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Theoretical study on magnetic and spectral properties of binuclear copper (II) complexes

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Abstract

The density functional theory (DFT) is used to calculate magnetic coupling constants and electronic absorption spectra of binuclear copper (II) complexes. The calculated results show that the increase in electronegativity of the terminal ligands can weaken the antiferromagnetic interaction, and can make the maximum absorption wavelength red-shift. In addition, the influence of conjugate structure between magnetic center and bridging atom on magnetic coupling interactions and electronic absorption spectra has also been analyzed. The calculated results may be useful as theoretical references for synthesis of the new functional complex and the molecular assembly analysis.

Keywords: Binuclear copper (II) complex; Magnetic coupling; TDDFT; Electronic absorption spectra

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1. Introduction

The theoretical study of the magnetic behaviors of polynuclear systems represents a great challenge to quantum chemical calculation due to the existence of a manifold of states separated by small differences. In recent years, the study on the magnetostructural correlation of polynuclear systems has drawn much attention for elucidating the magnetic phenomena, designing new molecular magnetic materials and investigating the role of the polymetallic active sites in biological processes [1–5]. Up to now, the theoretical study on this field is mainly focused on binuclear systems of transition metals. The bridged copper (II) binuclear system is of particular interest because only one electron per magnetic center participates in the magnetic interaction. The *ab initio* calculation of molecular magnetism has been firstly reported by Daubey et al. [6], who used CI approach to study the magnetic interaction for methyloxo-bridged Cu (II) dimers. Ruiz et al. [7,8] have used DFT-BS(broken-symmetry) method to study the magnetic behavior of hydroxo- and alkoxo- bridged Cu dimers, and their results have showed a correlation between magnetic coupling constant *J* and the Cu–O–Cu bridging angle and with the out-of-plane displacement of the hydroxo or alkoxo groups. From second-order perturbation theory, Hay et al. [9] concluded that antiferromagnetic interaction would decrease when electron density was removed from the bridging atom. In this paper, in order to further examine the exchange coupling phenomenon in the binuclear copper (II) compounds, the influence of atomic electronegativity in terminal ligands and that of the conjugated structure between magnetic center and the bridging atom on magnetic coupling interactions have been studied with DFT-BS(broken-symmetry) and model compounds. On the other hand, in order to get the information of photochemical properties, the electronic spectra were calculated and simulated with time dependent density functional theory (TDDFT) method, and it will help to understand the relationship between structures and luminescence properties of binuclear copper (II) compounds.

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2. Computational details

For Cu (II) binuclear systems, using $\hat{H} = -2J\hat{S}_1 \bullet \hat{S}_2$, We evaluate the magnetic constant J by the following equation:

$$E_T - E_S = -2J \tag{1}$$

where E_T and E_S denote the energies of triplet and singlet states, respectively. Positive J value means ferromagnetic behavior, and negative one means antiferromagnetic behavior.

The broken symmetry approach within the framework of the density functional theory is efficient to calculate the coupling constant J within a monodeterminant. A single configuration representing the essential features of the resulting antiferromagnetic state is developed in this method. When magnetic orbitals are allowed to interact by overlapping in a self-consistent field (SCF) procedure, a state of mixed spin symmetry and lowered space symmetry, named as a mixed spin or broken symmetry state, is obtained. The energy of the mixed spin state is a specific weighed average of the energies of pure spin multiplets. The broken symmetry wave function as a single determinant is not eigenstate of $\hat{S}^2$ but corresponds to a total $M_S = 0$ state or, more generally, to the minimum M_S value. The Heisenberg exchange coupling constant J for binuclear systems can be determined from the energies of the mixed spin state and the highest spin multiplet state, as proposed by Noodleman. [10]

$$E(S_{\max}) - E_{BS} = -S^2_{\max}J \tag{2}$$

For binuclear Cu (II) systems,

$$E_T - E_{BS} = -J \tag{3}$$

According to the calculation experience of Ruiz et al. [11–13], the result obtained from the following Eq. (4) formula is often more satisfied with experimental exchange constants.

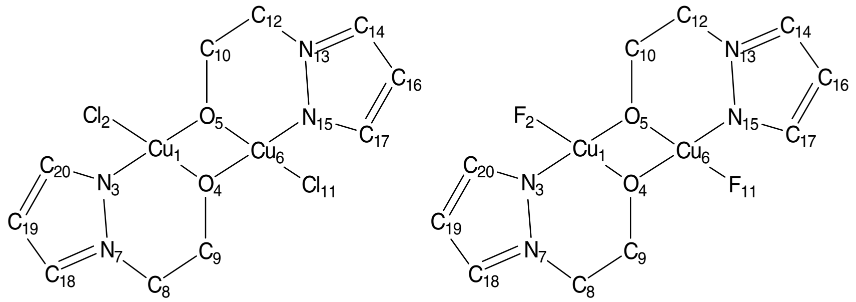
$$E_T - E_{BS} = -2J \tag{4}$$

All calculated exchange constants J in our work are obtained from formula Eq. (4). In order to investigate molecular photochemical properties, the low-lying excited states were calculated using TDDFT. In addition, vertical excitation energies were also calculated for the first 35 singlet excited states to obtain electronic absorption spectra.

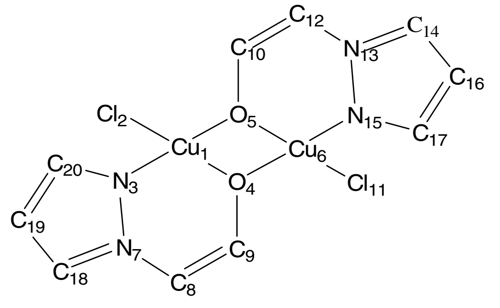
All calculations were preformed by means of the GAUSSIAN 98 suite of *ab initio* programs using the DFT-B3LYP functional in which Becke's hybrid exchange functional (B3) [14] and the correlation functional [15] of Lee, Yang, and Parr (LYP) are combined, and 6–31G** basis set was used for all atoms.

3. Model Complexes

In our calculations, the studied models 1–3 are showed in Fig. 1. As the magnetic behavior is sensitive to any tiny deviation of the molecular structure studied, the geometry structure of model 1 is directly taken from X-ray crystallography analysis [16] without optimization for structural parameters. That Cl atoms of model1 are substituted by F atoms leads to model 2 while keeping the bond length



model 1 model 2



model 3

Fig. 1. Structures of the models 1–3 (H atoms not shown).