Crystal Structure of Isothiocyanato-*N,N'*-diethyl-*N,N'*-bis(pyridine-2-ylmethyl)propanediaminecopper(II) Perchlorate

Takashi YOKOYAMA,*† Shintaroh HASE,* Masakazu YOSHISE,* Atsushi SHIOMI,* Takuya SHIBA,* Haruo AKASHI,** and Michio ZENKI*

*Department of Chemistry, Faculty of Science, Okayama University of Science,
1-1 Ridai-cho, Kita-ku, Okayama 700-0005, Japan

**Research Institute of Natural Sciences, Okayama University of Science,
1-1 Ridai-cho, Kita-ku, Okayama 700-0005, Japan

A new complex of an isothiocyanato-*N,N'*-diethyl-*N,N'*-bis(pyridine-2-ylmethyl)propanediaminecopper(II) perchlorate ($[\text{Cu}(\text{NCS})(\text{LEt}_2)]\text{ClO}_4$) was prepared. Its crystal structure was determined by single-crystal X-ray diffractometry. $[\text{Cu}(\text{NCS})(\text{LEt}_2)]\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ crystallized in a monoclinic system, and was characterized thus: $C2/c$, with $a = 20.8501(10)$, $b = 17.2174(9)$, $c = 15.0630(7)$ Å, $\beta = 119.049(3)^\circ$, $Z = 8$, $V = 4727.2(4)$ Å³. The crystal structure was solved by direct methods and refined by full-matrix least squares on F^2 to final values of $R1 = 0.0585$.

(Received August 9, 2011; Accepted September 28, 2011; Published on web November 10, 2011)

Crystal structures of *N,N'*-dimethyl-*N,N'*-bis(pyridine-2-ylmethyl)propanediaminecopper(II) perchlorate ($[\text{Cu}(\text{LMe}_2)](\text{ClO}_4)_2$)¹ and isothiocyanato-*N,N'*-dimethyl-*N,N'*-bis(pyridine-2-ylmethyl)propanediaminecopper(II) perchlorate ($[\text{Cu}(\text{NCS})(\text{LMe}_2)]\text{ClO}_4$)² have been reported. Each of the *N*-methyl groups is placed at a *trans*- and a *cis*-configuration for $[\text{Cu}(\text{LMe}_2)](\text{ClO}_4)_2$ and $[\text{Cu}(\text{NCS})(\text{LMe}_2)]\text{ClO}_4$, respectively. This would be a reason why a distortion of the complex cation was released to re-bind LMe_2 with Cu(II) after the dissociation of LMe_2 from $[\text{Cu}(\text{LMe}_2)]^{2+}$; as a result, the isothiocyanate ion strongly coordinated to $[\text{Cu}(\text{LMe}_2)]^{2+}$. When the two *N*-methyl groups were replaced at two *N*-ethyl groups, which might make a large steric hindrance in a peripheral ligand of Cu(II), it is interesting to investigate the configuration of the *N*-ethyl groups for *N,N'*-diethyl-*N,N'*-bis(pyridine-2-ylmethyl)propanediaminecopper(II) ($[\text{Cu}(\text{LEt}_2)]^{2+}$). Its crystal structure and preparation have not yet been reported. Therefore, the $[\text{Cu}(\text{LEt}_2)]^{2+}$ complex was prepared, and its crystal structure was determined in this work.

N,N'-Bis(pyridine-2-ylmethyl)propanediamine (LH_2) was prepared according to a published preparation method.^{2,3} The LH_2 of a liquid was purified through an amino silica gel (100 – 200 mesh, Fuji Silysia Chem., Aichi, Japan) column by an eluent-mixed ethyl acetate with hexane at a volume ratio of 1:1. The ligand *N,N'*-diethyl-*N,N'*-bis(pyridine-2-ylmethyl)propanediamine (LEt_2) was prepared by refluxing a mixture of LH_2 (0.08 mol) with ethyl bromide (0.48 mol, Wako) dissolved

Fig. 1 Chemical diagram of the title compound.

† To whom correspondence should be addressed.
E-mail: tyokoyam@chem.ous.ac.jp

Table 1 Crystal and experimental data

Chemical formula: $\text{C}_{20}\text{H}_{29}\text{N}_5\text{CuClO}_{4.5}\text{S}$	
Formula weight = 542.54	
$T = 296$ K	
Crystal system: monoclinic	Space group: $C2/c$
$a = 20.8501(10)$ Å	
$b = 17.2174(9)$ Å	$\beta = 119.049(3)^\circ$
$c = 15.0630(7)$ Å	
$V = 4727.2(4)$ Å ³	$Z = 8$
$D_x = 1.525$ g/cm ³	
Radiation: Mo $K\alpha$ ($\lambda = 0.71069$ Å)	
$\mu(\text{Mo } K\alpha) = 1.1646$ mm ⁻¹	$F(0\ 0\ 0) = 2256$
Crystal size = $0.10 \times 0.10 \times 0.10$ mm ³	
No. of reflections collected = 16857	
No. of independent reflections = 5215	
θ range for data collections = 1.8 to 27.5°	
Data/Restraints/Parameters = 5215/0/316	
Goodness-of-fit on $F^2 = 1.056$	
R indices $[I > (2\sigma(I))]$: $R1 = 0.0498$	
R indices (all data): $R1 = 0.0585$, $wR2 = 0.1188$	
$(\Delta\rho)_{\text{max}} = 0.000$	
$(\Delta\rho)_{\text{max}} = 0.76$ eÅ ⁻³	$(\Delta\rho)_{\text{min}} = -0.64$ eÅ ⁻³
Measurement: Rigaku RAXIS IV	
Program systems: CrystalStructure3.8, SHELXL97	
Structure determination: SIR2002	
CCDC deposition number: 827772

Fig. 2 ORTEP structure of $[\text{Cu}(\text{NCS})(\text{LEt}_2)]\text{ClO}_4$, showing 50% probability ellipsoids. Hydrogen atoms were omitted for clarity.

in 100 mL of distilled methanol at 70°C for 72 h. The ligand LEt_2 of a liquid was purified by the same method as in the purification of LH_2 . The yield of LEt_2 was 26%. Blue single crystals of $[\text{Cu}(\text{NCS})(\text{LEt}_2)]\text{ClO}_4$ were grown from a mixed methanolic solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich, Milwaukee, WI) and potassium thiocyanate (Wako) with LEt_2 at a mole ratio of 1:1:1.

The chemical structure of $[\text{Cu}(\text{NCS})(\text{LEt}_2)]\text{ClO}_4$ is illustrated in Fig. 1. Figure 2 shows a labeling diagram of $[\text{Cu}(\text{NCS})(\text{LEt}_2)]\text{ClO}_4$; water molecule is omitted in the crystal. The crystal data are summarized in Table 1. $[\text{Cu}(\text{NCS})(\text{LEt}_2)]\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ crystallized in a monoclinic system, and was characterized thus: $C2/c$, $a = 20.8501(10)$, $b = 17.2174(9)$, $c = 15.0630(7)\text{\AA}$, $\beta = 119.049(3)^\circ$, $Z = 8$, $V = 4727.2(4)\text{\AA}^3$. The crystal structure was solved by direct methods and refined by full-matrix least squares on F^2 to final values of $R1 = 0.0585$. The structures of the disordered perchlorate ion and water molecule in the crystal were determined by fixing the occupancy factors at the same values. The selected bond distances and angles for non-hydrogen atoms are summarized in Table 2. The atomic coordinates and the other bond distances and angles for non-hydrogen atoms are summarized in Tables S1 – S3 (Supporting Information).

The N -ethyl groups for $[\text{Cu}(\text{NCS})(\text{LEt}_2)]\text{ClO}_4$ were placed at a *cis* configuration to each other, as a configuration of the N -methyl groups for $[\text{Cu}(\text{NCS})(\text{LMe}_2)]\text{ClO}_4$. Since the

Table 2 Selected bond distances ($\text{\AA}$) and angles ($^\circ$)

Cu1-N1	2.064(2)	Cu1-N2	2.111(2)
Cu1-N3	1.993(2)	Cu1-N4	2.086(3)
Cu1-N5	2.050(3)		
N1-Cu1-N2	96.87(9)	N1-Cu1-N3	176.88(14)
N1-Cu1-N4	82.61(10)	N1-Cu1-N5	91.67(11)
N2-Cu1-N3	82.73(9)	N2-Cu1-N4	128.85(12)
N2-Cu1-N5	124.68(13)	N3-Cu1-N4	95.22(10)
N3-Cu1-N5	91.09(11)	N4-Cu1-N5	106.42(11)

perchlorate ion did not coordinate to the $[\text{Cu}(\text{NCS})(\text{LEt}_2)]^+$, it was a five-coordinated species of a trigonal bipyramidal geometry, as the geometry of the $[\text{Cu}(\text{NCS})(\text{LMe}_2)]^+$. The bond distances of Cu1-N and the angles of N-Cu1-N' for the $[\text{Cu}(\text{NCS})(\text{LEt}_2)]^+$ given in Table 2 were almost similar to those for the $[\text{Cu}(\text{NCS})(\text{LMe}_2)]^+$.² Therefore, the N -ethyl groups for the $[\text{Cu}(\text{NCS})(\text{LEt}_2)]^+$ would have an almost similar steric factor as the N -methyl groups for the $[\text{Cu}(\text{NCS})(\text{LMe}_2)]^+$.

Supporting Information

Atomic coordinates (Table S1) and bond distances (Table S2) and angles (Table S3) for non-hydrogen atoms. These materials are available free of charge on the Web at <http://www.jsac.or.jp/analscix/>.

Acknowledgments

We thank Mr. Ryoichi Yoshida for his helpful assistance.

References

1. T. Pandiyan, H. J. Guadalupe, J. Cruz, S. Bernès, V. M. Ugalde-Salvdivar, and I. González, *Eur. J. Inorg. Chem.*, **2008**, 3274.
2. T. Yokoyama, M. Yoshise, S. Hase, A. Kawate, H. Akashi, and M. Zenki, *X-ray Struct. Anal. Online*, **2011**, 27, 51.
3. C.-M. Che, W.-T. Tang, and C.-K. Li, *J. Chem. Soc., Dalton Trans.*, **1990**, 3735.