A Novel Stereochemical Form for Iron(III)

By B. F. HOSKINS* and B. P. KELLY

(Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria, 3052, Australia)

THE iron(III) derivatives of the dialkyldithiocarbamic acids exhibit anomalous magnetic behaviour.[1] The magnetic moments of these compounds are temperature-dependent and very sensitive to minor changes in the alkyl substituents of the co-ordinating groups. It was suggested that this behaviour could be explained in terms of an octahedral model for the iron atom and a thermal equilibrium between nearly equi-energetic high-spin ($^6A_1$) and low-spin ($^2T_2$) ground states.[2]

We have determined the crystal structure of tris-(*NN*-di-n-butyldithiocarbamato)iron(III) at room temperature; the effective magnetic moment at room temperature of the solid compound is 5·32 B.M. We have found that the iron atom is bonded to six sulphur atoms, and has a configuration which is far from octahedral and which is better described as intermediate between a trigonal prism and a trigonal antiprism, as is shown in the Figure.

Crystal data: $C_{22}H_{54}N_3S_6Fe$, $M = 669$, monoclinic, $a = 22{\cdot}46$, $b = 10{\cdot}50$, $c = 18{\cdot}40$ Å, $\beta = 120{\cdot}8°$, $U = 3782$ Å^3, $D_m = 1{\cdot}19$ (by flotation), $Z = 4$, $D_c = 1{\cdot}18$, space group $C\,2/c(C^6_{2h}$, No. 15); Co (unfiltered) radiation, single-crystal oscillation and equi-inclination Weissenberg photographs. The structure was solved by the usual heavy-atom method and refined initially by successive difference Fourier syntheses and then by the full-matrix least-squares method, using individual anisotropic temperature factors. At present, the R value is 0·10 based on observed reflections only.

Crystals of the compound are composed of discrete molecules of the neutral complex. The iron atoms occupy positions with site symmetry 2. The six sulphur donor atoms of the complex are equi-distant from the iron atom and are arranged in two parallel equilateral triangles, 2·87 Å apart. One triangle is rotated by an angle of 32° relative to the other, from the trigonal prismatic configuration. The average iron–sulphur bond length is 2·418 Å [with an estimated standard deviation (e.s.d.) of 0·006 Å]. Other molecular dimensions are shown in the Figure.

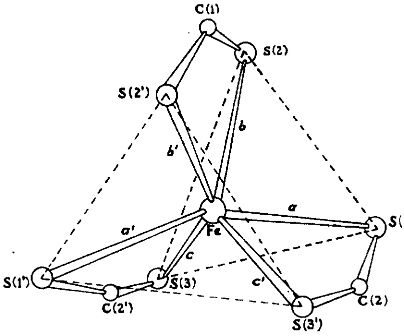

FIGURE. *The co-ordination sphere of tris-*(NN-*di-n-butyldithiocarbamato*)*iron*(III). *Measurements are;* $a = 2{\cdot}413$, $b = 2{\cdot}426$, $c = 2{\cdot}415$ Å; $\angle bb' = 72{\cdot}5°$, $\angle ac' = 72{\cdot}9$, $\angle cc' = 106{\cdot}0$, $\angle ab = 103{\cdot}5°$.

There are no significant differences in the dimensions of the crystallographically-independent ligand groups. The average sulphur–carbon bond length of 1·71 Å (with an e.s.d. of 0·02 Å) compares favourably with other dithiocarbamates, but the average carbon–nitrogen bond length of 1·41 Å (with an e.s.d. of 0·03 Å) is slightly longer than others previously reported for similar compounds. The dimensions observed for the dithiocarbamate group and the planar environment of the nitrogen atom indicate marked delocalisation of the π-electrons, which is consistent with previous i.r. studies[3] and structure determinations.[4]

Finally we note that each of the three crystallographically-independent n-butyl chains has a different conformation.

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[1] L. Cambi and L. Szego, *Ber.*, 1931, **64**, 2591; L. Cambi, A. Cagnasso, and A. Tanara, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1931, **13**, 254; L. Cabmi, L. Szego, and A. Cagnasso, *ibid.*, 1932, **15**, 266, 329; L. Cambi and L. Szego, *Ber.*, 1933, **66**, 656; L. Cambi and L. Malatesta, *ibid.*, 1937, **70**, 2067.

[2] A. H. White, R. Roper, E. Kokot, H. Waterman, and R. L. Martin, *Austral. J. Chem.*, 1964, **17**, 294.

[3] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Nature*, 1956, **177**, 1042.

[4] M. Bonamico, G. Mazzone, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, 1965, **19**, 898; M. Bonamico, G. Dessy, C. Mariani, A. Vaciago, and L. Zambonelli, *ibid.*, p. 619; M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, *ibid.*, p. 886.