able to us. This is by using the Bleaney–Bowers approximation,[15] where it is assumed that J_1 and J_2 (from excited states) in eq 6 are equal to each other and equal

$$D_{\text{exch}} = -(1/8)[(J_1(g_{\parallel} - 2)^2/4) - J_2(g_{\perp} - 2)^2] \quad (6)$$

to the ground-state $2J$ value. D_{exch} is calculated from eq 7, D_{dd} was calculated above using eq 5, and D_{exptl} is

$$D_{\text{exptl}} = D_{\text{dd}} + D_{\text{exch}} \quad (7)$$

obtained from epr data ($D_{\text{exptl}} = 0.028$). It can also be assumed that D_{exch} and D_{dd} have opposite signs.[16] The range of values of $|2J|$ calculated is 21–293 cm^{-1}. Our value of $+24.0$ cm^{-1} is located at the low end of that range.

The use of the modified Langevin equation (eq 2) should be reviewed. If the constant Θ has a finite value, it means that there are additional interactions present, most likely lattice (or sublattice) effects. A negative Θ indicates that the lattice tends to line the spins among the dimers in an antiparallel fashion. It should be obvious that the use of the Langevin equation without Θ would assume the nonexistence of any additional lattice effects and would actually lump all the additional effects together with the pairwise interaction in the value of $2J$. If, as is the case here, there are additional lattice antiferromagnetic effects, one would expect a smaller calculated value of $2J$ if Θ is disregarded That is what is seen, with the absolute values of $2J$ from ref 2 quite a bit lower than ours (7 and 1 *vs.* $+24.0$ cm^{-1}).

The energy value for this lattice interaction is small, about 1 cm^{-1}, but is quite noticeable at low temperatures, where the values of kT approach that value. It is interesting to note that the only other compound[17] with a positive $2J$ value reported outside this laboratory where appropriate data are available, bis(acetylacetonato)nickel(II), also shows a weak lattice antiferromagnetism at low temperatures. In that case $2J = +37$ cm^{-1} and $\Theta = -0.2°$. It appears, then, to be advisable when working in the low-temperature range, to test the experimental fit by using the Weiss constant Θ.

The biological implications of the type of spin interactions described here for $[\text{Cu(edtc)}_2]_2$ are not completely apparent at the present time. However, this same type of behavior might be displayed by other compounds of biological importance, where the out-of-plane coupling has been assumed weak or nonimportant. We are presently engaged in the study of some of these systems, in particular of tetrakis(tyrosinato)dicopper(II)[18] in order to shed some additional light on this important question.

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Proton Knight Shifts and Antiferromagnetic Exchange in Binuclear Oxo-Bridged Iron(III) Porphyrins

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The temperature dependence of the Knight shifts of the pyrrole protons in the binuclear porphyrins μ-oxo-tetraphenylporphineiron(III) and μ-oxo-tetra(p-methylphenyl)porphineiron(III) have been used as a direct measure of the isotropic exchange parameter J. The values obtained are somewhat larger than those obtained from magnetic susceptibility data obtained for similar compounds in the solid phase. It is proposed that the reason for the increased value of J is the slight increase in the Fe(III)–O–Fe(III) bond angle which it is considered could occur when these binuclear chelates exist in solution.

The solvent conditions permitting hemin aquation or heme autoxidation may frequently lead to the formation of binuclear oxo-bridged iron(III) porphyrins.[1] The synthesis, characterization, and structure of μ-oxo-bis(tetraphenylporphine)iron(III) was studied by Fleischer and Srivastava.[2] The magnetic data for this compound gave $\mu_{\text{eff}} = 1.15$ BM, clearly indicating an antiferromagnetic interaction between the iron(III) atoms. The Fe–O–Fe bond angle was found to be 168° involving a tilting of the porphyrin rings though the remainder of the tetraphenylporphyrin structure is much the same as for other porphyrins. The room-temperature magnetic data for μ-oxo-bis(tetraphenylporphineaquoiron(III)) ions reported by Cohen,[3] who determined μ_{eff} to be 1.74 BM per ion and interpreted the results of previous magnetic studies of hemins in terms of mixtures of high-spin hydroxo and low-spin oxo binuclear species.

The nmr spectra of iron(III) porphyrins have been studied to measure Fermi contact shifts,[4] contact shift

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interactions,[5] axial ligand interactions,[6] and the transmission of electronic effects.[7] It is the purpose of the present investigation to use the temperature dependence of the proton magnetic Knight shifts as a means of evaluating the isotropic exchange parameter J of the oxo-bridged binuclear iron(III) porphyrins.

Experimental Section

Tetraphenylporphineiron oxide $(FeTPP)_2O$ and tetra(p-methylphenyl)porphineiron oxide $(FeTpMPP)_2O$ were prepared by the method of Fleischer.[2] (Deuteroporphyrin IX dimethyl ester)iron oxide $(FeDPIXDME)_2O$ was prepared by the method of Caughey, *et al.*[1]

Proton nmr were obtained in $CDCl_3$ solutions on a Varian HA 100 spectrometer operating in an HR mode over a temperature range 250–320°K using a standard Varian variable-temperature control unit calibrated from the chemical shifts of methanol. The chemical shifts were relative to TMS and their positions were measured by the side-band technique. The free-base proton chemical shifts were measured for the ligands to give diamagnetic proton positions.

The Theory of Knight Shifts in Antiferromagnetic Iron(III) Complexes

The theory of the temperature dependence of proton Knight shifts for mononuclear paramagnetic complexes has been reported by Golding, *et al.*,[8] for a variety of ground states. Kurland and McGarvey[9] have extended these results and have given a more general formulation of the problem.

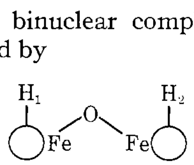
For high-spin octahedral iron(III) the ground state $^4A_{1g}$ is orbitally nondegenerate. The major interaction between such ions is then isotropic exchange: $-JS_1 \cdot S_2$ $(S_1 = S_2 = {}^5/_2)$. This interaction gives rise to a series of spin states $S_i' = 0, 1, 2, 3, 4$, and 5, of relative energies $0, -J, -3J, -6J, -10J$, and $-15J$, respectively.

For mononuclear complexes of high-spin iron(III) it can be shown that the proton Knight shift is given by

$$\Delta H = \frac{Ah\langle S_z\rangle}{g_n\beta_n}$$

where $\Delta H = H_{\text{exptl}} - H_{\text{diamag}}$, $\langle S_z\rangle$ is the time-averaged value of the z component of the spin S $(= {}^5/_2)$, and A is the hyperfine interaction constant. It has been assumed that the Knight shift has arisen from a Fermi contact interaction between the unpaired electrons on the molecule with the proton spin I. For $^6A_1$ ground states there is no contribution from pseudocontact terms unless the zero-field splitting is large, and for the cases considered here no contribution has been noted.[9]

In the case of a binuclear complex whose general structure is indicated by



with equivalent ligands on each iron(III) ion it is necessary to consider contributions to the contact shift from both ions.

Thus for proton 1 the Knight shift experienced may be written as the sum of the shifts due to ions 1 and 2

$$\Delta H_1 = \frac{h}{g_n\beta_n}[A_1\langle S_{1z}\rangle + A_2\langle S_{2z}\rangle]$$

where A_1 is the hyperfine constant due to ion 1 and A_2 that due to ion 2. A_2 may be considered small and hence

$$\Delta H_1 = \frac{A_1h}{g_n\beta_n}\langle S_{1z}\rangle$$

For a symmetric dimer $\langle S_{1z}\rangle = \langle S_{2z}\rangle = \langle S_z'\rangle/2$, where S_z' refers to the total spin $S' = S_1 + S_2$, so

$$\Delta H_1 = \frac{A_1h}{g_n\beta_n}\frac{\langle S_z'\rangle}{2}$$

Assuming a Boltzmann distribution $\langle S_z'\rangle$ may be evaluated as

$$\langle S_z'\rangle = \frac{\Sigma\langle S_z'\rangle_{S_i'}\exp(-E_{S_i'}/kT)}{\Sigma\exp(-E_{S_i'}/kT)}$$

On evaluation we obtain

$$\Delta H_1 = \frac{-A_1hg\beta H}{g_n\beta_nkT}F$$

where

$$F = \frac{\exp(J/kT) + 5\exp(3J/kT) + 14\exp(6J/kT) + 30\exp(10J/kT) + 55\exp(15J/kT)}{1 + 3\exp(J/kT) + 5\exp(3J/kT) + 7\exp(6J/kT) + 9\exp(10J/kT) + 11\exp(15J/kT)}$$

g is the electron g factor, β is the electronic Bohr Magneton, and J is the isotropic exchange parameter.

Results and Discussion

The proton nmr spectra of the binuclear iron(III) porphyrins are shown in Table I. Pyrrole protons on all three complexes showed downfield shifts of about 450 cps from the diamagnetic porphyrin. Protons on the meso phenyl groups occurred at the same field position and were upfield from their diamagnetic positions. The temperature variation over the range −20 to +50° for these protons was negligible while for the pyrrole protons shifts varied by about 60 cps. For the deuteroporphyrin IX dimethyl ester the pyrrole proton resonances were weak as there are only two compared to eight protons in the tetraphenylporphines. Other resonances are due to the methyl groups and propionic ester groups but were not used for calculations of J as they did not change with temperature considerably.

TABLE I

PROTON RESONANCE POSITIONS OF BINUCLEAR IRON(III) PORPHYRINS IN DEUTERIOCHLOROFORM SOLUTIONS AT 20° WITH TMS INTERNAL REFERENCE

	Pyrrole H	Meso phenyl H	Others
$(FeTPP)_2O$	−1344	−771	
$(FeTpMPP)_2O$	−1335	−742	−277 (pM)
$(FeDPIXDME)_2O$	−1340	. . .	−634, −521, −279

A computer program was constructed which fitted the temperature variation of the pyrrole proton Knight

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shifts for $(FeTPP)_2O$ and $(FeTpMPP)_2O$ by a nonlinear least-squares process, as a function of A and J. The results are shown in Table II.

TABLE II

TEMPERATURE DEPENDENCE OF KNIGHT SHIFT OF PYRROLE PROTONS AND COMPUTED SHIFTS FROM BEST-FIT LEAST-SQUARES PARAMETERS

$(FeTPP)_2O$			$(FeTpMPP)_2O$		
	ΔH, cps			ΔH, cps	
Temp, °K	Calcd[a]	Exptl	Temp, °K	Calcd[a]	Exptl
323.2	−480	−481	323.2	−480	−477
313.2	−475	−474	313.2	−474	−473
303.2	−469	−470	303.2	−467	−470
293.2	−463	−464	293.2	−459	−455
283.2	−456	−454	283.2	−452	−455
273.2	−448	−446	273.2	−443	−448
263.2	−440	−440	263.2	−434	−434
253.2	−431	−433	253.2	−423	−419

[a] Calculated from best-fit least-squares parameters: $(FeTPP)_2O$, $A = 1.29 \times 10^5$ cps, $J = -309\ cm^{-1}$; $(FeTpMPP)_2O$, $A = 1.44 \times 10^5$ cps, $J = -335\ cm^{-1}$.

Table II which outlines the temperature dependence of the Knight shift of pyrrole protons leads to a value of $J = -309$ and $-335\ cm^{-1}$ for $(Fe^{III}TPP)_2O$ and $(Fe^{III}TpMPP)_2O$, respectively. These values are somewhat larger than those obtained from magnetic susceptibility data of similar chelates in the solid state. The errors involved in measurement could account for some of the disparity between the two sets of results. The errors in the J values determined here are of the order $\pm 50\ cm^{-1}$. The increase in the value of J noted when the systems are in a solution phase could lie in a slight variation of the bond angle in the relevant Fe^{III}–O–Fe^{III} system, with the tendency to become more linear resulting in a higher J value. A reason for considering an increase in bond angle arises from a consideration of the interaction between the two porphyrin rings which could be influenced by packing in the solid state. It is envisaged that the process of solution could aleviate constraints imposed by packing considerations leading to a widening of the Fe^{III}–O–Fe^{III} bond angle. It must be pointed out that a factor neglected in the treatment of the data here, and which is a problem specific to the porphyrins, is the possibility of a shielding effect due to ring current effects on the protons in the other porphyrin ring. However, it is felt that such effects would be small.[10]

It has been noted by Cohen[3] that it is difficult to obtain preparations of the binuclear iron(III) porphyrins that do not contain small amounts of high-spin impurities. This fact, together with the large diamagnetic corrections for the porphine macrocycle make bulk susceptibility measurements on such systems difficult. The advantage of the nmr method lies in the fact that, even if small amounts of high-spin impurity are present, direct observations on the low-spin binuclear complex can be made to obtain the important magnetic parameters.

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The Electronic Spectra of Tetragonal Chromium(III) Complexes

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The polarized electronic spectra of *trans*-$[Cr(en)_2X_2]ClO_4$, X = Br and Cl, and *trans*-$[Cr(en)_2(H_2O)_2]Cl \cdot H_2O$ are reported and the quartet ligand field bands are assigned. The tetragonal ligand field parameter κ $(=Ds/Dt)$ is found to be $+0.8$, $+0.33$, and -0.8 for X = Br, Cl, and H_2O, respectively. The intensities of the ligand field bands are vibronic in origin and the temperature dependence of the intensity of the $^4E_g(^4T_{2g})$ band follows the coth law. The nature of the odd-parity states which give intensity to the ligand field transitions is discussed.

I. Introduction

It has been shown[1] that the magnitude of the tetragonal ligand field parameter, κ $(=Ds/Dt)$, can be rationalized by expressing κ in terms of the empirical molecular orbital parameters $\delta\sigma$ and $\delta\pi$[2,3] whose signs can often be predicted from the knowledge of the bonding capabilities of the ligands. This simple model failed in many cases to predict the sign of κ as this required the knowledge of the magnitude of $\delta\sigma$ relative to that of $\delta\pi$. The present work was carried out to establish the signs of these tetragonal parameters. In addition a more penetrating experimental study of the vibronic mechanism seemed possible with the available range of complexes. Quantitative work on the temperature dependence of the intensity of ligand field transitions has been limited to the broad bands in hexaaquo complexes[4] and certain sharp absorptions in $[(CH_3)_4N]_2UCl_6$.[5]

Previous work[6,7] has established that the intensities of the ligand field transitions in *trans*-$Co(en)_2X_2^+$ and *trans*-$Cr(en)_2F_2^+$ are predominantly vibronic in origin and that the electronic spectra can be interpreted using the effective point group D_{4h}. According to the vibronic selection rules only the $^4B_{1g} \rightarrow {}^4B_{2g}$, $^4A_{2g}$ transitions are forbidden, both in z polarization. Provided

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