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The Reaction of Fe(II) with Ethylthioxanthate: Isolation and X-ray Structural Characterization of $[(CH_3)_4N][Fe(S_2CSC_2H_5)_3]$

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The reaction of Fe^{3+} and thioxanthates ($RSCS_2^-$) has been well examined and leads to two types of products depending on the nature of R. With R = C_2H_5 the dimeric compound $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ has been isolated [1] and structurally characterized [2], while the monomeric complex $[Fe(S_2CSC_2H_5)_3]$ proposed as the initial reaction product could not be observed. In contrast, if R = t-C_4H_9 only the monomeric complex $[Fe(S_2CS{-}t{-}C_4H_9)_3]$ is formed [3, 4]. So far, however, no X-ray structures of Fe(II) thioxanthates are available. A similar lack of structural information exists for Fe(II) xanthates of which $[Fe(S_2COC_2H_5)_2]$ and $[Fe(S_2COC_2H_5)_3]^-$ have been reported [5]. In the case of the related N,N-diethyldithiocarbamato ligand the X-ray structure of the dimeric Fe(II) complex $[Fe(S_2CN(C_2H_5)_2)_2]_2$, has been determined [6].

We have investigated the reaction of $FeCl_2 \cdot 4H_2O$ and potassium ethylthioxanthate in organic solvents. In methanol or tetrahydrofuran the reaction mixtures are violet to reddish brown at a $C_2H_5SCS_2^-/Fe^{2+}$ ratio of 0.5–5:1. At considerably higher ratios the solutions are bluish-green. However, the only isolatable products which are formed after addition of R'_4NBr ($R' = CH_3$, C_2H_5) are the air-sensitive compounds $[R'_4N][Fe(S_2CSC_2H_5)_3]$, of which small crystals are bluish-green and larger ones appear black. The preparation of $[(C_2H_5)_4N][Fe(S_2CSC_2H_5)_3]$ (I), its conversion and the X-ray structure of the resulting $[(C_2H_5)_4N]_2[Fe(SC_2H_5)(S_2CSC_2H_5)(S_2CS)]_2$ are described elsewhere [7]. *Anal.* Calc. for I, ($C_{17}H_{35}FeNS_9$): C, 34.15; H, 5.90; N, 2.34%. Found: C, 34.05; H, 5.92; N, 2.30%.

Single crystals of $[(CH_3)_4N][Fe(S_2CSC_2H_5)_3]$ (II) suitable for X-ray structure determination were grown directly from a methanolic reaction mixture. The crystals are monoclinic, space group $P2_1/n$ with $a = 14.971(4)$, $b = 39.597(11)$, $c = 25.167(8)$ Å, $\beta = 105.37(3)°$, $V = 14385.6$ Å^3, $Z = 24$ and $D_x = 1.501$ gcm^{-3}.

Systematically weak reflexions indicate the presence of a superstructure with a unit cell volume three times as large as that of the corresponding subcell. If these weak reflexions are neglected, the translation *b* of the subcell is one third of the corresponding supercell value and the lattice appears to be *C*-centered. Systematic extinctions are characteristic for the space group *C2/c* or its acentric counterpart *Cc*. Due to the centrosymmetric lattice of the superstructure the acentric space group *Cc* can be excluded.

Three-dimensional intensity data neglecting the reflexions of the superstructure were collected on a SYNTEX $P2_1$ four-circle diffractometer (graphite monochromated Mo$K\alpha$ radiation, scintillation counter, $2\theta < 54°$, ω-scan, 5232 total reflexions including 3095 reflexions with $I > 1.96\ \sigma(I)$. During data collection the crystal was cooled to −133 °C by a stream of cold nitrogen.

The crystal structure was solved in the space group *C2/c*. The structural model derived in this way represents a superposition of six slightly different individual images that could be resolved into a set of two statistically–populated arrangements for the anions and the cations. Full-matrix least-squares refinement with anisotropic thermal vibrations of the Fe and S atoms and isotropic temperature factors of the C and N atoms converged at $R_1 = 0.074$ and $R_2 = 0.078$. The hydrogen atoms are not included in the final refinement. Crystals of II consist of discrete $[Fe(S_2CSC_2H_5)_3]^-$ anions and tetramethylammonium cations. The cation features the expected basic geometry and will not be discussed further.

Figure 1 shows the $[Fe(S_2CSC_2H_5)_3]^-$ anion (III) in one of the two possible orientations with the atomic labeling scheme. Distances and angles within the anion which are discussed in the following description are averaged over corresponding values of the two orientations. Selected structural parameters are given in Table I. The FeS_6 coordination unit of III is distorted from a regular octahedron towards a trigonal prism. This distortion can be described by an angle of twist θ between the two triangles which are defined by the sulfur atoms S(1), S(3), S(5) and S(2), S(4), S(6), respectively. The value of 30° corresponds to an undistorted octahedron while the value for a trigonal prism is 0°. Applying the method given by

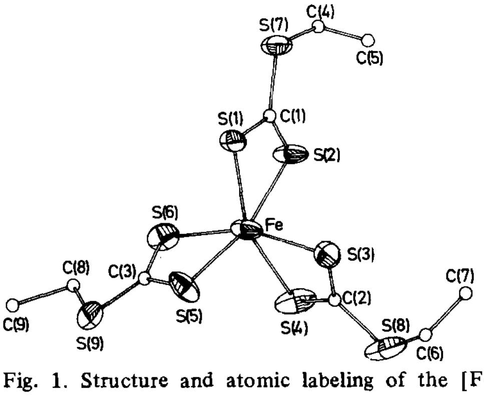

Fig. 1. Structure and atomic labeling of the $[Fe(S_2CSC_2H_5)_3]^-$ anion.

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TABLE I. Selected Average Structural Data of the $[Fe(S_2CSC_2H_5)_3]^-$ Anion.

Bond Lengths and Bite Distance (Å)[a]	
Fe–S	2.52
(Fe–)S–C	1.68
$(C_2H_5–)$S–C	1.73
$S–C_2H_5$	1.80
C–C	1.53
S···S (bite)	2.92
Bond Angles (°)[a]	
S–Fe–S (in the chelate)	71.0
Fe–S–C	84.1
S–C–S, endocyclic	120.5
exocyclic	123.4, 116.0
C–S–C	106.2

[a] Range of individual values with standard deviations: Fe–S 2.48(1)–2.56(1); (Fe–)S–C 1.63(2)–1.73(2); $(C_2H_5–)$S–C 1.69(2)–1.78(2); S–Fe–S 70.0(5)–72.1(5).

Healy and White [8], θ is calculated to be 19.1° for III. This is in good agreement with the value expected from theoretical considerations for a normalized bite of 1.16, as found in the present compound [9].

The average Fe–S bond length of 2.52 Å in III is nearly identical with the theoretical value calculated for Fe(II) in an octahedral sulfur environment [10].

In comparison with Fe–S bond lengths observed within the four-membered chelate rings of hexacoordinated Fe(III) thioxanthato (2.297 Å in $[Fe(S_2CS\text{-}t\text{-}C_4H_9)_3]$ [4], 2.338 Å in $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ [2]), trithiocarbonato (2.330 Å in $[Fe(SC_2H_5)(S_2CSC_2H_5)(S_2CS)]_2^{2-}$ [7]) and xanthato complexes (2.317 Å in $[Fe(S_2COC_2H_5)_3]$ [11]) the Fe(II)–S bond length in III appears to be *ca.* 0.2 Å longer. A structural study of two tris(N,N-dialkyldithiocarbamato)iron(III) complexes revealed a difference of *ca.* 0.1 Å in the mean Fe(III)–S bond lengths of the 'high-spin' (2.41 Å) and 'low-spin' (2.31 Å) states [8]. Compared to the Fe(II)–S distances observed in III the Fe(III)–S bond even in the high-spin state is significantly shorter. This fact must be attributed to the different oxidation states of Fe. A similar relation between Fe–S bond distances and Fe oxidation states is observed in tetrahedrally S-coordinated Fe complexes. In these cases the average Fe–S bond length increases from 2.233 Å to 2.370 Å on passing from Fe(III) to Fe(II) [10].

The angles within the four-membered chelate rings of III are 71.0° (S(1)–Fe–S(2), S(3)–Fe–S(4), S(5)–Fe–S(6)), 84.1° (Fe–S(1)–C(1), Fe–S(2)–C(1), Fe–S(3)–C(2), Fe–S(4)–C(2), Fe–S(5)–C(3), Fe–S(6)–C(3)) and 120.5° (S(1)–C(1)–S(2), S(3)–C(2)–S(4), S(5)–C(3)–S(6). The corresponding angles in $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ are 73.4, 87.0 and 112.6°, respectively [2]. The endocyclic C–S bond distances in the CS_2Fe rings of the two compounds are equal within the limits of experimental error (1.68 and 1.679 Å, respectively). The large S–C–S angle in III is correlated with an S···S bite distance of 2.92 Å which is markedly longer than in the dimeric complex (2.795(3) Å).

The sums of the S–C–S bond angles of the individual ligands of III range from 359.8 to 360.0° indicating planar CS_3 fragments. Two types of exocyclic S–C–S angles can be distinguished, of which the averages are 116.0 and 123.4° respectively. The larger angle opens to the side of the ethyl group. Corresponding observations on other iron thioxanthato complexes [2, 4, 7] have been explained by the steric requirements of the alkyl group. This also seems to be the most reasonable explanation in the case of III. As a result of partial p_π–p_π bonding the average exocyclic $C(sp^2)$–S bond with a length of 1.73 Å is shorter than a C–S single bond. The Pauling bond order-bond length relation as used by Merlino [12] gives partial double bond characters of 19% for the exocyclic C–S bond and 40.5% for each of the endocyclic ones. Similar values have been obtained for other thioxanthato and xanthato complexes [4].

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