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Strong Ferromagnetic Exchange Couplings in Copper(II) and Nickel(II) Complexes with a Paramagnetic Tridentate Chelate Ligand, 2,2′-Bipyridin-6-yl *tert*-Butyl Nitroxide

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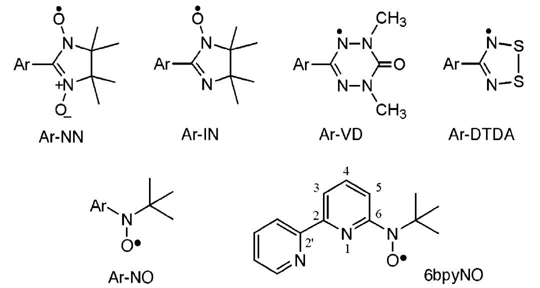
Metal-radical hybrid solids have been well investigated toward molecule-based magnets.[1] Various 2-pyridyl-substituted ligands containing paramagnetic nitronyl nitroxide (NN),[2] imino nitroxide (IN),[3] oxoverdazyl (VD),[4] and dithiadiazolyl (DTDA)[5] groups have been known to form chelate rings where a radical center is directly bonded to the metal ion (Chart 1). Herein we propose 2-azaaromatic *tert*-butyl nitroxide (ArNO; NO stands for the *tert*-butyl nitroxide group) radicals as a paramagnetic chelating ligand, but such reports have been missing in the literature. Heteroaromatic rings are known to have a weaker stabilizing effect than phenyl, as indicated by the fact that intact pyridyl-NOs are unisolable.[6] A new paramagnetic ligand, 2,2′-bipyridin-6-yl *tert*-butyl nitroxide (6bpyNO) is a synthetic target, whose stability would be improved owing to an additional aromatic ring. Furthermore, the NO group has some advantage. The spin density on the ligating O atom of ArNO is assumed to be almost twice as large as that of the other conventional radicals such as ArNN,[7] because of the almost half size of the spin-delocalizable π-conjugation in the radical groups (which also leads to the undesired instability of ArNO). Magnetic exchange coupling is proportional to the spin densities at the interacting atoms.[8] Thus, ArNO radicals are promising to bestow stronger exchange coupling to metal-radical hybrid solids.

Ligand 6bpyNO was prepared from 6-bromo-2,2′-bipyridine[9] according to the conventional method.[10,11] We found that 6bpyNO was sufficiently stable under ambient conditions. No decomposition has been observed for a few months when stored in a refrigerator. Copper(II) and nickel(II) complexes of 6bpyNO were obtained by mixing with a stoichiometric amount of metal salts in methanol.[12]

We successfully determined the crystal structures of $[\mathrm{Cu^{II}(6bpyNO)Cl_2}]$ (**1**) and $[\mathrm{Ni^{II}(6bpyNO)_2](PF_6)_2}$ (**2**) as shown in Figure 1.[13] The tridentate 6bpyNO was confirmed to work as a α,α′,α″-terpyridine-type chelate ligand. The $\mathrm{Cu^{II}}$ ion in **1** was pentacoordinated with 6bpyNO and two chloride anions. One axial position was occupied by Cl2 with the distance of 2.414(2) Å, which is longer than that of Cl1 (2.201(2) Å). The other axial site was vacant, leading to a pyramidalization of the copper basal plane; the N2−Cu1−Cl1 and O1−Cu1−N1 angles were 157.04(5) and 153.33(6)°, respectively. The chelate ring involving O1 and Cu1 was highly planar as indicated with the C10−N3−O1−Cu1 torsion angle of 10.7(2)°. We have proposed that the geometrical parameter of the $\mathrm{C_{Ar}}$−N−O−M torsion quantitatively indicates the degree of the planar structure around the metal-nitroxide bond.[2c] The Cu1−O1 distance was 2.109(1) Å.

The nickel ion in **2** had an octahedral geometry like usual bis(terpyridine) complexes (Figure 1b). There were two crystallographically independent molecules in a unit cell, and they were practically the same. Each $[\mathrm{Ni(6bpyNO)_2}]^{2+}$ complex ion had a pseudo-C_2 symmetry. The Ni−O distances range from 2.084(3) to 2.100(3) Å and the Ni−N distances from 1.965(3) to 2.086(4) Å, implying that they form an octahedron around a high-spin Ni ion. The C−N−O−Ni torsion angles within a metal-radical chelate ring were 4.8(4), 5.5(5), 4.6(5), and 4.9(5). These small torsion angles guarantee the planar structure of the chelate ring.

Chart 1



The magnetic properties of **1** and **2** were measured on a SQUID magnetometer (Figure 2). Upon cooling from 300 to 100 K, the $\chi_{\mathrm{mol}}T$ values increased and reached a plateau, indicating the presence of intramolecular ferromagnetic interactions in both compounds. The spin-only calculated values are 1.0 and 3.0 cm^3 K mol^{-1} for high-spin **1** ($S_{\mathrm{total}} = 1$) and **2** ($S_{\mathrm{total}} = 2$), respectively. The experimental $\chi_{\mathrm{mol}}T$ values of ca. 1.0 and 3.2 cm^3 K mol^{-1} for **1** and **2**, respectively, clearly indicate their high-spin states. Final drops of the $\chi_{\mathrm{mol}}T$ values are assigned to intermolecular antiferromagnetic couplings, as well as zero-field splitting for the $\mathrm{Ni^{II}}$ ions in **2**.

The singlet−triplet model[14] from the spin Hamiltonian $H = -2J\mathbf{S}_1\cdot\mathbf{S}_2$ was applied for **1** together with a Weiss mean field parameter θ, affording $J/k_{\mathrm{B}} = +202(12)$ K and $\theta = -3.52(6)$ K with $g_{\mathrm{avg}} = 2.062(4)$. Similarly, a three-centered model[15] ($H = -2J(\mathbf{S}_1\cdot\mathbf{S}_2 + \mathbf{S}_2\cdot\mathbf{S}_3)$) was applied to the analysis of **2** to give $J/k_{\mathrm{B}} = +192(2)$ K and $\theta = -0.67(1)$ K with $g_{\mathrm{avg}} = 2.082(1)$.

The observed ferromagnetic couplings were considerably large (the singlet−triplet energy gap of **1** corresponds to ca. 400 K), and can be explained simply in terms of the orbital orthogonality.[2,3] The 3d electron configurations of $\mathrm{Cu^{II}}$ and $\mathrm{Ni^{II}}$ are $(t_{2g})^6(e_g)^3$ and $(t_{2g})^6(e_g)^2$, respectively, and the magnetic e_g orbitals having σ-type symmetry are orthogonal to the nitroxide magnetic π^* orbital(s) (Figures 1S and 2S for the DFT calculation analysis). Even when we take into consideration a detour pathway through the pyridine ring, ferromagnetic coupling can be expected according to the spin-polarization mechanism on the π-conjugate systems,[16] as clarified in the isomeric $\mathrm{Cu^{II}}$ complexes using 4bpyNO and 5bpyNO[17] (for the 4- and 5-positions of bpy, see Chart 1).

In the literature, however, there have been several reports on antiferromagnetic cases using 2-pyridyl-substituted radical chelates with $\mathrm{Cu^{II}}$ or $\mathrm{Ni^{II}}$,[2,18] where the orbital orthogonality is violated because of steric reasons.[2c] The 2,2′-bipyridyl group has been

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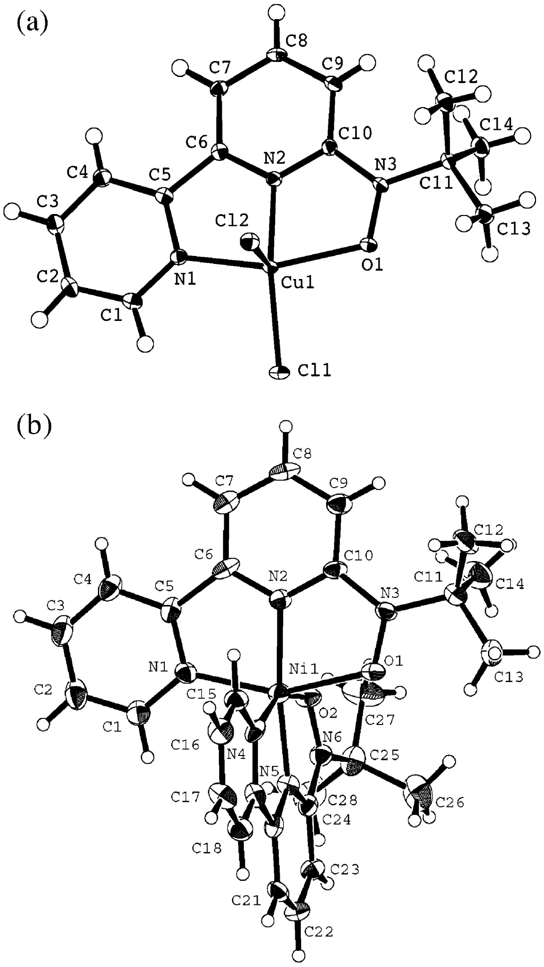

Figure 1. Ortep drawings for (a) [Cu(6bpyNO)Cl$_2$] (**1**) and (b) [Ni(6bpyNO)$_2$]$^{2+}$ moiety as one of two crystallographic independent units in **2**. Thermal ellipsoids are drawn at the 50% probability level for non-hydrogen atoms.

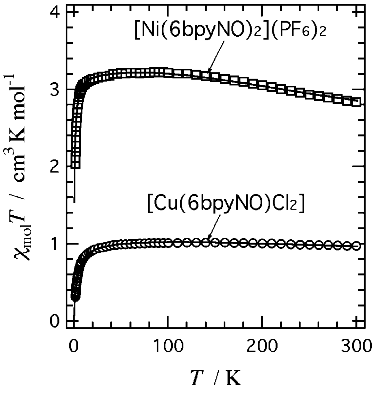

Figure 2. Temperature dependence of $\chi_{\mathrm{mol}}T$ for **1** and **2** measured at 5000 and 500 Oe, respectively. The solid lines represent calculated curves. See the text for the equations and optimized parameters.

introduced in the present complexes for improving stability compared with a simple pyridyl group. It also seems useful for the planar structure because of the tension operative in the fused five- and six-membered rings in the terpyridine-type chelation; for example, the N2−C10−N3, N2−C6−C5, and N1−C5−C6 angles in **1** were 112.81(17), 113.90(17), and 113.30(17)°, respectively, which favor 120° by nature. The following is another system showing a similar relation. The Ni$^{\mathrm{II}}$ complex containing 2,2′-bipyridine-6,6′-diyl-bis(NN) exhibited ferromagnetic coupling,[2a,b] whereas antiferromagnetic coupling was observed when 2-pyridyl-NN was applied.[18]

In summary, we have reported here the first examples of Cu$^{\mathrm{II}}$ and Ni$^{\mathrm{II}}$ complexes having ArNO chelate rings, both of which showed strong ferromagnetic interactions ($J/k_{\mathrm{B}} \cong 200$ K) owing to the high spin-density at the nitroxide oxygen atom and the highly planar chelate structures.

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Supporting Information Available: Figures 1S and 2S, experimental details (preparation of 6pbyNOH and **2**, crystal structure determination, and magnetic measurements), and CIF files of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) A precursor 6bpyNOH (*N*-2,2′-bipyridin-6-yl *N*-*tert*-butyl hydroxylamine) was obtained as colorless solids: mp 105−107 °C (hexane) (see Supporting Information). A mixture of 6bpyNOH (30 mg, 0.12 mmol) and freshly prepared Ag$_2$O (0.13 g, 3.3 mmol) in CHCl$_3$ (5 mL) was stirred at room temperature for 1 h, and a resultant red solution was passed through a silica gel column eluted with CH$_2$Cl$_2$. A red band was collected, and the solvent was removed under reduced pressure, to give a red oily product of 6bpyNO in 85% yield. ESR (room temperature, toluene): a_{N} = 10.5 G at g = 2.0060. IR (neat): 777, 1192, 1360, 1429, 1558, 2972 cm^{-1}. UV/vis (CHCl$_3$) λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1}): 474 (702), 513 (450).

(12) Preparation of **1**: A combined solution from 6bpyNO (36 mg, 0.15 mmol) in MeOH (2 mL) and CuCl$_2$·2H$_2$O (26 mg, 0.15 mmol) in MeOH (2 mL) was kept in a refrigerator for a few weeks. Black plates of **1** (16 mg, 0.043 mmol; yield 29%) were precipitated and separated on a filter. IR (KBr disc): 785, 1176, 1442, 1589, 3001 cm^{-1}. Anal. Calcd: C, 44.63; H, 4.28; N, 11.15%. Found: C, 45.31; H, 4.55; N, 11.29%. For the preparation of **2**, see Supporting Information.

(13) Selected crystallographic data: (**1**) C$_{14}$H$_{16}$Cl$_2$CuN$_3$O, monoclinic $P2_1/c$, $a = 11.965(8)$, $b = 9.611(7)$, $c = 12.86(1)$ Å, $\beta = 94.55(7)°$, $V = 1475(1)$ Å^3, $Z = 4$, $d_{\mathrm{calcd}} = 1.697$ g cm^{-3}, μ(Mo Kα) = 1.844 mm^{-1}, $T = 90$ K, $R_{\mathrm{int}} = 0.037$, $R(F)$ ($I > 2\sigma(I)$) = 0.0295, and $R_{\mathrm{w}}(F^2)$ (all data) = 0.0370 for 3380 unique reflections; (**2**) C$_{28}$H$_{32}$F$_{12}$N$_6$NiO$_2$P$_2$, orthorhombic, *Pbca*, $a = 25.214(6)$, $b = 13.624(4)$, $c = 40.469(9)$ Å, $V = 13902(6)$ Å^3, $Z = 16$, $d_{\mathrm{calcd}} = 1.592$ g cm^{-3}, μ(Cu Kα) = 2.612 mm^{-1}, $T = 90$ K, $R_{\mathrm{int}} = 0.089$, $R(F)$ ($I > 2\sigma(I)$) = 0.0569, and $R_{\mathrm{w}}(F^2)$ (all data) = 0.0562 for 12628 unique reflections.

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