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THEORETICAL STUDIES OF CT FERROMAGNETS AND FERRIMAGNETS: METALLOCENIUM-TCNE COMPLEXES

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Abstract An intermolecular orbital interaction theory presented previously has been applied to elucidate the mechanisms of spin alignments in the ferromagnetic or antiferromagnetic metallocenium(M)-TCNE complexes (M=V, Cr, Mn, Fe, Ni) and other CT complexes. It is found that spin polarization and super-exchange interactions play important roles for the ferro- and antiferro-magnetic spin alignments, respectively. Ab initio calculations have been carried out for model complexes.

INTRODUCTION

Previously ab initio molecular orbital (MO) calculations have been carried out for charge-transfer (CT) complexes consisted of organic donor cation radical (D^+) and tetracyanoethylene anion radical ($TCNE^-$) in order to investigate the sign and magnitude of the effective exchange integrals between them.[1] It was found that the spin polarization (SP) effect, which is a clue to the so-called McConnell's first model,[2] plays an important role for the ferromagnetic spin alignment in these complexes. Very recently Broderick and Hoffmann[3] have demonstrated that the SP effect is also important for reasonable explanation of the ferromagnetic interaction in the decamethylchromocenium-tetracyanoquinodimethane (TCNQ) complex, for which the so-called McConnell's second model breaks down. On the other hand, the superexchange (SE) mechanism is operative for the effective exchange interactions between transition metal ions through anions such as oxygen dianion.[4] As a continuation of the previous work[1,4-6] the intermolecular orbital interaction (IOI) theory[7] and ab initio method are applied to investigate possible mechanisms of the spin alignments in the metallocenium-TCNE (or TCNQ) complexes. The SP and superexchange (SE) models are found to be of particular importance for design of molecular ferromagnets.

INTERMOLECULAR ORBITAL INTERACTION (IOI) THEORY

The effective exchange interactions between open-shell species are classified into several components on the basis of the intermolecular orbital interaction theory.[7]
(1) the potential exchange (PE) interaction J(PE) between singly occupied MOs (SOMOs). This is rewritten by the first spin-density-product term (SDPI).
(2) the kinetic exchange (KE) interaction J(KE) between SOMOs. This is rewritten by the orbital-overlap (OO) term J(OO) in our model Hamiltonian.[8] The first-order term J(FOT) is given by the sum of PE and KE terms: J(FOT)= J(PE) + J(OO).
(3) the intermolecular charge-transfer (CT) interaction. This is the second-order interaction and is also the theoretical foundation for the McConnell's second-model.[9]
(4) the intramolecular SP effect plus intermolecular spin-delocalization (SD) effect. The third-order SP•SD term[7] is rewritten by the second SDP term (SDPII) used in the McConnell's first model.[2] The SDP term in our extended McConnell model [7] or IOI model involves the first and second SDP terms: J(SDP)=J(SDPI) + J(SDPII).
(4) the superexchange (SE) term J(SE) for the metal-anion-metal systems.[4]

QUALITATIVE ANALYSIS OF METALLOCENIUM-TCNE COMPLEXES

The above IOI theory was applied to the qualitative analysis of mechanisms of spin alignments in one-dimensional chains of metallocenium-TCNE complexes and related donor-acceptor (DA) systems. Figure 1 illustrates the molecular structure of the donor-acceptor (DA) chain and the MO levels for the DA pair.[10] The d-electron configurations for the metalloceniums (M=V, Cr, Mn, Fe, Ni) are illustrated in fig. 2.

First order term

The potential exchange term J(PE) between the unpaired d-electron(s) of $[M(L)_2]^+$ and the unpaired π-electron of $TCNE^-$ ($TCNQ^-$, etc.) is given by the Coulombic

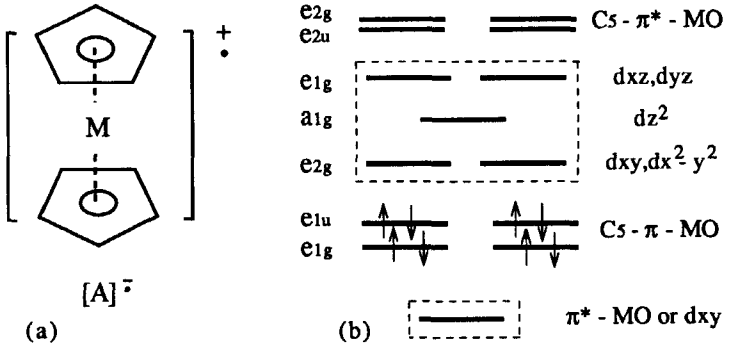

Fig 1 . (a) molecular structure of the one - dimensional chain $(D^+A^-)_n$ (D=M(L)2, A=TCNE,TCNQ,etc (b) molecular orbital (MO) energy levels for $[D^+A^-]$ complex

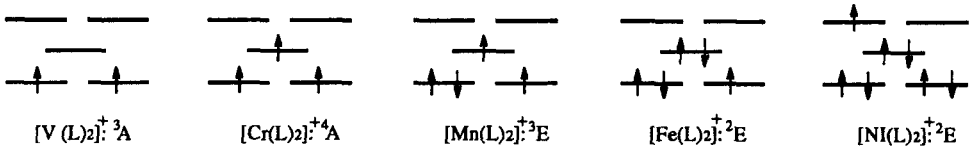

Fig 2. d - electron configurations for the decamethylmetalloceniums

exchange integral Kij and is always positive in sign.[7] The orbital overlap term J(OO) [8] between the unpaired d- and π-electrons is negative (antiferromagnetic) if they are nonorthogonal, while it vanishes if they are orthogonal. Therefore the J(OO) term is zero for the vanadium and iron complexes, indicating that the sign of the first-order term J(FOT) is positive in sign. The J(FOT) term is negative for the Cr, Mn and Ni complexes, since the nonzero J(OO) term usually overweighs the J(PE) term.[4,8] However, the magnitude of J(FOT) should be small since the distance between M^+ and A^- is long (over 5 A) in the case of the metalocenium-TCNE (TCNQ) complexes.[9] Table I summarizes the predicted results.

Second-order CT (McConnell) term

The spin state of the lowest charge-transfer (CT) state ($D^{2+}A^{2-}$) from D^+ and A^- is easily estimated from the d-electron configuration in fig. 2. The low spin (LS) CT state is predicted to be more stable than the high-spin (HS) CT state in the case of the V, Cr and Ni complexes, indicating that the McConnell term J(MM) is negative

TABLE I Signs of effective exchange integrals for metallocenium-TCNE (TCNQ) complexes estimated by the orbital interaction model.

	First-order term (FOT)			McConnell model (MM)			Jexp[c,d]	
System[a]	J(PE)	J(OO)	J(FOT)	G.S.[b),c]	CT[b),c]	J(MM)	A1	A2
$[V(L)_2]^+A^-$	≥0	0	≥0	$^{2,4}[^3A\bullet^2A]$	$^2[^2E\bullet^1A]$	<0		
$[Cr(L)_2]^+A^-$	≥0	≤0	≤0	$^{3,5}[^4A\bullet^2A]$	$^3[^3A\bullet^1A]$	<0	?	>0
$[Mn(L)_2]^+A^-$	≥0	≤0	≤0	$^{2,4}[^3E\bullet^2A]$	$^4[^4A\bullet^1A]$	>0	>0	>0
$[Fe(L)_2]^+A^-$	≥0	0	≥0	$^{1,3}[^2E\bullet^2A]$	$^3[^3E\bullet^1A]$	>0	>0	>0
$[Ni(L)_2]^+A^-$	≥0	≤0	≤0	$^{1,3}[^2E\bullet^2A]$	$^1[^1A\bullet^1A]$	<0	<0	?

a) L=C_5Me_5 and A^-=$TCNE^-$, b) G.S. = ground state and CT=lowest-excited state
c) $^a[^pD^{m+}\bullet^qAQ^{n-}]$ (D=M(L)2, A1=TCNE or A2=TCNQ), d) experimental value.

(antiferromagnetic). On the other hand, the J(MM) term should be ferromagnetic for the Mn and Fe complexes. Table I summarizes the predicted signs of the J(MM) term, together with those of the intrachain J values concluded from the Weiss temperatures observed for the metallocenium-A (TCNE, TCNQ, etc.) complexes.[9] From Table I, the McConnell's second-model cannot explain the positive (ferromagnetic) J value for the decamethylchromocenium-$TCNQ^-$ complex.

Spin polarization (SP) and spin delocalization (SD) terms

The ferromagnetism observed for the decamethylchromocenium-TCNQ complex may indicate that the higher order terms such as the SP•SD and superexchange (SE) terms are important for other metallocenium-A complexes as illustrated in fig. 3. Kahn et al.[11] have also emphasized that the SP effect plays an important role even for the ferrocenium-TCNE complex. In our IOI formalism, the SP•SD term is expressed by the intramolecular spin polarization (SP) of the cyclopentadienyl (Cp) ring by spin(s) of the transition metal ions (M^+) followed by the intermolecular CT interaction between Cp and A^-. The net effect is usually ferromagnetic as can be illustrated by the SP rule: $M^+(\uparrow)Cp(\downarrow)A^-(\uparrow)$.[7,8] On the other hand, Soos et al. [12] have discussed the important role of J(SE) for the metallocenium-A complexes. The SE term is given by the CT from Cp anion to the d-orbitals of M^+ followed by the effective exchange interaction J' between Cp radical and A^-. Therefore the sign of the J(SE) term depends on that of J'. The J' term should be positive (ferromagnetic) in the case of some acceptors of Ni and Pt complexes[9] since the SOMO of these species is the dx2-y2(dxy)-type.[6] On the other hand, J' should be negative for π-acceptors such as TCNQ and TCNE because of the nonzero orbital overlaps between the π-molecular orbital (MO) of Cp and π-MO of A. Therefore the J(SE) term is usually antiferromagnetic for the metallocenium-TNCE (TCNQ) complexes. The IOI

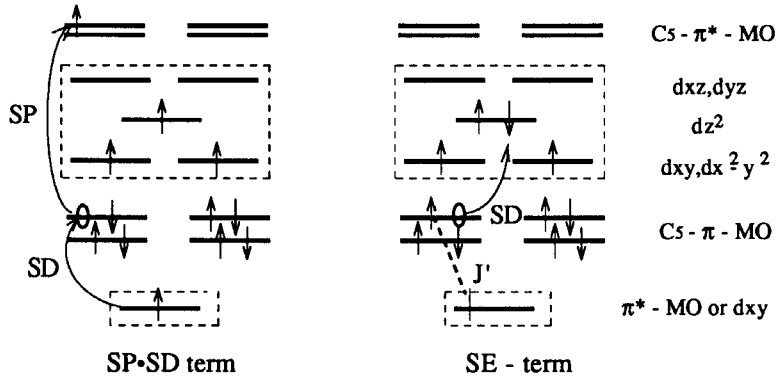

Fig 3. Two types of the third order magnetic interactions

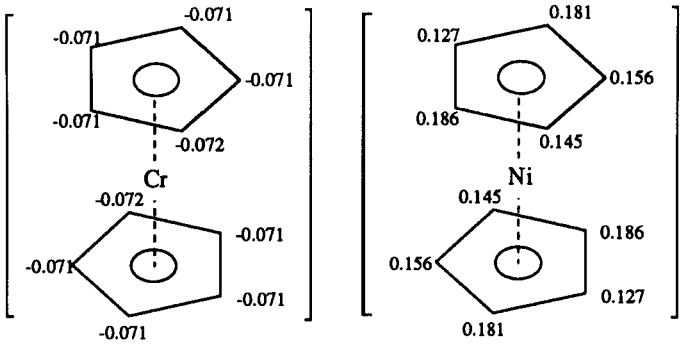

Fig.4 π–spin density of metallocene cations

Table II d-orbital spin denstiy (SD) and electron density (ED) of metallocene cations

d-AOs	$[CrL_2]^+$		$[NiL_2]^+$	
	SD	ED	SD	ED
d_0	0.969	1.025	-0.000	1.992
d_{+1}	0.326	0.781	-0.139	1.429
d_{-1}	0.327	0.781	-0.297	1.340
d_{+2}	0.966	0.983	-0.004	1.970
d_{-2}	0.966	0.983	-0.004	1.970

arguments[7] conclude that the ferro- and antiferro-magnetic exchange interactions observed for the chromocenium-TCNQ and the nickelocenium TCNE complexes can be, respectively, ascribed to the predominant roles of the spin polarization (SP) and superexchange (SE) effects since other terms such as the first-order term J(FOT) and the McConnell term J(MM) in Table 1 predict the antiferromagnetic interactions.

AB INITIO COMPUTATIONS OF MODEL COMPLEXES

Ab initio computations were carried out for model complexes in order to confirm the above qualitative predictions. Figure 4 illustrates the spin density populations calculated for $[Cr(Cp)_2]^+$ and $[Ni(Cp)_2]^+$ by the ab initio UHF (MINI-1 [13]) method.[4] Table II summarizes the d-orbital spin density and electron density for the Cr (III) and Ni(III) ions in the complexes. From fig.4, the negative spin density is induced on the Cp-ring in the case of $[Cr(Cp)_2]^+$ because of the SP effect, while the positive spin densities are populated on the Cp-ring of $[Ni(Cp)_2]^+$, indicating that the spin delocalization (SD) from the Cp anion to Ni(III) is extremely large. The latter arises from the lowering of the d-orbital level of the late transition metal ion and use of the MINI-1 basis set: note that the more flexible basis sets suppress the SD effects significantly. However, inspite of such a deficiency, the ab initio computations clearly indicate the difference of the Cr and Ni complexes, supporting the qualitative

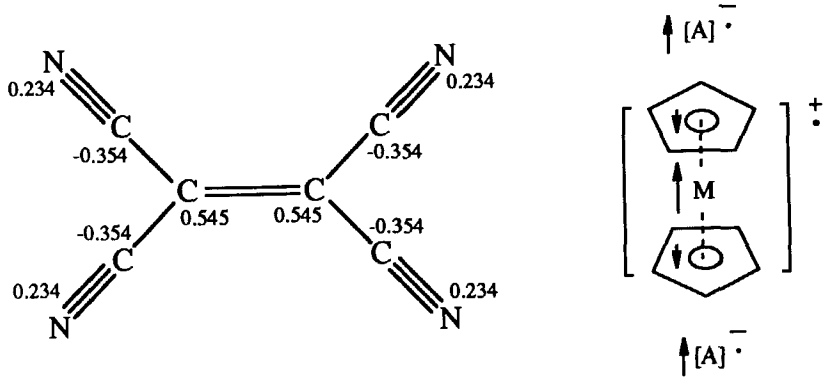

Fig. 5 π-spin density calculated for the TCNE anion and ferromagnetic 1D chain.

conclusions from the IOI theory.[7] The more refined computations will be published elsewhere, together with detailed numerical data.

Fig. 5 illustrates the population of π-spin densitites calculated for the TCNE anion by the ab initio UHF method. The negative spin densities appear on the carbon atoms of the cyano groups, showing the large SP effect. The situation is the same for the TCNQ anion. Therefore the ferromagnetic spin alignments are feasible for the one-dimensional (1D) column $\{[Cr(Cp_2)]^+A^-\}_n$ because of the SP effect as illustrated in fig. 5. On the other hand, very accurate ab initio computations for the dimer (n=1) are necessary in order to elucidate the predominant importance[9,11] between the McConell J(MM) and SP terms in the case of $\{[M(Cp_2)]^+A^-\}_n$ (M= Fe, Mn).

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