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ALTERNATING CHAIN MAGNETISM IN CATENA-μ-OXO-HEMIPORPHYRAZINATOIRON(IV), THE FIRST μ-OXO LINEAR CHAIN COMPLEX OF IRON

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Abstract X-ray studies, Mössbauer, and magnetism show FeOHp to be an antiferromagnetically coupled alternating chain with $J = -133\ \mathrm{cm}^{-1}$, $g = 2.3$ and an alternation parameter of 0.4.

INTRODUCTION

There has been great interest in the polymeric μ-oxo-phthalocyaninato complexes of silicon and germanium, since after being doped with iodine, the materials exhibit high electrical conductivities.[1] Corresponding complexes with titanium and vanadium are monomers with terminal oxo-ligands.[2] Tetraphenylporphinatoiron forms μ-oxo-bridged dimeric complexes $(TPPFe)_2O$.[3] We report $(FeOHp)_n$ (where H_2Hp = hemiporphyrazine) to be the first polymeric μ-oxo-bridged complex of iron. On the basis of chemical and

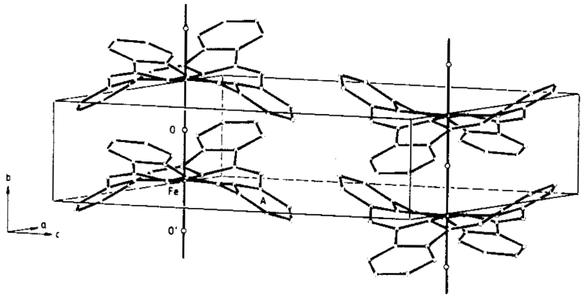

Figure 1. Antiparallel packing of FeOHp chains.

physical properties, we assign the iron an oxidation state of IV and a spin state S = 1.

EXPERIMENTAL

μ-Oxo-hemiporphyrazinatoiron (FeOHp) is prepared by treating hemiporphyrazine (H_2Hp) with iron(II) acetate in boiling nitrobenzene over a period of 30 minutes. Mössbauer effect spectra were recorded with a constant acceleration spectrometer equipped with a furnace and a liquid helium cryostat, and the measured spectra were fit to a sum of Lorentzian lines. Magnetic susceptibility data were collected with a vibrating sample magnetometer over the temperature range 3.35 to 294.8 K, and with a Gouy Balance over the temperature range 113.2 to 423 K. The data sets were in good agreement. Attempts to record an EPR spectrum (70 K to 300 K) were unsuccessful.

RESULTS

The FeOHp moieties are stacked up along the b axis (Figure 1) and are linked together with axially-bound oxygen

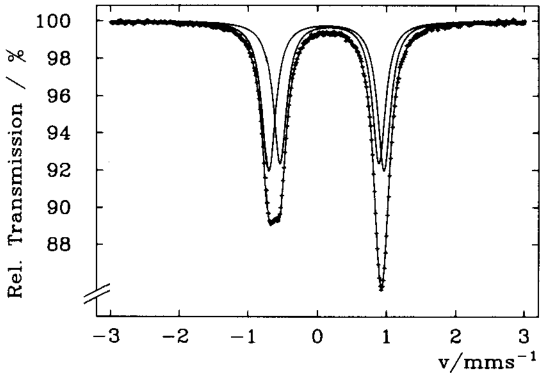

Figure 2. Mössbauer spectrum of FeOHp at 298 K.

bridges to form a linear chain.[4] 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 bridging oxygen atom is disordered into two crystallographically different sites (four positions due to the C_2 symmetry). The Fe-O_a and Fe-O_b bond distances range from 1.973 to 2.030 Å. The Fe-O-Fe bond angles are 158.2° and 170.5° for the two oxygen bridge types.

The Mössbauer spectrum of FeOHp at room temperature is shown in Figure 2. The identification of two distinct iron sites was unexpected in view of the X-ray structure results, which show the iron ions as translationally equivalent. Mössbauer spectra were also collected at 420 K and at 4.2 K, but only slight variations in the isomer shift and quadrupole splitting were observed. Above 420 K the sample decomposes.

The magnetic susceptibility (Figure 3) of FeOHp

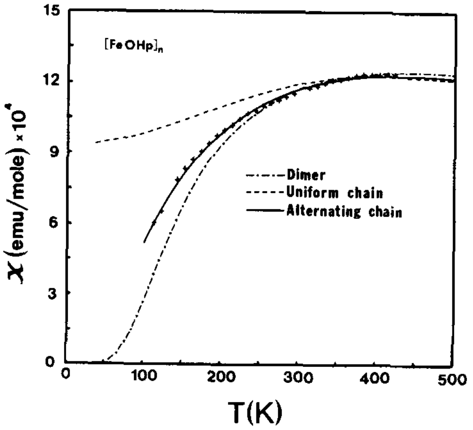

Figure 3. Magnetic susceptibility data for FeOHp.

decreases from 1.24×10^{-3} at 423 K towards 6×10^{-4} at 110 K. Below a minimum in the magnetic susceptibility near 65 K, the magnetic susceptibility increases with a further decrease in temperature. The low temperature data 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 (on the order of 0.4%).

It was anticipated that the magnetic susceptibility data above 65 K could be accounted for in terms of Heisenberg exchange of S = 1 ions within a linear chain, according to the Hamiltonian $H = -2J \Sigma \hat{S}_i \cdot \hat{S}_j$. Although there are no closed form solutions for the magnetic susceptibility of antiferromagnetically coupled S = 1 chains, Weng[5] has extended the work of Bonner and Fisher[6] and Fisher,[7] 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 Hall[8] for Heisenberg exchange in $S = 1/2$ ions, and by Kahn and co-workers[9] for $S = 1$ ions, we have fit[4] the function in Equation 1

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

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. The magnetic data above 110 K can not be fit with any of the linear chain equations for any spin value with reasonable J or g values. The magnetic susceptibility data above 110 K can not be fit satisfactorily with theory for antiferromagnetically exchange coupled pairs of any spin value.

The absence of an EPR resonance could signal a large zero-field splitting, and, in such cases, anisotropic exchange is common. Attempts to fit scaled versions of Ising exchange,[10] i.e. $H_{ex} = -2J\Sigma\, \hat{S}_i{}^z\, \hat{S}_j{}^z$, to the magnetic susceptibility data also failed.

Since the bridging oxygens are randomly distributed in four possible positions, it seemed likely that theory for random exchange[11] might be successful in accounting for the magnetic susceptibility. These expressions also fail to fit the experimental data with any reasonable values of J, g, and a J-value distribution.

The data can be fit with a scaled expression for exchange coupling in an alternating chain of $S = 1$ ions with $J = -133$ cm^{-1}, $g = 2.30$, and an alternation parameter of $\alpha = 0.4$. 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

$$H = -2J\sum_{i} [\hat{S}_{2i}\cdot\hat{S}_{2i-1} + \alpha\hat{S}_{2i}\cdot\hat{S}_{2i+1}] \qquad (2)$$

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 would be implied by a random exchange model.

DISCUSSION

The Mössbauer data for high spin (S = 2) iron(II) differ remarkably from those of FeOHp, and since the compound is paramagnetic with a magnetic moment of 2.05 μ_B at 423 K, this oxidation state can be eliminated. The Mössbauer data for high spin (S = 5/2) iron(III) are substantially different from those of FeOHp 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 moment of 2.05 μ_B (and rising) which is too large for a strongly exchange coupled S = 1/2 system. The weak temperature dependence of the Mössbauer ΔE_Q supports a spin Hamiltonian formalism using S = 1 for an iron(IV) system.[12] The Mössbauer parameters are also in agreement with tabulated data for other iron(IV) systems,[13-15] confirming our selection of oxidation state +IV and spin state S = 1 for FeOHp.

The applicability of the alternating chain model may

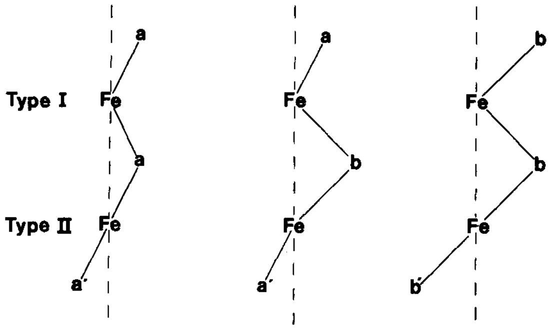

Figure 4. Disorder in the oxygen sites of FeOHp.

be understood in terms of the disorder in the oxygen positions. As shown schematically in Figure 4, all FeHp moieties are translationally equivalent, however the details of the iron site are dictated by the occupancy of the oxygen sites, which are labelled a, a', b, and b'. 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. 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,[16] and that 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 $Fe-O_a-Fe$ differs from that in $Fe-O_b-Fe$ (where the subscripts designate the site of the bridging oxygen), but that both are expected to have relatively large antiferromagnetic exchange coupling constants. The alternation parameter of 0.4 which resulted from the analysis of the magnetic susceptibility data provides 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 FeOHp in which the bridging oxygens are randomly distributed among four positions. These yield an infinite chain containing two different spin exchange bridging networks for superexchange interactions, and two different types of iron sites. Extensive magnetization studies and heat capacity studies at low temperatures will be necessary to verify the nature of the low temperature behavior.

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