

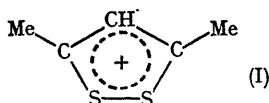
Dithiolylium Derivatives of some Transition Metals

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MONOMERIC SQUARE-PLANAR DITHIOACETYLACETONATO-COMPLEXES $[M \text{ saccac}_2]$, where $\text{saccac} = \text{MeCS}\cdot\text{CH}\cdot\text{CSMe}$ and $M^{\text{II}} = \text{Co}, \text{Ni}, \text{Pd}, \text{or Pt}$, have been isolated from the reaction of acidified alcoholic solutions of acetylacetonate with hydrogen sulphide in the presence of the appropriate metal ion.^{1,2} However, a similar reaction in the presence of ferrous³ or ferric^{3,4} ions gave a violet crystalline product, $\text{Fe}(\text{C}_5\text{H}_7\text{S}_2)_2\text{Cl}_4$, the deep colour of which led Knauer *et al.*,⁴ to suggest the presence of "Fe-SS co-ordination". Furuhashi *et al.*,⁵ supported this suggestion and, on the evidence of i.r. spectral data, assigned relative strengths to the proposed metal-sulphur bonds. However, the crystals transmit more light in the visible region than the very intensely coloured chelates, such as $[\text{Co saccac}_2]$ and $[\text{Fe saccac}_2]$, which contain metal-sulphur bonds.

We now present evidence which excludes the presence of iron-sulphur bonds and confirms that the compound is properly formulated as a tetrachloroferrate(II) salt of the 3,5-dimethyl 1,2-dithiolylium cation (I). This cation is, in



fact, the dominant ion observed in the mass spectra of all $[M \text{ saccac}_2]$ chelates,¹ and has been isolated as a picrate⁴ from an aqueous solution of the tetrachloroferrate.

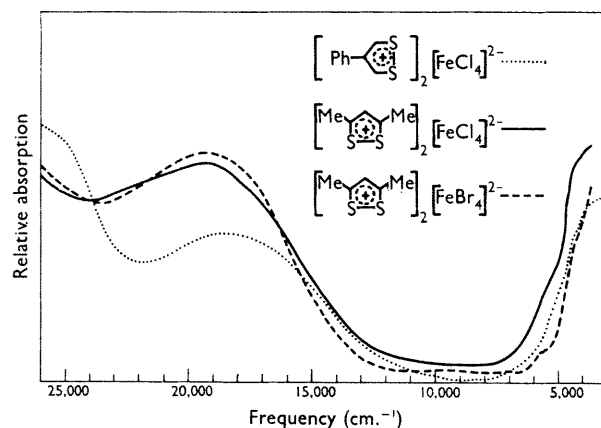
The iron complex is a member of an extended series of crystalline compounds $(\text{C}_5\text{H}_7\text{S}_2)_2\text{MX}_4$, which have been isolated^{6,7} for $M^{\text{II}} = \text{Mn}, \text{Fe}, \text{Co}, \text{or Ni}$, and $\text{X} = \text{Cl or Br}$; all have i.r. spectra ($2000\text{--}300 \text{ cm}^{-1}$) which are so closely similar that an isostructural series is likely. Manganese(II) and iron(II) complexes have been prepared previously; isolation of the cobalt(II) and nickel(II) halogeno-derivatives, however, requires oxidative addition of the simple chelates $[M \text{ saccac}_2]$ by a halogen,⁷ a method used for the preparation of the simple salts of the 3,5-dimethyl 1,2-dithiolylium cation (I^- , I_3^- , and ICl_2^-). The striking similarity between the i.r. spectra of the last-named compounds and those of the tetrahalogenometallates implies that the $[\text{C}_5\text{H}_7\text{S}_2]^+$ cation retains its identity in the latter.

Admixture in ethanol of 4-phenyl 1,2-dithiolylium chloride with metal chlorides yields an analogous series of complexes $(\text{C}_9\text{H}_7\text{S}_2)_2\text{MCl}_4$; since their magnetic and spectral properties

are closely similar to those of $(\text{C}_5\text{H}_7\text{S}_2)_2\text{MCl}_4$ no difference in their structure is likely. In this case, the synthetic procedure removes any doubt concerning their formulation as tetrachlorometallate(II) salts.

Diffuse reflectance spectra (especially for the cobalt and nickel compounds) and magnetic studies ($100\text{--}300^\circ \text{K}$) unequivocally confirm the existence of the tetrahedral $[\text{MX}_4]^{2-}$ anions in the crystalline state. Agreement between our work and the published data⁸ for these anions is excellent. For the $(\text{C}_5\text{H}_7\text{S}_2)_2\text{FeCl}_4$ complex, we observe $\mu_{\text{eff}}(293^\circ) = 5.30 \text{ B.M.}$, a value substantially higher than reported elsewhere⁵ and known to be typical of tetrahedral iron(II).⁹

Although the crystalline ferrate(II) complexes $(\text{C}_5\text{H}_7\text{S}_2)_2\text{FeCl}_4$, $(\text{C}_5\text{H}_7\text{S}_2)_2\text{FeBr}_4$, and $(\text{C}_9\text{H}_7\text{S}_2)_2\text{FeCl}_4$ are all deep violet, they yield nearly colourless solutions. Examination of the reflectance spectra (undiluted samples) reveals that the colour is due, in each case, to a broad absorption band centred near $20,000 \text{ cm}^{-1}$ (see Figure). Since neither the



FIGURE

dithiolylium cations nor $[\text{FeX}_4]^{2-}$ anions absorb light appreciably in the visible region, we conclude that the band in the solid has its origin in the transfer of charge from the strongly reducing tetrahalogenoferrous anion to the delocalised dithiolylium cation. The rather close contacts

observed between the Cl and S atoms (see following Communication) in the $(C_5H_7S_2)_2FeCl_4$ complex suggest a convenient pathway for this charge transfer.

Finally, the Mössbauer spectrum¹⁰ of $(C_5H_7S_2)FeCl_4$ at room temperature displays well-defined quadrupole splitting

into two lines ($\Delta E_Q = 1.46$ mm./sec.) which characterizes the spectra reported for tetrachloroferrate(II) salts of quite different cations.⁹

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