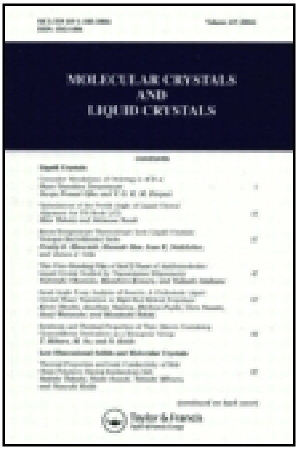

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Synthesis and Magnetic Properties of Bis(Hexafluoroacetylacetonato)Cop Complex with 5-Bromo-1,3-Phenylenebis(N-tert-Butylaminoxyl) as a Bridging Ligand

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Synthesis and Magnetic Properties of Bis(Hexafluoroacetylacetonato)Copper(II) Complex with 5-Bromo-1,3-Phenylenebis(*N*-*tert*-Butylaminoxyl) as a Bridging Ligand

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Bis(hexafluoroacetylacetonato)copper(II), Cu(hfac)$_2$ (= M) reacts with 5-bromo-1,3-phenylenebis(*N*-*tert*-butylaminoxyl), $\mathbf{1}_{\mathrm{Br}}$ to yield a complex of formula $[\mathrm{M}_3\bullet(\mathbf{1}_{\mathrm{Br}})_2]$. The X-ray crystal structure shows that it crystallizes in the space group $P1$, with a = 12.469(2) Å, b = 15.278(2) Å, c = 11.602(2) Å, α = 104.59(1)°, β = 111.86(1)°, γ = 88.32(1)°, and Z = 1. The crystal contains copper(II) trinuclear structure, M-$\mathbf{1}_{\mathrm{Br}}$-M-$\mathbf{1}_{\mathrm{Br}}$-M. The magnetic susceptibility measurements revealed a structural transition at ca. 48 K accompanied by a temperature hystereisis.

Keywords: triplet biradical; trinuclear complex; temperature hysterisis

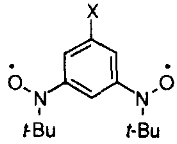
INTRODUCTION

We have introduced a new strategy of constructing extended systems by self-assembly of transition metal ions and high-spin (J_1 > 0) π-conjugated polyaminoxyls as ligands.[1] The dimensionality of the complex and the sign and magnitude of the exchange coupling between the neighboring spins can be readily tuned by this strategy. A *m*-Phenylenebis(*N*-*tert*-butylaminoxyl) derivatives $\mathbf{1}_{\mathrm{X}}$ (X= H, Cl, Br) with a triplet ground state (S = 1), *e.g.*, $\mathbf{1}_{\mathrm{H}}$,[2] would form with coordinatively doubly unsaturated metal ions a 1:1 complex having a 1D infinite chain structure. Since the exchange coupling between the ligands and the directly attached transition metal ions is typically antiferromagnetic [*J*(coordination) << 0] and the 2*p* and 3*d* spins tend to cancel each other out, a residual spin would be established for the repeating unit unless the spin of the letter is unity. Such a 1D array of spins would become an antiferro-, meta-, or ferromagnet depending on the nature of the interchain interaction. Some clusters which contained paramagnetic transition metal ions and nitronylnitroxide derivative was reported previously. [3] We wish to report here the crystal structure and magnetic properties of new trinuclear cluster which contains copper(II) ion and triplet bis(aminoxyl)benzene. [4] This complex exhibits the structural transition at ca. 48 K accompanied by a temperature hystereisis.

EXPERIMENTAL

Synthesis of complex

SCHEME I



$\mathbf{1}_X$ (X = H, Cl, Br)

Bisaminoxyl radical, $\mathbf{1}_{Br}$ (SCHEME I) was synthesized as previously reported. [5] To a solution of 2.25 g (4.54 mmol) of $Cu(hfac)_2$ in a mixture of 10 ml of diethyl ether and 90 ml *n*-heptane was added 0.994 g (3.02 mmol) of 5-bromo-1,3-phenylenebis(*N*-*tert*-butylaminoxyl) ($\mathbf{1}_{Br}$) in 20 ml of methylenechloride and 10 ml of diethyl ether. The solution was concentrated under reduced pressure to ca. 10 ml to give 2.50 g (1.20 mmol, 79.5 %) of dark-green powder of $[Cu(hfac)_2]_3 \cdot (\mathbf{1}_{Br})_2$ from a dark-green solution.

X-ray Crystal Structure Analysis

A dark-green block single crystal of complex $[Cu(hfac)_2]_3 \cdot (\mathbf{1}_{Br})_2$ in approximate dimensions 0.3 × 0.4 × 0.9 mm^3 was mounted on a glass fiber. Diffraction data were obtained with 2θ (max.) = 55.0 ° at 23 °C. The structure was solved in *P*1 to give the crystal data: $Cu_3Br_2N_4O_{16}C_{58}H_{48}F_{36}$, MW = 2091.42, triclinic, space group *P*1 (No. 1), a = 12.469(2) Å, b = 15.278(2) Å, c = 11.602(2) Å, α = 104.59(1)°, β = 111.86(1)°, γ = 88.32(1)°, V = 1980.0(6)

Å^3, and $D_X = 1.754$ g/cm^3 for $Z = 1$. All non-hydrogen atoms were refined anisotropically. Refinement converged at $R = 0.088$ and $R_w = 0.077$ for 5918 unique reflections, with $I > 0.5\ \sigma(I)$ and 1072 variables. GOF = 2.94.

Magnetic Susceptibility Measurement

Magnetic susceptibility was measured on a Quantum Design MPMS5S SQUID susceptometer. A microcrystalline sample (ca. 30 mg) of $[\mathrm{Cu(hfac)_2}]_3 \bullet (\mathbf{1}_{\mathrm{Br}})_2$ was place in a Japanese pharmacopoeia #5 gel capsule. The background data of the cell was measured separately and subtracted from the sample-in-cell data.

RESULTS AND DISCUSSION

Crystal structure of $[\mathrm{Cu(hfac)_2}]_3 \bullet (\mathbf{1}_{\mathrm{Br}})_2$ is shown in FIGURE 1.

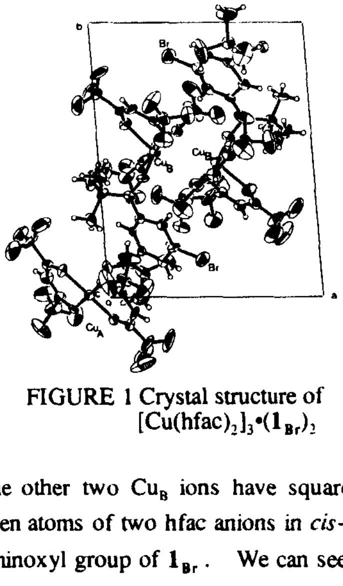


FIGURE 1 Crystal structure of $[\mathrm{Cu(hfac)_2}]_3 \bullet (\mathbf{1}_{\mathrm{Br}})_2$

Crystal involves three Cu ions crystallographically independent, which are categorized to two types, Cu$_A$ and Cu$_B$. (SCHEME II) One of these Cu ions, Cu$_A$ has an octahedral coordination with the four oxygen atoms of two hfac anions and the two oxygen atoms of the aminoxyl groups which coordinated *trans*- configuration of two different molecules of $\mathbf{1}_{\mathrm{Br}}$.

The other two Cu$_B$ ions have square pyramidal coordinations with four oxygen atoms of two hfac anions in *cis*-disposition and the one oxygen atom of aminoxyl group of $\mathbf{1}_{\mathrm{Br}}$. We can see the trinuclear copper(II) structure of Cu$_B$-$\mathbf{1}_{\mathrm{Br}}$-Cu$_A$-$\mathbf{1}_{\mathrm{Br}}$-Cu$_B$. The Cu$_A$ -- O distance are 1.9 - 2.0 Å for the oxygen atoms of hfac and 2.4 Å for the oxygen atoms of aminoxyl groups. The expected interactions between Cu$_A$ and NO group are ferromagnetic, because the $3d_{x^2-y^2}$ orbital of Cu(II) and $2p$ orbital of aminoxyl have no overlap in the coordination bond. [6] On the other hand, the Cu_B -- O distance are 1.9 - 1.96 Å for the oxygen atoms of aminoxyl groups, and strong antiferromagnetic interaction is expected because of a considerable overlap between the $3d_{x^2-y^2}$ orbital of Cu(II) and 2*p* orbital of aminoxyl. [7] The two Cu_B ions are not crystallographically equivalent, but the coordinations are very similar. The Cu_B-Cu_B distance between neighboring trinuclear clusters is 3.82 Å, for which negligibly small interaction is expected.

The paramagnetic susceptibility of unoriented microcrystalline samples of $[Cu(hfac)_2]_3 \cdot (\mathbf{1}_{Br})_2$ was investigated in the temperature range 2 - 300 K. The temperature dependence of the μ_{eff} values obtained in a field of 50000 Oe are given in FIGURE 2.

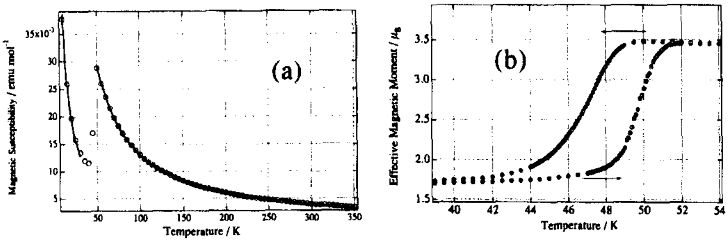
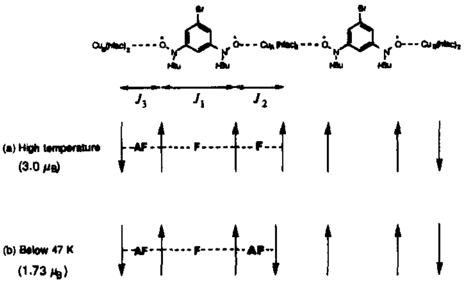


FIGURE 2 (a) χ_m vursus T plot for $[Cu(hfac)_2]_3 \cdot (\mathbf{1}_{Br})_2$ measured at a magnetic field of 50000 Oe.
(b) Observed μ_{eff} versus *T* plots in the temperature range 39 - 54 K. Solid lines are calculated on Curie-Weiss law (10 - 30 K) and the trinuclear complex model (50 - 350 K).

The μ_{eff} value of 3.08 μ_B at 350 K is equal to the theoretical value of 3.0 μ_B for three non-interacted paramagnetic 1/2 spins. Then the μ_{eff} value increased with decreasing temperature and showed a sharp decrease at 47 K. The μ_{eff} value change to 1.75 μ_B which value is correspond to the theoretical value of 1.73 μ_B for one paramagnetic 1/2 spin. When the measurement was carried out in raising temperature the jump of μ_{eff} value showed at 50 K. The μ_{eff} value near the room temperature is consistent with the magnetic model which have ferromagnetic interaction between Cu_A-$\mathbf{1}_{Br}$ and antiferromagnetic interaction between Cu_B-$\mathbf{1}_{Br}$. This magnetic structure is expected from the crystal structure as shown in SCHEME II(a). Due to the strong antiferromagnetic exchange interactions between Cu_B-$\mathbf{1}_{Br}$, only three spins are magnetically active. For the coordination of Cu_B-$\mathbf{1}_{Br}$, a large antiferromagnetic interaction of J >372 K can be expected. [7] For a system consisting of three spins arranged in a linear fashion as in the unit of NO -- Cu_A -- NO in high temperature region, the spin Hamiltonian is written as $H = -2J_2(S_{NO} \cdot S_{Cu} + S_{Cu} \cdot S_{NO})$, the molar susceptibility is given by eq. (1), where P is purity factor and other symbols have their usual meaning. For χ_m versus T plot, best fit parameters were $P = 0.980 \pm 0.01$ and $J_2 = 30.0$ K ± 0.43 and $g = 2.006$ in a temperature range of 55 - 350 K.

$$\chi = \frac{PNg^2\mu_B^2}{kT} \frac{10 + \exp(-J_2 / kT) + \exp(-3J_2 / kT)}{2 + \exp(-J_2 / kT) + \exp(-3J_2 / kT)} \qquad (1)$$

SCHEME II



In the low temperature region, the magnetic susceptibility behaves as a paramagnetic spin $S = 1/2$, this result indicates that one of these two ferromagnetic interactions change to antiferromagnetic interaction. Application of Curie-Weiss law to the temperature dependence of χ_{mol} gave $C = 0.385 \pm 0.04$ emu K mol^{-1} and $\theta = 0.01 \pm 0.00$ K in the range of 10 - 30 K. At room temperature, the coordinations of two aminoxyl radicals to the Cu_A ion are almost equivalent (SCHEME II-(a)). However, when temperature is decreased, it is assumed that one of this coordination length is shortened and the other is lengthened, and this shortened one would change interaction to antiferromagnetic from ferromagnetic (SCHEME II-(b)).

CONCLUSION

It is concluded that trinuclear copper(II) chain consisting of three different interaction ferro- (J_1, $J_2 > 0$) and antiferromagnetic ($J_3 << 0$) couplings has been realized. The exchange interaction value between Cu_A and NO group was estimated by linear three spin analysis. A structural transition occurred at ca. 48 K, the transition was assumed that the one of ferromagnetic interactions between three linear spins (NO -- Cu_A -- NO) changes to antiferomagnetic.

Acknowledgments

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