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Structural peculiarities of the [(2-amino-5-ethyl-1,3,4-thiadiazole)CuCl] complex

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Dedicated to Evgen I. Gladyshevskii (1924-2012)

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Crystals of the [Cu($C_4H_7N_3S$)Cl] (1) σ-complex were synthesized by solvothermal reaction of 2-amino-5-ethyl-1,3,4-thiadiazole ($C_4H_7N_3S$) with CuCl in hydrochloric acid solution, and studied by X-ray diffraction. The structure is monoclinic, space group $P2_1/c$, a = 6.1880(11), b = 11.6631(15), c = 10.5174(15) Å, β = 96.231(8)°, V = 754.6(2) Å^3 at 200 K, Z = 4. The Cu(I) atoms possess trigonal pyramidal coordination involving two N atoms from two adjacent organic ligands and two Cl atoms, one of which occupies the apical position of the coordination polyhedron. Forming a bridge, the halogen atoms connect organometallic {$Cu_2(C_4H_7N_3S)_2$} fragments into infinite {$Cu_2(C_4H_7N_3S)_2Cl_2$}$_n$ chains, which through (N)H...Cl hydrogen contacts are linked into a 3D-framework.

1,3,4-Thiadiazole / Copper(I) / Complex / Crystal structure

Introduction

1,3,4-Thiadiazole derivatives attract considerable attention due to their huge range of biological activity (anticancer, anti-inflammatory, analgesic, antifungal, anticonvulsant, *etc.* [1-5]), as well as owing to their unique role in self-organization of potential metal-organic complexes through coordination to different transition metal ions [6-11]. For example, 2-amino-1,3,4-thiadiazole easily undergoes a transition-metal-induced reductive coupling reaction with acetonitrile, resulting in Co(III) amidine complexes [6], while the bis(5-anilino-3-methyl-1,3,4-thiadiazol-3-ium) tetrachlorocuprate(II) salt has been prepared in a good yield by a Cu(II)-induced reaction of a thiosemicarbazide precursor ($PhNHCSNHNMe_2$) with $CuCl_2$ [11]. Despite the considerable interest in 1,3,4-thiadiazole derivatives, the research area of their complexation with copper halides is still rather poorly covered and the only hitherto synthesized and X-ray studied copper(I) chloride complex is [Cu(L2)Cl] (**2**) (L2 = 2-amino-5-methyl-1,3,4-thiadiazole) [12].

In order to evaluate the influence of the 5-substituting constituent on the coordination behavior of 2-amino-1,3,4-thiadiazole regarding CuCl, the new [Cu(L1)Cl] σ-complex with 2-amino-5-ethyl-1,3,4-thiadiazole (L1) (**1**) was synthesized and characterized by X-ray diffraction.

Experimental section

Preparation of [Cu(L1)Cl] (1)

Crystals of **1** were synthesized by a solvothermal reaction of copper(I) chloride with commercially available 2-amino-5-ethyl-1,3,4-thiadiazole (L1) in an aqueous solution of hydrochloric acid. The solution of 2-amino-5-ethyl-1,3,4-thiadiazole (2.01 mmol, 0.26 g) in 2.3 mL of 3 M hydrochloric acid was prepared at ~80 °C. Then an equimolar amount of freshly prepared CuCl (2.01 mmol, 0.20 g) was added to this solution. The solution was gradually cooled to room temperature and colorless crystals of complex **1** formed. The crystal density was measured by the flotation method in a chloroform-bromoform mixture.

Crystal structure determination

The crystallographic parameters and a summary of the data collection for **1** are presented in Table 1. Single-crystal data were collected on a Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector, using graphite monochromatized Mo K_α radiation. The structure of **1** was solved by direct methods using the SHELXS-97 program and refined with SHELXL-97 software [13]. The non-hydrogen atoms were found by the direct methods.

The positions of the H atoms of the amine group were derived from difference Fourier syntheses. Full-matrix least-squares refinements based on F^2 were carried out for the positional and thermal parameters of the atoms, employing an anisotropic mode of refinement for all the non-hydrogen atoms. The positions of the ethyl H atoms were treated as riding atoms and refined with fixed C–H distances and U_{iso}(H) values of 1.2U_{eq}(C) (Tables 2,3).

Results and discussion

In the structure of [Cu(L1)Cl] (**1**) the organic molecule 2-amino-5-ethyl-1,3,4-thiadiazole (L1) is coordinated to the Cu(I) atoms through two N atoms of the thiadiazole ring (Fig. 1). The Cu(I) atom possesses a trigonal pyramidal coordination environment formed by two N (N(1) and N(3)) and two Cl atoms, one of which is located at the apical position (Cu–Cl 2.668(1) Å) of the coordination polyhedron. The deviation of the copper atom from the basal plane of the trigonal pyramid is 0.24 Å. Thus, the L1 moiety acts as a N,N-bridged ligand, connecting two Cu(I) atoms into centrosymmetric $\{Cu_2(L1)_2\}$ fragments with a six-membered $\{Cu_2N_4\}$ cycle. Similar behavior of the heterocyclic core to form topologically similar fragments with Cu(I) has previously been found in [(L2)CuCl] (**2**) (L2 = 2-amino-5-methyl-1,3,4-thiadiazole) and

Table 1 Crystal data and structure refinement for the compound **1**.

Empirical formula	$C_4H_7ClCuN_3S$	Crystal size, mm	0.12 × 0.08 × 0.10
Formula weight	228.18 g/mol	Color, shape	colorless, irregular
Temperature, K	200(2)	Theta range for data collection, °	2.6-29.2
Wavelength, Å	0.71069		
Crystal system, space gr.	monoclinic, $P2_1/c$	Limiting indices	$-7 \leq h \leq 7$, $-15 \leq k \leq 15$, $-5 \leq l \leq 13$
Unit cell dimensions,			
a, Å	6.1880(11)	Refinement method	Full-matrix least-squares on F^2
b, Å	11.6631(15)	Measured reflections	3276
c, Å	10.5174(15)	Unique reflections	1708
α, °	90.00	R_{int} value	0.028
β, °	96.231(8)	Reflections used	1531
γ, °	90.00	Free parameters	92
V, Å^3	754.6(2)	Goodness-of-fit on F^2	1.08
Z	4	R values	$R_1 = 0.067$, $wR_2 = 0.198$
Absorption coeff., mm^{-1}	3.45	Largest diff. peak and hole, e/Å^3	0.78 and −0.90
Calculated density, g/cm^3	2.009		
F(000)	456	Measured density, g/cm^3	2.02

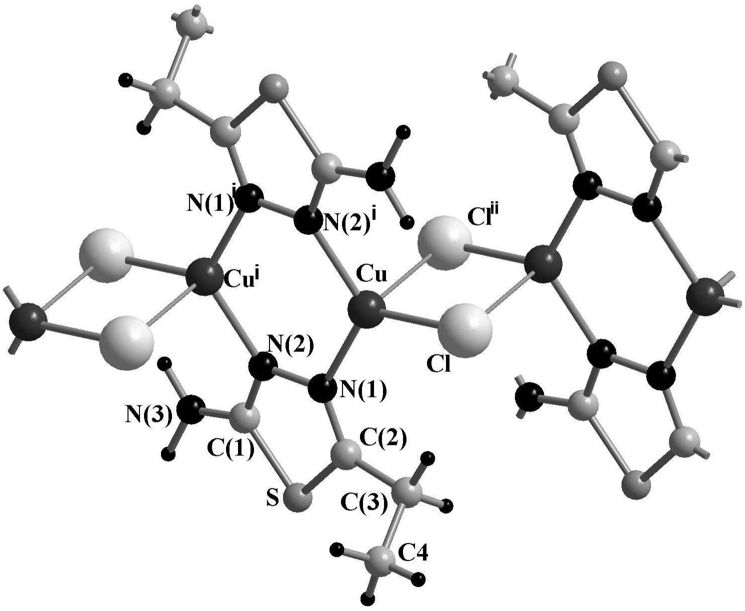

Fig. 1 Fragment of crystal structure of **1**. Symmetry codes: (i) $-x+1$, $-y$, $-z$; (ii) $-x+2$, $-y$, $-z$.

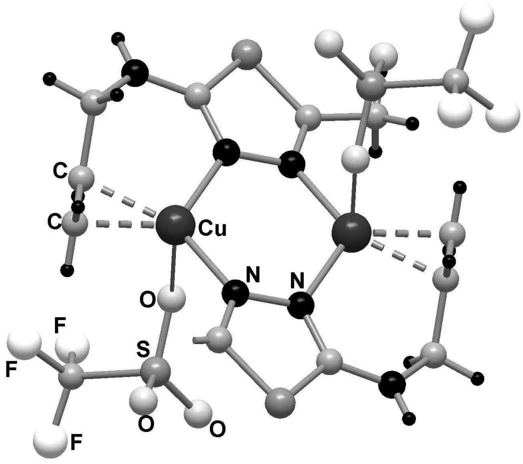

Fig. 2 Dimers in the structure of [Cu($C_6H_9N_3S$)CF_3SO_3].

in a number of N-allyl derivatives of 1,3,4-thiadiazole [14] and S-allyl derivatives of 5-aryl substituted 1*H*-tetrazoles [15,16], where an analogous equatorial copper(I) surrounding is formed by two heterocyclic N atoms, while the third equatorial position is occupied by an olefinic C=C bond, instead of a Cl atom as in [Cu(L1)Cl] (**1**) and [Cu(L2)Cl] (**2**). It may be noted that $\{Cu_2(L)_2\}^{2+}$ fragments are the main building blocks in crystal engineering of Cu(I) complexes with 1,3,4-thiadiazole ligands. The centrosymmetric fragment of a copper(I) π-complex with 2-(allyl)-amino-5-methyl-1,3,4-thiadiazole is shown for comparison in Fig. 2. The fourth position of the metal-centered trigonal pyramid in the structure of this π-compound is occupied by a weakly bonded O atom of the $CF_3SO_3^-$ anion. In compound **1** one of the Cl atoms is much more remote from the copper center than the other, up to 2.668(1) Å, and occupies the fourth (apical) position of the Cu(I) coordination polyhedron.

In both [Cu(L1)Cl] (**1**) and [Cu(L2)Cl] (**2**), two Cl atoms act as a bridge, connecting neighboring $\{Cu_2(L)_2\}$ tectons into endless organometallic $\{Cu_2(L)_2Cl_2\}_n$ chains, which may by considered as crosslinked $\{Cu_2N_4\}$ and $\{Cu_2Cl_2\}$ cycles (Fig. 1).

Hydrogen bonds play a significant role in the construction of the structures discussed here [17,18]. N-H...Cl hydrogen bonds, which occur between the NH_2 group of the organic molecule L1 and Cl atoms of neighboring $\{Cu_2(L)_2Cl_2\}_n$ chains, link the latter into a hydrogen-bonded 3D-network (Fig. 3, Table 4).

Acknowledgment

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Table 2 Fractional atomic coordinates and (equivalent) isotropic displacement parameters (Å^2) for **1.**

Atom	x	y	z	U_{eq}/U_{iso} [a]
Cu	0.74058(9)	0.03018(5)	−0.04543(5)	0.0352(2)
Cl	1.03669(17)	0.06890(8)	−0.15663(9)	0.0309(3)
S	0.4989(2)	0.31672(9)	0.18967(11)	0.0349(3)
N(1)	0.5943(6)	0.1492(3)	0.0513(3)	0.0265(7)
N(2)	0.4169(6)	0.1117(3)	0.1113(3)	0.0276(7)
N(3)	0.1888(7)	0.1741(3)	0.2616(4)	0.0361(9)
C(1)	0.3510(7)	0.1901(3)	0.1874(4)	0.0274(8)
C(2)	0.6543(7)	0.2531(3)	0.0808(4)	0.0275(8)
C(3)	0.8338(8)	0.3157(4)	0.0256(4)	0.0351(10)
C(4)	0.7525(9)	0.4211(5)	−0.0494(5)	0.0485(13)
H(31)	0.9029	0.2644	−0.0303	0.042 [b]
H(32)	0.9424	0.3386	0.0944	0.042 [b]
H(41)	0.708	0.478	0.0084	0.058 [b]
H(42)	0.6311	0.4005	−0.1098	0.058 [b]
H(43)	0.867	0.4514	−0.0942	0.058 [b]
H(1N3)	0.1154	0.1019	0.2563	0.058 [b]
H(2N3)	0.1126	0.2414	0.3133	0.058 [b]

[a] for non-hydrogen atoms U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor;
[b] for hydrogen U_{iso}.

Table 3 Selected bond lengths (in Å) and angles (in deg) in the structure of **1**.

Atoms	Bond length, Å	Atoms	Angle, °
Cu–N(1)	1.995(3)	N(1)–Cu–N(2)$^{i\ a}$	121.3(1)
Cu–N(2)$^{i\ a}$	2.005(3)	N(1)–Cu–Cl	123.2(1)
Cu–Cl	2.323(1)	N(2)^{i}–Cu–Cl	111.5(1)
Cu–Cl$^{ii\ a}$	2.668(1)	N(1)–Cu–Cl$^{ii\ a}$	96.9(1)
N(1)–C(2)	1.295(5)	N(2)^{i}–Cu–Cl$^{ii\ a}$	96.2(1)
N(1)–N(2)	1.395(5)	Cl–Cu–Cl(1)$^{ii\ a}$	96.76(4)
N(2)–C(1)	1.309(5)	C(2)–N(1)–N(2)	113.9(3)
S–C(1)	1.736(4)	N(2)–C(1)–S	113.8(3)

[a] symmetry codes: (*i*) $-x+1, -y, -z$; (*ii*) $-x+2, -y, -z$.

Table 4 Geometry of the hydrogen bonds in the crystal structure of **1**.

Atoms involved	Symmetry	Distances, Å			Angle, °
D−H···*A*		*D*···H	H···*A*	*D*···*A*	*D*−H···*A*
N(3)−H(1N3)···Cl	$1-x, -y, -z$	0.956(4)	2.396(4)	3.296(1)	156.9(2)
N(3)−H(2N3)···Cl	$-1+x, 1/2-y, 1/2+z$	1.090(4)	2.291(4)	3.284(1)	150.5(2)

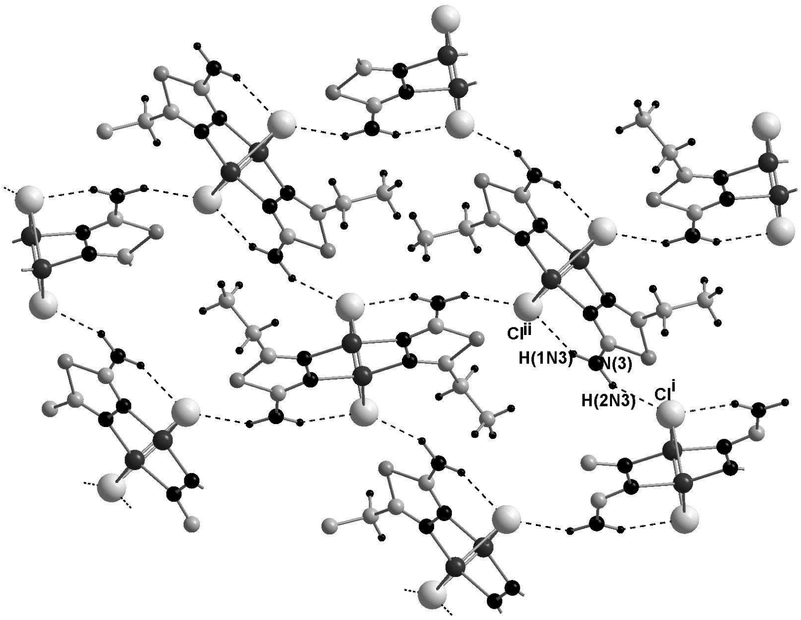

Fig. 3 3D hydrogen-bonded framework in complex **1**. Symmetry codes: (*i*) $-x+1, -y, -z$; (*ii*) $-x+2, -y, -z$.

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