

Spin-Transition-Like Behavior on One Side in a Nitroxide-Copper(II)-Nitroxide Triad System

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The ground spin-state of $[\text{Cu}(\text{phpyNO})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2$ was switched between $S_{\text{total}} = 1/2$ and $3/2$ across 175 K. On warming, the space group was changed from $P2_12_12_1$ to $C222_1$ in a single-crystal-to-single-crystal manner, and the transient structure could be monitored by means of the crystallographic analysis. The copper-radical exchange coupling changed from $2J/k_B = -463(3)$ to $+312(6)$ K with rather small $\text{Cu}-\text{O}-\text{N}-\text{C}_{2\text{py}}$ twisting deformation on one side, while practically no distortion occurred on the other.

Introduction

Bistable solid-state materials without any change in chemical composition (spin-crossover for an instance) are of increasing interest for future applications to switching, sensing, memory, display, and other devices.¹ Heterospin systems provide the wide diversity of the characters of paramagnetic centers including the symmetry of the lobes of magnetic orbitals.² Orthogonal arrangement of magnetic orbitals leads to ferromagnetic coupling between the spins.² Copper(II)–nitroxide coordination compounds are the best documented among the $d-\pi$ heterospin systems,³ and it is well-known that axial coordination favors moderate ferromagnetic coupling and equatorial coordination strong anti-ferromagnetic coupling (Scheme 1a). However, the latter has also been reported to show considerable ferromagnetic interaction (Scheme 1b).^{4–6} In the present paper, a new “spin-transition-like” Cu–nitroxide complex will be reported by

using *tert*-butyl 5-phenyl-2-pyridyl nitroxide (phpyNO)⁶ as a paramagnetic chelating ligand.

Results and Discussion

Compound $[\text{Cu}(\text{phpyNO})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2$ (**1**) was prepared by complexation of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ with the known phpyNO ligand.⁶ The spectroscopic and analytic characterizations were satisfactory, and finally the molecular structure was confirmed by X-ray diffraction study (Table 1 and Figure 1). The crystal-structure analysis clarified the structural phase transition occurred, and accordingly we determined the molecular structures at 204 and 94 K. The space group was orthorhombic $C222_1$ at 204 K, and a half of molecule corresponds to an asymmetric unit (Figure 1a). The Cu ion has an octahedral geometry with water molecules at the axial positions. The nitroxide oxygen atom is directly coordinate to the Cu^{2+} ion with the Cu–O distance of 1.945(2) Å. We have proposed the Cu–O–N– $\text{C}_{2\text{py}}$ torsion angle is a convenient indicator^{5,6} for orthogonal geometry between the nitroxide π^* and Cu^{2+} $3d_{x^2-y^2}$ orbitals. This angle is as small as $3.3(4)^\circ$ at 204 K; in other words, the 5-membered chelate is highly planar.

The low-temperature phase at 94 K lost the molecular symmetry in a space group of $P2_12_12_1$. It should be noted that the nitroxide coordination site remains to be equatorial. The Cu–O–N– $\text{C}_{2\text{py}}$ torsion angles are $3.1(4)$ and $31.1(3)^\circ$, indicating that one chelate plane is planar while the other forms an out-of-plane pleated ring (Scheme 2). The geometrical change is relatively small so that the transition took place in a single-crystal-to-single-crystal manner (see below).

Magnetic susceptibility of **1** was measured on a SQUID magnetometer (Figure 2). The $\chi_{\text{mol}}T$ value was 1.47 cm^3

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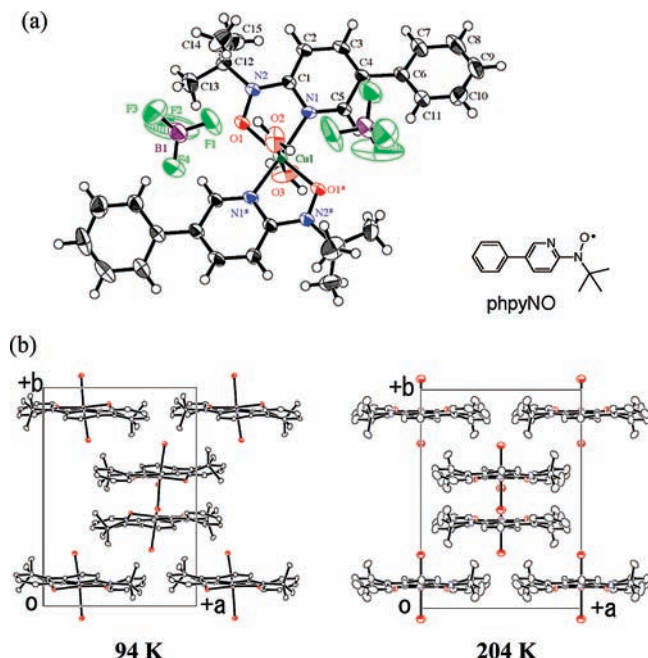


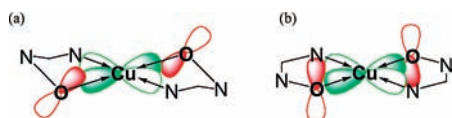
Figure 1. (a) X-ray crystal structure of **1** measured at 204 K. Thermal ellipsoids of non-hydrogen atoms are drawn at the 50% probability levels. Symmetry operation code of * stands for $-x, y, 1/2-z$. Structural formula of phpyNO is also shown (right). (b) Molecular arrangements at 94 K (left) and 204 K (right). Counter anions and hydrogen atoms are omitted.

Table 1. Selected Crystallographic Data for **1**

| | phases | |
|-----------------------------------------|------------------------------|------------------------------|
| | high-temperature phase | low-temperature phase |
| formula | $C_{30}H_{38}B_2CuF_8N_4O_4$ | $C_{30}H_{38}B_2CuF_8N_4O_4$ |
| crystal system | orthorhombic | orthorhombic |
| space group | $C222_1$ | $P2_12_12_1$ |
| $a/\text{\AA}$ | 11.734(7) | 11.256(5) |
| $b/\text{\AA}$ | 16.033(16) | 16.039(12) |
| $c/\text{\AA}$ | 18.492(9) | 18.490(8) |
| $V/\text{\AA}^3$ | 3479(4) | 3338(3) |
| Z | 4 | 4 |
| $d_{\text{calc}}/\text{g cm}^{-3}$ | 1.443 | 1.504 |
| $\mu(\text{Mo K}\alpha)/\text{mm}^{-1}$ | 0.711 | 0.741 |
| R_{int} | 0.074 | 0.091 |
| $R(F)^a$ ($I > 2\sigma(I)$) | 0.0524 | 0.0524 |
| $R_w(F^2)^b$ (all data) | 0.0665 | 0.0619 |
| unique reflections | 3992 | 7619 |
| T/K | 204 | 94 |

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Scheme 1. Orbital Overlap between π^* (N–O) and $3d_{x^2-y^2}$ (Cu) is Present (a) and Absent (b) in [Cu(2-pyridyl nitroxide)₂]-Type Spin Triads



K mol^{-1} at 300 K, which is much larger than the calculated spin-only value of three doublets ($1.13 \text{ cm}^3 \text{ K mol}^{-1}$). Upon cooling, the $\chi_{\text{mol}}T$ value continued to increase, indicating the presence of considerably large ferromagnetic coupling. On further cooling, we can find a distinct spin-transition-like behavior at 175 K. The $\chi_{\text{mol}}T$ value approached the value of one doublet ($0.38 \text{ cm}^3 \text{ K mol}^{-1}$), suggesting that the metal–radical coupling drastically changed to very strongly

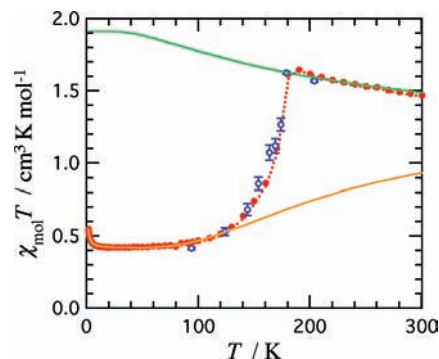
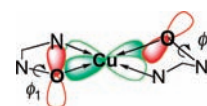


Figure 2. Temperature dependences of $\chi_{\text{mol}}T$ (red circles) for polycrystalline **1**. The applied magnetic fields were 500 Oe. A broken line is drawn only for a guide to the eye. The green and yellow solid lines correspond to the theoretical best fits on the data above 180 K and below 120 K, respectively. See the text for details on the equations and parameters. The blue open circles represent the calculated $\chi_{\text{mol}}T$ value from the Cu–O–N–C_{2py} torsion angle determined by means of X-ray crystallographic analysis.

Scheme 2. Asymmetric Chelate Structure of the Low-Temperature Phase of **1**



antiferromagnetic to form an $S_{\text{total}} = 1/2$ state. The phase transition was found to be completely reversible.

The exchange parameters were estimated by the Heisenberg spin-Hamiltonian, $H = -2J(S_1 \cdot S_2 + S_2 \cdot S_3)$, for the spin-triad system when each molecule is symmetric. The susceptibility is expressed as follows:⁷

$$\chi_{\text{mol}} = \frac{N_A g_{\text{avg}}^2 \mu_B^2}{4k_B T} \frac{\exp(-2J/k_B T) + 1 + 10 \exp(J/k_B T)}{\exp(-2J/k_B T) + 1 + 2 \exp(J/k_B T)}$$

Owing to the monotonic change of the $\chi_{\text{mol}}T$ value in the 180–300 K range, treatment of a variable g factor gave a large statistical deviation, and we had to assume the fixed value of $g_{\text{avg}} = 2.03$, which is reasonable from the known values of related systems.^{5,6,8} The exchange parameter could be estimated as $2J/k_B = +312(6) \text{ K}$.

An unsymmetrical model, $H = -2J_1 S_1 \cdot S_2 - 2J_2 S_2 \cdot S_3$, was applied in the 2–120 K range, which affords the following equation,⁹ with a modification of a Weiss mean-field parameter (θ):

$$\chi_{\text{mol}} = \frac{N_A g_{\text{avg}}^2 \mu_B^2}{4k_B(T - \theta)} \frac{A}{B}$$

with

$$A = \exp(-2(J_{12}^2 + J_{23}^2 - J_{12}J_{23})^{1/2}/k_B T) + 1$$

$$+ 10 \exp((J_{12} + J_{23} - (J_{12}^2 + J_{23}^2 - J_{12}J_{23})^{1/2})/k_B T)$$

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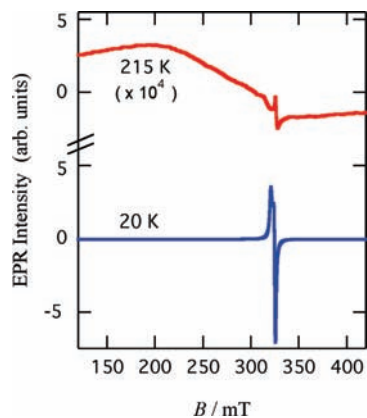


Figure 3. X-Band EPR spectra of **1** measured at 215 K (top) and 20 K (bottom).

and

$$B = \exp(-2(J_{12}^2 + J_{23}^2 - J_{12}J_{23})^{1/2}/k_B T) + 1 \\ + 2 \exp((J_{12} + J_{23} - (J_{12}^2 + J_{23}^2 - J_{12}J_{23})^{1/2})/k_B T)$$

The crystallographic study indicates that one chelate structure was pleated while the other was practically unchanged to remain planar. To reduce possible large statistical errors in the estimation of two J 's, the J_1 is assumed to be constant ($2J_1/k_B = +312$ K), and other parameters were optimized, giving $g_{\text{avg}} = 2.102(2)$, $2J_2/k_B = -463(3)$ K, and $\theta = +0.431(6)$ K. The positive θ implies the presence of intermolecular ferromagnetic interaction, observed as a small $\chi_{\text{mol}}T$ upsurge below 10 K, but it seems to be negligible for the present study. The calculated curves successfully reproduced the experimental data (solid lines in Figure 2).

The variable-temperature X-band electron paramagnetic resonance (EPR) measurements of **1** (Figure 3) were consistent with the SQUID result. The very broad peak was observed at 215 K, which is characteristic of exchange-coupled radical-copper-radical triad systems having $S = 3/2$,¹⁰ and it was difficult to estimate precisely the g value because of the broadness. A very weak and sharp peak was found at 326.6 mT ($g = 2.004$), which can be ascribed to a phpyNO radical impurity. In contrast, a sharp and strong peak due to a doublet species appeared with anisotropic g tensor of copper(II) ion in the low-temperature phase, and the broad band disappeared (Figure 3, bottom). The g_{\parallel} and g_{\perp} values at 20 K were 2.040 (320.9 mT) and 2.010 (325.6 mT), respectively. They seem to be slightly smaller than the usual values for copper(II) compounds. The ground state has an organic radical contribution in addition to the copper(II) spin character. The EPR spectra of high- and low-temperature phases were quite different from each other, and the structural

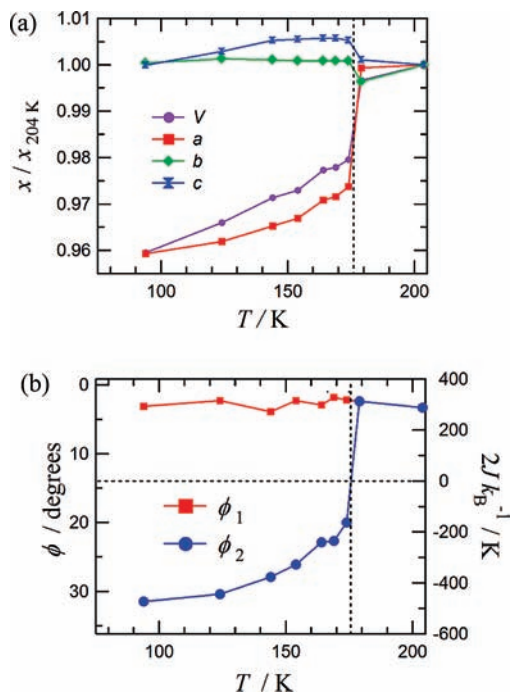


Figure 4. (a) Temperature dependence of the cell parameters of **1**. (b) Temperature dependence of the Cu–O–N–C_{2py} torsion angles (ϕ_1 , red squares, and ϕ_2 , blue circles) and calculated J_1 and J_2 from the linear magneto-structure relation. See the text for details on the equations and parameters. Solid lines are drawn for a guide to the eye.

phase transition accompanied by the change of the magnetic ground states was clearly confirmed.

There have been several reports on the Cu–nitroxide complexes showing spin-transition-like behavior.^{11,12} It has been suggested that the Cu–O bond lengths would change to convert the roles of axial and equatorial coordination sites,^{11,12} which brings about a switch from weak to anti-ferromagnetic interactions (e.g., $2J/hc = -20$ to -240 cm⁻¹ in a [Cu(hfac)₂(pyrazolylnitronyl nitroxide)] derivative¹³). On the other hand, **1** involves the considerably large couplings from the equatorial coordination throughout the phase transition.

Fortunately, the structural phase transition is gradual, and the intermediate structure is monitored as a function of temperature. The cell parameters exhibited abrupt changes at 175 K. The torsion angle (ϕ) around Cu–O–N–C_{2py} can be regarded as a reliable indicator for the plane geometry of chelates; namely, highly planar chelates defined by small ϕ exhibit ferromagnetic coupling.⁵ The Cu–O–N–C_{2py} torsion angles (ϕ_1 and ϕ_2) were tracked as a function of temperature by means of crystal structure determination at any given temperature (Figure 4). Supporting Information, Figure 1S depicts an animated X-ray crystal structure.

The ϕ value can be converted to J from the linear magneto-structure relation empirically proposed: $2J/k_B = a + b|\phi|$ with $a = 440(40)$ K and $b = -35(3)$ K deg⁻¹.^{5c,6} Figure 4b also shows the calculated J_1 and J_2 values. In the intermediate structures, the $\chi_{\text{mol}}T$ values were simulated according to the unsymmetrical model with J_1 and J_2 , and reproduced well the experimental $\chi_{\text{mol}}T$ values (blue circles in Figure 2).

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The proposed magneto-structure relationship holds for the intermediate structures entirely during the phase transition, as well as the terminal structures.

Another example of spin-transition-like Cu–nitroxide complexes, $[\text{Cu}^{2+}(\text{2pyNO}^-)(\text{2pyNO}^*)]_2(\text{BF}_4^-)_2$ (**2**), was reported very recently.¹⁴ In that case, the molecule has four spins and the ground S_{total} was switched between 0 to 2. The two Cu–O–N–C_{2py} distortions are synchronized on both sides, maintaining the molecular symmetry. In contrast, **1** showed a breakdown of the symmetry. The difference may reside in the driving force of the spin transition, in which the entropy term in $\Delta G = \Delta H - T\Delta S$ seems to play a major role. The spin multiplicity is responsible for the number of microstates. The $T\Delta S$ loss of **2** would be substantial when both exchange couplings simultaneously become antiferromagnetic to decrease the spin multiplicity to $S_{\text{total}} = 0$. On the other hand, the spin multiplicity of **1** does not alter (i.e., $S_{\text{total}} = 1/2$), whether antiferromagnetic coupling takes place on one side ($\uparrow\text{---}\uparrow\text{---}\downarrow$) or on both sides ($\uparrow\text{---}\downarrow\text{---}\uparrow$). Practically no gain or loss of the statistical entropy could not compensate another enthalpy cost of atomic displacement. The symmetry was lost in **1**. Thus, the present system is just like entropy-driven spin-crossover systems.^{1,15}

One may point out that the present spin-state change solely by magnetic coupling effects has no relation with spin-crossover. However, the high- and low-spin states are regulated by a balance of electron-pairing and building-up energies, which is in common for the one-centered case (spin-crossover compounds) and the two-centered case (metal-radical chelates). The very gradual structural phase transition is observed in the present study, as well as in another instance,¹⁴ being congruous with the term of a crossover.

Summary

The copper-radical exchange coupling on one side drastically changed from $2J/k_B = +312(6)$ to $-463(3)$ K at 175 K on cooling. Owing to the short distance and effective orbital interaction between the paramagnetic centers when coordinated equatorially, the magnetic couplings are notably large. Furthermore, the chemical composition of **1** did not change, being suitable for solid-state devices. There have been scarce reports on the structure monitored during the phase transition.^{14,16} Thanks to the small structural change, the present study afforded an example of the spin-transition materials which maintain the single-crystalline form.

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Experimental Section

Preparation of $[\text{Cu}(\text{phpyNO})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2$ (1**).** The paramagnetic ligand was prepared according to the literature method.⁶ A mixture of phpyNO (48.3 mg; 0.20 mmol) in 0.5 mL of dichloromethane and $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (34.5 mg; 0.10 mmol) in 0.5 mL of acetonitrile was allowed to stand at 0 °C for one night. The resultant dark purple crystalline solid was collected and washed on a filter, and dried under air. The yield was 38.5 mg (0.051 mmol; 51%). Mp. 126.5–128 °C. Anal. Calcd for $\text{C}_{30}\text{H}_{38}\text{B}_2\text{Cu}_1\text{F}_8\text{N}_4\text{O}_4$: C, 47.67; H, 5.07; N, 7.41%. Found: C, 47.52; H, 5.09; N, 7.58%. IR (neat) 3521, 2985, 1452, 1261, 1122, 1084, 1038, 768, and 698 cm^{-1} .

X-ray Crystallographic Analysis. X-ray diffraction data of **1** were collected on Rigaku R-axis RAPID and Saturn70 CCD diffractometers, respectively, with graphite monochromated $\text{Mo K}\alpha$ ($\lambda = 0.71070$ Å) radiation. The structures were directly solved, and the parameters were refined in the CrystalStructure program package.¹⁷ Numerical absorption correction was used. The thermal displacement parameters of non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at calculated positions, and their parameters were refined as “riding.” Table 1 summarizes the crystallographic data of **1**.

Magnetic Measurements. Magnetic susceptibilities of the polycrystalline samples of **1** were measured on a Quantum Design MPMS SQUID magnetometer at an applied magnetic field of 500 Oe in a temperature range 1.8–300 K. The magnetic response was corrected with diamagnetic blank data of the sample holder obtained separately. The diamagnetic contribution of the sample itself was estimated from Pascal’s constant.

EPR Measurements. EPR spectra were recorded on a JEOL JES-TE300 X-band (9.2 GHz) spectrometer equipped with a Heli-Tran model LTR-3 cryostat (APD Cryogenics) for low-temperature experiments. Saturation effects were carefully removed from the spectra by lowering the microwave power. The specimen in a quartz cell tube was evacuated by an oil rotary pump and then charged about 30 mmHg helium gas for heat exchange.

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Supporting Information Available: CIF files of **1** measured at 94 and 204 K including tables of selected geometrical parameters, and an animation of the phase transition of **1** (QT). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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