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This Week's Citation Classic

Smith D W & Williams R J P. The Spectra of ferric haems and haemoproteins. *Struct. Bond.* 7:1-45, 1970.
[Dept. Chemistry, University of Sheffield, Sheffield, and Inorganic Chemistry Lab., Oxford, England]

The electronic spectra of ferric haems and haemoproteins are reviewed. Their analysis requires explicit consideration of mixing between π-π* and charge transfer states, as well as the effects of axial coordination and the recognition of spin equilibria. The probe properties of spin equilibria are discussed. [The *SCI*® indicates that this paper has been cited over 120 times since 1970.]

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"In mid-1965, I began my doctoral work in Bob Williams's group in Oxford. I was then mainly interested in ligand field spectra, and I inherited from Andy Thomson a homemade microspectrophotometer for making single crystal measurements. It was a temperamental brute, driven by a battery of lead accumulators, but capable of good spectra given due care and attention. Measurements were best made-in the dead of night, and the hours I kept caused my landlady to harbour doubts about my morals and sobriety. Bob's infectious enthusiasm soon seduced me into bio-inorganic chemistry, and we decided upon a study of ferrimyoglobin crystals. We began by making an expedition to 'that other place' (i.e., Cambridge) to pick the protein experts' brains at the MRC laboratory. I began to have second thoughts about the whole thing when Chris Nobbs asked about our supplies of whale meat, and explained the elaborate extraction and crystallisation procedure. But in the end, he kindly donated to us a generous supply of beautiful crystals. These provided us with useful information about the much-neglected near infrared spectra of ferrimyoglobin and its derivatives; we were also able to make some measurements on cytochrome-c. We then turned to a general interpretation of the electronic spectra of ferric haems and haemoproteins. Bands could be identified as arising from the high-spin and low-spin forms, both present in equilibrium, and could be assigned as porphyrin π-π* transitions or as ligand-to-metal charge transfer transitions, with extensive configuration interaction. Peter Day's understanding of charge transfer spectra came in useful here. Gaussian analysis of the spectra made it possible to determine the relative amounts of the two spin states in several axiallysubstituted derivatives.

"The work on ferrimyoglobin was relevant to studies of other haemoproteins, and after completing my D. Phil, thesis in 1968 I suggested to Bob that we publish a review together. The first 30 pages of the article as it appeared in print were largely abstracted from my thesis, while the last section, dealing with the probe properties of spin equilibria, was entirely Bob's work.

"I would like to think that the article has been extensively cited because it presents a comprehensive analysis of Fe(III)-porphyrin spectra, useful in the study of spin equilibria and axial coordination in haemoproteins. But I suspect that the article's popularity owes more to the provocative speculations and penetrating insights in Bob's contribution. The use of electronic spectra in studies of haemoproteins has, to a great extent, been overtaken by the rapid developments in other techniques in the 1970s. These are reviewed in A.S. Brill's admirable monograph."[1]

1. **Brill A S.** *Transition metals in biochemistry*. Berlin: Springer-Verlag, 1977. p. 81-117.