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## Broken symmetry calculations of magnetic coupling constants in complexes of [M(PHTFAC)<sub>2</sub>(NITpPy)] (M=Co, Mn, Cu)

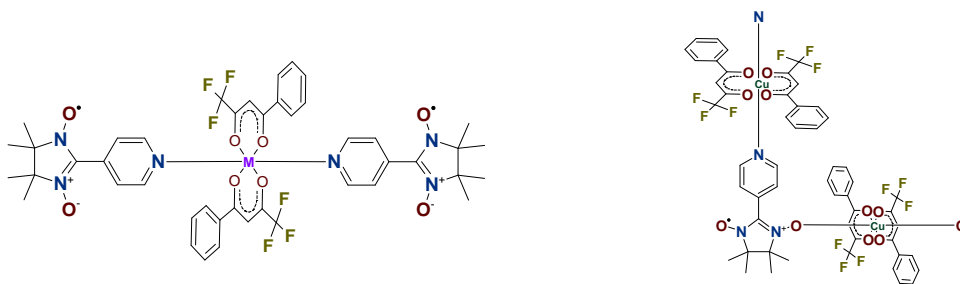
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**Abstract** – Three metallo- $\beta$ -diketonate complexes were synthesized. Their electronic structures were studied by DFT calculations (B3LYP/LANL2DZ/D95V). The Mn (II) and Co (II) complexes (A and B systems) have similar structures, but different magnetic behavior. Based on the electronic structure and broken symmetry approach it was possible to identify the pathway for magnetic interactions. The Cu(II) complex (C system) forms a zigzag chain, with two distinct coordination sites. The magnetic data fit, using an appropriated model, revealed ferromagnetic and antiferromagnetic interactions. Using the DFT calculations it was possible to indicate which of the two copper-radical sites is responsible for each magnetic interaction.

Molecular magnetic compounds have attracted the interest of many chemists and physicists in recent years. Due to the mild conditions of synthesis many of these compounds have been synthesized in recent years, with a variety of architectures. In the present communication we report on B3LYP/D95V/LanL2DZ calculations of magnetic coupling constant, using the broken symmetry approach, for the nitronyl nitroxide radical complexed to the metallo- $\beta$ -diketonate complex[1,2]. Combination of these blocks through coordination of the radical to the metal complex generates blocks with more than one magnetic center, as seen in Figure 1.



**Figure 1:** Sketch of complex [M(PHTFAC)<sub>2</sub>(NITpPy)]. For complex A, M=Co, for complex B, M=Mn.

The manganese (A) and cobalt (B) complexes (Figure 1) are structurally similar, with the metal center coordinated in an octahedral environment, two phenyltrifluoroacetylacetonate (phtfac) ligands in the *trans* orientation and two nitronyl nitroxide radicals coordinated through the pyridine ring in the axial positions. The adjustment of magnetic measurements showed ferromagnetic and antiferromagnetic interactions with coupling constant  $J_A^{\text{exp}} = 3.0 \text{ cm}^{-1}$  and  $J_B^{\text{exp}} = -4.6 \text{ cm}^{-1}$ , respectively. The copper complex (C) form a zigzag chain with two Cu(phtfac)<sub>2</sub> independent sites. In one site the radical is coordinated through the oxygen atom of the nitroxide group while in the other one the coordination is through the pyridine ring. The fit of the magnetic data indicate two constants  $J_c^{\text{exp}} = 29.4 \text{ cm}^{-1}$  and  $J_c^{\text{exp}} = -4.4 \text{ cm}^{-1}$ .

The geometries of A and B were fully optimized in the C<sub>i</sub> point group. Calculations of the magnetic coupling constant resulted in values of  $J_A^{\text{calc}} = 2.2 \text{ cm}^{-1}$  and  $J_B^{\text{calc}} = -46.0 \text{ cm}^{-1}$ . For C, the experimental geometry was used to determine the ground spin state followed by the broken symmetry calculation. Ferromagnetic interactions with coupling constant of  $33.2 \text{ cm}^{-1}$  were found for complexation *via* the oxygen atom, while antiferromagnetic interactions with coupling constant of  $-7.9 \text{ cm}^{-1}$  were found for complexation *via* the pyridine ring.

Analysis of the magnetic orbitals of the manganese complex reveals that interactions leading to ferromagnetic coupling are stronger than those resulting in antiferromagnetic coupling. For the cobalt complex, although the calculated coupling constant is considerably higher than the experimental value, both experiment and theory predict the same behavior. For the copper complex, calculations allowed determination of the pathway leading to the observed ferromagnetic and antiferromagnetic interactions.

## References

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