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Synthesis and Crystal Structure of Copper(II) Complex with Bis(2-aminoethyl)sulfide and Thiocyanate as Ligands

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The study of the copper(II) complexes has become a rapidly developing research area for the importance of the complexes in life science and material science. Although many kinds of tridentate ligands have been used to synthesize the copper(II) complexes, the complexes dealing with bis(2-aminoethyl)sulfide [L] as tridentate ligand has been very few [1–2]. In this paper the synthesis and structural features of the novel complex of copper(II) with bis(2-aminoethyl)sulfide and thiocyanate as ligands are reported.

A solution of bis(2-aminoethyl)sulfide (0.2540 g, 2.110 mmol) in methanol (10 cm^3) was added to a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.7828 g, 2.11 mmol) in H_2O (10 cm^3) and the solution was stirred for a few of minutes, then the solution of NaSCN (0.1374 g, 2.11 mmol) in methanol (10 cm^3) was added to the stirred solution in drops and the green microcrystals appeared immediately. After the mixture was stirred for 5 minutes and the green microcrystals were filtered, the microcrystals were dissolved in small amount of water and the deep green crystals for the following analyses were obtained a few of days later. Found: C, 24.10; H, 4.32; N, 18.43; Cu, 21.35%. Calc. for $C_6H_{12}N_4S_3Cu$: C, 24.02; H, 4.03; N, 18.68; Cu, 21.19%.

Details of crystal parameters, data collection and structure refinement are given in Table 1. All data reduction and structure refinement were performed using the SHELX 97 program system. Fractional coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms and selected bond lengths and angles are listed in Table 2 and 3, respectively.

Table 1. Crystallographic data and collection parameters for the complex.

Formula	$C_6H_{12}N_4S_3Cu$
Formula weight	299.944
Crystal system	orthorhombic
Space group	Pna2(1)
a (Å)	10.8594(17)

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Table 1 (continuation)

b (Å)	13.020(2)
c (Å)	8.2872(13)
$\alpha = \beta = \gamma$	90°
V (Å^3)	1171.7(3)
Dc (g/cm^3)	1.700
Crystal dimensions (mm)	0.5×0.5×0.4
Color	deep green
Temperature (K)	293(2)
Radiation wavelength (Å)	MoKα 0.71073
Absorption coefficient (mm^{-1})	2.385
F(000)	692
θ range for data collection	2.44 to 25.01
Limiting indices	$-12 \leq h \leq 12$, $-8 \leq k \leq 15$, $-9 \leq 1 \leq 9$
Reflections collected/unique	5821/2002 [R(int) = 0.0175]
Completeness to θ = 25.01	99.9%
Refinement method	Full-matrix least-square on F^2
Data/restraints/parameters	2002/1/175
Goodness-of-fit on F^2	0.999
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0189, wR2 = 0.0452
R indices (all data)	R1 = 0.0206, wR2 = 0.0458
Absolute structure parameter	0.033 (12)
Largest diff. peak and hole	0.202 and –0.151 e.Å^{-3}

Table 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) . U(eq.) defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cu(1)	9936(1)	6550(1)	4650(1)	42(1)
N(1)	8680(2)	5568(2)	5369(3)	61(1)
N(2)	9292(2)	6433(2)	2440(3)	62(1)
N(3)	11211(2)	7561(2)	3813(3)	52(1)
N(4)	10752(2)	6465(2)	6846(3)	47(1)
S(1)	7244(1)	3865(1)	6043(1)	60(1)
S(2)	8221(1)	5653(1)	–346(1)	62(1)
S(3)	8978(1)	8271(1)	5869(1)	52(1)
C(1)	8095(2)	4859(2)	5659(3)	43(1)

Table 2 (continuation)

C(2)	8842(2)	6117(2)	1281(3)	45(1)
C(3)	10669(3)	8560(3)	3398(4)	67(1)
C(4)	10057(3)	9079(2)	4798(7)	67(1)
C(5)	9743(3)	8034(3)	7784(4)	61(1)
C(6)	10926(3)	7445(2)	7686(3)	52(1)

Table 3. Selected bond lengths (Å) and angles (°).

Cu(1)–N(1)	1.963(2)	Cu(1)–N(2)	1.966(3)
Cu(1)–N(3)	2.032(3)	Cu(1)–N(4)	2.027(2)
Cu(1)–S(3)	2.6687(8)		
N(1)–Cu(1)–N(2)	89.13(10)	N(1)–Cu(1)–N(4)	89.75(10)
N(2)–Cu(1)–N(4)	170.89(10)	N(1)–Cu(1)–N(3)	177.65(11)
N(2)–Cu(1)–N(3)	88.52(11)	N(4)–Cu(1)–N(3)	92.57(11)
N(1)–Cu(1)–S(3)	99.26(8)	N(2)–Cu(1)–S(3)	106.18(8)
N(3)–Cu(1)–S(3)	81.45(8)	N(4)–Cu(1)–S(3)	82.92(7)

The complex crystallizes in the orthorhombic, space group $Pna2(1)$ with a = 10.8594(17), b = 13.020(2), c = 8.2872(13) Å, $\alpha = \beta = \gamma = 90°$, V = 1171.7(3) Å^3, Z = 4, Dc = 1.700 g/cm^3, and $F(000)$ = 692. Crystallographic data have been deposited at Cambridge Crystallographic Data Centre (no. CCDC 161874).

The ORTEP drawing of [CuL(NCS)$_2$] with the atom numbering scheme is shown in Fig. 1, while the unit cell and packing diagram is shown in Fig. 2. The X-ray structure reveals that the copper atom is pentacoordinated by one sulfur of L, two nitrogen

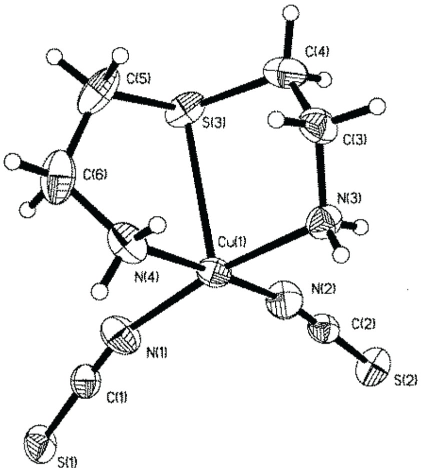

Figure 1. The ORTEP drawing of [Cu(L)(NCS)$_2$] with atom numbering scheme.

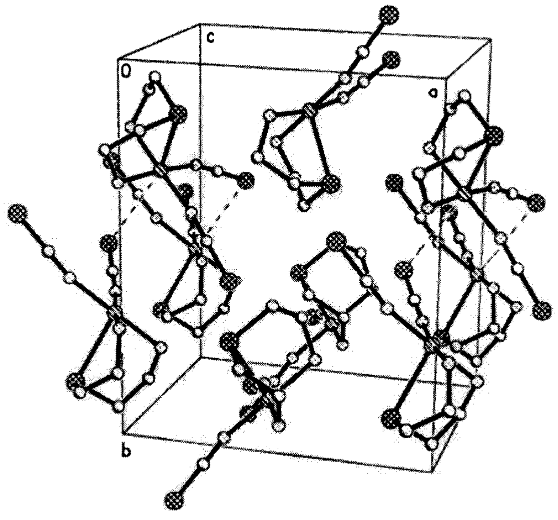

Figure 2. Unit cell and packing diagram for the complex.

atoms of L and another two nitrogen atoms of SCN^-. The coordination polyhedron of the copper(II) is square-pyramidal and the sulfur atom and the four nitrogen atoms locate on the axial position and the basal square plane, respectively. The distance of Cu–N is in the range of 1.963–2.032 Å and that of the Cu–S equals 2.6687(8) Å. To our knowledge the distance of Cu–S is one of the longer bonds in copper complexes with square-pyramidal coordination environment [3–4].

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