of 679-fold. If the electronic effects are not taken into consideration the apparent rate enhancement, i.e., $(k_e/k_n)_{obsd}$, is actually larger (6250). The corrected rate enhancements obtained by placing a phosphate moiety on either the epoxide inhibitors or the inhibitors in Figure 1 correspond to a $\Delta\Delta G^{\ddagger}$ value ($\Delta G^{\ddagger}_n - \Delta G^{\ddagger}_e$) of 3.8 ($\pm$0.1) kcal/mol. This is a measure of the specific interaction of the phosphate moiety with the enzyme in the transition state.

Conclusion

The interpretation of an enzymic rate enhancement is dependent on the choice of the model compound, The model compound (a) should have the same reactive residue as present in the enzyme, (b) should produce the same product as that formed by reaction with the enzyme, (c) should not deviate in reactivity relative to other similar model compounds except with respect to electronic effects, and (d) should be normalized to the same electronic effects present in the enzymic residue (i.e., have a pK_a similar to that of the enzymic residue). The substituent effects on the reaction of the inhibitor (or the substrate) with the enzyme which contribute to this rate enhancement can be separated into two general factors: "electronic" and "steric". A plot of the logarithm of the enzymic rate constants versus the logarithm of the nonenzymic rate constants for a variety of substituted inhibitors (or substrates) should yield a straight line (if there is no change in the rate-limiting step with changing substituents). The slope, λ, is an index of the difference in electronic sensitivities of the enzymic and nonenzymic reactions and any deviations from this line indicate factors other than electronic ones which contribute to this rate enhancement.

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Communications to the Editor

Paramagnetic Anisotropy and Zero-Field Splitting in Tetraphenylporphyrinatoiron(III) Chloride

Sir:

Tetraphenylporphyrinatoiron(III) chloride (TPPFeCl) is a synthetic analogue of naturally occurring chlorohemin and resembles it very closely at least as far as the magnetic properties and coordination around the iron atom are concerned. In TPPFeCl the ferric ion is in high spin state ($S = 5/2$) with $^6S_{5/2}$ electronic ground state. The degeneracy of the sextet is partly removed by the combined effect of spin-orbit coupling and axial ligand field, to give three Kramers doublets, namely $M_s = \pm 1/2$, $\pm 3/2$, and $\pm 5/2$. A spin Hamiltonian of the form

$$\mathcal{H} = DS_z^{\,2} \qquad (1)$$

gives the energy separation between the Kramers doublets $M_s = \pm 1/2$ and $M_s = \pm 3/2$ as $2D$, and that between $M_s = \pm 3/2$ and $M_s = \pm 5/2$ as $4D$, where D is the zero-field splitting (ZFS) parameter.

The ZFS is an important physical parameter in the high spin d^5 system. Its accurate determination has, therefore, evoked a continuing interest for a long time.[1] Several efforts have, for example, been made to determine accurately the ZFS in TPPFeCl and other hemin compounds. The average magnetic moment of TPPFeCl down to 2.2 K has been analyzed[2] on the basis of the above spin Hamiltonian, which gives $D = 11.8$ cm^{-1}. A similar value of D was obtained from the analysis of temperature dependence of isotropic proton shift studies on this compound.[3] The ZFS of a number of ferric porphyrins has also been determined directly by far-infrared techniques.[4] Though such measurements have not been reported for TPPFeCl, the ZFS in chlorohemin and protoporphyrin dimethyl ester iron(III) chloride has been determined very accurately by this technique, giving $D = 6.95$ cm^{-1} in both the compounds.[5] This value is evidently much smaller than the above value for the analogous TPPFeCl. The difference is especially surprising in the case of chlorohemin as its magnetic properties (down to 2.2 K) are very similar to TPPFeCl.[2] In view of this discrepancy and the interest in the ZFS in TPPFeCl, we have determined the ZFS in TPPFeCl from the measurements of paramagnetic anisotropy in the 80-300 K temperature range. Our measurements, contrary to the previous results, give $D = 5.9 \pm 0.1$ cm^{-1} in this compound.

TPPFeCl was prepared by the method described in the literature.[6] It was purified by column chromatography using a neutral silica-gel column (100–200 mesh) and using benzene solvent. The TPPFeCl gets adsorbed at the top of the column. It was eluted with benzene containing 10% (V/V) ethanol. The compound was characterized by elemental analysis and by its spectrum in the UV-visible region. The spectrum was taken in chloroform and was recorded on a Carl-Zeiss spectrophotometer. The peak positions agreed very well with those re-

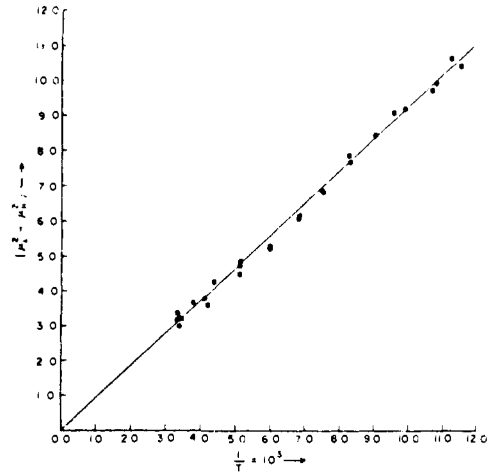

Figure 1, Temperature dependence of $(\mu_\perp^2 - \mu_\parallel^2)$ of TPPFeCl. The circles are experimental data, and the solid line is the theoretical plot for $D = 5.9$ cm^{-1}.

ported for TPPFeCl in the same solvent.[7] Large well-developed single crystals weighing up to 1-5 mg were grown from dichloromethane. The identity of the crystals was established by taking x-ray photographs and matching the unit cell constants and space group reported for TPPFeCl.[8] The unit cell constants matched, within the experimental errors, the reported values. The crystal anisotropies were measured by a null deflection method[9] using the equipment described earlier.[10] The overall error in the measurement is estimated to be not more than 2%. The single crystals of TPPFeCl belong to a tetragonal system, with the porphyrin skeletons of the different molecules so arranged in the unit cell that the Fe-Cl bond directions of all the molecules are parallel to the c axis of the crystal.[8] The crystal anisotropy is then the same as the molecular anisotropy $(K_\perp - K_\parallel)$; the parallel and perpendicular subscripts refer to the quantity parallel and perpendicular to the c axis of the crystal. The observed anisotropy must, however, be corrected for diamagnetic anisotropy due to the porphyrin skeleton, which is expected to be significant. The paramagnetic anisotropies were thus obtained by correcting the observed values by the diamagnetic anisotropy of nickel(II) tetraphenylporphyrin.[11] The corrected experimental anisotropies are plotted in Figure 1 in the form of $(\mu_\perp^2 - \mu_\parallel^2)$ vs. $1/T$. Here $(\mu_\perp^2 - \mu_\parallel^2) = 7.997(K_\perp - K_\parallel)_c T$; $(K_\perp - K_\parallel)_c$ is the experimentally measured corrected molecular anisotropy and μ_i, the principal magnetic moment.

The experimental results in Figure 1 show that $K_\perp > K_\parallel$, implying that D is positive.[1,12] Including the g anisotropy in eq 1, the principal magnetic moments μ_i are given by:

$$\mu_\parallel^2 = \frac{3g_\parallel^2[1 + 9e^{-x} + 25e^{-3x}]}{4[1 + e^{-x} + e^{-3x}]}$$

$$\mu_\perp^2 = \frac{3g_\perp^2[9 + (16 - 11e^{-x} - 5e^{-3x})/x]}{4[1 + e^{-x} + e^{-3x}]} \qquad (2)$$

where

$$x = 2D/kT$$

If $D/kT \ll 1$, which is generally true in the liquid nitrogen temperature range, eq 2 can be simplified and written as:

$$(\mu_\perp^2 - \mu_\parallel^2) = \frac{35}{4}(g_\perp^2 - g_\parallel^2) + (g_\perp^2 + 2g_\parallel^2)\frac{28D}{3kT} \qquad (3)$$

The intercept of the plot of $(\mu_\perp^2 - \mu_\parallel^2)$ vs. $1/T$ would give, according to eq 3 the g anisotropy. The experimental data so plotted in Figure 1 establish that the g anisotropy is almost zero in TPPFeCl. Thus taking $g_\perp = g_\parallel = 2$, the fit of the experimental data to eq 2 gives $D = 5.9 \pm 0.1$ cm^{-1}. In deducing this value, more stress was given in fitting the experimental data below 200 K, so that even large uncertainty in the diamagnetic anisotropy of TPPNi will not significantly affect the value.[13]

The value of the ZFS parameter for TPPFeCl, deduced from the measurements of paramagnetic anisotropy, is thus in disagreement with the values reported from the analysis of the low temperature average magnetic moment and isotropic proton shift studies. However, the present value, as expected, is very close to that of the analogous chlorohemin and protoporphyrin dimethyl ester ferric chloride. It is interesting to note that the analysis of average magnetic susceptibility data has also given an incorrect value of D for chlorohemin and an explanation of this discrepancy has earlier been given.[14]

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Modification of Chlorobenzene Photoreactivity through Exciplex Formation

Sir:

The photochemistry of aryl halides is believed to involve aryl radicals as reactive intermediates.[1] Most often, these radicals are proposed to arise through bond homolysis (eq 1), though in some cases there is evidence to suggest that electron transfer from a donor to the excited aryl halide can occur.[2,3] The resulting aryl halide radical anion then expels a halide ion[4] (eq 2).

$$\mathrm{ArX^*} \rightarrow \mathrm{Ar^\cdot} + \mathrm{X^\cdot} \qquad (1)$$

$$\mathrm{D} + \mathrm{ArX^*} \rightarrow \mathrm{D^{+\cdot}} + \mathrm{ArX^{-\cdot}} \rightarrow \mathrm{Ar^\cdot} + \mathrm{X^-} \qquad (2)$$

The fate of the aryl radical depends on the medium. In aromatic solvents, arylation occurs,[5] while in solvents liable to hydrogen abstraction, reductive dechlorination is the major reaction pathway.[2,3,6] Under certain circumstances, the aryl radical may combine with a nucleophile, leading ultimately to substitution by the $\mathrm{S_{RN}1}$ mechanism.[7]

Recently, Fox et al. suggested a third possible reaction pathway.[8] Photolysis of chlorobenzene in cyclohexane solution gave a remarkably high yield of chlorocyclohexane. Cleavage according to eq 1 seemed to be ruled out, on the grounds that both phenyl and chlorine are reactive radicals and should both