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Theoretical Studies on the Spin Exchange Interaction in Copper(II) Complexes Coordinated with Nitronyl Nitroxide

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Abstract: Nitronyl nitroxide radical **1**, NIT (4, 4, 5, 5-tetramethyl-4, 5-dihydro-1*H*-imidazolyl-1-oxyl-3-oxide) and copper(II) chloride complexes with nitronyl nitroxide **2**, [Cu(NITPh)$_2$Cl$_2$] (NITPh = 2-phenyl-4, 4, 5, 5-tetramethyl-imidazoline-1-oxyl-3-oxide) were studied with density functional theory (DFT). The magnetic orbital analysis reveals that the antiferromagnetic coupling for complex **2** is due to the antibonding σ*-orbital overlap between $d_{x^2-y^2}$ (Cu) and π* (NO) orbitals. Also, spin population and atomic charge distribution analysis suggest that for AFS of complex **2** the antiferromagnetic coupling between the radical ligands and the copper(II) ion originates from the spin delocalization induced by the α electron transfer from π*(NO) to $d_{x^2-y^2}$ (Cu) orbital.

Keywords: Density functional theory, spin exchange coupling, copper-radical complex.

In the recent years, a wide variety of transition metal complexes with the nitronyl radical ligands have been reported[1,2]. These systems display the various magnetic behaviors (ferro- or antiferro-magnetism) between the unpaired electrons on the radical ligands and on the paramagnetic metal ion center. However, few theoretical studies on the metal-radical complexes were reported and quite few are known about the nature of the exchange coupling interactions. In this work, we are interested in the electronic structure of the copper-radical complex. More attention was paid to magnetic exchange interaction pathway from the view of the molecular orbital theory, and the magnetic coupling mechanism from analysis of the spin population and net charge distributions.

Computational Details

All calculations were performed using ADF 2.0.1 quantum chemical software package. The IV basis sets, containing triple-ζ basis sets and a polarization function for all atoms and the relativistic effects for Cu, were used. Calculations were based on fully nonlocal self-consistent-field type and the local exchange-correlation potential of Vosko, Wilk and Nusair (VWN). The nonlocal exchange and correlation energy terms and

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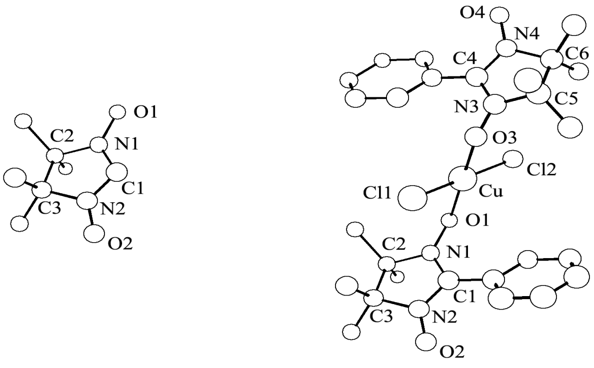
corresponding potentials are due to Becke and Perdew, respectively. It is experimentally well known that the measured exchange coupling interaction are affected largely by small deviations in bond angles and bond lengths, so the geometrical parameters of all the compounds studied were taken from the single-crystal X-ray data[1](**Figure 1**).

Figure 1 The schematic structure of NIT and $[Cu(NITPh)_2Cl_2]$



NIT $[Cu(NITPh)_2Cl_2]$

Results and Discussion

Spin population distribution and spin exchange mechanism

As a potential paramagnetic center, the radical **1** carries a single electronic spin, $S=1/2$. For radical **1**, the selected spin populations calculated are listed in **Table 1**, which shows the major spin population is located on the NO(O1-N1-C1-N2-O2) group. For the complex **2**, the Cu(II) ion formally carries an unpaired electron in the $d_{x^2-y^2}$ orbital, and the nitronyl nitroxides involving two radical moieties carry one unpaired electron each on π^* orbital of the NIT ring. So the complex **2** has three spin states with the different spin distributions: radical(↑)-Cu(↓)-radical(↑), radical(↑)-Cu(↑)-radical(↓) and radical(↑) -Cu(↑)-radical(↑). The calculations show that the first state is antiferromagnetic spin state (AFS) with the lower energy and the last state is the ferromagnetic spin state (FS) with the higher energy. The polarized neutron diffraction experiment had confirmed that complex **2** behaves a strong antiferromagnetic coupling[1,3]. For AFS of complex **2**, the spin populations were compared to those of radical **1**. **Table 1** shows that the spin populations on O1(0.0781) for complex **2** decreased greatly compared to that (0.3169) of radical **1**. While the spin population on O2 atom is changed slightly compared to that of radical **1**. Also, the spin populations on the nitrogen atoms are slightly decreased. It is worth noting that the total net spin population on the NO(O1-N1-C1-N2-O2) group in the AFS of complex **2** (+0.6757) are remarkably smaller than that of the radical **1** (+0.9724). The total net charge on the NO group is (-0.2172) for the AFS of the complex **2**, more positive than that for the FS(-0.2338), while the atomic charge on the copper ion is +0.4241 for the AFS, less positive than that for the AFS (+0.4383). The calculated results of spin population and net charges consistently suggest that the antiferromagnetic coupling favors α-electronic transfer from the ligand NO groups to Cu(II), keep in mind that in AFS of complex **2** the net spin population on Cu(II) is minus sign (namely β-spin state).

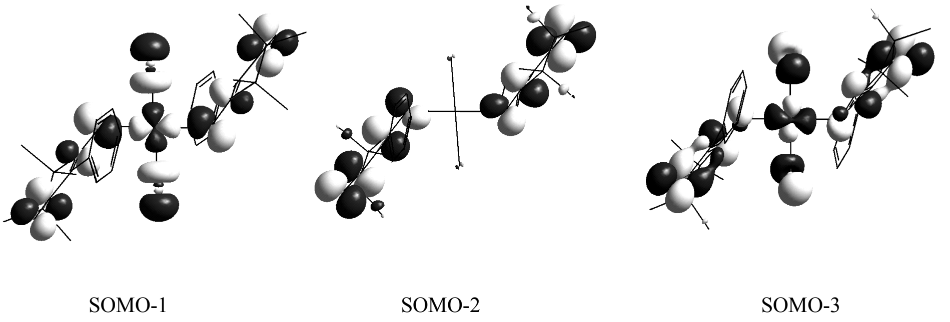
Table 1 Spin population and atomic charge (in parentheses) on the selected atoms

	Radical **1**		Complex **2**			
			FS		AFS	
Cu			0.5201	(0.4383)	-0.2511	(0.4241)
O1	0.3169	(-0.5276)	0.2426	(-0.5503)	0.0781	(-0.5296)
O2	0.3161	(-0.5285)	0.3888	(-0.4973)	0.2913	(-0.5044)
N1	0.2295	(0.2375)	0.2479	(0.2929)	0.1933	(0.2942)
N2	0.2283	(0.2335)	0.2498	(0.2560)	0.1834	(0.2620)
C1	-0.1184	(0.4416)	-0.0564	(0.2649)	-0.0704	(0.2606)
C2	-0.0097	(-0.0035)	-0.0039	(0.0813)	-0.0068	(0.0800)
C3	-0.0095	(-0.0019)	-0.0081	(0.0965)	-0.0073	(0.0961)

Molecular orbital analysis and spin exchange pathway

The singly occupied molecular orbital (SOMO) of radical **1** is an antibonding molecular orbital(π^*) formed by the $2p_z$ orbitals of the nitrogen atoms and the oxygen atoms perpendicular to the plane of the NIT ring, which is the local magnetic orbital of the radical ligand in the complex **2** (**Figure 2**). It should be noted that the orbital overlap style between the local magnetic orbital of the radical ligand and the transition metal ion largely affects the molecular magnetic behaviors. As the magnetic orbital, the SOMO always can give the enough information for the magnetic exchange pathway. The schematic structure of complex **2** was depicted in **Figure 1**, where the copper(II) ion, two chlorine anions (Cl1,Cl2) and oxygen atoms (O1,O3) form a mean plane. The dihedral angle between the plane and the plane composed of NIT ring is about ~84°. Such the geometrical conformation makes it possible to form the σ-type orbital between $d_{x^2-y^2}$ (Cu) and $2p_z$(O1,O3) on the NO groups, keep in mind that here the *z*-orientation in p_z(O1,O3) is perpendicular to the NIT rings. It should be pointed out that experimental results had verified that the magnetic orbital component on the two oxygen atoms (O1,O3) of the O-N-C-N-O group is rotated and hybridized[4]. So the deviation of p_z (O1,O3) favors the formation of the σ-type bonding or antibonding orbitals. It is evident in **Figure 2** that the SOMO-1 is combined with the weak σ^*-type antibonding style between $d_{x^2-y^2}$ (Cu) and p_z (O1,O3). The SOMO-2 is largely composed of the π^*(NO). And the SOMO-3 exhibits σ^*-type antibonding combination between metal-ligand, but there is obvious deviation for the p_z(O1,O3) from the perpendicular orientation of the NIT rings. It is consistent with the experimental results mentioned above. Therefore, the experimentally strong antiferromagnetic coupling is due to the σ^*-type overlap between the $d_{x^2-y^2}$ (Cu) and p_z (O1,O3).

Figure 2 Isodensity surface of the magnetic orbitals for AFS of [Cu(NITPh)$_2$Cl$_2$]



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