tert-Butyl 2-Pyridyl Nitroxide Available as a Paramagnetic Chelate Ligand for Strongly Exchange-Coupled Metal−Radical Compounds

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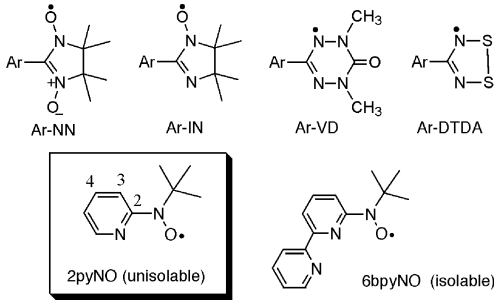
Metal−radical hybrid solids have been well investigated toward molecule-based magnets, where a radical center is directly bonded to the metal ion, affording appreciable magnetic exchange coupling.[1] Various 2-pyridyl-substituted ligands containing a paramagnetic center such as nitronyl nitroxide (NN),[2,3] imino nitroxide (IN),[4] oxoverdazyl (VD),[5] and dithiadiazolyl (DTDA)[6] groups have been known to form chelate rings (see Chart 1 for their structural formulas). We propose here *tert*-butyl 2-pyridyl nitroxide (2pyNO; NO stands for the *tert*-butyl nitroxide group) as a promissing candidate for strongly correlated metal−radical materials. The spin density on the ligating oxygen atom of ArNO is assumed to be almost twice as large as that of the other conventional radicals such as ArNN, owing to an almost half size of the spin-delocalizable π-conjugation in the radical groups, which also leads to the undesired instability of ArNO. There have been no reports on the chelate compounds involving 2pyNO despite many efforts because of synthetic difficulty; the simple pyridyl-NOs are not isolable.[7] Thanks to the stabilization from an extended aromatic ring, 6bpyNO has been available for synthesis of $[Ni(6bpyNO)_2](PF_6)_2$ and $[Cu(6bpyNO)Cl_2]$.[8] Complexation with metal ions stabilizes the radicals, as demonstrated by the isolation of H−IN,[1d,9] 3pyNO, and 4pyNO[10] compounds. This technique has been widely utilized for unstable functional groups by means of steric protection as well as electronic perturbation.[11] We supposed that the synthesis of 2pyNO complexes would be challenging, and actually we have succeeded in the preparation of $[Ni^{II}(2pyNO)_2(H_2O)_2]\cdot(ClO_4)_2$ (**1**) and $[Cu^{II}(2pyNO)_2(ClO_4)_2]$ (**2**).

Chart 1. Structural Formulas



A precursory hydroxylamine (2pyNOH) was prepared from 2-bromopyridine and 2-methyl-2-nitrosobutane via the conventional organo-lithium method. Crude 2pyNO, obtained from oxidation of 2pyNOH with Ag_2O, was introduced to a subsequent complexation without isolation, giving **1** and **2** by use of a stoichiometric amount of nickel(II) and copper(II) perchlorates, respectively (see Supporting Information for experimental details). The present complexes are sufficiently stable during storage under ambient conditions for several months.

The chelate rings involving 2pyNO are clearly depicted in Figure 1.[12] The dicationic moiety of **1** (abbreviated as $\mathbf{1}^{2+}$) has a twofold symmetry around the O2−Ni1−O3 bond (Figure 1a). Two water molecules occupy the axial position with respect to the chelate plane, while the counter ClO_4^- anions are located in clearance of the crystal. An octahedron is characterized by the O1−Ni1, N1−Ni1, O2−Ni1, and O3−Ni1 distances of 2.008(2), 2.018(3), 2.080(4), and 2.052(4) Å, respectively, suggesting the high spin center with $S_{Ni} = 1$. The chelate ring is highly planar as indicated with the small C1−N2−O1−Ni1 torsion angle (3.9(3)°). We have proposed the C_{Ar}−N−O−M torsion as a convenient indicator for orthogonal arrangement of metal $3d\sigma$ and oxygen $2p_z$ orbitals.[3]

Compound **2** has a centrosymmetry (Figure 1b). The copper(II) ion forms an elongated octahedron with the somewhat long axial Cu1−O2 distance (2.478(4) Å) com-

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(12) Selected crystallographic data. **1**: $C_{18}H_{30}Cl_2N_4O_{12}Ni$, orthorhombic, *Pcca*, $a = 21.697(8)$, $b = 8.534(3)$, $c = 14.165(6)$ Å, $V = 2622.8(17)$ Å^3, $Z = 4$, $d_{calcd} = 1.580$ g cm^{-3}, μ(Mo Kα) = 1.009 mm^{-1}, $T = 100$ K, $R_{int} = 0.060$, $R(F)$ ($I > 2\sigma(I)$) = 0.0540, and $R_w(F^2) = 0.0667$ for 2992 unique reflections. **2**: $C_{18}H_{26}Cl_2CuN_4O_{10}$, monoclinic, $P2_1/n$, $a = 6.176(3)$, $b = 20.503(10)$, $c = 9.516(4)$ Å, $\beta = 104.33(4)°$, $V = 1167.4(10)$ Å^3, $Z = 2$, $d_{calcd} = 1.686$ g cm^{-3}, μ(Mo Kα) = 1.227 mm^{-1}, $T = 90$ K, $R_{int} = 0.063$, $R(F)$ ($I > 2\sigma(I)$) = 0.0592, and $R_w(F^2) = 0.1085$ for 3349 unique reflections.

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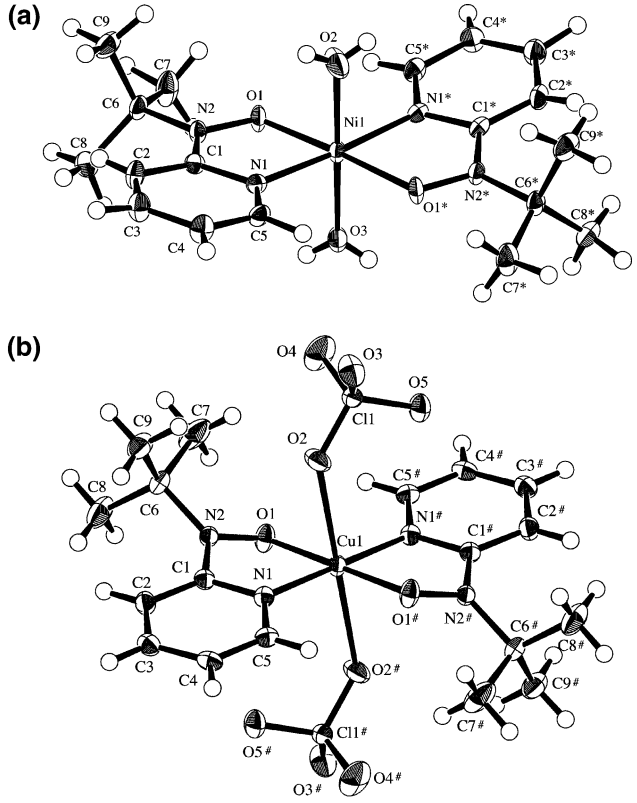

Figure 1. Ortep drawings for (a) $[Ni(2pyNO)_2(H_2O)_2]^{2+}$ in **1** and (b) $[Cu(2pyNO)_2(ClO_4)_2]$ (**2**). Thermal ellipsoids are drawn at the 50% probability level for non-hydrogen atoms. Symmetry operation codes for * and # are $(-x, +y, 1/2 - z)$ and $(-x, -y, -z)$, respectively.

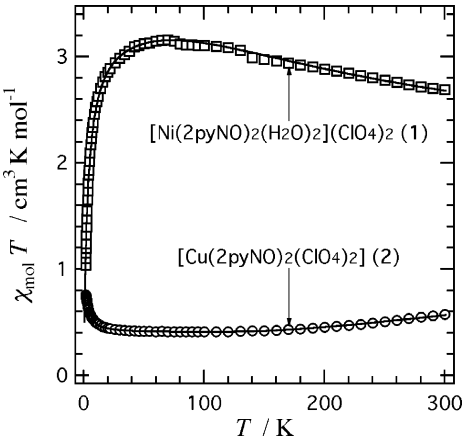

Figure 2. Temperature dependence of $\chi_{mol}T$ for **1** and **2** measured at 500 and 5000 Oe, respectively. The solid lines represent calculated curves. See the text for the equations and optimized parameters.

pared with the equatorial bonds (1.942(4) and 1.935(3) Å for O1−Cu1 and N1−Cu1, respectively). The axial direction is considerably canted from the normal of the basal plane as indicated by the O1−Cu1−O2 and N1−Cu1−O2 angles (85.6(2) and 83.4(2)°, respectively), probably owing to the steric effect from the perchlorate ligand. The C1−N2−O1−Cu1 torsion angle is 25.9(5)°, which may violate orthogonality between the copper(II) and nitroxide magnetic orbitals (see below).

Magnetic susceptibilities of **1** and **2** were measured on a SQUID magnetometer (Figure 2). Upon cooling from 300 to 70 K, the $\chi_{mol}T$ value of **1** increased up to 3.2 cm^3 K mol^{-1}, indicating the presence of intramolecular ferromagnetic interaction.[13] A linear-arrayed three-centered model[14] (the spin Hamiltonian $H = -2J(S_1 \cdot S_2 + S_2 \cdot S_3)$) was applied to the analysis of **1** together with a Weiss mean field parameter θ. Fitting to the resultant expression (eq 1) afforded the opimized parameters $J/k_B = +126(3)$ K and $\theta = -3.45(5)$ K with $g_{avg} = 2.112(4)$. A final drop of the $\chi_{mol}T$ value can be assigned to Ni^{II} zero-field splitting as well as intermolecular antiferromagnetic couplings, both of which were confined to θ.

$$\chi_{mol} = \frac{2Ng^2\mu_B{}^2}{k_B(T-\theta)} \frac{\exp(-2J/k_BT) + 1 + 5\exp(2J/k_BT)}{\exp(-4J/k_BT) + 3\exp(-2J/k_BT) + 3 + 5\exp(2J/k_BT)} \quad (1)$$

In sharp contrast to the results on **1**, the $\chi_{mol}T$ value of **2** decreased and reached a plateau at 0.4 cm^3 K mol^{-1} on cooling, indicating the presence of intramolecular antiferromagnetic interaction.[13] A final upsurge can be ascribed to intermolecular ferromagnetic interaction. We applied a doublet-quartet model based on a linear array (eq 2),[15] with a modification using a Weiss temperature (θ), to give the parameters $J/k_B = -137(1)$ K, $\theta = +1.88(2)$ K, and $g_{avg} = 2.064(2)$. The calculated curves well-reproduced the experimental data for both **1** and **2**.

$$\chi_{mol} = \frac{Ng^2\mu_B{}^2}{4k_B(T-\theta)} \frac{\exp(-2J/k_BT) + 1 + 10\exp(J/k_BT)}{\exp(-2J/k_BT) + 1 + 2\exp(J/k_BT)} \quad (2)$$

A density functional theory calculation supported the above analysis. We applied an unrestricted density functional method (UB3LYP/6-31G(d,p)) in the Gaussian 03 program[16] (see Supporting Information for details) to the molecular geometries determined above. The converged self-consistent field energies of the singlet and quintet of $\mathbf{1}^{2+}$ showed the gap of 3.41×10^{-3} au with the ground quintet state. On the other hand, the doublet state of **2** was lower in energy than the quartet one by 3.46×10^{-3} au. The intramolecular magnetic coupling constants of $\mathbf{1}^{2+}$ and **2** were estimated as

(13) The Curie−Weiss equation ($\chi_{mol} = C/(T - \theta_{CW})$) was applied to the data in 100−300 K, giving $C = 2.51$ cm^3 K mol^{-1} and $\theta_{CW} = +23$ K for **1** and $C = 0.72$ cm^3 K mol^{-1} and $\theta_{CW} = -104$ K for **2**. In this analysis, the θ_{CW} value implies the dominant interaction, that is, intramolecular coupling. The positive and negative θ_{CW} values clearly indicate the presence of intramolecular ferro- and antiferromagnetic couplings, respectively.

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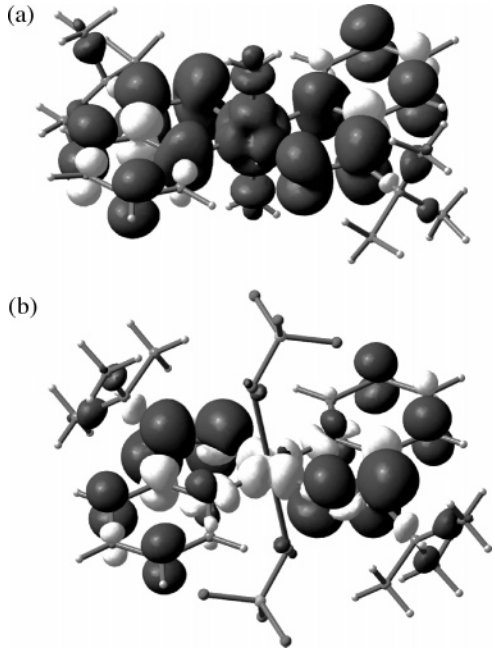

Figure 3. Spin density surfaces of (a) the quintet state of $\mathbf{1}^{2+}$ and (b) the doublet state of **2**, calculated on the UB3LYP/6-31G(d,p) level. Dark gray, positive spin; light gray, negative spin. See Figure 1 for the atom labels.

$J/k_B = +179$ and -364 K, respectively. Though the calculated J values were somewhat overestimated, the ground spin states were correctly predicted. The spin density surfaces of the ground states of $\mathbf{1}^{2+}$ and **2** are shown in Figure 3. Qualitatively the same results were obtained using the Lanl2dz basis set.

These spin density maps approximately represent the singly occupied molecular orbitals, which carry a σ character at the metal ions and a π^* character at the nitroxide groups. As previously proposed,[2−4,17] the metal−radical ferromagnetic couplings observed can be explained in terms of the orbital orthogonality between them. Compound **1** showed the ferromagnetic coupling owing to the small torsion angle around C_{Ar}−N−O−M (3.9°). Similarly, the nickel(II)− and copper(II)−6bpyNO complexes having the small torsion (4.6−5.5° and 10.7°, respectively) exhibited the strong ferromagnetic couplings.[8] On the other hand, **2** has a considerably large torsion (25.9°), and accordingly the antiferromagnetic coupling was operative.

We can also find that polarized spin densities on the pyridine ring are appreciable (Figure 3). A possible mechanism of the intermolecular ferromagnetic coupling in the crystal of **2** should be noticed. The C3 and C4 (Figure 1b) carry negative (−0.0445) and positive (+0.0928) spin densities, respectively (Figure 3b), in good agreement with the spin-polarization scheme on an aromatic ring.[18] The relatively short intermolecular distances of 3.274(8) Å are found between C3···C4* and C4···C3*, which is smaller than the sum of the van der Waals radii (3.40 Å)[19] (the symmetry operation code for * is $1 - x, -y, 1 - z$). McConnell proposed the intermolecular exchange coupling in the π-stacking dimer where the spin density was polarized.[20,21] The intermolecular ferromagnetic coupling of **2** was observed as expected from this model. In the crystal of **1**, we can find hydrogen bonds between water and pyridine hydrogen atoms and perchlorate oxygen atoms. The intermolecular antiferromagnetic coupling observed seems consistent with these intermolecular contacts.

In summary, we have reported here the first examples of Ni^{II} and Cu^{II} complexes having 2pyNO chelate rings, both of which showed considerably strong exchange couplings. The spin is polarized from the NO group onto the pyridine ring (Figure 3), in contrast to the case of nitronyl nitroxide and other radicals,[22] leading to magnetic coupling in an intermolecular fashion. This work encourages us to develop more studies on metal−radical hybrid materials using fragile radicals which have been set aside so far because of the preconceived notion that they were unavailable.

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Supporting Information Available: Experimental and calculation details (PDF) and CIF files (including selected geometrical tables) of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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