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mechanisms. We infer that this similarity suggests a "side-by-side" positioning of the ferrocene derivatives in the transition state rather than a "sitting on top" arrangement. The rapid reactions of the carbollyl derivatives support this proposal, for a "side-by-side" configuration would not require electron transfer over such great distances or through the B-H framework of the carbollyl compound.

Acknowledgment. We are grateful to Professor Harlan H. Higginbotham III of Northeast Missouri State College for making the initial rate measurements on $\text{Fe}^{3+} + \text{Fe}(\text{C}_5\text{H}_5)_2$, and to Mr. D. F. Dustin and Professor M. F. Hawthorne for the gift of the carborane used to prepare some of the compounds studied. We are pleased to acknowledge interesting and helpful discussions with Professor A. C. Wahl.

Proton Magnetic Resonance Investigation of Antiferromagnetic Oxo-Bridged Ferric Dimers and Related High-Spin Monomeric Ferric Complexes

Gerd N. La Mar,^{*1} G. R. Eaton,² R. H. Holm,² and F. Ann Walker³

*Contribution from the Departments of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139,
University of California, Davis, California 95616,
and California State University, San Francisco, California 94132.
Received June 1, 1972*

Abstract: The pmr spectra of several types of antiferromagnetic Fe(III) dimeric complexes containing the non-linear unit Fe-O-Fe have been investigated. The systems studied are of the $[\text{Fe}(\text{salen})]_2\text{O}$ and $[\text{Fe}(\text{P})]_2\text{O}$ types (P = tetraphenylporphine (TPP), tetra-*p*-tolylporphine (TTP), tetra-*n*-propylporphine, and octaethylporphyrin) and also include the structurally related high-spin monomers $\text{Fe}(\text{salen})\text{OAc}$ and $\text{Fe}(\text{P})\text{Cl}$. An expression (eq 6) has been obtained for the temperature dependence of the contact shifts of a magnetically isotropic spin-coupled ($^6/2$, $^5/2$) dimer which admits different hyperfine coupling constants A_i for the different spin levels S'_i of the dimer ($i = 0, 1, 2, \dots$) and is valid provided the Curie law holds for each spin level. Isotropic shifts of salen monomers exhibit a Curie dependence and their signs and relative magnitudes are consistent with π -spin delocalization, indicating that the shifts are contact in origin and zero-field splittings (ZFS) are small. Shifts of salen dimers, whose patterns are similar to the monomer shifts, are treated as contact shifts. The temperature-dependent magnetic susceptibilities of $[\text{Fe}(\text{salen})]_2\text{O}$ and $[\text{Fe}(\text{salen})]_2\text{O} \cdot \text{CH}_2\text{Cl}_2$ (solid state) and $[\text{Fe}(\text{5tBu-salen})]_2\text{O}$ (dichloromethane) do not superimpose with the contact shifts of the latter in dichloromethane solution when normalized at ca. 300°K. The direction of the deviation is shown to be consistent with $A_1 < A_2$. Isotropic shifts of the porphyrin monomer $\text{Fe}(\text{TTP})\text{Cl}$ are non-Curie and deviations from Curie behavior have been analyzed in terms of a dipolar (T^{-2}) contribution. The ZFS parameter D has been estimated from the pmr data and its value ($+11 \text{ cm}^{-1}$) is comparable to those directly determined for other porphyrin monomers by far-infrared methods. Using this value of D , dipolar shifts have been calculated for $\text{Fe}(\text{TPP})\text{Cl}$ and $\text{Fe}(\text{TTP})\text{Cl}$ and are found to be significant fractions of the total isotropic shifts. The probable existence of ZFS effects of comparable magnitude in porphyrin dimers indicates that their shifts cannot be treated in terms of eq 6 with or without all A_i equal. The results obtained in this work show that accurate values of the antiferromagnetic spin-spin coupling constant J for μ -oxo-salicylaldimine and porphyrin iron(III) dimers cannot be obtained from a simple two-parameter fit of the temperature dependence of the isotropic shifts, as has been done previously.

It is now well established that antiferromagnetic spin coupling between metal centers is operative in a variety of important biological macromolecules.⁴⁻⁶

The reported cases invariably involve iron, usually in the ferric state, coupled to another iron^{4,5} or, in one case, to copper.⁶ The most prominent class of metalloproteins exhibiting this behavior is the iron-sulfur proteins, for which pmr isotropic shifts,^{4a} Mössbauer data,^{4b} and magnetic susceptibility studies^{4c} all indicate significant antiferromagnetic coupling. For two-iron systems this coupling occurs in both the reduced $[\text{Fe}(\text{II})-\text{Fe}(\text{III})]$ and oxidized $[\text{Fe}(\text{III})-\text{Fe}(\text{III})]$ forms of the proteins.

Proton magnetic resonance spectra⁷ in such antiferromagnetic systems may be expected to lead to useful information on the electronic states of the coupled metal centers, inasmuch as monitoring the

(1) University of California; Alfred P. Sloan Foundation Fellow, 1972-1974.

(2) Massachusetts Institute of Technology.

(3) San Francisco State University.

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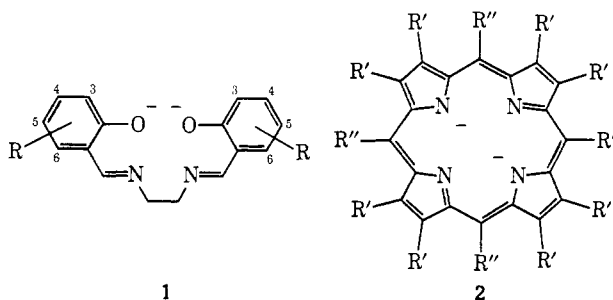
temperature dependence of the isotropic shifts of nuclei close to the metal centers permits a detailed characterization of the local spin magnetization⁷ without interference from the bulk diamagnetism of the protein or paramagnetic impurities.

Pmr studies on a variety of binuclear antiferromagnetic iron systems, including ferredoxins^{4a,8} and oxo-bridged dimers of porphyrins,⁹⁻¹² *o*-phenanthroline,¹³ bipyridyl,¹⁴ and salicylaldehydes,¹⁵ have been reported. In the case of the ferredoxins full resolution of the isotropically shifted spectra has not been achieved in all cases. A recent theoretical treatment¹⁶ of the pmr spectra of these proteins has led to qualitative predictions of the locations of some of the unobserved resonances. This treatment, which is the most detailed yet presented for any binuclear system, yielded a value of the antiferromagnetic coupling constant J which appears significantly lower than that found compatible with bulk susceptibility measurements. If the spectra of biological systems of comparable or greater complexity are to be elucidated, it is desirable to interpret in more detail than heretofore the spectra of relatively simple antiferromagnetically coupled iron dimers.

Some of the interpretations of the pmr data for dimeric Fe(III) complexes^{9,15} have relied on a number of assumptions which have not been adequately tested and which we show here to be invalid in a number of cases. The major assumption is that the contact shift has the same temperature dependence as the paramagnetic susceptibility, such that J may be obtained from a simple two-parameter fit. This is identical with assuming that the Fermi coupling constant, A , for any given nucleus is independent of the spin state for the dimer. Consideration of two alternative models¹⁷⁻²⁰ for describing molecular antiferromagnetism suggests that this need not be the case, and data will be presented here which substantiates a dependence of A on spin state. A second important assumption, implied in most of the previous studies, is that the isotropic shifts are purely contact in origin and that the shifts arising from the high-spin ($S = 5/2$) metal centers follow the Curie law accurately. Justification of this assumption is usually based on the fact that the ^6A ground state of high-spin Fe(III) exhibits negligible g -tensor anisotropy,²¹ with $g_{\parallel} = g_{\perp} = 2.0$. However,

the detailed theoretical treatment by Kurland and McGarvey⁷ has demonstrated that significant dipolar shifts can arise in high-spin d^5 systems due to the presence of large zero-field splittings (ZFS), in spite of the near isotropy of the g tensor. More importantly, these dipolar shifts arising from lifting of electronic degeneracy in the absence of an applied field are predicted⁷ to vary as T^{-2} . Hence, the temperature dependence of the isotropic shift for such a system may be expected to exhibit both T^{-1} and T^{-2} components, even though the bulk susceptibility may follow the Curie law accurately over the same temperature range. Therefore, even if A is identical for each spin-state of the dimer, J may not be extracted from the temperature dependence of the isotropic shift without explicit consideration of the contributions from the ZFS for each thermally accessible spin state. The importance of such ZFS contributions can be established by characterizing the non-Curie behavior of the observed shift for any one spin state. The present analysis will demonstrate that these contributions can be substantial in some previously studied systems.

The two systems selected for this investigation are the oxo-bridged Fe(III) dimers derived from the Schiff base **1** ($R = \text{alkyl}$) and the synthetic porphyrins **2** ($R' = \text{H}$, $R'' = \text{aryl, alkyl}$; $R' = \text{alkyl}$, $R'' = \text{H}$).²²



This choice was dictated by the ability to observe well-resolved pmr spectra for both the oxo-bridged dimers and the structurally closely related high-spin square-pyramidal monomers, as well as by the availability of magnetic susceptibility^{23,24} and X-ray structural data^{23c,24a,25,26} for these systems. Susceptibilities

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Table I. Characterization Data for Mono- and Binuclear Iron(III) Salicylaldiminates

Compound	Mp, ^a °C	Calcd, %			Found, %		
		C	H	N	C	H	N
[Fe(3Me-salen)] ₂ O	335–340	60.36	5.07	7.82	60.42	5.15	7.89
[Fe(4Me-salen)] ₂ O	>360	60.36	5.07	7.82	60.67	5.23	7.82
[Fe(5 <i>t</i> Bu-salen)] ₂ O	>360	65.17	6.84	6.33	64.94 ^b	6.90 ^b	6.14 ^b
					64.98 ^c	6.69 ^c	6.36 ^c
[Fe(4Me-salpn)] ₂ O	330–335	61.31	5.42	7.53	61.09	5.50	7.65
Fe(3Me-salen)(OAc)	213	58.70	5.17	6.85	58.88	5.12	6.89
Fe(4Me-salen)(OAc)	274–275	58.70	5.17	6.85	58.84	5.29	6.94
Fe(4Me-salen)(OAc- <i>d</i> ₃)	272–273	58.27		6.80	58.13		6.87
Fe(4Me-salpn)(OAc- <i>d</i> ₃)	224	59.17		6.57	58.97		6.71
Fe(5 <i>t</i> Bu-salen)(OAc)	>360	63.29	6.74	5.68	63.07	6.76	5.86

^a Sealed tube, *in vacuo*; all compounds decomposed at the melting point. ^b Recrystallized from chloroform. ^c Recrystallized from dichloromethane.

of monomeric complexes of the types Fe(salen)X^{23b,e} and Fe(P)X^{24a,b,e,f} have been shown to obey the Curie law in the solid state over the temperature interval pertinent to this study, with magnetic moments typical of magnetically dilute high-spin Fe(III)²⁷ (*ca.* 5.9–6.0 BM). For the salen μ -oxo dimers [Fe(salen)]₂O magnetic moments in the range 1.9–2.0 BM/Fe at 300°K and $J \approx -90$ to -100 cm⁻¹ have been reported.^{23a,c} Single-crystal X-ray studies reveal bent Fe–O–Fe bridges with angles of *ca.* 140°. ^{23c, 25a} Magnetic properties of the analogous porphyrin dimers [Fe(P)]₂O are not as well characterized. The room temperature moment for [Fe(TPP)]₂O is *ca.* 1.8–1.9 BM.^{24b,c} The bridge angle in this complex is 174.5°. ^{24a} An accurate low-temperature study of the oxodimer of protoporphyrin IX dimethyl ester has yielded $\mu = 1.55$ BM (296°) and $J = -132$ cm⁻¹. ^{24d} A comparable value of J may be anticipated for the porphyrin dimers studied in this work, which is primarily concerned with developing a sounder interpretation of the isotropic shifts of the μ -oxo antiferromagnetic Fe(III) dimers derived from **1** and **2**.

Experimental Section

Preparation of Compounds. (a) **Salicylaldimine Complexes.** Fe(salen)Cl,²⁸ Fe(salen)OAc,²⁹ and [Fe(salen)]₂O^{23a} were prepared by published methods. Substituted salicylaldehydes were obtained from the corresponding phenols by the Duff reaction.³⁰ Characterization data for new complexes are listed in Table I. The Schiff bases H₂(R-salen) (R = 3-Me, 4-Me, 5-*t*Bu) and H₂(4Me-salpn) were prepared by mixing ethanol solutions containing stoichiometric amounts of the substituted salicylaldehyde and diamine. The yellow crystalline products were identified by their pmr spectra.

Fe(R-salen)Cl and Fe(4Me-salpn)Cl. The compounds (R = 3-Me, 4-Me, 5-*t*Bu) were made from the preformed Schiff bases by procedures analogous to that reported for Fe(salen)Cl.²⁸ Fe(5*t*Bu-salen)Cl was not isolated prior to conversion to the acetate because of its high solubility. The other complexes were collected by filtration and used without further purification in the following preparations.

[Fe(R-salen)]₂O (R = 3-Me, 4-Me, 5-*t*Bu) and [Fe(4Me-salpn)]₂O. Synthesis of these compounds followed a procedure analogous to that reported^{23a} for other [Fe(R-salen)]₂O complexes. The ap-

propriate chloride was slurried in ethanol with excess freshly prepared silver(I) oxide until the color changed from reddish purple to yellow-brown. The solvent was removed and the resulting solid was extracted with chloroform (dichloromethane used for [Fe(4Me-salpn)]₂O). The extract was filtered and the volume reduced until solid formed. The products were repeatedly recrystallized from chloroform–hexane ([Fe(5-*t*Bu-salen)]₂O), chloroform ([Fe(3Me-salen)]₂O, [Fe(4Me-salpn)]₂O), or dichloromethane–hexane ([Fe(4Me-salen)]₂O), washed with hexane, and dried under vacuum at 65°. In a typical preparation *ca.* 1.0 g (2.6 mmol) of Fe(4Me-salen)Cl was slurried in 100 ml of ethanol with *ca.* 1.7 g (7 mmol) of freshly prepared Ag₂O for 3 hr. The solvent was removed and the residue was extracted with 300 ml of dichloromethane. The solution volume was reduced to *ca.* 10 ml and hexane was added. The resulting solid was collected by filtration and recrystallized twice from filtered dichloromethane–hexane solutions. After drying 0.63 g (67% yield) of yellow-brown needles were obtained.

Fe(R-salen)OAc (R = 3-Me, 4-Me, 5-*t*Bu) and Fe(4Me-salpn)(OAc-*d*₃). As in the reported synthesis of Fe(salen)OAc,²⁹ these compounds were prepared by allowing the appropriate oxo-bridged dimer to react with excess glacial acetic acid at room temperature. The deuterated compounds were prepared from acetic acid-*d*₄. In a typical preparation, 100 mg (0.14 mmol) of [Fe(4Me-salen)]₂O was stirred with *ca.* 1 ml (17 mmol) of acetic acid-*d*₄ for 2 hr during which time the color changed from yellow-brown to red-purple, and then the slurry was evaporated to dryness in a stream of nitrogen. The residue was recrystallized three times by dissolving in *ca.* 3 ml of chloroform, reducing the volume to *ca.* 1 ml, and slowly adding *ca.* 1–2 ml of hexane. The product was collected by filtration and dried under vacuum at methanol reflux temperature, yielding 112 mg (96%).

(b) Porphyrin Complexes. Fe(T-*n*PrP)Cl was obtained from Dr. A. Adler and Fe(OEP)Cl, [Sc(TPP)]₂O, and [Sc(OEP)]₂O from Dr. D. Dolphin. Fe(TPP)Cl,³¹ Fe(TTP)Cl,³¹ [Fe(TPP)]₂O^{24a} were prepared according to published methods, except that xylene was omitted in the recrystallization of the dimers. [Fe(T-*n*PrP)]₂O and [Fe(OEP)]₂O were obtained from the corresponding chlorides by a method analogous to that reported for [Fe(TPP)]₂O.^{24a}

Pmr Measurements. Pmr spectra were recorded on a Varian HA-100 spectrometer modified to operate with variable frequency modulation, using audiofrequency sidebands for calibration, in conjunction with a Varian V-4343 temperature control unit pre-calibrated against methanol and ethylene glycol. TMS was used as the internal reference in all cases. Isotropic shifts obtained at 100 MHz are reported in ppm and are referenced against appropriate diamagnetic compounds. For salen monomers and dimers the free ligands were used as diamagnetic references inasmuch as their shifts differed insignificantly (≤ 0.005 ppm) from those of the corresponding planar Ni(II) complexes. In the case of Fe(P)X complexes, the diamagnetic Ni(P) shifts were employed as references, except for Fe(T-*n*PrP)X where free ligand shifts were used. For dimeric porphyrin complexes, in which ring current effects are significant, dimeric diamagnetic complexes were employed as references (*vide infra*). Line widths (δ), defined as the full peak width at half-height, are given in Hz at 100 MHz. It was observed that in all cases the pmr spectrum of a monomer was unaffected by the addition of the related dimer, and *vice versa*, indicating that any

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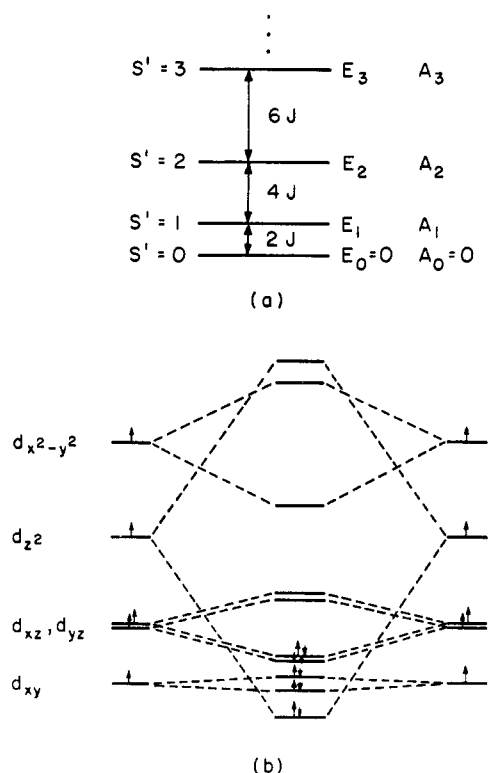


Figure 1. (a) Energy levels of the $S_1 = S_2 = 5/2$ case predicted by the HDVV model. Notation of the hyperfine coupling constants for each level is indicated. (b) Illustrative d-orbital energy level scheme for two interacting metal ions. An electron configuration for the $S' = 0$ ground state of the dimer is shown. More detailed schemes including bridge atom orbitals and a nonlinear M-O-M arrangement are considered elsewhere.^{19,20}

dynamic equilibrium which may exist between them in the presence of small amounts of water or base must proceed at a rate which is slow on the pmr time scale ($\tau^{-1} \ll 10^2 \text{ sec}^{-1}$).

Solution Magnetic Susceptibility Measurements. Measurements were made by the usual nmr method³² using concentric tubes and chloroform or dichloromethane solutions containing 2% by volume of TMS. It is noted that in Evans' equation³² for susceptibility determined by this technique, extensive solution and solvent properties (density, concentration, and susceptibility) are temperature dependent. Accurate data are not available for densities and susceptibilities of the solvents used over the entire temperature range of interest. In this work the published room temperature magnetic susceptibilities and temperature-dependent densities for dichloromethane, chloroform, and TMS were used.³³ The estimated uncertainty in the measured susceptibilities is $\lesssim 4\%$.

Theory

Antiferromagnetism in Dimers. Antiferromagnetism can be treated by either the Heisenberg-Dirac-Van Vleck (HDVV) or dipolar model¹⁷ or by the molecular orbital model.¹⁸⁻²⁰ In the HDVV approach the spins are localized on the metal centers with the exchange interaction given by the Hamiltonian $\mathcal{H} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2$, where \mathbf{S}_1 and \mathbf{S}_2 are the spin vectors for centers 1 and 2. The separation between spin states k and l for the antiferromagnetic dimer is given by

$$E_{kl} = -J[S'_k(S'_k + 1) - S'_l(S'_l + 1)] \quad (1)$$

(32) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

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where S' is obtained by the addition rule for the two spin vectors. For the case with $S_1 = S_2 = 5/2$ the ground state is diamagnetic and there are five excited states, $S' = 1, 2, 3, 4, 5$, with spacings $2J, 4J, 6J, 8J$, and $10J$. The complete energy level manifold is then described in terms of a single parameter, J .

The alternative interpretation of antiferromagnetism in such systems is based on the MO description¹⁸⁻²⁰ of dimer formation. The two high-spin monomers interact to give rise to bonding and antibonding linear combinations of the MO's for the monomers. Neglecting, for simplicity, the filled orbitals of the bridge atom and including only the metal d orbitals, ten energy levels result. The ground state is diamagnetic, with ten spins paired in five linear combinations, and a manifold of excited states exists with spin multiplicities identical with those predicted by the HDVV model. The HDVV energy levels and a possible energy scheme for d-orbital interaction are illustrated in Figure 1.

There are important distinctions between these two models of antiferromagnetism. Unlike the HDVV model, in which a single parameter describes the spin-state energy manifold, the spacings of energy levels in the MO model are not necessarily systematic¹⁸⁻²⁰ and should reflect the specific bonding characteristics of a given system. More importantly, the MO model leads to prediction of the symmetry of the d orbitals which contain the unpaired electrons for any given spin state. Thus for the $S' = 1$ state, the unpaired spins could reside in σ - and/or π -type d orbitals so that the state could be characterized as $\sigma\sigma$, $\sigma\pi$, or $\pi\pi$. Since the delocalization of unpaired spins depends on the d-orbital symmetry,³⁴ the coupling constant for a given nucleus could be critically dependent upon the location of the unpaired spins in any spin state. A similar dependence of A on spin state could also occur in the HDVV model if there exists unequal dipolar coupling between the different spins on the two centers.

In order to treat the general case, equations will be obtained for the susceptibility and contact shift of a ($3/2, 5/2$) dimer in terms of a spin-state energy manifold with arbitrary spacings having $E_{S'} = E_0, E_1, E_2, \dots, E_5$ corresponding to $S' = 0, 1, 2, \dots, 5$. Taking the g value to be 2.0 for the spin-free ion, as observed for the $S' = 2$ state of a ferric dimer³⁵ and assuming a Boltzmann distribution over the energy levels, a magnetic observable ω for the dimer is given by

$$\omega = \sum_i \omega_i p_i e^{-x_i} / \sum_i p_i e^{-x_i} \quad (2)$$

where $x_i = E_i/kT$ and $p_i = (2S'_i + 1)$, the degeneracy of the spin state. The susceptibility of a given spin state²⁷ is

$$\chi_i = \frac{g^2 \beta^2 N}{3kT} S'_i(S'_i + 1) \quad (3)$$

which yields for the dimer

$$\chi = \frac{K \sum_i (2S'_i + 1) S'_i(S'_i + 1) e^{-E_i/kT}}{\sum_i (2S'_i + 1) e^{-E_i/kT}} \quad (4)$$

(34) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965).

(35) M. Y. Okamura and B. M. Hoffman, *J. Chem. Phys.*, **51**, 3128 (1969).

where $K = g^2\beta^2N/3k$. The proton contact shift for a given spin state for which the Curie law is valid may be expressed^{7,34,36} as

$$\Delta H_i = -\frac{A_i}{\gamma_H\hbar}\langle S_{zi} \rangle = -\frac{A_i}{\gamma_H\hbar} \frac{\langle S' \rangle}{2} = -\frac{A_i}{\gamma_H\hbar} \frac{g\beta S'_i(S'_i + 1)H_0}{6kT} \quad (5)$$

where $\langle S_{zi} \rangle = \langle S_{z2} \rangle$ is the average spin magnetization of either metal center and $\langle S' \rangle$ is the spin magnetization for the dimer. The net contact shift for the dimer therefore is

$$\frac{\Delta H}{H_0} = \frac{P}{T} \frac{\sum_i A_i (2S'_i + 1) S'_i (S'_i + 1) e^{-E_i/kT}}{\sum_i (2S'_i + 1) e^{-E_i/kT}} \quad (6)$$

with $P = -g\beta/6\gamma_H\hbar k$. It is emphasized that eq 6 holds only if it can be demonstrated that the Curie law is valid for the individual spin states. Note that in the HDVV model J may be directly obtained by a one-parameter fit of eq 4 to $\chi(T)$ data.^{23a,37} If all $A_i = A$, then J and A may be determined by a two-parameter fit of eq 6 to the temperature dependence of contact shift. However, if A_i depends upon the spin state, J cannot be determined from the contact shift without explicit knowledge of the A_i 's for the thermally accessible states.

If all A_i are equal, eq 4 and 6 yield a relationship which is valid at all temperatures

$$\chi = R(\Delta H/H_0) \quad (7)$$

where the constant ($R = K/PA$) is independent of temperature. Hence the temperature dependence of $\Delta H/H_0$ and χ will superimpose over the complete temperature range if the latter is scaled by R . Equation 7 holds even if all g_i are not equal to 2.0, since identical g_i 's would appear within the sums of both eq 4 and 6. The effect of variable A_i on the difference between the temperature dependence of χ and $\Delta H/H_0$ cannot be generalized without a knowledge of all A_i 's. To demonstrate the effect of different coupling constants a three-level system³⁸ is used as an illustration. In this case

$$\chi = \frac{6K}{T} \left[\frac{e^{-E_1/kT} + 5e^{-E_2/kT}}{1 + 3e^{-E_1/kT} + 5e^{-E_2/kT}} \right] \quad (8)$$

and

$$\frac{\Delta H}{H_0} = \frac{6P}{T} \left[\frac{A_1 e^{-E_1/kT} + 5A_2 e^{-E_2/kT}}{1 + 3e^{-E_1/kT} + 5e^{-E_2/kT}} \right] \quad (9)$$

The analog to eq 7 then becomes

$$\chi = R' \left(\frac{\Delta H}{H_0} \right) \left[\frac{e^{-E_1/kT} + 5e^{-E_2/kT}}{(A_1/A_2)e^{-E_1/kT} + 5e^{-E_2/kT}} \right] \quad (10)$$

where $R' = K/PA_2$. When $A_1 = A_2$, the scaled curves

(36) It is assumed that $\langle S_{z2} \rangle$ ($\langle S_{z1} \rangle$) does not cause a significant coupling constant for any proton in the ligand attached to metal center 1(2). This assumption will not affect the predicted temperature dependence of contact shift as discussed in the text, but it would influence any detailed interpretation of coupling constants in terms of bonding and spin delocalization.

(37) A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 396 (1961).

(38) For the dimers considered in this study $|J| \approx 100 \text{ cm}^{-1}$ and only the lowest three states are significantly populated at and below 300°K. In terms of the HDVV model with $E_0 = 0$, $E_1 = 200$, $E_2 = 600$, and $E_3 = 1200 \text{ cm}^{-1}$, there is a 0.8% population of the E_3 state at 300°K.

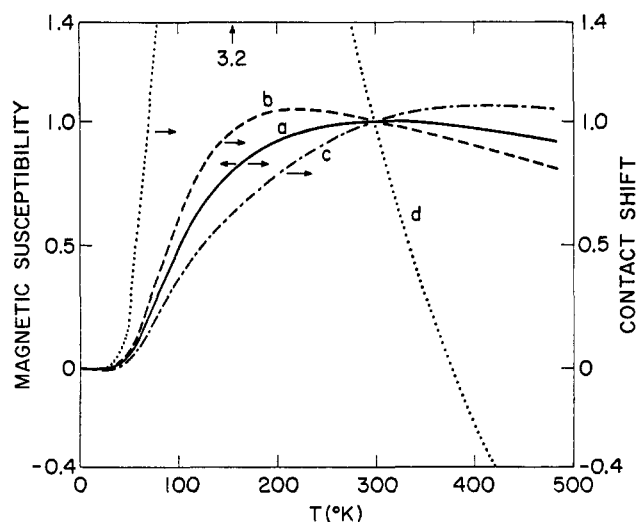


Figure 2. Temperature dependence of magnetic susceptibility and contact shift for an antiferromagnetically coupled dimer, normalized at 300°K, for a three-level manifold with $E_0 = 0$, $E_1 = 200$, and $E_2 = 600 \text{ cm}^{-1}$: a, $A_1 = A_2$; b, $A_1 = 2A_2$; c, $A_1 = 1/2A_2$; d, $A_1 = -A_2$.

of $\Delta H/H_0$ and χ coincide at all temperatures, as indicated by curve a in Figure 2. In the more general case, if $\Delta H/H_0$ is scaled by R' so that it superimposes χ at some arbitrary high temperature (taken as $\sim 300^\circ\text{K}$ in our cases), the contact shift deviates from the susceptibility as the temperature is lowered in the direction indicated by curve b if $A_1 > A_2$, while the deviation for $A_1 < A_2$ is depicted by curve c. Test calculations show that for the possible case where A_1 and A_2 have different signs, the contact shift dependence can simulate ferromagnetic behavior over a limited temperature range, as shown by curve d. Once the ratio A_1/A_2 is determined by fitting the contact shift curve, A_1 and A_2 can be simply obtained from eq 9.

It is therefore concluded that J cannot be obtained directly from contact shift data unless the relative magnitude of the coupling constants are known. In a qualitative sense the observed deviation between χ and $\Delta H/H_0$ such as shown in Figure 2 could lead to useful information on the relative sizes of the coupling constants for the different spin states, which in favorable cases could serve to elucidate the mechanism of spin interaction in the MO model.

Isotropic Shifts in Monomers. The observed isotropic shift may arise from contact and/or dipolar interactions, i.e., $(\Delta H/H_0)^{\text{iso}} = (\Delta H/H_0)^{\text{con}} + (\Delta H/H_0)^{\text{dip}}$.⁷ The dipolar shift, which is a consequence of the magnetic anisotropy of the complex, was originally associated solely with g -tensor anisotropy.³⁹ In spin-free monomeric ferric complexes the usually isotropic g tensor²¹ suggests negligible dipolar shifts. However, the recent detailed analysis by Kurland and McGarvey⁷ has shown that ZFS can also lead to sizable dipolar shifts. Far-infrared studies have demonstrated that a number of Fe(III) complexes, including high-spin porphyrins, exhibit quite large ZFS effects.⁴⁰ The contact shift for a high-spin d^5 complex with an isotropic

(39) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(40) G. C. Brackett, P. L. Richards, and W. S. Caughey, *ibid.*, **54**, 4383 (1971).

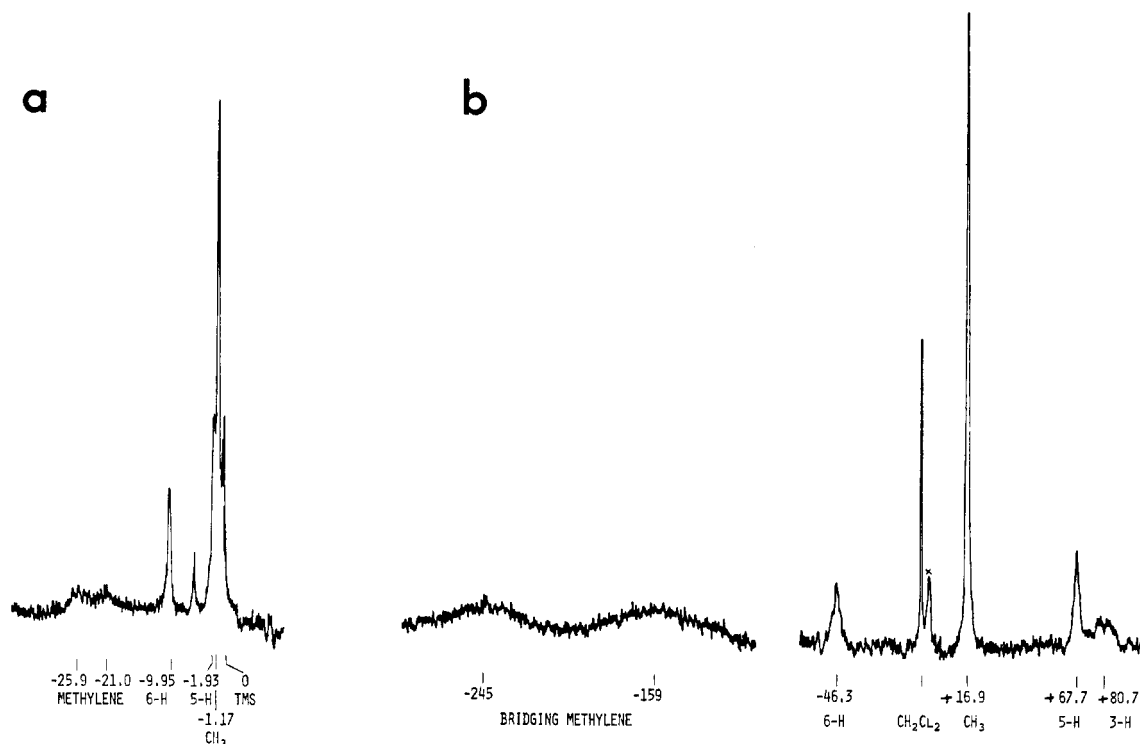


Figure 3. PMR spectra (100 MHz) of (a) $[\text{Fe}(\text{4Me-salen})]_2\text{O}$ and (b) $\text{Fe}(\text{4Me-salen})(\text{OAc-}d_3)$ in CD_2Cl_2 solution at $\sim 29^\circ$. Magnetic field increases from left to right.

g tensor takes the form⁷

$$\left(\frac{\Delta H}{H_0}\right)^{\text{con}} = -\left(\frac{A}{h}\right)\frac{F}{T} \quad (11)$$

where $F = 35 g\beta/(12k\gamma_{\text{H}}/2\pi)$ and (A/h) is the Fermi coupling constant in Hz. For the same case the dipolar shift is given by⁷

$$\left(\frac{\Delta H}{H_0}\right)^{\text{dip}} = B \left[\frac{3 \cos^2 \theta - 1}{r^3} \right] \frac{D}{T^2} \quad (12)$$

where D is the ZFS parameter, $B = 28g^2\beta^2/9k^2$, and the bracketed term is the usual geometric factor in which r is the length of the metal-proton vector and θ is the angle between this vector and the unique magnetic axis (the C_4 axis for the porphyrins). Because the contact shift varies as T^{-1} , while the dipolar shift depends on T^{-2} , the presence of sizable dipolar contributions to the observed isotropic shifts can be established by detection of curvature in a Curie plot. In cases where significant dipolar shifts can be demonstrated for any given spin state, dipolar shifts of variable magnitude may be expected for the different spin states in the antiferromagnetic dimer. In such cases, unless D is known for each spin state, the temperature dependence of the isotropic shift in the dimer is unlikely to lead to meaningful estimates for J .

To date no results have been presented which unambiguously establish the presence of the quadratic temperature term. The nonzero intercept observed for the isotropic shifts of some hemins has been suggested to arise from such terms.⁴¹ However, the limited temperature range in the DMSO solvent prevented the

observation of shifts over a sufficiently wide temperature range⁴¹ so as actually to detect any possible curvature in the Curie plot. Aside from permitting a more quantitative assessment of the isotropic shifts, the characterization of a quadratic component to the observed shift would permit direct determination of D from solution nmr spectra.⁴²

Results and Discussion

In the following sections the isotropic shifts of high-spin monomeric and μ -oxo dimeric salen and porphyrin complexes are considered in terms of the foregoing theory. As already pointed out, a detailed analysis of the shifts of a dimer requires characterization of the temperature dependence of the contact shift for each occupied spin state S'_i . In the case of insignificant g -tensor anisotropy any deviation from the Curie behavior (eq 5) assumed in eq 6–10 is expected to arise mainly from ZFS effects. In the absence of directly determined³⁵ D values for the dimers considered here, any ZFS effects evident in the pmr spectra of the monomers are considered to be qualitative indicators of the presence of effects of similar magnitude in the weakly spin-coupled dimers. The magnitude of D in the present cases is primarily dependent on the strength of the axial ligand field component.⁴⁰ The close similarities in coordination geometry of related

(41) R. J. Kurland, R. G. Little, D. G. Davis, and C. Ho, *Biochemistry*, **10**, 2237 (1971).

(42) It is noted that characterization of a quadratic temperature term is relevant to the interpretation of the large shifts induced by lanthanide shift reagents, inasmuch as Bleaney⁴³ has shown that dipolar shifts in such systems do not result from g -tensor anisotropy, but arise primarily from lifting of the electronic degeneracy by ligand field interactions. Hence, the temperature dependence of the observed shifts in well defined adducts of shift reagents may be expected to provide an index of the relative importance of contact vs. dipolar shifts.

(43) B. Bleaney, *J. Magn. Resonance*, **8**, 91 (1972).

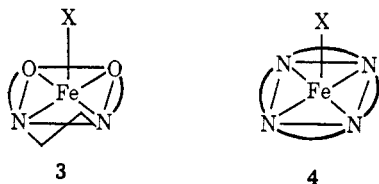
Table II. Isotropic Proton Shifts^a (ppm) of Monomeric and Oxo-Bridged Dimeric Iron(III) Salicylaldiminates in CD₂Cl₂ Solution at ~29°

Complex	Ring				Bridge	Acetate ^e
	3	4	5	6		
Fe(salen)OAc ^d	+89.9	-69.5	+74.3	-39.9	<i>f</i>	-136
Fe(3Me-salen)OAc	(-57.0) ^b	-78.6	+78.5	-42.0	<i>f</i>	-136
Fe(4Me-salen)OAc	+87.4	(+19.2) ^b	+74.3	-39.3	-155, -241 ^g	-134
Fe(5 <i>t</i> Bu-salen)OAc	+91.0	-67.7	(-2.7) ^c	-39.8	<i>f</i>	-137
[Fe(salen)] ₂ O	+6.45	-5.93	+4.74	-2.97	-16.9, -22.0	
[Fe(3Me-salen)] ₂ O	(-3.75) ^b	-7.09	+5.02	-3.20	-18.0, -22.9	
[Fe(4Me-salen)] ₂ O	<i>f</i>	(+1.14) ^b	+4.75	-2.82	-17.1, -22.0	
[Fe(5 <i>t</i> Bu-salen)] ₂ O ⁱ	<i>f</i>	-5.45	(-0.29) ^c	-2.75	-17.1, -21.1	
[Fe(4Me-salpn)] ₂ O ^h	<i>f</i>	(+0.99) ^b	+4.45	-2.67	-14.3, -19.4, -24.8	

^a Shifts are reported relative to those of the free ligands; negative values indicate shifts to lower field than free ligand. ^b Methyl. ^c *tert*-Butyl. ^d Line width (Hz) for the indicated resonance: 700 (3-H), 300 (4-H), 250 (5-H), 400 (6-H). ^e Based on -2 ppm as diamagnetic reference. ^f Not observed or not measured. ^g Observable only in the -OAc-*d*₃ complex. ^h Bridge methyl shift *ca.* -1.6 ppm. ⁱ Line width (Hz) for the indicated resonance: 45 (4-H), 80 (6-H).

monomers^{25b, 26, 44} and dimers^{23c, 24a, 25a, 26} suggests that their ZFS are likely to be comparable.

High-Spin Monomers. Salen and porphyrin iron(III) complexes of this type have the general square-pyramidal structures **3**^{25b} and **4**,^{26, 44} respectively, with the metal ion displaced out of the mean coordination plane by 0.38–0.48 Å.



(a) **Salen Complexes.** The pmr spectrum of a representative complex, Fe(4Me-salen)(OAc-*d*₃), is given in Figure 3b. Although the lines are broad (~250 Hz), the chemical shifts are quite large, so that a relatively well resolved spectrum is realized. The nonequivalent methylene protons appear considerably downfield of other signals, with line widths in excess of 1000 Hz. The somewhat larger area of the resonance at -160 ppm suggests that it may contain the azomethine proton signal, for which no clearly resolvable peak is found in the range ±350 ppm from TMS. Signal assignments in this series were made on the basis of alkyl substitution at three of the four ring positions. Isotropic shifts are set out in Table II.

In Figure 4 the observed isotropic shift is plotted vs. T^{-1} for Fe(3Me-salen)(OAc-*d*₃). Linear relationships are found which extrapolate through the origin within experimental error, indicating that the Curie law is obeyed quite accurately. This is also true for Fe(salen)OAc in the solid state.^{23e} The shifts must be essentially contact in origin⁷ and the ZFS parameter, D , in eq 12 must be relatively small. The broader peaks, when compared to porphyrin monomers (*vide infra*), also suggest a small D .⁴⁵

The absence of substantial dipolar shifts is also supported by comparison of observed isotropic shifts with calculated spin densities for the salicylaldiminato

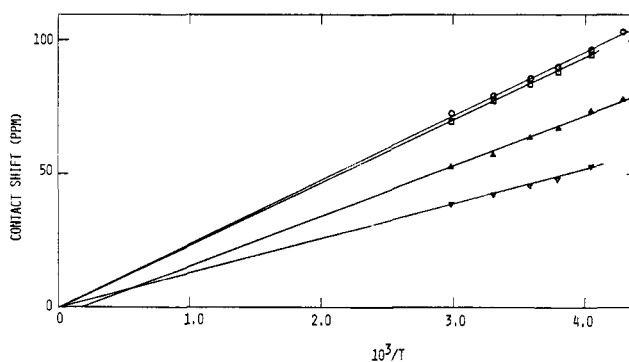


Figure 4. Plot of contact shift vs. T^{-1} for Fe(3Me-salen)OAc in CD₂Cl₂ solution. Shifts of 5-H are positive and those of 3-Me, 4-H, and 6-H are negative.

Table III. Observed and Calculated Relative Proton Contact Shifts for Iron(III) Salicylaldiminates

Complex	Ring				Bridge
	3	4	5	6	
Fe(salen)OAc ^a	+10.0	-7.7	+8.3	-4.5	-17.2, -26.7 ^c
[Fe(salen)] ₂ O ^a	+10.0	-9.2	+7.4	-4.6	-26.2, -34.1
Calcd ^b	+10.0	-5.7	+11.2	-6.3	

^a Contact shifts from Table II are normalized such that the 3-H shift is +10.0. ^b Based on spin densities for salicylaldimino π radical estimated by a VB calculation (*cf.*, ref 46). ^c Based on shifts of Fe(4Me-salen)(OAc-*d*₃).

π radical.⁴⁶ The data in Table III reveal that the relative shifts parallel the relative calculated spin densities for the highest bonding MO. Existence of π spin density is also evidenced by the opposite signs⁴⁷ for proton and methyl shifts at a given ring position. The spin density may therefore be considered to arise mainly from $L \rightarrow M$ π charge transfer. Due to the possible significant contributions of the second-order Zeeman term⁷ to the contact shifts, no spin densities have been evaluated from the measured shifts. The large downfield shifts for the bridging methylene protons probably reflect spin transfer in the σ system.

The observation of accurate Curie behavior for the shifts of a high-spin monomer **3** establishes the validity of eq 5 for a single spin state and supports the applica-

(44) (a) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Amer. Chem. Soc.*, **89**, 1992 (1967); (b) J. L. Hoard, M. J. Hamor, T. A. Hamor, and W. S. Caughey, *ibid.*, **87**, 2312 (1965); (c) D. F. Koenig, *Acta Crystallogr.*, **18**, 663 (1965).

(45) G. N. La Mar and F. A. Walker, results to be submitted for publication.

(46) R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Amer. Chem. Soc.*, **86**, 379 (1964).

(47) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956); A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

Table IV. Isotropic Shifts for High-Spin Iron(III) Porphyrin Chloride Complexes

Complex	Shifts, ^a ppm				
	Pyrrole-H	<i>o</i> -H	<i>meso</i> <i>m</i> -H	<i>p</i> -H	CH ₂
Fe(TPP)Cl ^b	-70.2	~+1.7 ^d	-4.50 -5.62	+1.45	
Fe(TTP)Cl ^b	-70.2	+1.8 ^d	-4.71 -5.76		-3.80
Fe(T-nPrP)Cl ^{b,e}	-76.8 ^e		α -CH ₃ -57.2	β -CH ₂ ~0	γ -CH ₂ -1.3
Fe(OEP)Cl ^{c,e}	CH ₂ -35.4 -39.0	CH ₃ -4.7		H +65	

^a CDCl₃ solution, ~29°. ^b Referenced against analogous diamagnetic nickel(II) porphyrin. ^c Referenced against free ligand. ^d Expected splitting not observable. ^e For discussion of spectra, cf. ref 48.

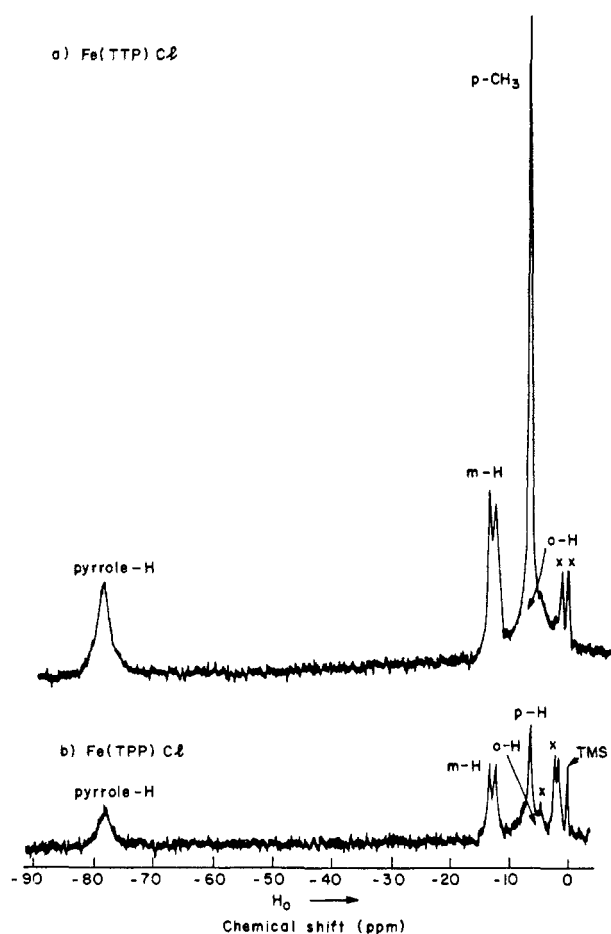


Figure 5. PMR spectra (100 MHz) of (a) Fe(TTP)Cl and (b) Fe(TPP)Cl in CDCl₃ solution at ~29°.

bility of eq 6 to the dimers. A comparison of the temperature dependence of the contact shift and susceptibility for the dimer may therefore be expected to shed light on the validity of the assumption of equal coupling constants for all spin states.

(b) **Porphyrin Complexes.** The monomeric species studied here are of the type Fe(P)Cl. While an apical oxygen donor ligand would simulate more closely the coordination environment in the dimer, it will be shown that the conclusions reached for the chloride complexes are relevant to those containing oxygen ligands. PMR traces for Fe(TPP)Cl and Fe(TTP)Cl are shown in Figure 5. All phenyl resonances were assigned by

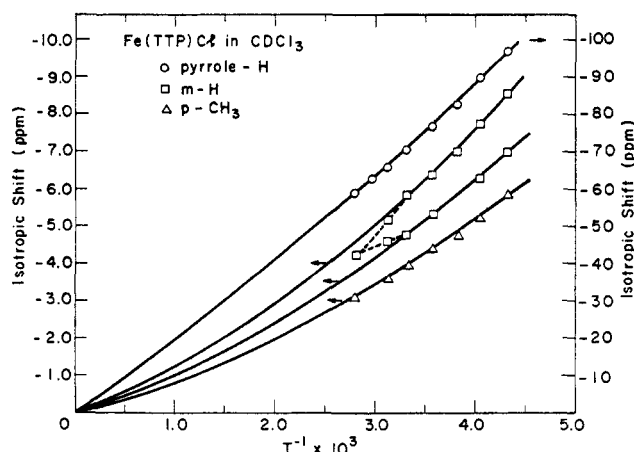


Figure 6. Plot of the temperature dependence of the isotropic shifts of Fe(TTP)Cl in CDCl₃ solution. The solid line for pyr-H was obtained from a fit to eq 13 and the solid lines through the *m*-H and *p*-CH₃ data points were calculated as described in the text.

methyl substitution.⁴⁸ The two *m*-H signals observed below ca. 60° occur because of the nonequivalence of these protons in structure 4 when phenyl group rotation is slow.⁴⁹ The temperature dependence of the pyr-H, *m*-H, and *p*-CH₃ signals of Fe(TTP)Cl is plotted in Figure 6. Other porphyrin complexes of this type possess similar spectra, which will be discussed elsewhere.⁴⁸ Isotropic shifts at ambient temperature are collected in Table IV. Inspection of Figure 6 reveals that the shifts do not conform to strict T^{-1} dependence, but tend to exhibit curvature such that they increase faster than T^{-1} as the temperature is decreased. The curvature is variable, being least for pyr-H and largest for the two *m*-H peaks (slow exchange region).

The curvatures in Figure 6 are interpreted in terms of simultaneous contributions from the contact (eq 11) and dipolar terms (eq 12), in which case the net shift takes the form

$$\left(\frac{\Delta H}{H_0}\right) = \frac{\alpha}{T} + \frac{\epsilon}{T^2} \quad (13)$$

where $\alpha = -(A/h)F$ and $\epsilon = B(3 \cos^2 \theta - 1)r^{-3}D$. Fitting the pyr-H isotropic shifts to eq 13 permits the

(48) F. A. Walker and G. N. La Mar, *Ann. N. Y. Acad. Sci.*, in press.
(49) For pmr studies relevant to Ph group rotation in metalloporphyrins, cf. F. A. Walker and G. L. Avery, *Tetrahedron Lett.*, **52**, 4949 (1971); S. S. Eaton, G. R. Eaton, and R. H. Holm, *J. Organometal. Chem.*, **39**, 179 (1972).

Table V. Calculated Dipolar and Contact Shifts for High-Spin Iron(III) Porphyrin Chloride Complexes

Resonance signal	$[(3 \cos^2 \theta - 1)/r^3] \times 10^{24}$	Rel geom factor	Calcd $(\Delta H/H_0)^{\text{dip}}$	Obsd ^a $(\Delta H/H_0)^{\text{iso}}$	Net $(\Delta H/H_0)^{\text{con}}$
Pyrrole-H <i>meso</i> -Ph	-670	-1.000	-9.6	-70.2	-60.6
<i>o</i> -H	-436	-0.650	-6.3	} $\sim +1.7^b$	$\sim +8.0$
	-224	-0.335	-3.2		$\sim +4.9$
<i>m</i> -H	-182	-0.271	-2.6	-5.8	-3.2
	-139	-0.207	-2.0	-4.7	-2.7
<i>p</i> -H	-146	-0.219	-2.1	+1.45	+3.6
<i>p</i> -Me	-113	-0.167	-1.6	-3.80	-2.2

^a Data for Fe(TPP)Cl and Fe(TTP)Cl (Table IV). ^b Expected splitting not observable.

determination of α and ϵ , and therefore (A/h) and D since the geometrical factor can be evaluated from available X-ray data.^{44a} This fit yields $(A/h)_{\text{pyr-H}} \cong 2.0 \times 10^5$ Hz and $D \cong 11.3 \pm 1.0$ cm⁻¹. The theoretical temperature dependence generated by these values is indicated by the solid line in Figure 6. With this value of D the relative dipolar shifts for other protons are determined solely by the relative geometric factors. Values for the contact and dipolar contributions to the observed shifts at 25° are given in Table V. Geometrical factors for *o*-H and *m*-H were calculated assuming the phenyl rings to be perpendicular to the porphyrin plane and are not significantly affected by limited oscillations. The temperature dependence predicted for the phenyl protons was determined by imposing a T^{-1} dependence for the contact contributions and a T^{-2} dependence for the dipolar contributions, leading to the solid lines through the data points in Figure 6. A good fit for all resonances is obtained in this manner, with the relative magnitudes of the observed deviations from Curie behavior consistent with the relative importance of dipolar *vs.* contact⁵⁰ contributions at a given ligand position. The pattern of net contact shifts for the phenyl group (Table V) is characteristic of delocalized π spin density.

The D value obtained from the pmr data is of the same sign and comparable magnitude to those reported for some natural porphyrin iron(III) chloride complexes (*ca.* 7–9 cm⁻¹) obtained using far-infrared techniques.⁴⁰ The present analysis is the first case of the determination of a ZFS parameter by nmr. The far-ir studies have also shown that D is a sensitive function of the nature of the axial ligand X, decreasing in the order I > Br > Cl > F for complexes of several natural porphyrins.⁴⁰ The same order appears to hold in the Fe(TTP)X series. Analysis of Curie plot curvature of the pyr-H shift has yielded $D \approx 14$ cm⁻¹ for the iodide complex.⁴⁸

These results demonstrate that isotropic shifts of the high-spin porphyrin monomers do not follow the Curie law due to the presence of dipolar shifts with a T^{-2} dependence, arising from D values significantly larger than in salen monomers.⁵¹ Thus, eq 5 and 6 are

(50) If $g_{\parallel} \neq g_{\perp}$ contact shifts for the $S = 5/2$ case can also show a small T^{-2} dependence.⁷ Assuming $g = 2.0$, for the deviation in contact shift from eq 11 to be as large as 1% at 200°K, $|(g_{\parallel} - g_{\perp})D|$ must be *ca.* 4. If $(g_{\parallel} - g_{\perp}) = 0.10$ as an upper limit, $D = 40$ cm⁻¹, a value much larger than found thus far for Fe(P)X complexes,⁴⁰ thereby further indicating that the observed Curie law deviations arise principally from dipolar contributions.

(51) The difference in D values for the two types of monomers is further supported by line width considerations. For salen complexes $\delta_{\text{pyr-H}}$ is approximately the same as $\delta_{\text{pyr-H}}$ of the porphyrins even though $r_{\text{Fe-H}} \sim 6.5$ Å and $r_{\text{Fe-pyr-H}} \sim 5.3$ Å. For dipolar relaxation in the

unlikely to be strictly applicable to the porphyrin μ -oxo dimers and an analysis⁹ of their shifts in terms of a single parameter, J , is of questionable validity. While this conclusion might be more appropriately based on results for an apical oxygen-donor monomer, far-ir data indicate that $D(\text{met-Mb}) > D(\text{MbF})$ and that the value of the former (9.5 cm⁻¹) is comparable to those of other porphyrin chloride complexes.⁴⁰

Antiferromagnetic Dimers. (a) **Salen Dimers.** The pmr spectrum of [Fe(4Me-salen)]₂O at $\sim 29^\circ$ is shown in Figure 3a. Signal assignments were made by alkyl substitution and isotropic shifts are listed in Table II. [Fe(5*t*Bu-salen)]₂O was prepared in order to obtain a dimer sufficiently soluble for accurate nmr determination³² of temperature-dependent susceptibility. [Fe(salen)]₂O itself proved insufficiently soluble for shift or susceptibility measurements over an adequate temperature range in either chloroform or dichloromethane.

Although the shifts of the dimers are concentration independent, they were found to depend upon solvent. For both [Fe(salen)]₂O and [Fe(5*t*Bu-salen)]₂O it was observed that at ambient temperature the shifts are ~ 5 –10% larger and line widths ~ 5 –10% smaller in dichloromethane than in chloroform. The larger shifts in the former solvent suggest greater paramagnetism and, hence, a smaller J . This is in agreement with the previous observation^{23a} that the dichloromethane solvate, [Fe(salen)]₂O·CH₂Cl₂, exhibits a slightly larger magnetic moment than the unsolvated form. The solvate molecule in the former lies near the bridging oxygen^{23c} such that a small effect on J is not surprising. The temperature dependence of the shifts of the 5-*t*Bu complex in dichloromethane and chloroform are identical in that scaling the shifts to coincide at any one temperature causes the shifts to superimpose over the entire temperature interval of measurement.

The pattern of ring proton shifts is consistent with dominant contact interactions. Relative shifts for dimer and monomer are quite similar (Table III) and the mode of spin-delocalization is presumably the same in both. If the dimers experienced any dipolar shifts, the relative ring proton shifts in the dimers and monomers would not be expected to be so similar. Single-

fast motion limit,⁵² proton line widths are proportional to the electron spin relaxation time (T_{1e}), indicating that T_{1e} is longer in the salen monomers. It has also been shown^{45,53} that T_{1e} in such high-spin d^5 systems is determined by modulation of D by the tumbling of the complex, such that $T_{1e} \propto D^{-2}$. Because the salen complexes are smaller, their solution motions should be more rapid than for the porphyrins, and it can be concluded that D for the salen monomers must be smaller than for the porphyrin monomers.

(52) N. Bloembergen, *Phys. Rev.*, **99**, 559 (1955).

(53) M. Rubinstein, A. Baram, and Z. Luz, *Mol. Phys.*, **20**, 67 (1971).

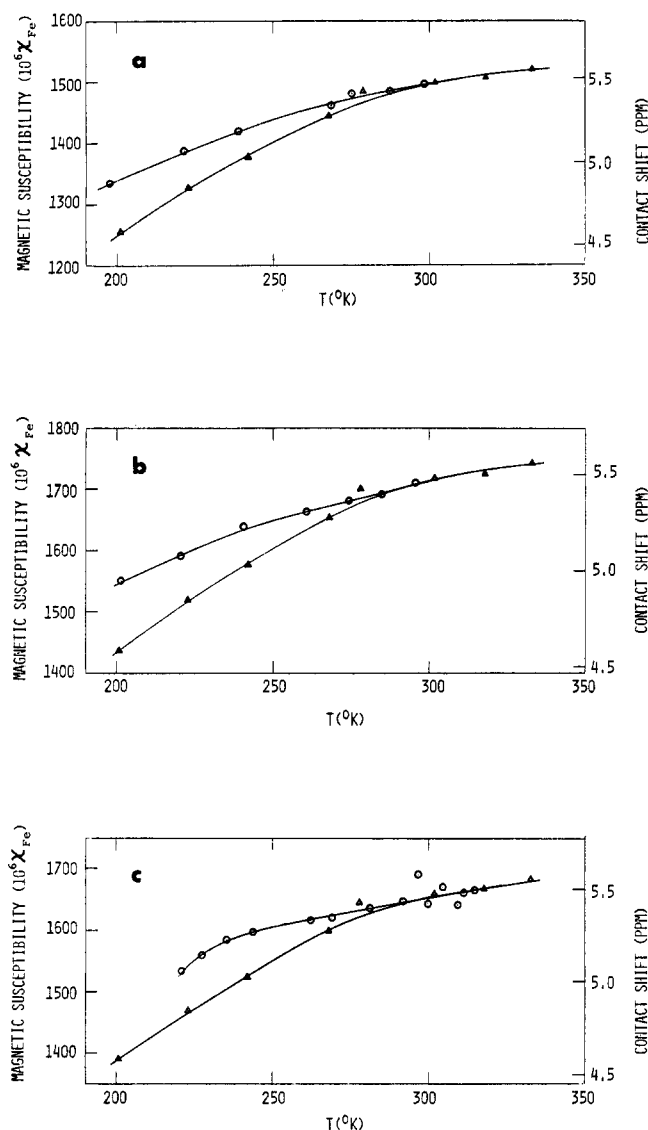


Figure 7. Temperature dependence of the 4-H contact shifts of [Fe(5tBu-salen)]₂O in CH₂Cl₂ (▲) with the magnetic susceptibility per iron of (a) [Fe(salen)]₂O in the solid state,^{23a} (b) [Fe(salen)]₂O · CH₂Cl₂ in the solid state,^{23a} and (c) [Fe(5tBu-salen)]₂O in CH₂Cl₂ solution measured by pmr. The scales were arbitrarily chosen such that χ_{Fe} and $\Delta H/H_0$ coincide at (a) 302, (b) 302, (c) 318°K.

crystal magnetic measurements of [Fe(salen)]₂O · CH₂Cl₂ demonstrate extremely small magnetic anisotropy.^{23c} In view of these results and the very small D values in the monomers, dipolar shifts should be negligible so that a comparison of χ and $\Delta H/H_0$ should serve to indicate whether or not $A_1 = A_2$.

Comparison of the 4-H contact shifts of [Fe(5tBu-salen)]₂O with susceptibility data is shown in Figure 7. Comparison with the unsubstituted dimer is appropriate since χ for a series of salen dimers has been shown to be relatively insensitive to substitution at the five-position.^{23a} While the solid state susceptibilities of the solvated and unsolvated dimers do differ slightly, their temperature dependencies essentially superimpose when χ_{Fe} values are scaled to coincide at ca. 300°K. In the three cases illustrated, the contact shift decreases faster than χ_{Fe} as the temperature is lowered. From eq 10 and Figure 2 this result indicates that $A_2 > A_1$. Similar conclusions can be reached using the 6-H shifts, although their smaller values introduce more

uncertainty into the magnitude of the deviation from χ_{Fe} . Moderate to good fits of the results in Figures 7a and 7b can be obtained using energy level separations predicted by the HDVV model and variable A_i values. For example, taking $J = -87$ cm⁻¹, determined for solid [Fe(salen)]₂O · CH₂Cl₂,^{23a} to apply to [Fe(5tBu-salen)]₂O in dichloromethane the data in Figure 7b can be fit with the following ranges of parameters: $A_1/A_2 = 0.40$ to 0.60 , $A_3/A_2 = -0.20$ to 0.50 . Adequate fits were obtained only with inclusion of the E_3 level.⁵⁴

It is therefore concluded that for dimers of the [Fe(salen)]₂O type the coupling constants are observably dependent on spin state, and that J may not be directly extracted from the contact shift data even though eq 5 and 6 are valid. Recently, a pmr study of the dimer [Fe(*n*Pr-sal)]₂O has been reported¹⁵ in which a solution J value was determined from the temperature dependence of the contact shifts using eq 6 with a single coupling constant A . A plot of $(\Delta H/H_0)_{4H}$ vs. χ_{Fe} measured in the solid state⁵⁵ reveals the same type of deviation as shown in Figure 7a-c for the salen systems. The larger apparent value of J found in solution¹⁵ compared to that in the solid⁵⁵ (HDVV model) is not unambiguously interpretable, and the lack of agreement between the two values probably reflects in part a dependence of A_i on spin state similar to that found for the salen systems.

(b) **Porphyrin Dimers.** Pmr spectra for the dimers [Fe(TPP)]₂O, [Fe(T-*n*PrP)]₂O, and [Fe(OEP)]₂O at ambient temperature are illustrated in Figures 8 and 9. Chemical shifts are collected in Table VI. Those of [Fe(TPP)]₂O have been reported independently⁹ and our data are in good agreement. More than one phenyl signal for this compound was found only in toluene solution, where two signals of intensity ratio 3:2 were observed. The assignments of this pair given in Table VI are tentative. The pyr-H signal of [Fe(T-*n*PrP)]₂O was assigned by analogy with [Fe(TPP)]₂O and the *n*-Pr resonances were assigned on the basis of line widths and relative intensities. In the spectrum of [Fe(OEP)]₂O at room temperature the *meso*-H signal is not clearly resolved. However, at ca. -80° a shoulder appeared on the low-field side of the methylene doublet near the expected pyr-H diamagnetic position while at ca. +90° a shoulder appeared on the high-field side of this doublet. Hence the *meso*-H shift indicated in Figure 9 and Table VI is approximate. The inequivalence of the methylene protons in this dimer is clearly resolved (Figure 9), as is the case for Fe(OEP)Cl (Table IV).

In obtaining accurate isotropic shifts for porphyrin dimers, it is necessary to employ as references the chemical shifts of structurally related diamagnetic dimers due to ring current effects of one porphyrin

(54) The best fit using the three level scheme ($S = 0, 1, 2$) and $J = -87$ cm⁻¹ yields $A_1/h = 1.04 \times 10^5$ and $A_2/h = 2.32 \times 10^5$ Hz. The fit is improved by also including the $S = 3$ level, obtaining $A_1/h = 1.10 \times 10^5$, $A_2/h = 2.21 \times 10^5$, and $A_3/h = 0.44 \times 10^5$ Hz. For $J = -95$ cm⁻¹, obtained from the susceptibility studies of [Fe(salen)]₂O (ref 1a), the three-level fit yields $A_1/h = 1.32 \times 10^5$ and $A_2/h = 2.40 \times 10^5$ Hz, while the four-parameter fit gives $A_1/h = 1.37 \times 10^5$, $A_2/h = 2.29 \times 10^5$, and $A_3/h = 0.46 \times 10^5$ Hz. It is observed that A_1/h and A_2/h are changed by approximately 5% upon inclusion of the $S = 3$ level. In view of the number of independent variables and the anticipated ambiguity of the uniqueness of the resulting parameters, not too much emphasis should be placed on the numerical values.

(55) A. van den Bergen, K. S. Murray, and B. O. West, *Aust. J. Chem.*, **21**, 1517 (1968).

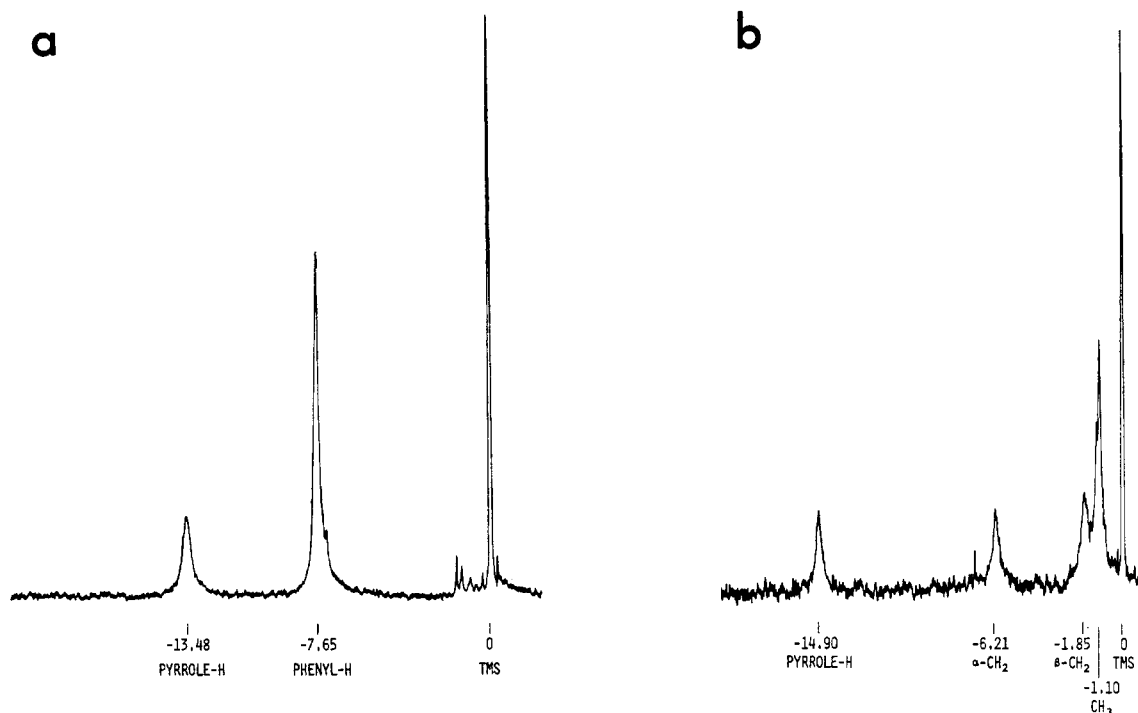


Figure 8. PMR spectra (100 MHz) of (a) $[\text{Fe}(\text{TPP})]_2\text{O}$ and (b) $[\text{Fe}(\text{T-}n\text{PrP})]_2\text{O}$ in CDCl_3 solution to $\sim 29^\circ$. Magnetic field increases from left to right. Peaks not labeled are due to impurities. Shifts are in ppm.

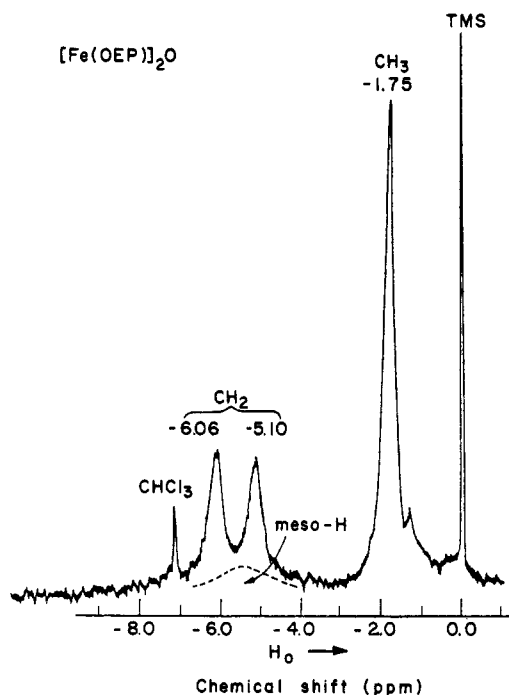


Figure 9. PMR spectra (100 MHz) of $[\text{Fe}(\text{OEP})]_2\text{O}$ in CDCl_3 solution at $\sim 29^\circ$.

ring on the shifts of the other.⁵⁶ With respect to their positions in diamagnetic monomeric $\text{Ni}(\text{II})$ analogs,⁴⁵ the *meso*-H, CH_2 , and pyr-H signals of the TPP and OEP μ -oxo $\text{Sc}(\text{III})$ dimers (Table VI) are shifted up-

(56) For related studies on μ -oxo-phthalocyanine complexes, cf. T. R. Janson, A. R. Kane, J. F. Sullivan, K. Knox, and M. E. Kenney, *J. Amer. Chem. Soc.*, **91**, 5210 (1969). Also, compare the shifts of $\text{Sc}(\text{OEP})\text{OAc}^{\text{57}}$ (CH_2 , -4.07 , -4.19 ; CH_3 , -1.85 ; *meso*-H, -10.37 ppm, CDCl_3) with those of $[\text{Sc}(\text{OEP})]_2\text{O}$ in Table VI.

(57) K. W. Buchler, G. Eikermann, L. Puppe, K. Rohbock, H. H. Schneehage, and D. Weck, *Justus Liebigs Ann. Chem.*, **745**, 135 (1971).

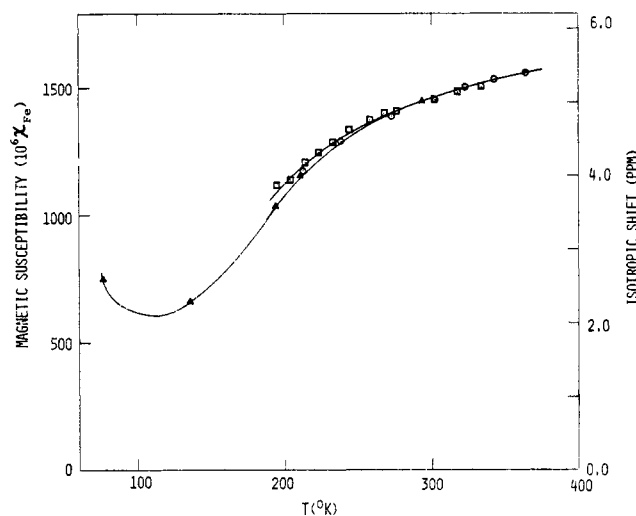


Figure 10. Temperature dependence of the pyr-H isotropic shifts of $[\text{Fe}(\text{TPP})]_2\text{O}$ in CD_2Cl_2 (\square) and CDCl_3 (\circ) and χ_{Fe} in the solid state.^{24b} Isotropic shifts are negative. The scale was arbitrarily chosen such that the shift and χ_{Fe} coincide at 294°K . Note that the originally published^{24a} susceptibility data for this complex have been revised.^{24b}

field by *ca.* 0.7, 0.3, and 0.3 ppm, respectively. In a previous study⁹ of $[\text{Fe}(\text{TPP})]_2\text{O}$ the free ligand was used as the diamagnetic reference, and it is estimated that the reported contact shifts are in error by *ca.* 7–8% in the temperature interval employed due to this choice of reference. The error is propagated in J values determined from the shifts even if, as assumed, eq 6 is valid and all A_i are equal.

The temperature dependence of the pyr-H isotropic shift and solid state susceptibility^{24b} of $[\text{Fe}(\text{TPP})]_2\text{O}$ are compared in Figure 10. Data were obtained in both chloroform and dichloromethane, with the latter

Table VI. Pmr Chemical Shifts of Oxo-Bridged Iron(III) Porphyrin Complexes at $\sim 29^\circ$

Complex	Solvent	Shift, ppm			
		Pyrrole-H		Phenyl	
[Fe(TPP)] ₂ O	Toluene- <i>d</i> ₈	-13.60		-7.45 (<i>m</i> -, <i>p</i> -H)	
				-7.65 (<i>o</i> -H)	
	CD ₂ Cl ₂	-13.49		-7.65	
[Sc(TPP)] ₂ O ^a	CDCl ₃	-13.48		-7.65	
	CDCl ₃	-8.46		-7.70	
	CDCl ₃	-5.02		$\sim +0.05$	
[Fe(OEP)] ₂ O		<i>meso</i> -H	-CH ₂ -CH ₃		-CH ₂ -CH ₃
	CDCl ₃	~ -5.5	-6.06, -5.10		-1.75
	CDCl ₃	-9.40	-3.80		-1.56
[Sc(OEP)] ₂ O	CDCl ₃	$\sim +3.9$	-2.26, -1.30		-0.19
[Fe(T-nPrP)] ₂ O		Pyrrole-H	α -CH ₂	β -CH ₂	CH ₃
	CDCl ₃	-14.90	-6.22	-1.81	-1.05
	CDCl ₃	~ -6.3	~ -1.3	$\sim +0.5$	~ 0

^a D. Dolphin, unpublished results. ^b Isotropic shifts given as the difference between chemical shifts of Fe and Sc complexes. ^c [Sc(TPP)]₂O was used as the diamagnetic reference of the pyrrole-H shift, and the free ligand was used for the *meso*-*n*-Pr shifts.

solvent used to extend the temperature range to -75° . Accurate solution susceptibilities were not obtained due to the limited solubility of the complex and a small extent of monomer formation in the optimum solvent, chloroform. The increase in χ_{Fe} at low temperature indicates some high-spin monomer impurity. The comparison is still of utility since the deviation observed is a lower limit to the actual difference due to the presence of the impurity. The isotropic shifts of the dimer are not affected by monomer impurity (*vide supra*). The deviation of shift and susceptibility is consistent with $A_1 > A_2$.⁵⁸ Because the quadratic temperature term due to ZFS causes the isotropic shifts of the high-spin monomer to increase faster than predicted by Curie behavior as the temperature is lowered, a similar behavior for the individual populated spin states of the dimer⁵⁹ could alternatively account for the direction of the deviation of isotropic shift from χ_{Fe} in Figure 10. The significantly different isotropic shift pattern for the dimers, as compared with either the isotropic shift or the contact shift pattern⁴⁸ for the monomers, given in Table VII, is also suggestive of the presence of some dipolar contribution to the observed shifts of the dimer,⁶² though different spin

(58) The possibility of unequal coupling constants in porphyrin dimers has been recognized in other work,¹² where it is claimed that A_1 is slightly larger than A_2 .

(59) One of the referees suggested that the dipolar shift must be negligible and that $D = 0$ for the dimer, since it has been reported⁶⁰ that the far-infrared spectrum for the deuteriohemine dimer failed to reveal any ZFS transitions. However, as discussed elsewhere (ref 40) the need for long electron spin relaxation times to yield narrow far-ir spectra requires the use of temperatures in the range 1.3–50°K. At the upper limit, the populations of the $S = 1$ and $S = 2$ levels are 0.15 and 10–8%, respectively, using $-2J = 380^\circ\text{K}$, as obtained in ref 24d. Since the signal-to-noise in far-ir magnetic spectroscopy is often very low even for paramagnetic complexes, resolution of the ZFS transitions for the $S = 1$ level are very unlikely, and for the $S = 2$ level, impossible. At a lower temperature, 20°K, where spin relaxation would have decreased to yield narrower lines, the population of the $S = 1$ level drops to 10–6%. Moreover, the observed absence of magnetic broadening of the Mössbauer peaks of ferric porphyrin dimers⁶¹ has been interpreted as arising from rapid spin relaxation due to the antiferromagnetic coupling, even at 4.2°K. It is therefore very unlikely that any limits can be placed on the probable magnitudes of the D values for the various spin levels based on available spectroscopic data.

(60) N. Sadasivan, H. I. Eberspaecher, W. H. Fuchsman, and W. S. Caughey, *Biochemistry*, **8**, 534 (1969).

(61) M. A. Torrens, D. K. Straub, and L. M. Epstein, *J. Amer. Chem. Soc.*, **94**, 4100 (1972).

(62) An estimate of the dipolar shift for the $S = 2$ level, assuming a value for D only 10% of that for the monomers, still yields ~ 0.5 ppm. Since this accounts for $\sim 10\%$ of the observed shift, the hazards of discounting the ZFS for the dimer at this time are obvious.

Table VII. Comparison of Relative Shifts^a in High-Spin Monomeric and Antiferromagnetic Dimeric Porphyrin Complexes

Resonance signal	Monomer		Dimer
	($\Delta H/H_0$) ^{iso}	($\Delta H/H_0$) ^{con}	($\Delta H/H_0$) ^{iso}
Pyrrole H ^b	-10.0	-10.0	-10.0
CH ₂ ^c	-5.0, -5.6	-5.3 ^d	-4.4, -2.6
CH ₃ ^c	-0.7		-0.4
<i>meso</i> H ^c	+9.3	+13.3 ^d	+6.8
α -CH ₂ ^e	-7.5	-7.6 ^d	~ -2.2
β -CH ₂ ^e	~ 0		$\sim +0.8$
γ -CH ₃ ^e	-0.2		~ 0

^a Data from Tables IV and VI; shifts for pyr-H normalized to -10.0. ^b Fe(TPP)Cl. ^c Fe(OEP)Cl. ^d Reference 48. ^e Fe(T-nPrP)Cl.

delocalization mechanisms could also account for the difference. This difference in monomer and dimer shift patterns for the porphyrins is contrasted to the similarity of the two patterns for the salen complexes (Table III).

The preceding results indicate that a straightforward analysis of the isotropic shifts of porphyrin dimers assuming negligible dipolar interactions and ZFS effects is clearly an oversimplification, and that interpretations of this type^{9,12} are unlikely to lead to accurate values for J . A more detailed analysis of dimer shifts is not advisable at this time and must await direct determination of D values for monomers or, preferably, the dimers themselves. This information together with an expanded theoretical treatment should permit corrections in eq 5 and 6 for the temperature dependence of the individual spin states, leading to a more satisfactory description of isotropic shifts of porphyrin monomers and dimers than is possible at present.

The absence of significant ZFS effects in the salen dimers has allowed the conclusion that $A_2 > A_1$ and permits, within the MO description, some qualitative predictions about the nature of the d orbitals which contain the unpaired spins in the excited $S' = 1, 2$ states. Since the aromatic proton shifts reflect π spin delocalization, $A_2 > A_1$ indicates that the probability of finding unpaired spins in a d orbital of proper symmetry to mix with ligand π MO's is somewhat larger in the $S' = 2$ than in the $S' = 1$ state. The highest filled π MO of the salicylaldiminate has an

even number of nodes so that it will interact mainly with d_{zz} (the z axis is perpendicular to the O_2N_2 plane and the x axis bisects the $O-Fe-N$ angle). Hence d_{zz} must be placed in the MO diagram for the dimer (Figure 1b) such that it has a higher spin population in the $S' = 2$ state. Although an approximate MO diagram for some bent μ -oxo dimers has been proposed,²⁰ the low symmetry of the system and the lack of information concerning the exact ordering of the levels in the monomers renders any detailed analysis unrealistic at this stage. It is emphasized that none of the results obtained in this work imply that an MO description is to be preferred to the HDVV treatment of the electronic properties of the antiferromagnetic dimers. Studies of the related μ -oxo Fe(III) dimers derived from HEDTA^{35,63,64} and EDTA⁶⁴ indicate that their magnetic and spectral properties can be adequately interpreted on the basis of high-spin ferric ions coupled by spin-spin interactions, with the separation of the $S' = 0, 1, 2$ states in accord with the predictions of the HDVV model.⁶³

(63) M. Okamura, personal communication to G. N. L.

(64) H. J. Schugar, G. R. Rossman, C. G. Barraclough, and H. B. Gray, *J. Amer. Chem. Soc.*, **94**, 2683 (1972).

Lastly, it has been suggested that pmr spectra of oxo-bridged dimers in solution are well-resolved because magnetic exchange coupling decreases the electron spin relaxation time in the dimer relative to that in a related high-spin monomer. Although such coupling can lead to considerable decreases in T_{1e} for the metal center in some cases, T_{1e} for salen dimers is actually longer than for the monomers. In the fast motion limit the line width is given⁵² by $\delta \propto \mu_e^2 T_{1e}$. Taking $\mu_e \approx 6$ BM for the monomer and ~ 2 BM for the dimer and using the experimental 4-H line widths in Table II, T_{1e} (monomer) $\sim 0.7T_{1e}$ (dimer). Hence, relaxation in the monomer is more efficient, and the narrower lines in the dimer arise primarily from the appreciable population of the diamagnetic ground state. The improved resolution of the monomer spectrum compared to that of the dimer is evident in Figure 3.

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Stereochemically Nonrigid Six-Coordinate Molecules.¹

III. The Temperature-Dependent ¹H and ³¹P Nuclear Magnetic Resonance Spectra of Some Iron and Ruthenium Dihydrides

P. Meakin, E. L. Muetterties, and J. P. Jesson*

Contribution No. 1947 from the Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898. Received June 20, 1972

Abstract: Stereochemical nonrigidity in a class of six-coordinate hydrides has been examined using ¹H and ³¹P nmr techniques. These hydrides are of the type H_2ML_4 , where M is iron or ruthenium and L is a phosphite, phosphine, phosphinite, or phosphonite. The stereochemical behavior in solution for these complexes is of two types: (1) the cis stereoisomer with essentially no trans form present and (2) cis and trans forms present in equilibrium and both detectable by nmr. The rearrangement barriers for the iron complexes proved relatively insensitive to wide variations in the steric and electronic character of the phosphorus ligands. This situation also prevailed in the ruthenium set, but ruthenium barriers were larger than those for iron. The intramolecular rearrangements are discussed in terms of the "tetrahedral jump" model with consideration of the range of potential energy surfaces available for these fluxional molecules. A similar study was also carried out for complexes of the form H_2ML_3L' ($L' = CO, C_6H_5CN$).

Stereochemical nonrigidity is an established, common feature of five-, seven-, eight-, and nine-coordinate molecules or ions.²⁻⁵ This is a primary reflection of the nondominance of any idealized coordination polyhedron in these coordination classes and the close physical relationships among the plau-

sible, idealized coordination polyhedra within a class.²⁻⁵ In contrast, six-coordinate molecules are much less prone to facile intramolecular rearrangement.²⁻⁶ For this coordination number there is one predominant coordination polyhedron, the octahedron.^{4,6} Recently we showed that a group of transition metal hydrides, of the type H_2ML_4 , are stereochemically nonrigid.⁷⁻⁹ This was the first¹⁰ unequivocal demon-

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