Pyrimidine-Bridged Cobalt(II) Complexes with a Chiral 3-D Network Showing Weak Ferromagnetism

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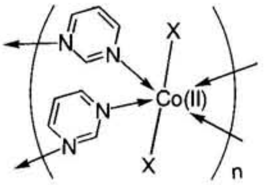
The reaction of CoX_2 (X = Br, Cl) and pyrimidine (PM) in H_2O gave crystals of $CoPM_2X_2$. The crystal structure analysis revealed a chiral three-dimensional network of the Co(II) ions. Weak ferromagnetism with relatively large spontaneous magnetization was observed below 5 K for both compounds.

Molecular magnetic materials having organic π-conjugated bridging ligands have been extensively studied in recent years.[1] The cyanide-bridged bimetallic systems[2] and *N,N'*-dicyanoquinonediimine-bridged copper salts[3] are typical instances of the developments of magnetic and conducting materials. Although the binary metallic materials[2,4] and metal-radical systems[5] having three-dimensional networks were developed for bulk magnetisms, molecular magnets containing a single spin species are rare.[6] In connection with the studies on *m*-phenylene-bridged poly-radical or -carbene species,[7] we[8] and other groups[9] investigated the magnetic interactions in pyrimidine(PM)-bridged transition-metal complexes, among which various geometrical and magnetic structures were found.[10] We report here a novel three-dimensional network of Co(II) ions in PM-bridged complexes $CoPM_2X_2$ [X = Br (**1**), Cl (**2**)] showing low-temperature weak ferromagnetism.



$CoPM_2X_2$

1 : X = Br
2 : X = Cl

To a concentrated aqueous solution of $CoBr_2$ was added dropwise a two-molar amount of PM, and the resultant solution was allowed to stand for a week. The violet single crystals of **1** were precipitated. A similar procedure replacing $CoBr_2$ with $CoCl_2$ gave the crystals of **2**. They were analytically pure[11] and suitable for the structure analysis. The X-ray diffraction data were collected on RIGAKU AFC-7R and -5R diffractometers and analyzed on programs in a package of SHELX-97.[12] The magnetic properties were measured on a Quantum Design MPMS SQUID magnetometer.

The crystal structure analysis revealed that the crystals of **1** and **2** were chiral and that their crystal structures were practically the same.[13] The Co ion is coordinated with four nitrogen atoms of PM and two halogen anions at the equatorial and axial positions, respectively, to form an octahedral geometry. One halogen and Co ions and a half of PM are crystallographically independent. The Co-halogen bond lengths are 2.579(1) and 2.407(1) Å for **1** and **2**, respectively, and the Co-N bond lengths are 2.208(7) Å and 2.206(3) Å for **1** and **2**, respectively. The neighboring Co atoms are bridged by PM ligands. Figure 1a shows the chiral 4_3 screw structure of the $CoPMBr_2$ moieties. Since the crystal is chiral, no enanthiomeric helical structure is found in the crystal.

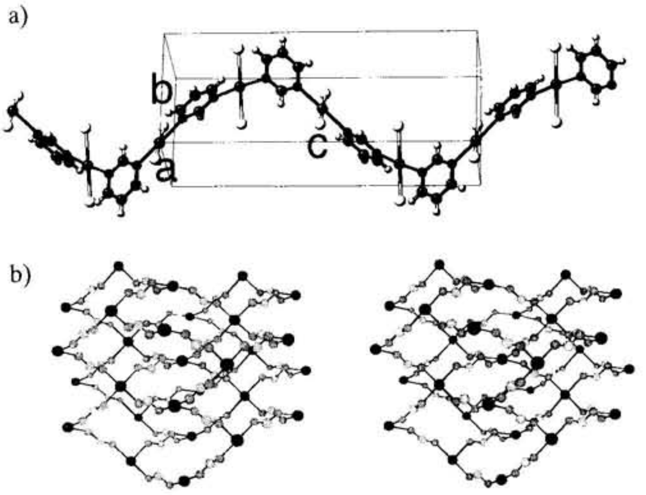


Figure 1. a) $CoPMBr_2$ moieties in **1** related by a 4_3 symmetry operation along the *c* axis. PM bridges among the chains are omitted for the sake of clarity. b) Stereo-view of the three-dimensional network of Co ions (solid circles) and N-C=N moieties (shaded circles).

The PM rings omitted in Figure 1a also bridge the Co ions among the helixes to build a close three-dimensional network. Figure 1b shows the Co ions and N-C=N moieties in the crystal of **1**. They form a chiral macrocyclic motif $(N\text{-}C\text{=}N\text{-}Co\text{-})_6$, and, therefore, the Co ions are connected like a distorted diamond structure by PM bridges. The nearest neighboring Co···Co distances are 6.2506(4) and 6.213(1) Å for **1** and **2**, respectively.

The $1/\chi_p$ vs. T plot of **1** was drawn from the magnetic susceptibility measured at 0.5 T over a temperature range 1.8 - 300 K. The data above 20 K was analyzed with a Curie-Weiss expression $[\chi_p = C/(T-\theta)]$ to give $C = 4.01$ cm^3 K mol^{-1} and $\theta = -27$ K. The Curie constant (C) suggests $S = 3/2$ and $g = 2.92$. Similar measurement and analysis for **2** gave $C = 3.59$ cm^3 K mol^{-1}, $\theta = -17$ K, and $g = 2.77$. Below about 20 K the magnetic susceptibilities for both complexes deviated from the Curie-Weiss behavior, and the effective magnetic moment (or the product χ_pT) increased with decreasing temperature.

The magnetic phase transition of **1** was found at 5 K. As Figure 2a shows, the field-cooled magnetization (FCM) of **1**, measured at an applied field of 3 Oe, started to diverge at around 5 K. The remnant magnetization (RM), measured on heating after the FCM measurement, gradually decreased and turned negative at 4.7 K. The origin of this critical behavior is not clear at present. The RM disappeared at 5 K. The zero-field-cooled magnetization (ZFCM), measured on heating at an applied field of 3 Oe, showed a maximum at 4.7 K and coincided with FCM at above 4.7 K.

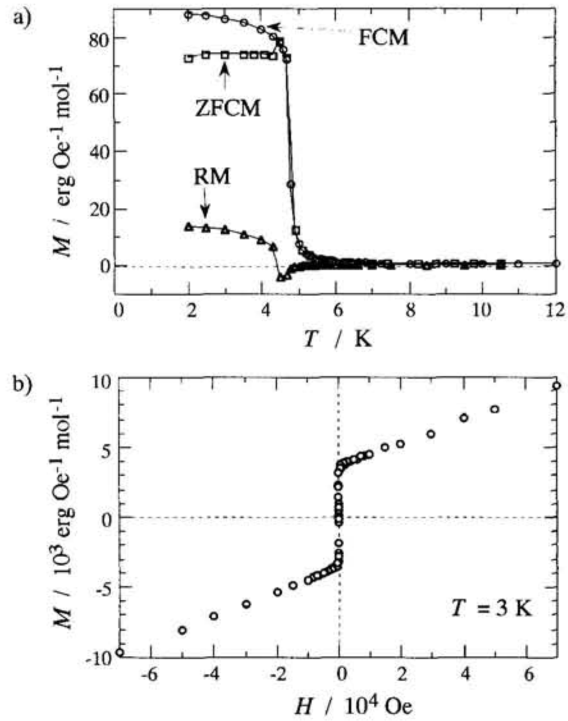


Figure 2. a) Temperature dependence of the field-cooled magnetization (FCM, circles) measured at an applied magnetic field of 3 Oe, the remnant magnetization (RM, triangles) measured after the field-cooling, and the zero-field cooled magnetization (ZFCM, squares) at an applied field of 3 Oe for **1**. b) Magnetization curve of **1** measured at 3.0 K.

In order to determine the nature of the phase transition, the magnetization curve of **1** was measured at 3.0 K below the transition temperature (Figure 2b). A hysteresis loop was observed with a small coercive field of 15 Oe, indicating that the specimen has a very soft character. The magnetization varied linearly up to the maximum field strength studied (7 T), owing to rather strong antiferromagnetic interaction. The spontaneous magnetization extrapolated to H → 0 (M_S) was 3700 erg Oe^{-1} mol^{-1}, which is only 15% of the theoretical value (24500 erg Oe^{-1} mol^{-1}). This behavior is typical of a weak ferromagnet.

The magnetism of **2** was quite similar to that of **1**. The phase transition temperature of **2**, defined by the upsurge of FCM, was also 5 K in spite of a slight difference in the cell parameters. The ZFCM had a maximum at 4.5 K. The coersive field of **2** was also 15 Oe at 3.0 K. The M_S was 3800 erg Oe^{-1} mol^{-1}, which is 16% of the theoretical value.

The nitrogen lone-pairs in PM are coordinated to the equatorial site in Co(II). In our previous works on polymeric PM-Cu(II) complexes in which all of the PM-nitrogen atoms are equatorially coordinated,[10] we found that the Cu(II) spins were antiferromagnetically coupled in contrast to our initial expectation.[8] This coupling could be explained in terms of an orbital overlap between a PM molecular orbital contributed by two nitrogen lone-pairs and Cu(II) magnetic $d_{x^2-y^2}$ orbitals on both sides in the PM ring. The PM ring in **1** and **2** is supposed to play the role of an antiferromagnetic coupler, because of the similar orbital overlap between the nitrogen lone-pair and Co(II) $d_{x^2-y^2}$ orbitals. Actually, the negative Weiss temperatures (θ's) and the magnetization curves indicate that the Co(II) spins are antiferromagnetically correlated. However, the spins become not completely antiparallel. Dzjaloshinsky-Moriya antisymmetric exchange interaction may occur in the chiral crystals,[14,15] giving rise to spin canting. The cant angles of **1** and **2** are estimated to be 9° at 3.0 K, assuming that the M_S's are attributed to the residual moment from the spin canting.[16]

In conclusion, the three-dimensional network was easily obtained by use of bidentate PM ligands. The weak ferromagnetism observed in **1** and **2** is due to the asymmetry of the crystals and also due to the relatively strong antiferromagnetic coupling through the unsaturated π-system in pyrimidine.

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11 Elemental Analysis (C, H, N) and IR spectra of **1** and **2** satisfied the chemical formula. Mps. >220°C (dec).

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13 The crystallographic data are as follows. **1**: tetragonal, $I4_122$, a = 7.576(1), c = 19.889(2) Å, V = 1141.4(2) Å^3, Z = 4, D_{calc} = 2.205 g cm^{-3}, $R(F)$ = 0.044, and $R_w(F^2)$ = 0.119 for 348 reflections [$I > 2\sigma(I)$]. **2**: tetragonal, $I4_322$, a = 7.419(1) , c = 19.938(5) Å, V = 1097.3(4) Å^3, Z = 4, D_{calc} = 1.756 g cm^{-3}, $R(F)$ = 0.027, and $R_w(F^2)$ = 0.062 for 370 reflections [$I > 2\sigma(I)$]. The refinements were performed with all 420 and 408 independent reflections in $\sin\theta/\lambda < 0.65$ for **1** and **2**, respectively. The enantiomorph of the crystals was determined by anomalous scattering of MoK_α radiation.

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16 The magnitude of M_S of weak ferromagnets is usually very small (typically 10^{-2} - 10^{-3} of the nominal value for d-spin species). Since the Dzjaloshinsky-Moriya interaction can be drawn as $D \cdot (S_i \times S_j)$ where the constant vector D is approximately proportional to $(\Delta g/g)J$,[15] the relatively large M_S's in the present study may be caused by the large superexchange interaction J through the PM bridge, as well as by the spin-orbit coupling of Co(II) spins (indicated by the large deviations of the g values from 2).