

## The Crystal Structure of Bis(dithioacetylacetonate) Tetrachloroferrate(II) [Bis(3,5-dimethyl-1,2-dithiolium) Tetrachloroferrate(II)]

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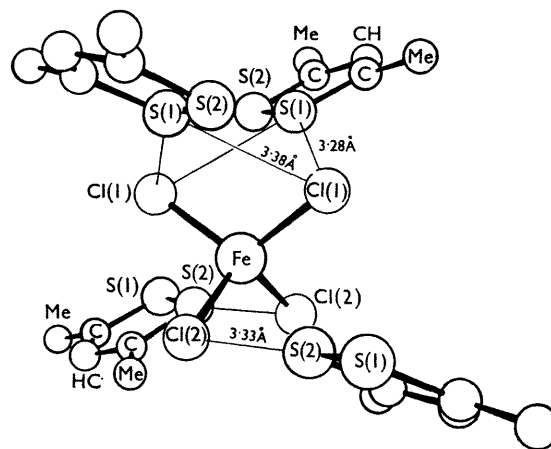
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THE preparation<sup>1</sup> of complexes of the type  $M^{II} \text{sacsac}_2$  [ $\text{sacsacH} = \text{dithioacetylacetonate}$ ], and the structure analysis<sup>2</sup> of the complex in which  $M = \text{Co}$ , suggested<sup>3</sup> that a  $\text{Fe}^{II}$  complex of the same ligand might be a structural model for biological systems in which  $\text{Fe}(\frac{2}{8})$  clusters are believed to play a part. A complex with the composition  $\text{Fe saccac}_2 \text{Cl}_4$ , prepared under the same reaction conditions as  $\text{Co saccac}_2$ , appeared to fit this role. The subjective evaluation of its colour as being "schwarzrot"<sup>3a</sup> or "violet"<sup>3b</sup> led to two tentative structural assignments<sup>3</sup> in both of which disulphide groups were shown as participating in the co-ordination.

An X-ray crystal structure analysis has now shown that  $\text{Fe saccac}_2 \text{Cl}_4$  consists of 3,5-dimethyl-1,2-dithiolium [ $= \text{saccac}^+$ ] cations and  $\text{Fe}^{II} \text{Cl}_4^{2-}$  anions. The structure is shown in the Figure. A two-fold symmetry axis passes through the Fe atom. The tetrachloroferrate(II) ion is tetrahedral [ $\text{Fe}-\text{Cl}(1) = 2.34(1)$ ,  $\text{Fe}-\text{Cl}(2) = 2.31(1) \text{ \AA}$ ], the angles subtended at the Fe atom by the pairs of symmetry-related chlorine atoms being  $116^\circ$  [ $\text{Cl}(1)-\text{Fe}-\text{Cl}(1)$ ] and  $112^\circ$  [ $\text{Cl}(2)-\text{Fe}-\text{Cl}(2)$ ], respectively.

The 3,5-dimethyl-1,2-dithiolium cations are planar and (at the present level of refinement) have dimensions which do not differ significantly from the corresponding values in the iodide salts of the 3-phenyl,<sup>4</sup> 4-phenyl,<sup>5</sup> and 3,5-diamino-1,2-dithiolium<sup>6</sup> cations. The mean bond-lengths in  $\text{saccac}^+$  (and their estimated standard deviations) are S-S,  $2.03(1)$ ; S-C,  $1.69(2)$ ; C-CH,  $1.36(3)$ ; and C-CH<sub>3</sub>,  $1.53(3) \text{ \AA}$ . The mean bond-angles (standard deviation =  $1-1.5^\circ$ ) are S-C-CH,  $118^\circ$ ; S-C-CH<sub>3</sub>,  $117^\circ$ ; CH<sub>3</sub>-C-CH,  $125^\circ$ ; C-CH-C,  $115^\circ$ , and C-S-S,  $94.5^\circ$ . From a survey of the structures of compounds with sulphur-sulphur and carbon-sulphur bonds, Hordvik<sup>7</sup> has assigned standard bond-lengths of  $2.10$ ,  $1.89$ ,  $1.82$  and  $1.61 \text{ \AA}$  to pure S-S (*cis*-planar), S=S, C-S, and C=S bonds, respectively. In agreement with the description of other 1,2-dithiolium cations,<sup>7,8</sup> the S-S bonds in  $\text{saccac}^+$  then have significant (0.33) double-bond character and the C=S bonds have considerable (0.67) double-bond character. We note that,

with the exception of  $l(\text{S}-\text{S})$ , the bond-lengths in the free cation are not significantly different from those in the chelated dithioacetylacetonato [ $= \text{saccac}^-$ ] anion;<sup>2</sup> the bond-angles necessarily differ.



FIGURE

The five atoms of the tetrachloroferrate(II) ion all make their closest contacts with sulphur atoms of four surrounding  $\text{saccac}^+$  cations. The Fe atom has two S(1) neighbours at  $3.52 \text{ \AA}$ . The Cl atoms likewise make contacts of the types  $\text{Cl}(1) \cdots \text{S}(1) = 3.28$ ,  $\text{Cl}(1) \cdots \text{S}(1) = 3.38$ , and  $\text{Cl}(2) \cdots \text{S}(2) = 3.33 \text{ \AA}$ , respectively.

The structure reported here entirely confirms that suggested independently by Heath, Martin, and Stewart<sup>9,10</sup> on the basis of new spectroscopic and magnetic measurements for this and related complexes. It also provides a reason why a crystal composed of two types of almost colourless complexes should appear to have such an intense absorption in the visible spectral region. Each  $\text{FeCl}_4^{2-}$  anion makes six, and each  $\text{saccac}^+$  cation three,  $\text{Cl} \cdots \text{S}$

contacts which are significantly shorter than the sum of the conventional van der Waals radii<sup>11</sup> of S and Cl, 3.65 Å. This implies that charge-transfer absorption is taking place. An analogous charge-transfer effect occurs<sup>12</sup> in the intensely coloured crystalline FeCl<sub>4</sub><sup>2-</sup> salt of 4-(*N*-methylpyridinio)-*N*-methylpyridinium dication, where the chlorine-nitrogen contacts are abnormally short. Charge transfer has likewise been given as the reason for the short S · · I<sup>-</sup> distances found in 4-phenyl-1,2-dithiolylium iodide.<sup>5</sup>

Crystal data: Bis(dithioacetylacetonate)tetrachloroferate(II) crystallised in the form of deep red (nearly black) prisms from aqueous solution:<sup>3</sup> C<sub>10</sub>H<sub>14</sub>Cl<sub>4</sub>FeS<sub>4</sub>, *M* = 460.2, monoclinic, *a* = 17.71(1), *b* = 7.67(1), *c* = 15.86(1) Å,

$\beta = 122.2(1)^\circ$ , *D*<sub>m</sub> = 1.68, *Z* = 4, *D*<sub>c</sub> = 1.68 g.cm.<sup>-3</sup>,  $\mu = 161$  cm.<sup>-1</sup>; space group *C2/c*; 1537 reflections, of which 438 were unobservably weak, were recorded with Cu-K<sub>α</sub> radiation by a computer-controlled Supper equi-inclination diffractometer. The structure was solved by standard Patterson and Fourier methods, and has been partially refined by full matrix least-squares. The present residual *R* is 0.12 (for the observed reflections alone).

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<sup>9</sup> Preceding Communication.

<sup>10</sup> Dr. H. A. O. Hill (Oxford) has informed us that his recent measurements of the Mössbauer spectrum of Fe sacsa<sub>2</sub> Cl<sub>4</sub> also lead to the same result (H. A. O. Hill, C. E. Johnson and R. Rickards, to be published).

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