THE CRYSTAL STRUCTURE OF TRIS(DIALLYLDITHIOCARBAMATO) IRON(III)

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The crystal and molecular structure of $[Fe(S_2CN(C_3H_5)_2)_3]$ was solved by X-ray structural analysis and refined by the least squares method to give $R = 0{\cdot}09$ for 1 834 observed reflections. The compound crystallizes in the $C2/c$ space group and the monoclinic unit cell has dimensions of $a = 18{\cdot}709$ (6), $b = 10{\cdot}217$ (3), $c = 15{\cdot}546$ (6) . 10^{-10} m, $\beta = 106{\cdot}03$ (3)°. The experimentally observed density is 1·35 Mg m^{-3} and the calculated value for $Z = 4$ is 1·33 Mg m^{-3}. In the structure the iron atom occupies a special position on the two-fold axis and is coordinated by six sulphur atoms in a trigonally deformed octahedron: Fe-S1 2·340 (6), Fe-S2 2·367 (7), Fe-S3 2·323 (6) . 10^{-10} m. The S_2CNC_2 ligands are approximately planar.

Difficulties encountered in structural studies of the metal(III) dithiocarbamates[1-3] have been shown to result from the fact that unsolvated complexes cannot form good crystals, while the solvated crystals lose solvent molecules frequently without change in molar volume. This problem has been overcome for the tris(diallyldithiocarbamato)iron complex.

EXPERIMENTAL AND RESULTS

Crystals of the compound $[Fe(S_2CN(C_3H_5)_2)_3]$ (molecular mass 572·7) were prepared with the following elemental analysis:

Element	C	H	N	S
% calculated	44·04	5·28	7·33	33·59
% found	44·10	5·48	7·13	33·41

The crystals are needles with approximate dimensions 0·45 × 0·3 × 0·1 mm^3. The approximate dimensions of the unit cell, obtained from rotation and Weissenberg photographs, were refined by the least squares method using a Syntex $P2_1$ diffractometer. Ten exactly centred reflections yielded the following values: $a = 18{\cdot}709$ (6), $b = 10{\cdot}217$ (3), $c = 15{\cdot}546$ (6). 10^{-10} m, $\beta = 106{\cdot}03$ (3)°.

The experimentally observed density $D_0 = 1{\cdot}35$ Mg m^{-3} (measured in a bromoform–ethanol mixture) is in good agreement with the value calculated assuming four formula units per unit cell ($D_c = 1{\cdot}33$ Mg m^{-3}).

The diffraction intensities were measured on a Syntex P2_1, diffractometer using the $\Theta - 2\Theta$ scanning technique with a take-off angle of 1·5°. The scan rate was variable and was set automatically on the basis of preliminary (20° min^{-1}) two-second intensity measurement. The profile of each reflection was scanned in 48 steps at a minimal rate of 4·88° min^{-1} when the number of pulses was less than 150 s^{-1} and at a maximal rate of 29·3° min^{-1} when the number of pulses was greater than 1 500 s^{-1}. The background counts were measured for half the total scan time at each end of the scan range. Two standard reflections were measured for each 100 reflection intervals. No deviation in intensities was recorded. The intensities were corrected for te Lorentz and polarization factors but not for absorption or extinction ($\mu = 9{\cdot}3$ cm^{-1}).

Altogether, 3 267 symmetrically independent reflections were measured, of which 1 834 with $I > 1{\cdot}96\sigma(I)$ were classified as observed (56·3%). Only observed reflections were used for the final structure solution.

Systematic extinction of the reflections of the types hkl, $h + k = 2n + 1$ and $h0l$, $l = 2n + 1$ indicated two possible space groups, $C2/c$ or Cc. The average statistical values $\langle|E_{\bar{h}}|^2\rangle$, $\langle|E^2| - 1\rangle$, $\langle E\text{-}\rangle$ and distribution of $\langle E_{\bar{h}}\rangle$ unambiguously favoured the $C2/c$ space group.

TABLE I

Refined atomic coordinates in the [Fe($S_2CN(C_3H_5)_2)_3$] crystal structure (standard deviations given in parentheses) and their isotropic equivalent thermal parameters B_{eq}^{+}

Atom	x/a	y/b	z/c	B_{eq} (nm^2 . 10^2)
Fe	0	0·0833 (1)	0·25	4·83
S1	0·0729 (8)	0·2650 (1)	0·3100 (1)	5·47
C1	0	0·3560 (8)	0·25	4·84
N1	0	0·4877 (7)	0·25	5·05
C2	0·0621 (6)	0·5615 (9)	0·3088 (4)	5·87
C3	0·0500 (4)	0·5753 (8)	0·4035 (5)	6·98
C4	0·0468 (4)	0·6811 (8)	0·4414 (5)	8·11
S2	0·1009 (9)	−0·0654 (6)	0·2858 (1)	5·52
S3	0·0362 (9)	0·0592 (9)	0·1195 (1)	6·00
C5	0·1040 (3)	−0·0410 (6)	0·1768 (3)	5·73
N2	0·1558 (2)	−0·0959 (6)	0·1427 (3)	6·26
C9	0·1565 (4)	−0·0640 (10)	0·0489 (4)	7·20
C10	0·2072 (4)	0·0650 (3)	0·0537 (6)	8·47
C11	0·2460 (9)	0·0816 (26)	0·0557 (14)	10·44
C12	0·2180 (4)	−0·1744 (8)	0·1971 (5)	7·06
C13	0·2088 (6)	−0·3197 (9)	0·1710 (6)	8·23
C14	0·1741 (7)	−0·3828 (13)	0·1325 (8)	9·27

* $B_{eq} = \frac{4}{3} \sum_i \sum_j B_{ij} \bar{a}_i , \vec{a}_j$.

Choice of $C2/c$ was confirmed by successful structural refinement. It follows from the number of formula units and the space group that the Fe atom occupies a special position on the two-fold axis in the structure. The phase problem was solved by Patterson and Fourier synthesis. The Fe, Cl and N atoms were located on the two-fold axis and the other atoms in general positions. The subsequent three Fourier syntheses yielded the positions of all nonhydrogen atoms, assuming a thermal coefficient of 0·043 nm^2. The positional parameters of the nonhydrogen atoms were refined by the full matrix least squares method, the minimized function $\sum w(|F_0| - |F_c|)^2$ and a unit weighting scheme. After three refinement cycles using isotropic thermal parameters factor R converged to a value of 0·23. Introduction of anisotropic thermal parameters decreased R after two refinement cycles to a value of 0·09. In the final cycle the shifts of all positional parameters were less than $0{\cdot}1\sigma$ and thermal parameters $<0{\cdot}2\sigma$. The hydrogen atoms were not located. The refined positional coordinates of all nonhydrogen atoms are given in Table I. The interatomic bond lengths and valence angles are given in Tables II—V. Projection of the molecule onto the (001) plane is depicted in Fig. 1. The values of observed and calculated structural factors and coefficients of thermal vibration for all the atoms are available on request from the authors.

All the calculations were carried out on a Siemens 4004/150 computer in the Computer Centre of Comenius University.

DISCUSSION

Designation of the atoms in the coordination polyhedron of FeS_6 is apparent from Fig. 2; the interatomic distances and angles in this coordination polyhedron are listed in Tables II and III.

TABLE II

Interatomic distances in the FeS_6 coordination polyhedron (. 10^{10} m)

Fe—S1	2·340 (6)	S1—S2	3·45 (1)
Fe—S2	2·367 (7)	S1—S3′	3·37 (1)
Fe—S3	2·323 (6)	S2—S3′	3·41 (1)
S1—S1′	2·84 (1)	S1—S3	3·59 (1)
S2—S3	2·85 (1)	S2—S2′	3·60 (1)

TABLE III

Valence angles in the FeS_6 coordination polyhedron (°)

S1—Fe—S1′	75·0 (2)	S1—Fe—S3	98·9 (2)
S2—Fe—S3	74·4 (2)	S2—Fe—S2′	100·1 (2)
S1—Fe—S2	94·4 (2)	S1—Fe—S2′	160·4 (2)
S1—Fe—S3′	90·8 (2)	S3—Fe—S3′	167·8 (2)
S2—Fe—S3′	97·6 (2)		

As can be seen from Table II, the dithiocarbamate ligands (dtc) are symmetrically bidentate coordinated to the Fe atom. All the Fe–S bond lengths are approximately equal with an average value of $2{\cdot}343 \,.\, 10^{-10}$ m. The coordination sphere of the FeS_6 polyhedron is similar to that of other symmetrically bidentate coordinated

TABLE IV

Interatomic distances in the ligands ($.\ 10^{10}$ m)

S1—C1	1·70 (2)	N2—C12	1·47 (3)
C1—N1	1·35 (3)	N2—C9	1·50 (3)
N1—C2	1·47 (3)	C12—C13	1·54 (4)
C2—C3	1·55 (4)	C13—C14	1·20 (4)
C3—C4	1·24 (4)	C9—C10	1·61 (4)
S3—C5	1·68 (2)	C10—C11	1·15 (4)
S2—C5	1·73 (2)	C5—N2	1·35 (3)

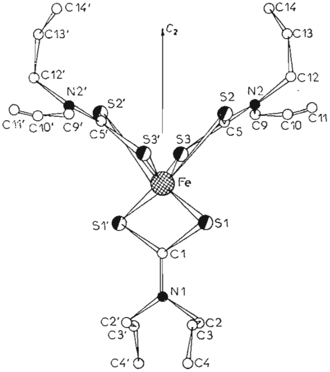

FIG. 1

Projection of the $Fe(S_2CN(C_3H_5)_2)_3$ molecule onto the (001) plane

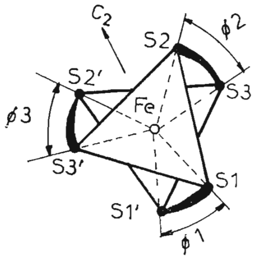

FIG. 2

View of the FeS_6 coordination polyhedron along the pseudo-C_3 symmetry axis with designation of atoms tris-dtc complexes of transition metals shifted from the octahedral geometry towards the trigonal-prismatic. The twist angle ϕ was calculated individually for each chelate ring (Fig. 2) similarly as in work[4]. The three ϕ_i values are 36·5, 41·5 and 41·5° (average value 39·8°). It can be seen that ϕ_1 differs considerably from ϕ_2 and ϕ_3, indicating that in the studied complex distortion $D_3 \rightarrow C_2$ is superimposed on the usual $O_h \rightarrow D_3$ distortion. In tris-dtc complexes of Fe(III) a similar type of distortion was observed[5] only for the [Fe(MePh)$_3$] complex.

TABLE V

Valence angles in the ligands (°)

S1—C1—S1′	114·0 (1)	S2—C5—S3	113·0 (1)
Fe—S1—C1	85·6 (7)	S2—C5—N2	123·0 (2)
S1—C1—N1	123·0 (1)	S3—C5—N2	124·0 (1)
C1—N1—C2	121·0 (2)	C5—N2—C12	112·0 (2)
N1—C2—C3	110·0 (2)	C5—N2—C9	119·0 (2)
C2—C3—C4	124·0 (1)	N2—C12—C13	110·0 (2)
Fe—S2—C5	85·2 (8)	C12—C13—C14	123·0 (4)
Fe—S3—C5	87·5 (6)	N2—C9—C10	109·0 (3)
C9—C10—C11	123·0 (4)		

TABLE VI

Deviations of some atoms (. 10^{10} m) from the plane constructred by the least squares method through the designated fragments

Fragment Fe S1 S1′ C1 N1 C2 C2′

Fe −0·02, S1 0·025, S1′ −0·014, C1 0·018, N1 0·036
C2 −0·065, C2′ 0·021, C3 1·531, C3′ −1·531

Fragment Fe S2 S3 C5 N2 C12 C9

Fe −0·073, S2 0·048, S3 0·029, C5 0·044, N2 0·041
C12 −0·031, C9 −0·057, C13 −1·593, C10 1·365

Fragment S1 S1′ C1 N1

S1 0·0, S1′ 0·0, C1 0·0, N1 0·0, C2 −0·109, Fe 0·0

Fragment S2 S3 C5 N2

S2 −0·001, C5 0·004, N2 −0·002, C12 −0·066, C9 −0·109
Fe −0·110

Distortion of the complex can also be described in terms of various types of S–Fe–S angles (Table III), namely: *1*) Chelate angle α has an average value of 74·6°; *2*) the average value of angle ξ (the angle between Fe and two sulphur atoms in the same triangle) is 94·3°; *3*) The ζ angle (the angle between Fe and two "cis" sulphur atoms in different triangles) has an average value of 99·3°; *4*) The average value of angle γ (the angle between Fe and two "*trans*" sulphur atoms in different triangles) is 162·9°. The distortion of the FeS_6 coordination sphere is not only of trigonal nature; trigonal-prismatic complexes with sulphur-containing ligands are known[6,7] with a compression ratio s/h of 1·00, where s is the length of the edge of a triangular face and h is the height of the trigonal prism or antiprism (Fig. 2). For an ideal octahedron[8], ratio $s/h = 1{\cdot}22$. Compression ratio s/h for the $[Fe(S_2CN(C_3H_5)_2)_3]$ complex is 1·37, *i.e.* the three S_2C chelate fragments are not only trigonally twisted with respect to the octahedron but also compressed towards the metal atom.

The interatomic distances and valence angles in the dtc ligands are given in Tables IV and V. The average bond lengths in the S_2CNC_2 ligand fragment are: C—S 1·715, S_2C—N 1·35, CN—C_2 1·48 . 10^{-10} m, which is consistent with a high degree of π-conjugation in the S_2CN chelate ligand fragments.

The β-carbon atoms of the allyl groups are in mutual *trans*-configuration with respect to the trigonal S_2CN plane. In this respect, the $[Fe^{III}(S_2CN(C_3H_5)_2)_3]$ complex is similar to the $[Fe(Et_2dtc)_3]$ complex[9] and differs from the $[Fe(n\text{-}Bu_2dtc)_3]$ complex[10] in which the β-carbon atoms of two ligands are in the *cis*-configuration. The high degree of π-conjugation in the S_2CNC_2 ligand fragment is reflected in the planarity of these fragments, as can be seen in Table VI. In contrast to many other dtc complexes[4], the metal atom lies in the plane of the S1S1′C1N1 ligand and is only slightly shifted from the plane of the S2S3C5N2 ligand (0·1 . . 10^{-10} m). This fact documents the relatively free packing of the moleculs in the structure with weak van der Waals intermolecular interactions which is in agreement with the high thermal vibrations of the carbon atoms of the allyl groups.

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