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Structures and Magnetic Properties of the Complexes Made up by CU(HFAC)$_2$ and Bisnitroxide Radical Derivatives

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The trinuclear complexes are synthesized by Cu(hfac)$_2$ and 5-substituted-1,3-bis(*N-tert*-butylaminoxyl)benzene (**1**$_X$; X= H, F and Cl), π-conjugated bis-aminoxyl radical with a triplet ground state[1]. It is found that the [Cu(hfac)$_2$]$_3$(**1**$_X$)$_2$ complexes are paramagnetic and have a trinuclear cluster crystal structure. They have symmetric structure whereas the complex with X = Br is asymmetric.[2] While the complex with X = Br shows a ferromagnetic interaction within central three spins (J/k_B = 33.9 K) and exhibits a first-order type structural transition around 48 K and below this temperature it has an S=1/2 ground state, the complexes with X = F and Cl do not show any transformation. The intracluster exchanges for X = F and Cl are characterized by larger exchange parameters J/k_B = 40.5 K and 41.6 K, respectively. They keep ferromagnetic interaction within the trimers down to lowest temperatures and their ground states have S = 3/2.

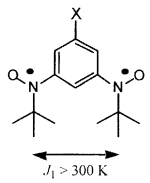
Keywords molecule based magnet; bisnitroxide; copper complex; trinuclear complex; ferromagnetic interaction

INTRODUCTION

We have recently developed a strategy of constructing extended systems by self-assembly of transition metal ions with high-spin ($J_1 > 0$) π-conjugated polyaminoxyls as ligands. 5-substituted-1,3-bis(*N-tert*-butyl-*N*-aminoxyl)benzene (**1**$_X$, SCHEME 1) with a triplet ground state, for example, formed with Mn(hfac)$_2$ (hfac = hexafluoroacetylacetonato) a polymeric one-dimensional ferrimagnetic alternate chain.[3] An assembly of these chains became a metamagnets below 5.5 K and 5.3 K (X = H and F), became a

ferrimagnets below 4.8 K and 5.3 K (X = Cl and Br) by virtue of a weak interchain interaction. During the course of our systematic attempts to obtain low-dimensional magnetic materials using $\mathbf{1}_X$ (X = H, F, Cl and Br) and transition metal ions (Mn^{2+} and Cu^{2+}), we obtained a compound of formula $[Cu(hfac)_2]_3\bullet(\mathbf{1}_X)_2$. We have reported the magnetic property and crystal structure of the seven-spins system trinuclear complex of formula $[Cu(hfac)_2]_3\bullet(\mathbf{1}_{Br})_2$ for which a similarly strong intramolecular exchange interaction (J_1/k_B > 300 K,[1] where J_1 is defined as an intramolecular exchange coupling parameter in the Heisenberg Hamiltonian $H = -2J'S_a\bullet S_b$ for the NO• group spin operators S_a and S_b of the biradical molecule) which exhibits structural transition at *ca.* 48 K accompanied by a temperature hysteresis.[2] In this paper, we report the structures and magnetic behavior of complexes between $Cu(hfac)_2$ ion and $\mathbf{1}_X$ (X = F and Cl).

SCHEME 1



$\mathbf{1}_X$

EXPERIMENTAL

A CH_2Cl_2 solution of $\mathbf{1}_X$ (X = H, F and Cl) was added to a suspension of 1.5 times molar of $Cu(hfac)_2$ in hexane and the mixture was concentrated under reduced pressure until some dark-green crystals of $[Cu(hfac)_2]_3\bullet(\mathbf{1}_X)_2$ precipitate out. For X-ray structure analysis, the dark-green single crystals were grown from the mixture of CH_2Cl_2 and hexane at –30 °C.

RESULTS AND DISCUSSION

Structures

X-ray crystallographic analysis has revealed that all the complexes crystallize in a trinuclear cluster structure. Three isostructural complexes (X = H, F and Cl) have an inversion center at their central Cu_A ions, whereas

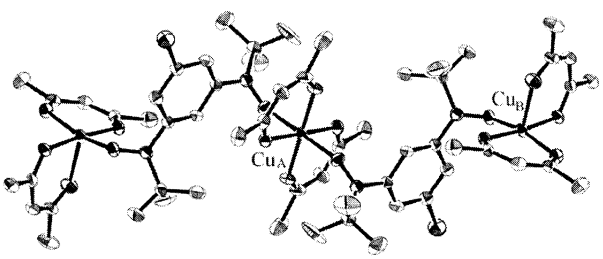


FIGURE 1 Structure of $[Cu(hfac)_2]_3\bullet(\mathbf{1}_{Cl})_2$. Hydrogen and fluorine atoms are omitted for clarity.

$[Cu(hfac)_2]_3 \bullet (\mathbf{1}_{Br})_2$ has an asymmetric structure. The ORTEP view of $[Cu(hfac)_2]_3 \bullet (\mathbf{1}_{Cl})_2$ is given in FIGURE 1.[4]

The coordination around the central Cu_A ion is arranged octahedral. The axial bonds to $\mathbf{1}_X$ are much longer than the equatorial bonds. Bond distances and angles in the hfac$^-$ are normal. The selected bond lengths and intercluster contacts are listed in TABLE 1.

TABLE 1 Selected bond and contact lengths (Å) for the complexes.

	X=H	F	Cl
Cu_A - •ON	2.411(9)	2.357(5)	2.402(6)
Cu_B - •ON	1.919(9)	1.870(4)	1.950(6)
Intercluster Cu-Cu contact	4.812(3)	4.374(2)	3.843(3)

The expected exchange interaction between Cu_A and the aminoxyl groups of $\mathbf{1}_X$ is ferromagnetic ($J_2>0$) because the $3d_{x^2-y^2}$ orbital of Cu_A and the $2p$ orbital of aminoxyl group have no overlap in the coordination bond.[5] On the other hand, the nitroxide of $\mathbf{1}_X$ occupies an equatorial position in the square pyramid of other two Cu_B. For these coordination bonds, a strong antiferromagnetic interaction is expected because of a considerable overlap between the $3d_{x^2-y^2}$ orbital of Cu_B and $2p$ orbital of the aminoxyl groups. The intermolecular Cu-Cu lengths are longer than at least 3.8 Å, for which negligibly small interactions are expected.

Magnetic properties

The field dependence of magnetization was measured at the temperature 1.8 K. In contrast with $[Cu(hfac)_2]_3 \bullet (\mathbf{1}_{Br})_2$, other three complexes do not exhibit any structural transition. The magnetization curves of two complexes are shown in FIGURE 2. They are in good agreement with the theoretical curves are represented by the Brillouin function with S taken 3/2. These results indicate that the ground state of these compounds answers $S = 3/2$ and the spins are aligned ferromagnetically. The μ_{eff} versus T curve for the complex $[Cu(hfac)_2]_3 \bullet (\mathbf{1}_F)_2$ is displayed in FIGURE 2. That for X = F and Cl has similar behavior. The high temperature values of μ_{eff} after the diamagnetic corrections were taken into account are 3.17 and 3.05 μ_B for X = F and Cl, respectively. These values are equal to the theoretical value for three non-interacting paramagnetic spins. The μ_B values increase with decreasing temperature. The numerical fit to the experimental $\chi_m T$ variation shown in FIGURE 2 with the use of a seven spin Heisenberg Hamiltonian was unsuccessful, since the parameters associated with the strong antiferromagnetic coupling between Cu_B and NO diverged.

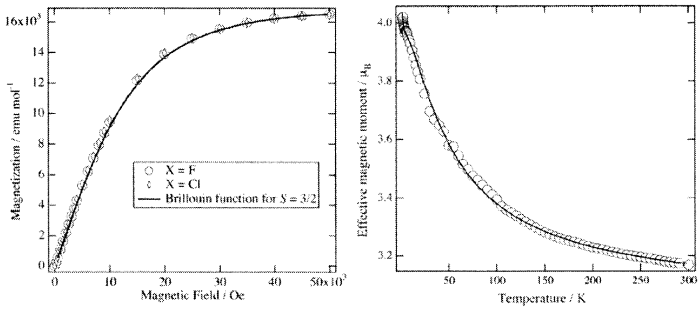


FIGURE 2 The magnetization curves for X = F and Cl (T = 1.8 K) and μ_{eff} versus T for X = F (applied field = 0.5 tesla).

Therefore the theoretical fit was performed by the equation for a three-spin system, Eq. 1. Where $\gamma = J_2/J_2'$, and the other symbols indicate usual meanings. The intercluster interaction was taken into account by introducing a mean field correction parameter λ as Eq.2. Note, in these compounds the contribution into the susceptibility from diamagnetic ions is substantial (*ca.* 35 % at 300 K). The Eq. 1 includes therefore a term $(\chi T)_{dia}$ which takes into account this contribution.

$$\chi = P\frac{Ng^2\mu_B^2}{4kT}\frac{10+\{1+\exp(-2J_2/kT)\}\exp\{-J_2(2\gamma-1)/kT\}}{2+\{1+\exp(-2J_2/kT)\}\exp\{-J_2(2\gamma-1)/kT\}} \quad \text{(Eq.1)}$$

$$\chi_m T = \frac{1}{(\chi_0 T)^{-1}+\lambda/T} + (\chi T)_{dia} \quad \text{(Eq.2)}$$

In the fitting process, γ value converged to unity, which indicates that $J_2 \approx J_2'$, *i.e.* both the complexes can be considered as uniform trimer spin systems (γ = 1). Unfortunately, the magnetically pure sample of the compound X = H could not obtain because of the tendency toward an isomorphism. The exchange parameters thus obtained are listed in TABLE 2.

TABLE 2 The fitting parameters of $[Cu(hfac)_2]_3\bullet(\mathbf{1}_X)_2$

	X = F	X = Cl
J_2/k_B	40.5 ± 0.8 K	41.6 ± 0.8 K
λ	0.095 ± 0.008	0.12 ± 0.01
χ_{dia}(fitted)	1653 × 10^{-6}	1376 × 10^{-6}

They show that these compounds behave as paramagnetic trinuclear cluster complexes with a ferromagnetic intercluster interaction. As compared with

the bromine complex, the intercluster exchange parameters are larger in these complexes. Taking into account shorter coordination bonds in these compounds, this observation is reasonable. Due to this circumstance, the overlap between the magnetic orbitals is more considerable for X = F and Cl. As it is expected from the coordination environments of copper(II) and the nitroxide radicals there is a weak ferromagnetic interaction between them. The positivity of this exchange can hence explain the low temperature values of μ_{eff}. Without this intercluster interaction μ_{eff} must reach the theoretical value 3.87 μ_B at low temperature.

In summary, it is found that the $[Cu(hfac)_2]_3 \bullet (\mathbf{1}_X)_2$ complexes are paramagnetic and have a trinuclear cluster crystal structure. The complexes with X = F and Cl do not show any transformation while the complex with X = Br exhibits structural transition around 48 K. The intracluster exchanges for X = F and Cl are characterized as $J_2 / k_B = 40.5 \pm 0.8$ K and 41.6 ± 0.8 K, respectively. They keep ferromagnetic interaction within the trimers down to lowest temperatures and their ground states have $S = 3/2$.

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G.O.F.= 5.31. For X=Cl; a= 12.505(4)Å, b= 15.402(4)Å, c= 11.567(3)Å, α= 104.36(2)°, β= 112.16(2)°, γ= 88.36(3)°, V= 1993(1)Å^3, R= 0.070, R_w= 0.079 and G.O.F.= 2.45.

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