The Structure of a Dianionic Nitrosyl Dithiolene Complex of Iron

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THE dianionic nitrosyl dithiolene complex $[Fe(NO)S_4C_4(CN)_4]$ has been prepared as part of an investigation into the properties of five-co-ordinate dithiolene nitrosyl species.[1,2] The compound crystallises in the space group $P2_1$ with two anions in a unit cell of dimensions: $a = 7{\cdot}511$, $b = 14{\cdot}214$, $c = 15{\cdot}084$ Å, $\beta = 92°24'$. The crystal structure has been solved by the usual combination of Patterson and Fourier methods on the basis of 877 non-equivalent reflexions measured using a "Pailred" automatic single crystal diffractometer. Refinement by block-diagonal least-squares has yielded a reliability index, $R = 0{\cdot}089$. Anisotropic thermal motion was allowed for in the case of the iron and sulphur atoms only and the contribution to the structure factors of both the real and the imaginary parts of the anomalous scattering factor of iron were included.

The structure and geometry of the anion are shown in the Figure. The average standard deviations in the bond lengths range from 0·01 Å in the case of Fe–S to 0·06 Å for the C–C bonds. None of the differences between formally equivalent bonds are therefore significant and the bond lengths and angles in the dithiolene ligands are consistent with those found elsewhere.[3] The mean Fe–S bond is 1·27 Å and the iron is displaced 0·51 Å from the plane containing the four sulphurs.

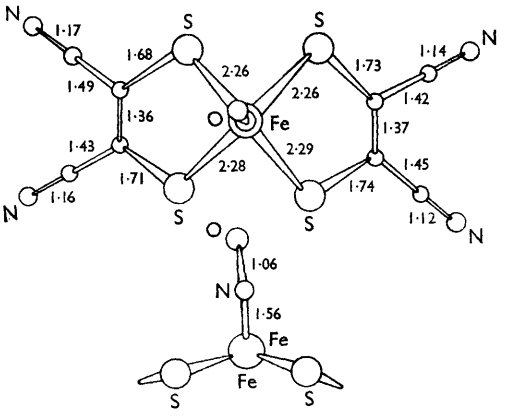

FIGURE. *The structure and geometry of* $Fe(NO)S_4C_4(CN)_4$; *all distances in* Å.

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Considerable interest centres on the geometry of the Fe–NO system. McCleverty *et al.*,[2] have studied the infrared spectrum of the compound and report an NO stretching frequency of between 1620 and 1650 cm.$^{-1}$. They point out that this has been taken as characteristic of a π-bonded M–NO system[4] such as is observed in the structure of nitrosobis-(*NN*-dimethyldithiocarbamate)cobalt.[5] In this molecule the nitrosyl group makes an angle of 137° with the axis of the square pyramid, the point of intersection being near the mid-point of the NO bond. In a recent structure analysis of nitrosyliron bis-(*NN*-diethyldithiocarbamate), however, the nitrogen lies on the pyramidal axis and the Fe–N–O angle is 174°—not significantly non-linear. In the present analysis, the nitrogen atom is not significantly displaced from the apical axis and the Fe–N–O angle equals 168°. Because of large thermal motion of the oxygen atom this value is within two standard deviations of 180° whereas changes in the nitrogen and oxygen positions of the order of 10 σ would be required to reproduce a geometry similar to that of the aforementioned cobalt complex.

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