Instrumental Achievements

Crystal Structure of Bis(2-mercaptotiazoline)copper(I) Chloride, [Cu(mtz)₂Cl]

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Since copper(I) favors a four-coordinate tetrahedral geometry, there has been a vast body of tetrahedral copper(I) complexes characterized crystallographically.¹ This is because the tetrahedral form is stable in copper(I) chemistry. On the other hand, although trigonal copper(I) complexes are coordinately unsaturated and unpopular, they often exist as reaction intermediates. It is important to add new structures to trigonal copper(I) chemistry. This work considered trigonal CuL_3 having a thione sulfur donor.

Colorless single crystals of $[\text{Cu}(\text{mtz})_2\text{Cl}]$ (**1**) were obtained from a mixture of CuCl (0.05 mmol) and mtz (0.10 mmol) in CH_3CN (10 ml). Diffraction data were collected on a Rigaku AFC-5R diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda=0.71069$ Å). The structure was solved by a direct method (MITHRIL)² and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. The positions of the hydrogen atoms were

obtained from difference Fourier syntheses. All of the calculations were performed using a TEXSAN crystallographic software package.³

The structure of complex **1** is shown in Fig. 1. This molecule has a two-fold symmetry along the Cu(1)–Cl(1) vector, which coincides with the crystallographic two-fold axis along the *b*-axis. The Cu(1) atom is coordinated by S atoms and a Cl ion, having a trigonal planar geometry. The mtz ligand has two coordination forms due to its tautomerism. One is a neutral thione sulfur form; the other is an anionic thiolate sulfur form. The molecular structure shows that the C(1)–S(1) distance is 1.693(4) Å, thus indicating the thione form. The Cu(1)–S(1) distance of 2.232(1) Å falls within the distances (2.206(2)–2.480(3) Å) of Cu^I complexes with the thione form.^{4a–h} The Cu(1)–Cl(1) distance of 2.283(2) Å is close to that (2.260 Å) of analogous Cu^I complexes [Cu(2-thiouracil)₂Cl].^{5a} The angles around the Cu(1) atom are nearly 120° in the range (109.1 –

Fig. 1 ORTEP view of [Cu(mtz)₂Cl] (1) and atomic numbering. Selected bond distances(Å) and bond angles(°). Cu(1)–Cl(1)=2.283(2), Cu(1)–S(1)=2.232(1), C(1)=S(1)=1.693(4), Cl(1)–Cu(1)–S(1)=117.96(3), S(1)–Cu(1)–S(1')=124.07(6).

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Table 1 Crystal and experimental data

Formula: CuClS ₄ N ₂ C ₆ H ₁₀
Formula weight: 337.40
Crystal system: monoclinic
Space group: C2/c Z=4
a=14.245(4) Å
b=6.342(2) Å
c=13.519(2) Å
β=101.01(1)°
V=1178.7(5) Å ³
D _{calc} =1.901 g/cm ³
R=0.036 Rw=0.044
No. of reflection used=1536 (I>3σ(I))
Measurement: Rigaku AFC-5R
Program system: TEXSAN
Structure determination: direct method (MITHRIL)
Refinement: full-matrix least-squares

Table 2 Final atomic coordinates and equivalent isotropic thermal parameters $B_{eq}(\text{\AA}^2)$ of non-hydrogen atoms

Atom	x	y	z	B_{eq}
Cu(1)	1.0000	0.0469(1)	0.2500	3.18(3)
Cl(1)	1.0000	0.4068(2)	0.2500	4.11(6)
S(1)	1.08696(7)	-0.1181(1)	0.38994(7)	3.13(4)
S(2)	1.1784(1)	-0.0122(2)	0.60728(8)	4.56(5)
N(1)	1.1092(2)	0.2684(5)	0.4758(2)	3.0(1)
C(1)	1.1209(2)	0.0646(6)	0.4838(3)	2.6(1)
C(2)	1.1932(3)	0.2543(7)	0.6535(3)	3.9(2)
C(3)	1.1393(3)	0.3943(7)	0.5676(3)	3.8(2)

$$B_{eq} = (4/3) \sum_i \sum_j \beta_{ij} (a_i \cdot a_j).$$

135.4 Å) of Cu^I complexes^{5a-f} having a trigonal planar geometry. In the intermolecule, the N-H group of two mtz ligand has two hydrogen bonds between the Cl atom, whose N(1)⋯Cl(1) distance is 3.165(3) Å. This hydrogen-bond distance is similar to those (3.079–3.33 Å) of analogous Cu^I complexes^{4a-c} having a thioamide framework. This is associated with the stability of the trigonal structure.

This work was supported in part by a Grant-in-Aid for Science Research (No. 04453049, 05453131 and 05453046) from the Ministry of Education, Science and Culture in Japan.

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(Received August 9, 1993)

(Accepted August 26, 1993)