

Supporting Information

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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General method

Solvents and reagents were used as received from commercial sources unless otherwise noted. Bis(3,5-dichloro-4-pyridyl)(2,4,6-trichlorophenyl)methyl radical (bisPyTM) was prepared according to previously reported protocol.¹ Elemental analysis measurements were performed by the elemental analysis center of the university of Tokyo.

Synthesis of [Cu^{II}(hfac)₂(bisPyTM)]_n

Under a nitrogen atmosphere, Cu^{II}(hfac)₂·nH₂O (36.4 mg, 0.071 mmol for n = 2) was dissolved in dry hexane (24 mL) under reflux. bisPyTM (31.7 mg, 0.065 mmol) in dry dichloromethane and dry hexane (3 mL and 5 mL) was added dropwise to the solution at 70°C, and stirred in the dark overnight. The solvent was evaporated, dried, and the subsequent recrystallization from dichloromethane–hexane afforded [Cu^{II}(hfac)₂(bisPyTM)]_n (30.4 mg, 0.032 mmol) as dark red crystals in 49% yield.

Anal. calcd for C₂₇H₈Cl₇F₁₂N₂O₄Cu: C, 33.64; H, 0.84; N, 2.91. Found: C, 33.86; H, 1.33; N, 2.90.

DFT Calculations

The calculations were carried out using the Gaussian09 program package.² The geometry of the Cu^{II}(hfac)₂(bisPyTM)₂ moiety was extracted from the crystallographic data at 93 K and 298 K. Single-point calculations were performed assuming either quartet or doublet states for Cu^{II}(hfac)₂(bisPyTM)₂ using three-parameterized Becke-Lee-Yang-Parr (B3LYP) hybrid exchange-correlation functional³⁻⁵ with LANL2DZ (Hay-Wadt ECP) basis set⁶ for the Cu atom and the 6-31G(d) basis set^{7,8} for the other atoms. The open-shell electronic structures were approximated by spin-unrestricted method. The intramolecular exchange interactions were considered within the broken-symmetry framework proposed by Yamaguchi and co-workers.^{9,10}

Single crystal X-ray diffraction

Diffraction data for X-ray analysis were collected at 93, 110, 120, 130, 140, 150 and 298 K on a Rigaku Saturn724 (Varimax dual) diffractometer with multi-layer mirror monochromated MoK α radiation ($\lambda = 0.71075$ Å). Lorentz-polarization and empirical absorption corrections were performed with the program Crystal Clear 2.0.

Structures were solved by the direct method using SIR2004¹¹ and refined against F^2 using SHELXL-97.¹²

All the other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in idealized positions and were refined using a riding model with fixed thermal parameters. The crystallographic data are listed in Table S1. The cif files (CCDC No. 1884411, 1884445, 1884446, 1884447, 1884448, 1884449 and 1884450 for at 93, 110, 120, 130, 140, 150 and 298 K, respectively) can be obtained free of charge from The Cambridge Crystallographic via

www.ccdc.cam.ac.uk/data_request/cif.

Magnetic Measurements by SQUID.

The temperature dependence of the magnetic susceptibility of complexes was measured with a Quantum Design MPMS SQUID magnetometer. Aluminum foil was used as a sample container, whose magnetic contribution was subtracted as background by measuring its own magnetic susceptibilities in every measurement. The diamagnetic correction χ_{dia} for the sample was carried out with Pascal's constants. χ_{dia} : $3.54 \times 10^{-4} \text{ emu} \cdot \text{mol}^{-1}$ for $\text{Cu}^{\text{II}}(\text{hfac})_2(\text{bisPyTM})$.

ESR spectroscopy.

ESR spectra were recorded with a JEOL JES-FA200 spectrometer with X-band microwave at temperature in the range of 4.3 to 297 K. Observed g -values were calibrated with the $\text{Mn}^{2+}/\text{MgO}$ standard. Powdered samples charged in a 5 mm ϕ sample tube were used for measurements.

Table S1. Crystallographic data

[Cu^{II}(hfac)₂(bisPyTM)]_n			
Empirical formula	C ₂₇ H ₈ Cl ₇ CuF ₁₂ N ₂ O ₄		
<i>F</i> _w / g mol ⁻¹	964.07		
Crystal dimension / mm	0.14 × 0.07 × 0.03		
<i>T</i> / K	93 K	110 K	120 K
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> / Å	15.3530(17)	15.3431(18)	15.3379(18)
<i>b</i> / Å	11.0280(10)	11.0404(10)	11.0460(10)
<i>c</i> / Å	20.812(3)	20.877(3)	20.900(3)
<i>α</i> / °	90	90	90
<i>β</i> / °	102.899(6)	102.735(6)	102.657(6)
<i>γ</i> / °	90	90	90
<i>V</i> / Å ³	3434.8(7)	3449.4(7)	3454.9(7)
<i>Z</i>	4	4	4
<i>λ</i> / Å	0.71075	0.71075	0.71075
<i>μ</i> (Mo Kα) / mm ⁻¹	1.283	1.278	1.276
<i>ρ</i> _{calc} / g cm ⁻³	1.864	1.856	1.853
<i>R</i> _I ^a	0.0452	0.0452	0.0459
<i>wR</i> ₂ ^b	0.0959	0.0967	0.1016
<i>GOF</i> ^c	0.944	0.962	0.949

(a) $R_1 = \Sigma ||F^0| - |F^c|| / \Sigma |F^0|$ ($I > 2\sigma(I)$). (b) $wR_2 = [\Sigma (w(F^{02} - F^{c2})^2) / \Sigma w(F^{02})^2]^{1/2}$ ($I > 2\sigma(I)$). (c) $GOF = [\Sigma (w(F^{02} - F^{c2})^2) / \Sigma (N^t - N^p)^2]$.

[Cu^{II}(hfac)₂(bisPyTM)]_n			
Empirical formula	C ₂₇ H ₈ Cl ₇ CuF ₁₂ N ₂ O ₄		
<i>F</i> _w / g mol ⁻¹	964.07		
Crystal dimension / mm	0.14 × 0.07 × 0.03		
<i>T</i> / K	130 K	140 K	150 K
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> / Å	15.3404(18)	15.3428(18)	15.3536(19)
<i>b</i> / Å	11.0521(10)	11.0604(10)	11.0690(11)
<i>c</i> / Å	20.930(3)	20.949(3)	20.979(3)
<i>α</i> / °	90	90	90
<i>β</i> / °	102.584(6)	102.478(7)	102.497(6)
<i>γ</i> / °	90	90	90
<i>V</i> / Å ³	3463.3(7)	3471.0(7)	3480.9(7)
<i>Z</i>	4	4	4
<i>λ</i> / Å	0.71075	0.71075	0.71075
<i>μ</i> (Mo Kα) / mm ⁻¹	1.273	1.270	1.266
<i>ρ</i> _{calc} / g cm ⁻³	1.849	1.845	1.839
<i>R</i> _{<i>I</i>} ^a	0.0473	0.0487	0.0515
<i>wR</i> ₂ ^b	0.1029	0.1042	0.1123
<i>GOF</i> ^c	0.965	0.966	0.984

(a) $R_1 = \Sigma ||F^0| - |F^c|| / \Sigma |F^0|$ ($I > 2\sigma(I)$). (b) $wR_2 = [\Sigma (w(F^{02} - F^{c2})^2) / \Sigma w(F^{02})^2]^{1/2}$ ($I > 2\sigma(I)$). (c) $GOF = [\Sigma (w(F^{02} - F^{c2})^2) / \Sigma (N^t - N^p)^2]$.

[Cu^{II}(hfac)₂(bisPyTM)]_n	
Empirical formula	C ₂₇ H ₈ Cl ₇ CuF ₁₂ N ₂ O ₄
<i>F</i> _w / g mol ⁻¹	964.07
Crystal dimension / mm	0.14 × 0.07 × 0.03
<i>T</i> / K	298 K
Crystal system	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>
<i>a</i> / Å	15.566(14)
<i>b</i> / Å	11.161(9)
<i>c</i> / Å	21.302(16)
<i>α</i> / °	90
<i>β</i> / °	102.022(14)
<i>γ</i> / °	90
<i>V</i> / Å ³	3620(5)
<i>Z</i>	4
<i>λ</i> / Å	0.71075
<i>μ</i> (Mo Kα) / mm ⁻¹	1.218
<i>ρ</i> _{calc} / g cm ⁻³	1.769
<i>R</i> _{<i>I</i>} ^a	0.0943
<i>wR</i> ₂ ^b	0.2029
<i>GOF</i> ^c	1.098

(a) $R_1 = \Sigma ||F^0| - |F^c|| / \Sigma |F^0|$ ($I > 2\sigma(I)$). (b) $wR_2 = [\Sigma (w(F^{02} - F^{c2})^2) / \Sigma w(F^{02})^2]^{1/2}$ ($I > 2\sigma(I)$). (c) $GOF = [\Sigma (w(F^{02} - F^{c2})^2) / \Sigma (N^t - N^p)^2]$.

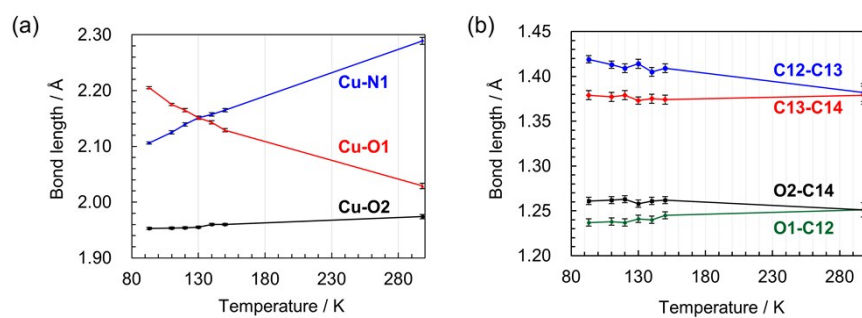


Fig. S1. Temperature dependence of bond lengths with standard deviations (Å) (a) around the Cu^{II} ion and (b) of the O-C-C-C-O moiety in hfac ligands in [Cu^{II}(hfac)₂(bisPyTM)]_n.

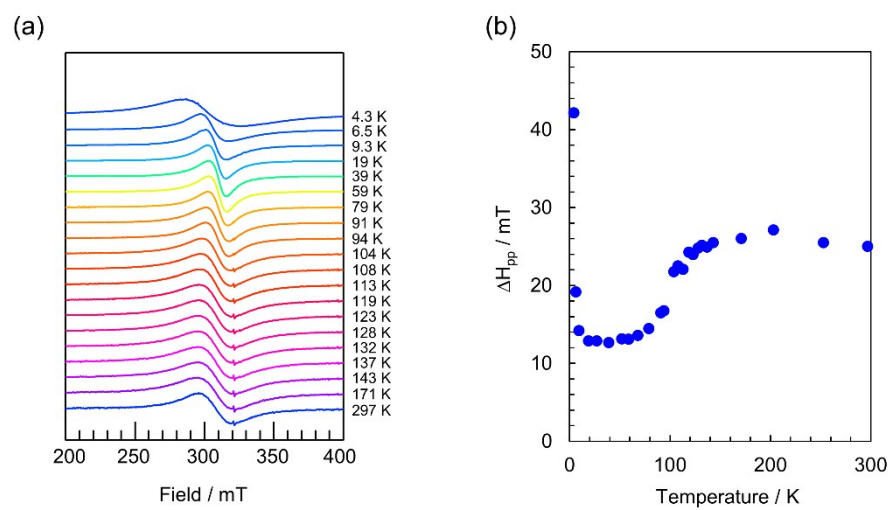


Fig. S2. Temperature-dependent (a) ESR spectra and (b) ΔH_{pp} of $[\text{Cu}^{\text{II}}(\text{hfac})_2(\text{bisPyTM})]_n$.

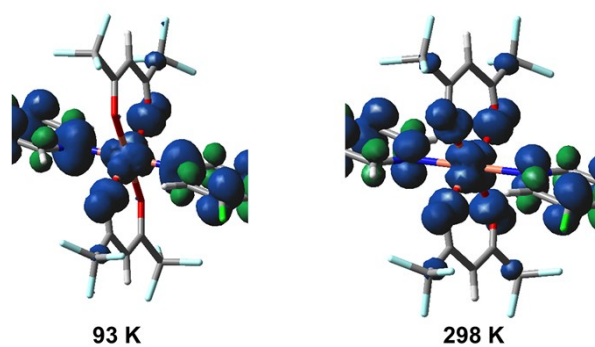


Fig. S3. Calculated spin density distribution around the Cu^{II} ion of a bisPyTM- $\text{Cu}^{\text{II}}(\text{hfac})_2$ -bisPyTM model structure at 93 K and 298 K.

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