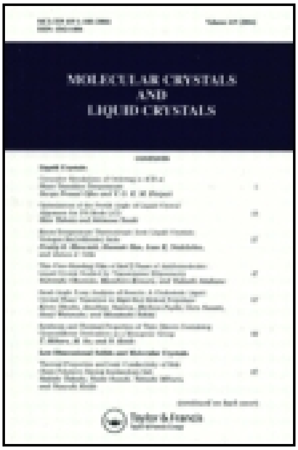

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Magnetic Properties of 4- and 5-Methylpyrimidine-Bridged Copper(II) Complexes

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MAGNETIC PROPERTIES OF 4- AND 5-METHYLPYRIMIDINE-BRIDGED COPPER(II) COMPLEXES

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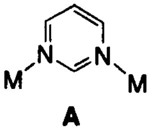
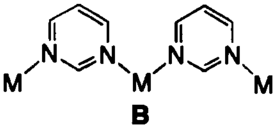
Abstract The magnetic measurements of $[L{\cdot}Cu(hfac)_2]_n$ (L = 4- and 5-MPM, MPM = methylpyrimidine) revealed the presence of ferromagnetic interactions among Cu(II) spins. However, Cu spins in di- and trinuclear complexes were proved to be paramagnetic. The crystal structures of $[4\text{-MPM}{\cdot}Cu(hfac)_2]_n$ and $(4\text{-MPM})_2{\cdot}[Cu(hfac)_2]_3$ were determined.

INTRODUCTION

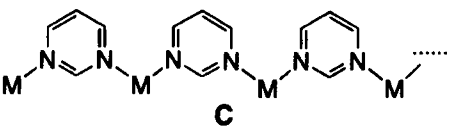
The intramolecular magnetic interactions of several dinuclear transition-metal complexes containing pyrimidines or related compounds have been investigated (for example, **A**) [1-3]. The superexchange interaction was discussed on the basis of spin polarization mechanisms on the π systems of the heteroaromatic ligands [2,3], just like those on the *m*-phenylenes in the organic high-spin poly(*m*-phenylenecarbenes) [4,5] and poly[*m*-phenylene(phenylmethyls)] [4,6]. We have investigated the magnetism of tri- and polynuclear complexes (**B**, **C**) as well as **A**, in which pyrimidine bridges may play a role of ferromagnetic exchange couplers. Polynuclear complexes $[L{\cdot}Cu(hfac)_2]_n$ (**1**) and trinuclear complexes $L_2{\cdot}[Cu(hfac)_2]_3$ (**2**) [L = 4-MPM (**a**) and 5-MPM (**b**) (MPM = methylpyrimidine), hfac = 1,1,1,5,5,5-hexafluoropentane-2,4-dionate] have been synthesized using a copper(II) ion as a spin source (S = 1/2). We report here their crystal structures and magnetic properties.



A



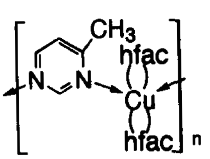
B



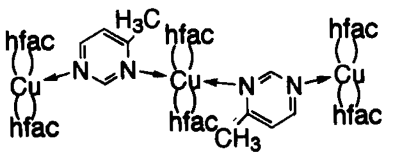
C

EXPERIMENTAL

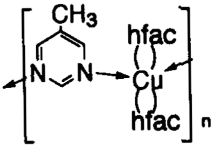
Polymer [4-MPM·Cu(hfac)$_2$]$_n$ (**1a**) was prepared according to the method previously reported [7]. Trinuclear **2a** was obtained as a by-product in recrystallization of **1a**. They were separated based on the difference of crystal shapes under a microscope. **1a**: green plates. Mp. 107-109°C (from heptane). Anal. Calcd for $C_{15}H_8CuF_{12}N_2O_4$: C, 31.51; H, 1.41; N, 4.90%. Found: C, 31.26; H, 1.48; N, 5.02%. **2a**: green needles. Mp. 129-131°C (from heptane). Anal. Calcd for $C_{40}H_{18}Cu_3F_{36}N_4O_{12}$: C, 29.64; H, 1.12; N, 3.46%. Found: C, 29.51; H, 1.28; N, 3.62%. The syntheses of **1b**, **2b**, (5-MPM)·[Cu(hfac)$_2$]$_2$ (**3b**), and (5-MPM)$_2$·Cu(hfac)$_2$ (**4b**) were described elsewhere [8]. Pyrazine(PZ)-bridged poly- and dinuclear complexes (**5** and **6**, respectively) were prepared according to the method in the literature [9].



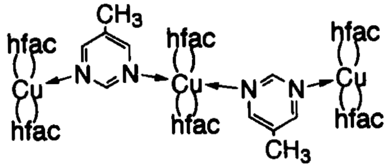
1a



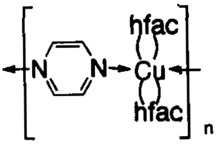
2a



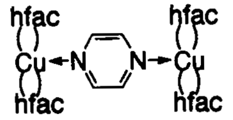
1b



2b

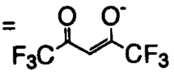


5



6

hfac$^-$ =



The X-ray diffraction data of **1a** and **2a** were recorded on a RIGAKU AFC7R four-circle diffractometer using Mo K_α radiation. The paramagnetic susceptibility was measured on an MPMS-7 SQUID magnetometer (Quantum Design) down to 1.8 K at 0.5 T. The diamagnetic and temperature-independent magnetic contributions were corrected.

RESULTS

Crystal Structures

The X-ray crystallography confirmed the poly- and trinuclear structures for **1a** and **2a** respectively (Figure 1) [10]. The 4-MPM rings and Cu(II) ions in **1a** build a head-to-tail uniform chain with 4_1 symmetry along the *c* axis. The linear structure is similar to that of [PM·Cu(hfac)$_2$]$_n$ (PM = unsubstituted pyrimidine) in spite of a different space group [7]. Since the inter-chain Cu···Cu distances are much longer (9.63, 9.88, and 10.57 Å) than the intra-chain one (6.10 Å), the crystal of **1a** can be regarded as a 1-dimensional structure. The N(1) and N(3) are located on the equatorial and axial positions respectively; Cu-N(1) and Cu-N(3) bond lengths are 2.03 and 2.62 Å respectively.

On the other hand, the 4-MPM rings in **2a** are arranged in a head-to-head fashion; an inversion center resides at the hexacoordinated Cu(II) ion. The intramolecular Cu···Cu distance is 6.17 Å. The neighboring molecules are arranged along a diagonal (1 -1 1) direction in the crystal, in which the terminal Cu(hfac)$_2$ moieties are facing each other in parallel. This intermolecular Cu···Cu distance is 5.33 Å. In other words, the Cu(hfac)$_2$ and 4-MPM moieties are arranged to form a pseudo-1-dimensional chain, where 4-MPM bridges are missing every third unit.

The crystal structure of **2b** [8] was similar to that of **2a** except for the geometry around the central Cu ion. This geometry was susceptible to the steric effect of methyl groups. Whereas N(3) in **2a** coordinates at an axial position of the central Cu ion with an N-Cu bond length of 2.48 Å, the corresponding nitrogen atom in **2b** does at an equatorial position with that of 2.23 Å. The intra- and intermolecular Cu···Cu distance in a pseudo-chain of **2b** is 5.98 and 5.89 Å respectively.

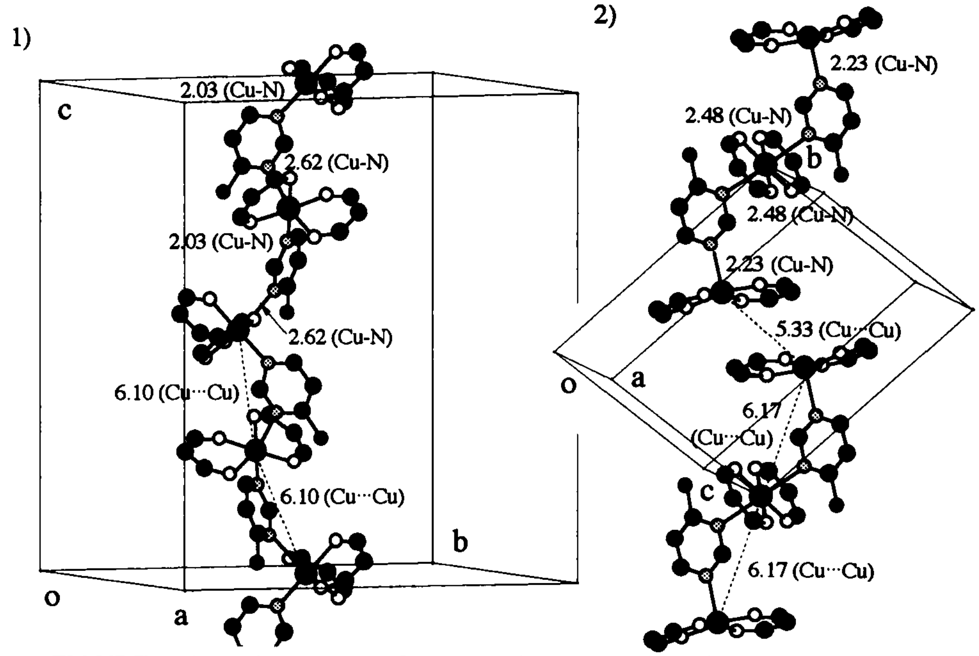


FIGURE 1 Crystal structures of **1a** (1) and **2a** (2). Selected atomic distances are shown in Å. Hydrogen atoms and trifluoromethyl groups are omitted for clarity.

Magnetic Properties

The SQUID measurements of **1a** and **1b** revealed the presence of ferromagnetic interactions between the Cu(II) spins, as indicated by the increase of the effective magnetic moment with a decrease of temperature [Figure 2 (1)].

The exchange parameter J between the neighboring Cu(II) spins can be estimated from the best fit to the Padé series expansion on the basis of a uniform 1-dimensional ferromagnetic chain [11]. We obtained $J/k_B = +0.29$ K and the Landé g factor of 2.26 from the data of **1a** in 2.2 - 10 K. The calculated curve reproduces well the experimental data in this temperature region. A similar analysis for **1b** gave $J/k_B = +0.73$ K and g = 2.14. These values are close to those of the polymers $[QZ{\cdot}Cu(hfac)_2]_n$ (QZ = quinazoline), $[PM{\cdot}Cu(hfac)_2]_n$ [7], and $[PM_2{\cdot}Cu(NO_3)_2]_n$ [12].

The magnetization curves of **1a** and **1b** were measured at 1.8 - 2.0 K. They were found to exceed the theoretical Brillouin function of S = 1/2. The data of **1a** appeared between S = 1/2 and S = 1 curves, and the data of **1b** between S = 1 and S = 3/2 ones. These findings confirm the presence of ferromagnetic interaction in the crystals of **1a** and **1b**. Thus, pyrimidine rings can be regarded as ferromagnetic exchange couplers in these polymer systems.

On the other hand, the crystals of **2a** and **2b** exhibited very weak antiferromagnetic behaviors [Figure 2 (2)]. The effective magnetic moments showed practically no temperature dependence above ca. 5 K, and they were 3.29 and 3.00 μ_B per molecule for **2a** and **2b**, respectively. These experimental values are incompatible with the spin-only value of 3.87 μ_B (g = 2) or 4.2 μ_B (g = 2.2 [13]) for quartet molecules, but reasonably interpreted as S = 1/2 paramagnetisms with g = 2.19 for **2a** and 2.00 for **2b**.

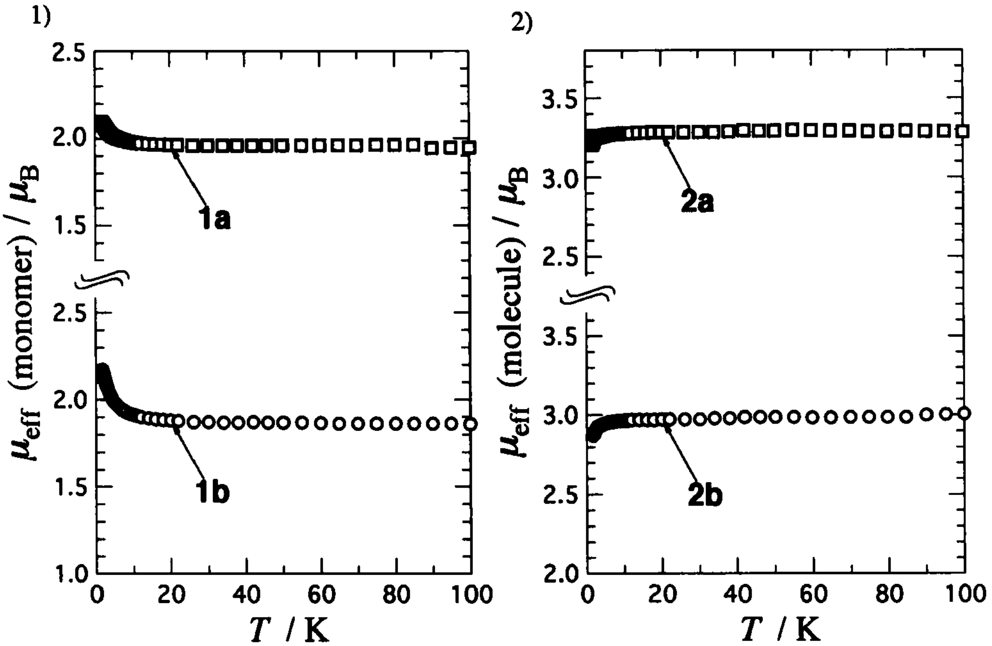


FIGURE 2. Temperature dependences of the effective magnetic moments of polymer complexes **1a** and **1b** (1) and trinuclear complexes **2a** and **2b** (2).

We also investigated the magnetic properties of dinuclear complexes. The magnetic behavior was similar; the effective magnetic moments were almost constant with temperature, and the values 2.63 μ_B for **3a** and 2.67 μ_B for **3b** indicated that the Cu(II) spins were paramagnetic with g = 2.15 and 2.18, respectively [14]. The pyrimidine bridges did not work as magnetic couplers in di- and trinuclear $Cu(hfac)_2$ complexes, unlike the case of polymers.

On the basis of our molecular design [3,7], PZ bridges are expected to be antiferromagnetic exchange couplers. Hatfield and co-workers reported that **5** obeyed the Curie-Weiss law with the Weiss constant of -0.54±0.5 K [9]. We re-examined the magnetisms of **5** and **6**. We obtained Curie and Weiss constants of 0.470 $cm^3\ K\ mol^{-1}$ and -0.06 K respectively for **5**, indicating that **5** was almost paramagnetic. The g value was determined to be 2.23 (lit. [9] g = 2.24). A similar analysis of **6** gave Curie and Weiss constants of 0.906 $cm^3\ K\ mol^{-1}$ and -0.11 K respectively (g = 2.19). Complexes **5** and **6** showed only slight antiferromagnetic behaviors below ca. 5 K.

DISCUSSION

The magnetic studies of complexes using 4-MPM and 5-MPM qualitatively gave the same results. We can conclude that ferromagnetic couplings were observed only in pyrimidine-bridged polymers. Trinuclear **2a** and **2b** are not ground quartet molecules, although the organic triradicals bridged by *m*-phenylenes were known to be ground high-spin molecules [15]. The polymer form is essential for ferromagnetic interaction.

The symmetry of the crystal and the geometry of nitrogen ligation may be important factors for magnetic properties. However, $[QZ{\cdot}Cu(hfac)_2]_n$ which exhibited ferromagnetic interaction has inversion centers at Cu(II) ions and both of the QZ nitrogens coordinate at axial positions [7] just like paramagnetic **2a**. The following explanation is plausible. The di- and trinuclear complexes include pentacoordinated Cu(II) ions. The energy levels of SOMO in $Cu(hfac)_2$ moieties are varied by the coordination of the nitrogen atoms. Superexchange interaction decreases by a possible mismatch of energy levels between SOMOs of the penta- and hexacoordinated copper ions and also between SOMO of the pentacoordinated copper ion and HOMO of the pyrimidine bridge. In the polymers, all of the SOMOs should have exactly the same energy level, and consequently parallel spin alignment is preferable by Hund's rule.

PM and PZ bridges were proved to be potential ferro- and antiferromagnetic exchange couplers respectively. The PZ-bridged Cu(II) complexes showed very weak antiferromagnetic interaction. Through-bond interactions in the PZ-bridged complexes must be small, because the copper ions are separated by one more carbon atom in comparison with those in the PM-bridged complexes.

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14. Similar μ_{eff} and g values were obtained in L·[Cu(hfac)$_2$]$_2$: L = PM, μ_{eff} = 2.71 μ_B, g = 2.21; L = 4,6-dimethyl-PM, μ_{eff} = 2.66 μ_B, g = 2.17; L = 5-bromo-PM, μ_{eff} = 2.69 μ_B, g = 2.20. S.-i. Mitsubori, T. Ishida, and T. Nogami, unpublished results.
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