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A One-Dimensional Helical Copper(II) Imino Nitroxide

Hiroki Oshio,* Takashi Watanabe, Akihiro Ohto, and Tasuku Ito

Department of Chemistry, Graduate School of Science, Tohoku University,
Aoba-ku, Sendai 980-77, Japan

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The reaction of $[Cu^I(CH_3CN)_4](PF_6)$ with a biradical of imino nitroxide in methanol yielded a copper(II) complex $[Cu^{II}(imapy)](PF6)$ (**2**) (Himapy = 2-(1′-oxy-4′,4′,5′,5′-tetramethyl-4′,5′-dihydro-1′*H*-imidazol-2′-yl)-6-(1″-oxyl-4″,4″,5″,5″-tetramethyl-4″,5″-dihydro-1″*H*-imidazol-2″-yl)pyridine)). In **2** one of the nitroxides in the ligand was reduced to a hydroxyamino anion and the Cu^I ion was oxidized. Complex **2** crystallizes in tetragonal space group $P4_32_12$ with $a = 14.341(3)$ Å, $c = 24.282(5)$ Å, $V = 4993(1)$ Å^3, and $Z = 8$, and the absolute structure for this crystal was determined by using Flack's parameter. Square planar coordination sites of the Cu^{II} ion are occupied by two nitrogen and two oxygen atoms, where one of the coordinated oxygen atoms comes from the hydroxyamino group in the next molecule. The Cu^{II} ions are bridged by the imino−hydroxyamino anion to form a one-dimensional structure with each Cu^{II} ion having the coordinated imino nitroxide. Complex molecules locate on the 4-fold screw axis, which results in a counterclockwise helical arrangement of the imino nitroxides. Magnetic susceptibility measurements revealed that antiferromagnetic interactions are operative. The system was treated as the one-dimensional chain of the Cu^{II}−radical species, and coupling constants J_1 and J_2 for the intrachain and Cu^{II}−radical interactions were estimated to be −6 and −23 cm^{-1}, respectively.

Introduction

Supramolecular chemistry of coordination compounds is the subject of intense research.[1] It has been known for several years that self-assembly of oligopyridyl strands and Cu^I ions yielded a well-organized molecular architecture as seen in helical complexes.[2] General features of the Cu^I ion as a component of the self-assembled system are that the tetrahedral coordination of the Cu^I ion can give helicate formation of the oligopyridyl strands and that the Cu^I ions mediate electronic interactions between organic components.[3] On the other hand, magnetochemistry of metal complexes with organic radicals like nitroxides has been extensively studied, and some such complexes have revealed spontaneous magnetization.[4] Therefore, an assembly of polypyridyl type imino nitroxides by means of metal ions may yield magnetically coupled molecular solids. We report here the helical structure and magnetic properties of a Cu^{II}-imino nitroxide, $[Cu^{II}(imapy)](PF_6)$ (**2**) (Himapy = 2-(1′-oxy-4′,4′,5′,5′-tetramethyl-4′,5′-dihydro-1′*H*-imidazol-2′-yl)-6-(1″-oxyl-4″,4″,5″,5″-tetramethyl-4″,5″-dihydro-1″*H*-imidazol-2″-yl)pyridine)), which was prepared by the reaction of $[Cu^I(CH_3CN)_4](PF_6)$ with a multidentate imino nitroxide.

Experimental Section

Preparation of the Complex. Ligand **1** (2,6-bis(1′-oxyl-4′,4′,5′,5′-tetramethyl-4′,5′-dihydro-1′*H*-imidazol-2′-yl)pyridine)[5] and $[Cu^I(CH_3CN)_4](PF_6)$[6] were prepared by the reported methods. **1** (50 mg, 0.14 mmol) was added to a solution of $[Cu^I(CH_3CN)_4](PF_6)$ (50 mg, 0.14 mmol) in methanol (3 mL) under a nitrogen atmosphere. After standing overnight, dark red tablets of $[Cu^{II}(imapy)](PF_6)$ (**2**) (28 mg, 35%) were filtered out, and one of them was subjected to an X-ray structural analysis. Anal. Calcd for $C_{19}H_{27}CuF_6N_5O_2P$ (**2**): C, 40.32; H, 4.81; N, 12.37. Found: C, 40.67; H, 4.95; N, 12.05.

Physical Measurements. Magnetic susceptibility data were collected in the temperature range 2.0−300 K in a applied 1 T with the use of a Quantum Design Model MPMS SQUID magnetometer. Pascal's constants were used to determine the constituent atom diamagnetism.[7] The X-ray photoelectron spectrum (XPS) was recorded on a Shimazu ESCA-750.

X-ray Crystallography. A crystal of $[Cu^{II}(imapy)](PF_6)$ (**2**) with dimensions of 0.1 × 0.1 × 0.05 mm^3 was used for the data collection. Diffraction data were collected on a Rigaku AFC5R four-circle diffractometer equipped with graphite monochromatized Cu Kα ($\lambda = 1.541\ 78$ Å) radiation at −50 °C. Three standard reflections were measured every 200 data collections and revealed no fluctuation in intensities. The lattice constants were optimized from a least-squares refinement of the settings of 25 carefully centered Bragg reflections in the range of $50° < 2\theta < 60°$. The number of measured ($8° < 2\theta < 125°$) and unique reflections were 4469 and 2358, respectively. Crystallographic data are collected in Table 1. Structure analysis and refinement data were corrected for Lorentz and polarization. An empirical absorption correction using the program DIFABS was applied which resulted in transmission factors ranging from 0.75 to 1.3. The structure was solved by a conventional heavy-atom method and refined by a full-matrix least-squares method with anisotropic thermal parameters for Cu, P, and F atoms and isotropic parameters for the others. Final $R = 0.084$ and $R_w = 0.083$, for 2944 unique reflections with $I_o > 3\sigma(I_o)$ and 181 parameters, were obtained. The final Fourier difference synthesis showed a maximum of +0.79 and −0.92 e Å^{-3}. Final atomic parameters and equivalent isotropic thermal parameters are listed in Table 2. All calculations except for the calculation of Flack's parameters were performed by using the teXsan crystallographic software package of the Molecular Structure Corp.

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Table 1. Crystallographic Data for [Cu(imapy)](PF$_6$) (**2**)

chem formula	$C_{19}H_{27}CuF_6N_5O_2P$
fw	565.96
temp (°C)	−50
cryst system	tetragonal
space group	$P4_32_12$ (No. 96)
a (Å)	14.341(3)
c (Å)	24.282(5)
V (Å^3)	4993(1)
Z	8
ρ_{calc} (g cm^{-3})	1.505
ρ_{obsd} (g cm^{-3})	1.51
μ(Cu Kα) (cm^{-1})	24.90
R^a	0.084
$R_w{}^b$	0.083

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)]^{1/2}$. Function minimized: $\sum w(|F_o| - |F_c|)^2$. Least-squares weights: $1/\sigma^2(F_o) = [\sigma^2(F_o) + p^2F_o{}^2/4]^{-1}$. p-factor: 0.015.

Table 2. Fractional Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) of Non-Hydrogen Atoms of [Cu(imapy)](PF6) (**2**)

atom	x	y	z	$B_{eq}{}^a$
Cu(1)	0.4225(1)	0.0291(1)	0.02782(6)	1.62(4)
P(1)	0.2263(3)	0.2263	0.0000	2.52(6)
P(2)	0.1092(2)	0.1092	−0.5000	1.95(5)
F(1)	0.3029(7)	0.3029	0.0000	8.5(3)
F(2)	0.1482(6)	0.1482	0.0000	6.0(2)
F(3)	0.1598(6)	0.2912(6)	−0.0363(3)	4.8(2)
F(4)	0.2682(6)	0.1827(7)	−0.0545(3)	5.8(3)
F(5)	0.0306(6)	0.0306	−0.5000	6.9(2)
F(6)	0.1836(6)	0.1836	−0.5000	6.1(2)
F(7)	0.1842(5)	0.0290(5)	−0.5033(3)	3.6(2)
F(8)	0.1115(7)	0.1115(9)	−0.4352(3)	6.5(4)
O(1)	0.3658(6)	−0.0193(6)	0.0939(3)	2.2(2)
O(2)	0.4211(6)	0.0271(6)	−0.1827(3)	2.0(1)
N(1)	0.3216(6)	−0.0300(6)	−0.0196(3)	1.2(2)
N(2)	0.2757(7)	−0.0381(7)	0.0954(3)	1.9(2)
N(3)	0.1331(7)	−0.0893(7)	0.0745(4)	1.9(2)
N(4)	0.4720(7)	0.0682(6)	−0.0443(3)	1.6(2)
N(5)	0.4664(7)	0.0455(6)	−0.1340(4)	2.1(2)
C(1)	0.3424(8)	−0.0275(8)	−0.0740(4)	1.5(2)
C(2)	0.2887(8)	−0.0715(9)	−0.1133(4)	2.0(2)
C(3)	0.2066(9)	−0.1196(9)	−0.0949(5)	2.4(3)
C(4)	0.1841(9)	−0.1210(9)	−0.0389(5)	2.3(3)
C(5)	0.2455(8)	−0.0723(8)	−0.0032(4)	1.5(2)
C(6)	0.2212(9)	−0.0661(9)	0.0564(4)	1.7(2)
C(7)	0.2299(9)	−0.0512(8)	0.1511(5)	2.1(3)
C(8)	0.1234(9)	−0.0484(9)	0.1323(5)	2.6(3)
C(9)	0.2611(10)	−0.1452(10)	0.1730(5)	3.1(3)
C(10)	0.258(1)	0.030(1)	0.1879(5)	4.1(3)
C(11)	0.0606(9)	−0.1110(9)	0.1656(5)	2.6(3)
C(12)	0.081(1)	0.051(1)	0.1269(5)	4.0(3)
C(13)	0.4257(8)	0.0263(8)	−0.0850(4)	1.6(2)
C(14)	0.5573(8)	0.1145(9)	−0.0652(4)	2.3(2)
C(15)	0.5247(9)	0.1300(8)	−0.1292(4)	2.1(2)
C(16)	0.6383(9)	0.0505(8)	−0.0586(4)	2.3(3)
C(17)	0.5712(10)	0.2095(10)	−0.0372(5)	3.4(3)
C(18)	0.6086(9)	0.1205(9)	−0.1697(5)	2.7(3)
C(19)	0.4676(9)	0.2151(8)	−0.1390(4)	2.0(2)

[a] $B_{eq} = {}^8/_3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{12}aa^*cc^* \cos\beta + 2U_{12}bb^*cc^* \cos\alpha)$.

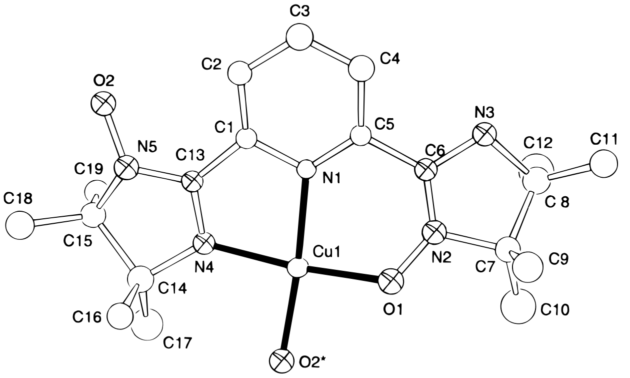


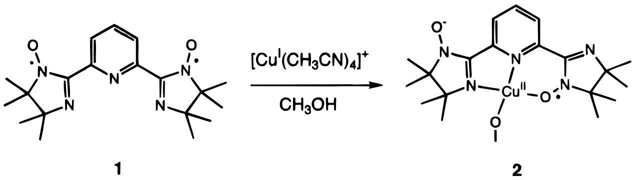
Figure 1. Structure of [Cu^{II}(imapy)]$^+$ showing 30% thermal ellipsoids and the atom-labeling system.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of [Cu(imapy)](PF$_6$) (**2**)

Cu(1)−O(1)	1.929(7)	Cu(1)−O(2)	1.917(8)
Cu(1)−N(1)	2.035(9)	Cu(1)−N(4)	1.970(8)
O(1)−N(2)	1.32(1)	O(2)−N(5)	1.38(1)
N(2)−C(6)	1.29(1)	N(3)−C(6)	1.38(1)
N(4)−C(13)	1.33(1)	N(5)−C(13)	1.35(1)

O(1)−Cu(1)−O(2)	92.8(3)	O(1)−Cu(1)−N(1)	91.2(3)
O(1)−Cu(1)−N(4)	173.5(4)	O(2)−Cu(1)−N(1)	173.9(3)
O(2)−Cu(1)−N(4)	93.3(3)	N(1)−Cu(1)−N(4)	82.6(4)
Cu(1)−O(1)−N(2)	120.5(7)	Cu(1)−O(2)−N(5)	113.9(6)
O(1)−N(2)−C(6)	129.5(10)	O(2)−N(5)−C(13)	120.9(9)
N(2)−C(6)−N(3)	113.4(10)	N(4)−C(13)−N(5)	110.5(10)

Scheme 1



Results and Discussion

The reaction of [Cu^I(CH$_3$CN)$_4$](PF$_6$) with the biradical **1** of imino nitroxide gave dark red crystals of [Cu^{II}(imapy)](PF$_6$) (**2**). During the reaction, the Cu^I ion was oxidized to a Cu^{II} ion, while the one of the imino nitroxides was reduced to the imino−hydroxyamino anion (Scheme 1).

The oxidation state of the Cu ion in **2** was confirmed by XPS with three peaks at 934, 936, and 944 eV characteristic of Cu^{II} species.[8] The redox properties of Cu ions strongly depend on the coordination geometry.[9] A geometrical requirement of a tridentate ligands in **1**, which compels the Cu ion to have square planar coordination, prompts oxidation of the Cu^I ion.

Complex **2** crystallizes in the noncentrosymmetric tetragonal space group P4$_3$2$_1$2. The absolute structure has been determined by using Flack's parameter,[10] which was estimated to be −0.1(1) for the presented space group. It should be noted that the powdered sample of **2** does not show circular dichromism and this leads us to conclude that **2** is a 1:1 mixture of crystals with the space groups of $P4_32_12$ and $P4_12_12$. An ORTEP diagram is depicted in Figure 1, and selected bond distances and angles are listed in Table 3. The coordination geometry about the Cu^{II} ion is square planar with two nitrogen and two oxygen atoms, where one of the oxygen atoms comes from the imino−hydroxyamino anion of the next molecule. The Cu−N and Cu−O bond lengths are in the range 1.917(8)−2.035(9) Å, and the Cu^{II} ion is displaced by 0.023 Å above the N_2O_2 plane. The N−O bond length (N5−O2 = 1.38(1) Å) of the hydroxyamino anion is longer than that (N2−O1 = 1.32(1) Å) of the nitroxide. The Cu^{II} ions are bridged by the imino−hydroxyamino anion to form a one-dimensional structure along the c-axis, and each Cu^{II} ion has a coordinated imino nitroxide. The complex molecule is located on a crystallographic 4-fold screw axis so that imino nitroxides associated with Cu^{II} chain have a counter-clockwise helical arrangement in the crystalline (Figure 2).

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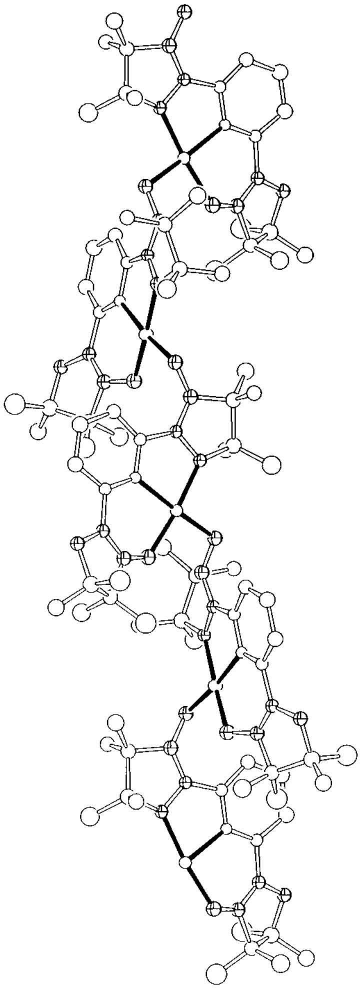


Figure 2. One-dimensional helical structure of [Cu^{II}(imapy)]$^+$.

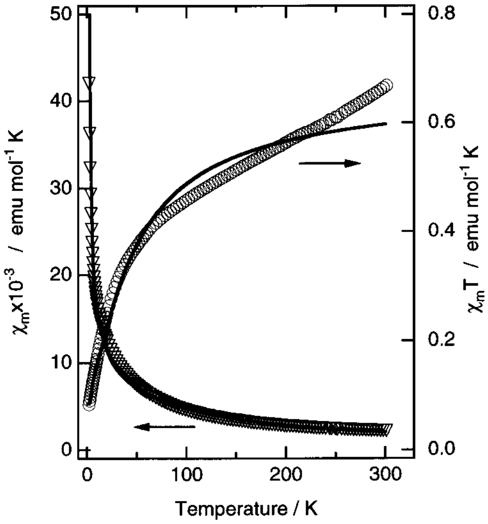
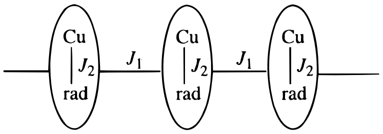


Figure 3. Temperature dependence of χ_mT and χ_m for [Cu^{II}(imapy)]-(PF$_6$). The solid line corresponds to the best fitted curves by using the parameters described in the text.

The magnetic susceptibility data for **2** are shown in Figure 3 in the form of χ_mT and χ_m vs T plots. χ_mT values decrease as the temperature is lowered, which is indicative of antiferromagnetic interactions. In **2**, the Cu^{II} ions form a chain structure and each Cu^{II} ion has a coordinated imino−nitroxyl group. Therefore, both intrachain (J_1) and the Cu^{II}−radical (J_2) interactions should be included in analyzing the magnetic behavior. The system was treated as a one-dimensional chain of a Cu^{II}−radical species (Scheme 2).

Scheme 2



The modified Fisher's model for the classical-spin chain system was applied for the analysis of the magnetic data,[11] although the system is appropriate to be treated as a quantum spin system. An exchange Hamiltonian for the system has the form of

$$H_{\text{chain}} = -J_1 \sum S_{D_i} \cdot S_{D_{i+1}}$$

where S_D represents temperature-dependent spin of the Cu^{II}-radical species. The temperature dependence of the total $\chi_m T$ value denoted as $(\chi_m T)_{\text{chain}}$ can be expressed as

$$(\chi_m T)_{\text{chain}} = \frac{Ng^2\beta^2}{3k}[S_D(S_D + 1)]\frac{1 + u}{1 - u}$$

$$u = \coth[J_1 S_D(S_D + 1)/kT] - kT/[J_1 S_D(S_D + 1)]$$

$$S_D(S_D + 1) = \frac{6 \exp(2J_2/kT)}{1 + 3 \exp(2J_2/kT)}$$

where the symbols have their usual meaning. The least-squares fitting of the observed data led to $J_1 = -6(1)$ cm^{-1} and $J_2 = -23(1)$ cm^{-1} with 0.1(1) of paramagnetic impurity, where the *g* value was fixed to 2.00 in this calculation. It should be noted that an EPR measurement for the powdered sample of **2** at 77 K shows only a weak signal at 0.33 T attributable to a radical impurity.

The results presented here suggest that the polypyridyl type imino nitroxide can be self-assembled by the Cu ion. We have reported that the Cu^I ion in [Cu^I(immepy)$_2$](PF$_6$) (immepy = bidentate imino nitroxide) propagates a fairly strong ferromagnetic interaction ($2J = 103$ cm^{-1}, where $H = -2JS_1 \cdot S_2$) between the coordinated imino nitroxides.[12] More effort is justified to prepare polypyridyl type imino nitroxides assembled by the Cu^I ion, which may have the intermolecular ferromagnetic interaction. This approach may offer promising perspectives on synthesizing novel magnetic materials like helical and chiral magnets.

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Supporting Information Available: Tables S1−S4, listing the detailed crystallographic data, anisotropic temperature factors, and bond lengths and angles, and Figures S1 and S2, showing ORTEP diagrams (6 pages). Ordering information is given on any current masthead page.

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