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Magnetism of Pyrimidine-Bridged Metal(II) Halide Complexes

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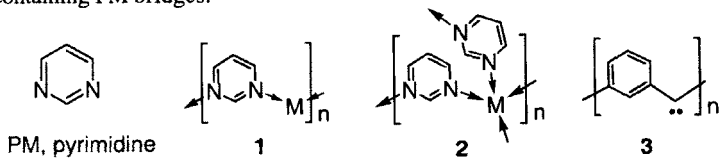
Magnetic phase transitions of $PM_2{\bullet}CoCl_2$, $PM_2{\bullet}CoBr_2$, and $PM_2{\bullet}FeCl_2$ (PM = pyrimidine) were observed at T_N = 4.4, 4.7, and 6.1 K, respectively, as defined by the peak of $\chi^{ac'}$. They are characterized to be isomorphous, belonging to the space group $I4_122$, and canted antiferromagnets below T_N. The neutron diffraction study supports the principally antiferromagnetic structure.

Keywords: weak ferromagnet; canted antiferromagnet; X-ray diffraction; neutron diffraction

INTRODUCTION

The control of magnetic interactions among the metal spins through bridging ligands is of great interest for materials chemistry. We have reported the magnetism of pyrimidine-bridged transition metal complexes (**1** and **2**) in connection with the organic high-spin *m*-phenylene-bridged poly-carbenes and -radicals (for example, **3**) [1]. Indeed the pyrimidines work as a ferromagnetic coupler, as demonstrated by bisoxovanadium(IV) [2] and linear polycopper(II) complexes [3] bridged by various pyrimidines. Only a few pyrimidine-bridged Ti(III) and Co(II) complexes are reported to show ferromagnetic coupling [4]. The magnetic couplings in dinuclear Mo(I) complexes bridged by bipyridyls were interpreted in terms of the spin polarization mechanism [5]. However, the pyrimidines can also play a role of an antiferromagnetic coupler, depending on geometry between nitrogen lone-pair and magnetic orbitals [6,7].

The cobalt(II) halide complexes $PM_2{\cdot}CoCl_2$ and $PM_2{\cdot}CoBr_2$ (PM = pyrimidine) have been reported to possess a chiral 3-dimensional network of cobalt ions and exhibit weak ferromagnetism below 5 K [8]. We have investigated the magnetisms of various metal(II) chloride complexes containing PM bridges.



RESULTS AND DISCUSSION

$PM_n{\cdot}MCl_2$ (n = 1, 2) complexes

Polycrystalline samples of PM-bridged complexes were obtained by mixing PM and metal(II) chloride in water, methanol, or ethanol. The formulas were determined by the elemental analysis (C,H,N).

Figure 1 shows the temperature dependence of $M_{mol}TH^{-1}$ measured at 0.5 T for the complexes obtained here. The 2:1 complexes $PM_2{\cdot}MCl_2$ (M = Fe, Co) showed peaks at around 5 and 4 K, respectively. Since details of $PM_2{\cdot}CoCl_2$ have been described elsewhere [8], those of $PM_2{\cdot}FeCl_2$ are stated

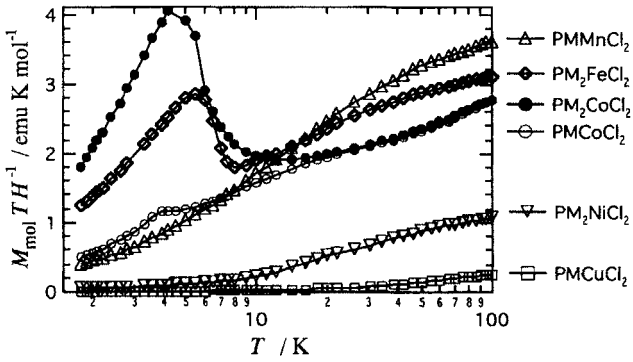


FIGURE 1 Temperature dependence of $M_{mol}TH^{-1}$ for PM/MCl_2 complexes.

here. The Curie-Weiss expression [$\chi = C/(T - \theta)$] with C = 3.40 emu K mol^{-1} and θ = -9.2 K reproduces the data in a temperature range 20 - 300 K. The isotropic Landé g factor is estimated to be 2.13 with S = 2. The magnetism at lower temperatures is described in the following section. The M_{mol} of PM_2•$NiCl_2$ showed a λ-type cusp at 16 K (not shown), suggesting an antiferromagnetic phase transition at about 16 K.

The 1:1 complexes PM•MCl_2 (M = Mn, Co, Cu) exhibited antiferromagnetic coupling without any phase transition down to 1.8 K. A shoulder of the $M_{mol}TH^{-1}$ of PM•$CoCl_2$ at 4 K is due to contamination of PM_2•$CoCl_2$.

Weak ferromagnetism of PM_2•$FeCl_2$

In order to clarify the nature of the anomaly of PM_2•$FeCl_2$, we measured the field-cooled magnetization (FCM), remnant magnetization (RM), and zero-field-cooled magnetization (ZFCM). The FCM (3 Oe) showed an upsurge at 6.4 K on cooling, and, after removal of the applied field at 4.5 K, the RM completely disappeared at 6.3 K on heating. The ZFCM (3 Oe) increased with increasing temperature and exhibited a peak at 6.1 K.

Figure 2a shows the temperature dependence of the χ_{ac}' (in-phase component) and χ_{ac}'' (out-of-phase component) at an applied field of 1 Oe with 10^4 Hz. A sharp peak of the χ_{ac}' and small hump of the χ_{ac}'' at 6.1 K, which we define as a transition temperature T_N, were observed. Under the same conditions, T_N's of PM_2•$CoCl_2$ and PM_2•$CoBr_2$ were 4.4 K and 4.7 K, respectively.

The M-H curves of PM_2•$FeCl_2$ were measured below T_N. As Figure 2b shows, together with an S-shape magnetization curve in a low-field region, a linear field dependence up to 7 T due to strong antiferromagnetic interaction was observed at 2.0 K. This behavior is typical of a weak ferromagnet [10,11]. The spontaneous magnetizations estimated by H → 0 extrapolation were 2.5 x10^3 erg Oe^{-1} mol^{-1} at 2.0 and 3.0 K, which are 11% of a theoretical value. Assuming that the spontaneous magnetization is attributed to the residual moment from the spin canting, the cant angle is 6°. Similar measurements of PM_2•$CoCl_2$ and PM_2•$CoBr_2$ revealed the cant angle of 9° at 3.0 K [8].

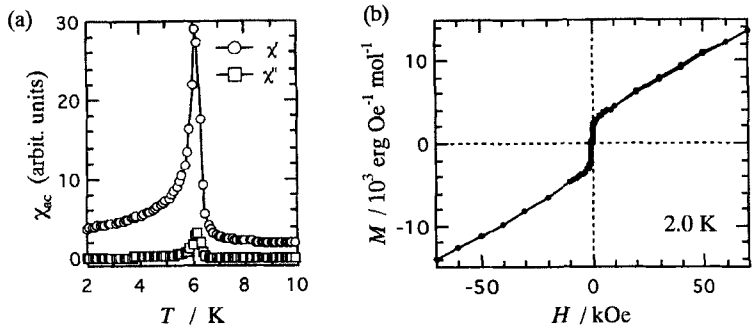


FIGURE 2 (a) Temperature dependence of ac susceptibilities of PM_2•$FeCl_2$. (b) Magnetization curve of PM_2•$FeCl_2$ measured at 2.0 K.

Crystal structure of PM_2•$FeCl_2$

Combined X-ray and neutron diffraction of PM_2•$FeCl_2$ and the Rietveld refinement gave satisfactory results; PM_2•$FeCl_2$ has an isostructure of PM_2•$CoCl_2$ (tetragonal, $I4_122$) [8] with $a = b = 7.4292(3)$ Å, $c = 20.364(1)$ Å. The Fe-N and Fe-Cl distances are estimated to be 2.26 and 2.39 Å, respectively.

Attention must be paid to the local FeN_4Cl_2 geometry, in which all of PM nitrogen atoms are equatorially coordinated. We have pointed out that the electron spins in magnetic $d_{x^2-y^2}$ orbitals are antiferromagnetically correlated through the PM molecular orbital(s), i.e., by a superexchange mechanism [9], when the nitrogen lone pair and $d_{x^2-y^2}$ orbitals have an appreciable orbital overlaps on both sides [6,7]. In spite of partly different d-electron configurations ($t_{2g}^4e_g^2$ for Fe(II) vs. $t_{2g}^5e_g^2$ for Co(II)), magnetic correlations due to e_g orbitals may be found similar to each other.

Magnetic structure of PM_2•$FeCl_2$, PM_2•$CoCl_2$, and PM_2•$CoBr_2$

Neutron powder diffraction has been carried out on the diffractometers E2 and E6 (HMI) at various temperatures using non-deuterated samples. The difference diffractogram of PM_2•$FeCl_2$ (Figure 3) shows the additional Bragg intensities produced by the long-range magnetic ordering. The rule $h+k+l$ = even for the observed magnetic Bragg reflections (hkl) indicates that in priciple the body centering is conserved. The presence and strengths of the reflections

(00*l*) suggest that the magnetic moments lie perpendicular to the c axis. The solid line is a fit of the magnetic structure model shown in Figure 4. The ordered moment is 3.8 ± 0.3 μ_B at 1.6 K. The intensity of the magnetic reflections decreased continuously with rising temperature and vanished at 6.4 ± 0.2 K. The diffraction measurements on PM_2•$CoCl_2$ and PM_2•$CoBr_2$ afforded similar results indicating the long-range antiferromagnetic ordering with 2.7 and 1.7 μ_B ordered moments, respectively.

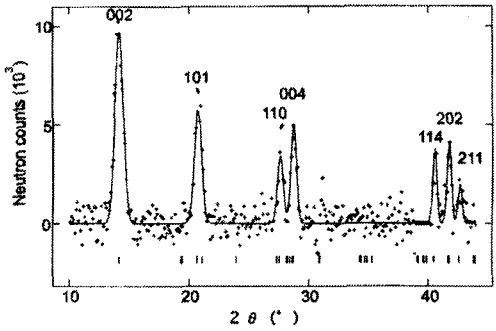


FIGURE 3 Difference of the two neutron powder diffractograms measured at 1.6 K (below T_N) and 7.0 K (above T_N) for PM_2•$FeCl_2$. The wavelength was 2.448 Å.

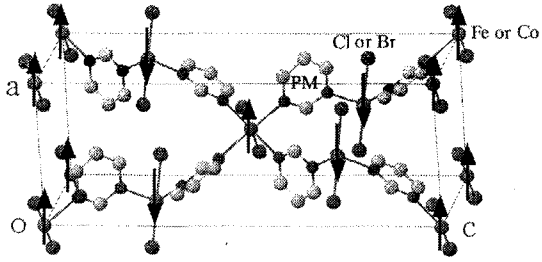


FIGURE 4 Model for a basic magnetic structure. Small canting is omitted.

The antiferromagnetic coupling through PM bridges is clearly indicated. However, canting direction can not be determined only by these diffraction data. The residual moment is suggested to survive along the unique c direction

for symmetry reasons [11]; a small canting towards the c axis from the starting structure (Figure 4) would lead the observed weak ferromagnetism.

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