the Jahn–Teller stabilization energy E_{JT} never exceeds the energy of a quantum $h\nu$ of the corresponding active vibrational modes substantially. The degree of covalent delocalization of the singly occupied degenerate metal 3d orbital over the ligand rings correlates well with Jahn–Teller distortion increasing strongly along the series $Fe(cp)_2^+ < Mn(cp)_2 < Co(cp)_2 < Ni(cp)_2^+$.

This finding agrees with the predictions of semiempirical MO calculations. In the solid state, by systematic variation of the host lattice we were able to observe a stepwise transition from a purely dynamic Jahn–Teller effect to the static distortion limit in the case of cobaltocene. Alkyl substituents at the rings influenced the cobaltocene EPR spectra in the same way as asymmetric lattice potentials.

Electrical Anharmonicity for the OH Stretching Vibration of Methanol and its Hydrogen Bonded Complexes

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We have calculated the first and second dipole moment derivatives for a number of hydrogen bonded systems involving methanol and a variety of organic bases. Herman and Shuler's [1] expressions for the intensities of fundamental and first overtone are employed for the calculations. Both ++ and +– combinations of experimental values of transition moment integrals R_0^1 and R_0^2 are considered. Given below are the typical values of μ_1 and μ_2 for the two sign combinations in the case of dilute solutions of CH_3OH in CCl_4 representing free OH and CD_3OH in DMSO-d_6 as well as self associated CD_3OH in CD_3OD. It is found that for all the systems considered both for ++ and +– combinations μ_1 as well as μ_2 increase on hydrogen bonding. Often a reference is made in the literature that the intensity of the first overtone band of XH stretching vibration decreases on hydrogen bonding whereas that of the fundamental increases. On the basis of these observations a decrease in the overtone intensity can be explained on the basis of the fact that the negative contribution to the overtone intensity from an increase in the first derivative of the dipole moment supersedes the positive contribution from the increase in the second derivative of the dipole moment. This explanation is quite justified as it can be noticed from the above values that whereas μ_1 increases about 4 to 5 times on hydrogen bonding in the cases considered in these studies, μ_2 only increases by 50 to 10%.

This observation is similar to the prediction made by Di Paolo, Bourderon and Sandorfy [2] on the basis of their theoretical model calculations on the influence of Electrical Anharmonicity on infrared intensities in hydrogen bonded systems. However, contrary to their predictions it is rather clear from these studies that the decreasing intensities of first overtones on hydrogen bonding can be explained by taking +– combinations as nicely as from ++ combinations of transition moment values.

Methanol in	++ comb.		+– comb.	
	$\mu_1 \times 10^{20}$	$\mu_2 \times 10^{20}$	$\mu_1 \times 10^{20}$	$\mu_2 \times 10^{21}$
CCl_4	4.567	1.017	4.770	8.094
DMSO-d_6	20.443	1.641	20.750	3.943
CD_3OD	23.545	2.033	23.952	4.936

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Synthetic Models for Cytochrome-C Oxidase: Magnetic and Mössbauer Effect Studies of Binuclear Fe(III) Porphyrin–Cu(II) Complexes

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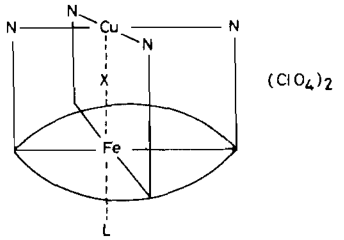
Recent e.s.r., magnetic susceptibility and m.c.d. measurements have indicated the presence of a strongly magnetically coupled Fe(III)–Cu(II) centre at the cytochorme a_3 active site in the oxidized form of cytochrome c oxidase [1]. In an attempt to mimic the essential features of this centre we have 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 $g \sim 6$ and $g \sim 2$ 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.

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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.