

between the exchange coupling constant and the angle between the O-H vector and the bridging Cr_2O_2 plane. In all cases where J is large, the angle is small and vice versa. Basically, as the angle increases, the lone pair on oxygen is shifted out and away from the Cr_2O_2 exchange-coupled unit, and in this manner, the lone pair is less effective in transmitting the superexchange interaction. This interesting observation can be precisely examined in the case of alkoxo-bridged complexes, as can the effect of electron density on the bridging oxygen atom since this latter quantity is governed by the hydrocarbon substituent and may be varied over a limited range at least. While major structural and chemical factors that affect exchange coupling may be determined from systematic studies⁵² of which this work forms an integral part, there are a number of features that give rise to subtle changes, and these may prove to be very difficult to detect. In addition, the exchange cou-

pling constant is slightly temperature dependent in some of these compounds,⁵³ and this property may tend to complicate a highly refined treatment.

Conclusion. The major conclusion to be drawn from this work is that exchange coupling in the tris(μ -hydroxo)-bridged chromium(III) complex $[\text{LCr}(\text{OH})_3\text{CrL}](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ results in the largest exchange coupling constant yet observed in hydroxo-bridged chromium(III) complexes, probably as a result of the symmetry and number of bridging ligands.

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Registry No. $[\text{Cr}_2(\text{OH})_3\text{L}_2](\text{ClO}_4)_3$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane), 81915-52-8.

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Single-Crystal Magnetic Study on Ferromagnetic Manganese(II) Phthalocyaninate

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A magnetic study has been carried out in the temperature range 1.2–25 K and magnetic field range 0–50 kOe on single crystals of manganese(II) phthalocyaninate. At higher temperatures the magnetic properties of manganese(II) phthalocyaninate exhibit chainlike characteristics, which may be understood in terms of ferromagnetic intrachain exchange of $S = 3/2$ ions with a weak antiferromagnetic interchain interaction. In the ordered state, $T_C = 8.3$ K, MnPc is a canted ferromagnet with easy axes of magnetization being along χ_1 and χ_3 directions. A zero-field splitting of the single-ion 4A_2 state of the manganese(II) ion gives rise to canted ferromagnetism, which does not show complete saturation at the high-field range of these experiments (50 kOe). The spin structure of manganese(II) phthalocyaninate at low temperature is discussed.

Introduction

Manganese(II) phthalocyaninate (MnPc) is a planar molecule and is known to be isostructural with other divalent metal phthalocyaninates.^{2,3} The stacking of the planar MnPc molecules in the crystal lattice is shown in Figure 1. The figure shows that the two pyrrole nitrogen atoms of each molecule lie exactly above or below the Mn belonging to nearest neighbors. The distance between these axially located nitrogen atoms and the Mn atom is 3.4 Å and thus may provide a possible pathway for magnetic exchange interactions. The Mn(II) ions lie on linear arrays parallel to the b axis of the molecule such that MnPc may be considered as containing magnetic linear chains along the b axis of the crystal.

Magnetic susceptibility and magnetization measurements on MnPc down to 1.4 K have established that the Mn(II) ion in MnPc is in an $S = 3/2$ spin state and that MnPc behaves as a molecular ferromagnet at low temperatures.⁴ A qualitative explanation for the ferromagnetism was given in terms

of the overlap of d orbitals of the Mn(II) ion and the π -system of the phthalocyanine ring.⁴ The data were later quantitatively explained in terms of a model for an $S = 3/2$ linear chain exhibiting ferromagnetic interactions, and a value for the exchange energy of $J = +7.6$ cm⁻¹ was deduced.⁵ Existence of ferromagnetism in MnPc was subsequently confirmed by Miyoshi et al.,^{6,7} who also determined the Curie temperature to be 8.6 K.

To determine the easy axis of magnetization in MnPc, Miyoshi⁸ measured the single-crystal magnetization at 4.2 K. MnPc belongs to the monoclinic system with two crystallographically inequivalent molecules in the unit cell, and crystals generally grow as long flat needles elongated along the b axis. Crystals used by Miyoshi were very small, weighing less than 10⁻² mg. The "single-crystal" magnetization measurements were therefore made on a bundle of single crystals oriented along the long b axis of the crystals. Miyoshi measured magnetization along the perpendicular to the long axis (i.e., b axis) of this bundle and concluded that the easy axis of magnetization lies along the b axis of the crystals.

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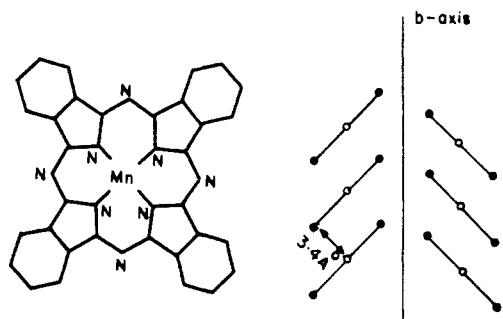


Figure 1. Stacking arrangement of planar manganese(II) phthalocyaninate molecules along the crystallographic *b* axis.

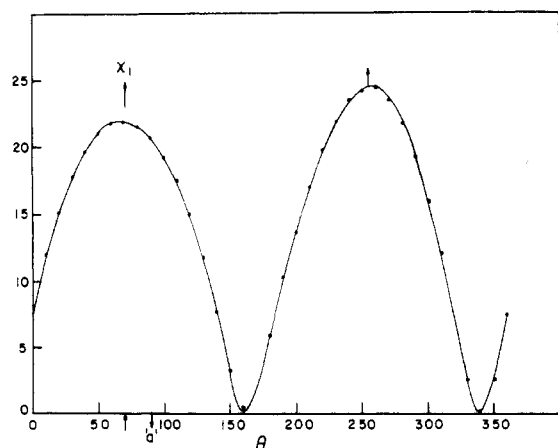


Figure 2. Angular dependence of the moment as a function of crystal orientation at 4.2 K. In these measurements, rotations were made about the *b* axis, which was perpendicular to the magnetic field. It may be seen that the principal direction, designated χ_1 , is rotated 20° from the *a* axis. The susceptibility is given in arbitrary units marked on the *y* axis.

Magnetic anisotropy measurements on individual single crystals of MnPc in the temperature ranges 80–300⁴ and 20–100 K⁹ have revealed that the *ac* plane of the MnPc crystal is highly anisotropic. In the above measurements of Miyoshi, the anisotropy in the *ac* plane was averaged to zero because of the random orientation of the crystallites. Thus, conclusions derived from the measurements were subject to ambiguities.

An accurate magnetic measurement on a single crystal of MnPc at low temperatures therefore was desirable in order to determine the spin structure in the ferromagnetic region. The present paper describes results of magnetization measurements in the 2–15 K temperature range on large, well-developed individual single crystals of MnPc.

Techniques

Single crystals of MnPc were grown by a vacuum sublimation technique. The monoclinic crystals grow as long, thick plates with well-developed (001) faces. The crystals used in the present measurements weighed between 4 and 7 mg.

Single-crystal susceptibilities were measured with a vibrating-sample magnetometer (VSM).¹⁰ In a monoclinic crystal one of the three principal susceptibilities, e.g. χ_3 , lies along the *b* axis of the crystal, with the other two, χ_1 and χ_2 , being in the *ac* plane at some angle to the *a* and *c* axes. This angle must be determined by experiment. In this work the orientations of χ_1 and χ_2 were determined, and χ_1 , χ_2 , and χ_3 were determined as functions of temperature and external magnetic field.

A single crystal of MnPc weighing about 5 mg was mounted on a Lucite goniometer head of the VSM probe with the *b* axis vertical so that the *ac* plane containing χ_1 and χ_2 was lying in the horizontal

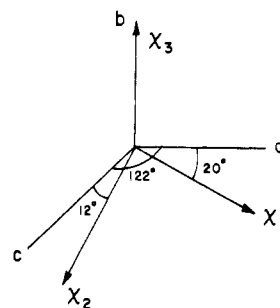


Figure 3. Relative orientation of the three principal magnetic susceptibilities of manganese(II) phthalocyaninate at 4.2 K.

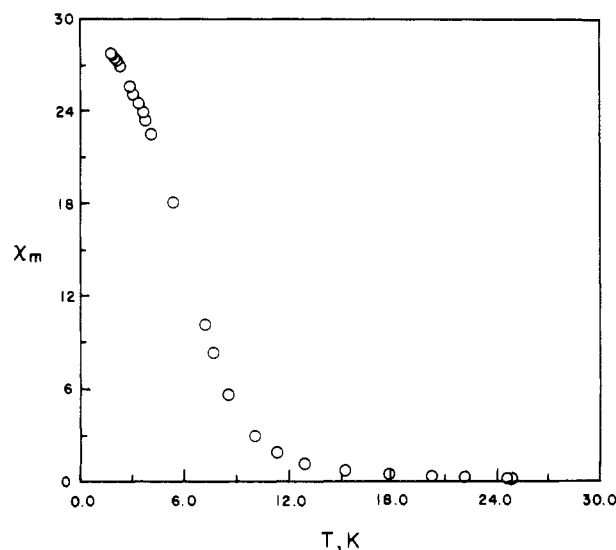


Figure 4. Temperature dependence of the average magnetic susceptibility (emu mol^{-1}) of manganese(II) phthalocyaninate in the temperature range 2–25 K.

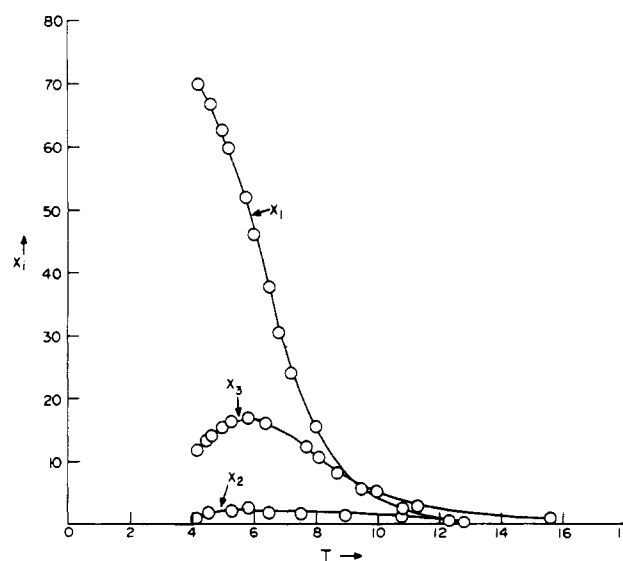


Figure 5. Temperature dependence of the principal magnetic susceptibilities (emu mol^{-1}) of manganese(II) phthalocyaninate in the temperature range 4–16 K.

magnetic field. The temperature was held constant at 4.2 K. The crystal was then rotated through the graduated goniometer head, and the moment (or susceptibility) was measured at an interval of every 10° . A plot of the angular dependence of the moment is shown in Figure 2. It is apparent that the maximum moment direction (e.g. χ_1) lies ca. 20° from the *a* axis of the crystal. The relative orientation of the three principal susceptibilities at 4.2 K is shown in Figure 3. Magnetization along these susceptibility directions was easily measured with varying field and temperature by setting these crystal directions

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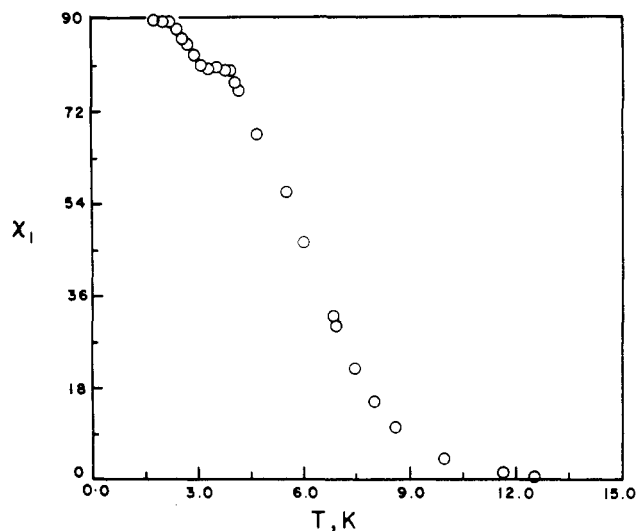


Figure 6. Temperature dependence of χ_1 , which shows a kink in the χ_1 vs. T curve at ~ 3 K, and the temperature independence of χ_1 below 2 K.

along the magnetic field. The magnetization up to 50 kOe along the long b axis (χ_3 direction) was also measured with a second VSM assembly equipped with a superconducting magnet.

Results

The temperature dependencies of the average (2–25 K) and principal susceptibilities (4–15 K) are shown in Figures 4 and 5. The measurements were done at a magnetic field of 30 Oe for $\bar{\chi}$ and at 50 Oe for the principal susceptibilities, χ_i ($i = 1, 2, 3$). The data at lower magnetic fields become slightly less accurate particularly for the single crystals above 10 K or so, but the data show similar temperature dependencies. The $\bar{\chi}$, as expected, shows an abrupt large increase below 9 K, and the magnitude of $\bar{\chi}$ does not maximize even at the lowest temperature of the measurements, ca. 2 K. The Curie temperature was obtained from the point of inflection in the χ vs. T plot. We obtained $T_c = 8.3$ K, in good agreement with the value of $T_c = 8.6$ K obtained previously from broad-line NMR studies. The temperature dependence of the principal susceptibilities shows a large anisotropy in χ_1 and χ_2 , with χ_1 increasing very rapidly below 8 K. $\chi_3 (= \chi_b)$ and particularly χ_2 are relatively much smaller in magnitude and show much less variation with temperature. The results of Figure 5 clearly establish that χ_1 is the direction of the easy axis of spin alignment. For a molecular ferromagnet χ_1 should have been independent of the temperature below T_c ^{11,12} however, MnPc does not show such behavior down to 4 K. We measured χ_1 therefore below 4 K and observed that at ca. 2 K χ_1 becomes almost independent of temperature (Figure 6). Further, a small but reproducible kink is observed in the χ_1 vs. T plot at 3.5 K. A possible explanation of these observations is that a small but finite antiferromagnetic exchange interaction exists between the chains, in addition to the apparently dominant ferromagnetic intrachain interaction. Above 3.5 K this ferromagnetism dominates the weak interchain antiferromagnetic interaction, with the kink in the χ_1 vs. T curve presumably representing this latter interaction.

Figure 7 summarizes the single-crystal magnetization data at 4.2 K along χ_1 (σ_1), χ_2 (σ_2), and χ_3 (σ_3) directions, as well as the average magnetization ($\bar{\sigma}$) of a powdered sample. Several features of the results are noteworthy. First, the data confirm that χ_1 is an easy axis of magnetization though the

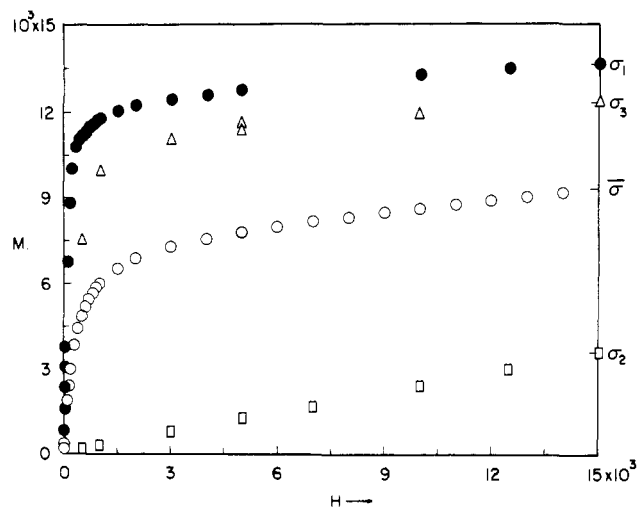


Figure 7. Single-crystal magnetization data at 4.2 K along χ_1 (σ_1), χ_2 (σ_2), and χ_3 (σ_3) directions in magnetic fields up to 15 kOe.

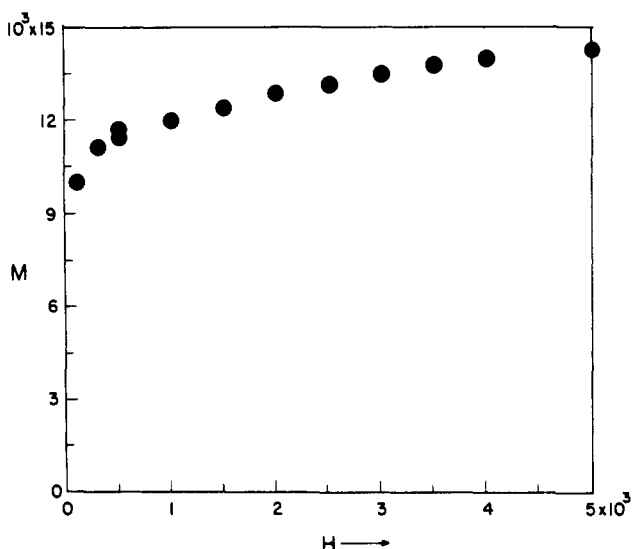


Figure 8. Single-crystal magnetization data for manganese(II) phthalocyaninate at 4.2 K in magnetic fields up to 50 kOe.

sample can be magnetized nearly as easily along χ_3 as well. Further, the large anisotropy and difference in magnetization behavior between σ_1 and σ_2 are consistent with their corresponding temperature dependencies. The most significant result is that although σ_1 reaches a near-saturation value even at a magnetic field at ca. 3 kOe, complete saturation is not reached up to a magnetic field of 15 kOe. The same behavior obtains for σ_2 and σ_3 . In fact, σ_3 does not reach complete saturation at 4.2 K in a magnetic field of 50 kOe (Figure 8).

Discussion

First, we compare our results with those of Miyoshi.^{6,7} There are some significant differences in the magnetization data. Our magnetization data (as well as χ_i vs. T data) show that the σ_1 direction is most easily magnetized. The reason for the discrepancy between our work on a single crystal and the earlier work^{6,7} may be understood in terms of the anisotropy of the material. We find that the magnetization in the ac plane of MnPc, which contains σ_1 and σ_2 , is extremely anisotropic. In the earlier work, measurements were made on a bundle of crystals that were randomly oriented in the ac plane, with measurements being made parallel (σ_{\parallel}) and perpendicular (σ_{\perp}) to the bundle axis (i.e., the b axis). The σ_{\parallel} from the earlier work^{6,7} corresponds to our σ_3 , and the σ_{\perp} corresponds to some average of our σ_1 and σ_2 . Since σ_1 and σ_2 are very different in magnitude, the experimentally observed

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average, that is σ_{\perp} , came out to be smaller than σ_{\parallel} , and consequently, an erroneous conclusion concerning the easy direction was arrived at. The value for σ_{\parallel} from the earlier work^{6,7} is in reasonable agreement with our σ_3 ; at 4.2 K we obtained a value of 12×10^3 emu for σ_3 , while Miyoshi obtained a value of 14×10^3 for σ_{\parallel} at the same temperature. The discrepancy arises from the relatively large uncertainties inherent in the measurements on the bundle of MnPc crystals.

The fact that the magnetization of the MnPc increases linearly with the magnetic field at higher fields and does not show complete saturation even up to 50 kOe is indicative of a canted ferromagnetic spin structure. The canted moments are assumed to rotate gradually with increasing magnetic field in a single domain region. With use of the formula $\sigma = \sigma_0 + \chi H$, the spontaneous magnetization σ_0 can be obtained from Figure 7. For powdered and single-crystal samples, the values are $\bar{\sigma}_0 = 12.5$ emu/g and $\sigma_0^{\chi_1} = 21.4$ emu/g. Since $\bar{\sigma}_0$ is the spatial average $\bar{\sigma} = 0.57\sigma_0^{\chi_1}$. Taking the above value for $\sigma_0^{\chi_1}$, we calculate $\bar{\sigma} = 12.2$ emu/g, in good agreement with the observed value.

$\sigma_0^{\chi_1}$ corresponds to the moment $\langle \mu \rangle = 2.17 \mu_B/\text{ion}$, which is less than $3.0 \mu_B/\text{ion}$ expected for an $S = 3/2$ spin state of MnPc. If the magnetic moments are assumed to align along their tetragonal axes making the angle between them nearly 90° , the resultant ferromagnetic moment will be $2.12 \mu_B/\text{ion}$, in agreement with the observation.

We now discuss the spin structure of MnPc at low temperatures. We have mentioned earlier that MnPc has two crystallographically inequivalent magnetic sites with each site constituting a magnetic chain. The magnetic moments within the chain interact ferromagnetically (J positive).⁵ There appears to be a feeble interchain interaction (J'), and the results shown in Figure 5 suggest that it is antiferromagnetic. Above about 3 K the interchain ferromagnetic interaction overtakes this interchain interaction. The magnetic properties of MnPc can then be discussed by using the Hamiltonian^{6,7}

$$\mathcal{H} = -2\sum_{ij} J\hat{S}_i\hat{S}_j - 2\sum_{jk} J'\hat{S}_j\hat{S}_k + \sum_j D(\hat{S}_j^x)^2 + \sum_k D(\hat{S}_k^y)^2$$

The first and second terms are exchange interactions in and between the chains, respectively, and the experimental results show that J is positive and J' is negative. The third and fourth terms are the single-ion anisotropies at the two sites, D being the zero-field splitting parameter of the ground 4A_2 state of the $S = 3/2$ manganese(II) ion in MnPc. At 4.2 K the relative orientation and magnitude (i.e., $\chi_1 > \chi_2$) of the principal susceptibilities suggest, on the basis of crystal field theory,⁵ that D is negative. Miyoshi has discussed the spin structure of MnPc on a two-sublattice model and shown that, for both J' and D negative, the spins are perpendicular to the χ_2 axis. As a result, the spins on the two sublattices are not antiparallel to each other, and the residual moment gives rise to canted ferromagnetism. Hence, the negative D is responsible for the canted ferromagnetism in MnPc, with both χ_1 and χ_3 directions being easy magnetization directions (see Figure 7). This canting of spins causes the magnetic moment to rotate in an external magnetic field, and the magnetization does not show complete saturation even at very high fields. For $g = 2$ the resulting magnetic moment is given by⁸

$$\mu = S\beta\left\{\left[1 + \left(\frac{A^2}{A^2 + 4}\right)^{1/2}\right]^{1/2} \pm \left[1 - \left(\frac{A^2}{A^2 + 4}\right)^{1/2}\right]^{1/2}\right\}$$

where $A = D/4J'$. For J' negative the magnetic moment varies from 0 to $2.1 \mu_B$. Since $|D| \gg |J'|$, a limiting value for the moment of $2.1 \mu_B$ is predicted, a value that is in good agreement with the experimentally observed magnetic moment.

In this case the magnetic moments are aligned nearly along their tetragonal axes. As shown in Figure 9, this alignment

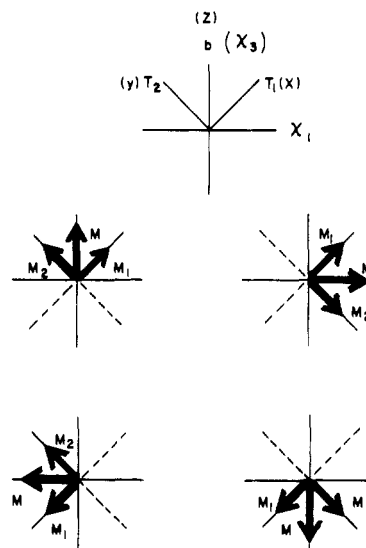


Figure 9. Four kinds of spin structures in manganese(II) phthalocyaninate at low temperatures. The resultant moments are seen to lie along χ_1 and χ_3 . T_1 and T_2 represent the two sites for the tetragonal MnPc molecules.

of magnetic moments gives rise to four kinds of spin structures at low temperatures. It may be seen that the resulting moments lie along χ_1 or χ_3 directions. The four kinds of spin structures are not equienergetic and equally populated. The resulting moments lie along χ_1 and χ_3 in high magnetic fields. However, in low applied fields, χ_1 is the easy and preferred axis.

Concluding Remarks

The ferromagnetism observed in MnPc is rather unique among metal phthalocyaninates. For example, even among isostructural analogues, CoPc shows only feeble antiferromagnetism while CuPc behaves as a normal paramagnet down to 1 K.^{4,6} The ground state of FePc is effectively nonmagnetic, and there is no evidence of magnetic ordering down to 1 K. The ferromagnetism in MnPc can be understood, at least qualitatively, in terms of the electronic configuration and the 90° superexchange mechanism, (the Mn-N-Mn angle is nearly 90°). The d-electron configuration of the Mn^{2+} ion in MnPc is $(b_{2g})^2(e_g)^2(a_{1g})^1$. It has been shown⁴ that the overlap of e_g and a_{1g} orbitals containing unpaired d electrons with phthalocyanine molecular orbitals of A_{2u} , E_g , B_{2u} , and B_{1u} symmetry will lead to ferromagnetism, as indeed is observed in MnPc.⁴

The spins in MnPc are appreciably canted, arising from the substantially large zero-field splitting of the 4A_2 ground state of the Mn^{2+} ion. An earlier crystal field calculation,⁵ based on the high-temperature (80–300 K) single-crystal susceptibility data, has shown that the splitting is about 40 cm^{-1} in MnPc and that ${}^4A_2(\pm 1/2)$ lies below the ${}^4A_2(\pm 3/2)$ state. It is however of interest to note that the directions of χ_1 and χ_2 have interchanged in the ordered state with respect to the high-temperature directions, giving rise to negative zero-field splitting (i.e., ${}^4A_2(\pm 3/2)$ lying below ${}^4A_2(\pm 1/2)$). It is this large negative zero-field splitting that is responsible for the canted ferromagnetism. Thus, the unusual magnetic behavior of MnPc appears to derive from the combination of magnetic interactions, the electronic configuration of the manganese ion, the low-symmetry structure of the compound, and crystal field effects.

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