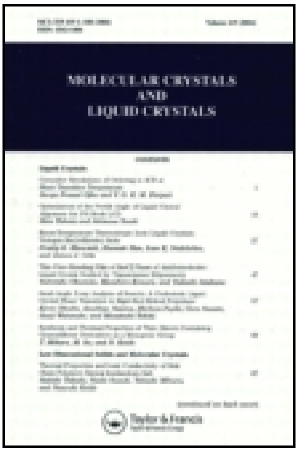

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Electron Density Distributions of Pyrimidine Bridged Cu, Fe, and Co Complexes Showing Magnetic Properties

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Electron Density Distributions of Pyrimidine-Bridged Cu, Fe, and Co Complexes Showing Magnetic Properties

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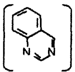
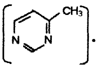
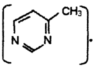
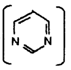
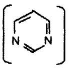
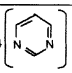
Experimental electron density distributions of $[Cu(NO_3)_2(H_2O)_2(pm)_2]$ (**1**) and $[MCl_2(pm)_2]$ (**2**:M=Co, **3**:M=Fe) (pm=pyrimidine) showing antiferromagnetic interactions were determined by the X-ray diffraction method using the multipole expansion refinement. In the crystal structures, the pyrimidine ligand bridges metal atoms to form one-dimensional chains in **1**, and three-dimensional networks in **2** and **3**. The electron populations in the d-orbitals calculated from the multipole population parameters revealed that the unpaired electrons are located in $d_{x^2-y^2}$ orbital for each complex. These results show that the strong interactions between the bridging ligand and the unpaired electrons cause the antiferromagnetic interactions mediated by the bridging ligands.

Keywords electron density distributions organomagnetic material X-ray diffraction multipole expansion method

INTRODUCTION

Organomagnetic substances are of great interest in materials science and physical chemistry. Some of the transition metal complexes containing the pyrimidine derivative as a bridging ligand showed intermolecular ferromagnetic interactions at an extremely low temperature [1, 2, 3]. Table 1 shows structural features [4, 5] and magnetic properties of these complexes. The pyrimidine derivatives were expected to mediate ferromagnetic interactions on the basis of spin polarization mechanisms on the π systems [6]. In the case of the complexes showing ferromagnetic properties, the transition atoms are bridged by the pyrimidine derivatives to form a one-dimensional chain, while the trinuclear complex showed only the paramagnetic interaction. Thus the chain structure is essential for the magnetic interaction. In the case of the antiferromagnetic complex (**1**), the pyrimidine ligand is also bridging Cu atoms to form a one-dimensional chain. Further more, the pyrimidine ligands connect metal atoms to construct the three-dimensional network structure in Co (**2**) [7] and Fe (**3**) complexes showing strong antiferromagnetic interactions. The key factor for which interactions will be mediated by the bridging ligand can be ascribed to the position of these ligands. In the complexes showing the ferromagnetic properties, at least one bridging ligand occupies an axial position, while all bridging ligands occupy the equatorial positions in the antiferromagnetic complexes. To elucidate the interactions between the ligands and the metal atoms, we carried out the analyses of electron density distributions of the complexes **1**, **2**, and **3**.

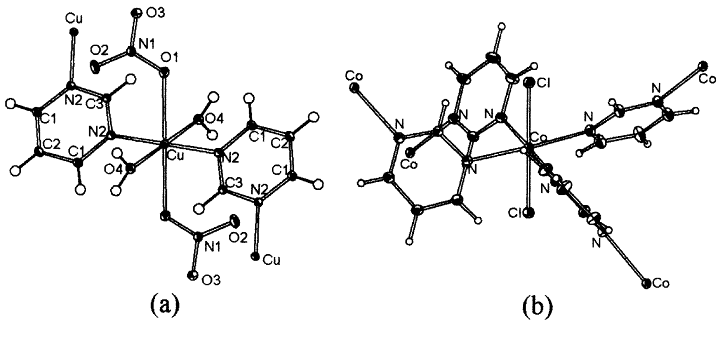
TABLE 1. Structural features and magnetic properties for Cu, Co, and Fe complexes

Compound*	 · $Cu(hfac)_2$	 · $Cu(hfac)_2$	2  · $3Cu(hfac)_2$	2  · $Cu(NO_3)_2$	 · $Cu(NO_3)_2(H_2O)_2$ **1**	4  · MCl_2 **2**:M=Co¶, **3**:M=Fe
Magnetic properties	Ferromagnet	Ferro-magnetic interaction	Para-magnetic interaction	Ferro-magnetic interaction	Antiferro-magnetic interaction	Antiferro-magnetic interaction
A feature of structure	One-dimensional polymer†	One-dimensional polymer†	Trinuclear complex†	One-dimensional polymer†	One-dimensional polymer‡	Three-dimensional polymer
Positions of bridging ligands	axial, axial	axial, equatorial	axial, axial	axial, equatorial	equatorial, equatorial	equatorial, equatorial

* hfac=1,1,1,5,5,5-hexafluoropentane-2,4-dionate
† reference 4, ‡reference 5, ¶ reference 7

EXPERIMENTAL

Crystal data: **1**: $CuC_4H_8N_4O_8$, Mw=303.68, Monoclinic, $C2/c$, a=12.232(2), b=11.472(2), c=7.485(2)Å, β=114.131(14)°, V=958.5(3)Å^3, Z=4; **2**: $CoC_8H_8Cl_2N_4$, Mw=290.01, Tetragonal, $I4_122$, a=7.3775(15), c=19.914(4) Å, V=1083.9(3) Å^3, Z=4; **3**: $FeC_8H_8Cl_2N_4$, Mw=286.93, Tetragonal, $I4_122$, a=7.3744(7), c=20.3359(12)Å, V=1105.9(2)Å^3, Z=4. Diffraction data were collected on a four-circle diffractometer at 100K with a low temperature device. The θ maximum is 60 degrees for Mo$K\alpha$ radiation. Unique reflections observed with $Io > 2\sigma(I)$ were 5893, 3693, and 3715 out of 14938, 8872, and 9050 measured reflections for **1**, **2**, and **3**, respectively. Using room-temperature results as starting atomic parameters, structures were refined by the program SHELXL-97 [8]. R-factors converged to 0.0240, 0.0236, and 0.0227 for 5893, 3693, and 3715 reflections ($Io > 2\sigma$(I)) for **1**, **2**, and **3**, respectively. Atomic positions and temperature factors for non-H atoms were refined using reflections with $\sin\theta/\lambda > 0.8$, to avoid the effect of the valence electrons on the atomic scattering factors. At this stage, R-values were 0.0284, 0.0314,and 0.0287 for 4153, 2615,and 2553 reflections for **1**, **2**, and **3**, respectively. Structure refinements were then performed using the multipole expansion method using the program MOLLY [9]. Metal and chlorine atoms were expanded to the hexadecapole level. Other non-H atoms were up to the octapole level. The refinements were reasonably converged to give R-factors of 0.0205, 0.0233, and 0.0215 for **1**, **2**, and **3**, respectively.



(a) (b)

FIGURE 1. ORTEP drawings around the metal atoms for (a) Cu complex **1**, (b) Co complex **2**. The Co and Fe complexes are isomorphous to each other.

RESULTS AND DISCUSSIONS

Figure 1 shows the molecular structures of **1** and **2**. After the multipole refinement, the overall residual densities gave satisfactorily featureless for each complex, although small peaks and holes remain especially at the central metal atoms. Figure 2 shows model-deformation maps around the central metal atoms. Lone pairs of the N and O atoms are clearly observed to direct to the Cu atom in the section of the equatorial plane in Fig. 2a. Positive peaks on the Cu atom look like to avoid these lone pair electrons. In the sections including axial ligands, positive peaks elongate toward the axial ligands (Fig. 2c). Around the Cu atom, shallow negative holes can be seen, which are adjacent to the lone pair electrons of ligated atoms (Figs. 2a~2c). Positive peaks on the Cu atoms can be assigned to the d-orbitals. Schematic representation of these peaks is shown in Fig. 3a. In the equatorial plane, there are four peaks. Upper and lower side of equatorial plane, there are two slightly diffused peaks. The model deformation densities of the Co complex (**2**) are shown in Figs 2d~2f.

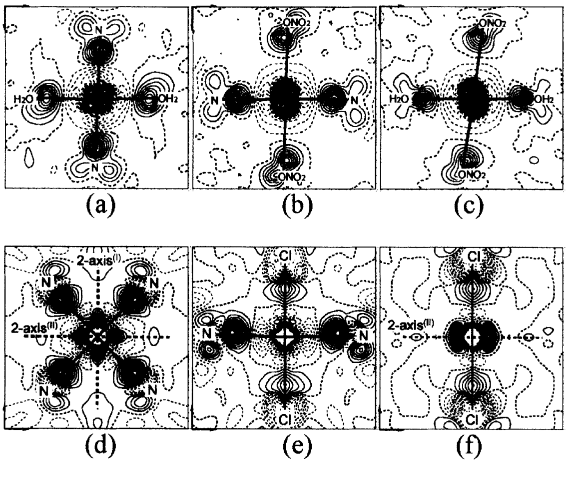
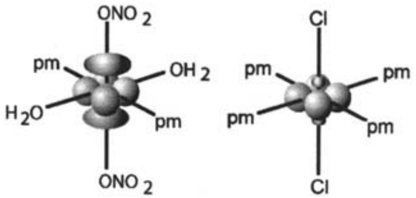


FIGURE 2. Model-deformation maps, $\Delta\rho = \rho_{[\mathrm{calc,\ multipole}]} - \rho_{[\mathrm{calc,\ spherical}]}$. (a) Section of the equatorial plane of **1**. (b) Section of the plane including axial ligands and two pyrimidines of **1**. (c) Section of the plane including axial ligands and two water molecules of **1**. (d) Section of the equatorial plane of **2**. (e) Section of the plane including two Cl and two N atoms of **2**. (f) Section of the plane including two Cl and 2-fold axis in the equatorial plane of **2**.



(a) (b)

FIGURE 3. (a), (b) :Schematic illustrations of d-orbitals for **1** and **2**, respectively.

Overall features of the Fe complex are the same with those of the Co complex. In the equatorial plane, four lone pair electrons direct toward the metal center, and positive peaks around the metal center look like to avoid the ligands (Fig. 2d). Positive peaks on the metal atoms can be illustrated as Fig. 3b. Upper and lower side of equatorial plane, there are two small peaks. Populations of the d-orbital electrons were calculated from the multipole population parameters. Although the symmetry of Cu atoms is crystallographically $\bar{1}$ in **1**, this calculation was performed on the assumption that the symmetry of the Cu atom can be regarded as 4/m in which the cross terms between the d-orbitals are neglected. The population in the dx^2-y^2 is 1.28, while others have values of 1.8 to 1.9. These values are comparable with the expected ones. The bridging ligand will interact with the dx^2-y^2 orbital which is occupied by the unpaired electron. Same calculations are performed on the Co (**2**) and Fe (**3**) complexes (table 2). The populations of b_1 and a_1 orbitals have the values of about 1 for both complexes. These values coincide with those expected for the high spin state. The b_2 and e_g, however, are far from the expected values, that is the b_2 is larger and e_g is smaller than the expected values. These differences may be ascribed to the interactions between the metal atoms and the ligands. The difference between **2** and **3** can be seen in the e_g orbital in which the

TABLE 2. Populations of d-orbital electrons.

	2			**3**		
	obs.	expected		obs.	expected	
		high	low		high	low
$b_1(dx^2-y^2)$	0.88	1	0	0.89	1	0
$a_1(dz^2)$	1.13	1	1	1.17	1	0
$b_2(dxy)$	1.66	1	2	1.67	1	2
$e_g(dxz,dyz)$	2.74	4	4	1.88	3	4
total	6.41	7	7	5.62	6	6

Co atom has larger value as much as one electron than the Fe atom. In the case of these complexes, the bridging ligand will also interact with the $d_{x^2-y^2}$ orbital which is occupied by the unpaired electron.

CONCLUSION

The unpaired electrons were determined to occupy the $d_{x^2-y^2}$ orbital which will interact with the bridging ligand, pyrimidine. The antiferromagnetic interaction is mediated by the bridging ligand which has strong interaction with the unpaired electron. The ferromagnetic interactions can be mediated by the ligand which has little interaction with the spin source.

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