C(21)–N(21)–C(22)	123·2 (1·8)
Br–Fe–S(12)	104·3 (0·2)	C(11)–N(11)–C(12)	121·0 (2·0)
Br–Fe–S(22)	105·4 (0·2)	C(21)–N(21)–C(24)	121·3 (1·8)
Fe–S(11)–C(11)	87·6 (0·8)	C(14)–N(11)–C(12)	119·3 (2·0)
Fe–S(21)–C(21)	85·2 (0·7)	C(22)–N(21)–C(24)	115·5 (1·7)
Fe–S(12)–C(11)	86·9 (0·7)	N(11)–C(14)–C(15)	105·6 (2·8)
Fe–S(22)–C(21)	86·6 (0·7)	N(21)–C(22)–C(23)	112·8 (2·0)
S(11)–C(11)–N(11)	126·4 (1·7)	N(11)–C(12)–C(13)	112·5 (1·8)
S(21)–C(21)–N(21)	121·1 (1·6)	N(21)–C(24)–C(25)	107·1 (2·2)

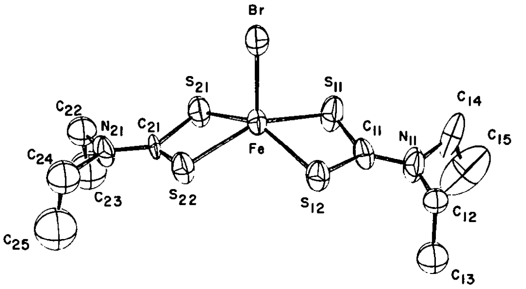

Fig. 1. A perspective view of the molecule (modification II) showing 33% thermal ellipsoids [atoms C(12), C(13), C(22), C(23), C(24) and C(25) were refined isotropically].

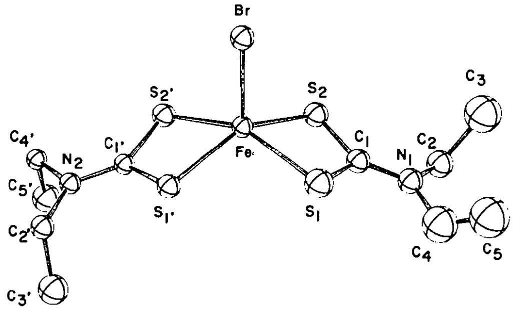

Fig. 2. A perspective view of the molecule (modification I) showing 33% thermal spheres.

Table 1. *Fractional atomic coordinates* (*non-hydrogen atoms*) *and isotropic thermal parameters with e.s.d.'s*

	x	y	z	B_{eq} or B(Å^2)
Br	0·3723 (2)	0·6539 (1)	0·6017 (5)	8·7 (2)*
Fe	0·3727 (2)	0·7931 (2)	0·6161 (5)	5·3 (2)*
S(11)	0·2332 (4)	0·8238 (4)	0·4933 (9)	7·4 (4)*
S(12)	0·3003 (3)	0·8214 (3)	0·8860 (8)	5·9 (4)*
S(21)	0·4406 (4)	0·8384 (4)	0·3536 (8)	6·5 (4)*
S(22)	0·5112 (3)	0·8261 (3)	0·7449 (9)	6·1 (4)*
N(11)	0·1282 (13)	0·8453 (13)	0·7851 (30)	7·7 (1·3)*
N(21)	0·6113 (11)	0·8648 (11)	0·4557 (24)	6·0 (1·1)*
C(11)	0·2060 (13)	0·8337 (12)	0·7291 (31)	5·5 (1·3)*
C(12)	0·1141 (13)	0·8543 (13)	0·9916 (30)	5·1 (5)
C(13)	0·1258 (15)	0·9361 (13)	1·0599 (33)	8·0 (6)
C(14)	0·0472 (19)	0·8413 (20)	0·6342 (45)	10·9 (2·2)*
C(15)	0·0210 (25)	0·9118 (24)	0·6084 (47)	16·7 (3·2)*
C(21)	0·5335 (11)	0·8481 (12)	0·5166 (31)	5·4 (1·2)*
C(22)	0·6249 (15)	0·8843 (14)	0·2482 (34)	6·7 (6)
C(23)	0·6091 (18)	0·9655 (16)	0·2037 (39)	11·2 (8)
C(24)	0·6949 (16)	0·8654 (15)	0·5962 (36)	8·9 (7)
C(25)	0·7127 (21)	0·9415 (20)	0·6443 (44)	14·4 (1·1)

* $B(\mathrm{eq}) = (B_{11} + B_{22} + B_{33})/3$. B_{ij} are the coefficients in the temperature function expression $\exp(-\sum_i\sum_j B_{ij}a_i^*a_j^*h_ih_j/4)$.

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† Lists of non-H anisotropic thermal parameters, positional and thermal parameters for H atoms, H-atom geometries, intermolecular distances, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38473 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

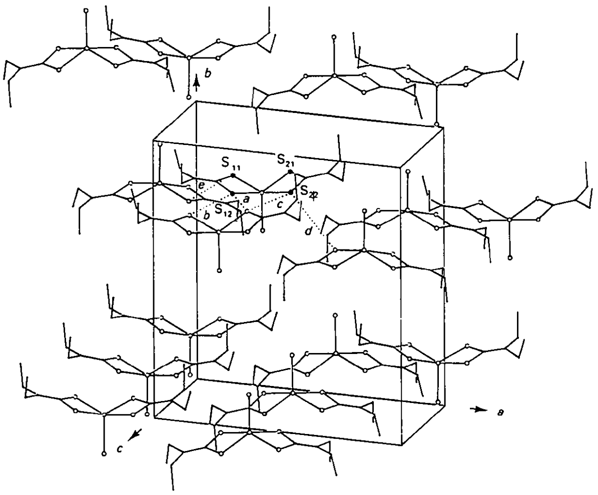

Fig. 3. Packing of the molecules in modification II. Intermolecular distances (Å) are: $a = S(12)\cdots S(21) = 3{\cdot}724\ (9)$; $b = S(12)\cdots S(11) = 4{\cdot}375\ (8)$; $c = S(22)\cdots S(21) = 4{\cdot}407\ (8)$; $d = e = S(22)\cdots S(11) = 4{\cdot}481\ (9)$.

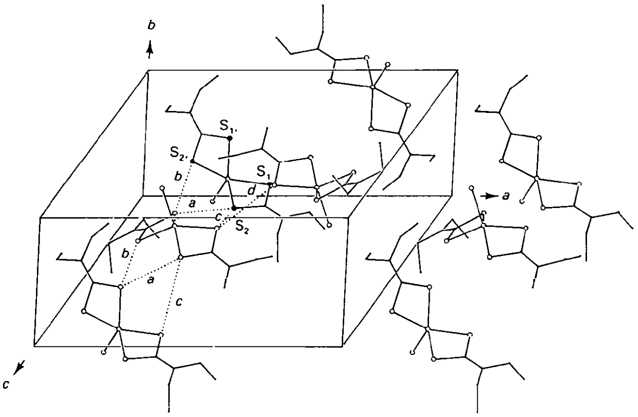

Fig. 4. Packing of the molecules in modification I. The labelled intermolecular distances (Å) have the following values: $a = 3{\cdot}60\ (1)$; $b = 3{\cdot}82\ (1)$; $c = 4{\cdot}36\ (1)$; $d = 3{\cdot}96\ (1)$.

In modification I (Fig. 2) the ethyl groups point in opposite directions at the two ends of the molecule with respect to the ligand planes. In modification II all four ethyl groups point in the same direction, opposite to the Br atom. The intramolecular distances and bond angles cover about the same range as observed before for modification I, the isomorphous chloride (Hoskins & White, 1970), the iodide (Healy *et al.*, 1972) and the isocyanide (Raston *et al.*, 1980) derivatives. The thermal parameters are higher than those observed for modification I, but agree rather closely with those observed for the isocyanide. In all derivatives at least one of the outer C atoms of the ethyl groups has a B value larger than 10·0 Å^2. The C(14)–C(15) distance of 1·29 (5) Å is somewhat short [comparable distance of 1·31 (7) Å in the chloride]. The short distance between C(15) atoms related by a symmetry center [final value 3·44 (6) Å] prompted anisotropic refinement of the C atoms of the C(14)–C(15) ethyl group. The large anisotropy observed for these atoms may indicate local disorder in this group which could result in an effective increase in the $C(15)\cdots C(15^{VII})$ distance. There are no other unusually short intermolecular distances.

On comparing the packing arrangements of the two modifications we note some distinct differences. Looking parallel to the c axis, we recognize in modification II, due to the small c value, a repetition of just one molecule and therefore a very regular packing arrangement (Fig. 3). The comparable view in modification I reveals an alternation in the Fe—Br direction for successive molecules (Fig. 4).

Structural features such as intermolecular contact distances are important for magnetic behavior. In these compounds the Fe···Fe and the Fe—Br···Fe distances are generally too large for a significant contribution to the exchange interactions. Therefore of primary interest are the intermolecular S···S linkages which can lead to an Fe—S···S—Fe interaction. In modification I there are three intermolecular S···S contacts with values less than 4 Å; the shortest is 3·60 (1) Å. In modification II there exists just one short intermolecular S···S contact, with a value of 3·724 (9) Å. As a whole, with respect to these S···S contacts, the molecules are farther apart from each other in modification II. This suggests a reduced critical temperature (weaker superexchange) compared with modification I. To pursue this point, Mössbauer experiments, with absorber temperatures as low as 1·2 K, were carried out with modification II. Only a simple quadrupole doublet was observed at all temperatures [$\Delta E_Q = 2{\cdot}87\ (1)\ \mathrm{mm\ s^{-1}}$; $\delta E = 0{\cdot}49\ (1)\ \mathrm{mm\ s^{-1}}$ at $T = 77$ K]. It is therefore very likely that T_c for modification II (as crystallized above) is below 1·2 K, *i.e.* lower than T_c for modification I.

It should be noted that despite the absence of magnetic h.f.s. in the Mössbauer spectra, some caution should be exercised in drawing conclusions about long-range order in modification II. For example, early preparations of modification I did not show magnetic h.f.s. However, later workers, using different crystallization techniques (Yoshikawa *et al.*, 1981; Decurtins *et al.*, 1982) observed a T_c of 1·34 K and 1·52 K respectively. Thus we cannot rule out the possibility that different crystallization methods might produce material displaying magnetic h.f.s.

It should also be noted that the discussion of superexchange paths is based on room-temperature X-ray data. The relevance of these data to the structure at 4 K or below is not *a priori* obvious. Some information on this point is provided by properties of modification I. This material has a destructive structural phase transition near 220 K (Ganguli *et al.* 1975).

Examination of T_c values for chloride–bromide mixed crystals, which do not have a phase transition (Malliaris & Simopoulos, 1975; DeFotis, Palacio & Carlin, 1979), shows that the extrapolated value for the pure bromide, modification I, is 1·5 K. This is very close to the value we observe in materials crystallized from benzene. This is an indication that between room temperature and helium temperatures the significant intermolecular distances and molecular environments do not change in ways that drastically alter exchange paths observed in the room-temperature data.

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Structure of Bis(1,10-phenanthroline)bis(2,4,6-trinitrophenolato)barium(II) Acetone (1:1), $[Ba(C_{12}H_8N_2)_2(C_6H_2N_3O_7)_2].C_3H_6O$

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Abstract. $M_r = 1011·98$, orthorhombic, *Pbca*, $a = 18·314$ (8), $b = 17·340$ (4), $c = 24·629$ (3) Å, $V = 7821$ (4) Å^3, $Z = 8$, $D_m = 1·72$, $D_x = 1·72$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 10·63 cm^{-1}, $F(000) = 4048$, $T = 294$ K, $R = 0·042$ for 6444 observed reflections. The coordination sphere about Ba consists of four N and four O atoms which form a distorted pentagonal-base trigonal-cap. The two neighbouring phenanthroline molecules act as bidentate ligands through their N atoms, the phenolic O atom and an O atom of an *ortho* nitro group of one of the picrates act as the third bidentate ligand and the coordination is completed by the phenolic O atom of the other picrate and the O atom of the acetone solvate molecule. The angle between the planar phenanthrolines is 60·5 (1)°, that between the picrates is 40·6 (2)°. The benzene rings of both picrates show a similar appreciable distortion from hexagonal symmetry and in both picrates one of the *ortho* nitro groups is severely twisted out of the least-squares plane, 28·6 (2) and 38·9 (2)°, respectively.

Introduction. Complexes of Na$^+$, K$^+$ and Rb$^+$ have been described with a combination of various chelating anionic and neutral ligands such as salicylate, picrate, *o*-nitrophenolate, polyethers and 1,10-phenanthroline (Layton, Nyholm, Banerjee, Fenton, Lestas & Truter, 1970; Truter, 1971; Poonia & Truter, 1973; Poonia, 1975*a*,*b*; Jones, Milburn, Sawyer & Hughes, 1981). In order to study the coordination of alkaline-earth-cation complexes with picrate and 1,10-phenanthroline, the analysis of the title compound was undertaken.

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