Exchange Coupling in Binuclear Oxy-bridged Iron(III) Protoporphyrin IX Dimethyl Ester

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Summary μ-Oxo-bis[protoporphyrin IX dimethyl ester iron(III)] gave magnetic susceptibility data from 1·5 to 293 K which fit a model dimer with strong anti-ferromagnetic exchange coupling (2*J* 380 K) between high-spin iron(III) atoms.

Recent studies of dimeric iron(III) complexes of porphyrins[1] and other ligands[2] with μ-oxo-linkages suggest a possible function for such linkages in heme and other iron proteins. The importance of exchange-coupled metal 'clusters' in metalloproteins[3-6] has recently emphasized the need for understanding the relationship between structure of polynuclear metal compounds and their biochemical function. We report here the detailed magnetic properties of a dimer of protoporphyrin IX (prepared nearly free of ferromagnetic impurity), a porphyrin widely found in heme proteins. Chlorohemin was esterified by methanol–sulphuric acid and chromatographed on alumina to yield μ-oxo-bis[protoporphyrin IX dimethyl ester iron(III)] with λ_{max} (ϵ_{mM}) of 397(138), 573(15·3), and 601 nm (13·0) in benzene and ^{1}H chemical shifts in p.p.m. from Me_4Si of 9·3 ($CH\!:\!CH_2$), 5·86 ($CH\!:\!CH_2$), 5·21 (ring Me), 6·29 (α-CH_2), and 2·83 (β-CH_2) in $CDCl_3$ at 30°.

Magnetic studies were performed with material (*ca.* 200 mg) on a vibrating sample susceptometer[7] (77—1·5 K) or a conventional Faraday balance[8] (2·2—300 K). Measurements of magnetic moments were made as a function of field at nine points from 2 to 18 kG for temperatures $> 2{\cdot}2$ K. The moments were linear in field to 3 kG even at 2·2 K and no indication of ferromagnetic impurities was obtained. At temperatures > 10 K moments were linear in field to 18 kG. At $\leqslant 2{\cdot}2$ K moments were measured from 500 to 3 kG and susceptibilities were calculated from the low-field linear part of the moment *vs.* field curve. Identical data were obtained on two occasions.

The results are shown in the Figure and the Table. The theoretical susceptibilities as functions of temperature were calculated in standard fashion.[9] The most significant aspect of the data is the typical antiferromagnetic behaviour of increasing paramagnetism with increasing temperature, and the accuracy with which it can theoretically fit the Heisenberg $2J\bar{S}_1.\bar{S}_2$ model of antiferromagnetic interaction. This permits not only a choice between the cases of coupled spins 1/2 or 5/2, but also an accurate determination of the coupling energy, 2*J*. Only a model of coupled spins 5/2 fits the data. Any value of 2*J* for coupled spins 1/2 which yields the increase of paramagnetism observed at high temperatures would be a maximum at < 200 K, in disagreement with experiment. The high-spin model implies a relatively weak ligand field at iron, consistent with there being no ligand *trans* to the oxygen bridge and the idea that the iron atoms are significantly out of the plane of porphyrin nitrogens (as in other high-spin hemins[10]) in the direction of the interior of the 'hemin sandwich'.

Table

Magnetic moments for μ-oxo-bis[protoporphyrin IX *dimethyl ester iron*(III)]

T/K	μ^2/BM^2 [a]
296	2·4
213	1·5
78	0·09

[a] For definition see ref. 3. Paramagnetism attributed to a small amount of paramagnetic impurity has been substracted to obtain these values. It has a value 0·1 BM^2 at 293 K.

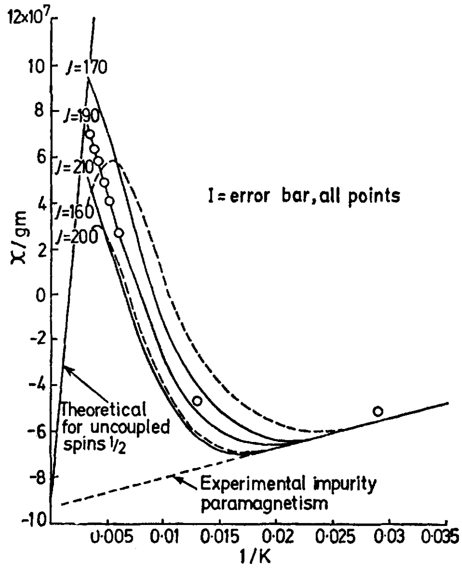
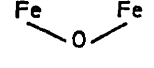


Figure. *Temperature dependence of* χ *the magnetic susceptibility of μ-oxo-bis[protoporphyrin* IX *dimethyl ester iron*(III)], *with theoretical curves for various coupling strengths. Theoretical curves for coupled high-spin ions* (—), *for low-spins* (- - - -). *Data points* (O). 2J = *energy splitting to first excited* (*magnetic*) *state of coupled spin system.*

The coupling obtained (2*J* 380 K) is extraordinarily strong. Such values have been observed for superexchange coupling between ions with half-filled orbitals through a single bridging oxygen atom[11] in a linear system. It is not within the range of couplings observed for ions bridged by two ligands at 45° to the metal–metal axis (I).



(I)

The small Curie law paramagnetism (linear in T^{-1} to 1·5 K) is almost certainly due to a small amount of paramagnetic impurity. By measuring the temperature dependence of the susceptibility to 1·5 K, (far below the temperature at which uncoupling of the paired iron spins takes place) we have obtained the impurity contribution and subtracted it in the data analysis to obtain $2J$. This paramagnetism corresponds to $< 1\%$ of the total iron with spin 5/2. In earlier, less pure samples, problems in reducing the paramagnetic impurities were encountered which resulted in difficulty in detecting uncoupling of the sample spins and, in general, created uncertainties in interpreting fundamental antiferromagnetic properties. Studies of bridged compounds in which susceptibilities are measured at a single temperature suffer severely from these uncertainties. Intermediate susceptibilities for possible Fe–O–Fe bridged compounds have been measured at room temperature and interpreted[12] as '$S = 1$ dimers'. Our data indicate that either small amounts of impurities, or the onset of thermal disordering of a coupled spin system could also produce the intermediate values. The data also indicate that it is possible for all ten d electrons to be coupled in an $\mathrm{Fe^{III}}$ dimer with weak-field ligands (in contrast to reasoning in ref. 12).

Susceptibility values at three temperatures [$\mu_{\mathrm{eff}} = 1{\cdot}15$ (293), 0·76 (195), and 0·45 (77 K)] were obtained by Fleischer and Srivastava[1c] for a dimeric iron tetraphenylporphyrin. These values were lower than the free spin values and increased with increasing temperature, indicating antiferromagnetism in that system. These values do not fit theoretical predictions for a system of paired spins 1/2 or 5/2, however, probably indicating small amounts of paramagnetic impurities in the sample. If the moment at 77 K is taken as a measure of the impurity and subtracted from the higher temperature values, the system agrees with a coupled spin 5/2 with an even greater $2J$ value, 550 K, than those which are observed in our work.

Because we can measure the coupling paramater so accurately in dimeric hemins, here within 3—5%, and because the orbital overlap causing such exchange is extremely sensitive to bond distances, bond types, and angles, this may be a fruitful system for studies on the basic mechanisms of exchange coupling.

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