Crystal Structure of Chlorobis(*R*-1-pyridine-2-ylethylamine)copper(II) Chloride

Hiromasa KUROSAKI,^{*,†} Koki MATSUDA,^{*} Naoki YAMAKAWA,^{*} Yoshihiro YAMAGUCHI,^{**} and Tulio CHAVEZ-GIL^{***}

^{*}Graduate School of Pharmaceutical Sciences, Kumamoto University,
Oe-honmachi 5-1, Kumamoto 862-0973, Japan

^{**}Environmental Safety Center, Kumamoto University, 39-1 Kurokami 2-Chome, Kumamoto 860-8555, Japan

^{***}Department of Biology, Chemistry and Environmental Science, Inter-American University of Puerto Rico,
San German, PR 00683-9801, USA

The title copper(II) complex crystallized in the monoclinic space group $P2_1$ with $a = 8.821(1)$, $b = 7.168(2)$, $c = 15.134(1)$ Å, $\beta = 100.636(8)^\circ$, $V = 940.5(2)$ Å³, and $Z = 2$. The complex is a distorted square pyramidal geometry around the copper atom with four nitrogen atoms of two bidentate ligands and one axial Cl atom.

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A number of copper(II) complexes derived from 2-aminomethylpyridine derivatives have been synthesized and characterized in order to investigate the structural correlations towards spectroscopy in conjunction with X-ray crystallography,¹ and superoxide dismutase (SOD)-mimetic activity.² Recently, we extended our efforts and prepared a copper(II) complex with a chiral ligand, *R*-1-pyridine-2-ylethylamine (= *R*-pye), in order to study biological superoxide dismutase (SOD)-mimetic SOD-mimetic activity.

Herein, we describe the crystal structure of a chiral copper(II) complex of *R*-pye. The ligand *R*-pye was synthesized as described in the literature.³ The copper(II) complex was prepared as follows: to a solution of $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ (0.300 g, 1.97 mmol) in 2.0 mL of water was added to a solution of *R*-pye ligand (0.460 g, 3.77 mmol) in 5.0 mL of acetonitrile. The formation of crystals was observed immediately, and the mixture was left standing at room temperature overnight, yielding bluish single crystals of $[\text{Cu}(\text{R-pye})_2\text{Cl}]\text{Cl} \cdot 2\text{H}_2\text{O}$ (0.710 g, 88%) ($1 \cdot 2\text{H}_2\text{O}$; Fig. 1). The crystals were collected on a filter, washed with diethyl ether, and dried under calcium chloride and phosphorous pentoxide.

Data collections were performed at 293 K with graphite-

monochromated Mo K_α radiation on a Rigaku AFC7R diffractometer ($\lambda = 0.71069$ Å). The complex was solved by heavy-atom Patterson methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares based on F^2 . Hydrogen atoms were located by geometrical calculations, and were not refined. All calculations were performed using teXsan crystallographic software.⁴ The crystal data and experimental data are listed in Table 1. The atomic coordinates and temperature factors for non-H atoms are given in Table 2, and selected bond distances and angles are listed in Table 3. A molecular structure of the cationic part of $1 \cdot 2\text{H}_2\text{O}$ is depicted in

Fig. 1 Chemical structure of $1 \cdot 2\text{H}_2\text{O}$.

[†] To whom correspondence should be addressed.
E-mail: ayasaya@gpo.kumamoto-u.ac.jp.

Table 1 Crystal data and experimental data

Empirical formula: $\text{CuCl}_2\text{H}_{24}\text{C}_{14}\text{N}_4\text{O}_2$	
Formula weight = 414.82	
Crystal system	monoclinic
Space group: $P2_1$	$Z = 2$
$a = 8.821(1)$ Å	
$b = 7.168(2)$ Å	$\beta = 100.636(8)^\circ$
$c = 15.134(1)$ Å	
$V = 940.5(2)$ Å ³	
$D_{\text{calc}} = 1.465$ g/cm ³	
No. measured reflections = 2472 (unique: 2327 ($R_{\text{int}} = 0.019$))	
$2\theta_{\text{max}} = 55^\circ$ with Mo K_α	
$R_1 = 0.033$	
$R_w = 0.038$	
Goodness-of-fit = 1.42	
$(\Delta/\sigma)_{\text{max}} = 0.114$	
$(\Delta\rho)_{\text{max}} = 0.55$ e Å ⁻³	
$(\Delta\rho)_{\text{min}} = -0.35$ e Å ⁻³	
Measurement: Rigaku AFC7R	
Program system: Rigaku teXsan	
Structure determination: Patterson method (DIRDIF94 PATTY)	
Refinement: full-matrix least-squares on F^2	
CCDC deposition number: 693422	

Table 2 Atomic coordinates and equivalent isotropic thermal parameters B_{eq}

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
Cu(1)	0.19524(4)	0.4998(1)	0.24663(2)	2.343(6)
Cl(1)	0.2335(1)	0.1569(2)	0.28999(6)	3.52(2)
Cl(2)	-0.2988(1)	0.2523(2)	0.22417(6)	3.71(2)
O(1)	-0.0642(4)	0.9261(5)	0.2957(2)	5.25(8)
O(2)	0.5497(4)	0.4309(5)	0.8090(2)	6.09(8)
N(1)	0.2878(3)	0.5874(4)	0.3729(2)	2.59(5)
N(2)	0.0019(3)	0.5236(5)	0.2967(2)	2.45(5)
N(3)	0.0951(3)	0.4919(6)	0.1153(2)	2.57(4)
N(4)	0.3861(3)	0.5284(5)	0.1944(2)	2.48(5)
C(1)	0.1938(4)	0.5617(5)	0.4324(2)	2.49(6)
C(2)	0.2457(4)	0.5926(6)	0.5234(2)	3.39(7)
C(3)	0.3949(4)	0.6512(7)	0.5528(2)	3.71(8)
C(4)	0.4896(5)	0.6787(6)	0.4916(3)	3.76(8)
C(5)	0.4320(4)	0.6467(6)	0.4023(2)	3.43(7)
C(6)	0.0360(3)	0.4856(6)	0.3937(2)	2.59(6)
C(7)	-0.0932(4)	0.5556(6)	0.4408(2)	3.56(8)
C(8)	0.1943(3)	0.4891(6)	0.0579(2)	2.51(5)
C(9)	0.1408(4)	0.4972(9)	-0.0343(2)	3.86(7)
C(10)	-0.0146(4)	0.5033(9)	-0.0670(2)	4.06(7)
C(11)	-0.1156(4)	0.5016(9)	-0.0090(2)	3.80(7)
C(12)	-0.0564(4)	0.4972(8)	0.0818(2)	3.42(6)
C(13)	0.3621(4)	0.4683(5)	0.0994(2)	2.72(7)
C(14)	0.4714(4)	0.5664(6)	0.0480(2)	4.17(9)

$$B_{\text{eq}} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha).$$

Table 3 Selected bond distances (Å) and angles (°)

Cu(1)–Cl(1)	2.550(2)	Cu(1)–N(1)	2.034(3)
Cu(1)–N(2)	1.997(3)	Cu(1)–N(3)	2.022(3)
Cu(1)–N(4)	1.998(3)		
Cl(1)–Cu(1)–N(1)	92.6(1)	Cl(1)–Cu(1)–N(2)	93.8(1)
Cl(1)–Cu(1)–N(3)	103.8(1)	Cl(1)–Cu(1)–N(4)	96.9(1)
N(1)–Cu(1)–N(2)	80.8(1)	N(1)–Cu(1)–N(3)	163.6(2)
N(1)–Cu(1)–N(4)	96.8(1)	N(2)–Cu(1)–N(3)	97.3(1)
N(2)–Cu(1)–N(4)	169.2(2)	N(3)–Cu(1)–N(4)	82.0(1)

Fig. 2. The cationic part of $1 \cdot 2\text{H}_2\text{O}$ consists of a Cu atom bonded to four nitrogen atoms of two bidentate ligands that are *trans* relative to each other, and one Cl atom, forming a distorted square pyramidal environment. The four nitrogen atoms occupy equatorial positions, forming a five-membered chelate ring with bite angles of 80.8(1) and 82.0(1)°, whereas the Cl atom, Cl(1), occupies the axial position. The Cu atom is displaced 0.236(2) Å above the mean basal plane in the direction of an axial Cl(1). Two methyl groups are placed in equatorial positions with respect to the coordination plane. The Cu–N bond distances (1.997(3) – 2.034(3) Å) are similar to those reported for related compounds (1.9948(17) – 2.021(2) Å),⁵ whereas the longest distance corresponds to the Cu(1)–Cl(1) distance (2.551(2) Å), which indicates tetragonal distortion.

In the crystal structure of $1 \cdot 2\text{H}_2\text{O}$ (Fig. 3), two water molecules are hydrogen bonded to the primary amine of *R*-pye [N(2)–H(9)···O(1)ⁱ = 2.020 Å, N(4)–H(20)···O(2)ⁱⁱ = 2.009 Å; symmetry

Fig. 2 ORTEP drawing of the cationic part of $1 \cdot 2\text{H}_2\text{O}$ with thermal ellipsoids drawn at the 50% probability level. Fig. 3 Crystal packing diagram of $1 \cdot 2\text{H}_2\text{O}$.

code, (i) *x*, *y*, *z* (ii) $-x+1$, $y+1/2$, $-z+1$]. Moreover, hydrogen bonds [N(2)–H(10)···Cl(2)ⁱ = 2.370 Å and N(4)–H(19)···Cl(2)ⁱⁱⁱ = 2.528 Å; symmetry code, (i) *x*, *y*, *z* (iii) $x+1$, *y*, *z*] are formed between the Cl atoms and the primary amine of *R*-pye.

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