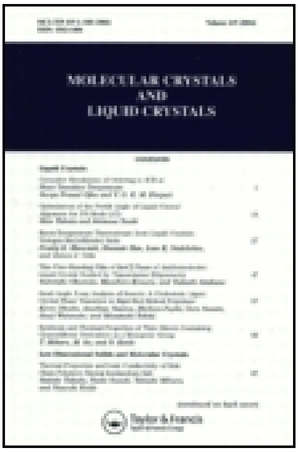

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Theoretical Study on the Exchange Interaction Between Metal Ion and Organic Radical Through Pyridine, Bipyridine and Terpyridine Ligands

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To cite this article: Jingping Zhang, Madoka Suehiro, Akira Sakane, Satoru Karasawa, Takeyuki Akita & Noboru Koga (2002): Theoretical Study on the Exchange Interaction Between Metal Ion and Organic Radical Through Pyridine, Bipyridine and Terpyridine Ligands, Molecular Crystals and Liquid Crystals, 376:1, 431-436

To link to this article: http://dx.doi.org/10.1080/713738426

Mol. Cryst. Liq. Cryst., Vol. 376, pp. 431-436
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1058-725X/02 $12.00 + .00

Theoretical Study on the Exchange Interaction Between Metal Ion and Organic Radical Through Pyridine, Bipyridine and Terpyridine Ligands

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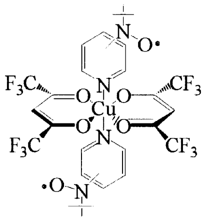
Ab initio total energy calculations with the DFT framework based on the geometries obtained by X-ray data were carried out for five complexes composed by copper(II) ion and organic radicals (eg. aminoxyl and carbene) through pyridine, bipyridine and terpyridine rings. It was found that the copper(II) complex having radical substituted at 4-position of aromatic ligand favors ferromagnetic coupling between organic radical and paramagnetic copper(II) ion.

Keywords DFT calculations; Molecular-based magnets; Organic radicals; Paramagnetic ions

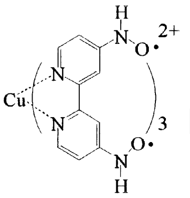
INTRODUCTION

For the construction of super high-spin complex in heterospin system, it is important to understand the spin exchange coupling between organic spin and 3d spin of metal ion. Recently we have prepared five copper complexes, bis(hexafluoroacetylacetonato)copper(II) coordinated with 4- and 3-(*N*-*tert*-butyloxyamino)pyridine (**1**) and (**2**), tris{4,4’ -(*N*-*tert*-butyloxyamino)-2,2’ -bipyridine}copper(II) (**3**), 4-

(α-diazobenzyl)terpyridinatocopper(II)dichloride (**4d**), and bis(4-(α-diazobenzyl)-terpyridinato)copper(II) (**5d**) as model complexes for the super high-spin complex. Their molecular structures (**1-3**, **4d** and **5d**) and magnetic properties (**1-5**) have been investigated by X-ray analysis and SQUID magneto/susceptometry, respectively. In this work, for full characterization of magnetic coupling between copper (II) ion and organic radicals, ab initio total energy calculations with the density function theory (DFT) framework [1, 2] were carried out for these complexes possessing multi spin centers.



1; 4NOPy
2; 3NOPy



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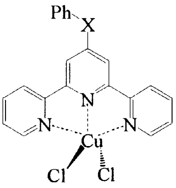
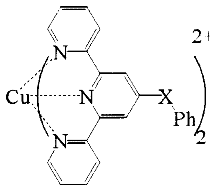


4d; X= C=N$_2$
4; X= C:



5d; X= C=N$_2$
5; X= C:

METHODOLOGY

Hybrid-DFT technique was used, which was the B3LYP functional employing the Lee-Yang-Parr correlation functional in conjunction with a hybrid exchange functional, contained in the GAUSSIAN98 package [3]. The basis used for atoms was 6-31G with the polarization functions (6-31G*) for investigated models. In order to get original SOMO orbital results, the geometries of investigated complexes were exactly based on X-ray crystal data. The counter anions (PF_6^-) for complex **5** were considered as well.

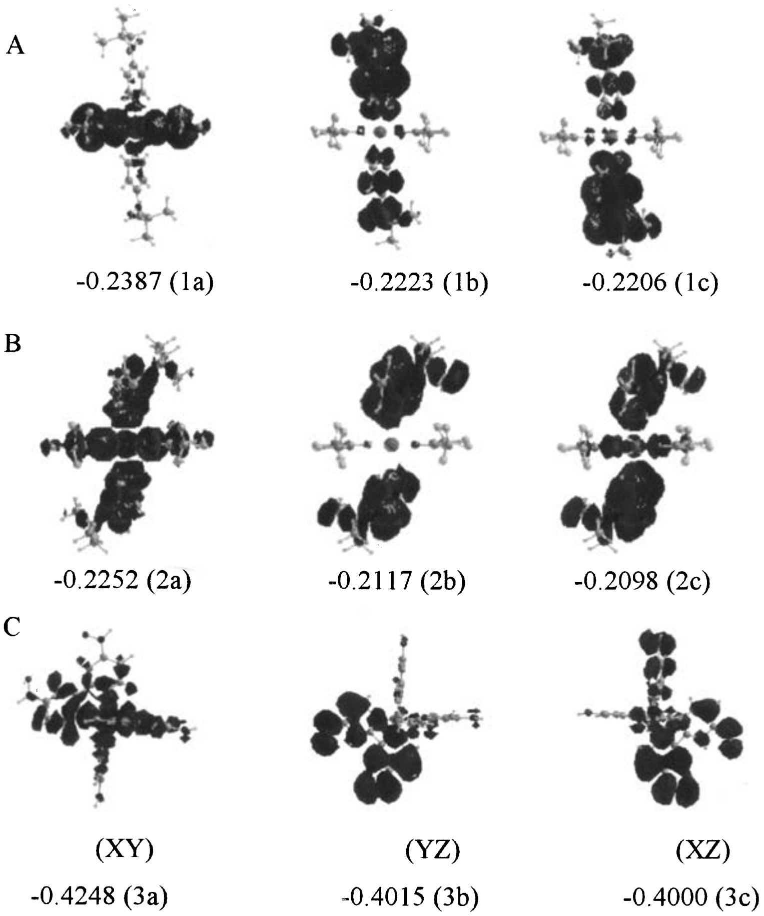
CALCULATED RESULTS AND DISCUSSION

The spin multiplicity and its relative stability can be obtained based on the calculated energy gap $\Delta E_{L\text{-}H}$ between the states of highest spin multiplicity (H) and the next lowest lying low-spin state (L). $\Delta E_{L\text{-}H} > 0$ corresponds to a high-spin ground state. The $\Delta E_{L\text{-}H}$ values for complexes **1** and **2** are 0.364 a.u. and –0.025 a.u., indicating strong ferro- and weak antiferromagnetic coupling (or near degenerate high- and low-spin ground states), respectively. The intramolecular ferromagnetic coupling for complex **1** is consistent with experimental result [4]. The total angular momentums of spin state X (L – low-spin state, H – high-spin state) denoted as $^{X}<S^2>$ and the expected values ($^{XE}<S^2>$) for each complex are given in Table 1. As can be seen from Table 1, DFT method here offers negligibly small spin contamination for all high-spin states and significant spin contamination for low-spin states in complexes **2-5** compared with the expected $<S^2>$ values. Therefore, the SOMO orbitals for high-spin states can be used to demonstrate the nature of interaction between ferromagnetic orbitals. The calculated natural SOMOs for investigated complexes together with their orbital energies (in a.u.) are schematically illustrated in Figure 1. In order to show the d orbitals of Cu^{II}, SOMO orbitals for **1** (1A) and **2** (1B) are rotated around axes of Y. As the J value for complex **1** based on ΔE_{L-H} is much larger than that obtained from experiment, it is worth to note that we should pay more attention to the SOMO results of high-spin state in stead of the absolute value of ΔE_{L-H} for such large complexes as investigated here.

TABLE 1 The calculated ($^{X}<S^2>$) and expected ($^{XE}<S^2>$) total angular momentum of each spin state for complexes **1-5**.

Complexes	$^{H}<S^2>$	$^{HE}<S^2>$	$^{L}<S^2>$	$^{LE}<S^2>$
1	3.77	3.75	0.76	0.75
2	3.76	3.75	1.75	0.75
3	15.79	15.75	5.80	3.75
4	3.78	3.75	1.76	0.75
5	8.82	8.75	4.69	3.75

The different interaction between complexes **1** and **2** can be explained by SOMO orbital distribution in Figure 1A and 1B. SOMO results for complex **1** (1a-c) offer such visional image that magnetic orbitals are consisting of $d_{X^2-Y^2}$ atomic orbital (AO) on Cu^{II} (1a) and P_z AOs on ligand radical parts (1b, 1c). According to the coefficients of AOs for three SOMO, they are orthogonal to each other. Hence, near degenerate and orthogonal SOMOs in complex **1** contribute to form the ferromagnetic coupling between three hetero-spin centers. In the SOMO orbitals of complex **2** in quartet state (2a-c), only P_Y in stead of P_Z AOs on the ligated pyridyl nitrogen atoms are found, indicating that the nodes for P_Z orbital on pyridyl nitrogen exist in complex **2**. Observed nodes of Pz AOs on pyridyl nitrogen result in the weak interaction between $d_{X^2-Y^2}$ AO on Cu^{II} and aminoxyls through pyridine rings to produce the near degenerate high- and low-spin ground state. Because the strong intermolecular antiferromagnetic coupling hindered to determine *J* value for complex **2** [4], calculation result suggests near degenerate high- and low-spin ground state here.



-0.2387 (1a) -0.2223 (1b) -0.2206 (1c)

-0.2252 (2a) -0.2117 (2b) -0.2098 (2c)

(XY) (YZ) (XZ)

-0.4248 (3a) -0.4015 (3b) -0.4000 (3c)

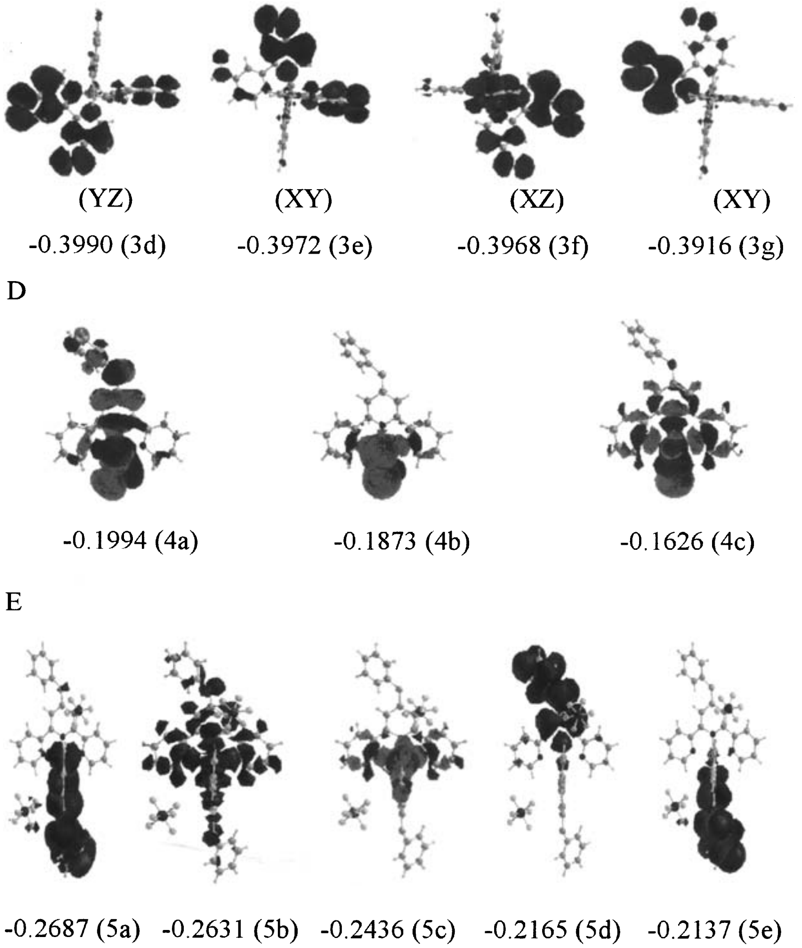


FIGURE1 The distribution of SOMO for complexes **1-5** (A-E)

For complex **3**, the SOMO results (see Figure 1C) illustrate that only the magnetic orbitals in XY plane (3e, 3g) are localized on each mono-radical parts of bipyridine ligands and are orthogonal to $d_{X^2-Y^2}$ AO on Cu^{II} (3a). On the other hand, the distribution of SOMOs on YZ (3b, 3d) and XZ (3c, 3f) planes shows disjoint characteristic, favoring antiferromagnetic coupling, between radical centers within each bipyridine ligand. As a total result, quartet ground state should be obtained, which is consistent with the experimental result.

The magnetic orbitals (see Figure 1D) for five coordinated complex **4** demonstrate that the magnetic orbitals are consisting of P_Z orbitals of organic radical (4a), P AOs of two Cl^- (4b), and $d_{X^2-Y^2}$ AO on Cu^{II}(4c). Furthermore, the P AOs of Cl^- anion appear in all magnetic orbitals, due to the strong interaction between two Cl^- anions and Cu^{II} ion. As a result, the interaction between carbene and Cu^{II} should be reduced to produce a less stable high-spin ground state.

For six coordinated complex **5**, the magnetic orbitals are three MOs from organic radical centers (5a, 5d, 5e), two AOs from Cu^{II}, i.e. $d_{X^2-Y^2}$ (5c) and d_{Z^2} (5b). As complex **5** has near ideal octahedral structure, leading to the near degenerate $d_{X^2-Y^2}$ and d_{Z^2} for Cu^{II}. Therefore, one spin from radical centers might be transferred to d_{Z^2} AO. High-spin ground state should be favored for complex **5**.

CONCLUSION

DFT calculation offers a visional image for SOMO orbitals of high spin states, by which the nature of interaction between ferromagnetic orbitals can be demonstrated. It is shown that the copper(II) complex having radical substituted at 4-position of aromatic ligand favors ferromagnetic coupling.

Acknowledgements

This work has been partially supported by Ministry of Education, Science, Sports and Culture, Japan (#08CE2005), National Natural Science Foundation of China (Grant No. 29804002), and Fok Ying Tung Education Foundation (Grant No. 71013).

References

[1] J. M. Seminario, (Ed.), Density Functional Theory, Adv. Quantum Chem., Vol. **33**, Academic, San Diego, 1998.
[2] D. P. Chong, (Ed.), Recent Advance in Density Functional Methods, World Scientific, Singapore, 1995; Part I.
[3] Gaussian 98 (Revision A.3), M. J. Frisch, et al, Gaussian, Inc., Pittsburgh PA, 1998.
[4] Y. Ishimaru, M. Kitano, H. Kumada, N. Koga, H. Iwamura, Inorg. Chem. **37**, 2273 (1998).