Preparation of Cu(I) Complexes with *N*-Bonded or *O*-Bonded *p*-Cyanophenoxido Ligand and Their Structures in Soild State and in Solution

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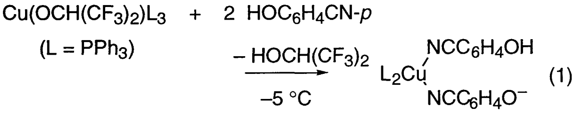
Reaction of *p*-cyanophenol with $[Cu(OCH(CF_3)_2)L_3]$ (L=PPh$_3$) gives $[Cu(N\text{–}NCC_6H_4O)(N\text{-}NCC_6H_4OH)L_2]$ (**1**), which possesses intermolecular O-H···O hydrogen bonding between the cyanophenoxido and cyanophenol ligands in the solid state and in solution.

Alkoxidocopper(I) complexes have attracted considerable attention as the intermediates of several synthetic organic reactions catalyzed by Cu(I) compounds.[1] Only a little is known on chemical properties and dynamic behavior of the complexes in solution partly because of versatility of coordination number as well as lability of the d^{10} Cu(I) center. In this paper we report reaction of an alkoxidocopper(I) complex and *p*-cyanophenol to afford the Cu(I) complex with *N*-bonded cyanophenoxido ligand rather than that with *O*-bonded ligand.

A 2:1 reaction of *p*-cyanophenol with $[Cu(OCH(CF_3)_2)L_3]$ $(L=PPh_3)^2$ at -5 °C gives a complex formulated as $[Cu(N\text{-}NCC_6H_4O)(N\text{-}NCC_6H_4OH)L_2]$ (**1**).[3]



$$Cu(OCH(CF_3)_2)L_3 + 2\ HOC_6H_4CN\text{-}p \quad (L = PPh_3) \xrightarrow[-5\ °C]{-\ HOCH(CF_3)_2} L_2Cu(NCC_6H_4OH)(NCC_6H_4O^-) \qquad (1)$$

1

X-ray crystallography[4] has revealed the molecular structure with tetrahedral coordination around the Cu(I) center that is bonded to two P and two N atoms. Molecules of **1** in the crystal form an infinite zigzag structure through intermolecular O-H···O hydrogen bonding as shown in Figure 1. Non-bonding distances between the oxygen atoms are in the range, 2.52–2.62 Å, which are consistent with the presence of hydrogen bonding.[5]

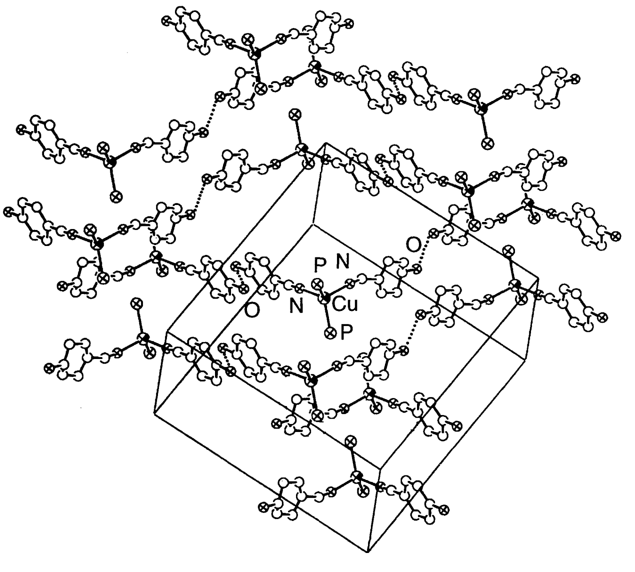
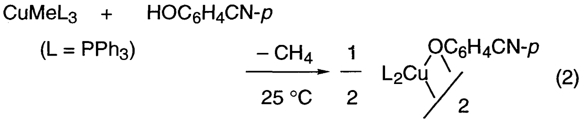


Figure 1. Crystal structure of $1\bullet(THF)_2(H_2O)(CD_2Cl_2)$. Phenyl group of PPh$_3$ and solvent molecules are omitted for clarity. Dotted lines between O atoms show hydrogen bonding.

Previously Darensbourg and his co-workers[6] have reported that reaction of $CuMeL_3$[7] with cyanoacetic acid gives $[Cu(N\text{-}NCCH_2COO)(N\text{-}NCCH_2COOH)L_2]$, the crystal of which contains similar intermolecular O-H···O hydrogen bonding between the cyanoacetate and cyanoacetic acid ligands. Reaction of $CuMeL_3$ with *p*-cyanophenol, however, gives the copper(I) complex with *O*-bonded cyanophenoxido ligands, $[Cu(OC_6H_4CN\text{-}p)L_2]_n$ (**2**) as shown in eq. 2.[8]



$$CuMeL_3 + HOC_6H_4CN\text{-}p \quad (L = PPh_3) \xrightarrow[25\ °C]{-\ CH_4} \frac{1}{2}\,[L_2Cu(OC_6H_4CN\text{-}p)]_2 \qquad (2)$$

2

Complexes **1** and **2** are distiguished from each other with the IR spectra in KBr disks. Peaks due to ν(C≡N) vibrations of **1** and **2** appear at 2210 cm^{-1} and 2202 cm^{-1}, respectively. A broad peak due to ν(C-O) of **1** is observed at 1286 cm^{-1}, while **2** shows the corresponding peak at 1368 cm^{-1} in the considerably smaller intensity.

The complexes show different ^1H NMR spectra. Figure 2 shows the ^1H NMR spectra of **1** in CD_2Cl_2at three temperatures.

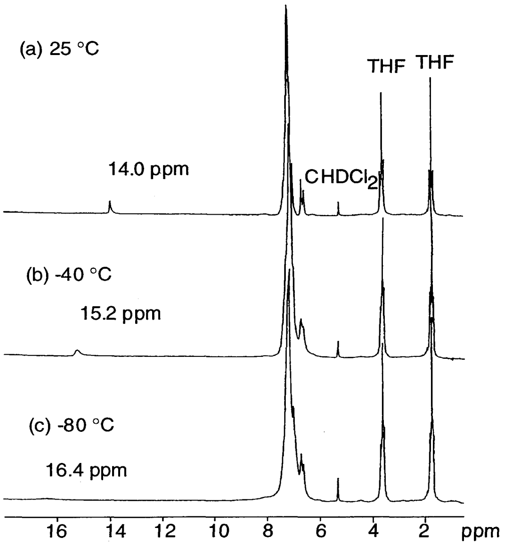


Figure 2. ^1H NMR spectra of $1\bullet(THF)_2$ at (a) 25 °C, (b) -40 °C, and (c) -80 °C in CD_2Cl_2.

A peak due to OH hydrogen of the coordinated cyanophenol appears at δ 14.0-16.4 ppm in the temperature range, 25 °C- –80 °C. The extremely low magnetic field position indicates the presence of strong intermolecular O-H···O hydrogen bonding between the cyanophenoxido and cyanophenol ligands also in the solution.[9] High solubility of the complexes in CD_2Cl_2 suggests that the infinite zigzag structure in the crystals is not maintained in the solution. Molecules of **1** in the solution form intermolecular hydrogen bonding to make cyclic oligomers probably.

The NMR spectra of an equimolar mixture of **2** and *p*-cyanophenol ([Cu] = ca. 60 mmol/dm^3) show the OH hydrogen peak of the cyanophenol at δ 9.1 ppm (60 °C), 9.9 ppm (0 °C) and 10.8 ppm (-70 °C). The low magnetic filed peak position is ascribed to reversible formation of O-H···O hydrogen bonding between the coordinated oxygen and OH group of the added cyanophenol similarly to aryloxido complexes of late transition metals.[2a,10] Significant difference of the OH peak positions from those of **1** indicates that **2** does not undergo its structural change into **1** even in the presence of *p*-cyanophenol.

In summary, Cu(I) complexes with *N*-bonded and that with *O*-bonded cyanophenoxido ligands have been prepared independently. Molecules of the former complex are bound with strong O-H···O hydrogen bonding both in the solid and in solution. Structural change between the *N*- and *O*-coordination is not observed in the solution, indicating high stability of the coordination bonds.

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3 Data for **1**: Isolated as **1**•(THF)$_2$ by recrystallization from THF. Yield 73%. ^{1}H NMR (90 MHz in CD_2Cl_2 at 25 °C) δ 14.0 (s, 1H, O*H*), 7.6-7.2 (m, 30H, C_6H_5), 7.1 (d, 4H, J = 8 Hz), 6.7 (d, 4H, J = 8 Hz), 3.7 (m, 8H, OCH_2), 1.8 (m, 8H, CH_2). Anal. Found: C, 71.44; H,5.41; N: 2.99%. Calcd. for $C_{58}H_{55}N_2O_4P_2Cu$: C, 71.85; H, 5.72; N: 2.89%.

4 Recrystallization of **1**•(THF)$_2$ from CD_2Cl_2 containing H_2O at -20 °C gave crystals of **1**•(THF)$_2$(CD_2Cl_2)(H_2O) suited for diffraction study. Crystal data $C_{59}Cl_2D_2H_{57}O_5P_2Cu$, triclinic, P $\bar{1}$ (No. 2), a = 15.632(4) Å, b = 15.912(5) Å, c = 12.909(4) Å, α = 102.81(3)°, β = 103.68(3)°, γ = 97.28(3)°, V = 2987 Å^{-3}, Z = 2, D_c = 1.164 g cm^{-1}, $F(000)$ = 1092, μ = 5.49 cm^{-1}for Mo-Kα radiation (λ = 0.71069 Å), R = 0.117, Rw = 0.093 for 2965 reflections ($I > 3\sigma(I)$) and 357 parameters. Insufficient convergence is mainly due to severe disorder of one of the two cyanophenoxido groups and of solvent molecules.

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8 Data for **2**: Yield 80%. ^{1}H NMR (90 MHz in CD_2Cl_2 at 25 °C) δ 7.4-7.2 (m, 30H, C_6H_5), 7.1 (d, 4H, J = 9 Hz), 6.7 (d, 4H, J = 9 Hz). Anal. Found: C, 73.08; H, 4.98; N: 2.40%. Calcd. for $C_{43}H_{34}NOP_2Cu$: C, 73.13; H, 4.85; N: 1.98%. The complex is most probably assigned as the dimer with two bridging cyanophenoxido ligands based on similarity of the IR peaks in the range, 1200-1600 cm^{-1}, to those of $[Cu(OPh)(PPh_3)_2]_2$ whose dinuclear structure has been established by X-ray crystallography (Ref. 2a). Equimolar reaction of $[Cu(OCHPh_2)(PPh_3)_3]$ with *p*-cyanophenol at 25 °C in Et_2O gave **2** in 90%. The reason for formation of **1** or **2** from the reactions in the present study depending on the starting materials and conditions is not clear at present.

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