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to π -Conjugation and Magnetic Properties**

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One-Dimensional Magnetic Chain Composed of Cu^{II} and Polychlorinated Dipyridylphenylmethyl Radical: Temperature-Dependent Jahn-Teller Distortion Correlated to π -Conjugation and Magnetic Properties

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The one-dimensional coordination polymer composed of Cu^{II} and an organic radical bisPyTM displayed temperature dependent Jahn-Teller distortion, which is correlated to the π -conjugation mode at the ligand as well as the magnetic properties. The ferromagnetic bisPyTM-Cu^{II} interaction was enhanced by the reorientation of the Cu^{II} $d_{x^2-y^2}$ orbital at low temperature.

Jahn-Teller (JT) and pseudo-JT distortion modulates the bonding geometry around the metal ion to decrease (stabilize) the energy of an electronic system,^{1,2} thereby affecting the physical properties of materials. Controlling the JT distortion is one promising approach to develop tunable physical properties or to reveal structure-property relationships.³ Among several transition metal compounds, certain Cu^{II}-based one dimensional (1D) chain complexes display unique pressure-^{4,5} or temperature-responsive^{6,7} JT distortion. Cu^{II} has a 3d⁹ electronic configuration and possesses an unpaired electron on its $d_{x^2-y^2}$ orbital in an elongated octahedral coordination geometry. External stimuli affect the coordination geometry around the Cu^{II}, causing rotation of the JT axis, which corresponds to the direction parallel to the elongated bonds on Cu^{II}. This change potentially facilitates reorientation of the spin orbital,⁴ thereby affecting the magnetic properties of the materials. For example, pressure-enhanced antiferromagnetic (AFM) interaction was observed in [Cu^{II}F₂(OH₂)₂(μ -pyrazine)]⁵, and Cu^{II}(hfac)₂ (hfac = hexafluoroacetylacetonato) with pyrazolyl-substituted nitronyl nitroxide displayed switching of Cu^{II}-radical exchange coupling from weakly ferromagnetic (FM) to strongly AFM with decreasing temperature.^{6,7} The JT distortion was correlated to the magnetic properties in these complexes; however, such examples are limited to date.

Here, we report on a new class of 1D chain complexes [Cu^{II}(hfac)₂(bisPyTM)]_n that exhibit temperature-responsive JT-distortion. The Cu^{II} ions are bridged by the organic radical ligand bis(3,5-dichloro-4-pyridyl)(2,4,6-trichlorophenyl)methyl radical

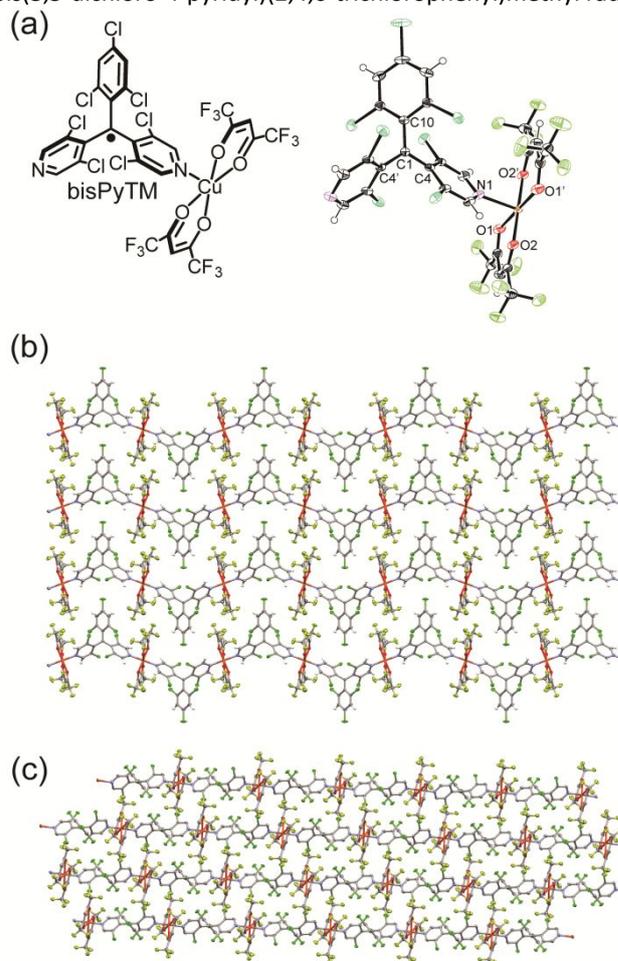


Fig. 1. Chemical and crystal structures of [Cu^{II}(hfac)₂(bisPyTM)]_n at 93 K. (a) Chemical structure and Ortep diagram of a Cu^{II}(hfac)₂(bisPyTM) unit, with views (b) perpendicular and (c) parallel to the *b*-axis.

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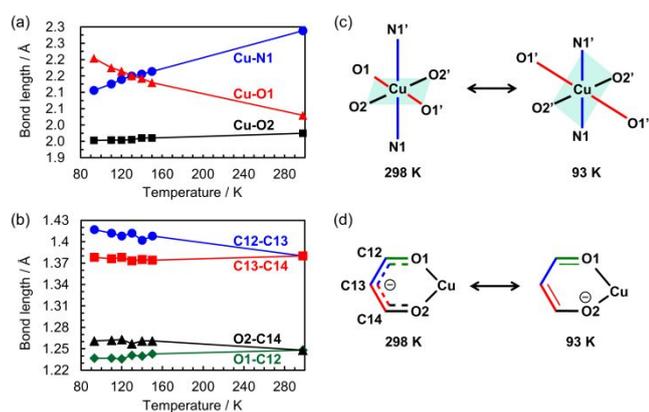


Fig. 2. Temperature dependence of bond lengths (Å) (a) around a Cu^{II} ion and (b) of an O-C-C-C-O moiety in hfac ligands in [Cu^{II}(hfac)₂(bisPyTM)]_n. Schematic representation of temperature-induced structural changes (c) around the Cu^{II} ion and (d) in the O-C-C-C-O moiety.

(bisPyTM),⁸ with dominant Cu^{II}-bisPyTM FM interaction. The distinct characteristics of the present complex are that (i) the temperature-dependent JT distortion around the Cu^{II} ion correlates with the π -conjugation mode in the hfac moiety and (ii) the Cu^{II}-radical FM interaction is enhanced by the reorientation of the JT axis with decreasing temperature.

[Cu^{II}(hfac)₂(bisPyTM)]_n was prepared using the procedure described in the Electronic Supplementary Information. The crystal structure analysed using single-crystal X-ray diffraction (SC-XRD) at 93 K is presented in Fig. 1.⁹ Half of the Cu^{II} ion, half of bisPyTM, and one hfac ligand are crystallographically independent. The Cu^{II} ion is located at the inversion center and is coordinated by four oxygen atoms (O1, O2, O1', O2') from two hfac ligands and two nitrogen atoms (N1, N1') from two bisPyTM radicals.

In bisPyTM, the central carbon atom C1 lies within the plane constructed by the neighbouring three carbon atoms (C4, C4', C10) and is sp²-hybridized, indicating its radical character.⁸ The three aromatic rings form a propeller-like conformation because of the steric repulsion from the chlorine atoms. bisPyTM bridges two Cu^{II} ions via the nitrogen atoms, forming a 1D -Cu^{II}(hfac)₂-bisPyTM- type zigzag chain structure developed along the *a*+*c* direction (Fig. 1b). These 1D chains assemble along the *b*-axis to form a layered structure (Fig. 1c). F \cdots Cl (3.208(3) Å) and F \cdots C (3.165(2) Å) atomic contacts are detected between the chains, which would mediate the interchain AFM interaction suggested by the magnetic studies discussed below.

Temperature-dependent SC-XRD studies revealed that the coordination geometry around the Cu^{II} atom changed with temperature (Fig. 2a). At 298 K, the Cu-N1 bond (2.289(6) Å) was longer than the Cu-O1 and Cu-O2 bonds (2.029(5) and 1.974(4) Å, respectively), indicating distortion of the octahedral coordination geometry elongated along the Cu-N bonds. Notably, the Cu-O1 bond was lengthened whereas the Cu-N1 bond was shortened with decreasing temperature; the former then became longer than the latter below 130 K (Fig. 2a). The changes in bond length were continuous without structural phase transition. Consequently, the JT axis rotated from the Cu-N1 bond direction at 298 K to the Cu-O1 bond direction at 93 K

(Fig. 2c). This result provides a new example of a magnetic chain exhibiting temperature-responsive JT distortion. The rotation is expected to result in the reorientation of the spin orbital ($d_{x^2-y^2}$ orbital) on the Cu^{II} ion, as suggested by the magnetic investigations discussed below.

We detected changes in the bond lengths involved in π -conjugation in the hfac moiety with decreasing temperature (Fig. 2b). The C12-C13 and C13-C14 bond lengths were nearly identical, and the former was elongated and the latter was shortened upon decreasing the temperature to 93 K. Similarly, the two C-O bonds were similar in length at 298 K; however, the C14-O2 bond was elongated and the C12-O1 bond was shortened at 93 K. These changes in bond lengths and symmetry of the O1-C12-C13-C14-O2 skeleton indicate that the negative charge is delocalized and fully π -conjugated at 298 K, whereas the charge is partly localized on the O2 atom and the π -conjugation mode favours one of the several resonant structures at 93 K (Fig. 2d); that is, the π -conjugated [O1-C12-C13-C14-O2]⁻ skeleton becomes O1=C12-C13=C14-O2⁻. This change in the π -conjugation is consistent with the changes in the Cu-O2 and Cu-O1 bond lengths, where the two bonds have similar lengths at 298 K and the former becomes distinctly shorter than the latter at 93 K. Namely, the change in the π -conjugation mode is correlated to the JT distortion around the Cu^{II} ion. The strong effect of the JT distortion on the electronic system indicates that the change in the π -conjugation is induced by the temperature-dependent JT distortion. This system is a rare example of the JT distortion being correlated to the degree of freedom of π -conjugation. This change was not observed in the discrete (i.e., 0D) Cu^{II}(hfac)₂(PyBTM)₂.¹⁰

The magnetic properties of [Cu^{II}(hfac)₂(bisPyTM)]_n are strongly affected by structural JT distortion. The room-temperature χT value (0.78 cm³·K·mol⁻¹) measured using a SQUID magnetometer is slightly higher than that expected from the sum of the two non-interacting $S = 1/2$ spins (0.75 cm³·K·mol⁻¹ with $g = 2.00$), confirming the existence of two spins on a [Cu^{II}(hfac)₂(bisPyTM)] unit (Fig. 3a). Upon cooling, the χT value increased and reached a maximum near 7 K, revealing a FM interaction between the spins on Cu^{II} and bisPyTM. The decrease in χT upon further cooling is presumably attributed to the interchain AFM interaction. An unusual increase in χT was detected at approximately 100-130 K, where the FM interaction is dominant in both the LT ($T < 90$ K) and HT ($T > 150$ K) phases, with a greater strength in the former than in the latter. The exchange interaction constant between the Cu^{II} and bisPyTM ($J_{\text{Cu-R}}$) for the LT and HT phases was estimated by simulating the temperature dependence of χT using the 1D chain model with $H = -2J_{\text{Cu-R}}(S_{\text{Cu}}S_{\text{R}} + S_{\text{R}}S_{\text{Cu}})$ and $S_{\text{R}} = S_{\text{Cu}} = 1/2$, where the interchain interaction zJ' was introduced by mean-field approximation.^{9,11,12} The simulation gave $J_{\text{Cu-R}}/k_{\text{B}}$ and zJ'/k_{B} values of 46 K and -2.0 K, respectively, with $g = 2.08$ for the LT phase and 11 K and 0 K respectively, with $g = 2.09$ for the HT phase. The J/k_{B} value was positive and four times larger in the LT phase than the HT phase, indicating that the FM bisPyTM-Cu^{II} interaction was enhanced in the LT phase.

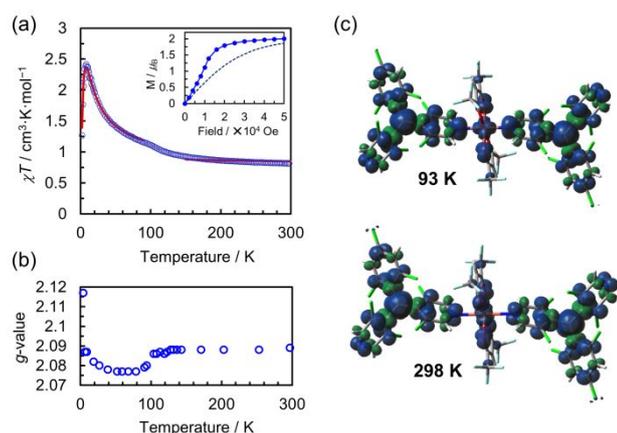


Fig. 3. Temperature-dependent (a) χT at 1 T and (b) g -value of $[\text{Cu}^{\text{II}}(\text{hfac})_2(\text{bisPyTM})]_n$. Red lines in (a) are fitting curves. Inset of (a) shows a M-H curve at 2 K with doubled Brillouin function for $S = 1/2$ (dashed line).¹³ (c) Calculated spin density distribution of a bisPyTM-Cu^{II}(hfac)₂-bisPyTM model structure at 93 K and 298 K.

The change in the strength of the FM interaction at approximately 100–130 K is associated with the temperature-dependent JT structural distortion of $[\text{Cu}^{\text{II}}(\text{hfac})_2(\text{bisPyTM})]_n$. As discussed above, the JT axis on the Cu^{II} ion is considered to rotate below 130 K to facilitate reorientation of the spin orbital on the Cu^{II} ion. The $d_{x^2-y^2}$ orbital that is extended along the Cu-O1 and Cu-O2 bond directions in the HT phase is distributed toward the Cu-O2 and Cu-N1 bond directions in the LT phase. Importantly, in both phases the $d_{x^2-y^2}$ orbital on the Cu^{II} ion is roughly orthogonal to the spin orbital (SOMO) on the nitrogen atom of bisPyTM that possesses a π character. This situation enables FM interaction to be achieved in both the HT and LT phases. The enhanced FM interaction at the LT phase is presumably attributed to the shorter Cu-O1 distance, which can increase the overlap density between the two spin orbitals.

The enhanced FM interaction in the LT phase differs from that in 1D chain Cu^{II}(hfac)₂-nitronyl nitroxide complexes, which changes from a weakly FM to strongly AFM interaction.^{6,7} The sign (AFM or FM) and strength of the interaction are determined by the degree of orthogonality/overlap between the two spin orbitals. For the present compound, FM interaction was maintained because of the better orthogonality between the two spin orbitals before and after the reorientation of the spin orbital on Cu^{II}.

The reorientation of the spin orbital is supported by a temperature-dependent g -value estimated by ESR spectroscopy (Fig. S2a). The g -value of 2.09 at 297 K gradually decreased below 130 K then dropped sharply to 2.08 around 100 K (Fig. 2b) with decreasing temperature. Similar temperature-dependence was confirmed on ΔH_{pp} of the ESR signal (Fig. S2b). These observations reflect the changes in the symmetry and/or distribution of Cu^{II} spin, potentially suggesting its reorientation, although high-frequency ESR spectroscopy using a single crystal is necessary to obtain a detailed information on the disposition of the spin orbital.

Electronic structure calculations based on density functional theory (DFT) were performed for the model structure, a

bisPyTM-Cu^{II}(hfac)₂-bisPyTM unit, to examine the FM bisPyTM-Cu^{II} interaction and the reorientation of the spin orbital.¹⁴ The model structure was constructed from crystallographic data obtained at 93 K and 298 K.

At both temperatures, the model complex was shown to have a quartet ground state. The spin densities on the Cu^{II} and the central carbon atom (C1) of bisPyTM were of the same sign, indicating FM exchange interaction between the spins (Fig. 3c). The spin density distribution indicates that the spins were located in the $3d_{x^2-y^2}$ orbital on the Cu^{II} ion and in the SOMOs on the two bisPyTM molecules. Importantly, the $3d_{x^2-y^2}$ orbital was distributed along the Cu-O1 and Cu-O2 bonds at 298 K but along the Cu-O2 and Cu-N1 bonds at 93 K, indicating the occurrence of spin orbital reorientation (Figs. 3c and S3). The $J_{\text{Cu-R}}/k_{\text{B}}$ values were calculated to be 4.7 K and 36.5 K at 298 K and 93 K, respectively, using the broken-symmetry approach.^{15,16} The value at 93 K was larger than that at 298 K, which is qualitatively consistent with the magnetic investigations discussed above. The calculations reproduced the experimental results well, indicating the reorientation of the spin orbital on Cu^{II} with increased FM exchange interaction in the LT phase.

In conclusion, the JT distortion, degree of freedom of π -conjugation, and magnetic properties in $[\text{Cu}^{\text{II}}(\text{hfac})_2(\text{bisPyTM})]_n$ were coupled, resulting in unique temperature-dependent properties. The reorientation of the spin orbital resulted in enhanced FM interaction between the spins on the Cu^{II} ion and bisPyTM, which has not been previously observed for JT-active Cu^{II} crystals. The present study expands the scope of JT-active magnetic molecular compounds displaying controllable properties.

Conflicts of interest

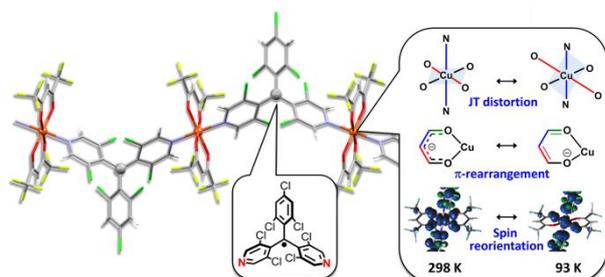
There are no conflicts to declare.

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The Jahn-Teller distortion, π -conjugation mode, and magnetic properties were coupled in the ferromagnetic Cu^{II} -radical chain, resulting in unique temperature-dependent properties.