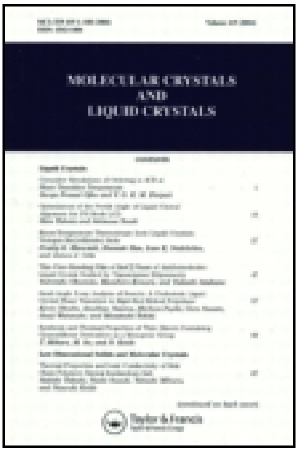

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Radical-Copper Macrocycles and Related Compounds

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Radical-Copper Macrocycles and Related Compounds

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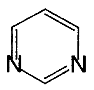
4-Pyrimidinyl nitronyl nitroxide (4PMNN) was synthesized and characterized, and four 4PMNN-metal(II) chloride complexes were investigated. Hexanuclear macrocyclic $[CuCl_2{\bullet}(4PMNN)]_6$ shows intermolecular ferromagnetic interaction. $MnCl_2{\bullet}(4PMNN)$ exhibits antiferromagnetic interaction. Mononuclear $CoCl_2{\bullet}(4PMNN)_2$ shows ferrimagnetic phase transition at ca. 3 K. $NiCl_2{\bullet}(4PMNN)_2$ are practically diamagnetic below 100 K.

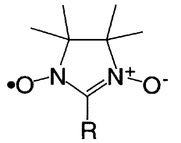
Keywords: X-ray diffraction, magnetic phase transition, pyrimidine, radical, nitronyl nitroxide

INTRODUCTION

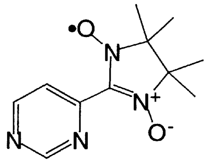
The metal-radical approach has been successful to design ferrimagnetic compounds that show magnetic order at low temperatures [1]. We have reported the magnetism of pyrimidine-bridged transition metal complexes [2,3,4] in connection with the organic high-spin *m*-phenylene-bridged poly-carbenes and -radicals [5]. In the course of our study on the role of radical-substituted pyrimidine as ferro- and antiferromagnetic couplers across the μ-1,3-NCN bridges, we have found that hexanuclear arrays $[(4PMNN){\bullet}CuX_2]_6$ (**1**: X = Br, **2**: X = Cl; 4PMNN = 4-pyrimidinyl nitronyl nitroxide) exhibited ferromagnetic intermolecular interactions [6]. We report here the magnetic properties of 4PMNN-MCl_2 complexes (M = Mn, Co, Ni) together with that of the 4PMNN ligand itself.



pyrimidine
(PM)



R-nitronyl nitroxide
(RNN)



4PMNN

EXPERIMENTAL

4-pyrimidinecarboxaldehyde was prepared according to the method previously reported [7] by using *N,N*-dimethylformamide diethyl acetal and pyruvic aldehyde dimethyl acetal as starting materials. The formyl group was converted to a nitronyl nitroxide group by Ullman's method [8], giving blue plates of 4PMNN in 76% yield from the aldehyde (mp. 128-131 °C, recrystallized from ether-hexane). Anal. Found: C, 56.64; H, 6.48; N, 23.63%. Calc.: C, 56.16; H, 6.43; 23.82%. MS (EI, 70 eV) *m/z* 236 (68%, MH^+), 106 (100%). ESR (benzene, room temperature) g = 2.0065, a_N = 7.1 G (quintet).

The typical procedure of complexation is as follows. A methanol solution (10 ml) containing 34 mg of 4PMNN and 35 mg of $CuBr_2$ was allowed to stand at room temperature for a week. Dark green needles (18 mg) of $CuCl_2$•(4PMNN) were precipitated and collected on a filter, which are suitable for magnetic studies. The composition was determined by means of elemental analysis (C, H, N).

X-Ray diffraction data were collected on a Rigaku Raxis-Rapid IP diffractometer with monochromated Mo$K\alpha$ and Cu$K\alpha$ radiations. Structures were solved by direct methods and the atomic positions were refined by full-matrix least-squares methods using all of the reflections. Magnetic properties were measured on Quantum Design MPMS SQUID and PPMS ac/dc magnetometers equipped with 7 and 9 T superconducting magnets, respectively. Diamagnetic contribution of the sample itself was estimated from Pascal's constants.

RESULTS AND DISCUSSION

4PMNN

X-Ray crystal structure analysis of 4PMNN [9] indicates that there are 8 molecules in a unit cell, only two molecules of which are shown in Figure 1 for the sake of clarity. The dotted lines represent intermolecular contacts within the sum of the van der Waals radii; 3.23 Å for O···C_{6PM} and 3.29 Å for O···N_{1PM}.

Figure 2 shows the temperature dependences of the product $\chi_{mol}T$ and $1/\chi_{mol}$. The $\chi_{mol}T$ value at 100 K was 0.38 cm^3 K mol^{-1}, clearly indicating the purity of the specimen. The Weiss temperature was -1.6 K. Semi-empirical UHF/PM3 calculation [10] on 4PMNN with the determined atomic coordinates suggests that spin polarization takes place along the conjugated skeleton, and the spin density of C_{6PM} is slightly positive. According to the McConnell theory [11], the O···C_{6PM} contact gives rise to intermolecular antiferromagnetic interaction.

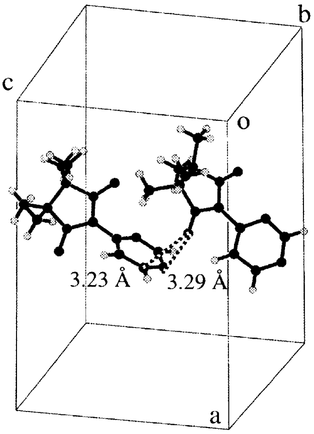


FIGURE 1 Crystal structure of 4PMNN.

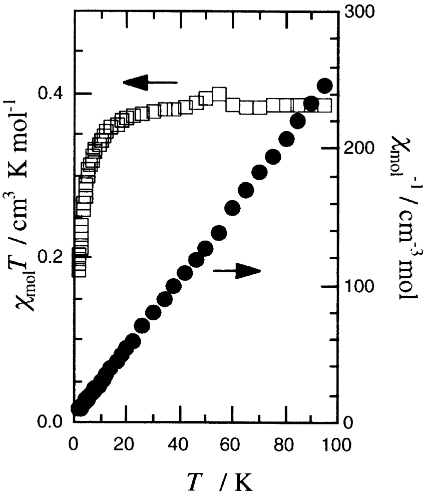


FIGURE 2 Temperature dependences of $\chi_{mol}T$ and $1/\chi_{mol}$ for 4PMNN.

MCl_2•(4PMNN)

There are two types of ligand/metal ratios (1:1 and 2:1) found in complexes obtained from 4PMNN and metal(II) chlorides. Elemental analysis revealed that the complexes obtained from 4PMNN with $MnCl_2$ and $CuCl_2$ has a ligand/metal ratio of 1:1. Figure 3 shows temperature dependence of $\chi_{mol}T$ for $MnCl_2$•(4PMNN) and $CuCl_2$•(4PMNN) measured at 5 kOe. The $\chi_{mol}T$ value of the former monotonically decreases with a decrease of temperature and almost obeys the Curie-Weiss law with the constants of 3.59 cm^3 K mol^{-1} and -14 K. On the other hand, the $\chi_{mol}T$ value of $CuCl_2$•(4PMNN) increases with a decrease of temperature, and below 8 K the $\chi_{mol}T$ value decreases.

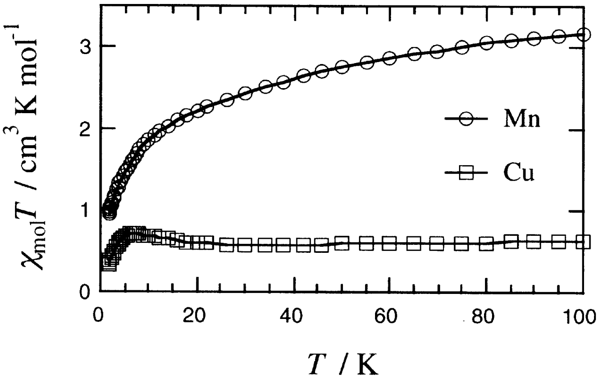


FIGURE 3 Temperature dependence of $\chi_{mol}T$ for $MnCl_2$•(4PMNN) and $CuCl_2$•(4PMNN) measured at 5 kOe. The solid lines are shown for a guide to the eye.

The crystal structure of $CuCl_2$•(4PMNN) was determined (Figure 4); the molecule consists of a head-to-tail hexamer and the hexamers construct a one-dimensional columnar structure [6]. The magnetic behavior is explained by competitive intramolecular antiferromagnetic interaction and intermolecular ferromagnetic interaction [6]. This compound did not show any magnetic phase transition down to 1.8 K. Possible supramolecular control of the magnetism is proposed by means of the guest-molecule inclusion into the cavity of $CuCl_2$•(4PMNN) [12].

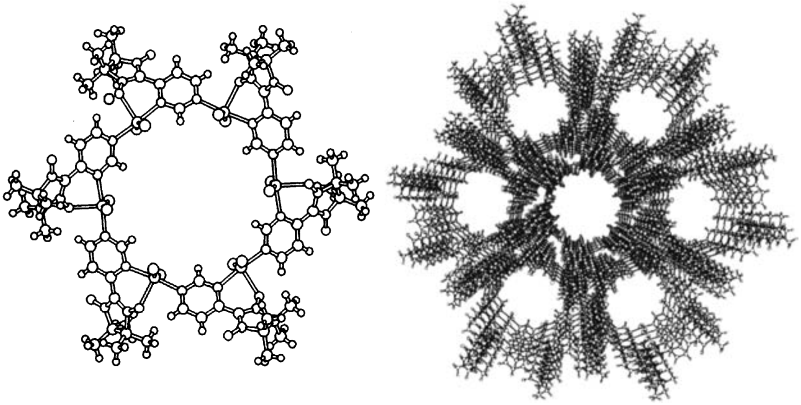


FIGURE 4 Molecular (left) and crystal structures (right) of hexameric $CuCl_2$•(4PMNN).

MCl_2•(4PMNN)$_2$

Elemental analysis revealed that the complexes obtained from 4PMNN with $CoCl_2$ and $NiCl_2$ had a ligand/metal ratio of 2:1. Figure 5 shows temperature dependence of $\chi_{mol}T$ for $CoCl_2$•(4PMNN)$_2$ and $NiCl_2$•(4PMNN)$_2$ measured at 5 kOe. The $\chi_{mol}T$ value of $NiCl_2$•(4PMNN)$_2$ was small and constant just like a diamagnetic compound, owing to fairy large antiferromagnetic interaction. There are two possible explanations: when a nickel(II) ion has a low spin state ($S_{Ni} = 0$), two 4PMNN moieties are antiferromagnetically coupled each other. It is more likely that each 4PMNN moiety correlates antiferromagnetically with a high-spin nickel(II). Crystal structure analysis of $NiCl_2$•(4PMNN)$_2$ is now underway.

On the other hand, a decrease of $\chi_{mol}T$ was found in lowering temperature for $CoCl_2$•(4PMNN)$_2$ (Figure 5). This behavior can be attributed to antiferromagnetic interaction, although the effects of the orbital angular momentum in cobalt(II) ions can not be eliminated at this stage. The $\chi_{mol}T$ value at 100 K indicates that the presence of three $S = 1/2$ spins, i.e., the cobalt(II) ion has a low spin state. A clear anomaly is found below 5 K and the $\chi_{mol}T$ curve has a peak at ca. 3 K. Figure 6 shows the magnetization curve of $CoCl_2$•(4PMNN)$_2$ measured at 1.8 K,

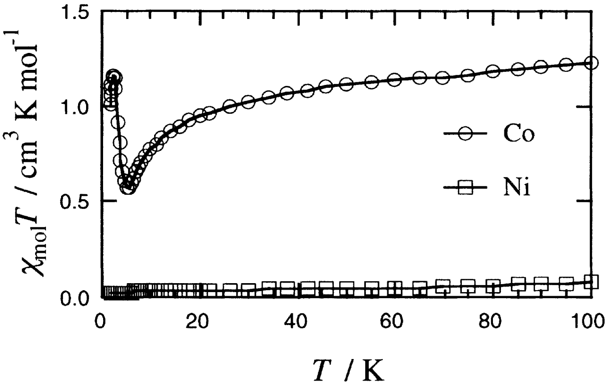


FIGURE 5 Temperature dependence of $\chi_{mol}T$ for $CoCl_2$•$(4PMNN)_2$ and $NiCl_2$•$(4PMNN)_2$ measured at 5 kOe. The solid lines are shown for a guide to the eye.

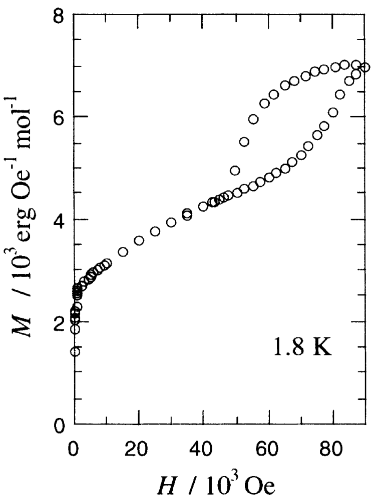


FIGURE 6 Magnetization curve of $CoCl_2$•$(4PMNN)_2$ measured at 1.8 K.

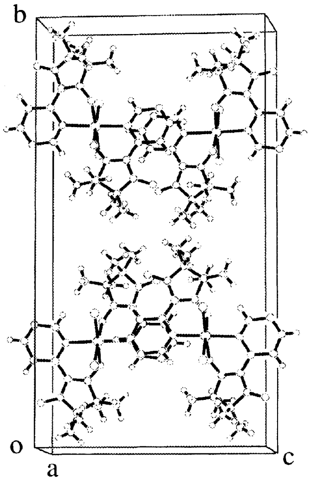


FIGURE 7 Crystal structure of $CoCl_2$•$(4PMNN)_2$.

which exhibits a spontaneous magnetization of 2.6 x 10^3 erg Oe^{-1} mol^{-1}. With an increase of the applied field, the magnetization increased and reached to ca. 5.0 x 10^3 erg Oe^{-1} mol^{-1} around 65 kOe, which is close to the theoretical saturation value of $S_{\mathrm{total}} = 1/2$. Therefore antiferromagnetic coupling is present in the three spin system. The magnetization started again to increase at ca. 65 kOe, which seems to be ferri- to ferromagnetic transition. Hysteresis behavior found in a high field region supports the ferromagnetic phase in this region.

The X-ray crystal structure analysis of $CoCl_2$•$(4PMNN)_2$ revealed that the complex consists of discrete mononuclear molecules; the N_{3PM} atom contribute a six-membered chelate but the N_{1PM} atom does not work as an N-donor (Figure 7) [13]. Intermolecular atomic contacts were found between the nitronyl nitroxide oxygen and methyl hydrogen atoms. Assuming that negative spin densities are polarized on methyl hydrogen atoms, the through-space interaction is ferromagnetic. A possible spin polarization is superposed to selected moieties of two adjacent molecules in Figure 8.

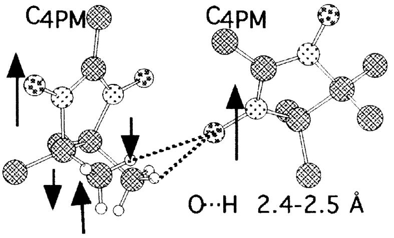


FIGURE 8 Intermolecular ferromagnetic exchange mechanism.

Similar magnetic interactions are reported on TEMPO-based ferromagnetic materials [14]. The magnetic ground state of $CoCl_2$•$(4PMNN)_2$ is schematically drawn as: $[\uparrow_{\mathrm{NN}} - \downarrow_{\mathrm{Co}} - \uparrow_{\mathrm{NN}}] \cdots [\uparrow_{\mathrm{NN}} - \downarrow_{\mathrm{Co}} - \uparrow_{\mathrm{NN}}] \cdots$, where "···" denotes intermolecular H···O interaction. These contacts are found in two directions parallel to the *ac*-plane.

SUMMARY

As the crystal structure analysis of $CuCl_2$•(4PMNN) and $CoCl_2$•$(4PMNN)_2$ clarified, they do not have polymeric structures. The intermolecular interactions are found to be ferromagnetic and the mechanisms are proposed based on the geometry of intermolecular van der Waals contacts. The mechanisms for purely organic ferromagnetic materials can be applied to molecular crystals of metal-radical complexes because the organic moieties in the periphery of the complex serve interactive sites between molecules.

Acknowledgments

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