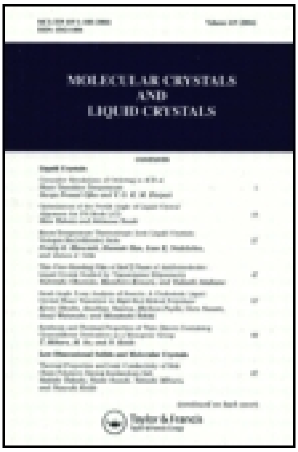

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Ferromagnetism of Pyrimidine - Bridged Copper(II) Complexes

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FERROMAGNETISM OF PYRIMIDINE - BRIDGED COPPER(II) COMPLEXES

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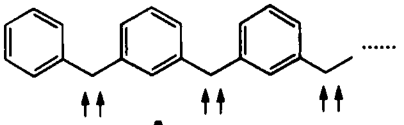
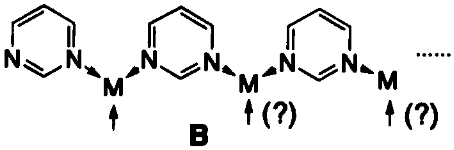
Abstract The magnetic measurements of polymeric complexes $[L{\cdot}Cu(hfac)_2]_n$, (L = pyrimidine, 4-methylpyrimidine, and quinazoline) revealed the presence of ferromagnetic interactions among the copper spins. The X-ray crystal-structure analysis of the pyrimidine and quinazoline complexes showed a copper-ligand alternating chain. The ferromagnetic transition of the quinazoline complex was observed at about 0.12 K. Pyrimidine$_2$-Cu(ClO$_4$)$_2$ complex was found to be a ferromagnet with a transition temperature of about 10 K.

INTRODUCTION

It is well-known that oligo-carbenes and -radicals linked with *m*-phenylenes have high-spin ground states (**A**).[1] However, it is not sufficiently clear whether an analogous rule holds for organic coordination compounds containing transition metals as spin sources (**B**). A few dinuclear transition-metal complexes containing pyrimidines or related compounds have been investigated.[2-5] The superexchange interactions were discussed on the basis of spin polarization mechanisms on the π systems of the heteroaromatic ligands, just like those on the *m*-phenylenes in the organic high-spin molecules.[3-5] We have recently found that the pyrimidine-bridged bis(oxovanadium) complexes are high-spin (triplet) molecules in their ground states.[5] One of them showed a ferromagnetic transition at 0.14 K, and this result was interpreted as ferromagnetic assembly of high-



A

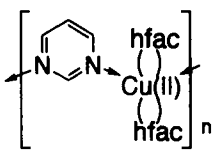


B

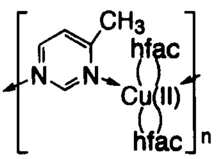
spin molecules.[5] We extended the investigation from dinuclear complexes to polynuclear complexes in which pyrimidines play a role of ferromagnetic exchange couplers. We report here the magnetic properties and crystal structures of a series of polymeric pyrimidine-bridged Cu(II) complexes, $[\mathrm{L{\cdot}Cu(hfac)_2}]_n$ (L = pyrimidine and its derivatives, hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate), and also report preliminary results on the complexes containing less bulky inorganic anions instead of hfac.

EXPERIMENTAL

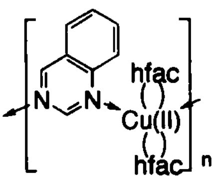
Commercially available starting materials were used without further purification. The complexes $[\mathrm{L{\cdot}Cu(hfac)_2}]_n$ (**1** - **3**) were prepared by refluxing a dichloromethane solution containing the bridging ligand [L = pyrimidine (PM), 4-methylpyrimidine (MPM), and quinazoline (QZ)] and $\mathrm{Cu(hfac)_2}$ with a 1:1 molar ratio. Addition of hexane followed by the slow evaporation of the solvent gave stable green needles. They were collected by filtration and purified by recrystallization from a dichloromethane- or chloroform-hexane mixed solvent. **1**: yield 54%, mp. 117-118°C. Anal. Calcd for $\mathrm{C_{14}H_6CuF_{12}N_2O_4}$: C, 30.15; H, 1.08; N, 5.02%. Found: C, 29.95; H, 1.08; N, 5.15%. **2**: yield 30%, mp. 106-107°C. Anal. Calcd for $\mathrm{C_{15}H_8CuF_{12}N_2O_4}$: C, 31.51; H, 1.41; N, 4.90%. Found: C, 30.95; H, 1.34; N, 4.49%. **3**: yield 85%, mp. 138-140°C. Anal. Calcd for $\mathrm{C_{18}H_8CuF_{12}N_2O_4}$: C, 35.57; H, 1.33; N, 4.61%. Found: C, 35.41; H, 1.48; N, 4.90%.



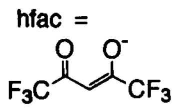
$[\mathrm{PM{\cdot}Cu(hfac)_2}]_n$ (**1**)



$[\mathrm{MPM{\cdot}Cu(hfac)_2}]_n$ (**2**)



$[\mathrm{QZ{\cdot}Cu(hfac)_2}]_n$ (**3**)



Complex $[\mathrm{PM_2{\cdot}Cu(ClO_4)_2}]_n{\cdot}2\mathrm{H_2O}$ (**4**) was obtained by dropping of an equimolar amount of pyrimidine to an ethanolic solution of $\mathrm{Cu(ClO_4)_2{\cdot}6H_2O}$. Green precipitates were collected, washed with absolute ethanol, and dried under vacuum. Anal. Calcd for $\mathrm{C_8H_{12}Cl_2CuN_4O_{10}}$: C, 20.95; H, 2.64; N, 12.21%. Found: C, 20.95; H, 2.14; N, 11.69%.

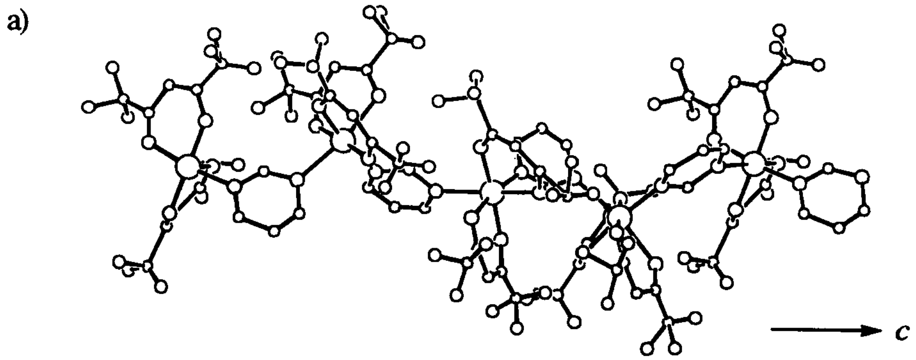
The X-ray diffraction data of **1** and **3** were recorded on a RIGAKU AFC-7R four-circle diffractometer using Mo $K\alpha$ radiation. Crystallographic data are as follows. **1**: $\mathrm{C_{14}H_6CuF_{12}N_2O_4}$, tetragonal, $I4_1cd$, $a = b = 18.598(1)$, $c = 22.331(3)$ Å, $V = 7724(1)$ Å^3, $Z = 16$, $\mu = 1.266\ \mathrm{mm^{-1}}$, $D_{\mathrm{calc}} = 1.918\ \mathrm{g\ cm^{-3}}$, $R = 0.057$, and $wR = 0.049$ for 1559 observed reflections. **3**: $C_{18}H_8CuF_{12}N_2O_4$, monoclinic, $P2_1/n$, a = 12.300(2), b = 12.123(2), c = 15.155(2) Å, β = 102.46(1)°, V = 2206.6(5) Å^3, Z = 4, μ = 1.114 mm^{-1}, D_{calc} = 1.829 g cm^{-3}, R = 0.043, and wR = 0.040 for 2937 observed reflections.

The static magnetic susceptibility was measured on an MPMS-7 SQUID magnetometer (Quantum Design) down to 1.8 K at 0.5 T. The diamagnetic contribution was estimated from Pascal's constants. The ac magnetic susceptibility of **3** was measured down to about 0.055 K at an ac magnetic field of about 35 mOe (127 Hz). The experimental details on the measurements of ac magnetic susceptibility and magnetization curves in a temperature region of a ^{3}He-^{4}He dilution refrigerator were described elsewhere.[6]

RESULTS AND DISCUSSION

Crystal Structures

Figure 1 shows the X-ray crystal structures of **1**. Each PM ligand coordinates two copper ions with the nitrogen lone pairs; the copper ions and pyrimidine rings construct an alternate linear polymer along the c axis (Figure 1a). All of the copper ions are symmetrically equivalent; the neighboring Cu···Cu distances are 6.01 Å within a chain. In spite of symmetry of PM, one nitrogen coordinates an axial position and the other an



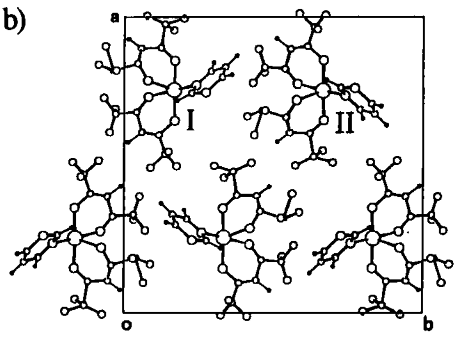


FIGURE 1 a) Alternating arrangement of copper ions and pyrimidine bridges within a chain in the crystal of **1**.

b) Crystal structure viewed along the c axis.

equatorial position. The axial bond lengths are 2.36 Å for Cu···N(1) and 2.25 Å for Cu···O(1) which are longer than the equatorial ones (1.86 - 2.12 Å). However, the octahedral structure was largely deformed, as indicated by the atomic deviations from the least-squares-plane defined by the copper ion and equatorial oxygen and nitrogen atoms; Cu: -0.04, O(2): -0.16, O(3): -0.06, O(4): 0.14, and N(2): 0.14 Å. The coordination of the axial nitrogen was canted by an angle of 5.9° from the perpendicular direction of the above plane.

Figure 1b shows the chain arrangement in the crystal of **1**. The nearest chains are located along the *b* axis (chains I and II in Figure 1b) with the shortest Cu···Cu distance of 9.30 Å.

In the crystal of **3**, the copper ions and QZ rings similarly construct an alternate linear polymer along the *b* axis (Figure 2a). There are two types of crystallographically independent copper ions which are located on the centers of symmetry. All of the neighboring Cu···Cu distances are 6.06 Å within a chain. The QZ molecules are arranged in a head-to-head fashion; the atomic sequence in the polymer backbone consists of repeating N(1)-Cu(1)-N(1) and N(2)-Cu(2)-N(2) units, where N(1) and N(2) denote the nitrogen atoms at 1- and 3-positions of QZ respectively. The atomic distance of N(2)-Cu(2) (2.45 Å) is longer than that of N(1)-Cu(1) (2.19 Å), probably due to the steric hindrance of the condensed benzene ring.

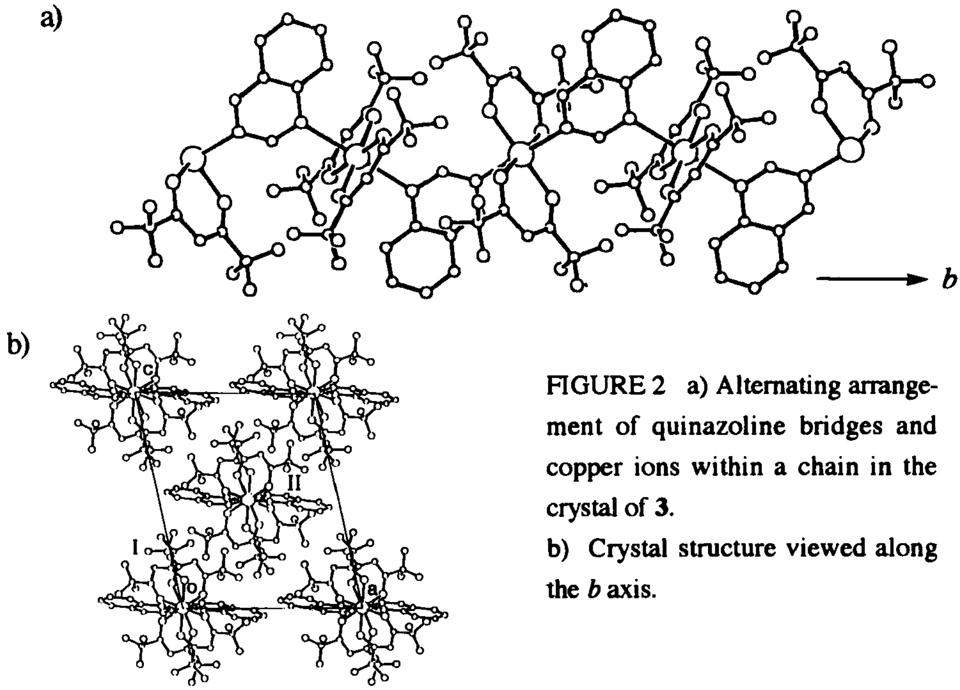


FIGURE 2 a) Alternating arrangement of quinazoline bridges and copper ions within a chain in the crystal of **3**.
b) Crystal structure viewed along the *b* axis.

The $Cu(hfac)_2$ moieties are almost coplanar with maximum atomic deviations of 0.11 Å for Cu(1) and 0.02 Å for Cu(2) from the least-squares-planes defined by the corresponding doubly chelating $Cu(O_2C_3)_2$ atoms. The $Cu(hfac)_2$ planes are mutually tilted by an angle of 104.3° in a chain. Both QZ nitrogen atoms are located at the axial positions to $Cu(hfac)_2$ planes. The Cu-O bond lengths are 2.00 and 2.07 Å for Cu(1) and 1.96 and 1.97 Å for Cu(2), which are shorter than Cu-N bond lengths for both cases. The coordination of the pyrimidine nitrogens were canted by angles of 11.3° for N(1) and 2.0° for N(2) from the perpendicular directions of the averaged $Cu(hfac)_2$ planes.

Figure 2b shows the chain arrangement in the crystal of **3**. The nearest chains are located along the *ac* diagonal direction (chains I and II in Figure 2b) with the shortest Cu···Cu distances of 8.67 Å.

For both crystal structures of **1** and **3**, the inter-chain Cu···Cu distances are much longer than the intra-chain Cu···Cu distance. No appreciable overlap was observed among the π-orbitals of the heteroaromatic rings or hfac chelating ligands and no atomic distances within the sum of van der Waals radii in any inter-chain directions. Thus, these structures can be regarded as quasi-one-dimensional systems.

Magnetic Properties

Figure 3 shows the temperature dependences of the effective magnetic moments of **1** - **3**. The increases of the effective magnetic moments (μ_{eff}) with decreasing temperature indicate the presence of the ferromagnetic interactions.

In the case of **1**, with decreasing temperature the moment reached to a maximum 2.08 μ_B at 2.2 K and then decreased in the lower temperature region, probably owing to the presence of relatively weak antiferromagnetic interaction. Based on a 1-dimensional Heisenberg ferromagnetic chain, the exchange parameter J between the neighboring copper ions can be estimated from the best fit to the Padé series expansion (eq.1).[7] We obtained $J / k_B = 0.30$ K and $g = 2.27$ from the data of **1** in 2.2 - 10 K. The calculated curve reproduces well the experimental data in this temperature region. The weak antiferromagnetic interaction found below 2.2 K is ascribable to inter-chain exchange interaction.

$$\chi_{dc} = (Ng^2\mu_B{}^2/4k_BT)\,[\,(\,1.0 + 5.7979916x + 16.902653x^2 + 29.376885x^3 + 29.832959x^4 + 14{,}036918x^5\,)\,/\,(\,1.0 + 2.7979916x + 7.0086780x^2 + 8.6538644x^3 + 4.5743114x^4\,)\,]^{2/3} \qquad \text{with } x = J/2k_BT \tag{1}$$

The effective magnetic moment of **2** continued to increase with decreasing temperature down to 1.8 K. The analysis of the data by eq.1 gave $J / k_B = 0.33$ K and $g =$

2.25. The calculated curve is well fitted to the experimental data; however, the experimental data slightly deviated downward from the calculated curve below about 2 K, probably due to the presence of very weak antiferromagnetic interaction.

The increasing tendency of the effective moment of **3** was most significant in the three complexes. Although the g value in a high temperature region is similar to those of the above two complexes (the calculation based on non-interacting S = 1/2 species gave g = 2.24 at 100 K), with decreasing temperature the moment very gradually decreases down to about 8 K. This finding can hardly be explained so far, but some structural deformation around copper ion may occur, resulting the variation of the g value. The

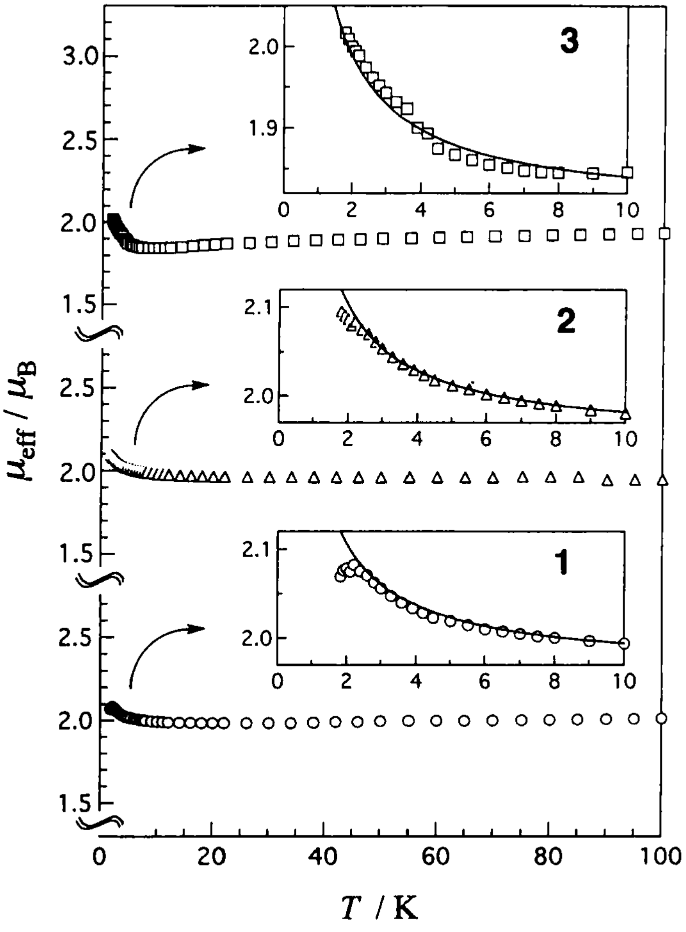


FIGURE 3 Temperature dependences of the effective magnetic moments of **1** - **3**. Insets: magnifications of a temperature region below 10 K. The solid curves represent the best fits to the Padé series expansion (see the text).

moment below 8 K increased with decreasing temperature, indicating the presence of predominant ferromagnetic interaction. The calculated curve with the best fit parameters $J / k_B = 0.45$ K and $g = 2.08$ almost reproduces the experimental data. The effective moment reached 2.02 μ_B at 1.8 K and seems to continue increasing below 1.8 K.

We extended the magnetic measurement of **3** to a temperature region of a ^{3}He-^{4}He dilution refrigerator. Figure 4a shows the temperature dependence of the ac magnetic susceptibility, χ_{ac}. Although neither saturation nor peak of the signal was confirmed in the temperature range of the present experiment, we observed an upsurge of χ_{ac} below about 0.12 K which we define the magnetic phase transition temperature (T_C). In order to elucidate the nature of the magnetic phase transition of **3**, we measured *M-H* curves below and above T_C. As Fig. 4b shows, a typical S-shaped ferromagnetic *M-H* curve was obtained at 43 mK (below T_C) with a small hysteresis, while a linear paramagnetic feature was observed at 512 mK (above T_C). These facts demonstrate that the specimen is a bulk ferromagnet in which the high-spin polymer chains are correlated ferromagnetically.

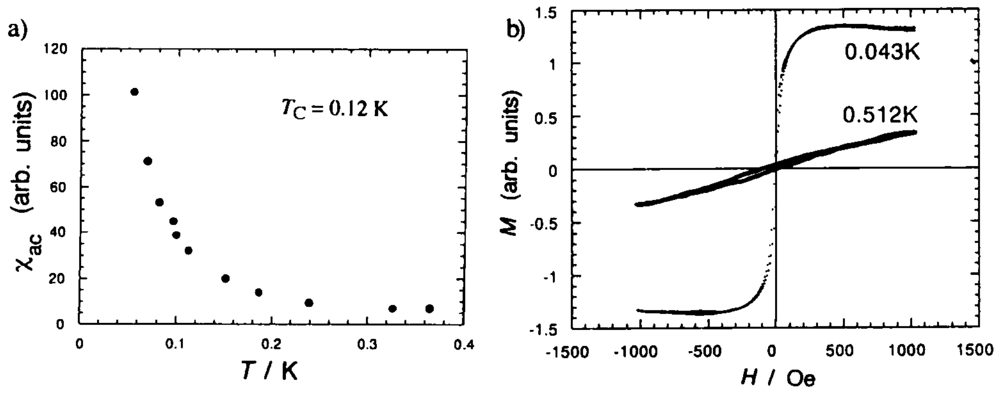


FIGURE 4 a) Temperature dependence of the ac magnetic susceptibility of **3** below 0.4 K, showing the ferromagnetic transition at 0.12 K (T_C). b) The *M-H* curves measured at 43 mK (below T_C) and at 512 mK (above T_C).

The hfac ligands are sterically bulky, causing inter-chain distances long. Thus, through-space inter-chain interactions are much weaker than the intra-chain ones. The weak interactions are responsible for the low T_C (0.12 K) of **3**.

In order to bestow strong inter-chain interaction in our system, less bulky inorganic anions were planned to be introduced. The magnetic properties were measured on powdery samples of $(PM)_n[CuX_2]$ ($X = Cl^-$, Br^-, NO_3^-, ClO_4^- etc.). Elemental analysis revealed that some complexes contained more than one pyrimidine molecules in a composition formula, suggesting the presence of more than one dimensional networks of copper ions. Among them, $(PM)_2[Cu(ClO_4)_2]\cdot 2H_2O$ (**4**) showed a ferromagnetic transition at about 10 K, which was confirmed by the measurements of field-cooled magnetization (FCM) and remnant magnetization (RM) (Figure 5a). The FCM gradually increased below 16 K with decreasing temperature and the slope, $-dM/dT$, had a maximum at about 7.4 K. The RM monotonously decreased on warming from 4.5 K and completely disappeared at 12 K. The hysteresis curve of **4** was obtained at 4.5 K (below T_C) with a coersive field of about 50 G (Figure 5b). The magnetization at 1000 Oe seems to be saturated to about 700 erg Oe^{-1} mol^{-1}, which is only 12% of the theoretical value (about 6000 erg Oe^{-1} mol^{-1}). The investigations of the detailed magnetic phenomena and crystal structures are now underway.

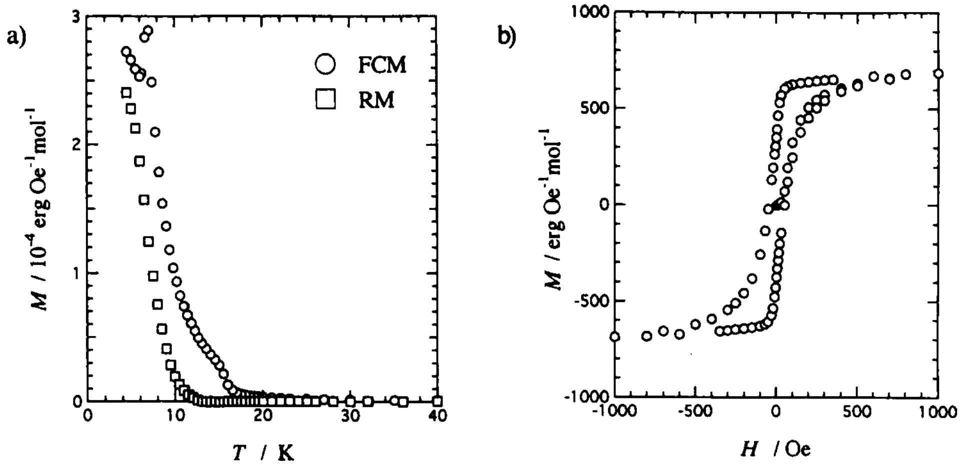


FIGURE 5 a) Field-cooled magnetization (FCM) and remnant magnetization (RM) of **4**. FCM was recorded in an external field of 3 Oe. b) Hysteresis curve recorded at 4.5 K.

Mechanism

The predominant ferromagnetic interaction of **1** - **3** must be ascribable to intra-chain interaction. The pyrimidine rings were concluded to work as ferromagnetic exchange couplers. On the other hand, it was reported that the isomeric pyrazine ring played a role of antiferromagnetic couplers in $[PZ\cdot Cu(hfac)_2]_n$[8] and $[PZ\cdot Cu(NO_3)_2]_n$[9] (PZ = pyrazine). The spin polarization rules analogous to organic π-electron systems described as **A** seem to hold for **1** - **3**.

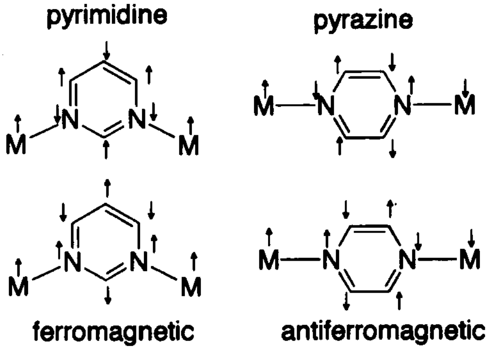
The crystallographic analysis revealed that the magnetic orbital of the copper(II) ion was ascribed to $d_{x^2-y^2}$ on the equatorial plane. When the nitrogen coordinates at equatorial sites, the direct magnetic interaction can be expected between the $d_{x^2-y^2}$ and nitrogen lone pair. Inoue *et al.* reasonably presented some mechanisms for the spin delocalization from copper(II) ions to ligand molecules in $[PZ\cdot Cu(NO_3)_2]_n$ and its derivatives,[9] in which pyrazine nitrogens coordinate to copper ions at equatorial sites. However, in the case of the axial coordinations, the pyrimidine nitrogens coordinate to fully occupied d_{z^2} orbital sites. Possible mechanisms of the spin polarization are proposed as follows: 1) interaction through a π-type overlap between spin-polarized $d_{yz}(Cu)$ - or $d_{xz}(Cu)$ - $p\pi(N)$ orbitals, and 2) interaction through direct overlap between $d_{x^2-y^2}(Cu)$ and $p\pi(N)$ orbitals.

1) Theoretical consideration on a spin-orbit coupling tells us that the α spin in the $d_{x^2-y^2}$ orbital induces β spin in d_{yz} and d_{xz} orbitals.[10] Since the d_{yz} and d_{xz} orbitals overlap with nitrogen π-orbitals, α spin is assumed to be induced on the nitrogen $p\pi$-orbitals.

2) In the present systems the angle between the axial bond and the equatorial plane is deviated from 90° (especially in the crystal of **1**, the octahedral structure was largely distorted). The overlap between the $d_{x^2-y^2}$ orbital and the π-orbital on the axial ligand was discussed in connection with Cu···O-N angles for the copper(II)-nitroxide complex.[11] Their computational analysis showed the non-zero overlaps for the coordination from a canted direction.[11] This direct overlap may induce β spin on the nitrogen $p\pi$-orbital. The nitrogen $n\sigma$-orbital also seems to have an overlap with the copper $d_{x^2-y^2}$ orbital and to result in similar polarization *via* the nitrogen lone pair.

Although the above mechanisms 1) and 2) suggest opposite spin polarizations on the nitrogen $p\pi$-orbitals, both of them cause the ferromagnetic coupling among the copper spins. These mechanisms lead to the conclusion that the magnetic couplings through the coordinations of 1,3- and 1,4-positions must be ferro- and antiferro-magnetic, respectively, from the topological point of view (Scheme 1).

SCHEME 1



SUMMARY

The polynuclear copper(II) complexes were designed on the analogy of organic high-spin materials such as poly-*m*-phenylene-carbenes or -radicals, and the ferromagnetic interactions were realized in the present systems. The ferromagnet **3** is an example of ferromagnetic assembly of ground high-spin polymers. Compounds **3** and **4** are new members of molecular-based ferromagnets containing single spin species.

ACKNOWLEDGEMENT

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REFERENCES

1. N. Mataga, Theor. Chim. Acta, 10, 372 (1967); A. A. Ovchinnikov, ibid., 47, 297 (1978). H. Iwamura, Adv. Phys. Org. Chem., 26, 179 (1990).
2. D. R. Corbin, L. C. Francesconi, D. N. Hendrickson, and G. D. Stucky, Inorg. Chem., 18, 3069, 3074 (1979).
3. H. Oshio and H. Ichida, J. Phys. Chem., 99, 3294 (1995); H. Oshio, J. Chem. Soc., Chem. Commun., 240 (1991).
4. T. Ishida, S.-i. Mitsubori, T. Nogami, and H. Iwamura, Mol. Cryst. Liq. Cryst., 233, 345 (1993); T. Ishida, S.-i. Mitsubori, T. Nogami, Y. Ishikawa, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda, and M. Ishikawa, Synth. Met. (Proceedings of International Conference on Science and Technology of Synthetic Metals '94), 71, 1791 (1995).
5. S.-i. Mitsubori, T. Ishida, T. Nogami, and H. Iwamura, Chem. Lett., 285 (1994); S.-i. Mitsubori, T. Ishida, T. Nogami, H. Iwamura, N. Takeda, and M. Ishikawa, Chem. Lett., 685 (1994).
6. T. Nogami, K. Tomioka, T. Ishida, H. Yoshikawa, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda, and M. Ishikawa, Chem. Lett., 29 (1994); Y. Nakazawa, M. Tamura, N. Shirakawa, D. Shiomi, M. Takahashi, M. Kinoshita, and M. Ishikawa, Phys. Rev. B, 46, 8906 (1992).
7. G. A. Baker, Jr., G. S. Rushbrooke, and H. E. Gilbert, Phys. Rev., 135A, 1272 (1964).
8. H. W. Richardson, J. R. Wasson, and W. E. Hatfield, Inorg. Chem., 16, 484 (1977).
9. H. Kuramoto, M. Inoue, S. Emori, and S. Sugiyama, Inorg. Chim. Acta, 32, 209 (1979).
10. C. J. Ballhausen, Introduction to Ligand Field Theory, McGraw Hill, Inc. (1962).
11. A. Caneschi, D. Gatteschi, A. Grand, J. Laugier, P. Rey, L. Pardi, Inorg. Chem., 27, 1031 (1988).