Large Mössbauer Quadrupole Splittings in High-spin Iron(II) Complexes: the Structure of Di-iodo-1,5,9,13-tetrathiahexadecaneiron(II) [or 1,5,9,13-Tetrathiahexadecaneiron(II) Di-iodide]

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The adducts FeI_2·(16[ane]S_4) and $FeBr_2$·(16[ane]S_4) are high-spin complexes with temperature-independent quadrupole splittings *ca.* 4.0 mm s^{-1} of a type that has been previously associated with five-co-ordination; *X*-ray analysis shows that this structure is better described as covalent octahedral or ionic square planar.

We have synthesized new adducts FeI_2·(16[ane]S_4) and $FeBr_2$·(16[ane]S_4) by direct reaction of the thioether with the iron(II) halide in acetonitrile under reflux. Under the same conditions, the iron(II) chloride is unreactive. The complexes are 2 : 1 electrolytes in nitromethane or in acetonitrile, and in the solid state at room temperature have magnetic moments of 5.13 (iodide) and 5.80 (bromide) μ_B. The Mössbauer spectra at 77 K and at room temperature are very similar. The iodide at 77 K has a chemical shift (*vs.* natural iron) of 0.94(1) mm s^{-1} and a quadrupole splitting (q.s.) of 4.10(1) mm s^{-1} [corresponding values at room temperature are 0.82(1) and 4.06(1) mm s^{-1}]. The values for the bromide are 0.96(1) and 3.60(1) mm s^{-1}, respectively, at 77 K.

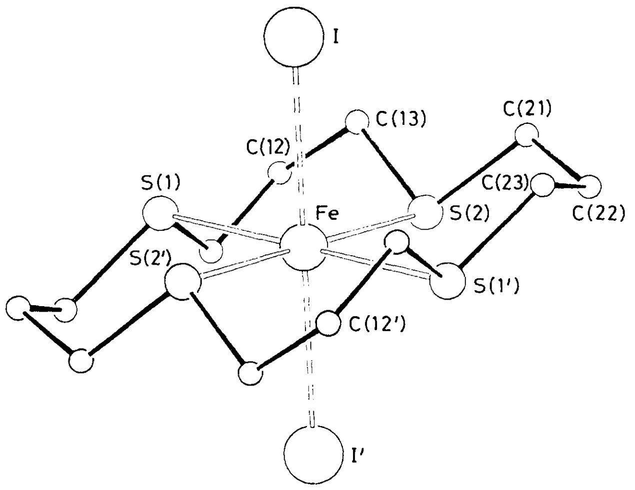

Figure 1. View of the complex FeI_2·(16[ane]S_4) showing the basic square planar (or octahedral) co-ordination.

These data suggest high-spin iron(II) in a five-co-ordinate square pyramidal environment.[1] To confirm that this is the case, we determined the structure, with the results shown in Figure 1.†

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† *Crystal data:* $C_{12}H_{24}FeI_2S_4$, $M = 606.2$. Monoclinic, space group $P2_1/c$ (no. 14), $a = 7.4831(6)$, $b = 13.6242(8)$, $c = 9.3983(6)$ Å, $\beta = 91.133(6)°$, $U = 958.0$ Å^3. $Z = 2$, $D_c = 2.101$ g cm^{-3}. $F(000) = 584$, μ(Mo-K_α) = 43.8 cm^{-1}, λ(Mo-$K\bar{\alpha}$) = 0.71069 Å.

Crystals are small yellow parallelpipeds. Preliminary *X*-ray photographic examination. Cell dimensions (from settings of 25 reflections with θ *ca.* 14°) and diffraction measurements (to $\theta_{max} = 25°$) on our Enraf-Nonius CAD4 diffractometer (with monochromated radiation). Corrections applied for Lorentz, polarisation and absorption effects; no crystal deterioration detected. Structure determined by heavy atom method,[9] and refined by full-matrix least-squares methods to convergence, $R = R_w = 0.019$[9] for all 1685 unique data, weighted $w = \sigma_F^{-2}$. Hydrogen atoms refined independently with isotropic thermal parameters; other atoms refined anisotropically. Scattering factors for neutral atoms from ref. 10. Computer programs, as above and in Table 4 of ref. 11, run on the MicroVAX II in the N.F.L. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Figure 1 suggests that there is octahedral co-ordination around the iron. In this centrosymmetric structure, the iron is in the plane of the four sulphur atoms and the Fe–S distances are 2.475(1) and 2.485(1) Å, which are longer by *ca.* 0.1 Å than usual iron–sulphur (thioether) separations, as far as we can judge,[2] though these are not for high-spin compounds. There is little apparent strain in the thioether ring (which has a novel conformation for derivatives of this cyclic ligand). The Fe–I separations are 2.8896(2) Å, which is close to the sum of the ionic radii of Fe^{2+} and I^- (*ca.* 2.92 Å).[3] The usual range of covalent Fe–I separations is 2.6 ± 0.1 Å.[4] There are close contacts between the iodine atoms and some of the methylene hydrogen atoms, but no apparent steric pressure that would force such a large iron–iodine separation. On this basis we conclude that the iron–iodine bond is largely ionic and that the co-ordination about iron is equally well described as square planar.

If the structure is taken to be tetragonally distorted octahedral, the splitting of the d-orbitals and their occupancy should be in the increasing order $d_{xy}^2 < d_{xz}^1, d_{yz}^1 < d_{x^2-y^2}^1 < d_{z^2}^1$, with the large q.s. arising from a large separation of the d_{xz}, d_{yz} degenerate pair and the d_{xy} orbitals.[5] On the other hand, if we consider the structure to be square planar, the order of orbitals should be $d_{z^2}^2 < d_{xz}^1, d_{yz}^1 < d_{xy}^1 < d_{x^2-y^2}^1$. Whether the iron–iodine bonds are better described as ionic or as covalent is a matter of opinion. This question should be resolvable by determining the sign of the field gradient. Nevertheless, it is quite clear that q.s. values of *ca.* 4 mm s^{-1} in high-spin iron(II) compounds are not a reliable criterion of five co-ordination as previously considered for high-spin porphyrin complexes.[6–8] However, high-spin iron(II) has not yet been found bound fully in the plane of the porphyrin.[1]

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