

Synthesis and Crystal Structure of the π Copper(I) Cyanide Complex with N,N'-Diallyl Thiocarbamide $2\text{CuCN} \cdot (\text{C}_3\text{H}_5\text{NH})_2\text{CS}$

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Received October 12, 2006

Abstract—Crystals of the π copper(I) cyanide complex with N,N'-diallyl thiocarbamide, $2\text{CuCN} \cdot (\text{C}_3\text{H}_5\text{NH})_2\text{CS}$ (**I**), are synthesized from an aqueous-methanol solution of potassium nitroprusside, diallyl thiocarbamide on a copper electrode using the method of alternating-current electrochemical synthesis. The crystals are monoclinic: space group $P2_1/n$, $a = 6.9440(5)$ Å, $b = 13.760(1)$ Å, $c = 12.733(1)$ Å, $\beta = 97.280(9)^\circ$, $V = 1206.8(2)$ Å³, $Z = 4$, $R = 0.0361$, $R_w = 0.0362$ for 2836 independent reflections with $F \geq 4\sigma(F)$. A unique polymeric structure is built due to the Cu(I)–(C=C) π bond and the bridging function of the thioamide S atom of the ligand molecule and one of the two independent cyano groups.

DOI: 10.1134/S1070328407110048

INTRODUCTION

The earlier studies of the complex formation of copper(I) salts with allyl thiourea (ATU) – $[\text{Cu}(\text{ATU})(\text{CH}_3\text{CN})]\text{NO}_3$ (**II**) [1], $[\text{Cu}_2(\mu\text{-ATU})_2(\text{ATU})_4]\text{SiF}_6$ [2], $4\text{CuCl} \cdot 6\text{ATU}$ [3], and N,N'-diallyl thiourea (DATU) – $[\text{Cu}_2(\mu\text{-DATU})_2(\text{DATU})_4](\text{NO}_3)_2$ (**III**) [4], showed that in these complexes, except for the first one, the C=C double bond in the presence of the thioamide sulfur atom is incapable of π -coordinating with the Cu(I) atom. Therefore, it seemed of interest to study the behavior of DATU toward the metal atom with the copper(I) pseudo-halide CuCN. The more so, the latter forms complexes, for instance, with imidazole derivatives [5], 2,3-dihydroxyquinoxaline (L, $\text{CuCN} \cdot \text{L}$) [6], and 4,4-dipyridine ($[(\text{CuCN})_2(4,4\text{-Bipy})]$) [7], each of which is characterized by an original polymeric composition.

In this work, we synthesized the copper(I) cyanide complex with DATU $2\text{CuCN} \cdot \text{C}_3\text{H}_5\text{NH}(\text{CS})\text{NHC}_3\text{H}_5$ (**I**) and studied its crystal structure.

EXPERIMENTAL

Synthesis. N,N'-Diallyl thiourea (DATU, $(\text{C}_3\text{H}_5\text{NH})_2\text{CS}$) was synthesized by the direct interaction of allyl amine and mustard oil according to a described procedure [8].

The qualitative single crystals of complex **I** for X-ray diffraction analysis were obtained by the method of alternating-current electrochemical synthesis [9]

from an aqueous-methanol solution of potassium nitroprusside $\text{K}_2[\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$, DATU on the copper electrodes. Colorless crystals of complex **I**, which are rather stable in air and suitable for X-ray diffraction analysis, were formed during two weeks on the electrodes.

The density of the crystals was determined by the flotation method in a chloroform–bromoform mixture.

X-ray diffraction analysis. After the crystals were preliminarily studied by the photomethod, a diffraction set obtained on a CAD-4 single-crystal diffractometer (MoK_α radiation) was used to determine the structure.

The structure was determined by direct methods, and light atoms and hydrogen atoms were localized from the difference Fourier syntheses. The structure was refined by the least-squares method in the full-matrix anisotropic approximation (for hydrogen atoms, in the isotropic approximation). All calculations were performed using the CSD program package. An absorption correction was applied.

The crystallographic data and detection parameters for complex **I** are given in Table 1. The coordinates and thermal parameters of atoms are presented in Table 2. The bond lengths and bond angles are given in Table 3, and the torsion angles are given in Table 4.

RESULTS AND DISCUSSION

In the structure of π complex **I**, two independent copper(I) atoms differ in their environment. The coordination sphere of the Cu(1) atom as a trigonal pyramid is formed by two carbon atoms of the cyano groups

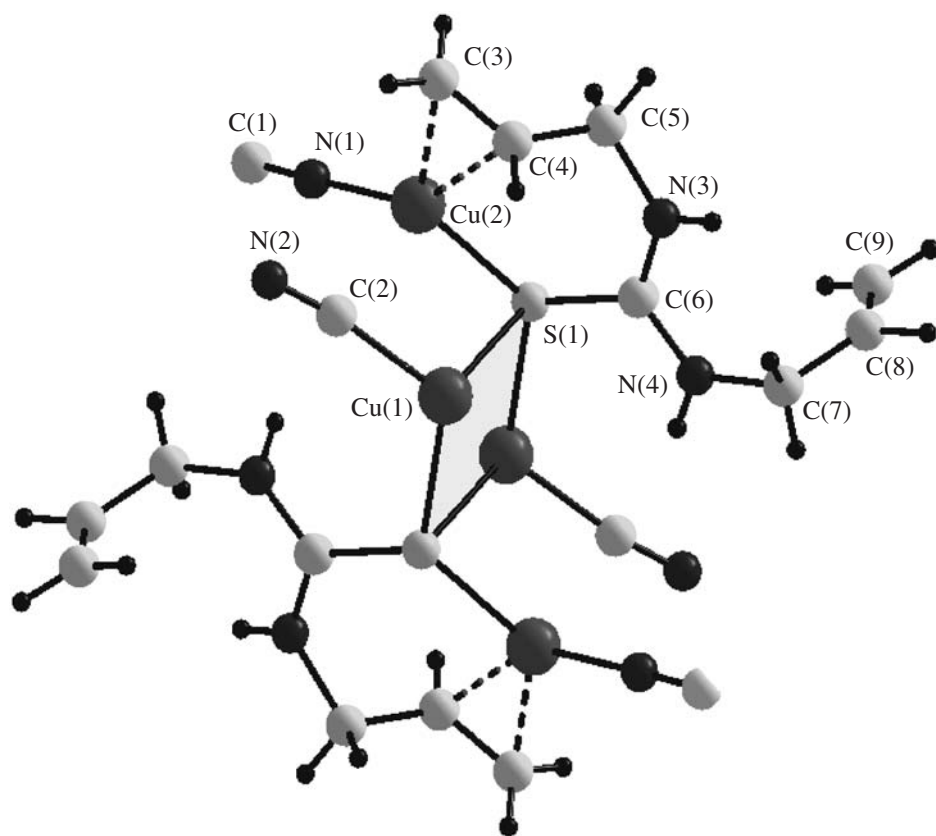


Fig. 1. Fragment of structure I.

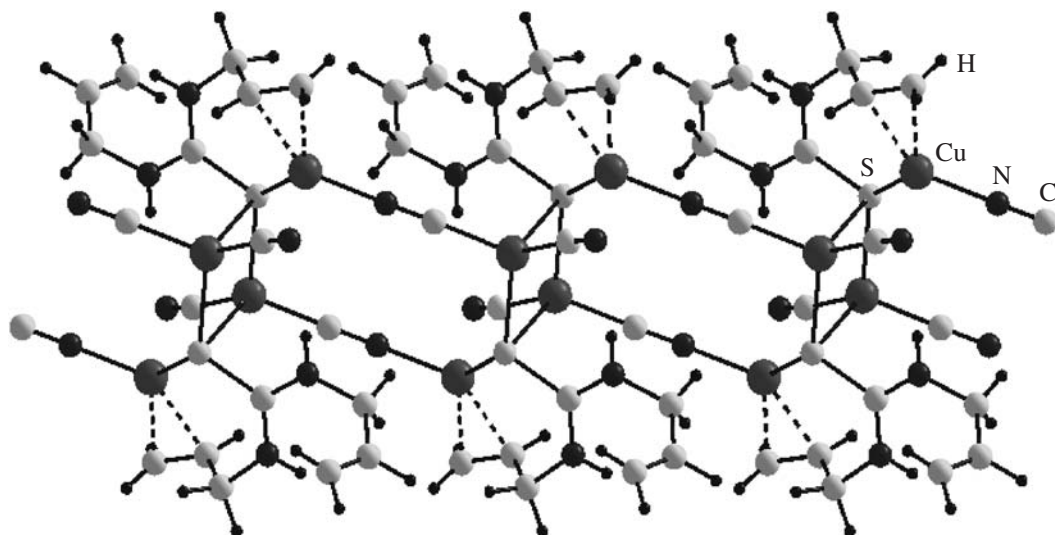


Fig. 2. Polymeric structure I.

(bridging and terminal groups) and two sulfur atoms of the DATU molecules, one of which occupies the apical position (Cu(1)–S(1) 2.810(2) Å). The quasi-planar trigonal environment of the Cu(2) atom is formed by the elongated to 1.355(7) Å C(3)=C(4) bond of one of the two allyl groups and the sulfur atom of DATU and by the N atom of the bridging CN group, whose carbon atom is bound to the Cu(1) atom. The triply bridging S atom is coordinated by two atoms of the Cu(1) type and the Cu(2) atom (Fig. 1). Thus, the polymeric structure of complex **I** is formed due to the bridging function of both the thioamide sulfur atom of DATU and one of the two independent cyano groups. In this structure, a DATU molecule acts as a chelating π,σ ligand toward the Cu(2) atom (Fig. 2). This rare example of the Cu(I)–(C=C) interaction is observed in the presence of the strongly donating thioamide sulfur atom and has the precursor: the CuCN complex with 3,3,6,6-tetramethyl-1-thia-4-cycloheptyne (**L**), [Cu(CN) · (**L**)₄ · THF [10], where the Cu(I)–(C≡C) bond is also formed but in the presence of a less donating thioether sulfur atom. It is most likely that the dual donor–acceptor nature of the cyano group favoring electron density withdrawing from the Cu(2) atom is imparted by the thioamide sulfur atom of the DATU and favors the Cu(I)–(C=C) interaction to occur in compound **I**. The same fact (the presence of the acetonitrile molecule coordinated to the Cu(I) atom and the presence of the NO₃[−] anions in the compound) favors the Cu(I)–(C=C) interaction to occur

Table 1. Crystallographic data and experimental and refinement parameters for structure I

Parameter	Value
Empirical formula	C ₉ H ₁₂ Cu ₂ N ₄ S
FW	335.4
Space group	<i>P</i> 2 ₁ / <i>n</i>
Temperature, K	100
Unit cell parameters:	
<i>a</i> , Å	6.9440(5)
<i>b</i> , Å	13.760(1)
<i>c</i> , Å	12.733(1)
β , deg	97.280(9)
<i>V</i> , Å ³	1206.8(2)
<i>F</i> (000)	672
<i>Z</i>	4
ρ_{meas} , g/cm ³	1.84(1)
ρ_{calcd} , g/cm ³	1.8458(5)
μ_{Mo} , cm ^{−1}	37.97
2 θ_{max} , deg	56.3
Number of reflections:	
measured	7248
independent with $F \geq 4\sigma(F)$	2836
Number of refined parameters	197
<i>R</i> , <i>R</i> _w	0.0361, 0.0362
Weighing scheme	[$\sigma(F_o)^2 + 0.0011(F_o)^2$] ^{−1}

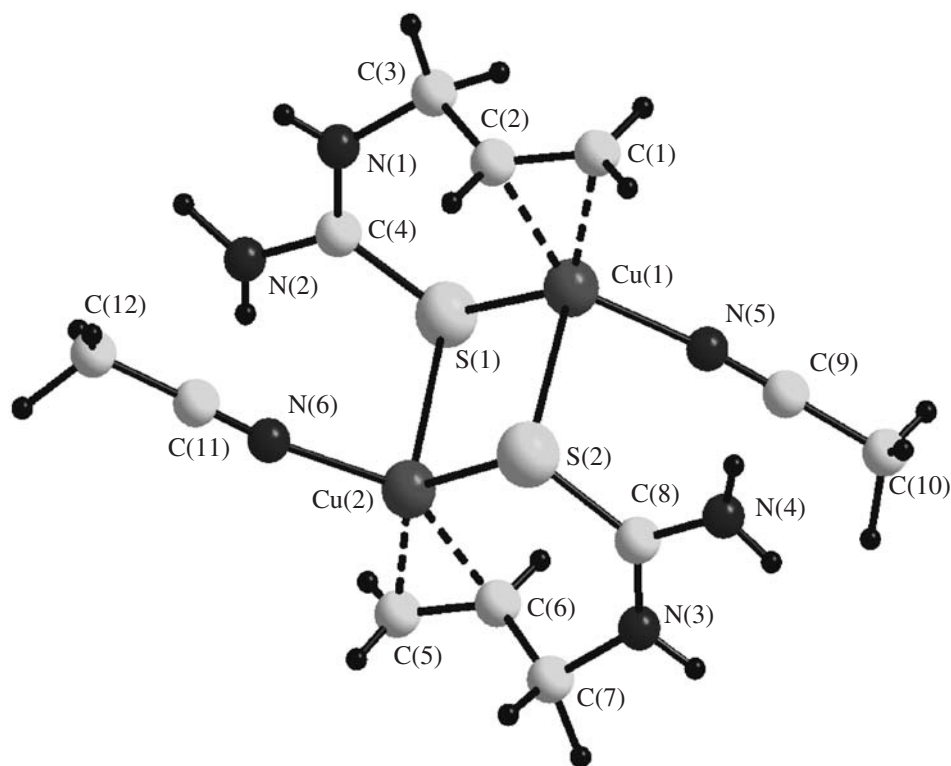


Fig. 3. Fragment of structure **II**.

Table 2. Coordinates of atoms and temperature parameters $U_{\text{eq/iso}}^*$ Å²

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq/iso}}^*$, Å ²
Cu(1)	0.08687(8)	0.88405(3)	0.03705(4)	0.0275(1)
Cu(2)	0.26367(8)	1.16874(3)	0.08951(4)	0.0264(1)
S	0.1294(1)	1.02589(7)	0.13774(8)	0.0234(1)
N(1)	0.5149(7)	1.1466(3)	0.0412(3)	0.0362(3)
N(2)	-0.1470(6)	0.7203(3)	0.1224(3)	0.0354(3)
N(3)	-0.0626(5)	1.1253(2)	0.2724(3)	0.0253(2)
N(4)	-0.1999(5)	0.9814(2)	0.2107(3)	0.0229(2)
C(1)	0.3346(6)	0.8665(2)	-0.0143(3)	0.0181(3)
C(2)	-0.0753(6)	0.7822(3)	0.0826(3)	0.0247(4)
C(3)	0.2632(7)	1.3057(3)	0.1652(3)	0.0286(4)
C(4)	0.1022(7)	1.2564(3)	0.1842(3)	0.0270(4)
C(5)	0.0865(7)	1.2014(3)	0.2848(3)	0.0277(4)
C(6)	-0.0592(6)	1.0471(3)	0.2135(3)	0.0214(4)
C(7)	-0.3742(7)	0.9926(4)	0.2634(4)	0.0317(4)
C(8)	-0.3524(8)	0.9741(4)	0.3785(4)	0.0413(5)
C(9)	-0.2053(10)	0.9357(5)	0.4349(5)	0.0550(5)
H(1)	0.368(7)	1.307(3)	0.216(3)	0.025(4)
H(2)	0.254(8)	1.350(3)	0.110(4)	0.038(5)
H(3)	-0.015(8)	1.262(3)	0.142(4)	0.031(5)
H(4)	0.219(8)	1.173(3)	0.313(4)	0.030(5)
H(5)	0.047(7)	1.248(3)	0.341(4)	0.029(4)
H(6)	-0.164(7)	1.135(3)	0.303(3)	0.019(4)
H(7)	-0.203(7)	0.935(3)	0.168(4)	0.026(5)
H(8)	-0.461(8)	0.954(4)	0.232(4)	0.039(5)
H(9)	-0.429(9)	1.067(5)	0.249(6)	0.075(7)
H(10)	-0.480(9)	0.990(5)	0.415(6)	0.082(7)
H(11)	-0.104(9)	0.917(5)	0.406(6)	0.083(7)
H(12)	-0.218(10)	0.936(6)	0.508(7)	0.089(8)

* For non-hydrogen atoms $U_{\text{eq/iso}} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* (\vec{a}_i \vec{a}_j)$.

Table 3. Bond lengths and bond angles in structure I

Bond	<i>d</i> , Å	Angle	ω , deg
Cu(1)–S(1)	2.333(2)	S(1)Cu(1)S(1)'	94.81(5)
Cu(1)–S(1)'	2.810(2)	S(1)Cu(1)C(2)	118.7(1)
Cu(1)–C(1)	1.931(4)	S(1)'Cu(1)C(2)	106.5(1)
Cu(1)–C(2)	1.932(4)	S(1)Cu(1)C(1)	103.6(1)
Cu(2)–S(1)	2.293(2)	S(1)'Cu(1)C(1)	101.3(1)
Cu(2)–N(1)	1.946(3)	C(1)Cu(1)C(2)	126.1(2)
Cu(2)–C(3)	2.117(4)	S(1)Cu(2)N(1)	111.2(1)
Cu(2)–C(4)	2.124(4)	S(1)Cu(2) <i>m</i> (3,4)	111.3(2)
Cu(2)– <i>m</i> (3,4)*	2.008(4)	S(1)Cu(2)N(1)	111.2(1)
S(1)–C(6)	1.746(1)	N(1)Cu(2) <i>m</i> (3,4)	127.9(2)
N(1)–C(1)	1.155(6)	C(3)Cu(2)C(4)	37.3(2)
N(2)–C(2)	1.138(6)	C(5)N(3)C(6)	125.7(4)
N(3)–C(5)	1.467(6)	C(6)N(3)H(6)	117(3)
N(3)–C(6)	1.314(5)	C(5)N(3)H(6)	117(3)
N(3)–H(6)	0.85(5)	C(6)N(4)C(7)	124.4(4)
N(4)–C(6)	1.327(5)	C(7)N(4)H(7)	115(3)
N(4)–C(7)	1.464(6)	C(6)N(4)H(7)	120(3)
N(4)–H(7)	0.84(4)	C(4)C(3)H(1)	119(3)
C(3)–C(4)	1.355(7)	C(4)C(3)H(2)	120(4)
C(3)–H(1)	0.91(5)	H(1)C(3)H(2)	120(4)
C(3)–H(2)	0.93(5)	C(3)C(4)C(5)	123.7(4)
C(4)–C(5)	1.504(6)	C(3)C(4)H(3)	123(3)
C(4)–H(3)	0.92(5)	C(5)C(4)H(3)	112(3)
C(5)–H(4)	1.02(5)	N(3)C(5)C(4)	113.2(4)
C(5)–H(5)	1.02(5)	N(3)C(5)H(5)	106(3)
C(7)–C(8)	1.476(7)	C(4)C(5)H(5)	109(3)
C(7)–H(8)	0.86(6)	N(3)C(5)H(4)	111(3)
C(7)–H(9)	1.10(7)	C(4)C(5)H(4)	109(3)
C(8)–C(9)	1.285(9)	H(4)C(5)H(5)	107(4)
C(8)–H(10)	1.07(8)	S(1)C(6)N(3)	121.4(3)
C(9)–H(11)	0.87(8)	S(1)C(6)N(4)	118.2(3)
C(9)–H(12)	0.95(9)	N(3)C(6)N(4)	120.4(4)
		N(4)C(7)C(8)	116.8(4)
		N(4)C(7)H(9)	108(4)
		C(8)C(7)H(9)	108(4)
		N(4)C(7)H(8)	107(7)
		C(8)C(7)H(8)	109(4)
		H(8)C(7)H(9)	107(5)
		C(7)C(8)C(9)	127(6)
		C(9)C(8)H(10)	119(4)
		C(7)C(8)H(10)	114(4)
		C(8)C(9)H(11)	120(5)
		C(8)C(9)H(12)	112(5)
		H(11)C(9)H(12)	127(7)

* *m*(3,4) is the midpoint of the C(3)=C(4) multiple bond.

Table 4. Torsion angles in structure I

Angle	τ , deg
Cu(2)N(1)C(1)Cu(1)	140.8
S(1)Cu(1)S(1)Cu(2)	56.1
C(3)C(4)C(5)N(3)	157.4
N(4)C(7)C(8)C(9)	–11.0
S(1)Cu(1)S(1)Cu(1)'	0
C(6)N(3)C(5)C(4)	–65.4
C(7)N(4)C(6)S(1)	175.2
C(5)N(3)C(6)S(1)	–1.7
C(7)N(4)C(6)N(3)	5.1
S(1)Cu(1)S(1)'Cu(2)'	–133.6

Note: Symmetry transformations: (') $-x, 2-y, -z$.

in the [Cu(ATU)(CH₃CN)]NO₃ complex (**II**) (Fig. 3), whereas no such π bond is observed in the [Cu(DATU)₃]NO₃ compound (**III**). Thus, in the absence of strongly withdrawing coligands in the coordination environment of copper(I) no Cu(I)–(C=C) bond (in the presence of the thioamide sulfur atom) is observed [11].

In the structure of π complex **I**, the C and N atoms of the cyano group are completely ordered, unlike those in a series of the CuCN σ complexes, for example, in the compounds [Cu₂(CN)₂(Bpym)] (Bpym is 2,2'-dipyrimidine) and [Fe(Bipy)₂(CN)₄Cu₂] (Bipy is 2,2'-dipyridine) [12].

No effective hydrogen bonds, except for the N(3)–H(6)···N(2) bond (H(6)···N(2) 2.08(4) Å, NHN angle 154(4)°, are observed due to the bridging function of the ligands that favor the formation of 3D structure **I**.

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