

Scientific paper

First N-allyl-aminothiadiazole Copper(I) π -Complexes: Synthesis and Structural Peculiarities of $[\text{Cu}(\text{L})\text{CF}_3\text{SO}_3]$ and $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2](\text{SiF}_6) \cdot 2.5\text{H}_2\text{O}$ Compounds ($\text{L} = 2\text{-(allyl)-amino-5-methyl-1,3,4-thiadiazole}$)

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We dedicate this paper to Professor Boris Žemva in honour of his receiving the 2011 Zois Award

Abstract

By means of alternating current electrochemical technique two crystalline copper(I) π -complexes with fluorine containing anions $[\text{Cu}(\text{L})\text{CF}_3\text{SO}_3]$ (**1**) and $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2](\text{SiF}_6) \cdot 2.5\text{H}_2\text{O}$ (**2**) ($\text{L} = 2\text{-(allyl)-amino-5-methyl-1,3,4-thiadiazole}$) have been obtained and characterized by X-ray single crystal diffraction and Raman spectroscopy. In both structures the organic molecule L acts as chelate-bridging tridentate ligand being connected to copper(I) by two N atoms of thiadiazole ring and C=C bond from allyl group resulting in a formation of stable cationic dimers $\{[\text{Cu}(\text{L})]_2\}^{2+}$. In the structure **1** oxygen atom from triflate-anion occupies an apical position of the metal coordination polyhedron, while in **2** located far from the metal centre hexafluorosilicate anion allows an appearance of the H_2O molecule in copper environment. Hydrogen bonds (D)–H \cdots A (where D = O, N, C; A = O, F) play a significant role in formation of 2D- (**1**) and 3D- (**2**) frameworks.

Keywords: Thiadiazole; copper(I); π -complex; crystal structure; alternating-current synthesis

1. Introduction

1,3,4-Thiadiazoles both are well known class of heterocycles that possess a huge range of biological activity (antimicrobial,¹ anticancer,² antioxidant,³ radioprotective⁴ etc.) as well as efficient building blocks for crystal engineering of metal-organic complexes.^{5–7} Unfortunately, this tool has not revealed all its coordination possibilities especially in the presence of the C=C-containing groups. Recent research on π -complexation of copper(I) with allyl derivatives of heterocyclic and acyclic compounds showed that the olefinic C=C bond and donor atoms of the ligand can determine the formation of extremely rare or unknown inorganic fragments.⁸ Moreover, the thiadiazole core shows a good affinity for such soft acid as copper(I) which, in turn, is able to engage an effective interaction with C=C bond. In this context, the compounds contain-

ing both 1,3,4-thiadiazole cycle and allyl group appear to be rather suitable for crystal engineering. Therefore, this paper presents the first results on coordination behavior of 2-(allyl)-amino-5-methyl-1,3,4-thiadiazole with regard to copper(I) in the presence of fluorine-containing CF_3SO_3^- and SiF_6^{2-} anions.

2. Experimental

2.1. Preparation of 2-(allyl)-amino-5-methyl-1,3,4-thiadiazole

2.1.1. Synthesis of 4-allylthiosemicarbazide

A solution of allylthiocyanate (20.0 mL, 0.206 mol) in 20 mL of ethanol was slowly added through backflow condenser to efficiently cooled by running water

hydrazine hydrate (10.0 mL, 0.206 mol) in 10 mL of ethanol. Obtained white dense suspension was stirred over 10 min., filtered with suction, washed by ethanol and dried on air. Recrystallization from acetonitrile yielded white needles of product. Yield: 17.3 g (64%), m.p. 76 °C.⁹

2. 1. 2. Synthesis of 2-(allyl)-amino-5-methyl-1,3,4-thiadiazole

2-(Allyl)-amino-5-methyl-1,3,4-thiadiazole (*L*) was obtained using the classical Pulvermaher procedure by the reaction of 4-allylthiosemicarbazide with acetyl chloride.¹⁰ An excess of acetyl chloride (8.25 g, 0.105 mol) was added to powdered 4-allylthiosemicarbazide (3.93 g, 0.03 mol) supporting the room temperature of the mixture (cooling by cold water). Then the reaction vessel was equipped by calcium chloride tube and the mixture was stirred for 20 hours. After that ice-cold water (20 mL) was poured into the cooled mixture, neutralized with potassium hydroxide solution (20%) (to pH ≈ 7.5) to precipitate product. A crude product was filtered, washed with small quantities of cold water and recrystallized from water to yield of 62% (2.89 g). NMR ¹H (400 MHz, CDCl₃), δ, p.p.m. 6.36 (s, 1H, NH), 5.97–5.87 (m, 1H, =CH), 5.32 (d, *J* = 17.2, 1H, -CH₂-), 5.22 (d, *J* = 10.4, 1H, -CH₂-), 3.94 (d, *J* = 5.6, 2H, CH₂=), 2.57 (s, 3H, CH₃).

2. 2. Synthesis of copper(I) π-complexes

Crystals of complexes were obtained under conditions of the alternating-current electrochemical synthesis¹¹ starting from the solution of *L* and the corresponding copper(II) fluorine-containing salt.

2. 2. 1. Preparation of [Cu(L)CF₃SO₃] (1)

To 3.5 ml of ethanol solution of Cu(CF₃SO₃)₂ (0.71 mmol, 0.26 g) 1 ml of ethanol solution of 2-(allyl)-amino-5-methyl-1,3,4-thiadiazole (0.97 mmol, 0.15 g) was added. The prepared dark green solution was placed into a small 5 ml test-tube and then copper-wire electrodes in cork were inserted. Under applied alternating current tension (frequency 50 Hz) of 0.60 V for 3 days the solution was discoloured and after that the reactor was stored in a refrigerator at -20 °C for 4 days and good quality colorless crystals of **1** appeared on copper electrodes. The yield was about 40%.

2. 2. 2. Preparation of [Cu₂(L)₂(H₂O)₂](SiF₆) · 2.5H₂O (2)

To 3.3 ml of acetonitrile solution of 2-(allyl)-amino-5-methyl-1,3,4-thiadiazole (1.3 mmol, 0.20 g) 1 ml of water saturated solution of CuSiF₆ · 4H₂O and 0.3 ml of ethanol were added. The resulting mixture consisted of top dark almost colorless (based on acetonitrile) and lower

dark-green (based on water) layers was subjected to alternating current (frequency 50 Hz, tension 0.60 V) and after 10 days the mixture became homogeneous. Good quality colorless crystals of **2** appeared on copper electrodes. The yield was near 70%.

2. 3. Raman Spectroscopy

Raman spectra from crystals of **1** and **2** and from pure ligand were recorded with a Horiba Jobin-Yvon LabRAM HR spectrometer by using the 632.81 nm excitation line of a He-Ne laser (17 mW).

2. 4. X-Ray Crystal Structure Determination

The crystallographic parameters and summaries of data collection for **1** and **2** are presented in Table 1. Single-crystal data were collected on a Rigaku AFC7 diffractometer (using graphite monochromatized MoK_α radiation) equipped by Oxford diffraction cryo-system and a Mercury CCD area detector. Data were treated using the Rigaku CrystalClear software suite program package.¹² Both structures were solved by direct methods using SIR-92 and SHELXS-97 programs (teXan crystallographic software package of Molecular Structure Corporation) and refined with SHELXL-97 software, implemented in program package WinGX.^{13–16} In both structures non-hydrogen atoms were found by direct methods and hydrogen ones – geometrically. Full-matrix least-squares refinements based on *F*² were carried out for the positional and thermal parameters for all non-hydrogen atoms. A multi-scan absorption correction was applied to all data sets. For **1** and **2** structures positions of carbon H atoms were treated as riding atoms and refined with C–H fixed distances and with *U*_{iso}(H) values of 1.2*U*_{eq}(C). Positions of hydrogen atoms attached to O and N were refined with »soft« restrictions and fixed before final cycles of refinement. One may note, that the low crystal quality of **2** apparently caused by partial losing of crystalline water molecules. Strongly disordered fluorine atoms of the second independent SiF₆²⁻ anion in **2** indicate an existence of their alternative positions due to the hydrogen bonds formation. One can add that earlier similar behaviour of the hexafluorosilicate anion was found in the [Cu₂(C₃H₅)₂NCN(H₂O)₃CH₃OH]SiF₆ π-complexes.¹⁷ The figures were prepared using DIAMOND 3.1 software.¹⁸

3. Results and Discussion

3. 1. Crystal Structures

In the crystal structure of [Cu(L)CF₃SO₃] (**1**) copper(I) atom possesses trigonal pyramidal environment arranged by N(3) and N(4) atoms of the adjacent thiadiazole cores, the C=C bond from N-allyl group of the same

Table 1. Crystal data and structure refinement for the compounds **1** and **2**.^a

	1	2
Empirical formula	C ₁₄ H ₁₈ Cu ₂ F ₆ N ₆ O ₆ S ₄	C ₁₂ H ₂₇ Cu ₂ F ₆ N ₆ O _{4.5} S ₂ Si
Formula weight	735.72 g/mol	660.68 g/mol
Temperature, K	200(2)	200(2)
Wavelength	0.71069 Å	0.71069 Å
Crystal system, space group	monoclinic, <i>P</i> 2 ₁ / <i>n</i>	triclinic, <i>P</i> -1
Unit cell dimensions, Å		
<i>a</i> , Å	7.6412(10)	13.0493(10)
<i>b</i> , Å	20.7907(18)	13.3386(6)
<i>c</i> , Å	8.6997(11)	15.0976(8)
α , °	90	71.95(7)
β , °	113.168(5)	68.93(6)
γ , °	90	77.39(7)
<i>V</i> , Å ³	1270.6(3)	2314.6(2)
<i>Z</i>	2	4
Calculated density, g/cm ³	1.92	1.90
Absorption coeff., mm ⁻¹	2.091	2.154
Absorption correction	multi-scan	multi-scan
Transmission, <i>T</i> _{min} , <i>T</i> _{max}	0.781, 0.826	0.521, 0.585
<i>F</i> (000)	736	1340
Crystal size, mm	0.12 × 0.1 × 0.09	0.12 × 0.1 × 0.1
Color	colorless	colorless
Theta range for data collection	2.73° to 29.03°	1.49° to 28.39°
Limiting indices	-9 ≤ <i>h</i> ≤ 10, -28 ≤ <i>k</i> ≤ 26, -11 ≤ <i>l</i> ≤ 6	-17 ≤ <i>h</i> ≤ 16, -17 ≤ <i>k</i> ≤ 17, -18 ≤ <i>l</i> ≤ 18
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Measured reflections	5591	15081
Used in refinement	2874	15081
Free parameters	172	623
Goodness-of-fit on <i>F</i> ²	1.01	1.20
<i>R</i> indices	<i>R</i> ₁ = 0.0537, <i>wR</i> ₂ = 0.1497	<i>R</i> ₁ = 0.0936, <i>wR</i> ₂ = 0.226
Largest diff. peak and hole	0.60 and -0.59 e Å ⁻³	1.89 and -1.07 e Å ⁻³

^a CCDC 873525, 873526 contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on applications to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code +(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

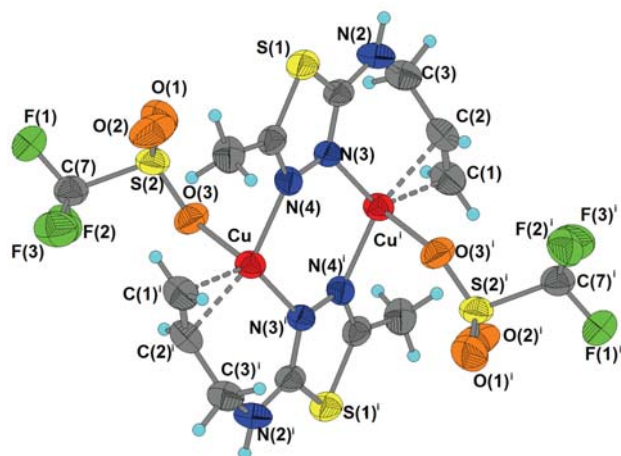


Figure 1. Fragment of crystal structure **1**. Symmetry codes: (i) $-x+2, -y, -z+1$.

ligand and one O atom of CF_3SO_3^- anion located at the apical position of the coordination polyhedron (Figure 1). Thus, organic molecule *L* plays a role of N,N,(N-C₃H₅) chelate-bridging ligand connecting two Cu(I) atoms into centrosymmetric dimer $\{\text{Cu}(\text{L})\text{CF}_3\text{SO}_3\}_2$ containing two six-membered CuC_4N_2 (considering C=C bond as one coordinating site) and one six-membered Cu_2N_4 rings. The latter was earlier found in the structure of copper(I) π -complexes with 5-(S-allyl)-1*H*-tetrazole derivatives, where copper(I) centers connect two most nucleophilic N(3) and N(4) atoms of adjacent tetrazole rings.^{19,20}

In the structure of $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2](\text{SiF}_6) \cdot 2.5\text{H}_2\text{O}$ (**2**) (with doubly charged hexafluorosilicate anion) molecule *L* plays the same role as in **1** being connected to Cu(I) atoms through N(3) and N(4) atoms of the thiadiazole core and C=C bond from N-allyl group (Figure 2). Cu(I) atom in **2** also possesses trigonal pyramidal coordination environment, but in this case an apical position of the

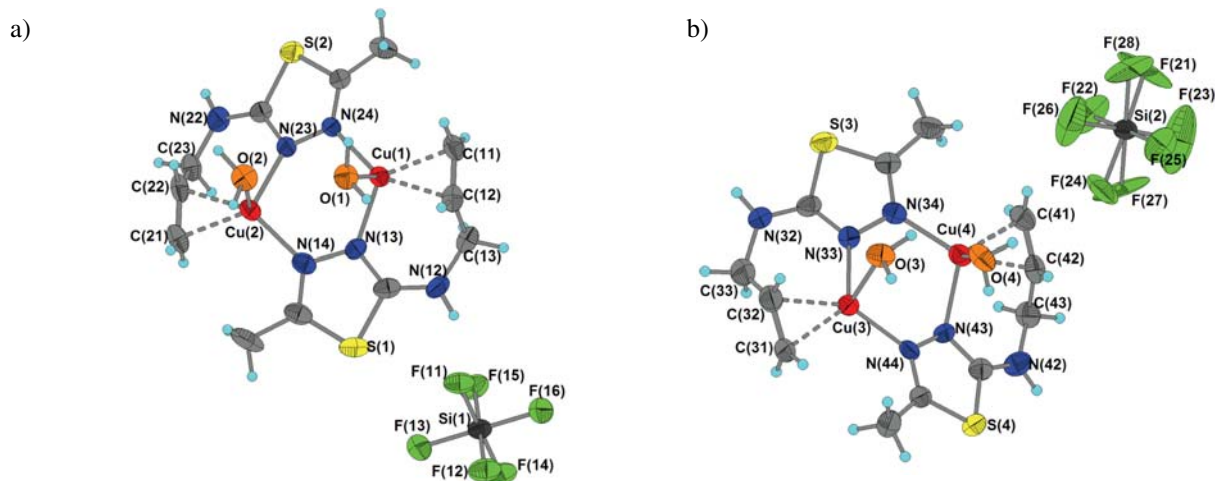


Figure 2. Two crystallographically independent fragments of structure **2** based on Cu(1)–Cu(2) (a) and Cu(3)–Cu(4) (b) atoms; F-atoms in $[\text{Si}(2)\text{F}_6]^{2-}$ are disordered.

Table 2. Selected bond length (in Å) and angle (in deg) values in the structure **1**.

$\text{Cu}-m^i$ [a]	1.959(6)	$\text{N}(3)-\text{Cu}-m$	111.3(2)
$\text{Cu}-\text{N}(3)^i$	2.015(4)	$\text{N}(4)-\text{Cu}-m$	132.6(2)
$\text{Cu}-\text{N}(4)$	1.981(4)	$\text{O}(3)-\text{Cu}-m$	101.2(2)
$\text{Cu}-\text{O}(3)$	2.442(5)	$\text{C}(1)-\text{Cu}-\text{C}(2)$	38.3(2)
$\text{C}(1)=\text{C}(2)$	1.360(8)	$\text{C}(1)=\text{C}(2)-\text{C}(3)$	123.3(6)

[a] Symmetry codes: (i) $-x+2, -y, -z+1$; m – middle point of $\text{C}(1)=\text{C}(2)$ bond.

Table 3. Selected bond length (in Å) and angle (in deg) values in the **2** structure.

$\text{Cu}(1)-m1$ [a]	1.948(8)	$\text{N}(13)-\text{Cu}(1)-m1$	112.1(3)
$\text{Cu}(1)-\text{N}(13)$	1.994(6)	$\text{N}(24)-\text{Cu}(1)-m1$	132.3(3)
$\text{Cu}(1)-\text{N}(24)$	1.987(6)	$\text{O}(1)-\text{Cu}(1)-m1$	98.6(3)
$\text{Cu}(1)-\text{O}(1)$	2.483(5)	$\text{C}(11)-\text{Cu}(1)-\text{C}(12)$	38.4(3)
$\text{C}(11)=\text{C}(12)$	1.355(11)	$\text{C}(11)=\text{C}(12)-\text{C}(13)$	123.2(7)
$\text{Cu}(2)-m2$ [a]	1.944(7)	$\text{N}(14)-\text{Cu}(2)-m2$	132.8(3)
$\text{Cu}(2)-\text{N}(14)$	1.987(6)	$\text{N}(23)-\text{Cu}(2)-m2$	111.3(3)
$\text{Cu}(2)-\text{N}(23)$	2.012(5)	$\text{O}(2)-\text{Cu}(2)-m2$	104.2(3)
$\text{Cu}(2)-\text{O}(2)$	2.218(5)	$\text{C}(21)-\text{Cu}(2)-\text{C}(22)$	37.9(3)
$\text{C}(21)=\text{C}(22)$	1.336(11)	$\text{C}(21)=\text{C}(22)-\text{C}(23)$	122.0(7)
$\text{Cu}(3)-m3$ [a]	1.928(7)	$\text{N}(33)-\text{Cu}(3)-m3$	112.5(3)
$\text{Cu}(3)-\text{N}(33)$	2.008(6)	$\text{N}(44)-\text{Cu}(3)-m3$	129.9(3)
$\text{Cu}(3)-\text{N}(44)$	1.966(6)	$\text{O}(3)-\text{Cu}(3)-m3$	104.2(3)
$\text{Cu}(3)-\text{O}(3)$	2.273(5)	$\text{C}(31)-\text{Cu}(3)-\text{C}(32)$	38.6(3)
$\text{C}(31)=\text{C}(32)$	1.350(11)	$\text{C}(31)=\text{C}(32)-\text{C}(33)$	125.6(9)
$\text{Cu}(4)-m4$ [a]	1.936(7)	$\text{N}(34)-\text{Cu}(4)-m4$	134.7(3)
$\text{Cu}(4)-\text{N}(34)$	1.971(6)	$\text{N}(43)-\text{Cu}(4)-m4$	111.6(3)
$\text{Cu}(4)-\text{N}(43)$	2.017(6)	$\text{O}(4)-\text{Cu}(4)-m4$	101.8(3)
$\text{Cu}(4)-\text{O}(4)$	2.457(6)	$\text{C}(41)-\text{Cu}(4)-\text{C}(42)$	38.3(3)
$\text{C}(41)=\text{C}(42)$	1.346(11)	$\text{C}(41)=\text{C}(42)-\text{C}(43)$	122.3(8)

[a] $m1, m2, m3$ and $m4$ – middle points of $\text{C}(11)=\text{C}(12), \text{C}(21)=\text{C}(22), \text{C}(31)=\text{C}(32)$ & $\text{C}(41)=\text{C}(42)$ bonds.

Cu(I) coordination polyhedron is occupied by water molecule instead of CF_3SO_3^- O atom in **1**. It should be noted that two apical water molecules are located on the same side of Cu_2N_4 rings that is a marked difference from that of **1**. One can add that in the crystal structure **2** two crystallographically independent noncentrosymmetric cationic dimers $[\{\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2\}]^{2+}$ are mutually tilted at approximately 78° .

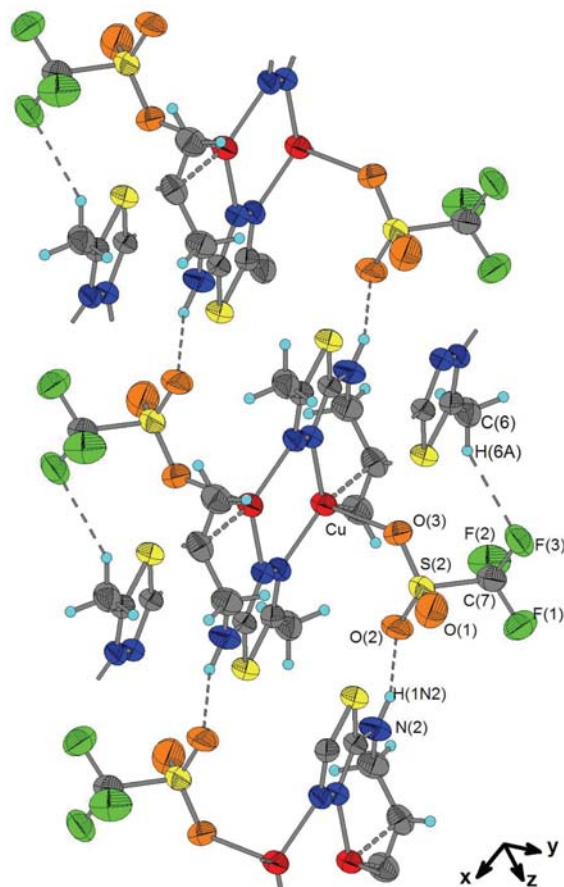
An efficiency of Cu(I)–(C=C) interaction is confirmed by the fact that Cu(I) deviates from a base of the trigonal pyramid by $\Delta = 0.140(1)$ Å and an angle between the C=C bond and the basal plane $\tau = 13.0(4)^\circ$ in **1**, while in **2** the same parameters are: $0.266(2)$ Å ($8.3(5)^\circ$), $0.326(2)$ Å ($7.0(5)^\circ$), $0.287(2)$ Å ($15.5(6)^\circ$) and $0.211(2)$ Å ($8.6(6)^\circ$) consequently for Cu(1), Cu(2), Cu(3) and Cu(4) atoms. Rather short Cu– m (m – a middle point of C=C bond) distances and moderately large C–Cu–C angles (Tables 2 and 3) also confirm these conclusions.

One may note that in crystal structure **2** the basal planes of copper(I) coordination polyhedra in the appropriate dimers $[\{\text{Cu}(\text{L})(\text{H}_2\text{O})\}_2]^{2+}$ are not coplanar and are bent by an angle of 16.3° (Cu(1)–Cu(2)) and 13.9° (Cu(3)–Cu(4)), while in **1** two corresponding planes are coplanar and are removed from each other by 2.26 Å. For comparison, such coplanar planes in the case of Cu(I) π -complexes with 5-(S-allyl)-1H-tetrazole derivatives are removed from each other by 0.11–4.23 Å.^{20,21}

Hydrogen bonds play a significant role in a construction of structures discussed.^{22,23} For example, in **1** two neighbouring $\{\text{Cu}(\text{L})\text{CF}_3\text{SO}_3\}_2$ blocks are connected by means of $\text{N}-\text{H}\cdots\text{O}(\text{S})$ hydrogen bonds into infinite chains, which, in turn, are connected by weak $\text{C}-\text{H}\cdots\text{F}$ contacts into layers lying in (101) plane (Figure 3, Table 4). Contrary to **1**, water molecules are involved into each cationic dimer in the structure **2**. The coordinated H_2O moiety acts as a bridge between dimers $[\{\text{Cu}(\text{L})\}_2]^{2+}$ and

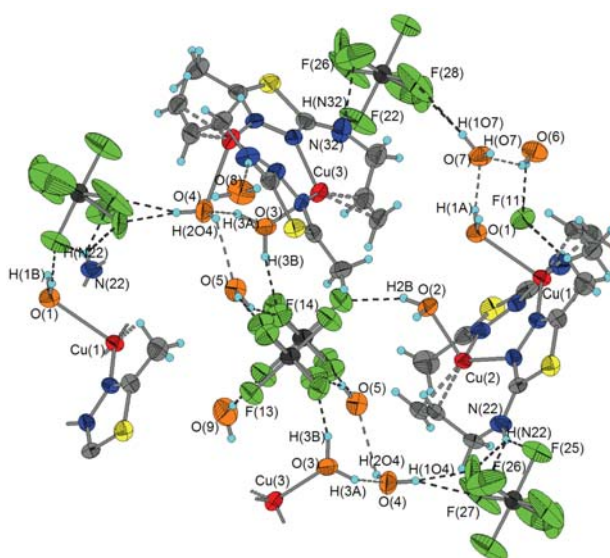
Table 4. Geometry of hydrogen bonds in the crystal structure **1**.

Atoms involved D-H...A	Symmetry	Distances, Å			Angle, ° D-H...A
		D...H	H...A	D...A	
N(2)-H(1N2)...O(1)	1-x, -y, -z	0.86	2.42	3.232(7)	158
N(2)-H(1N2)...O(2)	1-x, -y, -z	0.86	2.29	2.993(6)	139
C(6)-H(6A)...F(3)	-1+x, y, z	0.96	2.52	3.386(6)	150

**Figure 3.** Hydrogen bonds in structure **1**.

SiF_6^{2-} anions, whereas constitutional water molecules connect SiF_6^{2-} anions into 3D-framework (Figure 4, Table 5). One may note, that thermal motion of oxygen atoms (based on the size of respective thermal ellipsoids), belonging to attached to copper centres water molecules, is smaller than that for oxygens from uncoordinated water molecules. Such a predictable behaviour results also in imaginary shortening of respective O-H bonds in uncoordinated H_2O units.

Thus, despite the type of anion, 2-(allyl)-amino-5-methyl-1,3,4-thiadiazol tends to form stable dimers $[\{\text{Cu}(L)\}_2]^{2+}$ with Cu_2N_4 rings. However, the anions significantly affect the symmetry of the last. This may be caused by the fact that the fluorine anions are rather hard base that poorly correlates with soft acid Cu^+ and, as a result, CF_3SO_3^- anion is coordinated to the metal with O-atom in

**Figure 4.** Hydrogen bonded framework in **2**.

a centrosymmetric tectone $\{\text{Cu}(L)\text{CF}_3\text{SO}_3\}_2$, while SiF_6^{2-} with only hard F atoms does not enter into the internal surrounding of Cu(I) allowing O-atom of H_2O molecule to do it.

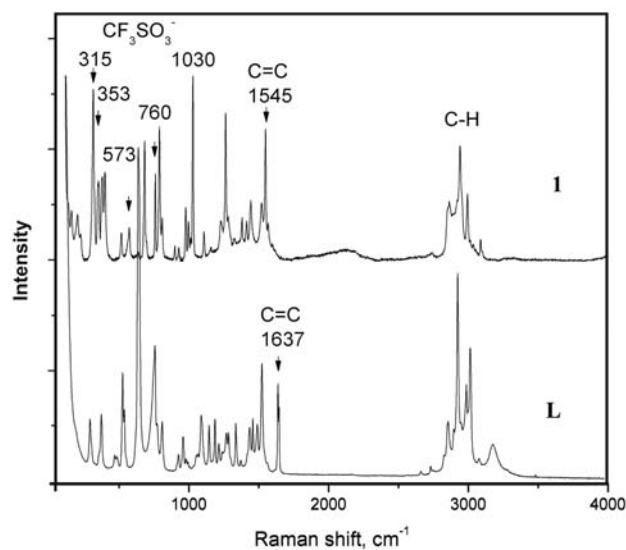
3. 2. Vibrational Spectra of **1** and **2** Compounds

Raman spectra of **1** and pure ligand are shown in Fig. 5, spectra of compound **2** and ligand are represented at Fig. 6. Although even the spectrum of *L* is quite complex, its comparison with Raman spectra of respective coordination compound leads to certain conclusions. The bands at 315, 353, 573, 760 and 1030 cm^{-1} in Raman spectrum of complex **1** are not present in the spectrum of pure *L*, and can therefore be assigned to the triflate-anion. The band at 760 cm^{-1} corresponds to the C-F symmetric deformation $\delta_s(\text{CF}_3)$. In $(\text{PEO})_3\text{LiCF}_3\text{SO}_3$ (PEO – (poly(ethylene oxide))), the corresponding band is observed at 766 cm^{-1} .²² The band at 1030 cm^{-1} may be assigned to the symmetric stretching mode $\nu_s(\text{S-O})$ of the triflate-anion, exactly as was observed in silver triflate in a mixed DMF/ acrylonitrile solution.²⁴ Bands at 315, 353 and 573 cm^{-1} can be attributed to C-S stretching, SO_3 rocking and CF_3 antisymmetric deformation respectively. Corresponding bands in solid $\text{NO}_2\text{CF}_3\text{SO}_3$ were observed at 322–324, 353–356 and 574–578 cm^{-1} .²⁵ The rest of the vibrational bands can be

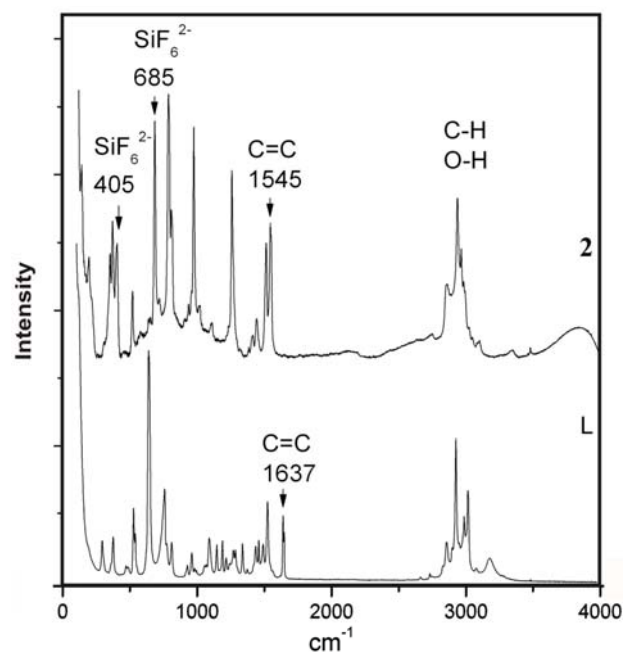
Table 5. Geometry of hydrogen bonds in the crystal structure **2**.

Atoms involved D–H...A	Symmetry	Distances, Å			Angle, ° D–H...A
		D...H	H...A	D...A	
O(1)–H(1A)···O(7)		0.96	2.07	3.022(8)	169
O(1)–H(1B)···F(25)		0.97	1.85	2.777(8)	160
O(2)–H(2B)···F(13)	1–x, 1–y, 1–z	0.96	1.94	2.737(8)	138
O(3)–H(3A)···O(4)		0.96	1.99	2.736(8)	133
O(3)–H(3A)···S(3)	–x, 2–y, 1–z	0.96	2.56	3.121(6)	117
O(3)–H(3B)···F(14)	1–x, 1–y, 1–z	0.97	1.87	2.806(8)	164
O(4)–H(1O4)···F(24)	x, 1+y, z	0.86	1.79	2.628(15)	166
O(4)–H(1O4)···F(27)	x, 1+y, z	0.86	2.11	2.94(3)	162
O(5)–H(1O5)···F(14)	1–x, –y, 1–z	0.86	2.06	2.784(8)	142
O(6)–H(1O6)···O(7)		0.87	2.11	2.857(9)	143
O(7)–H(1O7)···F(21)	–x, 1–y, 1–z	0.86	1.89	2.74(3)	165
O(7)–H(1O7)···F(28)	–x, 1–y, 1–z	0.86	2.20	3.06(2)	177
O(8)–H(1O8)···F(23)	–x, 1–y, 1–z	0.85	1.96	2.789(13)	166
O(9)–H(1O9)···F(16)	1–x, –y, 1–z	0.87	1.90	2.720(10)	156
O(4)–H(2O4)···O(5)	x, 1+y, z	0.86	2.28	2.751(9)	114
N(12)–H(N12)···F(11)		0.86	2.30	3.018(7)	141
N(12)–H(N12)···F(15)		0.86	2.08	2.830(8)	146
O(5)–H(2O5)···F(12)	x, y, –1+z	0.86	1.86	2.690(7)	161
O(6)–H(2O6)···F(11)		0.85	1.99	2.751(9)	148
O(7)–H(2O7)···F(26)		0.86	2.18	3.016(10)	163
O(7)–H(2O7)···F(28)		0.86	2.18	2.87(2)	138
O(9)–H(2O9)···N(34)	1+x, –1+y, z	0.86	2.56	3.219(11)	134
N(22)–H(N22)···F(24)	1–x, 1–y, –z	0.86	2.15	2.857(17)	134
N(22)–H(N22)···F(25)	1–x, 1–y, –z	0.86	2.24	3.035(9)	153
N(22)–H(N22)···F(27)	1–x, 1–y, –z	0.86	2.14	2.834(19)	137
N(32)–H(N32)···F(22)	–x, 1–y, 1–z	0.86	2.06	2.879(9)	158
N(32)–H(N32)···F(26)	–x, 1–y, 1–z	0.86	2.20	2.878(11)	136
N(42)–H(N42)···O(8)	x, 1+y, –1+z	0.86	1.91	2.738(9)	162

assigned to the ligand, for which the most prominent band was observed at 1545 cm^{-1} . This band arises from the C=C vibrations on the coordinated to the copper ion allyl group.²⁶ In pure ligand the C=C stretching mode is observed at 1637 cm^{-1} . This frequency decreases up to 100 cm^{-1}

**Figure 5.** Raman spectra of **1** and pure ligand **L**.

in copper(I) π -complexes with ethylene.²⁷ On the basis of the above results it can be concluded that the $\text{Cu}^+(\text{C}=\text{C})$

**Figure 6.** Raman spectra of **2** and pure ligand **L**.

interaction is strong enough.

The vibrational bands at 405 and 685 cm^{-1} in the spectrum of **2** are not present in the spectrum of pure *L*, and can therefore be assigned to the octahedral $[\text{SiF}_6]^{2-}$ anion. The vibrational band at 685 cm^{-1} results from symmetric stretching (ν_1), and the lower wavelength band at 405 cm^{-1} is the bending mode (ν_2) of the SiF_6^{2-} group. In $[(\text{C}_2\text{H}_5)\text{NH}_3]_2\text{SiF}_6$, the corresponding bands are observed at 395 and 665 cm^{-1} .²⁸ The vibrational bands of O–H stretching modes (around 3000 cm^{-1}) in **2** overlap with those of the C–H vibrations of coordinated ligands. The C=C stretching mode of the allyl group is also shifted to 1637 cm^{-1} . As was already mentioned, such a strong shift indicates moderately strong $\text{Cu}^+(\text{C}=\text{C})$ interaction, what is in a good agreement with the structural data.

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Povzetek

Dva nova bakrova(I) π -kompleksa $[\text{Cu}(\text{L})\text{CF}_3\text{SO}_3]$ (**1**) in $[\text{Cu}_2(\text{L})_2(\text{H}_2\text{O})_2](\text{SiF}_6)_2 \cdot 2.5\text{H}_2\text{O}$ (**2**) (*L* – 2-(alil)-amino-5-metil-1,3,4-thiadiazole) sta bila sintetizirana z elektrokemijskim postopkom in karakterizirana z rentgensko strukturno analizo na monokristalih ter ramansko spektroskopijo. V obeh strukturah organska molekula *L* deluje kot kelatno-mostovni trovalentni ligand, ki je povezan z bakrom (I) preko dveh N atomov tiadiazolnega obroča in C=C vezi iz alilne skupine, kar povzroči nastanek stabilnih kationskih dimerov $[\{\text{Cu}(\text{L})\}_2]^{2+}$.

V strukturi **1** se atom kisika iz triflatnega aniona nahaja v apikalnem položaju kovinskega koordinacijskega poliedra, v strukturi **2** dolge razdalje kovina – heksafluorosilikatni anion omogočajo koordinacijo H_2O molekule na bakrov atom. Vodikove vezi (E)–H \cdots Y (kjer je E = O, N, C, Y = O, F) igrajo pomembno vlogo pri oblikovanju 2D- (1) in 3D- (2) fragmentov.