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

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IN earlier work[1] we described a two-dimensional *X*-ray study of [Co(NO)(S_2CNMe_2)$_2$]; the molecule has the form of a rectangular-based pyramid, with the nitric oxide molecule at the apex, and we found that the angle Co–N–O was ~135°, and suggested that there might be a π-type interaction between the nitric oxide molecule and the metal atom, analogous to that in ethylene complexes. We later[2] examined the isomorphous analogue [Fe(NO)(S_2CNMe_2)$_2$] using partial three-dimensional diffraction data, and found the same molecular structure, but were unable to achieve satisfactory resolution of the nitric oxide group. We have now repeated the analysis. Meanwhile Colapietro *et al.*[3] have published the preliminary results of their analysis, using isotropic temperature factors, of the related complex [Fe(NO)(S_2CNEt_2)].

Crystal data: $C_6H_{12}FeN_3OS_4$, M = 326·1; monoclinic, a = 6·434 ± 0·003, b = 13·817 ± 0·005 c = 16·658 ± 0·005 Å, β = 117·27 ± 0·02°; U = 1316·4, D_m (by flotation) = $1{\cdot}65_3$ D_c = $1{\cdot}64_5$; Z = 4; space group $P2_1/c$ (C_{2h}^5, No. 14); Mo-K_α radiation. A Picker automatic diffractometer was used to measure all the reflections with $\sin\theta/\lambda < 0{\cdot}6$; 1651 independent structure factors of significant amplitude were used in the analysis, and refinement by the anisotropic least-squares method led to a final discrepancy index R of 0·104.

TABLE

Thermal parameters (Å^2) *derived by least-squares analysis assuming a single oxygen atom*

	U_{11}	$2U_{12}$	$2U_{13}$	U_{22}	$2U_{23}$	U_{33}
Fe	0·0390	−0·0012	0·0395	0·0511	0·0029	0·0351
N	0·0722	−0·0067	0·0713	0·0981	0·0153	0·0569
O	0·2872	−0·0204	0·1608	0·0955	0·0004	0·0789

Our results (see Figure) show a close similarity to those obtained by Colapietro *et al.* In particular we agree that the nitrogen atom lies on the pyramidal axis of the co-ordination polyhedron, the nitric oxide molecule being bound to the metal through the nitrogen atom only; there is clearly substantial π-character in the Fe–N bond, which is 0·1—0·2 Å shorter than any reasonable value of the single-bond radius sum, but there is no other π-type interaction between the N–O multiple bond and the metal atom. This result casts doubt on our earlier suggestion that such an interaction might occur in the cobalt analogue. Infrared spectra show that there is a considerable difference between the NO groups in [Co(NO)(S_2CNMe_2)$_2$] and its iron analogue [ν(N–O) = 1627 and 1690 cm.$^{-1}$ respectively] but not enough to suggest that the bonds are of different types.

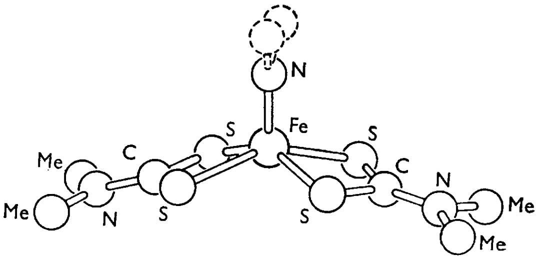

FIGURE. *The structure of* Fe(S_2CNMe_2)$_2$NO, *showing the probable disorder of the oxygen atoms.* [Fe–S = 2·294(2), S–C = 1·709(6), C–N = 1·34(1), N–Me = 1·48(1), Fe–N = 1·705(16) Å].

Colapietro *et al.* find the angle Fe–N–O = 174° (e.s.d. 4°) and N–O = 1·16 Å (e.s.d. 0·05 Å) in [Fe(NO)(S_2CNEt_2)$_2$]. Our results at the same stage of the analysis led to similar conclusions, but a study of the anisotropic thermal parameters (see Table) shows that the oxygen atom is subject to thermal vibrations of high amplitude (>0·5 Å r.m.s.) or to static disorder, along a direction approximately parallel to the crystallographic a axis. The electron density map, in which the electron cloud of the oxygen atom is greatly elongated in the x-direction can reasonably (but very imprecisely) be interpreted as the mean of two structures differing only in the position of the oxygen atom, and both having Fe–N–O ≈160° and N–O ≈1·1 Å. Our least-squares analysis, on the other hand, deduces the position of the oxygen atom to be mid-way between these two structures, giving the values Fe–N–O = 173·3° (e.s.d. 1·5°) and N–O = 1·02 Å (e.s.d. 0·02 Å).

The disordered structure is clearly closer to physical truth than that given by the least-squares method, in which both the molecular parameters for the NO group and their estimated standard deviations are misleading. The limits of error in all the studies referred to in this Communication are at present too wide to allow reliable conclusions to be drawn on the linearity of the M–N–O group, and we hope to repeat the analysis of $[Co(S_2CNMe_2)_2NO]$ and $[Fe(S_2CNMe_2)NO]$ at low temperatures in an attempt to clarify the bonding of the NO group in these complexes.

This work points to the need for caution in interpreting *X*-ray results, unless the anisotropic thermal parameters have been derived and critically examined.

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[1] (a) P. R. H. Alderman and P. G. Owston, *Nature*, **1956**, **178**, 1071; (b) P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *J. Chem. Soc.*, 1962, 668.

[2] P. G. Owston and J. M. Rowe, unpublished results.

[3] M. Colapietro, A. Domenicano, L. Scaramuzza, A. Vaciago, and L. Zambonelli, *Chem. Comm.*, 1967, 583.