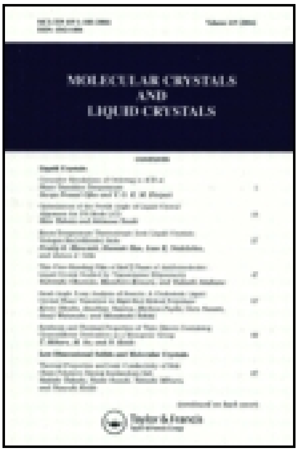

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Intramolecular Magnetic Interaction of Transition Metal ions in Complexes Containing Pyrimidine or Pyrazine as a Bridging Ligand

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INTRAMOLECULAR MAGNETIC INTERACTION OF TRANSITION METAL IONS IN COMPLEXES CONTAINING PYRIMIDINE OR PYRAZINE AS A BRIDGING LIGAND

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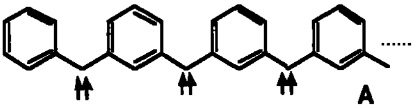
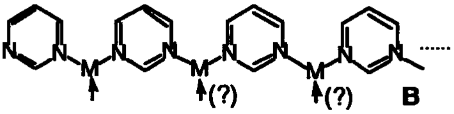
Abstract The magnetic interactions between transition metal ions bridged with 4,6-pyrimidinedicarboxylate, 4,6-dipyridylpyrimidine, 2,3-pyrazinedicarboxylate, or 2,3-dipyridylpyrazine were studied. Several dinuclear complexes containing Cu^{2+}, Ni^{2+}, Co^{2+}, or Mn^{2+} were synthesized and characterized. They were antiferromagnetically coupled in all cases.

INTRODUCTION

It is well known that oligo-carbenes or radicals linked with *m*-phenylenes have a high-spin ground state (**A**).[1] Although the spin polarization mechanism was shown to be valid for some oxygen or nitrogen perturbed systems,[2] the limitation of the application is not clear, especially for organic coordination compounds containing transition metals as spin sources (**B**). We synthesized systematically dinuclear complexes in which a pyrimidine or pyrazine ring was used as a bridging ligand and studied their magnetic properties.

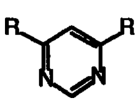




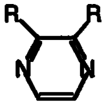
EXPERIMENTAL

4,6-Pyrimidinedicarboxylic acid (H_2PMDC)[3] and 4,6-dipyridylpyrimidine (DPPM)[4] were synthesized according to the literature methods. 2,3-Pyrazinedicarboxylic acid (H_2PZDC) and 2,3-dipyridylpyrazine (DPPZ) were purchased from Wako and Aldrich Co., Ltd. respectively. The complexes containing DPPM or DPPZ were obtained by mixing the corresponding chloroform solution of metal(II) hexafluoroacetylacetonate and that of the bridging ligand (molar ratio 2 : 1). The samples used for magnetic measurements were purified by repeated recrystallization. The complexes containing PMDC or PZDC were precipitated on mixing methanol solutions of the diacid and metal(II) acetylacetonate.

The susceptibilities of PMDC or PZDC complexes were measured on an Oxford Instruments Faraday-type magnetic balance in a field of 2 T with a field gradient of 5 T/m. Those of other complexes were measured on a Quantum Design MPMS SQUID susceptometer at 0.5 T. Their diamagnetic contribution was estimated from Pascal's constants.



PMDC R = CO_2^-
DPPM R = 2-Py

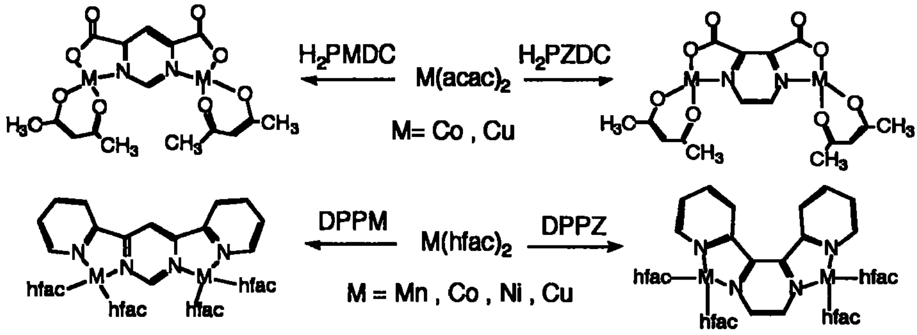


PZDC R = CO_2^-
DPPZ R = 2-Py

RESULTS AND DISCUSSION

All the complexes were easily obtained according to Scheme 1 and their yields, melting points, and elemental analyses are summarized in Table 1.

SCHEME 1



The elemental analyses of (acac)Cu(PMDC)Cu(acac) and (acac)Cu(PZDC)-Cu(acac) indicate that they contain some solvent molecules of crystallization or oligonuclear complexes as impurities. The temperature dependence of the magnetic susceptibility for the former complex shows that $\chi_g T$ decreases greatly as the temperature decreases, indicating that the two Cu spins are antiferromagnetically coupled. The latter complex shows very weak antiferromagnetic

TABLE 1 The yields, melting points, and elemental analyses of the complexes.

M	yield/%	color(shape)	mp/°C	recrys. solv.	Anal.C,H,N (calc)/%		
$(acac)_2M(PMDC)M(acac)_2$ a)							
Cu	10	greenish blue (powder)	256.2-259.7 (dec)	-b)	30.92 (39.11)	3.40 (3.28)	6.98 (5.70)
Co		pink (powder)		-b)		-c)	
$(acac)_2M(PZDC)M(acac)_2$ a)							
Cu	23	greenish yellow (powder)	256.2-259.7 (dec)	-b)	31.62 (39.11)	1.85 (3.28)	9.51 (5.70)
Co	25	pink (powder)	349.1-351.3(dec)	-b)		-c)	
$(hfac)_2M(DPPM)M(hfac)_2$ d)							
Mn	36e)	orange (needles)	263.1-264.0	C_6H_6-CH_3OH	35.45 (34.83)	1.33 (1.20)	4.26 (4.78)
Co	18	red (needles)	288.2(dec)	C_6H_6-CH_3OH	35.93 (34.60)	1.46 (1.20)	4.94 (4.75)
Ni	76	dark green (plates)	304.5-305.2 (dec)	C_6H_6-CH_3OH -CH_3COCH_3	36.29 (34.61)	1.62 (1.20)	5.01 (4.75)
Cu	20f)	green (needles)	217(dec)	C_6H_6-CH_3OH	35.57 (34.33)	1.41 (1.19)	4.63 (4.71)
$(hfac)_2M(DPPZ)M(hfac)_2$ d)							
Mn	53	orange (bricks)	158.5-160.8	$CHCl_3$-n-C_6H_{14}		-c)	
Co	60	red (needles)	220.5-222.5	$CHCl_3$-n-C_6H_{14}	34.56 (34.60)	1.35 (1.20)	5.00 (4.75)
Ni	66	dark green (bricks)	253.5-254.0	$CHCl_3$-CH_3OH	34.63 (34.61)	1.33 (1.20)	5.04 (4.75)
Cu	21	light green (powder)	80.1-82.5	C_6H_6	34.25 (34.33)	1.37 (1.19)	4.83 (4.71)

a) All the reactions were carried out in methanol at room temperature. b) Products could not be recrystallized because of their low solubility. c) Not determined yet. d) All the reactions were carried out in a refluxing chloroform-methanol mixed solvent for 1 h, unless otherwise noted. e) In chloroform-diethyl ether at room temperature. f) In chloroform at room temperature.

interaction between the two spins (Figure 1). Similar results were obtained from magnetic measurements of the dicopper complexes $(hfac)_2Cu(L)Cu(hfac)_2$ (L = DPPM and DPPZ) and the dicobalt complexes $(hfac)_2Co(L)Co(hfac)_2$ (L = DPPM and DPPZ). Kuramoto *et al.* reported[5] that the α spin was induced at a

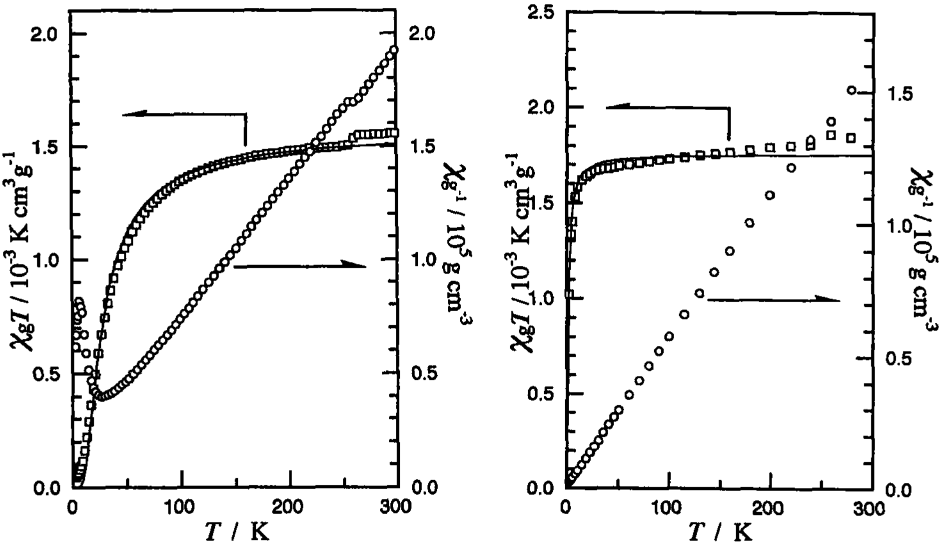


FIGURE 1 Temperature dependences of the product of the susceptibility and temperature (χ_gT) and the reciprocal susceptibility for (acac)Cu(PMDC)Cu(acac) [left] and (acac)Cu(PZDC)Cu(acac) [right]. Solid lines are the theoretical curves of the χ_gT.

coordinating nitrogen by the α spin of a copper(II) ion adjacent to it and that the spin polarization mechanism works well on pyrazine rings in an antiferromagnetic linear chain of an alternate polymeric complex pyrazine-Cu(NO_3)$_2$ as illustrated by Figure 2(A). Our results on Cu_2-pyrazine complexes are compatible with this interpretation. Oshio reported[6] that an Fe(III)$_2$-resorcinol complex exhibits ferromagnetic coupling between the two Fe ions and explained that the interaction was likewise caused by the spin polarization mechanism. However, attempts to induce ferromagnetic interactions through a bridging pyrimidine in place of pyrazine (Figure 2(B)) have been unsuccessful in our systems so far.

The temperature dependences of the effective moment for the pyrimidine complexes (hfac)$_2$M(DPPM)M(hfac)$_2$ (M = Cu, Ni, Co, and Mn) are summarized

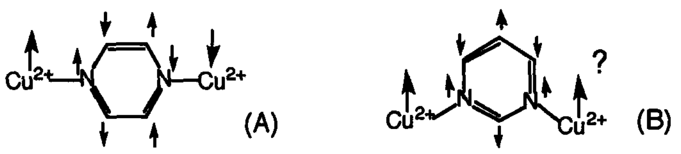


FIGURE 2 Spin polarization model for a Cu_2-pyrazine(A) or -pyrimidine(B) complex.

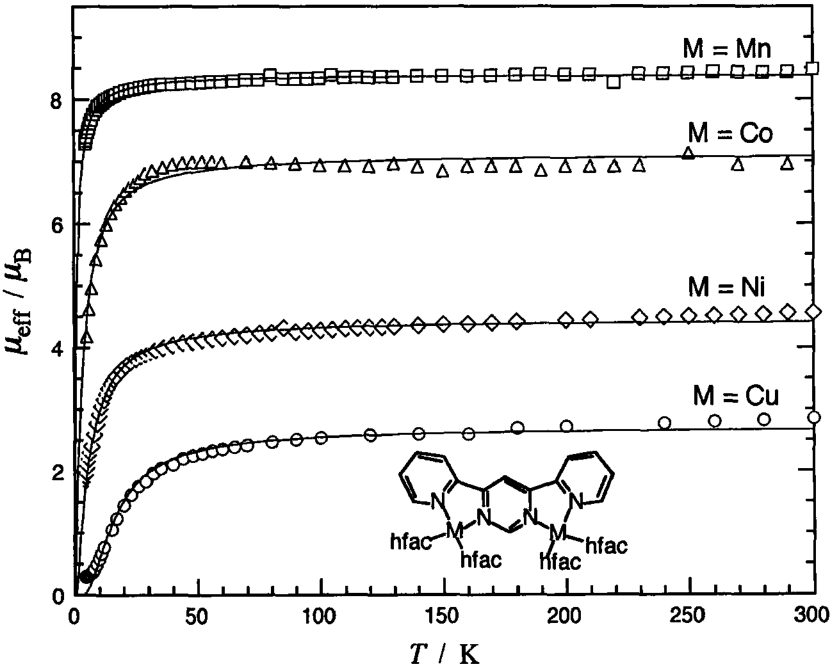


FIGURE 3 Temperature dependences of the effective moment for $(hfac)_2M$-(DMPM)$M(hfac)_2$ (M = Cu, Ni, Co, and Mn). Solid lines are the theoretical curves of the moment.

TABLE 2 Best fit parameters for (acac)Cu(L)Cu(acac) (L = PMDC and PZDC), $(hfac)_2M(DPPM)M(hfac)_2$ and $(hfac)_2M(DPPZ)M(hfac)_2$ (M = Cu, Ni, Co, and Mn).

complex	g value	J / k_B K[a]
(acac)Cu(PMDC)Cu(acac)	-[b]	-24.8
(acac)Cu(PZDC)Cu(acac)	-[b]	-1.81
$(hfac)_2Cu(DPPM)Cu(hfac)_2$	2.33	-22.9
$(hfac)_2Ni(DPPM)Ni(hfac)_2$	2.34	-4.55
$(hfac)_2Co(DPPM)Co(hfac)_2$	2.60	-1.54
$(hfac)_2Mn(DPPM)Mn(hfac)_2$	2.00	-0.20
$(hfac)_2Cu(DPPZ)Cu(hfac)_2$	2.20	-[c]
$(hfac)_2Co(DPPZ)Co(hfac)_2$	2.58	-[c]

[a] The exchange parameter J is defined by the spin Hamiltonian $-2JS_1 \cdot S_2$. [b] The g value could not be determined because of an ambiguity of the purity. [c] Very small.

in Figure 3. All the DPPM complexes investigated here showed antiferromagnetic interactions between the metal ions. Theoretical curves of the effective moment were analyzed by the Heisenberg model and the parameters in Table 2 were obtained. There were practically no intermolecular magnetic interactions, which is rationalized by the fact that the bulky hfac ligands separate neighboring molecules.

In general, the orthogonality of magnetic orbitals plays an important role in ferromagnetic coupling between spins. There are many approaches to obtain such orthogonality. For example, two different kinds of metal ions may be situated side-by-side whose magnetic orbital symmetries are different from each other. It is also possible that the geometry among the orbitals of the bridging ligands and metal ions is accidentally orthogonal and results in ferromagnetic coupling. The local geometry of the p_π - or n_σ -orbitals of the ligand and the d_π - or d_σ -orbitals of the transition metals can decide whether the interaction is ferromagnetic or antiferromagnetic. O'Connor *et al.* reported that the polymeric complex Cu(PZDC)(HCl) gave a linear ferromagnetic chain.[7] The introduction of HCl induces a change in the crystal structure which favors ferromagnetic coupling among the Cu spins. We are currently investigating the correlation between the molecular structure and the magnetic properties of the pyrimidine and pyrazine systems.

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REFERENCES

1) H. Iwamura, Adv. Phys. Org. Chem., 26, 179 (1990); N. Mataga, Theor. Chim. Acta, 10, 372 (1968).
2) T. Ishida and H. Iwamura, J. Am. Chem. Soc., 113, 4238 (1991); D. E. Seeger, P. M. Lahti, A. R. Rossi, and J. A. Berson, ibid., 108, 1251 (1986); E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo, and G. Smolinsky, ibid., 89, 5076 (1967); H. Tukada, K. Mutai, and H. Iwamura, J. Chem. Soc., Chem. Commun., 1159 (1987).
3) R. R. Hunt, J. F. W. McOmie, and E. R. Sayer, J. Chem. Soc., 525 (1959).
4) J. J. Lafferty and F. H. Case, J. Org. Chem., 32, 1591 (1967).
5) H.Kuramoto, M. Inoue, S. Emori, and S. Sugiyama, Inorg. Chim. Acta, 32, 209 (1979).
6) H. Oshio, J. Chem. Soc., Chem. Commun., 240 (1991).
7) C. J. O'Connor, C. L. Klein, R. J. Majeste, L. M. Trefonas, Inorg. Chem., 21, 64 (1982).