Axial Bonds in Copper(II) Cyclam with DMF Ligands

Ju Chang Kim [*] **and Alan J. Lough** [†]

Department of Chemistry, Pukyong National University, Pusan 608-737, Korea. [*]*E-mail: kimjc@pknu.ac.kr*
[†]*Department of Chemistry, University of Toronto, Toronto, ONT, Canada M5S 3H6*
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There have been many examples of copper(II) tetra-azamacrocycles, where the axial donors interact with copper(II) ions.[1-5] However, the complexes reported usually show considerably long Cu-axial donor distances with weak interactions between metal centers and axial donors. Even such weak interactions, it appears that the presence of hydrogen-bonding chelate rings comprised of axial donors, suitable anions and solvents, and secondary amines of the macrocycle is requisite for the stabilization of axial ligands to the central copper(II) ions.[1-4] In the present work, we describe the preparation and structure of *trans*-[Cu(**L**)-(DMF)$_2$](PF$_6$)$_2$ (**1**) (**L** = cyclam = 1,4,8,11-tetraazacyclo-tetradecane, DMF = N,N-dimethylformamide), where the complex shows fairly strong copper-axial donor interactions without the support of hydrogen-bonding chelate rings.

Experimental Section

Materials, methods and apparatus. All chemicals used in this work were of reagent grade and were used without further purification. Infrared spectra were measured as Nujol mulls between KBr plates using a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer over the range 4000 and 400 cm^{-1}. Solid state electronic spectra by the diffuse reflectance method were measured using Shimadzu 2401-PC UV/vis spectrophotometer. The complex [Cu(**L**)](ClO$_4$)$_2$ was prepared according to the literature procedures.[6]

***trans*-[Cu(L)(DMF)$_2$](PF$_6$)$_2$ (1).** Excess amount of NH$_4$PF$_6$ was added to a warm acetonitrile (20 mL) solution of [Cu(**L**)](ClO$_4$)$_2$ (0.3 g), then the complex was dissolved and white NH$_4$ClO$_4$ was precipitated. After the solids were removed by filtration, water was added to the filtrate until the purple crystals formed. [Cu(**L**)](PF$_6$)$_2$ was dissolved in a minimum amount of DMF/H$_2$O, which was allowed in an open beaker at room temperature. After several weeks, the target complex **1** was separated out as purple plates just before the solution was dried up. Suitable crystals of **1** for X-ray diffraction studies and subsequent spectroscopic measurements were manually collected under the microscope. Anal. Calcd. for C$_{16}$H$_{38}$CuF$_{12}$N$_6$O$_2$P$_2$ (**1**): C, 27.43; H, 5.43; N, 12.00. Found C, 27.42; H, 5.42; N, 12.41%. IR (Nujol, cm^{-1}): 3279 (νNH), 1650 (νCO).

X-ray crystallography. A summary of selected crystallographic data and selected interatomic distances and angles for **1** are given in Tables 1 and 2. X-ray data were collected on a Nonius Kappa CCD diffractometer, using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A combination of 1° phi and omega (with kappa offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.[7] The structure was solved and refined, using the SHELXTL\PC V5.1 package.[8] Refinement was performed by full-matrix least squares on F^2 using all data (negative intensities included). Hydrogen atoms were included in calculated positions, except for those involving hydrogen bonding specifically for the hydrogen atoms bonded to the nitrogen atoms, which were refined with isotropic thermal parameters.

Results and Discussion

Upon recrystallization of [Cu(**L**)](PF$_6$)$_2$ from DMF/H$_2$O, we obtained the DMF coordinated complex **1** as purple plates. The crystals of **1** retain their transparency for several weeks in a refrigerator, but they slowly decompose upon exposure to the atmosphere as evidenced by elemental analysis. The infrared spectrum and microanalysis for **1** clearly support the structure determined by the X-ray diffraction studies as described in the Experimental Section.

The crystal structure of **1** consists of a monomeric [Cu(**L**)(DMF)$_2$]$^{2+}$ cation and PF$_6$ anions (Figure 1). The

Table 1. Crystal data and structure refinement for **1**

Empirical formula	C$_{16}$H$_{38}$CuF$_{12}$N$_6$O$_2$P$_2$
Formula weight	700
Temperature (K)	150(1)
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 20.8877(5) Å
	b = 10.3326(3) Å
	c = 16.3753(3) Å
	β = 128.2320(10)°
Volume	2776.14(12) Å^3
Z	4
Density (calculated)	1.675 Mg/m^3
Absorption coefficient	1.010 mm^{-1}
Independent reflections	3158 [R(int) = 0.0338]
Goodness-of-fit on F^2	1.050
Final R indices [I > 2σ(I)]	R1 = 0.0392, wR2 = 0.0948
R indices (all data)	R1 = 0.0558, wR2 = 0.1053

R1 = $\Sigma \parallel F_o - F_c \parallel / \Sigma \mid F_o \mid$ and wR2 = [Σ [w(F$_o^2$–F$_c^2$)^2] / Σ [w(F$_o^2$)^2]]$^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°) for **1**

Cu1-N1	2.0306(19)	Cu1-N2	2.0277(19)
Cu1-O1	2.3985(17)	O1-C6	1.237(3)
N3-C6	1.323(3)		
N2#1-Cu1-N1#1	94.11(8)	N2-Cu1-N1#1	85.89(8)
N2-Cu1-O1	94.09(7)	N2-Cu1-O1#1	85.91(7)
N1-Cu1-O1	88.36(7)	N1-Cu1-O1#1	91.64(7)

Symmetry transformations used to generate equivalent atoms: #1 −x+1/2, −y+1/2, −z+1

macrocyclic ligand skeleton of the complex **1** takes the most stable "trans III" conformation with two chair form six-membered and two gauche five-membered chelate rings. An inversion center exists on the central copper(II) ion. Two DMF molecules are coordinated to the central copper(II) ion in axial sites. The coordination environment around the central copper(II) ion shows a tetragonally distorted octahedron with four Cu-N and two Cu-O bonds. The four Cu-N distances are in the range of 2.0306(19)-2.0277(19) Å. The Cu-O distance of 2.3985 (17) Å is considerably shorter than those found in related systems ([Cu(**L**)(H$_2$O)$_2$]F$_2$·4H$_2$O,[2] Cu-O = 2.484(6) Å; ([Cu(en)$_2$(H$_2$O)$_2$]F$_2$·4H$_2$O,[2] Cu-O = 2.571 (6) Å, en = ethylenediamine; ([Cu(**L1**)(H$_2$O)$_2$]Cl$_2$,[4] Cu-O = 2.649(2) Å, **L1** = 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0$^{1.18}$, 0$^{7.12}$] docosane; ([Cu(**L2**)(H$_2$O)$_2$]Cl$_2$,[3] Cu-O = 2.666(2) Å, **L2** = 3,5,10,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane; ([Cu(**L**)(CH$_3$CN)$_2$](CF$_3$SO$_3$)$_2$,[9] Cu-N$_{axial}$ = 2.570(5) Å; ([Cu(**L1**)(CH$_3$CN)$_2$](PF$_6$)$_2$,[5] Cu-N$_{axial}$ = 2.594(2) Å). One of the salient structural features found in **1** is the shortness of Cu-O distances. Although no hydrogen-bonding chelate rings are involved in **1**, the DMF molecules, which form stronger coordination than water molecules, preferentially coordinate to the copper(II) ion in DMF/H$_2$O cosolvents. The PF$_6$ anions mediate between the two [Cu(**L**)(DMF)$_2$]$^{2+}$ units through hydrogen bonding interactions (N(1)-H(1)···F(2) = 3.305(3) Å, (N(1)-H(1)···F(3) = 3.197(3) Å, (N(2)-H(2)···F(4)#2 = 3.181(3) Å, #2 x+1/2, y+1/2, −z+3/2),

resulting in the formation of hydrogen bonded polymer. The presence of PF$_6$ as anions appears to be crucial for the formation of DMF coordinated complex **1**. It was unsuccessful to obtain such a complex by using [Cu(**L**)](ClO$_4$)$_2$ instead of [Cu(**L**)](PF$_6$)$_2$. In the 14-membered copper(II) tetraazamacrocyclic systems, it has been generally recognized that the axial bonds are achieved when the hydrogen bonds play a role in stabilizing the coordination of an appropriate donor ligands to the central metal ions.[2-4] One of the exceptions is the interaction of CH$_3$CN to the copper(II) ion.[5,9] This is possibly due to the fairly good σ-donor and π-acceptor properties of CH$_3$CN. In the present complex **1**, the DMF molecule shows even stronger interactions to the copper(II) ion than CH$_3$CN ([Cu(**L**)(DMF)$_2$]-(PF$_6$)$_2$, Cu-O = 2.3985(17) Å; ([Cu(**L1**) (CH$_3$CN)$_2$](PF$_6$)$_2$,[5] Cu-N$_{axial}$ = 2.594(2) Å; [Cu(**L**)(CH$_3$CN)$_2$] (CF$_3$SO$_3$)$_2$,[11] Cu-N$_{axial}$ = 2.570(5) Å). For DMF ligands coordinated through oxygen, internal bond distances of C-O = 1.237(3) Å and C-N = 1.323(3) Å lengthen compared to those of the lattice DMF (C-O = 1.221(7) Å, C-N = 1.315(7) Å).[10] This is in accord with the band assigned as carbonyl stretch in the IR spectrum showing ~ 20 cm^{-1} to lower energies for **1** (νCO = 1650 cm^{-1}) compared to that of neat DMF (νCO = 1670 cm^{-1}). The solid state electronic spectrum in the visible region shows a band at 543 nm which represents a composite of the three transitions d$_{xy}$, d$_{xz}$, d$_{yz}$ → d$_{x^2-y^2}$. However, the lowest energy absorption due to the d$_{z^2}$ → d$_{x^2-y^2}$ transition was not observed in **1**. In general, the electronic spectra of octahedral copper(II) complexes exhibit a characteristic two-band pattern due to the Jahn-Teller induced tetragonal distortions.[11] On this account, the complex **1** containing two DMF ligands could be a good system for the understanding of probable copper(II) catalyzed hydrolysis of DMF. The behavior of the complex **1** in solvents of varying pH is currently under investigation.

Supplementary material. Crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC), CCDC No. 246464 for **1**.
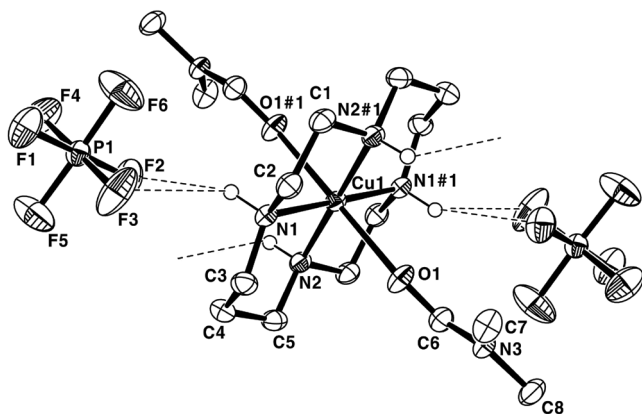

Figure 1. Molecular structure of **1** with atom-labeling scheme. Hydrogen atoms other than those participating in hydrogen bonding are omitted for clarity.

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