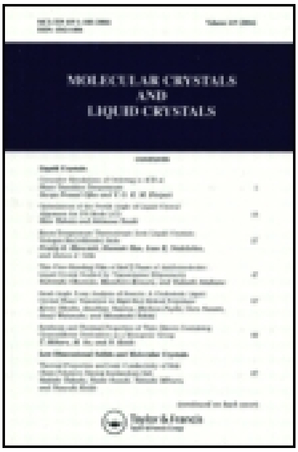

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Theoretical Studies on Magnetic Couplings of M-π Conjugated Systems via Pyrimidine Coupler

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The spin alignment rule for the magnetic couplings of d-π-d conjugated systems via pyrimidine has been proposed on the basis of the superexchange (SE) interaction and spin polarization (SP) effects in order to predict the sign of J_{ab} values between transition metal ions. This rule shows that the subtle balance of σ- and π- type SE interaction and SP effects determines the magnetic interaction of these systems.

Keywords: $M(II)_2$-pyrimidine; effective exchange interaction (J_{ab}); superexchange (SE) interaction; spin polarization (SP) effect

INTRODUCTION

Recently, many chemists have synthesized several binuclear transition metal complexes containing pyrimidine couplers.[1–4] Previously, we investigated the magnetic interactions of the simplest model complexes of d-π-d conjugated systems, i. e. M-π conjugated systems via pyrimidine as follows: $Mn(II)_2$-pyrimidine and $Cu(II)_2$-pyrimidine, by means of the UHF, UCCSD(T) and DFT such as UB2LYP, UB3LYP and UBLYP calculations, from the viewpoint of effective exchange interaction (J_{ab}), charge and spin density distributions and the shape and symmetry of natural orbitals.[5, 6] UHF showed ferromagnetic interaction between the Mn(II) ions via pyrimidine group due to overestimate of spin polarization (SP) effects. On the other hand, the J_{ab} values estimated by UBLYP and UCCSD(T) showed antiferromagnetic interactions. It was found that superexchange (SE) effect is crucial to investigate the magnetic interactions of Mn- π conjugated systems.

In this study, from these results, we have proposed the selection rule for the magnetic couplings of d-π-d conjugated systems via pyrimidine in the octahedral ligand field in order to predict the sign of J_{ab} values between transition metal ions The selection rule shows that the balance of σ- and π- type SE interaction and SP effects determines the magnetic interaction of these systems. Using *ab initio* UHF and DFT results and experimental ones for the several d-π-d conjugated systems, we have confirmed the selection rule.

SELECTION RULE FOR THE MAGNETIC COUPLINGS OF d-π-d CONJUGATED SYSTEMS VIA PYRIMIDINES

Through-bond d–d Orbital Interaction via Pyrimidine

Let us consider the through-bond interaction between transition metal ions via pyrimidine bridge. Since the two metal ions are far apart (R(M–M') ≅ 6.0 Å), the direct d–d interaction should be essentially zero. TABLE 1 summarizes the electronic configurations of transition metal ions in the octahedral ligand field. Hence, we have first considered SE interaction between two transition metal ions via pyrimidine. FIGURE 1 shows the possible d–d SE and SP interaction schemes via σ- and π-type molecular orbitals (MOs) of bridging pyrimidine. There are three different SE interactions: the first is the dσ–dσ SE interaction via σ-MO of pyrimidine, the second is the dπ–dπ SE one via π-MO, the last is the dσ–dπ SE one via π-MO. The dσ–dπ SE interaction via σ-MO of pyrimidine should be negligible because of very weak coupling between dπ-orbital and σ-MO. The charge transfer (CT) from the occupied MO of pyrimidine to the d-orbital generates the unpaired electron in the MO, which interacts with another

TABLE 1 Electronic configurations and possible states of transition metal ions

No.	d^n	Configurations	Spin states[a)]	Example
1	d^1	$(t_{2g})^1$	S = 1/2	Ti^{3+}, V^{4+}
2	d^2	$(t_{2g})^2$	S = 2/2 (HS), S = 0 (LS)	Ti^{2+}, V^{3+}
3	d^3	$(t_{2g})^3$	S = 3/2 (HS), S = 1/2 (LS)	V^{2+}, Cr^{3+}
4	d^4	$(t_{2g})^4$	S = 2/2 (IS), S = 0 (LS)	Cr^{2+}, Mn^{3+}
5	d^4	$(t_{2g})^3(e_g)^1$	S = 4/2 (HS)	Cr^{2+}, Mn^{3+}
6	d^5	$(t_{2g})^5$	S = 1/2 (LS)	Mn^{2+}, Fe^{3+}
7	d^5	$(t_{2g})^4(e_g)^1$	S = 3/2 (IS)	Mn^{2+}, Fe^{3+}
8	d^5	$(t_{2g})^3(e_g)^2$	S = 5/2 (HS)	Mn^{2+}, Fe^{3+}
9	d^6	$(t_{2g})^6$	S = 0 (LS)	Fe^{2+}, Co^{3+}
10	d^6	$(t_{2g})^5(e_g)^1$	S = 2/2 (IS)	Fe^{2+}, Co^{3+}
11	d^6	$(t_{2g})^4(e_g)^2$	S = 4/2 (HS)	Fe^{2+}, Co^{3+}
12	d^7	$(t_{2g})^6(e_g)^1$	S = 1/2 (LS)	Co^{2+}, Ni^{3+}
13	d^7	$(t_{2g})^5(e_g)^2$	S = 3/2 (HS)	Co^{2+}, Ni^{3+}
14	d^8	$(t_{2g})^6(e_g)^2$	S = 2/2 (HS), S = 0 (LS)	Ni^{2+}
15	d^9	$(t_{2g})^6(e_g)^3$	S = 1/2	Cu^{2+}

[a)] HS: highest-spin state, IS: intermediate spin state and LS: lowest-spin state.

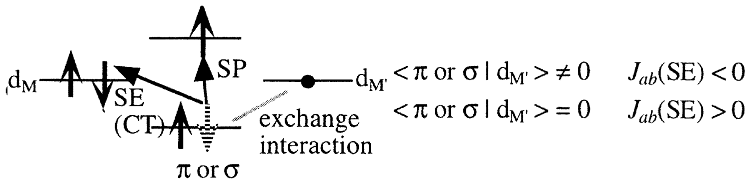


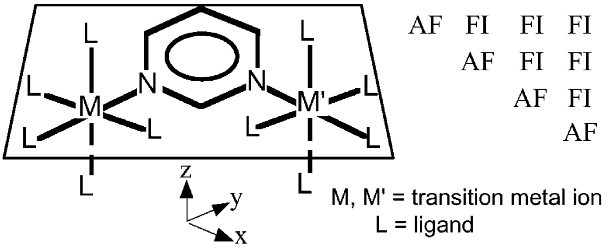
FIGURE 1 The superexchange (SE) interaction and spin polarization (SP) schemes of M_2-pyrimidine.

unpaired d-electron. If the orbital overlap between the open-shell d-orbital and π-MO occurs, this orbital-overlap term leads to the nonzero stabilization of the singlet state, namely J_{ab} (SE) < 0. On the other hand, if these radical orbitals are orthogonal, the potential exchange term leads to the ferromagnetic SE interaction; J_{ab} (SE) > 0. TABLE 2 lists the predicted spin alignments for the magnetic couplings of M_2-pyrimidine.

Next, the contribution of SP effects has been investigated in respect

TABLE 2 Spin alignmet rules for the magnetic couplings of M_2-pyrimidine based on SE interaction [a,b)]

	1	**2**	^{HS}**3**	^{LS}**3**	**5**	**6**	**7**	**8**	**10**	**11**	**12**	**13**	**14**	**15**	**X**
1	AF	FI	FI	AF	FI	AF	FI	FI	FI	FI	F	FI	F	F	P
2		AF	FI	FI	FI	FI	FI	FI	AF	FI	F	FI	F	F	P
^{HS}**3**			AF	FI	FI	FI	AF	FI	FI	FI	F	FI	F	F	P
^{LS}**3**				AF	FI	AF	FI	FI	FI	FI	F	FI	F	F	P
5					AF	FI	FI	FI	FI	AF	FI	FI	FI	FI	P
6						AF	FI	FI	FI	FI	F	FI	F	F	P
7							AF	FI	FI	FI	FI	FI	FI	FI	P
8								AF	FI	FI	FI	FI	FI	FI	P
10									AF	FI	FI	FI	AF	FI	P
11										AF	FI	FI	FI	FI	P
12											AF	FI	FI	FI	P
13												AF	FI	AF	P
14													AF	FI	P
15														AF	P
X															D



a) **X** = **2** (LS), **4** (LS), **9**, **14** (LS),

b) AF = antiferromagnetic, FI = ferrimagnetic, P = paramagnetic and D = diamagnetic

to the magnetic couplings. Spin flip excitation from σ- and π- occupied to unoccupied pyrimidine MOs is responsible for SP effects as illustrated in FIGURE 1. The through σ-bond interaction of the dσ spin via the SP of the σ-bond network of pyrimidine group provides net ferromagnetic exchange integrals as shown in FIGURE 3(A). The SP mechanisms through dπ(M)-π(pyrimidine)-dπ(M') and dσ(M)-π(pyrimidine)-dπ(M') networks

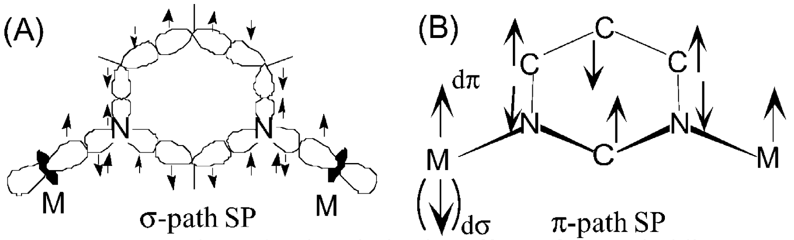


FIGURE 3 σ- and π-path spin polarization effects of M_2-pyrimidine

should provide ferromagnetic and an antiferromagnetic exchange interactions, respectively, as illustrated in FIGURE 3 (B).

Selection Rules for the Magnetic Couplings of M-π Conjugated Systems via Pyrimidine Coupler

Here, the selection rule for the magnetic couplings of the M-π conjugated systems has been proposed on the basis of these through-bond interactions such as SE and SP effects in order to predict the sign of J_{ab} values between transition metal ions, as shown in TABLE 3. In the previous study,[5–6] the calculated results showed that the dπ–π–dπ and dσ–σ–dσ SE interactions in d-π-d systems are more contributable to the coupling constants (J_{ab}) than their SP effects, in contrast to predominant role of the SP effect in p–π–p systems.[7] On the other hand, dπ–π–pπ conjugated systems show an intermediate character between d-π-d and p–π–p ones.[8] It is found from TABLE 3 that SE interaction and SP effect are competitive for M_2-pyrimidine systems. Therefore, the subtle balance of σ- and π- type SP effects and SE interaction is important for the magnetic couplings of these systems.

TABLE 3 Spin alignment rules for the magnetic couplings of M_2-pyrimidine derived for SP effects and SE interaction.

path	J_{ab}(SP)	J_{ab}(SE)	J_{ab}(total)
dπ–π–dπ	> 0	< 0	< 0
dσ–σ–dσ	> 0	< 0	< 0
dπ–π–dσ	< 0	> 0	< 0 or > 0

COMPARISON OF THE SELECTION RULE TO EXPERIMENTAL RESULTS

We have compared the spin alignment rule to the calculated and experimental values. TABLE 4 lists predicted magnetic interaction contributed by SP effect and SE interaction and calculated by UB3LYP and experimental magnetic couplings of several M_2-pyrimidine complexes. In the case of the complexes with the supposed structure(**I–III**), the couplings are antiferromagnetic because of the larger contribution of SE interaction than that of the SP effects. On the other hand, when the coordination ligands are distorted such as **IV**, dπ–π–dσ SE interaction probably contribute the ferromagnetic magnetic couplings. In addition, the insertion of O atom between transition metal ion and pyrimidine coupler strengthens the SP effects, leading to the ferromagnetic interaction of **V**. In order to predict the coupling constants considering the ligand coordination effects, we should examine the coordination ligand effects. Investigation of these results by ab initio calculation is under way.

TABLE 4 Predicted spin state and calculated and experimetal magnetic couplings of several M_2-pyrimidine complexes.

No.	M	M'	SP	SE	J_{ab}(UB3LYP)[a]	J_{ab}(exp.)[a]
I	Ti^{3+}(d^1)	Ti^{3+}(d^1)	F(σ)	AF(σ)		−1.4[c]
II	Mn^{2+}(d^5)	Mn^{2+}(d^5)	F(π)	AF(π)	−19.72[b]	−0.14[d]
III	Cu^{2+}(d^9)	Cu^{2+}(d^9)	F(σ)	AF(σ)	−169.3[b]	−16.0[d]
IV	V^{4+}(d^1)	V^{4+}(d^1)	F(σ)	AF(σ)		>0 [e]
V	Fe^{3+}(d^5)	Fe^{3+}(d^5)	F(π)	AF(π)		+0.65[f]

[a] J_{ab} are shown in cm^{-1}. [b] Ref. [5] and [6]. [c] Ref. [1]. [d] Ref. [2]. [e] Ref. [3]. [f] Ref. [4].

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