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SYNTHESIS STRUCTURE AND MAGNETIC PROPERTIES OF
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CHAPEL HILL DEPT OF CHEMISTRY W HILLER ET AL.
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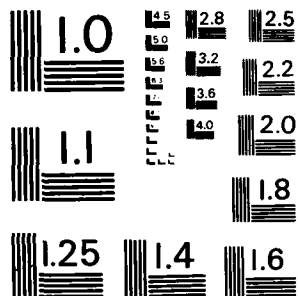
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The crystal and molecular structure of the compound catena--oxo-hemiporphyrizinatoiron(IV), $[\text{FeON}_8\text{C}_{26}\text{H}_{14}]_n$, has been determined from single-crystal, three-dimensional X-ray diffraction counter data. The compound crystallizes as blue-black needles in space group $P2_1/n$ with $Z = 2$ and having unit cell dimensions (at 210 K) $a = 16.090(3)\text{\AA}$, $b = 3.975(2)\text{\AA}$, $c = 16.070(3)\text{\AA}$, and $\beta = 92.97(1)^\circ$. The structure was refined by full-matrix least-squares techniques to a conventional R value of 0.054. Distorted hemiporphyrizinatoiron units stack along the b axis and are linked into

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20. Abstract

polymeric, uniformly spaced, linear chains by axially-bound oxygen bridges. The oxygen atoms are disordered into two crystallographically distinct sites lying about a central location which is normal to the C_2 axis collinear with the chain. The Fe-O-Fe angles are 158.2° and 170.5° , and the Fe-O bond distances range from $1.973\text{\AA}$ to $2.030\text{\AA}$. Mössbauer spectral studies at 4.2 K, room temperature and at 420 K reveal that there are two iron sites in the chain as a result of the disorder of the oxygen atoms, and the spectrum is essentially temperature independent. Magnetic susceptibility studies reveal that the iron ions are antiferromagnetically coupled in an alternating chain with $J = -133\text{ cm}^{-1}$, $g = 2.3$ and an alternation parameter of 0.4. ←

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Synthesis, Structure and Magnetic Properties of catena-
 μ -Oxo-Hemiporphyrazinatoiron(IV), the First Polymeric
 μ -Oxo-Bridged Complex of Iron

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Abstract: The crystal and molecular structure of the compound
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by full-matrix least-squares techniques to a conventional R

value of 0.054. Distorted hemiporphyrinatoiron units stack along the b axis and are linked into polymeric, uniformly spaced, linear chains by axially-bound oxygen bridges. The oxygen atoms are disordered into two crystallographically distinct sites lying about a central location which is normal to the C_2 axis collinear with the chain. The Fe-O-Fe angles are 158.2° and 170.5° , and the Fe-O bond distances range from 1.973 Å to 2.030 Å. Mössbauer spectral studies at 4.2 K, room temperature and at 420 K reveal that there are two iron sites in the chain as a result of the disorder of the oxygen atoms, and the spectrum is essentially temperature independent. Magnetic susceptibility studies reveal that the iron ions are antiferromagnetically coupled in an alternating chain with $J = -133 \text{ cm}^{-1}$, $g = 2.3$ and an alternation parameter of 0.4.

Introduction

In the last few years there has been great interest in the polymeric μ -oxo-phthalocyaninato complexes of silicon and germanium, since after being doped with iodine, the partially oxidized compounds exhibit high electrical conductivities (up to $10 \text{ ohm}^{-1} \text{ cm}^{-1}$).² Corresponding complexes with the transition metals titanium and vanadium are monomers with terminal oxo-ligands which exhibit strong π -bonds to the central atom.³ Tetraphenylporphyrinatoiron forms μ -oxo-bridged, dimeric

complexes $(\text{TPPFe})_2\text{O}$ (H_2TPP = tetraphenylporphyrin).⁴ An analogous dimeric μ -nitrido complex has also been reported in which the formal oxidation state of the iron is +3.5.⁵ It has been shown by cyclic voltammetric studies that $(\text{FeTPP})\text{Cl}$ and $(\text{FeTPP})_2\text{O}$ easily undergo reversible one-electron oxidations to Fe(IV) or Fe(III,IV) . An oxidation state of +IV for iron has recently been proposed for the tetraphenylporphyrinatoiron complex $[\text{Fe(O)(TPP)(1-methylimidazole)}]$.⁶ We report here the synthesis, structure and properties of $(\text{FeOHp})_n$ (where H_2Hp = hemiporphyrazine), the first polymeric μ -oxo-bridged complex of iron. Based on chemical and physical properties we assign a formal oxidation state of +IV and spin value $S = 1$ to the iron atom in this novel complex.

Experimental Section

Preparation and Characterization. Polymeric μ -oxo-hemiporphyrazinatoiron $[\text{FeOHp}]_n$ is prepared by treating hemiporphyrazine (H_2Hp) with iron(II) acetate in boiling nitrobenzene over a period of 30 minutes. Under these conditions nitrobenzene acts as an oxidizing agent, since $[\text{FeOHp}]_n$ is also obtained when the reaction is carried out in an inert atmosphere. Black, needle-like single crystals were formed on recrystallization of the crude product from nitrobenzene by slow cooling of the solution. The crystals were washed with methanol.

A solution of hemiporphyrinato-bis(pyridine)iron(II), $[\text{HpFe}(\text{py})_2]^7$ in pyridine is easily oxidized in air to $[\text{FeOHp}]_n$. The polymer $[\text{FeOHp}]_n$ is quite stable in bases (KOH, pyridine) but decomposes in the presence of strong acids with loss of the metal. There is a weight loss in the thermogravimetric analysis between 630 and 650 K which corresponds to the expected weight loss of an oxygen atom per FeHp unit. The ion of highest mass in the mass spectrum is FeOHp^+ ($m/e = 510$). The infrared spectrum of $[\text{FeOHp}]_n$ differs from that of $[\text{FeHp}]^7$ (which has been prepared in pure form for the first time) principally in the region between 700 and 900 cm^{-1} . ($[\text{FeHp}]$: 770w, 810m, 890w; $[\text{FeOHp}]_n$: 732s, 773s, 801w, 810m, 821s, 895vs).

Mössbauer effect spectra were recorded with a constant acceleration Mössbauer spectrometer equipped with a custom-built furnace and a liquid helium cryostat, and the fittings of sums of Lorentzian lines to the measured spectra were carried out using a least-squares iteration computer program.

Magnetic susceptibility data were collected in Mainz using a Foner type vibrating sample magnetometer over the temperature range 3.35 to 294.8 K, and in Tübingen using a Gouy Balance⁹ over the temperature range 113.2 to 423 K. The data sets were in good agreement. The vibrating sample magnetometer was operated at 10 kOe for the measurements and was calibrated with $\text{HgCo}(\text{NCS})_4$,⁸ while the magnetic equipment in Tübingen was calibrated with NiCl_2 .⁹ Diamagnetic corrections for the

constituent atoms were made using Pascal's constants.¹⁰ A flow type cryostat with an internal helium reservoir was used, and the temperatures were measured with a calibrated Au(0.3%Fe)/chromel thermocouple.

Although the compound is paramagnetic, attempts to record an EPR spectrum using a Varian E-112 EPR spectrometer at several temperatures (292 K, 113 K, 80 K) were unsuccessful.

Crystallographic Data and Structure Determination. The compound $(\text{FeOHp})_n$ crystallizes as blue-black needles. A single crystal with the approximate dimensions $0.15 \times 0.15 \times 0.9 \text{ mm}^3$ was chosen for the X-ray investigation. A monoclinic space group $P2_1/n$ was established on the basis of Buerger precession photographs. The lattice constants were determined accurately using an automatic single crystal diffractometer CAD4 (Enraf-Nonius, Delft) and 25 precisely centered high-angle reflections. Crystal data and data collection details are given in Table I. Two data sets were collected, one at room temperature, and one at 210 K. The CAD4 was operated in the needle mode. For the structure determination 9092 intensities were measured, with an ω/θ -scan from $\theta = 3^\circ$ to 30° at a temperature of 210 K. After averaging over the equivalent reflections of the reciprocal lattice, there remained 1459 reflections with intensities $I > 3\sigma(I)$. Intensity data were corrected for Lorentz and polarization effects and absorption.¹¹

Solution and Refinement of the Structure. The positions of the iron and nitrogen atoms N1 and N3 were deduced from a Patterson synthesis. When these positions were coupled with a difference Fourier synthesis, the missing nitrogen and carbon atoms were then located. Refinement of the positions of the iron, nitrogen, and carbon atoms with isotropic temperature factors led to an R-value of 0.158.^{12,13} The quantity minimized during refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The position of the bridging oxygen atom could not be determined from the data set that had been collected at room temperature. The second data set, which was collected at 210 K, allowed us to localize this position at 0.25, 0.6973, 0.25 from a difference Fourier synthesis. Upon inclusion of the anisotropic temperature parameters the reliability factor was improved to 0.072, whereupon a strong excursion of the oxygen's electron density vertical to the C_2 axis became apparent. When it was assumed that the oxygen was disordered in one site (two symmetry related positions) the reliability factor was 0.060. However, when it was assumed that the oxygen atom was disordered in two sites, that is, four positions which lie normal to the C_2 axis, the R-value was significantly improved to $R = 0.054$. A final difference Fourier analysis then showed no residual electron density at the original position. Incorporation of the calculated H atom positions in the structure-factor calculations led to a final R value of 0.045.

Positional and thermal parameters for the atoms are given in Tables IIA and IIB, and bond angles and bond distances are given in Table III. Tables of structure factors are available as supplementary material.

Results

Description of the Structure. The crystal structure is determined by the voluminous FeHp structural units shown in Figure 1. As shown in Figure 2, the FeHp moieties are stacked up along the *b* axis in translationally identical units, and these are linked together with axially-bound oxygen bridges to form a polymeric, linear chain with the iron atoms lying on the C_2 axes of the space group $P2/n$. The local C_2 symmetry is only fulfilled because of the disorder of the oxygen atoms and the actual molecular symmetry around a given iron is slightly distorted. Neighboring polymer chains are arranged antiparallel to each other (see Figure 2). There is a strong distortion of the (FeHp) units such that the isoindole units are twisted at angles of about 30° above the mean plane, and the pyridine rings are twisted about the same amount below that plane. The twisting probably arises from the space requirements of the central iron atom. This behavior is in sharp contrast to the planar GeHp unit in $[(Hp)Ge(C\equiv C-C(CH_3)_3)_2]$.¹⁴

The bridging oxygen atom is disordered into two crystallographically different sites (four sites overall due to

the C_2 symmetry). Corresponding distances and angles are, therefore, subject to considerable error. The Fe-O_a and Fe-O_b bond distances range from 1.973 to 2.030 Å, respectively, and are identical within the limits of error of the measurements. These distances are compatible with single covalent bonds. The Fe-O-Fe bond angles are 158.2 and 170.5 for the two different oxygen bridge types and can not be considered identical within error limits. This will be shown below to be an important factor in the determination of the magnetic properties.

Mössbauer Spectral Studies. The Mössbauer spectrum of [FeOHp]_n at room temperature is shown in Figure 3, and the isomer shift and quadrupole splitting data are given in Table IV. The identification of two distinct iron sites was unexpected in view of the results of the X-ray structural determination which shows that the iron ions are translationally equivalent. Mössbauer spectra were collected at 420 K, room temperature, and at 4.2 K, yet there were only slight variations in the isomer shift and quadrupole splitting as shown by the data in Table IV. These observations suggest that two predominant iron sites arise from the disorder in the oxygen sites and that these two iron sites exist over the entire temperature range 4.2 K to 420 K. These data also indicate that the two different oxygen bridge types are randomly disordered and occur throughout the entire temperature range. The oxygen sites are not averaged on the Mössbauer time

scale. At temperatures above 420 K, the sample begins to decompose and the Mössbauer spectra deteriorate in quality.

The increase of the isomer shift by ca. 0.2 mms^{-1} with decreasing temperature from 420 K to 4.2 K appears to be entirely due to the temperature dependence of the second order Doppler shift; there is no significant change in the chemical part of the observed isomer shift and thus no appreciable change in the electronic structure of the iron atom. The same argument derives from the quadrupole splitting data. The lack of a pronounced temperature dependence of the quadrupole splitting indicates that the energy gap between the d_{xy} orbital and the orbital doublet (d_{xz} , d_{yz}) is much larger than the thermal energy. The two quadrupole doublets are the result of two slightly different electric field gradients because of the disorder in the oxygen sites.

Magnetic Properties. As shown in Figure 4 the magnetic susceptibility of $[\text{FeOHp}]_n$ decreases from 1.24×10^{-3} at 423 K and approaches 6×10^{-4} at 110 K, the low temperature limit of the data collected at Tübingen. These data are in good agreement with a second set of data which were collected in Mainz. This second data set, which was collected in the temperature range 3.35 K to 294.8 K, revealed a minimum in the magnetic susceptibility near 65 K. Below that temperature the magnetic susceptibility increases with the decrease in temperature. The first attempt for the analysis of these data

was based on the structural information with the assumption that the increase in magnetic susceptibility at low temperatures arose from paramagnetic impurities, defects, and finite chain-length effects, and that the higher temperature data reflected antiferromagnetic exchange coupling in the linear chain.

The low temperature data were fit to a Curie-Weiss law, $\chi = C/(T - \theta)$ using a Simplex non-linear least squares fitting routine with the criterion of best fit being the minimum value of the function

$$F = \sum_i w_i (\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})^2$$

with the weights being assigned $w_i = (\chi_i^{\text{obsd}})^{-1}$. The data in the temperature range 18.3 K to 63.1 K, when corrected for the residual paramagnetism of the exchange coupled predominant component of the sample, may be fit precisely with the Curie-Weiss parameters $C = 0.06$ and $\theta = -25^\circ$. There is a sharp departure of the data at 12.8 K and lower temperatures from this Curie-Weiss law, and the lower temperature data may be fit with the parameters $C = 0.017$ and $\theta = 4^\circ$. The data in the temperature range 18.3 K to 63.1 K are thought to arise largely from a small amount of paramagnetic species which may be a combination of defects, end effects from finite chains, and impurities. These are estimated below to be on the order of

0.4%. Conjectures concerning the strong divergent behavior of the data at 12.8 K and lower temperatures are given below.

It was anticipated that the magnetic susceptibility data above 65 K, corrected for the residual Curie susceptibility of the assumed impurity, could be accounted for in terms of Heisenberg exchange of $S = 1$ ions within a linear chain, according to the Hamiltonian

$$H = -2J \sum_{i \neq j} \hat{S}_i \cdot \hat{S}_j$$

If, as we will show below, the iron ion is in formal oxidation state +IV, then a reasonable electronic configuration is $(d_{xy})^2(d_{xz}, d_{yz})^2$. This electronic configuration yields a singly (orbitally) degenerate, single-ion ground state, and frequently exchange between ions with such ground states is isotropic if zero-field splitting effects are not large.

Although there are no closed form solutions for the magnetic susceptibility of antiferromagnetically coupled $S = 1$ chains, Weng¹⁵ has extended the work of Bonner and Fisher¹⁶ and Fisher,¹⁷ and has given numerical results for exchange coupled chains of $S = 1, 3/2, 2, 5/2$, and 3 ions. Following the lead provided by Hall¹⁸ for Heisenberg exchange in $S = 1/2$ ions, and by Kahn and co-workers¹⁹ for $S = 1$ ions, we have fit the function in Equation 1

$$\chi_M = (Ng^2\mu_B^2/kT)[A + Bx^2][1 + Cx + Dx^3]^{-1} \quad (1)$$

where $x = |J|/kT$, to Weng's numerical results and have generated the coefficients for chains with spins $S = 1/2, 1, 2, 3/2, 5/2$, and 3 . These coefficients are given in Table V using five significant figures for each coefficient since these were the number of digits required to obtain precise fits. The equation for the analysis of magnetic susceptibility data of chains of $S = 1/2$ ions exhibiting antiferromagnetic Heisenberg exchange has been used extensively,²⁰ and Kahn and co-workers¹⁹ have been successful with the use of their equation for $S = 1$. Our equation is cast in a different form than that used by Kahn and co-workers¹⁹ and, as a result, the two sets of coefficients differ. The magnetic susceptibility data above 110 K can not be fit with any of the linear chain equations for any spin value with any values for the exchange coupling constant J and electron g value, see Figure 4.

As shown in Figure 4, the complete set of magnetic susceptibility data for $[\text{FeOHp}]_n$ above 110 K can also not be fit satisfactorily with theory for antiferromagnetically exchange coupled pairs of $S = 1$ ions. The best fit of the data to the equation for pair-wise exchange between $S = 1$ ions is obtained with the parameters $J = -150 \text{ cm}^{-1}$ and $g = 2.34$. Comparable equations for isotropic exchange coupling between

pairs of ions with spin values of $S = 2$, $3/2$, and $5/2$ ions gave equally unsatisfactory results.

As discussed below, there remained the possibility that the compound had iron in formal oxidation state +III with the hemiporphyrizine ligand being a radical anion, and that these were exchange coupled. This possibility was ruled out by the failure of equations for exchange coupling between an $S = 1/2$ ion and $S = 3/2$ or $S = 5/2$ ion to fit the magnetic susceptibility data. There are presently no available models for the magnetic behaviour of a uniform Heisenberg chain which has every ion in the chain interacting with an $S = 1/2$ ion exterior to the chain.

The absence of an EPR resonance could signal a large zero-field splitting, and, in such cases, anisotropic exchange is common. We attempted to fit scaled versions of the following equations for Ising exchange, i. e. $H_{\text{ex}} = -2J \sum_{i \neq j} \hat{S}_i^z \hat{S}_j^z$, to the magnetic susceptibility data:

$$\chi_{\parallel} = (Ng^2\mu_B^2/4k_B T) [\exp(-2|J|/k_B T)]$$

$$\chi_{\perp} = (Ng^2\mu_B^2/8|J|) \left[\tanh(|J|/k_B T) + (|J|/k_B T) \text{sech}^2[|J|/k_B T] \right]$$

The average susceptibility was calculated from $\chi_{\text{av}} = (1/3)(\chi_{\parallel} + 2\chi_{\perp})$. The scaled Ising equations failed to fit the experimental data.

Since the bridging oxygens are randomly distributed in four possible positions, it seemed likely that theory for random exchange might be successful in accounting for the magnetic susceptibility data. Scott et al.²¹ have modified Fisher's solution for the magnetic susceptibility of a chain of classical spins ($S = \infty$)¹⁷ and have developed the following expression for a chain in which the exchange coupling constant varies randomly with the bridge:

$$\chi_M = [Ng^2\mu_B^2 S(S+1)/3kT] \{ (1-\langle u \rangle) / (1+\langle u \rangle) \}$$

where

$$\begin{aligned} \langle u \rangle = & (-kT/2JS(S+1)) \ln \{ (2J + \lambda) \sinh[(2J-\lambda)S(S+1)/kT] \\ & \times ((2J - \lambda) \sinh[(2J+\lambda)S(S+1)/kT])^{-1} \} \end{aligned}$$

This expression does not fit the experimental data with any reasonable values of J , g , and λ for which it is valid. But this is not surprising since there are only two distinct oxygen bridges (and therefore only two exchange pathways corresponding to two exchange coupling constants) and not some thermally populated or averaged range of positions which could potentially lead to a distribution (i.e. randomly disposed about a mean value) of exchange constants.

As shown in Figure 4, the magnetic susceptibility data can be described by a scaled theoretical expression for exchange coupling in an alternating chain of $S = 1$ ions²² with $J = -133 \text{ cm}^{-1}$, $g = 2.30$, and the alternation parameter $\alpha = 0.4$. The data are shown down to 100 K since below $kT/J = 0.5$ the theoretical results are not reliable. The parameters are defined by the Hamiltonian

$$H = -2J \sum_{i=1}^{n/2} [\hat{S}_{2i} \cdot \hat{S}_{2i-1} + \alpha \hat{S}_{2i} \cdot \hat{S}_{2i+1}]$$

where J is the exchange integral between a spin and its right neighbor and αJ is the exchange integral between a spin and its left neighbor. The use of an alternating chain was suggested by the disorder in the oxygen position which yields two different Fe-O-Fe bridging networks in the chain. Therefore, there are only two values for the exchange coupling constant, and not a distribution of J values as implied by the random exchange model. The alternating chain model is discussed more fully in the Discussion section.

Discussion Section

Structure of $[\text{FeOHP}]_n$. Even with the severe distortion of the hemiporphyrazine system, the central iron atom and the four donor atoms N1, N3, N1', N3' form a planar configuration; the Fe-N distances of 1.910 and 2.135 Å are significantly different, and the shorter distances are those to the nitrogen atom of the isoindole units. This observation suggests that the basicity of the nitrogen atom N3 is enhanced by an interruption of the conjugation in the internal C(6-9)-N(3) ring. This conclusion is further supported by the bond distances C6-N2 and C9-N4, which are consistent with localized double bonds C6-N2 and C9-N4 which involve carbon atoms of the isoindole unit. The origin of the interference with the conjugation is the more stable electronic structure associated with intact 6 π systems of the pyridine rings and the six-membered rings B. Similar bonding relationships were found in $[\text{HpGe}\{\text{C}=\text{C}-\text{C}(\text{CH}_3)_3\}_2]$, where the Ge-N distances are 1.956 and 2.172 Å.¹⁴

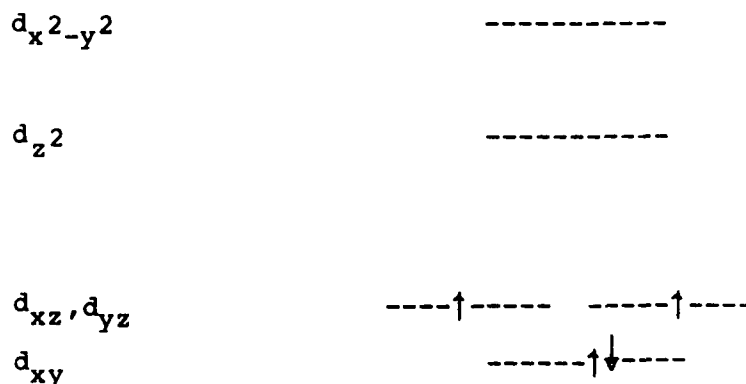
The saddle shape of the metallo-macrocycle is reminiscent of the same shape adopted by complexes of sterically hindered dibenzotetraaza[14]annulene ligands.²³ The dibenzotetraaza[14]annulene can be modified, with the exocyclic steric hindrance being removed, and strictly planar complexes are formed with first row²⁴ and second row²⁵ transition series metal ions. Since there is no exocyclic steric hindrance on the

hemiporphyrzine ligand, the saddle shape may arise from the small size and irregular shape of the four coordinate hole of the macrocyclic ligand relative to the size of the iron ion. Alternatively, there may be some special stability associated with an interaction between the axial oxygen ions and the π -clouds of the six-membered rings. Additional experimental work underway on other complexes of hemiporphyrzines may yield additional information on the origin of this structural feature.

Oxidation State and Electronic Configuration of Iron.

Formal oxidation states of +IV or +III can be assigned for the iron ion, but in the latter case, which corresponds to $\text{Hp}^1\text{-Fe}^{3+}\text{O}^{2-}$, the hemiporphyrzine ring would be a radical anion. Many such radical anions exhibit intense EPR signals in the area of the free electron g value.²⁶ No EPR absorptions were observed on a polycrystalline sample of $[\text{FeOHp}]_n$ at several different temperatures (292 K, 113 K, 80 K). This experimental observation, coupled with the failure of exchange models for an $S = 1/2$ ligand radical and an $S = 3/2$ or $S = 5/2$ metal ion to account for the magnetic susceptibility data, are strong supporting evidence for the +IV formal oxidation state indicated by the formula $[\text{FeOHp}]$. In addition, it is well known that it is difficult to detect EPR spectra in systems with even spin,²⁷ an additional observation which supports the oxidation state of +IV and spin state $S = 1$.

In planar macrocyclic complexes, only the d_{xz} and d_{yz} orbitals of the metal are capable of π bonding, and in fourfold symmetry these two orbitals transform as e_g . This degeneracy is lifted in the present case, but for the purposes of this discussion, it is sufficient to note that the energies of these two orbitals will be essentially the same. The $d_{x^2-y^2}$ is strongly σ antibonding, the d_{z^2} is weakly σ antibonding, and the d_{xy} is essentially nonbonding. This results in the following orbital splitting pattern:



Evidence for this array and spin state is provided by the Mössbauer spectra. The weak temperature dependence of ΔE_Q is consistent with a spin Hamiltonian formalism using $S = 1$ for an iron(IV) system.²⁸ The Mössbauer parameters in Table IV are also in agreement with the tabulated data for other iron(IV) systems.³¹⁻³³

In Figure 6 we have collected isomer shift and quadrupole splitting data for a number of iron porphyrin compounds with a range of oxidation states and spin multiplicities. We will now show that the Mössbauer data and/or the magnetic susceptibility data are consistent only with an oxidation state of +IV for iron. The Mössbauer data in Figure 6 for high spin ($S = 2$) iron(II) differ remarkably from those of $[\text{FeOHp}]_n$, and since the compound is paramagnetic with a magnetic moment of $2.05 \mu_B$ at 423 K, low spin ($S = 0$) iron(II) can be eliminated as a possibility. The magnetic and Mössbauer data eliminate $S = 0$ and $S = 2$ spin states and oxidation state +II for iron in $[\text{FeOHp}]_n$.

The Mössbauer data in Figure 6 for high spin ($S = 5/2$) iron(III) are substantially different from those of $[\text{FeOHp}]_n$ and this spin and oxidation state can be eliminated as a possibility. The most convincing evidence for the elimination of low spin ($S = 1/2$) iron(III) as a possibility is provided by the magnetic data. A magnetic moment of $2.05 \mu_B$ is much too large for a strongly exchange coupled $S = 1/2$ system. If we conclude from the data in Figure 4 that the magnetic susceptibility has reached its maximum value near 400 K, then a g value greater than 3 is required for an exchange-coupled pair of $S = 1/2$ ions to exhibit a magnetic moment of $2.05 \mu_B$ at 400 K. A g value greater than 4 is required for a chain of exchange-coupled $S = 1/2$ ions to exhibit the same moment. These g values

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are much too large to be realistic, and the low spin ($S = 1/2$) iron(III) possibility for $[\text{FeOHp}]_n$ can be eliminated.

As shown in Figure 6, the Mössbauer data for $[\text{FeOHp}]_n$ are similar to those reported for other iron(IV) compounds with established or proposed $S = 1$ spin states.

Exchange Coupling in $[\text{FeOHp}]_n$. The magnetic susceptibility data for $[\text{FeOHp}]_n$ may be described by an alternating chain model. The applicability of the model may be understood in terms of the structure and disorder in the oxygen positions. As shown schematically in Figure 5, all $[\text{FeHp}]$ moieties are translationally equivalent, however the details of the iron site is dictated by the occupancy of the oxygen sites, which are labelled a, a', b, and b' in Figure 5. A Type I iron site has oxygen neighbors arranged in a syn fashion, while a Type II iron site has oxygen neighbors arranged in an anti fashion. As shown in Figure 5, a Type I site can arise from adjacent oxygen occupancy in sites (a,a), (b,b), and (a,b), while a Type II site arises from adjacent oxygen occupancy in sites (a,a'), (b,b'), or (b,a'). Since the Mössbauer spectra provide evidence for only two iron sites, we conclude that the experiment is not sensitive enough to the three kinds of Type I and Type II sites to reflect their presence in the spectrum.

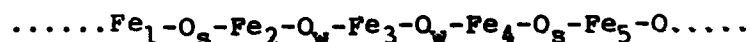
It has been well established that subtle changes in the superexchange pathway may have large effects on the exchange

coupling constant,²⁹ and the exchange coupling constant correlates well with the structural features of the bridge, specifically with the quotient ϕ/r_o where ϕ is the angle at the bridge and r_o is the bond distance. Since the ϕ/r_o values for the two bridges are 78.1 and 85.4, it may be expected that pairwise exchange in $\text{Fe-O}_a\text{-Fe}$ differs from that in $\text{Fe-O}_b\text{-Fe}$ (where the subscripts designate the site of the bridging oxygen), but that both are expected to have relatively large negative exchange coupling constants. The alternation parameter of 0.4 which resulted from the analysis of the magnetic susceptibility data provide experimental documentation for this conclusion.

The magnetic susceptibility behavior, the Mössbauer spectra, and the X-ray structural results are consistent with a chain structure for $[\text{FeOHpl}]_n$ in which the bridging oxygens are randomly distributed among four positions yielding an infinite chain containing two different spin exchange bridging networks for superexchange interactions and two different types of iron sites. Short sections of this infinite chain could probably be uniform chain-like segments containing only type a or type b oxygen bridges. However, the magnetic susceptibility data indicate, and it would be reasonable to expect on a statistical basis, that the predominate nature of the short segments would be alternating type a and type b oxygen bridges. Theoretical calculations³⁰ on small clusters of alternating $S = 1/2$ ions

have shown that the magnetic susceptibilities below χ_{max} of antiferromagnetically exchange-coupled short chains have substantially the same variation with temperature. It is not possible to determine a distribution of segment lengths from bulk magnetic susceptibility data.

There is a strong divergence of the magnetic susceptibility at the lowest temperatures. This may be understood in terms of a model in which there is random exchange between the "odd" iron ion, i. e. Fe_3 , in a segment such as



with similar ions in nearby segments. Here the subscripts s and w on the bridging oxygen designate stronger and weaker pairwise exchange coupling, respectively. Extensive magnetization studies and heat capacity studies at low temperatures will be necessary to verify this suggestion.

The Fe-O-Fe Bridging Angle. The presence of the bridging oxygen in two different crystallographic sites leads to two Fe-O-Fe bridging angles. The question of the features which control the bridging angle in μ -oxo-bridged iron compounds continues to attract attention.^{34,35} Data exist for a number of μ -oxo-bridged iron(III) compounds, and features such as ligand repulsions, electronic effects, and crystal packing have been

invoked to explain the usual nonlinearity of the Fe-O-Fe linkage.

The data for $[\text{FeOHp}]_n$ have a significant bearing on the question of the Fe-O-Fe angle. Ligand repulsions are identical and in-plane electronic effects are identical, and yet the two angles differ by about 12° , being $158.2(7)^\circ$ in one case and $170.5(7)^\circ$ in the other. An examination of the structural data do not reveal significant differences in the oxygen sites, and crystal-packing is unlikely to be important. Since the magnetic data suggest a regular alternation, it would appear that there is a significant out-of-plane trans-effect. Experiments which have been designed to yield information concerning this out-of-plane trans-effect are underway with analogous compounds.

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Registry No.

Supplementary Material Available. Tables of observed and calculated structure factors for $[\text{FeOHp}]_n$ (15 pages). Ordering information may be found on any current masthead page.

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Table I. Crystal Data and Data Collection Summary for $[\text{HpFeO}]_n$

Molecular formula	$\text{FeON}_8\text{C}_{26}\text{H}_{14}$	
Molecular weight	510.3	
Crystal class	monoclinic	
Space group	P2/n	
Lattice constants	at 210 K	at 293 K
	$a = 16.090(3) \text{ \AA}$	$a = 16.149(1) \text{ \AA}$
	$b = 3.975(2) \text{ \AA}$	$b = 3.992(1) \text{ \AA}$
	$c = 16.070(3) \text{ \AA}$	$c = 16.143(1) \text{ \AA}$
	$\beta = 92.97(1)^\circ$	$\beta = 92.94(1)^\circ$
Cell Volume	$1026.4 \text{ \AA}^3$	$1039.2 \text{ \AA}^3$
Density	$\rho_x = 1.651 \text{ g cm}^{-3}$	$\rho_x = 1.631 \text{ g cm}^{-3}$
Crystal dimensions	$0.15 \times 0.15 \times 0.9 \text{ mm}$	
Radiation	MoK_α	
μ , cm^{-1}	7.723	
2θ max, deg	30°	
Scan type	ω/θ	
Scan speed, deg min^{-1}	variable	
Background counting,		
deg offst	variable	
Final no. of parameters	167	
Formula units	$Z = 2$	
Observed Reflections	1459 with $I \geq 3\sigma(I)$	
R	0.045	

Table IIA. Atomic Positional Parameters and isotropic thermal parameters (in $\text{\AA}^2$) for $[\text{HpFeO}]_n$

Atom	x	y	z	B
Fe	0.2500	0.1943(5)	0.2500	3.33(3)
O ^a	0.2500	0.6973(25)	0.2500	11.9(4)
N1	0.2655(2)	0.1713(10)	0.3826(2)	2.53(9)
N2	0.1194(2)	0.2160(10)	0.4057(2)	2.7(1)
N3	0.1320(2)	0.2135(15)	0.2575(3)	3.9(1)
N4	0.0857(2)	0.2381(16)	0.1135(2)	2.7(1)
C1	0.3426(3)	0.1121(15)	0.4190(3)	2.3(1)
C2	0.3536(3)	-0.0553(15)	0.4948(3)	2.6(1)
C3	0.2848(3)	-0.1576(15)	0.5349(3)	2.9(1)
C4	0.2068(3)	-0.0752(15)	0.5028(3)	2.5(1)
C5	0.1988(3)	0.0993(15)	0.4276(3)	2.2(1)
C6	0.0932(3)	0.2758(15)	0.3305(3)	3.0(1)
C7	0.0102(3)	0.4241(15)	0.3096(3)	2.6(1)
C8	0.0015(3)	0.4337(15)	0.2238(3)	2.6(1)
C9	0.0775(3)	0.2918(15)	0.1914(3)	2.9(1)
C10	-0.0516(3)	0.5368(15)	0.3588(4)	2.9(1)
C11	-0.1230(3)	0.6659(15)	0.3181(4)	3.5(1)
C12	-0.1315(3)	0.6825(15)	0.2320(4)	3.2(1)
C13	-0.0689(3)	0.5672(16)	0.1827(4)	2.7(1)
H2	0.4079	-0.0964	0.5186	5.0
H3	0.2911	-0.2879	0.5846	5.0
H4	0.1589	-0.1349	0.5316	5.0
H10	-0.0457	0.5275	0.4179	5.0
H11	-0.1672	0.7422	0.3502	5.0

continued from Table IIA.

H12	-0.1808	0.7749	0.2063	5.0
H13	-0.0742	0.5810	0.1237	5.0

^aSplit positions :

O _a	0.270(1)	0.696(6)	0.264(2)	3.7(5) *
O _b	0.244(1)	0.700(4)	0.258(3)	3.4(5) *

Starred atoms were refined isotropically.

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as :

$$(4/3) \cdot [B_{11}a^{*2} + B_{22}b^{*2} + B_{33}c^{*2} + B_{12}a^*b^*\cos\gamma + B_{13}a^*c^*\cos\beta + B_{23}b^*c^*\cos\alpha]$$

Estimated standard deviations for the least significant figure are in parentheses. Parameters with no standard deviations were fixed by symmetry. Hydrogen atoms were introduced in calculated positions, fixed each 0.95 Å from the appropriate carbon atom.

Table IIB. Anisotropic Thermal Parameters B_{ij} (in $\text{\AA}^2 \cdot 10$)
for $[\text{HpFeO}]_n$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	14.9(3)	69.2(9)	16.0(3)	0.0	1.0(3)	0.0
O	162(9)	45(6)	151(9)	0.0	13(8)	0.0
N1	20(1)	40(3)	17(1)	-2(2)	1(1)	0(2)
N2	19(1)	39(3)	23(1)	-2(2)	3(1)	-1(2)
N3	17(1)	82(4)	20(1)	5(2)	1(1)	2(2)
N4	19(1)	39(3)	22(1)	-2(2)	0(1)	2(2)
C1	23(2)	26(3)	21(2)	1(2)	-1(1)	-4(2)
C2	28(2)	27(3)	22(2)	2(2)	-2(2)	-1(2)
C3	32(2)	31(3)	23(2)	0(2)	0(2)	4(2)
C4	29(2)	26(3)	22(2)	-2(2)	3(2)	-2(2)
C5	22(2)	25(3)	19(2)	-1(2)	3(1)	-4(2)
C6	20(2)	49(4)	22(2)	-3(2)	3(1)	0(2)
C7	17(2)	33(3)	28(2)	-4(2)	3(1)	0(2)
C8	17(2)	35(3)	25(2)	-4(2)	0(1)	0(2)
C9	18(1)	47(4)	22(2)	-1(2)	0(1)	3(2)
C10	22(2)	35(3)	31(2)	-7(2)	4(2)	-3(2)
C11	23(2)	43(4)	39(2)	3(2)	2(2)	-10(3)
C12	26(2)	28(3)	40(2)	5(2)	-5(2)	-7(3)
C13	23(2)	25(3)	32(2)	-3(2)	-3(2)	1(2)

The form of the anisotropic thermal parameter is :

$$\exp \left[- \frac{1}{4} (B_{11} h^2 a^{*2} + \dots + 2 B_{12} h k a^* b^* + \dots) \right]$$

Table III. Bond Lengths ($\text{\AA}$) and Angles (deg) for $[\text{HpFeO}]_n$
Standard deviations are in parentheses.

Bond lengths

Fe - N1	2.135(3)	C1 - C2	1.392(5)
Fe - N3	1.910(3)	C2 - C3	1.371(5)
Fe - O _a	2.03(3)	C3 - C4	1.371(5)
Fe - O' _a	2.02(3)	C4 - C5	1.388(5)
Fe - O _b	2.02(3)	C6 - C7	1.482(5)
Fe - O' _b	1.97(3)	C7 - C8	1.380(5)
N1 - C1	1.364(4)	C8 - C9	1.467(5)
N1 - C5	1.356(4)	C7 - C10	1.377(5)
N2 - C5	1.388(4)	C10 - C11	1.390(5)
N2 - C6	1.282(4)	C11 - C12	1.385(5)
N3 - C6	1.379(4)	C12 - C13	1.389(5)
N3 - C9	1.377(4)	C13 - C8	1.387(5)
N4 - C9	1.284(4)		
N4 - C1'	1.384(4)		

Bond angles

N1 - Fe - N1'	175.1(2)
N1 - Fe - N3	90.2(1)
N1 - Fe - N3'	89.9(1)
N3 - Fe - N3'	175.2(3)

continued from Table III.

Bond angles

N3 - Fe - N1'	89.9(1)
Fe - O _a - Fe	158.2(7)
Fe - O _b - Fe	170.5(7)
Fe - N1 - C1	119.5(2)
Fe - N1 - C5	119.1(2)
C1 - N1 - C5	117.6(3)
Fe - N3 - C6	123.9(2)
Fe - N3 - C9	123.7(2)
C6 - N3 - C9	108.5(3)
C5 - N2 - C6	123.7(3)
C9 - N4 - C1'	123.8(4)
N1 - C1 - N4'	122.3(4)
N1 - C1 - C2	121.9(4)
N4' - C1 - C2	115.6(4)
C1 - C2 - C3	119.0(4)
C2 - C3 - C4	119.8(4)
C3 - C4 - C5	119.2(4)
N1 - C5 - N2	122.7(4)
N1 - C5 - C4	121.8(4)
N2 - C5 - C4	115.4(3)
N2 - C6 - N3	128.9(4)
N2 - C6 - C7	122.4(4)
N3 - C6 - C7	108.8(4)
C6 - C7 - C8	106.3(4)
C6 - C7 - C10	132.0(4)
C8 - C7 - C10	121.7(4)

continued from Table III.

Bond angles

C7 - C8 - C9	107.5(4)
C7 - C8 - C13	121.6(4)
C9 - C8 - C13	130.9(4)
N3 - C9 - N4	128.5(4)
N3 - C9 - C8	108.8(3)
N4 - C9 - C8	122.6(4)
C7 - C10 - C11	117.0(4)
C10 - C11 - C12	121.6(4)
C11 - C12 - C13	121.1(4)
C12 - C13 - C8	117.0(4)

O - Fe - O angles of Type I :

O _a - Fe - O _a ^{''}	158(1)
O _a - Fe - O _b ^{''}	168(1)
O _b - Fe - O _b ^{''}	171(1)

O - Fe - O angles of Type II :

O _a - Fe - O _a [']	180(1)
O _b - Fe - O _a [']	168(1)
O _b - Fe - O _b [']	180(1)

Table IV. Mössbauer Parameters (Chemical Isomer Shift δ
 Relative to Metallic Iron, Electric Quadrupole Splitting ΔE_Q)
 for the Two Iron Sites I and II as a Function of Temperature

T, K	δ , mms ⁻¹		ΔE_Q	
	Site I	Site II	Site I	Site II
4.2	0.38(1)	0.34(1)	1.42(1)	1.72(1)
294	0.28(1)	0.22(1)	1.46(2)	1.64(1)
420	0.09(1)	0.07(2)	1.34(2)	1.60(5)

Table V. Coefficients for Magnetic Susceptibility Expressions
for Heisenberg Chains with $S = 1/2, 1, 3/2, 2, 5/2$, and 3 .

S	A	B	C	D
1/2	0.2500	0.18297	1.5467	3.4443
1	0.6667	2.5823	3.6035	39.558
3/2	1.2500	17.041	6.7360	238.47
2	2.0000	71.938	10.482	955.56
5/2	2.9167	208.04	15.543	2707.2
3	4.0000	595.00	20.811	7586.7

CAPTIONS FOR FIGURES

Figure 1. A view of the structural unit $[\text{FeOHp}]$ with the atom numbering scheme and labelling of the rings. The temperature factor of the oxygen atom is reduced to 50% for clarity.

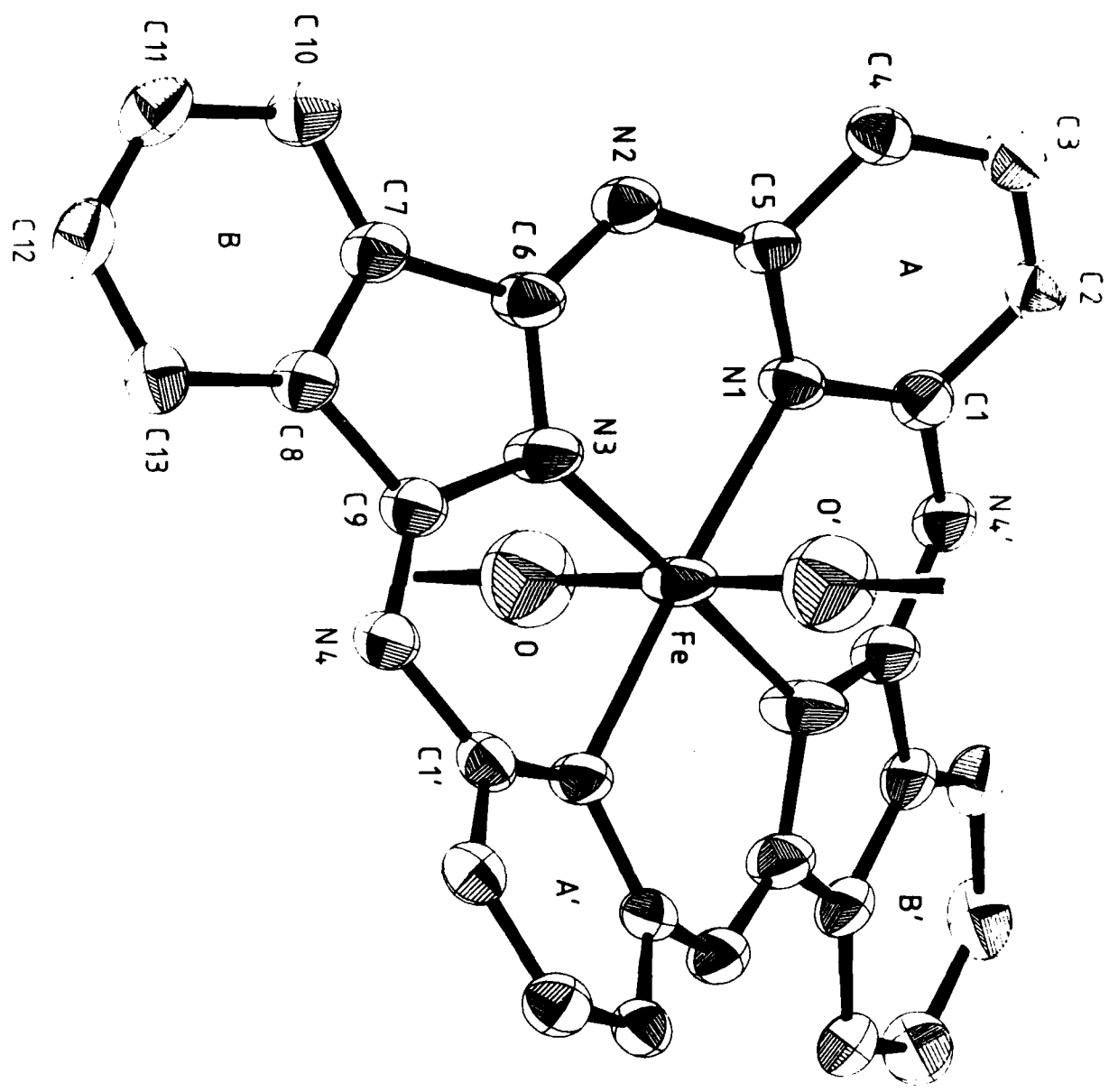
Figure 2. A view of the chain structure which shows the antiparallel arrangement of adjacent chains of $[\text{FeOHp}]_n$.

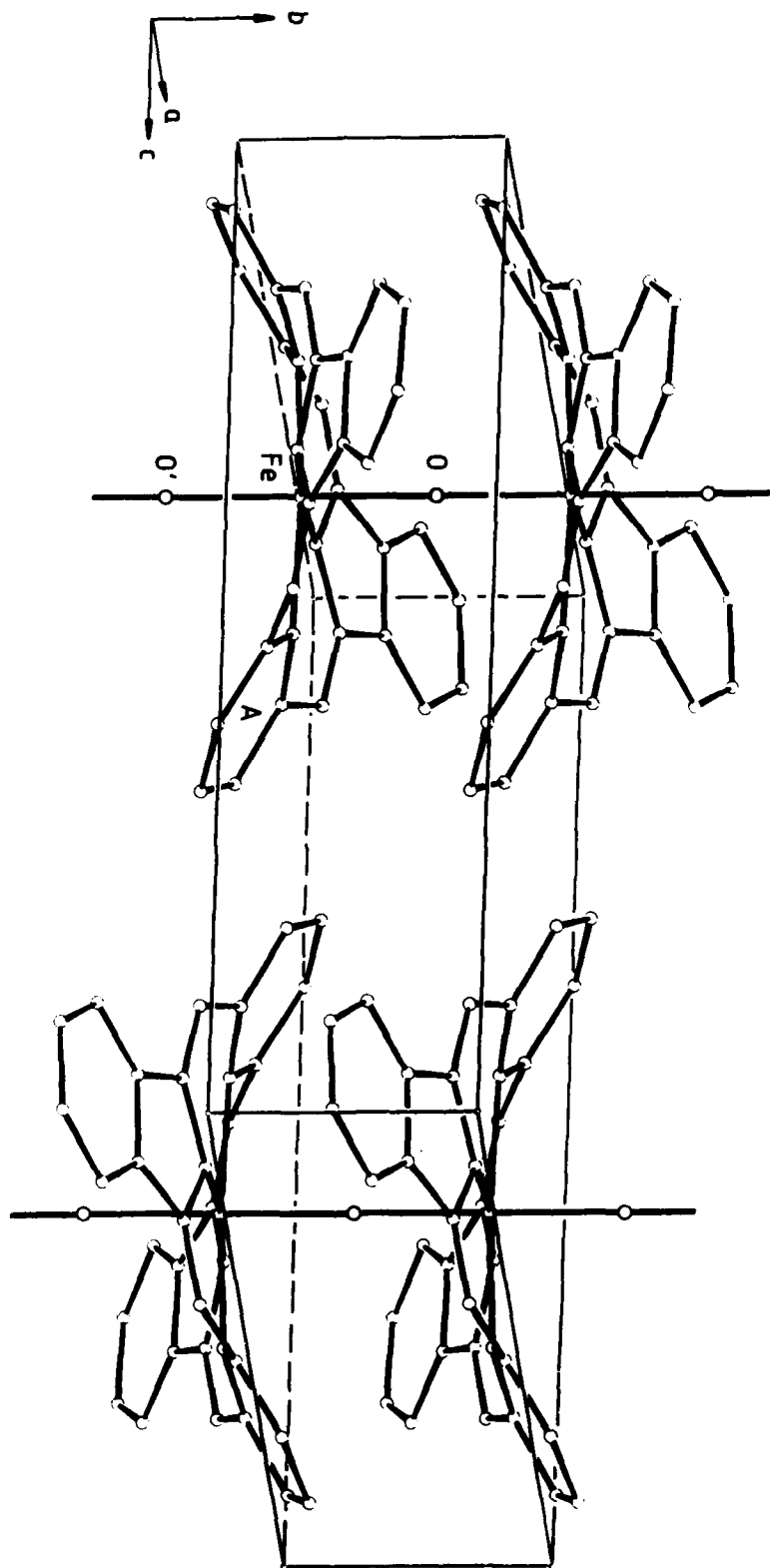
Figure 3. The Mössbauer spectrum of $[\text{FeOHp}]_n$ at room temperature. Calculated lines (two quadrupole doublets) arising from two iron sites are shown along with the experimental spectrum.

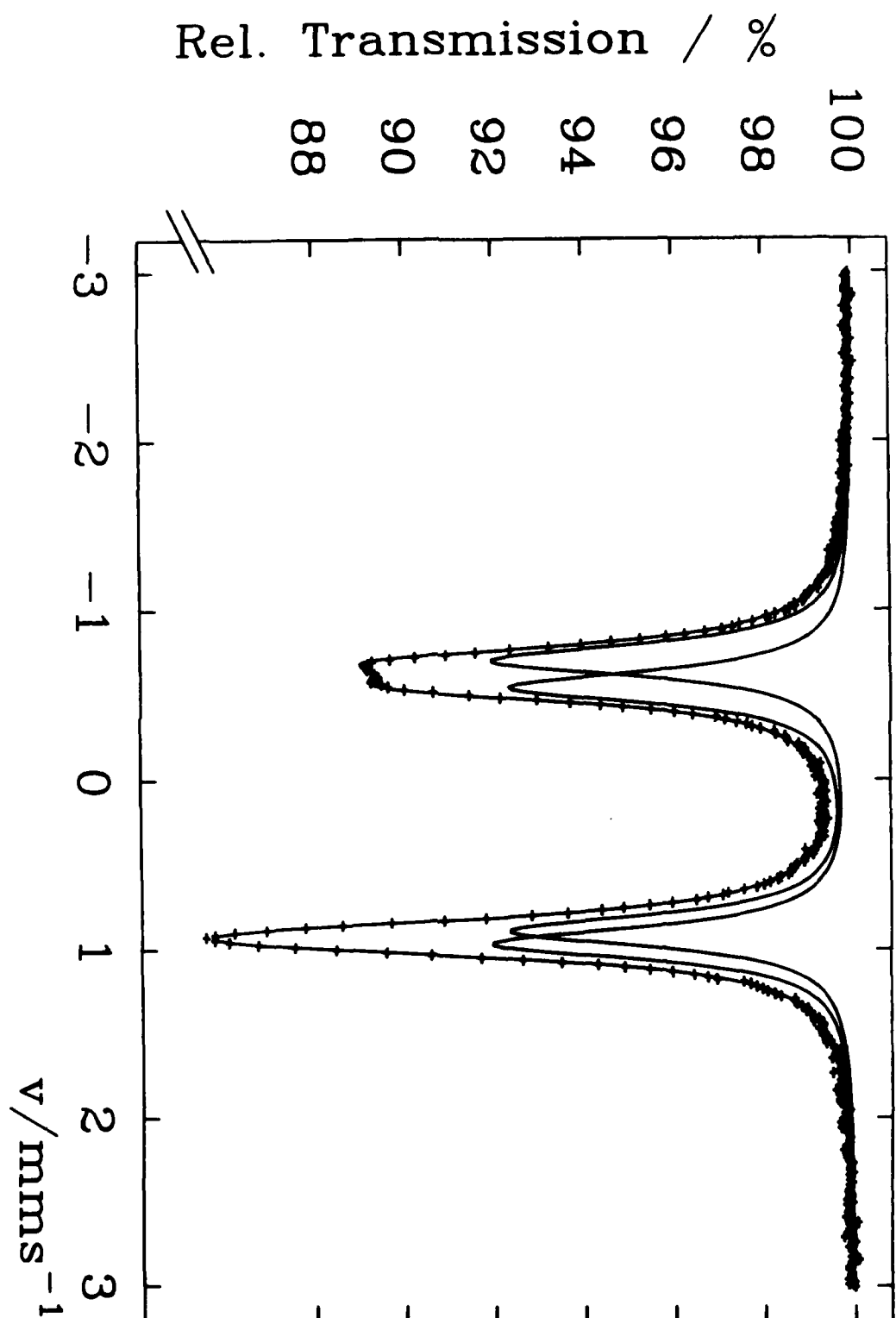
Figure 4. The magnetic susceptibility data for $[\text{FeOHp}]_n$. The full line was calculated from a scaled alternating chain model ($S = 1$) with the best fit parameters given in the text. The failure of the uniform chain model and the dimer model to fit the experimental data in best fit calculations is apparent.

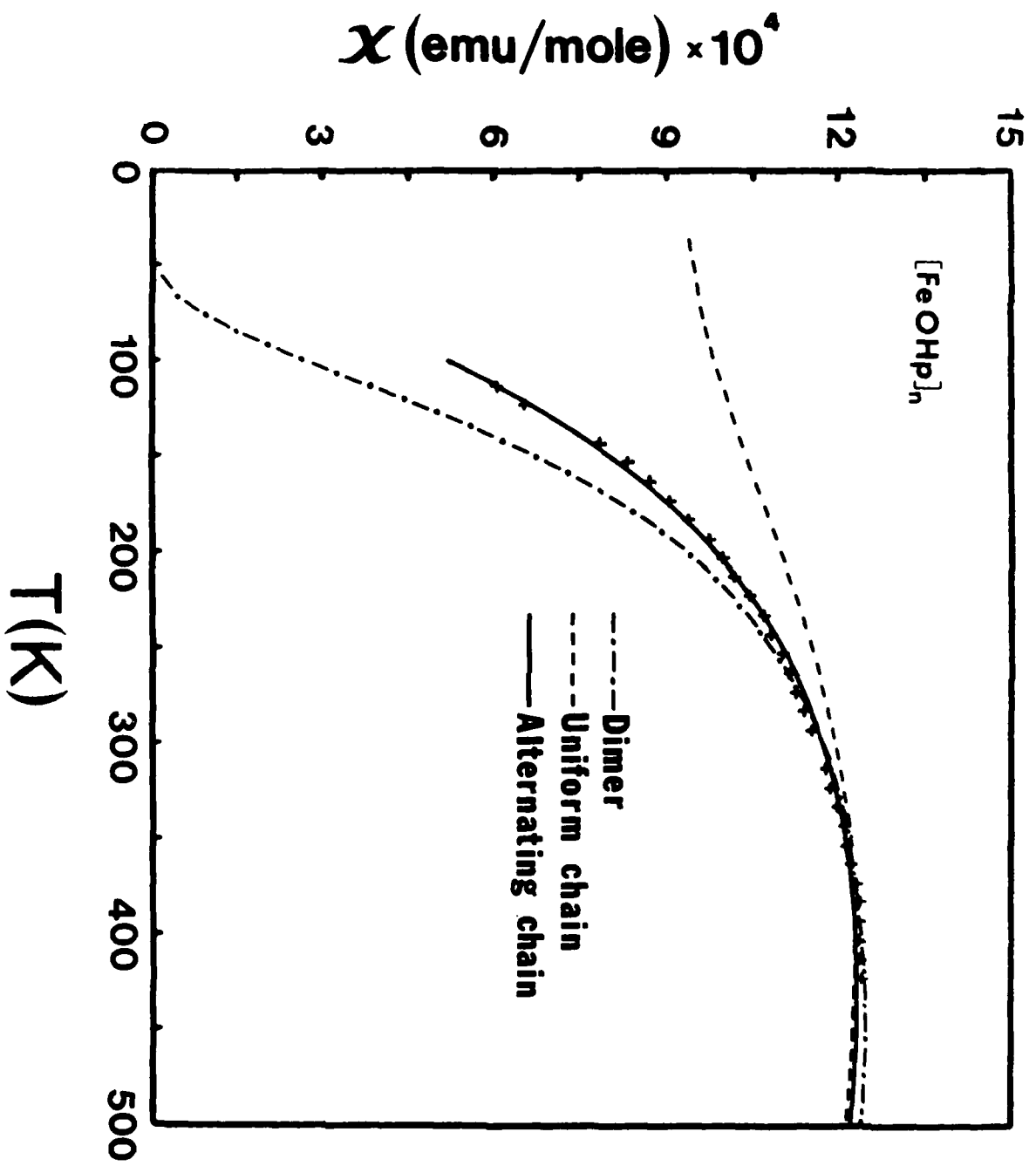
Figure 5. A schematic drawing of the chain which illustrates the disorder in the oxygen sites.

Figure 6. Isomer shifts δ and quadrupole splittings ΔE_q for several iron porphyrin compounds with oxidation states +II and +III. The Mössbauer data for $[\text{FeOHp}]_n$ are indicated by stars. The isomer shifts are relative to metallic iron as a standard, and data are given for various temperatures. See reference 33.

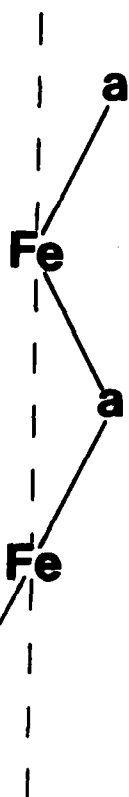




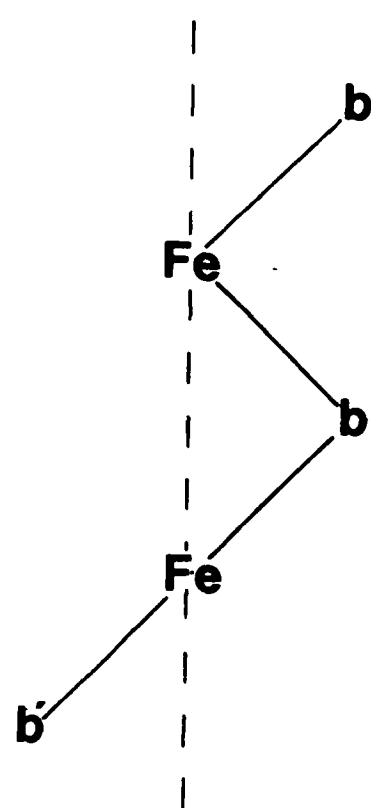
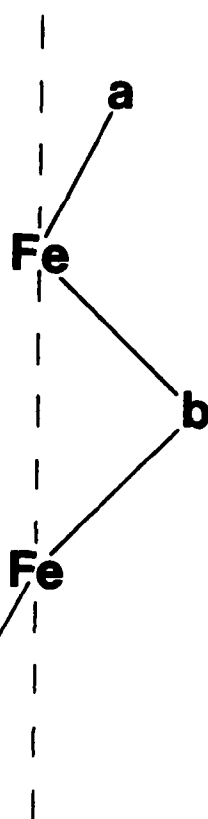


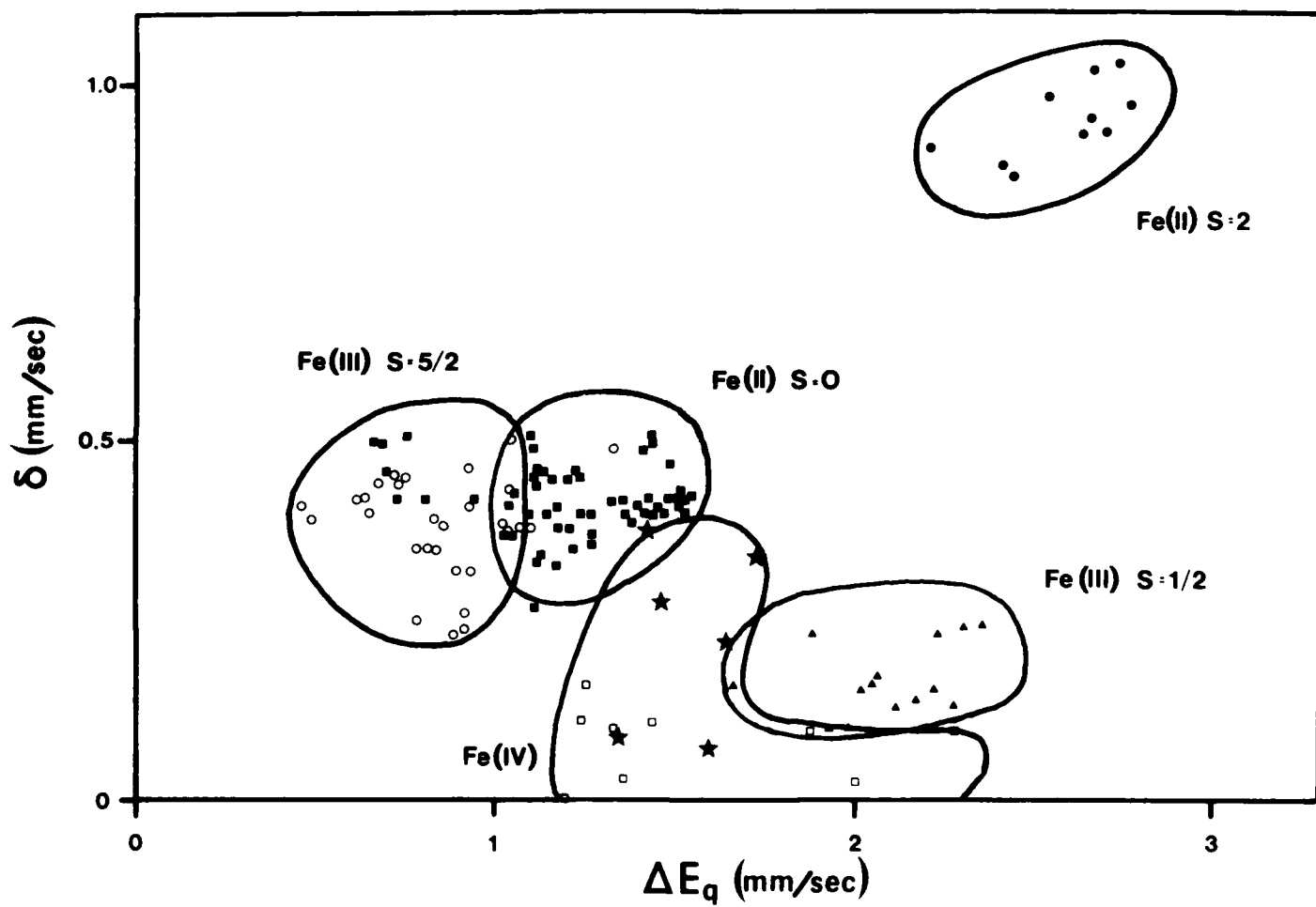


Type I



Type II





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