The Crystal and Molecular Structure of Nitrosyliron Bis-(*NN*-diethyldithiocarbamate)

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IN 1956 Alderman and Owston established, by two-dimensional *X*-ray techniques, the geometry of the complex [Co(NO)(S_2CNMe_2)$_2$] to be that of a rectangular-based pyramid.[1] They suggested that the nitric oxide molecule—which they found to occupy the apical position and to be inclined at an angle of approximately 135° to the vertical axis of the pyramid—might form an unsymmetrical π-bond with the cobalt atom. Later, in collaboration with J. M. Rowe,[2] they confirmed their previous hypothesis.

To our knowledge this remains the only example of interaction between the metal electrons and the π-electrons of the N–O multiple bond. We thought that the complex $[Fe(NO)(S_2CNEt_2)_2]$[3] might provide another example and we have therefore determined its crystal and molecular structure by three-dimensional *X*-ray techniques (also as a part of our research programme on the structure of metal dithiocarbamates).

Crystals of $[Fe(NO)(S_2CNEt_2)_2]$ are dark green and crystallize in the monoclinic system; $a = 14{\cdot}90 \pm 0{\cdot}02$, $b = 9{\cdot}44 \pm 0{\cdot}02$, $c = 12{\cdot}99 \pm 0{\cdot}02$ Å, $\beta = 108° \ 32' \pm 8'$; $U = 1732{\cdot}4$ Å^3; $D_m = 1{\cdot}46 \pm 0{\cdot}01$ g.cm.$^{-3}$ (by flotation); $Z = 4$; $D_c = 1{\cdot}466$ g.cm.$^{-3}$; $F(000) = 793{\cdot}1$. Space group: $P2_1/c$ from systematic absences. Data from Weissenberg photographs, Fe-K_α ($\lambda = 1{\cdot}9374$ Å) radiation.

The structure was solved by Patterson, trial, and Fourier methods, using 655 independent reflections from photographic records. Co-ordinates and isotropic temperature factors were refined by full-matrix least-squares to the present set of values, corresponding to $R = 0{\cdot}151$.

The co-ordination sphere of the complex is shown in the Figure. The iron atom is penta-co-ordinated, the co-ordination polyhedron being a rectangular-based pyramid with the nitric oxide molecule at the apex. The four sulphur atoms are coplanar within experimental error; the iron to sulphur distances are not significantly different and agree with recent literature values.[4] The iron atom is 0·63 Å above the basal plane of the co-ordination polyhedron. A very similar co-ordination geometry has recently been found[5] for the iron(III) complex $[FeCl(S_2CNEt_2)_2]$.

The iron, nitrogen, and oxygen atoms are approximately collinear within experimental error, as has been found for sodium nitroprusside.[6] Thus the geometry of the metal–(NO) system in $[Fe(NO)(S_2CNEt_2)_2]$ is different from that found in $[Co(NO)(S_2CNMe_2)_2]$, and no unsymmetrical metal–(NO) π-bond is formed, in spite of the close similarity of the remaining features of the structure. A detailed discussion of the geometry of the iron compound and of its bearing on the electronic structure of the metal–(NO) system is however deferred until further refinement based on a fuller set of diffractometer data is carried out.

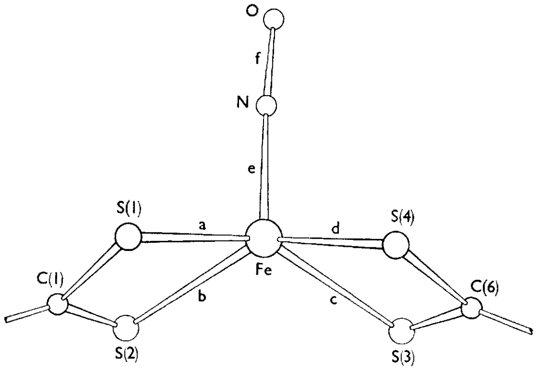

FIGURE. *The co-ordination sphere of nitrosyliron bis-*(NN-*diethyldithiocarbamate*). *Bond lengths are*: a = 2·28 (1), b = 2·30 (1), c = 2·30 (1), d = 2·26 (1), e = 1·69 (4), f = 1·16 (5) Å. *The angles* S(1)–Fe–S(2), S(3)–Fe–S(4), *and* Fe–N–O *are* 76·0° (0·5), 76·0° (0·5), *and* 174° (4) *respectively. Values in parentheses are estimated standard deviations.*

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[3] Compounds $[Fe(NO)(S_2CNR_2)_2]$ were first described by L. Cambi and A. Cagnasso, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1931, **VII**, **13**, 254, and by L. Cambi, *Z. anorg. Chem.*, 1941, **247**, 22. The electronic spectrum and structure of the methyl compound were discussed by H. B. Gray, I. Bernal, and E. Billig, *J. Amer. Chem. Soc.*, 1962, **84**, 3404, who also pointed out that the NO vibrational absorption at 1735 cm.$^{-1}$ indicates that the nitrosyl group can be considered as NO^+.

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