The Crystal and Molecular Structure of the Predominantly Low-spin Complex Tris-(*O*-ethylxanthato)iron(III)

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Summary The crystal structure of tris-(*O*-ethylxanthato)-iron(III) has been determined, and shows structural features of the co-ordination sphere about the iron atom which are significantly different from those found for tris-(*NN*-di-n-butyldithiocarbamato)iron(III).

Iron(III) derivatives of certain *NN*-substituted dithiocarbamates possess magnetic moments which are temperature[1] and pressure[2,3] dependent and which are very sensitive to minor changes in the nature of the substituents of the co-ordinating groups.[1] This anomalous behaviour has been explained in terms of a ligand-field "cross-over" situation involving a thermal equilibrium between the two possible ground states $^2T_2$ and $^6A_1$ which are usually separated by an energy difference of approximately kT.[1,2]

The magnetic measurements recorded for tris-(*O*-xanthato)- and tris(diphosphato)-complexes of iron(III) suggest that the xanthates, with the exception of the tris-(*O*-ethylxanthato)-complex, are characteristically low-spin (μ *ca.* 2·45 B.M. at room temperature) whereas the dithiophosphates are high-spin compounds (μ *ca.* 5·80 B.M. at room temperature).[2] Tris-(*O*-ethylxanthato)iron(III) ($\mu = 2{\cdot}19$

B M. at 108°K and 2 72 B M at 296°K)[2] has magnetic properties very closely related to those of the predominantly low-spin complex tris-(*NN*-di-isopropyldithiocarbamato)-iron(III) (μ = 2 10 B M at 109°K and 2 70 B M at 295°K)[1]

We report here the crystal structure of tris-(*O*-ethylxanthato)iron(III) which we have determined by *X*-ray diffraction methods at room temperature The six sulphur atoms of the xanthate complex are at almost equal distances from the iron atom, there being two independent crystallographic distances of 2 308 and 2 326 Å each with an estimated standard deviation (e s d) of 0 003 Å They are situated at the corners of two parallel equilateral triangles, 2 48 Å apart, where one triangle is rotated with respect to the other by 41° from the trigonal prismatic configuration as is shown in the Figure This configuration differs significantly from that reported[3] for the predominantly high-spin complex tris-(*NN*-di-n-butyldithiocarbamato)-iron(III) (μ = 5 32 B M at 264°K)[1] Here the sulphur atoms are at an average distance of 2 418 (0 006) Å from the iron atom situated at the corners of two parallel equilateral triangles, 2 87 Å apart, where one triangle is rotated relative to the other by only 32° from trigonal prismatic geometry For these two FeS_6-type complexes the iron-sulphur bond lengths differ by 0 10 Å This value is in excellent agreement with the earlier observations[2] based on the pressure dependence of magnetic susceptibility of iron(III) dithiocarbamates dissolved in non-polar solvents The transfer of two e_g electrons to t_{2g} orbitals in passing from the $^6A_1$ ($t_{2g}^3e_g^2$) to the $^2T_2$ ($t_{2g}^5e_g^0$) state was accompanied by an estimated contraction of the iron-sulphur distance of 0 1 Å

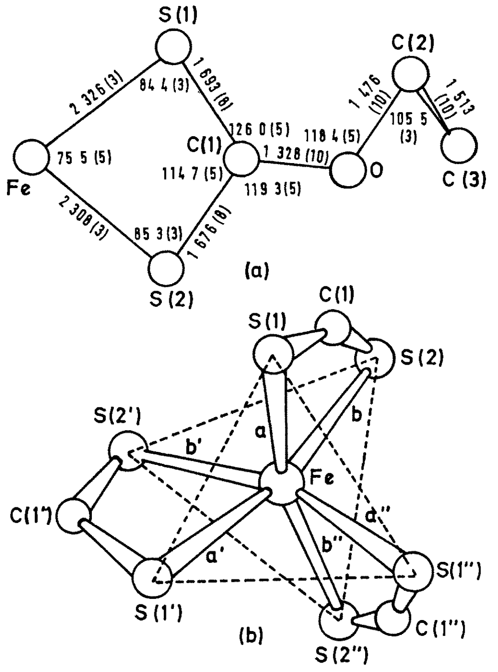

FIGURE (a) *Molecular dimensions of the independent ligand of tris-(O-ethylxanthato)iron(III) e s d 's are shown in brackets*

(b) *The co ordination sphere about the iron atom Dimensions are* a = 2 326, b = 2 308 Å, ∠aa' = 93 9, ∠bb' = 94 2, ∠ab' = 98 5, ∠a'b = 164 1°, ∠ab = 75 5°

The average carbon to sulphur bond length of 1 69 (0 008) Å agrees well with previously reported values found for structures involving this and similar ligands[3,4] The carbon to carbon bond distance of 1 51 (0 01) Å agrees well with previously reported values for the carbon to carbon single bond length[5]

There are two carbon to oxygen bonds in the xanthato-group, one has a length of 1 48 (0 01) Å and is the bond between the oxygen atom and a carbon atom of the ethyl group whereas the other has a length of 1 33 (0 01) Å and is the bond between the carbon atom of the S_2C-group and the oxygen atom The longer bond has a slightly greater length than the value of 1 426 Å given for carbon to oxygen single bond distances found in paraffinic alcohols[5] The bond of length 1 33 Å appears to possess considerable double bond character

Crystal data $C_9H_{15}S_6O_3Fe$, black hexagonal prisms, rhombohedral, $a_{\text{hex}} = 14\ 910 \pm 0\ 003$, $c_{\text{hex}} = 13\ 318 \pm 0\ 003$ Å $U_{\text{hex}} = 2564$ Å^3, $D_{\text{m}} = 1\ 62$ (by flotation), $Z_{\text{hex}} = 6$, $D_{\text{c}} = 1\ 63$ g cm $^{-3}$, space group $R\bar{3}$ (C_{3i}^2, No 148)

The intensities of 557 independent reflections were measured with a Siemens automatic diffractometer to a maximum θ of 70° using Fe-K_α radiation, 47 of these reflections were regarded as unobserved The crystal was coated with a thin layer of Shellac to prolong its life No significant variation in the intensities of the standard reflections was observed during the course of data collection Absorption corrections were made

The structure, excluding the hydrogen atoms, was solved using Patterson and Fourier methods and was refined by a full-matrix least-squares procedure applying anisotropic temperature factors to the individual atoms The *R* value at convergence was 0 067 The crystals are composed of discrete molecules of the neutral complex The iron atoms occupy positions of site symmetry 3 The molecular dimensions are shown in the Figure

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