Syntheses, Crystal Structures, and Magnetic Properties of a Stable Aminoxyl Radical and Its Copper(II) Complex

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A novel aminoxyl radical 4-(*N*-adamantanyloxyamino)-3,5-dichloropyridine (**1**), its hydroxylamine precursor (**2**) and copper(II) complex **3** with **1** were prepared and structurally characterized. The crystal structures of **1** and **3** showed the radical plane twists from pyridine ring. The density functional theory (DFT) calculation revealed that most of the spin (95.1%) locates on the radical group, while the pyridine nitrogen atom carries 0.4% spin. Temperature dependence of the magnetic susceptibilities (2–300 K) of **3** indicated intramolecular interaction between radical and copper(II) ion is ferromagnetic.

Hetero-spin systems have attracted a great deal of attention for their intrinsically interesting electronic structures and in particular as candidates of hybrid metal–organic magnetic materials. As the organic spin-active component, carbenes[1] and many kinds of organic radicals such as aminoxyls,[2] nitroxides,[3] and verdazyl radicals[4] as well as TCNE and TCNQ[5] radical anions, have been developed. For the construction of magnetic materials, a basic requirement for the radicals is that they must be stable enough to be used as building blocks. However, most of the aminoxyl radicals[2] have poor thermal stabilities due to high reactivity, which avoids the wide usage in complexation with transition-metal ions. In this paper, we report a novel organic radical which has high thermal stability.

Hydroxylamine, the precursor of radical, was prepared by coupling of nitrosoadamantane[6] with 3,5-dichloropyridyllithium (obtained in situ from a mixture of 3,5-dichloropyridine, diisopropylamine, and *n*-butyllithium) in THF solution below −70 °C.[7] Recrystallization from dichloromethane and hexane yielded hydroxylamine (**2**) as colorless single crystals. Oxidation of hydroxylamine by freshly prepared Ag_2O in ether followed by evaporation gave radical **1** as orange crystals with excellent yield. Single crystals suitable for X-ray analysis were obtained from slow evaporation of radical solution in methanol and water.[8] Slow evaporation of 1:2 (molar ratio) mixture of $Cu(hfac)_2$ and **1** in ether and hexane yielded yellowish-green prisms **3**.[9] Compound **1** and **3** crystallized in the triclinic space group $P\bar{1}$. The crystal structures of **1** and **3** are shown in Figure 1. Two crystallographically independent molecules are found in the asymmetric unit of **1**. The radical plane in each molecule is twisted from the pyridine ring, where the dihedral angle between O1–N2–C3 and C1–C3–C5 and that between O2–N4–C30 and C24–C25–C30 (not shown in Figure 1) are 75.93 and 86.68°, respectively. The bond angles around radical nitrogens (C3–N2–O1 = 115.8(4), C3–N2–C6 = 123.8(4), and O1–N2–C6 = 120.3(4)° for N2 and C30–N4–O2 = 116.4(4), C27–N4–C30 = 123.5(4), and O2–N4–C27 = 120.2(4)° for N4) and bond lengths of N2–O1 = 1.291(6) and N4–O2 = 1.278(6) Å indicate that the radical nitrogen is in an sp^2 hybrid state.

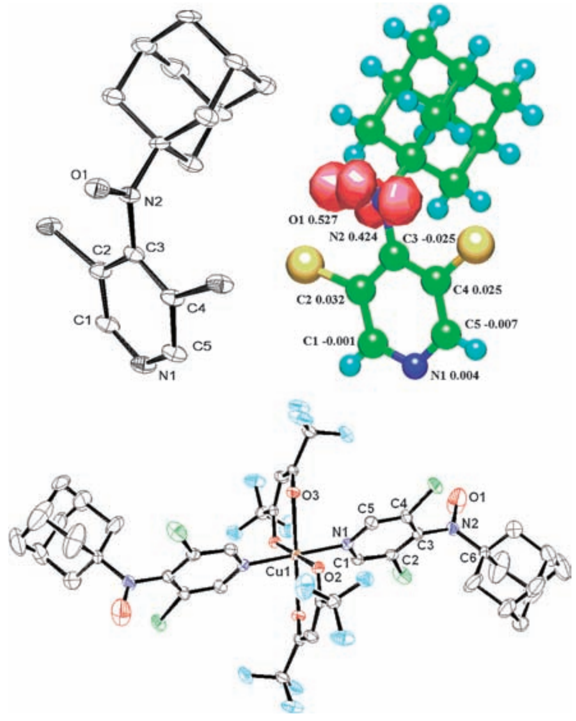

Figure 1. ORTEP drawing of the molecular structures for **1** (upper left) and **3** (bottom) showing 50% probabilities ellipsoids. Hydrogen atoms are omitted for clarity. The upper right shows the spin densities in radical **1**. The large red balls represent the positive spin densities. Only one of the two crystallographically independent molecules in **1** is shown here, because the two independent molecules have similar structures and similar spin densities each other.

Complex **3** has a trans configuration. The Cu^{II} atom is located at the crystallographic inversion center. The bond lengths around Cu^{II} are Cu1–O2 = 1.946(3), Cu1–N1 = 2.044(4), and Cu1–O3 = 2.294(3) Å. The dihedral angle between radical plane (C3–N2–O1) and pyridine ring is 84.66°, which lowers the spin polarization from radical moiety to two pyridine rings.

DFT (B3LYP/6-31G*) calculation was performed for the radical molecule **1**.[10] The Z-matrix was generated from X-ray crystal structure directly and fixed during calculation without geometry optimization. The Mulliken spin densities of selected atoms in one crystallographic-independent molecule are shown in Figure 1 (two independent molecules have similar spin density contribution). Radical oxygen atom carries 52.7% of the radical spin while the spin density at radical nitrogen atom is 42.4%,

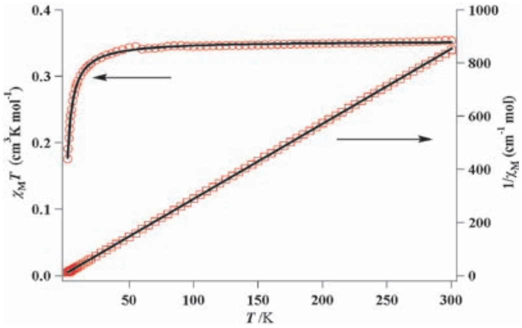

Figure 2. $\chi_M T$ vs. T (left) and $1/\chi_M$ vs. T (right) plots of **1**.

which indicates the radical group carries 95.1% of the spin. It is found the atoms of pyridine ring carry spins with alternate signs. The spin density at pyridine nitrogen atom is 0.4%, which can generate ferromagnetic interaction between radical and Cu^{II} ion in **3** owing to the magnetic orbital orthogonality.[2c] The low spin density at pyridine nitrogen atom might be due to the two chloro and adamantyl groups, which leads to large dihedral angle between radical plane and pyridine ring and lowering of the spin polarization effect from radical to pyridine ring.

The magnetic susceptibility of **1** and **3** were measured in 2.0–300 K range at 0.5 T field and were plotted as $\chi_M T$ vs. T in Figures 2 and 3, respectively. The $\chi_M T$ value of **1** at 300 K is 0.354 cm^3 K mol^{-1}, satisfied with the expected one for an isolated spin with $S = 1/2$. The $\chi_M T$ values in the range of 300–50 K were almost kept constant, which indicates the magnetic interaction between radical molecules in solid state is very weak. The fit of $1/\chi_M$ vs. T following Curie–Weiss law yielded $C = 0.354(1)$ cm^3 K mol^{-1}, $\theta = -2.1(1)$ K (Figure 2), which suggests the weak intermolecular antiferromagnetic interaction from the intermolecular short contacts between O1–H1B′ and O2–H24A′, etc.

The $\chi_M T$ value of **3** at 300 K is 1.12 cm^3 K mol^{-1}, in good agreement with the theoretical one (1.13 cm^3 K mol^{-1}) calculated for the three isolated spins with $S = 1/2$ in terms of the spin-only equation. As the temperature lowered, the $\chi_M T$ value increases slightly to 1.17 cm^3 K mol^{-1} at 50 K. Below 50 K, $\chi_M T$ value increases rapidly to reach a maximum as 1.44 cm^3 K mol^{-1} at 3 K, followed by a slight drop to 1.42 cm^3 K mol^{-1} at 2 K. This behavior indicates the intra- and intermolecular magnetic interaction are ferro- and antiferromagnetic, respectively. The $\chi_M T$ plot of **3** was analyzed quantitatively based on linear three spin model, R$_1$–Cu–R$_2$, $H = -2J(S_1S_{Cu} + S_2S_{Cu})$. The equation for three spins with $S_1 = S_2 = S_{Cu} = 1/2$ was fitted to the experimental data by the least-squares method.[2] The best fit gives $J/k_B = 4.02(7)$ K, $g = 2.005(1)$, and $\theta = -0.53(1)$ K. The theoretical curve is represented by a solid line in Figure 3.

Most of aminoxyl radicals are difficult to be handled and can be used only as solution from preparation reaction without isolation. In our work, radical **1** has high thermal stability. The melting point of **1** is 141–142 °C.[11] The solutions of radical in normal organic solvents are stable over months at room temperature. The radical crystals can be easily obtained from cooling or slow evaporation of the concentrated solution. Such stability may be ascribed to the presence of the adamantyl and chloro groups. Further studies are in progress in our group.

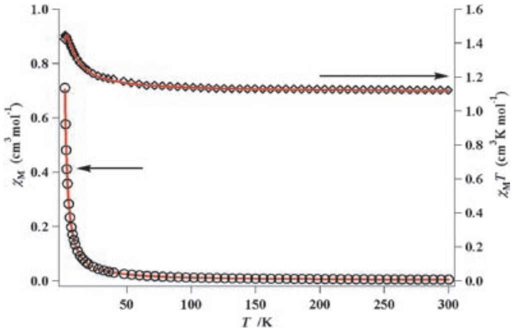

Figure 3. χ_M vs. T (left) and $\chi_M T$ vs. T (right) plots of **3**.

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References and Notes

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7 To a mixture of 0.8 mL of diisopropylamine, 3.6 mL of *n*-butyllithium (1.6 M) in 5 mL of dry THF was added 0.890 g of 3,5-dichloropyridine in 20 mL of THF under dry nitrogen atmosphere. The mixture was kept below −70 °C for 30 min. and quenched with 0.582 g 1-nitrosoadamantane in 55-mL THF. Usual workup yielded 0.665-g of hydroxylamine (**2**) (60.2%). Mp 222–223 °C (decomp.). Elementary analysis: Calcd for $C_{15}H_{18}Cl_2N_2O$: C, 57.52; H, 5.79; N, 8.84%. Found: C, 57.55; H, 5.72; N, 8.95%.

8 To a solution of 100 mg of **2** in 30 mL of ether was added 200 mg of fresh-prepared Ag_2O. The mixture was filtered after consumption of **2**. Evaporation of orange solution yielded **1** as needle crystals (96 mg, 96%). Mp 141–142 °C. Elementary analysis: Calcd for $C_{15}H_{17}Cl_2N_2O$: C, 57.70; H, 5.49; N, 8.97%. Found: C, 57.76; H, 5.41; N, 8.97%. Crystal data for **1**, triclinic, $P\bar{1}$, $a = 6.997(2)$, $b = 13.186(3)$, $c = 18.675(4)$ Å, $\alpha = 104.906(5)$, $\beta = 92.334(4)$, $\gamma = 105.037(4)°$, $V = 1426.3(6)$ Å^3, $T = 293$ K, $Z = 4$, $R(Rw) = 0.1122(0.2591)$, $GOF = 1.087$ for 4103 unique reflections with $I > 2\sigma(I)$ and 361 parameters. Crystallographic data have been deposited with CCDC No. 667903 under http://www.ccdc.cam.ac.uk.

9 Slow evaporation of a mixture of 105 mg of **1** and 86.3 mg of $Cu(hfac)_2(H_2O)_x$ in 10 mL of ether and 20 mL of hexane yielded 104.3 mg of yellowish green prism crystals (54%). Elementary analysis: Calcd for $C_{40}H_{36}Cl_4CuF_{12}N_4O_6$: C, 43.59; H, 3.29; N, 5.08%. Found: C, 43.44; H, 3.42; N, 5.15%. Crystal data for **3**, triclinic, $P\bar{1}$, $a = 8.207(1)$, $b = 10.213(2)$, $c = 14.360(2)$ Å, $\alpha = 72.422(3)$, $\beta = 81.118(3)$, $\gamma = 71.065(3)°$, $V = 1083.2(3)$ Å^3, $T = 293$ K, $Z = 1$, $R(Rw) = 0.075(0.204)$, $GOF = 1.439$ for 4717 unique reflections with $I > 2\sigma(I)$ and 308 parameters. Crystallographic data have been deposited with CCDC No. 667904 under http://www.ccdc.cam.ac.uk.

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11 Melting point is also confirmed by DSC and TG measurements. Decomposition temperature is ca. 145 °C.