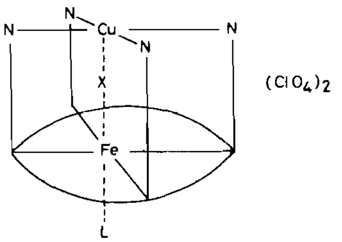
strongly magnetically coupled Fe(III)–Cu(II) centre at the cytochorme a_3 active site in the oxidized form of cytochrome c oxidase [1]. In an attempt to mimic the essential features of this centre we have synthesized [2] model complexes of a binucleating porphyrin, (P)–(N$_4$), where (N$_4$) is a tetrapyridine moiety covalently attached to the *meso*-phenyl groups of tetraphenylporphyrin. The structure adopted by a range of mixed Fe(III)/Cu(II) derivatives is shown schematically below and consists of an Fe(III) porphyrin bridged by an anion such as Cl^-, Br^-, N_3^- or CN^- to a Cupy$_4$-like group.



The X-ray structure of the X=Cl complex shows long Fe–Cl and Cu–Cl distances leading to a Cu–Fe distance of *ca.* 5 Å. The magnetic susceptibility of this complex was determined over the range 300–4.2°K and shows behaviour atypical of either exchange-coupled or magnetically isolated high-spin Fe(III)/Cu(II). E.s.r. signals at g ~ 6 and *g* ~ 2 are observed below 40 °K in agreement with the presence of high-spin Fe(III) and Cu(II). Mössbauer data, however, show the existence of two electronic states on the Fe, probably $S = 3/2$ and $S = 5/2$, the proportions of which vary with temperature. The bromo and azido bridged derivatives show similar X *vs.* T plots to the chloro but with lower μ_{eff} values at higher temperatures, and again with little evidence for any exchange-coupling, the CN^- bridged complex, however, shows markedly different magnetic behaviour, a preliminary interpretation of which is compatible with significant exchange-coupling between the metal centres. Calculations are in progress attempting to rationalize these data. They will be discussed together with comparisons between the magnetic behaviour of the model complexes and of the enzyme.

References

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Ab-initio Computations in Biomolecules: Electronic Charge Variations due to the Solvent Field

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A number of molecular systems like bases and base-pairs of nucleic acids, amino acids in the neutral and zwitterionic forms, have been studied theoretically (*ab-initio* SCF-LCAO-MO computations) in the gas phase at 0 K and solution at 300 K (Monte Carlo simulations). Most recently we have recomputed the charge density for such systems not in the gas phase (see above), but in presence of few hundreds water molecules, placed at positions obtained from the Monte Carlo simulations. The electronic charge densities are *different* from those computed in the gas phase; the differences are small in absolute value, but *very significant,* since they exhibit a very local character, that seems to be specific of the local region in a biomolecule (hydrophobic, hydrophilic regions). Additional work is in process, relating this analysis to reaction field formalism and simulations.

Stereochemical Lability: Inferences from Solid State Structural Data

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Electronic rearrangements by solvent interactions are almost always accompanied by significant changes in the molecular structure of the compound under consideration, *i.e.* electronic lability is accompanied by stereochemical lability. Thus, spin crossovers in transition metal compounds are accompanied by a change in metal to ligand bond distances or even a change in coordination number. In the Berry process observed for trigonal bipyramidal molecules, the two axial ligands with characteristic electron rich bonding are transformed into two equatorial ligands with more or less normal bonding and *vice versa.* Dynamically distorted Cu(II) compounds with six chemically equivalent ligands oscillate between three equal, isoenergetic structures. In each of the three structures a different pair of *trans*-positioned ligands shows long metal to ligand bond distances with corresponding differences in the ligand to metal σ-antibonding e_g-orbitals.