

Lattice- and spin-dimensionality crossovers in a linear-chain-molecule-based ferrimagnet with weak spin anisotropy

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[MnOEP][HCBD], a member of the metalloporphyrin family of donor-acceptor molecule-based magnets, consists of isolated ferrimagnetic chains of alternating $S=2$, [MnOEP], and $s=1/2$, [HCBD] units (OEP=octaethylporphyrinato and HCBD=hexacyanobutadiene). Analysis of the exchange pathways reveals an exchange along one interchain axis (J_{inter}) almost 3 orders of magnitude weaker than the intrachain exchange (J_{intra}), and a negligible exchange along the other interchain axis. From the susceptibility and magnetization data we determine J_{intra} and J_{inter} to be antiferromagnetic with values of -172 K and -0.4 K, respectively. At 19.6 K, the system undergoes both lattice and spin dimensionality crossovers in which the ferrimagnetic chains couple antiferromagnetically as two-dimensional Ising sheets. [S0163-1829(97)01625-1]

I. INTRODUCTION

The magnetic properties of low-dimensional systems is of intense current interest for reasons including questions regarding the Haldane gap,¹ the behavior of end-chain spins² in one-dimensional (1D) systems, and the nature of the excitations³ within 1D and 2D systems. One-dimensional systems with only nearest-neighbor interactions will not order above absolute zero regardless of the spin dimensionality of the system. Furthermore, if the lattice dimensionality is increased to two, only Ising systems will order at finite temperatures.⁴ The exploration of the middle ground between one and two dimensions is an area of growing interest. One approach is to investigate systems intermediate to one and two dimensions, e.g., ladder compounds.⁵ Another approach is to examine systems with large spatial anisotropy. Such systems behave in one manner at higher temperatures and change characteristics as the temperature (T) is lowered. For example, a system with very strong magnetic interactions along one axis relative to its other axes behaves one-dimensionally at high temperatures. However, as T is lowered, the weaker interchain interactions will eventually begin to dominate, forcing the system into a higher dimensional state. Renormalization-group (RG) theory gives substantial theoretical insights into such dimensionality crossovers,⁶ showing that, despite a small magnitude, the interchain interactions will ultimately dictate the relevant fixed point. The weaker terms in the Hamiltonian thus play an essential role in determining the critical behavior of a system. Hence, any deviation from pure one-dimensionality and pure Heisenberg spins will force a one-dimensional system to order at a finite temperature. Experimentally, there are several examples of lattice-dimensionality crossovers from 1D to 3D,⁷ however, few examples of a crossover from 1D to 2D exist.⁸ This paper reports such a crossover.

A major advantage of molecule-based magnets is their production via controllable molecular chemistry allowing fine-tuning of structures and magnetic behaviors. Thus, it is possible to modulate structural parameters in order to elucidate the important factors governing otherwise complex behavior. Using this “molecular engineering” approach, we have produced a family of metalloporphyrin donor-acceptor electron transfer salts. These salts are comprised of alternating $S=2$, $s=1/2$ ferrimagnetic linear chains with large intrachain interactions ($|J_{\text{intra}}| > 100$ K) and small interchain interactions ($|J_{\text{inter}}| < 1$ K) leading to 1D behavior at high temperatures. The large spin values and intrachain interactions enable observation of the effects of small interchain interactions at accessible temperatures. Structural differences among these compounds lead to the differences in interchain exchange and dipolar interactions as well as local spin anisotropies.

In this paper we report the unusual magnetic properties of the linear chain molecule-based magnet [MnOEP][HCBD] (OEP=octaethylporphyrinato and HCBD=hexacyanobutadiene). We attribute the high-temperature behavior and antiferromagnetic transition at 19.6 K to a simultaneous spin- and lattice-dimensionality crossover from 1D Heisenberg to 2D Ising. The temperature scale for this crossover behavior is set by the magnitude of the interchain exchange and the weak spin anisotropy. The outline of the paper is as follows. In Sec. II we discuss the measurement techniques. In Sec. III we present the structural properties of the [MnOEP][HCBD] compound and report magnetization and susceptibility data. In Sec. IV we extract exchange parameters from the magnetization data and compare the ordering temperature with predictions for Ising systems. Section V is a summary of our results.

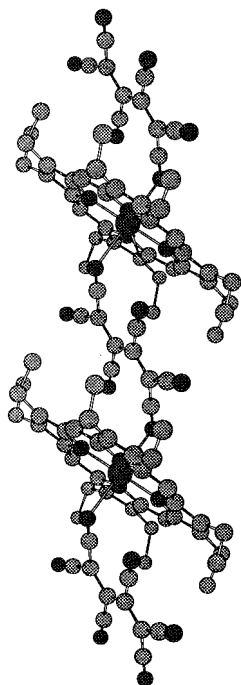


FIG. 1. Chain structure of $[\text{MnOEP}][\text{HCBD}]$. For clarity, H atoms are not shown.

II. EXPERIMENT

Magnetization (M) data were collected using a Quantum Design Model MPMS-5 SQUID magnetometer with a continuous flow cryostat and a 5.5 T superconducting solenoid. Susceptibility data were recorded on a Lake Shore Model 7225 ac susceptometer with an exchange cryostat and 5.0 T superconducting solenoid. The ac frequency of the driving field was varied from 5 to 10 000 Hz and phase-sensitive measurements were made using a lock-in amplifier. Calibration of the absolute magnitude of the susceptibility and its phases were made using the paramagnetic $\text{HgCo}(\text{SCN})_4$. All magnetic data were taken on powder samples that had been sealed under argon in quartz EPR tubes to avoid contamination with air. The largest uncertainties in the magnetic data ($\pm 2\%$) arose from the error in measuring the sample mass. The dc susceptibility, χ_{dc} , was taken as M/H , where the magnetic field $H = 5000$ Oe. The diamagnetic correction, $\chi^{\text{dia}} = -4.8 \times 10^{-4} \text{ emu}^3/\text{mol}$, was obtained from Pascal's constants.⁹ The diamagnetism of the quartz sample holders was separately measured and subtracted from the data.

III. RESULTS

A. Structural information and interchain exchange

The Mn^{III} octaethylporphyrin ($S = 2$) donor molecules are *trans*- μ_2 -bonded to HCBD ($s = 1/2$) acceptor ions in a linear chain structure.¹⁰ The covalent bonding between the Mn^{III} and an external N of the HCBD anion radical leads to a large antiferromagnetic exchange. Each chain has four nearest-neighbor chains. The bulkiness of the porphyrin ligand leads to relatively large interchain separations of 7.9 and 12.5 Å. These large distances along with the indirect interchain ex-

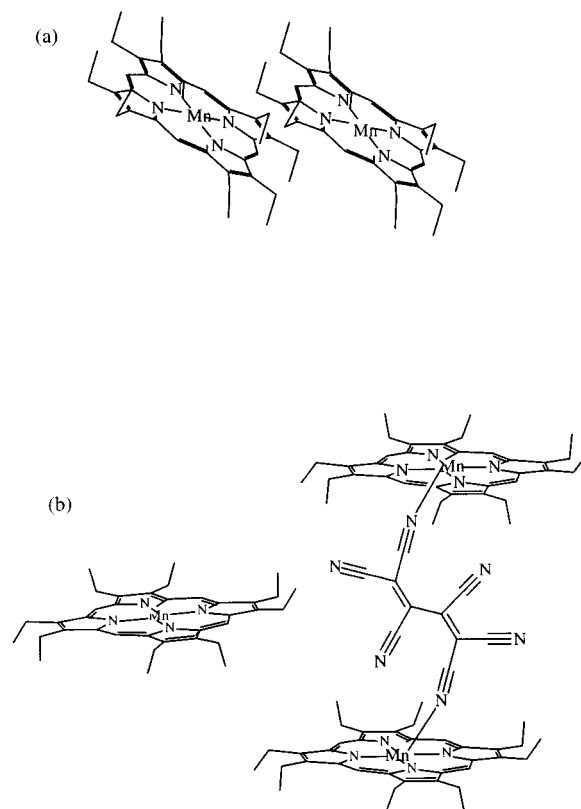


FIG. 2. Interchain exchange pathways between nearest-neighbor chains. (a) Between neighbor chains 7.9 Å apart, (b) between neighbor chains 12.5 Å apart. For clarity H atoms are not shown.

change routes lead to very weak interchain exchange. A side view of this chain structure is shown in Fig. 1. Figure 2 displays a view of the closest interchain exchange paths for the nearer [Fig. 2(a)] and farther [Fig. 2(b)] adjacent chains.

The spin density on the HCBD anion radical is delocalized throughout the molecule¹¹ with substantial spin density ($\sim 0.1\mu_B$) on the N that bonds to the Mn^{III} , whereas the spin density on the Mn^{III} porphyrin molecule resides primarily on the Mn^{III} site with only a small fraction ($0.02\mu_B$) residing on each of the outer sp^2 carbons.¹² We expect no appreciable spin density on the attached ethyl groups because of the lack of conjugation. Along the shorter interchain direction (7.9 Å), the parallel porphyrin planes partially interleave, with the closest C-C distance being 3.47 Å. The interchain exchange is estimated¹³ to be $\sim 10^{-1}$ K by comparison to calculations for cofacial overlap of benzene radicals in eclipsed¹⁴ and slipped^{15,16} geometries. In contrast, the exchange along the longer interchain direction is estimated to be *much less* than 10^{-1} K, with the closest exchange path being the Mn^{III} porphyrin-ethyl-HCBD, having a 3.5-Å ethyl-HCBD separation and essentially no spin density on the ethyl. In summary, the structure of the $[\text{MnOEP}][\text{HCBD}]$ supports strong magnetic coupling along the chains, weak 2D coupling between the chains making up a plane, and very much weaker exchange coupling between adjacent planes.

B. High-temperature dc susceptibility

The χ_{dc} measured at 0.5 T for 5–350 K is presented in Fig. 3(a) as $\chi_{\text{dc}}T$ versus T . The $\chi_{\text{dc}}T$ product increases with

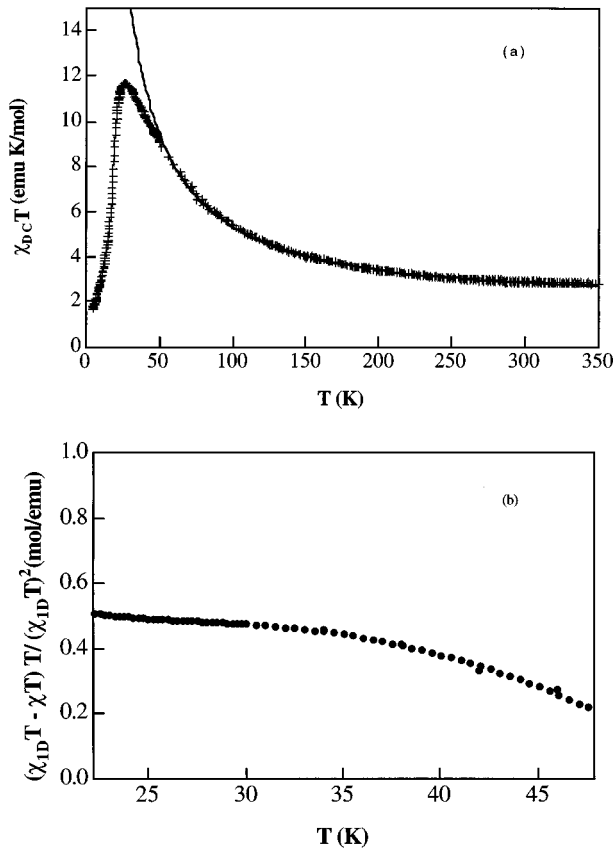


FIG. 3. $\chi_{dc}T$ vs T at 5000 Oe.

decreasing temperature to a maximum of 11.7 emu K/mol at 26.5 K. Due to the small interchain interactions, $\chi_{dc}T$ above 50 K was fit to a model developed by Seiden for isolated chains of alternating classical (S) and quantum-mechanical (s) spins.¹⁷ The Hamiltonian $H_{\text{intra}} = \sum_i -2J_{\text{intra}}[S_i + S_{i+1}]s_i$ leads to an expression for the susceptibility that has g_S , g_s , and J_{intra} as adjustable parameters, where g_S and g_s are the Landé g factors of S and s , respectively, and J_{intra} is the intrachain exchange. To compare our data with such predictions, we approximate the spin 2 of the Mn^{III} porphyrin molecule as classical, and fix the g_{HCBD} at 2.00, the free spin value.¹⁸ The fit gives excellent agreement for the two adjustable parameters $g_S = g_{\text{Mn}} = 1.92(4)$ and $J_{\text{intra}} = -172(3)$ K. The minimum in χT , characteristic of ferrimagnetic chains, is expected to occur above 350 K, outside the experimental temperature range. Below ~ 50 K, χT is substantially less than predicted by the one-dimensional model, indicating interchain antiferromagnetic coupling. The deviation from one-dimensionality is displayed as $(\chi_{1D}T - \chi T)T / (\chi_{1D}T)^2$ versus T , where χ_{1D} is the susceptibility predicted by Seiden's model [Fig. 3(b)].

C. Low-temperature ac susceptibility

The in- and out-of-phase ac susceptibilities, χ' and χ'' , respectively, measured from 2 to 40 K at frequencies of 5 to 10 000 Hz at an ac field of 1 Oe are reported in Fig. 4. χ' increases to a broad rounded maximum of 0.42 emu/mol at 22.5 K. The χ'' signal is essentially zero within the noise until 8 K is approached at which point a peak is observed.

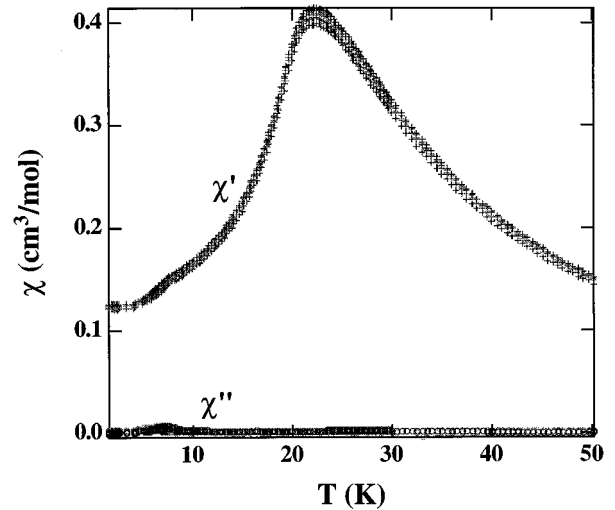


FIG. 4. The in-phase χ' and out-of-phase χ'' ac susceptibility vs T at various frequencies from 5 to 10 000 Hz. Data were recorded with an ac amplitude of 1 Oe.

No frequency dependence is observed within this temperature range. The lack of frequency dependence can be contrasted with other members of the metalloporphyrin family¹⁹ in which subtle chemical disorder leads to glassy behavior.

D. Low-temperature magnetization curves

The magnetization as a function of applied field measured from 0 to 5.5 T at constant temperature for temperatures from 5 to 25 K is shown in Fig. 5. The shape of the M versus H curve changes as the temperature is cooled below 20 K. Below 20 K, the rapid increase in M as H approaches 1 T indicates a metamagnetic transition due to antiferromagnetic (AFM) coupling between the chains. The magnetization approaches a saturation near 16 800 emu G/mol, consistent with a spin 2 strongly antiferromagnetically coupled with a spin 1/2. No hysteresis or other irreversibilities were observed for $T > 10$ K.²⁰

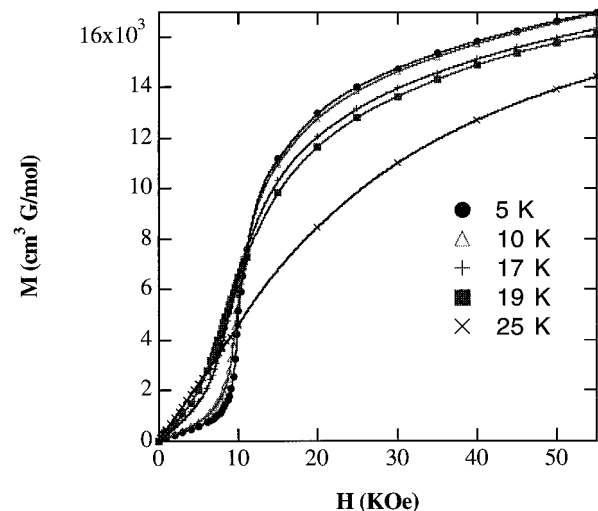


FIG. 5. The magnetization M as function of field H at various temperatures.

IV. DISCUSSION

A. Exchange and anisotropy energies

In light of the very small interplanar magnetic coupling, compared to exchange even between chains making up a plane, Fig. 2 and Sec. III A, we treat the transition at 19.6 K (see below) as a crossover from 1D to 2D. This is supported by a transition at lower temperatures attributed to a 2D to 3D crossover, and the critical exponent of the lower T transition.²⁰

The total Hamiltonian describing the important energies for the transition of interest here is

$$H = -2J_{\text{intra}} \sum_{ij} \mathbf{S}_{i,j} \cdot \mathbf{S}_{i,j+1} - 2J_{\text{inter}} \sum_{ij} \mathbf{S}_{i,j} \cdot \mathbf{S}_{i+1,j} + \sum_i DS_z^2. \quad (1)$$

Here J_{intra} is the intrachain exchange and J_{inter} is the interchain exchange in the closer interchain direction. The exchange in the third direction is taken as zero. The sum is over all spin sites i within chain j . DS_z^2 is the contribution of single-ion anisotropy. The first (intrachain) term, with $J_{\text{intra}} = -172$ K from the fit to the 1D predictions, is the largest term in the Hamiltonian. Given this large J_{intra} we use the approximation that $S_{\text{eff}} = S + s = 3/2$ at the low (~ 20 K) temperatures of interest. We now estimate J_{inter} and D .

The reduction of χT from the pure one-dimensional model below ~ 50 K implies a predominant AFM coupling between the chains. The absence of χ'' near the peak in χ' along with the lack of any observed irreversibilities further support predominant antiferromagnetic interchain exchange. Deviations of the data from the 1D model are used to estimate the AFM interchain exchange following similar estimations by de Jongh and Stanley.²¹ They describe a predominantly 1D or 2D system driven into a state of higher dimensionality via interchain or interlayer interactions. Following de Jongh and Stanley, it is straightforward to show that for two nearest neighbors ($z' = 2$)

$$J_{\text{inter}} = \frac{-C(\chi_{1D}T - \chi_{2D}T)T}{4(\chi_{1D}T)^2}. \quad (2)$$

A plot of the function on the RHS of Eq. (2) should be constant with temperature and yield a value for J_{inter} . We use the fit to Seiden's model as an estimate of χT_{1D} and our experimental data as χT_{2D} and plot the function $(\chi_{1D}T - \chi_{2D}T)T/(\chi_{1D}T)^2$ as a function of T [Fig. 3(b)]. The function is ~ 0.5 mol/emu from 20 to 35 K; above 35 K the function decreases gradually to 0.3 mol/emu likely due to roundoff errors caused by the small difference in χ_{1D} and χ_{2D} . Using the value 0.5 and a Curie constant for a spin-2, spin-1/2 system of 3.4, we obtain a value of $J_{\text{inter}} = (-0.5)(3.4)/4 = -0.43$ K.

An independent determination of J_{inter} is made by analyzing the field at which the metamagnetic transition occurs. Mean-field arguments²² relating the AFM exchange energy to the Zeeman energy give the relation between the field at which the zero-temperature metamagnetic transition occurs, $H_c(0)$, and the interchain exchange as

$$z'(-2J_{\text{inter}})S^2 = g\mu_B S H_c(0). \quad (3)$$

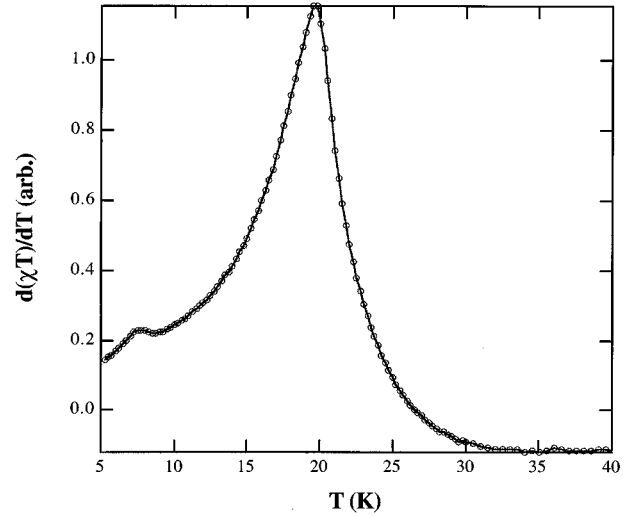


FIG. 6. The derivative with respect to T of the χT product as a function of temperature.

Rearranging for J_{inter} (using $z' = 2$) yields

$$J_{\text{inter}} = -g\mu_B H_c(0)/4S. \quad (4)$$

$H_c(0)$ is estimated from the magnetization curves to be 1 T. Using $S_{\text{eff}} = 3/2$ and $g = 2$ in Eq. (4) yields $J_{\text{inter}} = -0.45$ K, in good agreement with the value obtained above. We take the average of these two values, -0.44 K, as our best approximation of J_{inter} . It should also be noted that this is of the same order of magnitude as the estimates obtained by analyzing the exchange paths between chains.

We now estimate the sign and magnitude of D . Since the HCBd is magnetically isotropic, any anisotropy in the system should arise from the Mn^{III} ion²³ due to the ligand fields surrounding the Mn^{III} ion. The Mn^{III} ion local symmetry closely approximates octahedral with a small prolate tetrahedral distortion. Mn-N distances within the porphyrin plane are 2.003 Å, while the Mn-N distance to the CN groups above and below the porphyrin plane are 2.419 Å. There is also a small trigonal distortion of 3° , which we ignore here. The prolate distortion will favor an Ising-like anisotropy ($D < 0$) as opposed to the X-Y (easy plane, $D > 0$) anisotropy, which would be caused by an oblate distortion from octahedral symmetry. The Ising symmetry of the compound is supported by the absence of a T^2 functionality in the magnetic specific heat of the ordered state (refer to Fig. 6 in the next section). A T^2 functionality is expected⁴ in either X-Y or Heisenberg systems, in which spin-wave excitations occur.

The magnitude of the anisotropy in the Mn^{III} ion is small primarily because orbital angular momentum is quenched in ions with a $3d^4$ electronic configuration and intermediate ligand field strengths as would be expected in the Mn^{III} porphyrin system.²⁴ Magnetic studies of similar porphyrin systems estimate the value of D to be negative (Ising-like) and of order of a few K.²⁵ These numbers are consistent with estimates based on values of the spin-orbit constant for manganese and the ligand field splitting caused by the porphyrin and the CN groups,²⁶ and therefore should be similar to those in our system. The value of $g = 1.92(4)$ obtained from our fit

to the ferrimagnetic chain model is in the range of earlier reported g values (~ 1.96 and larger) of other Mn^{III} -based systems. The suppression of g below 2.00 supports the presence of a small nonzero anisotropy. We ignore the dipolar anisotropy in our discussion of the behavior near 20 K because it is significantly weaker ($\sim 10^{-2}$ K) (Ref. 13) than the single-ion anisotropy (~ 10 K).

B. Determination of T_c

The above estimations for the various energies describe a system with a large lattice anisotropy ($\sim 400:1$); ferrimagnetic chains are weakly antiferromagnetically coupled with one another. The spin anisotropy, on the other hand, is negligible at higher temperatures, $T \gg 20$ K, leading to Heisenberg-like behavior. However, as mentioned in the Introduction, the RG indicates that the weak terms in the Hamiltonian (i.e., the small anisotropy) govern the behavior at lower temperatures and particularly near the critical temperature.⁶ Thus this small anisotropy will ultimately drive the system into an Ising-like state and allow it to reach a state of long-range order.

χ' has a rounded maximum at $T_{\text{max}}=22.5$ K (along with an absence of χ'') similar to the behavior of low-dimensional AFM systems.⁷ Fisher has related the χT product to the magnetic energy of an antiferromagnet. The derivative, $d(\chi T)/dT$, is thus proportional to the magnetic specific heat,²⁷ which should diverge at T_c . The experimental $d(\chi T)/dT$ has a maximum at $T_c=19.6$ K, Fig. 6, below T_{max} , as expected in low-dimensional AFM's. The sharpness of the $d(\chi T)/dT$ divergence is consistent with Ising behavior as opposed to the rounded Schottky-type anomaly expected in Heisenberg systems.⁴ The value of $T_c=19.6$ K is consistent with the appearance of a metamagnetic transition in the magnetization data below this temperature.

By approximating the effective spin magnitude as $S_{\text{eff}}=S+s=3/2$ (below 20 K) and rescaling ($S_{\text{eff}}=3/2$) Onsag-

er's exact 2D rectangular $S=1/2$ model²⁸ relating the exchange strengths and T_c , we obtain $T_{c,\text{Ising}}=305$ K, approximately an order of magnitude larger than the observed 19.6 K ordering temperature. The origin of this large discrepancy may be the weak anisotropy of the system, implying a non-ideal Ising nature. At ~ 300 K the system is essentially Heisenberg-like; not until near and below the actual T_c is there Ising-like behavior.²⁹

V. CONCLUSIONS

In summary, the $[\text{MnOEP}][\text{HCBD}]$ salt is well represented as a system of ferrimagnetic chains consisting of alternating $S=2$, $s=1/2$ spins with strong intrachain exchange, and weak 2D AFM interchain interactions. The fit of the high-temperature susceptibility to Seiden's model for alternating quantum-classical ferrimagnetic chains yields $J_{\text{intra}}=-172$ K. The low-temperature magnetization and susceptibility data yield $J_{\text{inter}}=-0.43$ and -0.45 K, respectively, consistent with earlier estimates made by analyzing the exchange path, and thus $J_{\text{inter}}/J_{\text{intra}}=2.5 \times 10^{-3}$. The spin anisotropy is relatively weak, approximately a few K by comparison with similar Mn^{III} porphyrin compounds, and is due primarily to the single-ion anisotropy of the Mn^{III} ion. Both a lattice and a spin-dimensionality crossover are observed at $T_c=19.6$ K at which point the system undergoes a transition from a 1D Heisenberg ferrimagnet to a 2D Ising antiferromagnet.

ACKNOWLEDGMENTS

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