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Study on adjacent radicals short contact interaction, spin density, overlap integral and strong anti-ferromagnetic coupling strength

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ABSTRACT

Through theoretical calculations and magnetostructural study of nine radical compounds that exhibit strong anti-ferromagnetic coupling strength, it is revealed preliminarily that the overlap integral between adjacent radicals short contact atoms is relevant to associated strong anti-ferromagnetic coupling strength. It is also confirmed that spin density and overlap integral between adjacent radical short contact atoms are the two major factors that dominate intermolecular strong anti-ferromagnetic coupling strength. The study also reveals that the factor of the overlap integral can replace the factors of both interatomic short contact distance and slippage degrees of π-π stacking. The study also reveals for the first time that the overlap integral changes with different short contact atom and different central coordinated atom.

1. Introduction

Intermolecular magnetic interactions have been among the most studied topics in molecule-based magnetism research [1–6] and especially the strong anti-ferromagnetic interaction systems from adjacent radicals [7–9] have been intensively studied because of two reasons: (1) a few radical complexes exhibit strong intermolecular anti-ferromagnetic coupling strength, which are rarely observed in molecule-based magnetic coupling systems, and (2) some radical complexes display spin transitions [10–12], which are attributes of molecular switches and may lead to utilities in molecular electronics for memory or sensing applications. The intermolecular magnetic coupling mechanism has been investigated for several decades. For example, J. Ma and Q. J. Meng considered the relationship between the magnetic coupling strength and the intermolecular chemical bondings [13]; M. Deumal and J. J. Novoa have suggested that the magnetic coupling strength of π-π stacking systems decreases exponentially as the interatomic short contact distances increase [14]; However, as a reason of varying degrees of slippage in different π-π stacking systems, short contact distance alone is inadequate predictor of magnetic coupling strength. M. M. McConnell [15] proposed the magnetic coupling Hamiltonian operator of adjacent radicals: $H^{AB} = -S^A S^B \sum_{ij} J_{ij}^{AB} \rho_i^A \rho_j^B$, namely, McConnell I spin-polarization mechanism, which means that the magnetic coupling nature and strength are relevant to the spins on the adjacent radicals. But some experimental and theoretical calculation results are hard to be explained with McConnell I spin-polarization mechanism [16]. Toshiaki Enoki and Akira Miyazaki [17] correlated the weak anti-ferromagnetic coupling strength with the overlap integral through the theoretical calculations, in which the minimum S···S contact distance was limited within 3.8 Å for eliminating the effect of core repulsion [18]. When the S···S short contact distance equals or is larger than 3.8 Å, the anti-ferromagnetic strength is certainly very weak, and the meaningful interradical magnetic coupling comes from the shorter S···S contact [11]. Based on interradical magnetic coupling study of four π-π stacking radicals, Christos P. Constantinides and Jeremy M. Rawson point that the longer interradical distances result in smaller overlap integral and weaker exchange couplings [19], in which no data of the relevant overlap integral have been provided. Our previous study confirmed that the π-π stacking magnetic coupling strength is closely associated with the spin densities on relevant short contact atoms [20]. Further, we revealed that the weak magnetic coupling strength in non-radical π-π stacking systems can be attributed to the smaller spin densities on the relevant short contact atoms [20].

Based on the information above and the relevant consensus information, the spin density and overlap integral should be the two major factors that dominate intermolecular anti-ferromag-

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netic coupling strength [21]. But the correlation between anti-ferromagnetic coupling strength and the two factors remains unclear. Therefore, it should be more useful work to explore the correlation based on the crystal structures and the associated spin density and overlap integral. In this paper, the theoretical calculations and magnetostructural study are performed on the reported nine radical compounds that exhibit strong anti-ferromagnetic coupling strength due to adjacent radical short contacts, and herein, we report our research results.

2. Computational details

All the calculations are based on the relevant intermolecular short contact models, in which the bond length data, the associated angles, and the relevant locations of the adjacent short contact radicals were taken from the X-ray structures of the relevant crystals. The overlap integrals of the SOMOs were obtained using the orbital analysis. The calculations were performed using the Gaussian 09 program package [22] at the B3LYP level of theory, using the LANL2DZ basis set for the metallic cations and 6-31++G** basis set for the other non-metallic atoms. The theoretical calculations for the magnetic coupling strength were performed on the basis of density functional theory (DFT) and broken-symmetry approach [23–25] with program Orca 4.0.1 [26] coupling with the popular hybrid functional B3LYP proposed by Becke [27,28] and Lee et al. [29]. Triple-ζ with one polarization function TZVP [30,31] basis sets were used for all atoms, and zero order regular approximation (ZORA) was used for the scalar relativistic effect in the calculations. The exchange coupling constants J were evaluated by the energy difference between the high-spin state $E(HS)$ and the broken symmetry state $E(BS)$ with following formula:

$$J = -\frac{E(HS) - E(BS)}{[S_{Max} - (S_{Max} + 1)]}$$

and assuming the spin Hamiltonian is defined as:

$$H = -2JS_AS_B$$

3. Results and discussion

3.1. The spin densities, the overlap integral and associated strong anti-ferromagnetic coupling strength for radical complexes with mnt (mnt = 1,2-dicyanoethane-1,2-dithiolate) as ligand

Fig. 1 shows the intermolecular interactions of seven radical anions, in which R-1-1-1 through R-1-1-5 come from radical complex [RbzPy][Ni(mnt)$_2$] [32]; R-1-2-1 from radical [1-BrFBz-4-NH$_2$-Py][Pd(mnt)$_2$] [33]; R-1-3-1 from radical [F$_3$BzPy][Pd(mnt)$_2$] [11]; R-1-4-1 and R-1-4-2 from [*N*-hydrogenpyridinium][Pd(mnt)$_2$] [34]; R-1-5-1 and R-1-5-2 from FBzPy][Pd(mnt)$_2$] [35]; R-1-6-1 from [F$_3$BzPy][Pt(mnt)$_2$] [11]; R-1-7-1 and R-1-7-2 from[FBzPy][Pt(mnt)$_2$]·0.25-MeCN [36]. The spin densities of the adjacent radical atoms show in ESI and Table 1 displays the data of the spin densities of adjacent radical short contact atoms and associated overlap integrals from the theoretical calculations that are based on the models as shown in Fig. 1.

Literature reported the spin transition property at 185 K for the radical complex [RbzPy][Ni(mnt)$_2$] [32], which means that the complex displays paramagnetism above 184 K and diamagnetism below this temperature. Obviously, the spin transition property of the radical complex is relevant to the interactions of the adjacent radical anions. R-1-1-1 is a very weak adjacent radicals π-π stacking interaction that contains two pairs of weak contact atoms. Although the spin densities on the atoms of R-1-1-1 are larger than 0.1, the the sum of the absolute values of the overlap integral is very small (compared with that of following R-1-1-5). Therefore, the paramagnetism at 293 K should be attributed to the small overlap integral. The theoretical calculations give the magnetic coupling constant $2J = 28.36\ cm^{-1}$, which indicates that there is a weak ferromagnetic interaction between the weak adjacent radicals π-π stacking interaction. In comparison with the experimental paramagnetic property, the difference between the experimental paramagnetism and the theoretical calculation weak ferromagnetism may underestimate the stability of the broken symmetry [24]. R-1-1-2 through R-1-1-5 are four kinds of adjacent radical short contact [37] interactions at 89 K, in which R-1-1-2 to R-1-1-4 are non π-π stacking interaction and only R-1-1-5 belongs to π-π stacking interaction. The spin density on one of the atoms of the each short contact pair of R-1-1-2 is smaller than 0.1 and the overlap integral is also small, and therefore, R-1-1-2 does not result in strong anti-ferromagnetic coupling strength [20]. Compared with R-1-1-5, the overlap integral of R-1-1-3 is very small and therefore, R-1-1-3 also does not lead to strong anti-ferromagnetic coupling strength. The spin densities on the atoms of R-1-1-4 are smaller than 0.1 and the associated overlap integral is also small, and this short contact pair certainly does not lead to the strong anti-ferromagnetic coupling strength [20]. R-1-1-5 is different from the four models above and it possesses the large spin densities and the large sum of the absolute values of the overlap integrals (0.5453 for SOMO 2), and the diamagnetic property should be ascribed to both the large spin densities [20] and the large overlap integrals. The magnetic coupling constants ($2J\ cm^{-1}$) from the theoretical calculations at 89 K are $-1.60\ cm^{-1}$, $2.26\ cm^{-1}$, $3.16\ cm^{-1}$ and $-1580.94\ cm^{-1}$ for R-1-1-2 through R-1-1-5, respectively, which coincides with the analysis above.

The radical compound [33] [1-BrFBz-4-NH$_2$Py][Pd(mnt)$_2$] exhibits the diamagnetism over 5–300 K and the magnetic coupling constant of the theoretical calculation is $-3752.20\ cm^{-1}$, and R-1-2-1 displays its interadical short contact interaction at 293 K. The spin densities on the short contact atoms are larger than 0.2 and the absolute values of overlap integral SOMO (2) are as large as 0.3965–0.4380 and the sum of the absolute values of the overlap integral as large as 1.6677. Obviously, the diamagnetism should be contributed to both the large spin densities and the large overlap integrals.

As radical compound [1-BrFBz-4-NH$_2$Py][Pd(mnt)$_2$], the radical compound [11] ([F$_3$BzPy][Pd(mnt)$_2$] also exhibits diamagnetic property from 2 K to 350 K and the magnetic coupling constant from the theoretical calculation is $-4198.04\ cm^{-1}$ at 293 K and it coincides with the experimental diamagnetism. R-1-3-1 shows its adjacent radical short contact interaction at 293 K, and it is a π-π stacking short contact interaction. The spin densities on the short contact atoms change in the range of 0.17–0.27, which are much larger than 0.1, the absolute values of overlap integral of SOMO (2) are as large as 0.31 to 0.39, and the sum of the absolute values of the overlap integral is as large as 1.4. It is further confirm that the large sum of the absolute value of overlap integral results in the diamagnetism.

Literature also reports another palladium radical complex [34] [*N*-hydrogenpyridinium][Pd(mnt)$_2$] and it exhibits diamagnetism from 5 K to 300 K and R-1-4-1 and R-1-4-2 show the two kinds of interactions of the adjacent radical anions, in which R-1-4-1 is a non π-π stacking short contact interaction and R-1-4-2 is a π-π stacking short contact interaction. The spin densities on the short contact atoms of R-1-4-1 are far less 0.1 and it implies that the anti-ferromagnetic coupling strength from R-1-4-1 is very weak [20]. The spin densities on the four pairs of π-π stacking short contact atoms of R-1-4-2 are larger than 0.17 and the associated sum of the absolute values of the overlap integral of the SOMO (2) is also as large as 1.2994, which are similar to that of R-1-3-1. There-