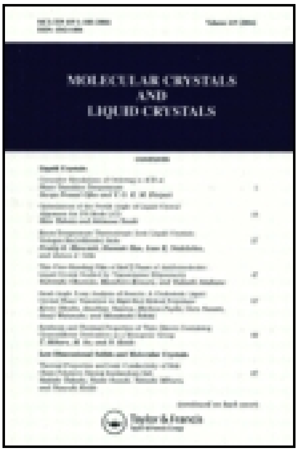

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Theoretical Studies on π-*d* Magnetic Interactions Between BETS Donor and Transition Metal Halides in κ-BETS$_2$MX$_4$ Crystals

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Cooperation of antiferromagnetism and superconductivity is achieved and reported by Kobayashi and his co-workers. For the BETS related crystals, κ-(BETS)$_2$FeCl$_4$ (BETS = bis (ethylenedithio) tetraselenafulvalene), effective exchange integrals (J_{ab}) between two BETS$^+$ molecules (Step I) and between BETS$^+$ and FeCl$_4^-$ molecules (Step II) are very important to reveal superconductivity and successfully evaluated in our treatments.

Keywords organic superconductor; effective exchange integral; BETS; ab initio MO; DFT

INTRODUCTION

The Intersection area between molecular magnets and conductors in intermediate or strong electron correlation regime has attracted much interest. For such species, peculiar molecular donors, i.e. BETS (BETS = bis (ethylenedithio) tetraselenafulvalene) and BEDT-TTF (BEDT-TTF = bis (ethylenedithio) tetrathiafulvalene) are very useful. Recently, antiferromagnetism and superconductivity have been achieved and reported by Kobayashi and his co-workers.[1] Certain types of BETS salts, i.e. κ-(BETS)$_2$MX$_4$ (M = metal atom, X = halogen atom), have been investigated by many groups widely. In addition, λ-phase crystals of these salts are useful to study another types of molecular arrangement. For such novel crystals, effective exchange integrals (J_{ab}) between two BETS$^+$

molecules (Step I) and between BETS$^+$ and MX_4^- molecules (Step II) are important in order to reveal superconductivity and magnetic features. In this study the theoretical calculations by using *ab initio* molecular orbital (MO) and density functional (DFT) methods were carried out in the two steps.

MOLECULAR STRUCTURE

For the crystals κ-BETS$_2$R (R = $FeCl_4$ (**1**), $FeBr_4$ and $GaCl_4$) and λ-BETS$_2$R (R = $FeCl_4$ (**1'**)) have been widely discussed.[1] In addition the crystals κ-(BEDT-TTF)$_2$R (X = Cu(NCS)$_2$, Cu[N(CN)$_2$]Cl, Cu[N(CN)$_2$]Br and Cu[N(CN)$_2$]I)[2] were also employed to evaluate the detailed intermolecular magnetic interaction in our previous papers.[3] The crystal structure of **1**, which was employed mainly in this study, is illustrated in Figure 1A and has the unit cells classified by a space group of Pnma and its cell parameter sets are (a = 11.693, b = 35.945 and c = 8.4914 Å). As shown in this figure this complex consist of each sheet of both donor molecules (BETS) and counter anions (transition metal halides : $FeCl_4$).

The more detailed molecular arrangement between each BETS molecule in two dimensional sheets is depicted in Figure 1B for the **1** crystal and eight molecules 1, 2, 3, 4, 5, 6, 7 and 8 are indicated. The molecules 1 and 2 contact each other with close face-to-face type stacking. Parameters A (= 1-2), B (2-5), p (2-7) and q (2-8), which are brought from

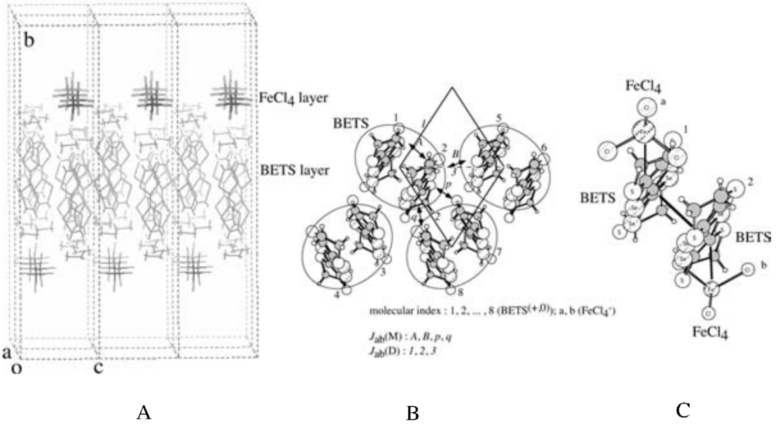


FIGURE 1 Crystal structure of **1** and molecular arrangement.

Hotta's[4] and Mori's[5] definition, are defined to indicate magnetic interaction between two molecules. Similar structure is usually found in the other crystals. We started our studies from treating only the sheet of BETS donors. In addition, molecular arrangement of molecules 1 and 2 of BETS$^{(+,0)}$ and molecules a and b of $FeCl_4^-$ in crystals **1** is depicted in Figure 1C. For the λ-phase of **1** spatial relation among these molecules is more complicated and we will treat it in another paper.

AB INITIO CALCULATIONS

Effective exchange integrals (J_{ab}(M)) in sheet of donors (Step I)

When we evaluate J_{ab} values between two donor molecules in two dimensional sheet, both J_{ab}(M) values between two BETS cations (namely, 2 holes in 2 molecules) and J_{ab}(D) values between two BETS dimers (namely, 2 holes in 4 molecules) are candidate to describe magnetic interaction as shown in Figure 1B.[3] In addition, other effective magnetic parameters (s_{ab}, t_{ab} and U_{eff}) can be evaluated with the calculated J_{ab}(M) values. However, here we focused our discussion on only J_{ab}(M) values.[3]

Ab initio MO and DFT methods with 6-31G basis sets were applied and the obtained results were -264, -31, -3 and -24 cm^{-1} (UHF); -822, -207, -6, -80 cm^{-1} (UB3LYP) for A, B, p and q, respectively. From these result all the J_{ab}(M) values are negative (antiferromagnetic) and the J_{ab}(M)(A) values for the nearest pair A were very small, showing the strong SOMO-SOMO interaction. The J_{ab}(M)(B) values for B-type pair are relatively small and the J_{ab}(M)(q) and J_{ab}(M)(p) values are reduced to zero in this order. Specially, dependency on the basis set is studied for A-type pair with UHF method and the obtained results are -55.3 (STO-3G), -287.0 (3-21G), -263.8 (6-31G), -270.8 (6-31G*), -270.7 (6-31G**) and -276.1 cm^{-1} (6-31++G). All the basis sets except for the STO-3G type reproduce large antiferromagnetic interaction. Polarization and diffuse functions reduce J_{ab} values slightly. Thus, it is concluded that our selection of the 6-31G basis set is suitable in our studies.

The *π-d* magnetic interaction between BETS donor and transition metal halides (Step II)

The magnetic interactions, which is the *π-d* contact between BETS donor and transition metal halides in crystal **1**, were also studied. The nearest pairs of BETS and $FeCl_4$ molecules with short intermolecular distance were treated as shown in Figure 1C. The J_{ab} values evaluated by UB3LYP and UHF methods for several spin structures are summarized in Table 1. Here MIDI ((53321/53/41)+4p for Fe) and 6-31G basis sets were employed. Three types of spin structure were defined as SS I, II and III, though SS I and (II and III) consist of molecules (a and 1) and (a, 1 and 2), respectively. Total spin momentum of septet and quintet are equivalent to the highest and lowest spin states. From these results it is found that almost all the J_{ab} values are very small but negative (antiferromagnetic), although we obtain positive values (ferromagnetic) in the case of SS I by UB3LYP method. The evaluated values for both methods increase in order of SS III, II and I.

Next, in order to explain and understand the above conclusions, especially SS I and II, let us consider the shape of spin densities by graphical representation. Figure 2 illustrates the spin densities for the result calculated by UB3LYP, where more stable spin states are employed for Figures 2A and C. The regions of up (alpha) and down (beta) densities were shown in dark and light gray color and cutoff threshold is set to be 0.002. From these results it is found that spin densities in all $FeCl_4^-$ molecules are alpha and isotropic. On the other hand, spin densities in $BETS^+$ molecules are delocalized and spread over whole atoms without alternation of spin phase. Concerning SS I the results in Figures 2A and 2B re-

TABLE 1 Evaluated results for spin structure (SS I, II and III).

Spin structure	J_{ab} /cm^{-1}	Charge density [c]			Spin density [c]		
		$FeCl_4$(a)	BETS(1)	BETS(2)	$FeCl_4$(a)	BETS(1)	BETS(2)
$FeCl_4^-$(5/2) - $BETS^+$(1/2)	15.2 [a]	-0.916	0.916		5.07	0.932	
(SS I)	(-0.101) [b]	(-0.991)	(0.991)		(5.00)	(-1.00)	
$FeCl_4^-$(5/2) - $BETS^+$(1/2) - $BETS^0$(0)	-0.330	-0.985	0.911	0.075	5.00	-0.945	-0.055
(SS II)	(-3.64)	(-0.985)	(0.911)	(0.074)	(5.00)	(-0.945)	(-0.055)
$FeCl_4^-$(5/2) - $BETS^0$(0) - $BETS^+$(1/2)	-3.39	-0.984	0.053	0.931	5.00	-0.033	-0.968
(SS III)	(-5.61)	(-0.984)	(0.053)	(0.931)	(5.00)	(-0.032)	(-0.968)

a UB3LYP method were employed.

b The results evaluated by UHF method are showed in parentheses.

c Quintet (septet for SS I with UB3LYP method) spin states were emplyed.

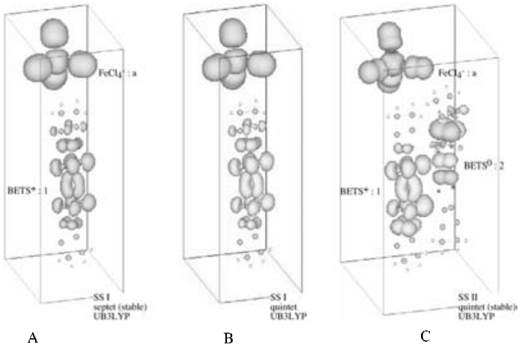
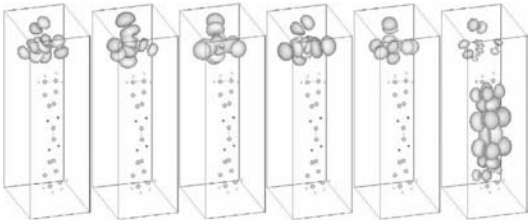


FIGURE 2 Graphical representation of the calculated spin densities.

semble each other except for spin phase in BETS$^+$ molecules. No spin densities appear in the H and C atoms in BETS$^+$ molecule where Cl atom in FeCl$_4^-$ contact. That might be the reason why only small $|J_{ab}|$ values are evaluated as listed in Table 1. When additional BETS^0(2) molecule is also taken into account, spin densities are induced in the next BETS^0 molecule as shown in Figure 2C.

In addition, in Table 1 the total charge/spin densities which were summed into molecules a, 1 and 2 are also listed by using both UB3LYP and UHF methods for all spin structures. From this table it is fount that complete distribution of total charge densities on each molecule is successfully accomplished, i.e. about 0.9 ~ 1.0 values of negative and positive are expected in FeCl$_4$(a) and BETS(1 for SS I and II; 2 for SS III), respectively. The BETS^0 molecules where neutral charge is expected have only a little charge densities. The results derived with both UB3LYP and UHF methods have same tendencies.

Finally, natural orbital (NO) analysis for septet state of SS I were carried out in order to study contribution of FeCl$_4$ and BETS$^+$ molecules to magnetic interaction. In Figure 3 NO coefficients for each orbital (HOMO, SOMO and LUMO) and their graphical representations are summarized for UB3LYP calculated results. For the solutions of septet spin state the occupation number for SOMO(n) (n = 1, 2, ... , 6) is 1.00000 and one electron occupies each orbital. On the other hand, the occupation numbers for HOMO and LUMO are about 2.0 and 0.0 and hardly contribute intermolecular magnetic interaction through indirect electron correla-



HOMO	SOMO(1)	SOMO(2)	SOMO(3)	SOMO(4)	SOMO(5)	SOMO(6)	LUMO
1.99911	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000	0.00089

FIGURE 3 Occupation number and graphical representation of the MOs.

tion correction. The lobes of only SOMO(6) spread over not only $FeCl_4$ but also $BETS^+$ molecules, though those of the other SOMOs are localized on $FeCl_4$ molecule. From these result it is concluded that the SOMO(6) and degenerated SOMOs play essential role in magnetic interaction.

CONCLUSION

These theoretical calculations can successfully evaluate all effective magnetic interactions between donors (Step I) and between donor and transition metal halides (Step 2). The obtained effective parameters can be adapted to the phase-diagrams of spin clusters. In these crystals there are the (super-)exchange coupling between two MX_4 molecules through two donor molecules (M-X - $(donor)_2^+$ - X-M). This means that studies about intersection area between molecular magnets and conductors become more important with π-*d* interaction and the other interactions.

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