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The Magnetic Properties of Manganese(II) Phthalocyanine. II

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The magnetic susceptibilities of manganese(II) phthalocyanine (PcMn) have been measured in the paramagnetic region between 13.8 and 280 K. The deviation from the Curie-Weiss law was found at a moderately high temperature (about 70 K), and the Weiss constant was obtained as 23 K. Comparing the ratio of T_c to θ (0.37) with that of the 2- or 3-dimensional lattice, the data were analysed on the basis of the ferro-magnetic linear-chain model. The magnitude of the intra-chain interaction (J) was deduced as $5.64k$ by comparison with Fisher's classical form of the theory of the ferromagnetic Heisenberg chain. We have also measured the magnetic susceptibilities of cobalt(II) phthalocyanine (PcCo) and of copper(II) phthalocyanine (PcCu), which are isomorphous with manganese(II) phthalocyanine, from 1.8 to 77 K. In PcCo, a broad maximum has been observed, and the data were analysed in terms of the theory of the antiferromagnetic Ising-chain model. On the other hand, PcCu obeyed the Curie law down to 1.8 K. A qualitative explanation of the exchange interactions in PcMn, PcCo, and PcCu was presented on the basis of their electronic states.

Most of the transition-metal phthalocyanines are known to be paramagnetic.[1] So far as the present author knows, most reports of their magnetic properties have been concentrated upon the investigation of their electronic structures within one molecule, though there have been a few of the intermolecular exchange interaction. However, the magnetic interaction revealed by the measurements of the magnetic susceptibility in the low-temperature region is of some interest, since the crystal is composed of discrete molecules at the van der Waals' radii; thus, the magnetic interaction is primarily intermolecular in origin.

Our earlier report[2] has shown that a ferromagnetic transition occurs in manganese(II) phthalocyanine $C_{32}H_{16}N_8Mn$ (hereafter simply denoted as PcMn) at T_c=8.6 K. However, no detailed measurements or discussion of the exchange interaction have been made.

Table 1. Constants of crystal structures[3]

	PcMn	PcCo	PcCu	PcNi
a Å	20.2	20.2	19.6	19.9
b	4.75	4.77	4.79	4.71
c	15.1	15.0	14.6	14.9
β°	121.7	121.3	120.6	121.9
Space group	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$
No of 3d-electron	5	7	9	8
Spin number	3/2	1/2	1/2	0

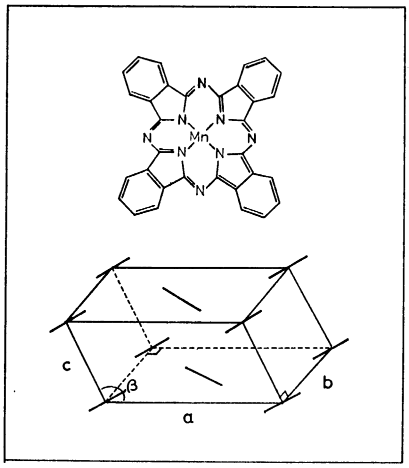

Fig. 1. Molecular and schematic crystal structures of PcMn. The molecular plane is approximately normal to the ab-plane.

To study the magnetic exchange interaction in the phthalocyanines, the magnetic susceptibilities of PcMn, PcCo, and PcCu were measured. They have been shown to be isomorphous with PcNi, whose structure is known[3] (see Table 1). The molecule is almost perfectly square-planar. The base-centered arrangement of two molecules per unit cell is shown in Fig. 1. The planar molecules are stacked along the short b axis at intervals of 4.7 Å, and the molecular planes are inclined to the ac plane at an angle of about 45°. The vertical distance between the nearest neighbors is 3.4 Å; this seems to be the minimum intermolecular separation when only van der Waals' forces are operative. As was pointed out by Mitra *et al.*,[4] this distance may provide a possible pathway for the magnetic exchange interaction. Therefore, the phthalocyanine may form magnetic linear chains along the b axis.

PcMn gives a large positive deviation from the Curie-Weiss law, and PcCo shows a broad maximum. These results are analysed in terms of the theory of linear-chain models. On the other hand, PcCu obeys the Curie law and may not form a magnetic linear chain. These results are also discussed on the basis of their electronic states.

Experimental

PcMn, PcCo and PcCu were prepared by the methods of Linstead *et al.*[5] and of McQueen *et al.*[6] The products were washed with benzene, ethanol, and acetone, and then sublimed at around 500 °C in an atmosphere of pure nitrogen. The single crystal grown by sublimation was in the shape of an elongated flat plate. The results of the elemental analysis of the carbon, hydrogen, and nitrogen of each sample corresponded closely to the calculated values. PcMn: Found: C, 67.70; H, 2.94; N, 19.67%, (Calcd: C, 67.73; H, 2.84; N, 19.75%), PcCo: Found: C, 67.86; H, 2.74; N, 19.57%, (Calcd: C, 67.76; H, 2.82; N, 19.61%), PcCu: Found: C, 66.87; H, 2.57; N, 19.42%, (Calcd: C, 66.72; H, 2.80; N, 19.45%).

All the measurements were carried out in the polycrystalline state. The static (dc) susceptibility measurements were done by means of a magnetic torsion balance described elsewhere[7] on the samples of 50—150 mg in a field of 10.2 kG. The measurements on PcMn were performed between 1.8 K and 280 K in the temperature region attainable by pumping out the liquid helium and liquid nitrogen. The measurements on PcCo and PcCu were carried out between 1.8 K and 77 K. The temperatures of the samples were measured with a carbon resistor and AuCo-Cu thermocouple calibrated by measuring not only the known magnetic susceptibility of Mn-Tutton salt, but also the vapor pressures of liquid helium, liquid hydrogen, and liquid nitrogen. The ac-susceptibility measurements of PcMn were done by means of a Hartshorn bridge zero-field method (90 Hz) between 13.8 K and 20.2 K by pumping out the liquid hydrogen. The temperature was determined from the susceptibility of the standard sample, $Cr(NH_3)_6Cl_3$,[8] and from the vapor pressures of liquid hydrogen. With this method, the initial susceptibility in the limit of zero field is fairly well approximated because the amplitude of the measuring field may be kept very small.

A diamagnetic correction of -290×10^{-6} emu/mol was used to correct the susceptibility data, following the recent results on diamagnetic PcNi reported by Mitra *et al.*[9]

Results and Discussion

a) PcMn. The dc susceptibility in 10.2 kG appears to deviate from the Curie-Weiss law below 70 K, as is shown in Fig. 2. Below 7 K, it reaches a constant maximum value dependent on the magnetic field strength, as has already been reported.[2] To study the magnetic behavior in the low-temperature region, it is more advantageous to plot $(\chi_m T)^{-1}$ against T^{-1}, which enlarges the deviation from the Curie-Weiss law.[10] The data are plotted as $1/\chi_m T$ to $1/T$ in Fig. 3. The molecular-field result (the Curie-Weiss law) appears as a straight line; $1/\chi_m T = 1/C - \theta/CT$. The deviation from the molecular-field result is very large. The Curie constant, C, and the Weiss constant, θ, are estimated as 2.13 and 23 K respectively in the high-temperature region. The susceptibility seems to become dependent on the field at $1/T=0.057$, ($T=17$ K). The results of ac-susceptibility measurements have been included in Fig. 3; they coincide with those measured in 10.2 kG above 17 K. This field dependence of the susceptibility is consistent with the results of the magnetization measurements[2] at 4.2, 11.1, and 20.2 K.

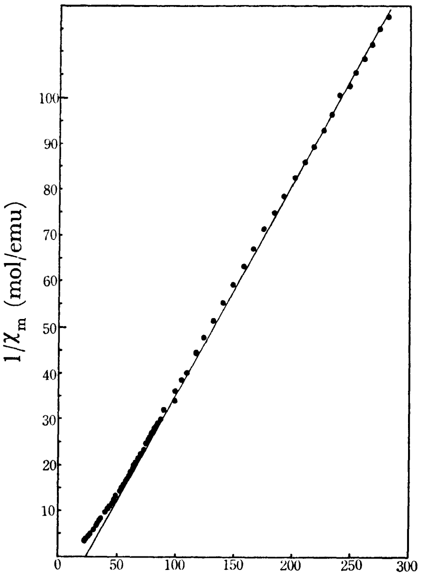

Fig. 2. Reciprocal susceptibilities of PcMn as a function of temperature ($H=10.2$ kG).

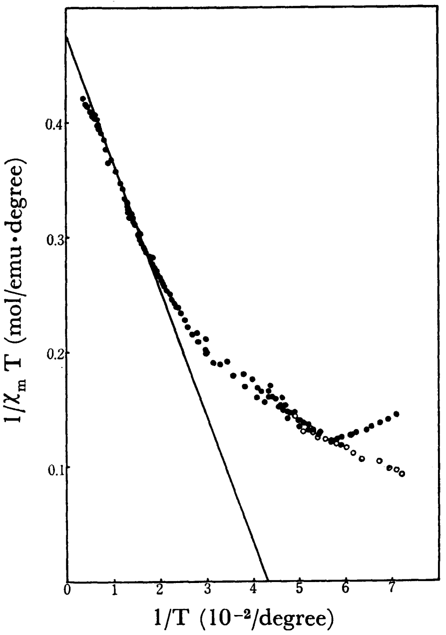

Fig. 3. Reciprocal susceptibilities ($1/\chi_m T$) of PcMn as a function of $1/T$. (●: $H=10.2$ kG, ○: $H\approx0$ G.)

It has been reported[1,4] that the ground electronic state of PcMn is a quartet ($S=3/2$). However, the ground state is not completely understood for the reason that no single crystal ESR data have been reported, though ESR measurements have been made of the powder sample ($g=2.0$).[11] Because of the lack of detailed information about the magnetic anisotropy, the exchange interaction in PcMn is assumed to be isotropic.

Now, let us compare the ratio of T_c to the θ of PcMn with that of the 2- or 3-dimensional lattice. On the Curie points of Heisenberg model magnetics, many theoretical studies have been made all along the line. Rushbrooke and Wood[12] have obtained an approximate formula for the Curie temperatures of 3-dimensional lattices for $S>1/2$; $T_c=(5/96)(z-1)[11S(S+1)-1](J/k)$, where z is the coordination number of the lattice. Moreover, Stanley and Kaplan[13] have

Table 2. The values of T_C/θ and kT_C/J[12-14]
(Heisenberg model of $S=3/2$)

Lattice	Dimension	z[a]	T_C/θ	kT_C/J
Simple cubic	3	6	0.68	10.48
b. c. c.	3	8	0.73	14.67
f. c. c.	3	4	0.77	6.28
triangle	2	6	0.43	6.5
quadratic	2	4	0.39	3.9
PcMn	—	2	0.37	1.53

a) the coordination number.

given the transition temperature in 2-dimensional lattices for $S>1/2$ as follows; $T_c=(1/5)(z-1)[2S(S+1)-1](J/k)$. The Weiss constant, θ, has also been obtained by the molecular-field model; $\theta=(2/3)zS(S+1)(J/k)$. Using these formulas, the (T_c/θ) ratio can be calculated theoretically in individual lattice. The results are tabulated for $S=3/2$ in Table 2. The experimentally-obtained ratio of PcMn is 0.37, much smaller than that of the 2- or 3-dimensional lattice. This suggests that the dominant exchange interactions in PcMn may form a magnetic linear-chain system.

In the second place, taking into account the crystal structure, PcMn is treated approximately as a ferromagnetic-chain system and the results are compared with the definite theory. At first sight, it seems plausible to apply Fisher's classical Heisenberg result.15) Fisher replaced the quantum mechanical spin operators with classical vectors. The resulting Hamiltonian for a chain of $N+1$ may be written in a magnetic field. H, as;

$$\mathscr{H} = -2JS(S+1)\sum_{i=1}^{N} \boldsymbol{s}_i \boldsymbol{s}_{i-1} - g\mu_{\mathrm{B}}[S(S+1)]^{1/2}\sum_{i=0}^{N} \boldsymbol{H}\cdot\boldsymbol{s}_i, \qquad (1)$$

where the unit vector, $\boldsymbol{s}_i$, is associated with the ith spin, whose magnetic moment is $g\mu_{\mathrm{B}}[S(S+1)]^{1/2}$. Fisher's expression for the magnetic susceptibility of the chain then becomes;16)

$$\chi_{\mathrm{m}} = Ng^2S(S+1)\mu_{\mathrm{B}}^2/3kT\cdot(1+\mathrm{u})/(1-\mathrm{u}), \qquad (2)$$

where $\mathrm{u}=\coth[2JS(S+1)/kT]-kT/2JS(S+1)$. If the interaction is ferromagnetic $(J>0)$, χ_{m} diverges as $T\rightarrow 0$. We may conveniently rewrite the above formula;

$$C/X_{\mathrm{m}}T = (1-\mathrm{u})/(1+\mathrm{u}). \qquad (3)$$

Using $S=3/2$ and the obtained C value of 2.13, Eq. (3) is fitted to the data in the high-temperature range by adjusting J. The best fit is obtained with $J=5.64k$. The resulting curve of $C/\chi_{\mathrm{m}}T$ *versus* J/kT is shown together with the data in Fig. 4. Although the theory is restricted within the classical limits and the real system of PcMn may be more complex, the data agree rather well with Fisher's theory over quite a wide temperature region. Using the value of $J=5.64k$, it is found that kT_c/J is 1.53 (8.6/5.64), smaller than the value of the theory of the 2- or 3-dimensional lattice (see Table 2).

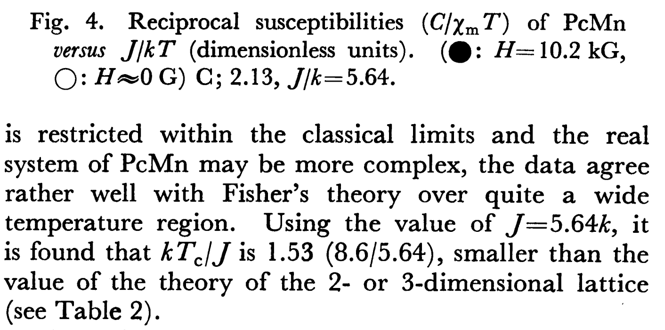

Fig. 4. Reciprocal susceptibilities $(C/\chi_{\mathrm{m}}T)$ of PcMn *versus* J/kT (dimensionless units). (●: $H=10.2$ kG, ○: $H\approx 0$ G) C; 2.13, $J/k=5.64$.

Thus, the preceding discussion confirms the 1-dimensionality of the dominant exchange interactions in PcMn. It is well known theoretically13,17) that isolated magnetic chains do not give rise to a magnetic transition, and that there occurs a magnetic transition in the presence of a small interaction between chains. Therefore, the magnetic transition in PcMn presumably results from an interchain interaction much smaller than the intrachain interaction.

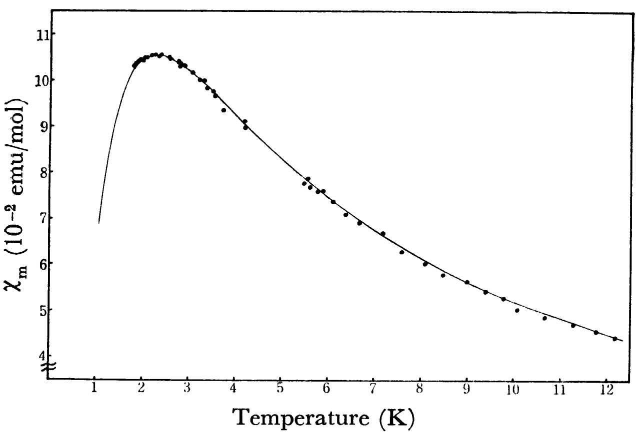

Fig. 5. Molar susceptibilities of PcCo as a function of temperature. The solid line; the parallel susceptibilities of the 1-dimensional Ising theory ($J/k=2.3$, $g=2.66$).

b) PcCo. The magnetic susceptibilities of PcCo are shown in Fig. 5. The results obey the Curie-Weiss law above 5 K. One feature of the results is the presence of antiferromagnetic interaction among molecules, suggested by the negative Weiss constant, $\theta(-3\ \mathrm{K})$. Another feature is the existence of a broad maximum at 2.3 K ($\chi_{\max}=10.55\times10^{-2}$ emu). Such a maximum can be expected for an antiferromagnetic linear-chain system. Of course, the broad susceptibility maxima could occur also in systems of isolated clusters or 2-dimensional sheets of spins. The structural consideration of phthalocyanines presented earlier does, however, favor the linear-chain model rather than any other one.

The electronic structure of PcCo has been studied by means of ESR measurements.18) The experimental results confirm that PcCo exists as a doublet $(S=1/2)$ and has anisotropic g values. The experimentally-obtained g-value (2.66), determined from the slope of $1/\chi_{\mathrm{m}}-T$ plots, is consistent with the reported data ($g_{/\!/}=1.89$, $g_{\perp}=2.94$).

Let us analyse the results using the theory of the 1-dimensional antiferromagnetic Ising model, because of the anisotropy shown in g values. The exchange interaction is represented as $-2JS_{\mathrm{iz}}S_{\mathrm{jz}}$. The expression for the magnetic susceptibility of the Ising chain thus becomes;19)

$$\left.\begin{aligned} \chi_{/\!/} &= (Ng^2\mu_{\mathrm{B}}^2/4kT)\exp(J/kT) \\ \chi_{\perp} &= (Ng^2\mu_{\mathrm{B}}^2/4|J|)[\tanh(|J|/2kT) \\ &\quad +(|J|/2kT)\,\mathrm{sech}^2(|J|/2kT)] \\ \chi_{\mathrm{p}} &= (\chi_{/\!/}/3) + (2\chi_{\perp}/3), \end{aligned}\right\} \qquad (4)$$

where $\chi_{/\!/}$, $\chi_{\perp}$, and χ_{p} indicate the parallel, perpendicular, and powder susceptibilities respectively. χ_{p} is the spatial average of $\chi_{/\!/}$ and $\chi_{\perp}$. χ_{p} has a broad maximum ($\chi_{\max}$) at $kT_{\max}/|J|\simeq 0.47$. By comparing the experimental and theoretical values of the temperature (T_{max}) which corresponds to the broad maximum (χ_{max}), the exchange interaction is estimated to be $J/k=-4.89$. However, using this value, the calculated maximum susceptibility (11.91×10^{-2} emu) does not agree with the experimental one (10.55×10^{-2} emu); this discrepancy is beyond the limits of experimental error. Strangely, the data are quantitatively in good accord with $\chi_{//}$ rather than with χ_p. $\chi_{//}$ exhibits a broad maximum at $kT_{max}=J$; thus, it is found that $J/k=-2.3$ K for $T_{max}=2.3$ K. Using the values of $g=2.66$ and $J=-2.3k$, the theoretical curve of $\chi_{//}$ is shown against T as a solid curve, together with the data shown in Fig. 5. The agreement is very good. The Weiss constant is expressed as $\theta=(2/3)zS(S+1)(J/k)$. By substituting the values of $\theta=-3$ K, $z=2$ and $S=1/2$, it is found that $J=-3k$, which is consistent with the value of $J=-2.3k$ rather than with that of $J=-4.89k$.

These facts can not be understood well, but they may come from the fact that PcCo is not the ideal Ising spin system, since the anisotropy of g values is small compared with those of the usual Co(II) compounds of the Ising type.[20]

c) PcCu. The results are subjected to the Curie law in the temperature region where the measurements were carried out (1.8—77 K). This implies that the exchange interaction in the PcCu crystal is very small; thus, PcCu may not form a magnetic linear chain. The g value was determined as 2.07 from the slope of the $1/\chi_m-T$ plots; this value is consistent with those obtained from the ESR measurements ($g_{//}=2.18$, $g_{\perp}=2.05$).[21]

d) Exchange Interactions in PcMn, PcCo, and PcCu. Through their crystal structures are isomorphous, the exchange interactions in PcMn, PcCo, and PcCu are multifarious. Because the nature of the magnetic interaction is dependent on the electronic configuration of each molecule, it will be useful to comment on the characteristics of the electronic state of the present system. The phthalocyanine ring has a well-developed π-system and generally has been treated by the molecular orbital method. The central metal orbitals interact weakly with the π-system. Let us consider the orbitals occupied by the unpaired electrons. Based upon the discussion of the results calculated by Gouterman *et al.*[22] and the results observed experimentally by ESR measurements, *etc.*[1,4,18,21] for PcCu, PcCo, and PcMn, the features can be described as follows.

The ordering of energy levels may be identical for the three compounds, as is shown in Fig. 6. The rise in the d_{zx} and d_{yz} levels above the d_{xy} level originates in the π-bonding with the phthalocyanine molecular orbitals.[21] In PcCu, the $d_{x^2-y^2}$ orbital is occupied by the unpaired electron which spreads into the molecular plane and has a σ-characteristic. In PcCo, the unparied electron is localized in a d_{z^2} orbital which is almost pure. This orbital has a characteristic of an out-of-plane spreading. In PcMn, three unpaired electrons occupy the d_{z^2}, d_{zx}, and d_{yz} orbitals. The unpaired electrons in the d_{zx} and d_{yz} orbitals can spread on the liganding phthalocyanine ring *via* the π-bonding.

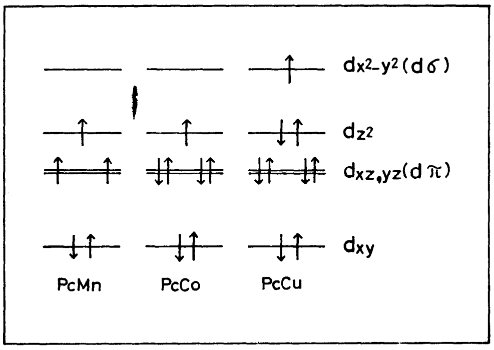

Fig. 6. Schematic representation of electronic structures of PcCu, PcCo, and PcMn.

In our previous report[2] on PcMn, the paramagnetic shifts of hydrogens were observed by means of proton magnetic resonance measurements (12 MHz) in the liquid-hydrogen-temperature region. These maesurements showed that the unpaired electrons in PcMn are spreading on the ligand. On the other hand, in PcCo and PcCu, only one nonshifted absorption is observed down to 1.8 K in the helium temperature range (PcCo: the linewidth is 9—10 G at 30 MHz; PcCu: the linewidth is 15—18 G at 17 MHz). These results support the above description of the electronic states.

The exchange interaction originates from an overlap of the wave function of the unpaired electrons. The nearest vertical distance between adjacent parallel molecules is 3.38 Å and may ensure a weak overlap of the out-of-plane orbitals. In PcCu, the $d_{x^2-y^2}$ unpaired orbital has a σ-characteristic; hence, the overlap of the wave function between adjacent molecules may be very small. Both PcCo and PcCu have out-of-plane unpaired orbitals; therefore, the overlap may be present. In PcCo, since the unpaired orbital d_{z^2} is almost pure, the overlap may be attributed to the direct one between the d_{z^2} orbitals of adjacent molecules. On the other hand, in PcMn there exists a delocalization of the unpaired spins onto the molecular plane *via* the π-bonding. This may enhance the overlap and afford the possibility of an exchange interaction between the nonparallel molecules (interchain interaction). However, for the nonparallel molecules, the metal-metal distance is 10.3 Å and the orbitals are at right angles to each other. Accordingly, the overlap of the wave functions between nonparallel molecules may be smaller than that between the parallel molecules.

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