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Intramolecular Ferromagnetic Radical–Cu^{II} Coupling in a Cu^{II} Complex Ligated with Pyridyl-Substituted Triarylmethyl Radicals

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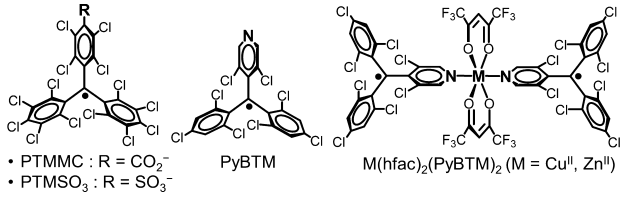
Supporting Information

ABSTRACT: Novel metal complexes $M(hfac)_2(PyBTM)_2$ [M = Cu^{II}, Zn^{II}; hfac = hexafluoroacetylacetonato; PyBTM = (3,5-dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical] were prepared. Both hexacoordinated complexes had elongated octahedral geometry, in which two PyBTM molecules coordinated at the equatorial positions in $Cu^{II}(hfac)_2(PyBTM)_2$ but at the axial positions in $Zn^{II}(hfac)_2(PyBTM)_2$. Magnetic studies revealed an intramolecular ferromagnetic exchange interaction between the spins on PyBTM and Cu^{II} (J_{Cu-R}/k_B = 47 K) based on the orthogonality of the two spin orbitals.

Open-shell radicals have been extensively studied in recent decades as potential components of functional molecular materials because of their magnetic, electron-conducting, optical, and redox properties.[1] In particular, combining organic radicals with paramagnetic transition-metal ions is a promising strategy to yield unusual magnetic systems based on radical–metal exchange interactions. Such systems include single-chain magnets,[1b] light-responsive breathing crystals,[1c] and stepwise neutral-to-ionic transitions with a sensitive magnetic response.[1d] To achieve these magnetic characteristics, it is important to understand key factors that dominate the magnetic interaction. A radical–metal magnetic interaction is often rationalized by the overlapping or orthogonality of two spin orbitals (one each from the radical and metal ion), which mediates antiferromagnetic (AFM) or ferromagnetic (FM) interactions, respectively. The coordination geometry of a radical ligand at a metal center affects the strength (J, an exchange constant) and sign (FM or AFM) of a through-bond radical–metal interaction because the geometry defines whether the spin orbitals are overlapping or orthogonal.[2]

Polychlorinated triphenylmethyl radicals (PTMs) have attracted much attention as useful components of functional electronic devices,[3] although only a small variety of magnetic metal complexes with PTM ligands have been reported. Veciana and co-workers prepared a Cu^{II} complex coordinated with two monocarboxylic PTMs (PTMMCs in Chart 1), $[Cu^{II}(PTMMC)_2(H_2O)_3]\cdot 6H_2O\cdot 2EtOH$, and reported an AFM PTMMC–Cu^{II} interaction with a J/k_B value of −23.1 K ($H = -2J\sum S_{Cu} S_{radical}$).[4a] The PTM–metal exchange interactions mediated through CO_2^- groups were also AFM in related complexes.[4b−e] A SO_3^--appended PTM, $PTMSO_3$ (Chart 1), coordinated to a Cu^{II} ion to afford $[Cu^{II}(cyclam)](PTMSO_3)_2$ (cyclam = 1,4,8,11-tetraazacyclotetradecane).[5] The complex exhibited an intramolecular AFM $PTMSO_3$–Cu^{II} interaction with J/k_B = −2.3 K. The magnetic mediations in PTM–metal complexes are mostly AFM. Although some complexes have displayed FM interactions, the mechanism is not fully understood.[6] A new approach for achieving promising FM mediation is necessary to expand the utility of the radicals; the combination of FM and AFM exchange pathways would provide complex magnetic systems with great diversity. The aim of this study is to develop a new method for achieving a definite FM metal–radical exchange coupling in metal complexes coordinated with this class of radical.

Chart 1. Chemical Structures of Molecules



We recently prepared a luminescent organic radical, (3,5-dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl radical (PyBTM), which has a nitrogen atom within the PTM skeleton (Chart 1).[7a] The nitrogen atom is capable of coordinating to metal ions.[7b] Our electron spin resonance (ESR) spectroscopic results and density functional theory (DFT) calculations have shown that the singly occupied molecular orbital (SOMO) is distributed on the pπ orbital of the nitrogen atom. Therefore, an efficient PyBTM–metal exchange interaction mediated by the nitrogen atom is expected in PyBTM-ligated complexes; the interaction would be greater than that mediated by CO_2^- or SO_3^- linkers. The correct choice of the metal ion (e.g., Cu^{II} with a spin on the orbital with σ-bonding nature) is expected to achieve a FM PyBTM–metal interaction because of the orbital orthogonality.

We report herein a novel Cu^{II} complex with coordinated PyBTM ligands, $Cu^{II}(hfac)_2(PyBTM)_2$ (hfac = hexafluoroacetylacetonato; Chart 1). An isostructural Zn^{II} complex, $Zn^{II}(hfac)_2(PyBTM)_2$, was prepared as a reference. The Cu^{II} complex showed a FM exchange interaction between the PyBTM radical and Cu^{II} ion with J/k_B = 47 K.

Details of the synthesis and characterization of the complexes are described in the Supporting Information (SI). Single-crystal X-ray diffraction studies revealed that the two $M(hfac)_2(PyBTM)_2$ (M = Cu^{II} and Zn^{II}) crystals are isostructural with each other. Each unit cell contains two crystallographically

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independent $M(hfac)_2(PyBTM)_2$ molecules, with the two structures nearly identical. One of the molecular structures of $Cu^{II}(hfac)_2(PyBTM)_2$ is shown in Figure 1a. The Cu^{II} ion is

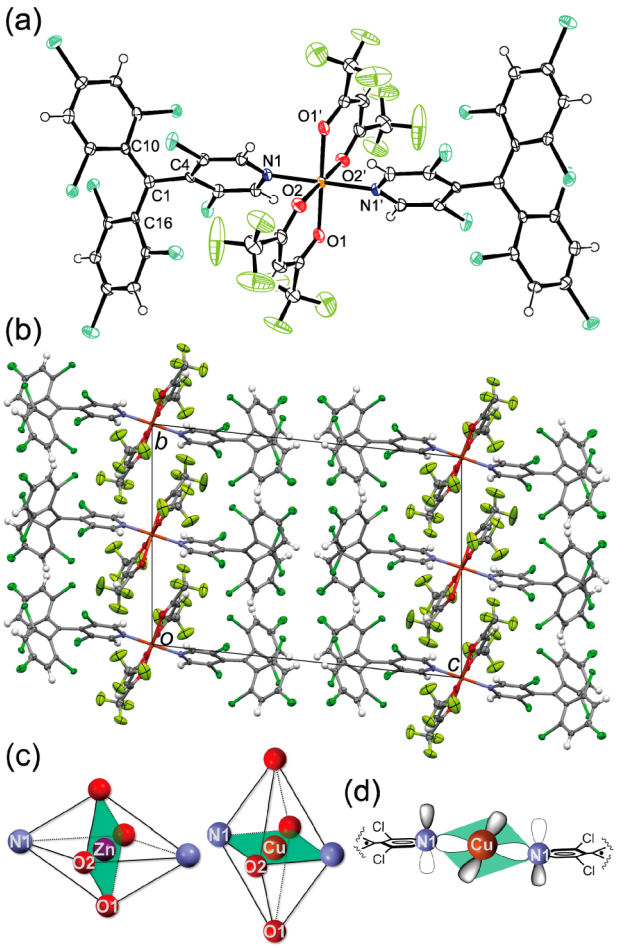

Figure 1. Molecular structure of $Cu^{II}(hfac)_2(PyBTM)_2$ (a) and the arrangement viewed along the *a* axis in the crystal (b). Schematic representation of the coordination geometry of the complexes (c) and the $3d_{x^2-y^2}$ orbital of Cu^{II} with the π orbitals at the nitrogen atom in PyBTM (d). Disorder of the trifluoromethyl groups is not shown for clarity.

located on an inversion center and forms a distorted octahedral coordination geometry in which two PyBTM molecules are coordinated in the trans configuration through the nitrogen atoms. The C1 atom in the PyBTM ligands lies in a C4−C10−C16 plane, confirming its sp^2 hybridization. This structural characteristic indicates that the PyBTM ligands maintain a radical character. In the hfac ligands, one of the two trifluoromethyl groups is disordered in two positions.

Although the two $M(hfac)_2(PyBTM)_2$ complexes are isostructural, they show differences in the distortion of the coordination geometry around the metal ion. The M−O1, M−O2, and M−N bond lengths (d_{M-O1}, d_{M-O2}, and d_{M-N}), which are the average lengths for the two crystallographically independent complexes, are d_{Cu-O1} = 2.219 Å, d_{Cu-O2} = 2.040 Å, and d_{Cu-N} = 2.012 Å in $Cu^{II}(hfac)_2(PyBTM)_2$ and d_{Zn-O1} = 2.078 Å, d_{Zn-O2} = 2.080 Å, and d_{Zn-N} = 2.153 Å in $Zn^{II}(hfac)_2(PyBTM)_2$. The octahedral coordination geometry is elongated in the Zn−N direction in the Zn^{II} complex but in the Cu−O direction in the Cu^{II} complex. The PyBTM radicals appear axially coordinated in the Zn^{II} complex and equatorially coordinated in the Cu^{II} complex (Figure 1c).

Such distortion determines the molecular orbital of the Cu^{II} ion on which the unpaired electron exists (i.e., the spin orbital). The $S = {}^1/_2$ spin on Cu^{II} in $Cu^{II}(hfac)_2(PyBTM)_2$ is expected to be in the $3d_{x^2-y^2}$-based orbital; this orbital is distributed along the equatorial Cu−O2 and Cu−N1 direction and shows σ-bonding character (Figure 1d). Meanwhile, the SOMO (spin orbital) of PyBTM on the nitrogen atom has $p\pi$ character.[7a] In this situation, the two spin orbitals are orthogonal with each other, possibly resulting in a FM interaction.

In the crystal, the two kinds of spin centers (Cu^{II} and C1 atoms) are sterically separated because of the bulkiness of the hfac and PyBTM moieties (Figure 1b). The shortest intermolecular M−M and C1−C1 distances are 8.558 and 8.526 Å in $Cu^{II}(hfac)_2(PyBTM)_2$ and 8.550 and 8.596 Å in $Zn^{II}(hfac)_2(PyBTM)_2$, respectively. Several intermolecular Cl···Cl, Cl···F, Cl···H, and F···F atomic contacts are detected that would be responsible for the intermolecular AFM interactions confirmed in the magnetic studies.

The magnetic properties of the complexes were investigated using a SQUID magnetometer. The room-temperature χT value of $Cu^{II}(hfac)_2(PyBTM)_2$ (1.21 $cm^3 \cdot K \cdot mol^{-1}$) was a little higher than that expected from three ideal $S = {}^1/_2$ spins (1.125 $cm^3 \cdot K \cdot mol^{-1}$ with g = 2.00), confirming the existence of three spins on the complex. The χT value increased upon cooling and reached a maximum at 20 K, indicating a dominant FM interaction between the spins. The subsequent decrease of the χT value below 20 K is attributed to the intermolecular AFM interaction, as discussed for the magnetic properties of $Zn^{II}(hfac)_2(PyBTM)_2$. The observed FM interaction results from the intramolecular exchange interaction between the Cu^{II} and PyBTM spins. The temperature dependence of χT was analyzed by a linear three-spin model with $H = -2J_{Cu-R}(S_{Cu}S_R + S_RS_{Cu})$, where $S_R = S_{Cu} = {}^1/_2$ and J_{Cu-R} indicates an exchange constant between the spins on Cu^{II} and PyBTM.[4a,8] The $\chi T-T$ plot was fitted using eq 1 (Figure 2). N, μ_B, and k_B indicate the

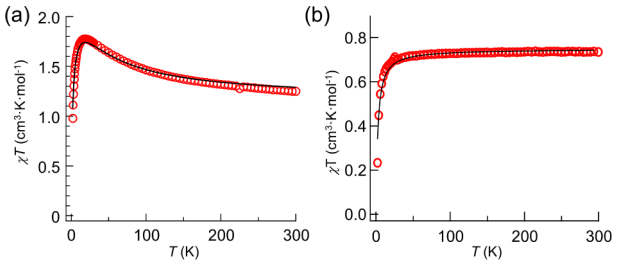

Figure 2. Temperature-dependent χT of $Cu^{II}(hfac)_2(PyBTM)_2$ (a) and $Zn^{II}(hfac)_2(PyBTM)_2$ (b) at 1 T. Black lines indicate fitting curves.

Avogadro constant, the Bohr magneton, and the Boltzmann constant, respectively; $\alpha = J_{Cu-R}/T$, and θ represents the intermolecular AFM interactions.[4a,8]

$$\chi T = [N\mu_B{}^2 g^2 T/3k_B(T-\theta)][60\exp(3\alpha) + 6\exp(2\alpha) + 6]/[16\exp(3\alpha) + 8\exp(2\alpha) + 8] \quad (1)$$

The fitting afforded values for J_{Cu-R}/k_B, g, and θ of 47 K, 2.05, and −1.7 K, respectively.[9,11] The large positive J_{Cu-R}/k_B value indicates an efficient FM PyBTM−Cu^{II} interaction that is much stronger than the interaction reported for a Cu^{II} complex with hexacarboxylic radical ligands (J_{Cu-R}/k_B = 2.1 K).[6b] This suggests

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that the pyridyl group within the triarylphenyl skeleton is superior to the CO_2^- group in achieving FM mediation. The origin of the FM coupling can be explained by the nearly orthogonal configuration of the two spin orbitals as discussed in the structural and theoretical studies.

The temperature-dependent χT of $Zn^{II}(hfac)_2(PyBTM)_2$ was analyzed by the Curie–Weiss law to afford a Curie constant (C) of 0.748 $cm^3 \cdot K \cdot mol^{-1}$ and a Weiss constant (θ) of −2.4 K (Figure 2b).[11] The C value indicates the presence of two PyBTM radicals with the nonmagnetic Zn^{II} ion. The negative θ value indicates an AFM interaction between the spin centers. The similarity of the θ values of the isostructural Cu^{II} and Zn^{II} complexes confirms the weak intermolecular AFM interaction in the crystals of $M(hfac)_2(PyBTM)_2$.

The intramolecular spin–spin interaction in both complexes could be reproduced by broken-symmetry DFT calculation (Figure 3),[10] in which the geometry of each complex was

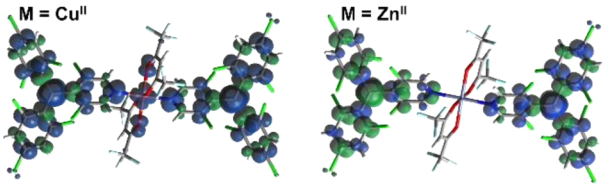

Figure 3. Spin-density distribution on $M(hfac)_2(PyBTM)_2$ calculated using DFT: uB3LYP/6-31g(d) for C, H, Cl, F, N, and Zn; LANL2DZ for Cu. One of the two crystallographically independent complexes is shown in each complex.

extracted from the crystallographic data. $Cu^{II}(hfac)_2(PyBTM)_2$ demonstrated a quartet ground state. The distribution of the spin density suggests that the spins are located at the $3d_{x^2-y^2}$-based orbital on the Cu^{II} ion and the SOMOs on the two PyBTM ligands. The identical sign of the spin density on the centering carbon atoms of the PyBTM ligands and the Cu^{II} ion represents a FM configuration of the spins. Calculated J_{Cu-R}/k_B values are 21 and 47 K for the two crystallographically independent molecules and are of the same order as the values obtained experimentally (Table S2 in the SI). $Zn^{II}(hfac)_2(PyBTM)_2$ was calculated to be in the singlet ground state, where intramolecular AFM interactions between the two PyBTM ligands were estimated to be negligible for the two crystallographically independent Zn^{II} complexes (J_{R-R}/k_B = −0.06 and −0.08 K). This suggests that the intermolecular AFM coupling would be the dominant factor in the AFM interactions observed in the magnetic studies.

In conclusion, $Cu^{II}(hfac)_2(PyBTM)_2$ and $Zn^{II}(hfac)_2(PyBTM)_2$ were newly prepared. Structural analysis indicated that they had different distortions of the octahedral coordination geometry. $Cu^{II}(hfac)_2(PyBTM)_2$ displayed efficient FM PyBTM–Cu^{II} interaction based on the orthogonality of the two spin orbitals.

■ ASSOCIATED CONTENT

Supporting Information

Preparation and characterization of complexes, crystallographic data, parameters calculated using DFT, ESR spectra, absorption and emission spectra, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(11) The θ values are converted to intermolecular exchange coupling constants zJ/k_B of −6.8 and −9.6 K for the Cu^{II} and Zn^{II} complexes, respectively, according to the relation of $\theta = zJS(S+1)/3k_B$ with $S = {}^1/_2$: Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.

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