Crystal and Molecular Structure of Bromobis(N,N-diisopropyldithiocarbamato)-iron(III)–Methylene Chloride Solvate

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The crystal and molecular structures of bromobis(N,N-diisopropyldithiocarbamato)iron(III)–methylene chloride solvate have been determined from three-dimensional X-ray diffraction data, collected on a computer-controlled Philips PW1100 single crystal diffractometer (477 observed reflections). The crystals are monoclinic, space group C2/c, with a *=* 16.579(3), b *=* 11.774(1), c *=* 14.533(2) *Å,* β *= 118.67(1)° and Z = 4. The structure was solved by direct phase determination with MULTAN and refined by least-squares calculations to a final* R *=* 0.092 *(*R_w *= 0.094). The configuration about the iron atom is approximately square pyramidal. The Fe atom lies 0.64 Å above the mean plane of the four S atoms of the dithiocarbamate ligands and the Br atom lies at the apex of the pyramide. The observed intraligand dimensions are normal for a bidentate dithiocarbamate [Fe–S 2.28(1) Å, S–Fe–S 76.0(4)°, S–C 1.74(2) and 1.68(4) Å, C–N 1.39(5) Å]. Also of interest is the Fe–Br bond [2.41(1) Å]. The crystal cohesion may be attributed to normal van der Waals forces.*

Introduction

The synthesis of the very interesting five-coordinated halogenobis(N,N-dialkyldithiocarbamato)iron(III) complexes by Wickman and Trozzolo [1] has stimulated extensive research on this class of compounds, from both experimental and theoretical points of view. Pasek and Straub [2], studying the reaction of iron(III) dithiocarbamates with iodine, were able to isolate complexes of the stoichiometry $Fe(R_2dtc)_2I_2$ which were found to be dimeric with an iodine bridge, linking two $Fe(R_2dtc)_2I$ units [3]. We thought it of interest to further develop synthetic routes to halogen-bridging dimers, and as a part of this program we report our results on the crystal structure of the title compound.

Experimental

Preparation of the Crystals

The complex was prepared by reacting the tris(N,N-diisopropyldithiocarbamato)iron(III) complex with excess of ferric bromide, according to the method of Wickman and Trozzolo [1], and was recrystallized from methylene chloride–petroleum ether.

Crystal Data

$[FeBr(S_2CNPr^i_2)_2]\cdot 0.7CH_2Cl_2$, $C_{14}H_{28}BrFeN_2S_4\cdot 0.7CH_2Cl_2$, FW = 547.8, monoclinic, space group $C2/c$, a = 16.579(3), b = 11.774(1), c = 14.533(2) Å, β = 118.67(1)°, V = 2489.05 Å^3, Z = 4, D_c = 1.46 g cm^{-3}, D_f = 1.42 g cm^{-3} (flotation), $F(000)$ = 1122, $\mu(MoK\alpha)$ = 26.7 cm^{-1}.

Collection of X-ray Data

The crystal selected for the X-ray study was a prism of dimensions 0.34 × 0.12 × 0.08 mm. During the preliminary X-ray measurements it was observed that the crystals were completely dissociated in about 24 hours, when exposed to radiation in air. To prevent decomposition during data collection the crystal was sealed in a glass capillary of 0.3 mm diameter and then centred on a computer-controlled Philips

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TABLE I. Positional Parameters ($\times 10^4$) and Isotropic Temperature Factors (Å^2).[a]

	x	*y*	*z*	*B*
Fe	0(0)	2623(7)	2500(0)	2.4(3)*
S(1)	762(6)	3229(10)	1639(7)	3.9(4)*
S(2)	1417(6)	3107(8)	3808(7)	3.0(4)*
Br	0(0)	577(7)	2500(0)	6.1(4)*
N	2507(19)	3983(24)	3027(23)	3.3(7)
C(1)	1683(19)	3510(30)	2875(22)	1.7(6)
C(2)	2694(24)	4381(34)	2140(30)	3.5(9)
C(3)	2091(28)	5407(38)	1529(32)	5.6(10)
C(4)	2725(25)	3397(40)	1531(31)	5.6(9)
C(5)	3240(23)	4158(32)	4148(26)	3.1(8)
C(6)	4041(22)	3521(34)	4308(26)	3.6(8)
C(7)	3304(25)	5349(36)	4332(29)	4.2(9)
Methylene Chloride				
Cl	444(15)	3373(23)	8599(17)	12.1(6)
C(8)	0(0)	4155(93)	7500(0)	8.3(31)

[a] B-values marked with an asterisk are equivalent isotropic temperature factors, defined by $B_{eq} = 8\pi^2/3\ \Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j$.

TABLE II. Interatomic Distances (Å) and Angles (°).

Fe–Br	2.41(1)	Br–Fe–S(1)	108.3(4)
Fe–S(1)	2.28(1)	Br–Fe–S(2)	104.5(3)
Fe–S(2)	2.28(1)	S(1)–Fe–S(2)	76.0(4)
S(1)–C(1)	1.74(2)	Fe–S(1)–C(1)	86.3(13)
S(2)–C(1)	1.68(4)	Fe–S(2)–C(1)	87.8(9)
C(1)–N	1.39(5)	S(1)–C(1)–S(2)	110(2)
N–C(2)	1.54(6)	S(1)–C(1)–N	123(3)
N–C(5)	1.51(4)	S(2)–C(1)–N	127(2)
C(2)–C(3)	1.55(5)	C(1)–N–C(2)	124(2)
C(2)–C(4)	1.47(6)	C(1)–N–C(5)	117(3)
C(5)–C(6)	1.44(5)	C(2)–N–C(5)	119(3)
C(5)–C(7)	1.42(6)	N–C(2)–C(3)	113(4)
		N–C(2)–C(4)	110(3)
Methylene Chloride		C(3)–C(2)–C(4)	118(3)
C(8)–Cl	1.68(6)	N–C(5)–C(6)	108(3)
		N–C(5)–C(7)	107(3)
		C(6)–C(5)–C(7)	120(3)
		Methylene chloride	
		Cl–C(8)–Cl′	113(6)

PW1100 four-circle single-crystal diffractometer. Precise determinations of lattice constants were carried out from the accurate setting of the angles of 32 unique reflections. Systematic absences lead to the space groups C2/c and Cc. The distribution of intensity statistics clearly favored a centrosymmetric structure and so the space group C2/c was chosen. Three-dimensional intensity data were collected with a scintillation counter of the PW1100 diffractometer in the $\theta/2\theta$ scan mode, using Mo Kα radiation, monochromated with a graphite monochromator. The intensities of 5594 reflections were measured and subsequently averaged to give 2186 unique reflections of which only 477 had $I > 3\sigma(I)$. These were considered as observed and used in the ensuing calculations. Integrated intensities were corrected for Lorentz and polarization effects, but not for absorption, and were further converted to Fo values using the special measurement-treatment program DATRED [4].

Structure Solution and Refinement

The structure was solved by direct phase determination with the MULTAN 77 system of programs [5] using 180 reflections with the largest E values. The E-map computed with the best combined figure of merit revealed clearly the position of all the heavy atoms of the complex. The rest of the atoms, as well as the solvate molecule of methylene chloride, were located by Fourier techniques. For all the subsequent calculations the X-ray 76 system of programs was used [6]. Atomic scattering factors for all atoms and anomalous dispersion corrections were taken from the 'International Tables for X-ray Crystallography' [7]. The structure refinement was carried out by a full-matrix least-squares procedure, in which the function minimized was $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme used was of the form $w = 1/\sigma^2(F_o)$. Using individual isotropic temperature factors for all atoms, and also an independent population parameter for the CH_2Cl_2 molecule, the conventional R factor converged to $R = 0.098$ ($R_w = 0.097$). Further refinement with anisotropic temperature factors resulted in non-positive definite temperature factors for some of the terminal atoms of the molecule, so that in the last stage of refinement only the heavy atoms were permitted to vibrate anisotropically. The refinement was stopped when the maximum shift/error was about 0.1. The final R value obtained was 0.092 ($R_w = 0.094$) while the population parameter for the solvate molecule was 0.70(2). The final positional and thermal parameters are listed in Table I. Bond lengths and bond angles are given in Table II. A list of anisotropic temperature factors of the heavy atoms and of the observed and calculated structure factors has been deposited with the Editor.

Description of the Structure and Discussion

A perspective drawing of the molecule is given in Fig. 1. The Fe atom is covalently bonded to four

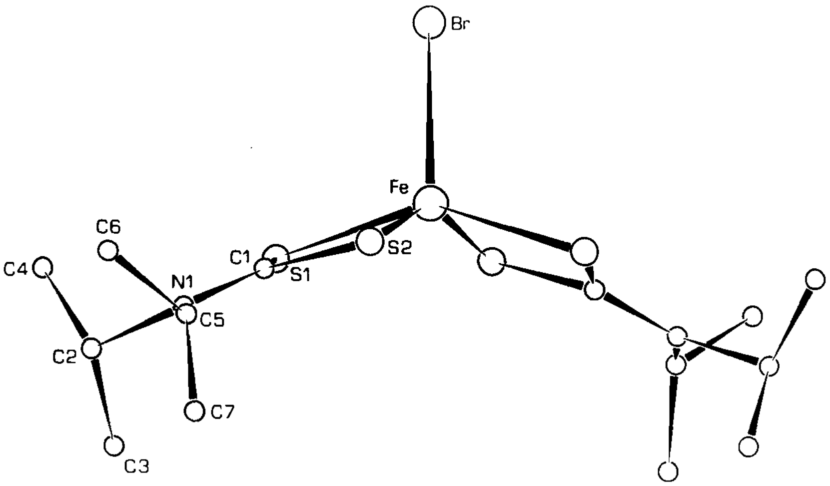

Fig. 1. Perspective view of the molecule.

TABLE III. Least Squares Planes with Displacements of Atoms from the Planes (A). The equation for a plane is in the form AX + BY + CZ = D and refers to orthogonal axes. The coordinates, X, Y, Z are expressed in A; D is the distance of the plane from the origin. Asterisks indicate atoms not included in the calculation on the plane. Mean estimated standard deviations of the atoms defining a plane are given in parentheses following the distances of the first atom.

Plane I:	central plane formed by S(1) and S(2) and their symmetrically equivalents in respect to the molecular twofold axis.	
	$-0.00226X + 1.00000Y + 0.00177Z = 3.73686$	
	S(1)	0.07(8)
	S(2)	−0.07
	S(1)′	0.07
	S(2)′	−0.07
	Fe*	−0.64
	Br*	−3.05
Plane II:	dithiocarbamato group	
	$-0.40698X + 0.91331Y - 0.01526Z = 3.39343$	
	S(1)	−0.002(4)
	S(2)	−0.002
	C(1)	0.006
	N	−0.002
	Fe*	0.088

S and one Br atom, forming a square pyramide with the Br atom lying at its apex. The whole molecule possesses a two-fold symmetry axis passing through the Fe and Br atoms. On the same axis lie also the C atoms of the methylene chloride molecule. The equations of the least-squares planes of the complex are given in Table III, where it can be seen that the four S atoms are nearly coplanar, while the Fe atom deviates 0.64 Å from their mean plane and in the direction of the Br atom. This is in very good agreement with the deviation of 0.62 Å observed in monochlorobis(diethyldithiocarbamato)iron(III) [8] and 0.65 Å observed in chlorobis(N,N-diisopropyldithiocarbamato)iron(III) [9]. As expected from other dithiocarbamates, the group S_2CN is strictly planar, within experimental error. In Table IV are given the observed Fe–S and Fe–X (X = halogen atom) distances for a number of known $Fe(dtc)_2X$ structures, from which it is deduced that the agreement with the corresponding distances of the compound under investigation is very satisfactory. Also the observed C–N and N–C distances in the dithiocarbamate ligand, 1.39 and 1.51–1.54 Å respectively, agree within experimental error with the corresponding distances observed in other dithiocarbamates [8, 11]. The molecular packing seems to be

TABLE IV. Fe–X(S) Distances (A) and X–Fe–S Angles (°) for $Fe(dtc)_2X$ Structures.

Compound	Space group	Fe–X	Fe–S	X–Fe–S	Ref.
$Fe(S_2CNEt_2)_2Cl$	$P2_1/c$	2.26 A	2.31, 2.29, 2.30, 2.30	105.4, 106.7, 105.1, 105.5	[8]
$Fe(S_2CNPr_2^i)_2Cl \cdot CHCl_3$	$P\bar{1}$	2.281	2.288, 2.284 2.283, 2.291	104.21, 104.58, 109.47, 107.71	[9]

(continued overleaf)

TABLE IV. *(continued)*

Compound	Space group	Fe–X	Fe–S	X–Fe–S	Ref.
$Fe(S_2CNEt_2)_2Br$	$P2_1/c$	2.42	2.28, 2.29, 2.30, 2.30	105.7, 106.0, 105.5, 104.7	[10]
$Fe(S_2CNPr_2^i)_2Br\cdot 0.7CH_2Cl_2$	C2/c	2.41	2.28, 2.28	108.3, 104.5	present work
$Fe(S_2CNEt_2)_2I$	$P2_1$	2.59	2.26, 2.28 2.27, 2.29	103.1, 109.9, 107.8, 99.4	[11]

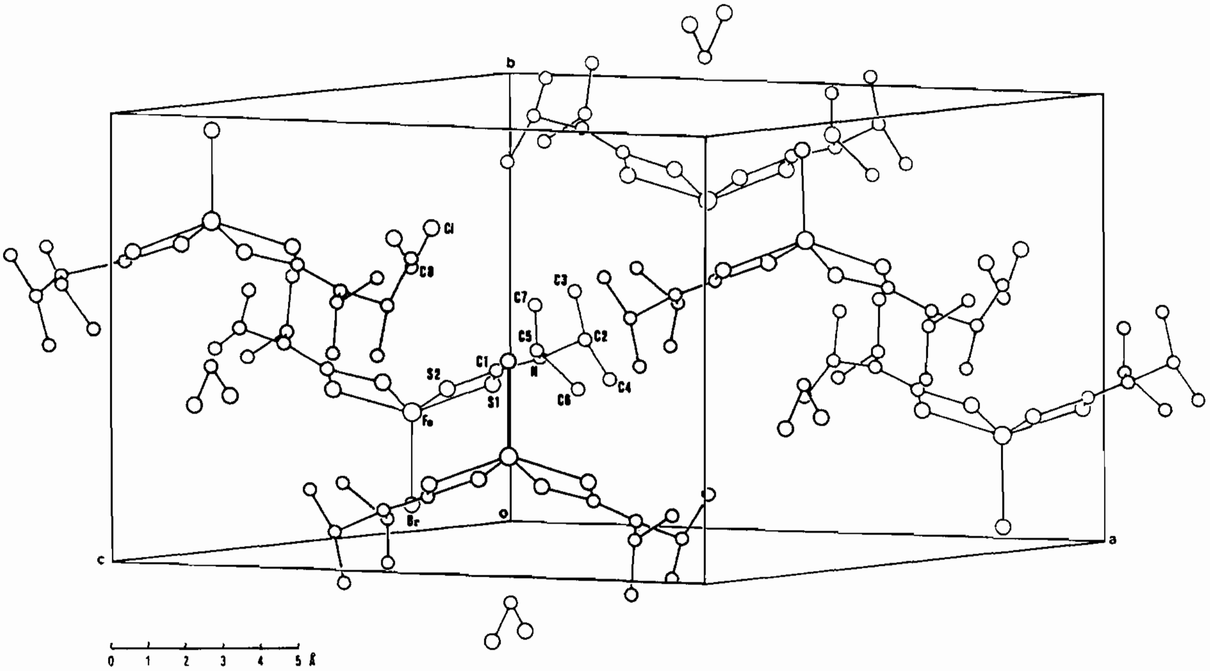

Fig. 2. Clinographic projection of the structure along [100].

TABLE V. Observed Intermolecular Contact Distances less than 4 A.

$Br-C(2^{I})$	3.87(4)
$Fe-C(8^{II})$	3.79(10)
$S(1)-C(6^{V})$	3.82(3)
$S(1)-C(8^{II})$	3.76(9)
$S(2)-C(8^{II})$	3.90(9)
$S(2)-S(2^{III})$	3.87(1)
$S(2)-C(5^{III})$	3.83(4)
$S(2)-C(6^{III})$	3.71(4)
$S(2)-C(3^{IV})$	3.96(5)
$Cl-C(4^{III})$	3.76(6)
$Cl(C(6^{VI})$	3.70(5)
$C(1)-C(8^{II})$	3.77(9)
$C(4)-C(7^{VII})$	3.91(6)

TABLE V. *(continued)*

Symmetry code	
I.	x – ½, y – ½, z
II.	–x, 1 – y, 1 – z
III.	½ – x, ½ – y, 1 – z
IV.	x, 1 – y, ½ + z
V.	–½ + x, ½ – y, ½ – z
VI.	–½ + x, ½ – y, ½ + z
VII.	½ – x, ½ + y, ½ – z

due mainly to normal van der Waals forces, since no unusually short intermolecular contact distances were observed, as can be seen from Table V. A clinographic projection of the structure is depicted in Fig. 2.

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