

Copper(I) complexes with 5-(allylthio)-1*H*-tetrazoles: synthesis and crystal structure of [Cu₂(C₁₀H₁₀N₄S)₂(H₂O)₂](BF₄)₂ and [Cu₂(C₁₀H₉ClN₄S)₂(H₂O)₂](BF₄)₂·C₂H₅OH π -compounds (C₁₀H₁₀N₄S and C₁₀H₉ClN₄S - 5-(allylthio)-1-phenyl- and 5-(allylthio)-1-(4-chlorophenyl)-1*H*-tetrazole)

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By means of the alternating current electrochemical technique, [Cu₂(*atpt*)₂(H₂O)₂](BF₄)₂ (1) (*atpt* = 5-(allylthio)-1-phenyl-1*H*-tetrazole, C₁₀H₁₀N₄S) and [Cu₂(*atcpt*)₂(H₂O)₂](BF₄)₂·C₂H₅OH (2) (*atcpt* = 5-(allylthio)-1-(4-chlorophenyl)-1*H*-tetrazole, C₁₀H₉ClN₄S) π -complexes have been synthesized and X-ray studied by the single crystal method. Crystals of 1 are monoclinic, space group *P*2₁/*n*, *a* = 10.4353(7), *b* = 10.9125(7), *c* = 12.9389(9) Å, β = 99.064(2)°, *V* = 1455.02(17) Å³ at 200 K, *Z* = 2, *R* = 0.067 for 2881 reflections; compound 2 crystallizes in the triclinic space group *P* $\bar{1}$, *a* = 10.925(2), *b* = 11.945(2), *c* = 15.168(3) Å, α = 75.89(1), β = 86.23(1), γ = 64.13(1)°, *V* = 1725.4(4) Å³ at 298 K, *Z* = 2, *R* = 0.066 for 2590 reflections. In these structures the metal atoms possess a trigonal pyramidal coordination environment involving N3 and N4 atoms from two adjacent organic ligands, an olefin C=C bond and a water molecule in apical position. Both the *atpt* and *atcpt* ligand molecules act as a tridentate N,N,(S-C₃H₂)-bridging ligand connecting two metal (*M*) atoms into centrosymmetric cationic [M₂(L)₂(H₂O)₂]²⁺ dimers with one six-membered {M₂N₄} cycle and two seven-membered {MNC₄S} rings. Effective O-H...F bonds occur between the coordinated water molecules and the BF₄⁻ anion.

Tetrazole / Copper(I) / Electrochemical technique / π -Complex / Crystal structure

1. Introduction

Metal tetrazole derivatives attract considerable attention due to their significant role in self-organization of particles through coordination to different transition metal ions, in particular, to copper(I) atoms [1]. Modification of the tetrazole molecule by an olefin-containing group being able to coordinate with Cu(I) atoms should promote the formation of more complex structures.

The recently investigated compounds [CuX(3*atpy*)] (3*atpy* = 3-(2-allyl-2*H*-tetrazole-5-yl)pyridine, X = Cl [2], Br [3]), [Cu₂Cl₂(4*atpy*)₂] (4*atpy* = 4-(2-allyl-2*H*-tetrazole-5-yl)pyridine) [4], [CuBr(4*atpy*)] [5] [Cu₂(*atcpt*)₂(H₂O)₂](NO₃)₂·C₂H₅OH and [Cu₃(*atcpt*)Cl₃] (*atcpt* = C₁₀H₉ClN₄S 5-(allylthio)-1-(4-chlorophenyl)-1*H*-tetrazole, C₁₀H₉ClN₄S) [6], appeared to be the only representatives among Cu(I)

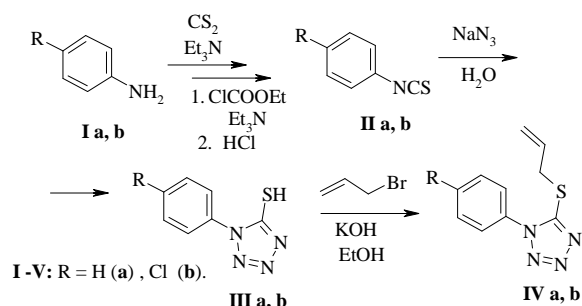
tetrazole π -compounds. It was shown that N-allyl derivatives of tetrazoles (3*atpy* [2,3] and 4*atpy* [4,5]) do not promote the inclusion of nitrogen atoms of the tetrazole ring in the metal coordination but the above-mentioned ligands are bonded to Cu(I) only by olefin C=C bonds and pyridine N atoms. Contrary to these ligands, the *atcpt* molecule is attached to the metal *via* two N atoms of the tetrazole core and by an olefin C=C bond from the S-allyl group in a chelating mode.

To continue a study of the coordination behaviour of 5-(allylthio)-1-phenyl-1*H*-tetrazoles regarding copper(I) ions we have obtained crystalline [Cu₂(*atpt*)₂(H₂O)₂](BF₄)₂ (1) (*atpt* = 5-(allylthio)-1-phenyl-1*H*-tetrazole (C₁₀H₁₀N₄S)) and [Cu₂(*atcpt*)₂(H₂O)₂](BF₄)₂·C₂H₅OH (2) (*atcpt* = 5-(allylthio)-1-(4-chlorophenyl)-1*H*-tetrazole (C₁₀H₉ClN₄S)) π -complexes and performed their single crystal X-ray structure characterization.

2. Experimental

2.1 Synthesis of C₁₀H₁₀N₄S and C₁₀H₉ClN₄S

The target ligands **IV** (C₁₀H₁₀N₄S (**a**) and C₁₀H₉ClN₄S (**b**)) were synthesized from commercially available aniline **I a** and 4-chloroaniline **I b** by several procedures (Scheme 1). Appropriate 4-R-aniline **I** was converted into 4-R-isothiocyanatobenzene **II** by the reaction with carbon disulfide and a consecutive treatment with ethyl chlorocarbonate and HCl according to the modified Kaluza method [7]. By a 1,3-dipolar cycloaddition reaction of the obtained isothiocyanatobenzene **II** with azide ions, 1-(4-R-phenyl)-1*H*-tetrazole-5-thiol **III** [8] was formed and readily reacted with 3-bromoprop-1-ene in the presence of KOH, yielding the corresponding ligand **IV** [9].



Scheme 1 Synthesis of C₁₀H₁₀N₄S and C₁₀H₉ClN₄S.

2.2 Preparation of [Cu₂(C₁₀H₁₀N₄S)₂(H₂O)₂](BF₄)₂

Crystals of **1** were obtained under conditions of the alternating-current electrochemical synthesis [10] starting from a methanol/water solution (3.5 ml methanol and 0.5 ml water) of Cu(BF₄)₂·6H₂O (1 mmol) and C₁₀H₁₀N₄S (2 mmol). The prepared solution was placed into a small test-tube and copper-wire electrodes in cork were inserted. After applying 0.50 V of alternating current (frequency 50 Hz) tension for 24 h, the initially muddy green colored solution was discolored and good-quality colorless prisms of **1** appeared on the copper-wire electrodes.

2.3 Preparation of [Cu₂(C₁₀H₉ClN₄S)₂(H₂O)₂](BF₄)₂·C₂H₅OH

Crystals of **2** were obtained under the same conditions of the alternating-current electrochemical synthesis starting from a methanol/2-butanol solution (3 ml methanol and 1 ml 2-butanol) of C₁₀H₉ClN₄S (2 mmol), previously titrated by HBF₄ to pH ~3.5, and Cu(BF₄)₂·6H₂O (1 mmol). After applying 0.50 V of alternating current (frequency 50 Hz) tension for 72 h, the muddy green-blue colored solution was discolored and good-quality colorless prisms of **2** appeared on the copper-wire electrodes.

3. X-Ray crystal structure determination

The crystallographic parameters and summaries of the data collection for **1** and **2** are presented in Table 1. Single crystal data for **1** were collected on a Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector, using graphite monochromated Mo K_α radiation; the data were treated using the Rigaku CrystalClear software suite program package [11]. The diffraction data for **2** were collected on a CAD-4 diffractometer (graphite monochromated Mo K_α radiation). Both structures were solved by direct methods using SIR-92 [12] and SHELXS-97 [13] programs (teXan crystallographic software package of the Molecular Structure Corporation [14]) and refined with SHELXL-97 [15] software, implemented in the program package WinGX [16]. In both structures the non-hydrogen atoms were found by direct methods and the hydrogen ones geometrically. Full-matrix least-squares refinements based on *F*² were carried out for the positional and thermal parameters of all non-hydrogen atoms. The positions of the 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). In both structures some of the fluorine atoms are disordered. The figures were prepared using DIAMOND 3.1 software [17]. Fractional atomic coordinates and displacement parameters for **1** and **2** are shown in Table 2 and 3.

4. Results and discussion

In the structure of [Cu₂(*atpt*)₂(H₂O)₂](BF₄)₂ (**1**) the *atpt* (5-(allylthio)-1-phenyl-1*H*-tetrazole, C₁₀H₁₀N₄S) ligand is coordinated to the Cu(I) atom through the C=C-bond of the allyl group and two N atoms of the tetrazole ring (Fig. 1). Similarly to the earlier studied π -complexes [Cu₂(*atcpt*)₂(H₂O)₂](NO₃)₂·C₂H₅OH (**3**) and [Cu₃(*atcpt*)Cl₃] (**4**) (*atcpt* = 5-(allylthio)-1-(4-chlorophenyl)-1*H*-tetrazole, C₁₀H₉ClN₄S) [6], the Cu(I) atom in **1** possesses a trigonal pyramidal coordination environment formed by two N3 and N4 atoms of the adjacent tetrazole core and a C=C bond from the S-allyl group. The apical position of the metal coordination polyhedron is occupied by a water molecule (Fig. 1, Table 4). The crystal structure packing of **1** is shown in Fig. 2. Although the coordination mode of the organic molecule in the related structures **1**, **3** and **4** appears to be the same, **4** differs from structures **1** and **3** by the bridging role of the apical Cl atom in the Cu(I) polyhedron.

The *atpt* moiety acts as a tridentate N,N,(S-C₃H₅)-bridging ligand connecting two Cu(I) atoms into centrosymmetric cationic [Cu₂(*atpt*)₂(H₂O)₂]²⁺ dimers with one six-membered almost planar {Cu₂N₄} cycle and two seven-membered {CuNC₄S} rings. This structure is somewhat similar to the σ -compounds {[Cu₁₀(μ_3 -N₄C₂H₃)₃(μ_4 -N₄C₂H₃)₇]-2H₂O}_{*n*} (where N₄C₂H₃ = 5-methyl tetrazolate) [18],

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

	1	2
Empirical formula	C ₂₀ H ₂₄ Cu ₂ N ₈ O ₂ S ₂ ·2(BF ₄)	C ₂₂ H ₂₄ Cl ₂ Cu ₂ N ₈ O ₃ S ₂ ·2(BF ₄)
Formula weight	773.33 g/mol	884.21 g/mol
Temperature, K	200(2)	298(2)
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	monoclinic, <i>P</i> 2 ₁ / <i>n</i>	triclinic, <i>P</i> -1
Unit cell dimensions,		
<i>a</i> , Å	10.4353(7)	10.925(2)
<i>b</i> , Å	10.9125(7)	11.945(2)
<i>c</i> , Å	12.9389(9)	15.168(3)
<i>α</i> , °	90	75.89(1)
<i>β</i> , °	99.064(2)	86.23(1)
<i>γ</i> , °	90	64.13(1)
<i>V</i> , Å ³	1455.02(17)	1725.4(4)
<i>Z</i>	2	2
Calculated density, g/cm ³	1.77	1.69
Absorption coeff., mm ⁻¹	1.69	1.59
<i>F</i> (000)	776	872
Crystal size, mm	0.12 × 0.12 × 0.1	0.27 × 0.18 × 0.11
Color, shape	colorless, unspecified	colorless, unspecified
Theta range for data collection	2-29 deg	2-21 deg
Limiting indices	-11 ≤ <i>h</i> ≤ 13, -14 ≤ <i>k</i> ≤ 14, -17 ≤ <i>l</i> ≤ 17	-10 ≤ <i>h</i> ≤ 11, -11 ≤ <i>k</i> ≤ 12, -3 ≤ <i>l</i> ≤ 15
Refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
Measured reflections	11582	3938
Unique reflections	3371	3674
Used in refinement	3371	3674
Free parameters	199	449
Goodness-of-fit on <i>F</i> ²	1.18	1.08
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.067, <i>wR</i> ₂ = 0.185	<i>R</i> ₁ = 0.066, <i>wR</i> ₂ = 0.164
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.076, <i>wR</i> ₂ = 0.198	<i>R</i> ₁ = 0.108, <i>wR</i> ₂ = 0.186
Largest diff. peak and hole	1.69 and -0.83 e·Å ⁻³	0.73 and -0.69 e·Å ⁻³

^a CCDC 772786, 772785 contain 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).

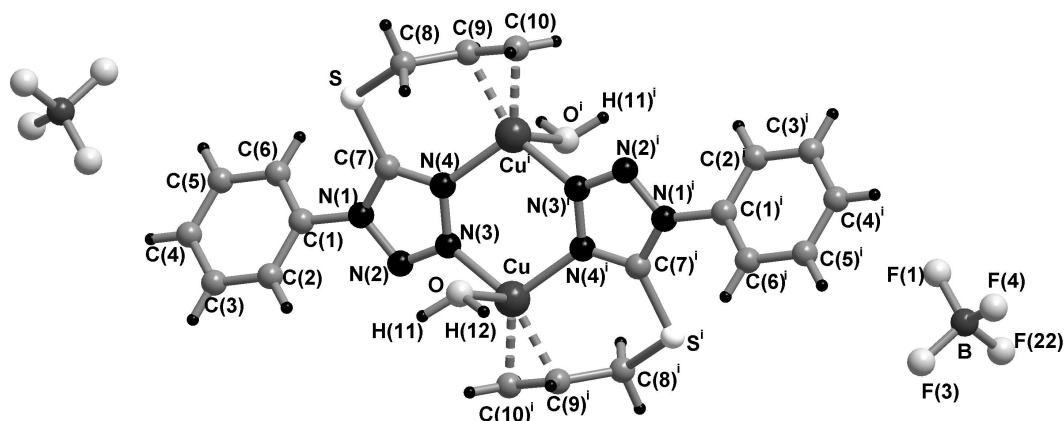


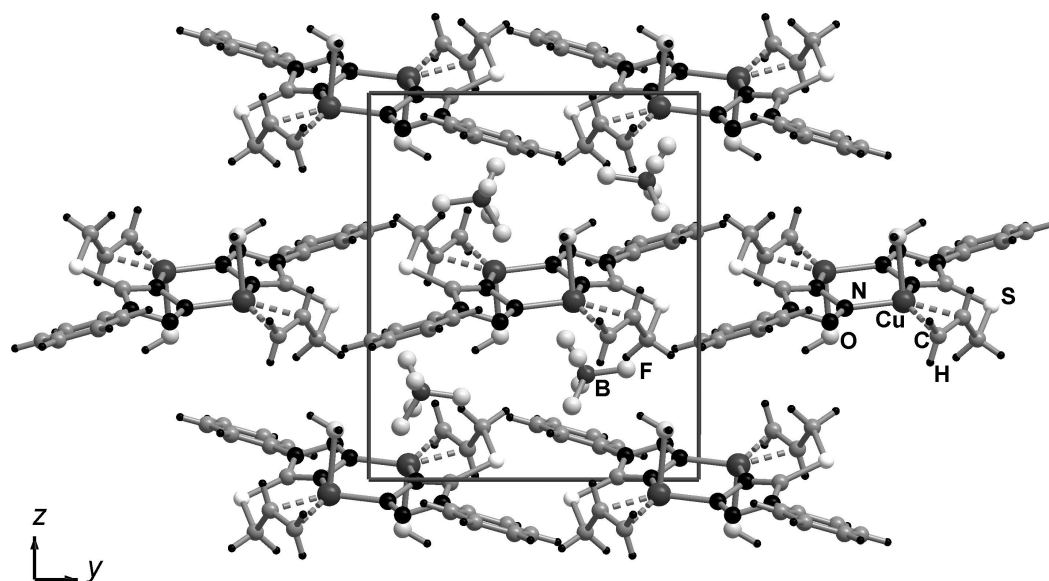
Fig. 1 Fragment of structure **1**. Symmetry code: (*i*) 1-*x*, -*y*, -*z*. Disorder of fluorine atoms is omitted for clarity.

Table 2 Fractional atomic coordinates and equivalent isotropic or isotropic^a displacement parameters (Å²) for **1**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}/U_{iso}^*{}^a$	Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}/U_{iso}^*{}^a$
Cu	0.39957(5)	0.12003(4)	0.03764(4)	0.0339(2)	C(7)	0.3568(3)	-0.2464(3)	0.0073(3)	0.0311(8)
S	0.38073(11)	0.38564(8)	0.04941(9)	0.0349(3)	C(8)	0.4951(4)	-0.3440(4)	-0.1358(3)	0.0374(9)
F(1)	0.1018(6)	-0.2800(4)	-0.2135(4)	0.1227(19)	C(9)	0.6246(4)	-0.2989(3)	-0.0795(3)	0.0336(8)
F(21) ^b	0.207(5)	-0.133(3)	-0.185(3)	0.116(3)	C(10)	0.7037(4)	-0.2251(4)	-0.1272(3)	0.0404(9)
F(22) ^b	0.1187(8)	-0.0966(6)	-0.1369(4)	0.116(3)	B	0.0822(5)	-0.1585(5)	-0.2275(4)	0.0424(11)
F(3)	-0.0441(5)	-0.1402(6)	-0.2545(5)	0.149(3)	H(11)	0.20620	0.09090	-0.12770	0.0690*
F(4)	0.1377(5)	-0.1156(4)	-0.3093(4)	0.1061(18)	H(12)	0.30810	0.17680	-0.16510	0.0690*
O	0.2965(4)	0.1024(3)	-0.1282(3)	0.0575(9)	H(2)	0.01840	-0.16730	0.06160	0.0460*
N(1)	0.2597(3)	-0.2220(3)	0.0616(3)	0.0314(7)	H(3)	-0.14570	-0.28700	0.10970	0.0500*
N(2)	0.2671(3)	-0.1028(3)	0.0918(3)	0.0351(8)	H(4)	-0.10580	-0.49000	0.15680	0.0540*
N(3)	0.3646(3)	-0.0577(3)	0.0561(3)	0.0347(7)	H(5)	0.09770	-0.57180	-0.16120	0.0510*
N(4)	0.4250(3)	-0.1437(3)	0.0039(3)	0.0322(7)	H(6)	0.26560	-0.45010	0.11980	0.0450*
C(1)	0.1566(4)	-0.2987(3)	0.0868(3)	0.0327(8)	H(81)	0.50980	-0.41490	-0.17760	0.0450*
C(2)	0.0343(4)	-0.2481(4)	0.0827(3)	0.0387(9)	H(82)	0.45670	-0.28040	-0.18310	0.0450*
C(3)	-0.0633(4)	-0.3199(4)	0.1103(3)	0.0419(9)	H(91)	0.65130	-0.32210	-0.01030	0.0400*
C(4)	-0.0391(5)	-0.4415(4)	0.1393(3)	0.0449(10)	H(101)	0.67850	-0.20110	-0.19630	0.0490*
C(5)	0.0823(5)	-0.4903(4)	0.1422(3)	0.0429(10)	H(102)	0.78280	-0.19890	-0.09040	0.0490*
C(6)	0.1825(4)	-0.4182(4)	0.1167(3)	0.0373(8)					

^a For non-hydrogen atoms U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor, for hydrogen U_{iso} .

^b Fluorine atoms are disordered and fill two sites with 0.155 and 0.845 occupation.

**Fig. 2** Projection of structure **1** on the *yz* plane.

$[\text{Cu}^{\text{II}}_2\text{Cu}^{\text{I}}_6(\text{N}_4\text{C}_2\text{H}_3)_9]\text{N}_3$ and $[\text{Cu}(\text{N}_4\text{CH})]$ ($\text{N}_4\text{CH} =$ tetrazolate anion) [19].

Replacement of *atpt* by *atcpt*, which contains a 4-chlorophenyl ring leads to the formation of $[\text{Cu}_2(\text{atcpt})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2 \cdot \text{C}_2\text{H}_5\text{OH}$ (**2**). It should be noted that the *atcpt* ligand does not change the coordination mode of the copper(I) ion, although two crystallographically independent $[\text{Cu}_2(\text{atcpt})_2(\text{H}_2\text{O})_2]^{2+}$ π -complex cations are formed. The structures **1** and **2** possess different crystal packings: the independent $[\text{Cu}_2(\text{C}_{10}\text{H}_9\text{ClN}_4\text{S})_2(\text{H}_2\text{O})_2]^{2+}$ cations in **2**

produce an original stacking in the [001] direction (Fig. 3).

In both of the π -compounds **1** and **2**, a small deviation of the metal atom from the basal plane of the trigonal pyramid (0.27 Å in **1** and 0.30 Å for Cu(1), 0.32 Å for Cu(2) in **2**), rather short Cu–*m* (*m* – midpoint of the C=C bond) distances and rather large C–Cu–C angles (Tables 4 and 5) indicate a sufficient efficiency of the Cu(I)–(C=C) interaction.

The structures of $[\text{Cu}_2(\text{atpt})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2$ (**1**) and $[\text{Cu}_2(\text{atcpt})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2 \cdot \text{C}_2\text{H}_5\text{OH}$ (**2**) are governed

Table 3 Fractional atomic coordinates and equivalent isotropic or isotropic^a displacement parameters (Å²) for **2**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}/U_{iso}^*{}^a$	Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}/U_{iso}^*{}^a$
Cu(1)	0.65604(12)	0.01989(13)	0.51056(9)	0.0490(5)	C(12)	0.2827(12)	-0.366(1)	1.1303(9)	0.058(3)
Cu(2)	0.35745(12)	0.11965(11)	0.91941(9)	0.0439(5)	C(13)	0.2200(12)	-0.4475(10)	1.1499(8)	0.056(3)
Cl(1)	0.9161(3)	-0.7340(3)	0.2542(3)	0.0751(10)	C(14)	0.1955(11)	-0.4933(10)	1.0846(8)	0.049(3)
Cl(2)	0.1185(3)	-0.5965(3)	1.1112(2)	0.0736(10)	C(15)	0.2301(13)	-0.4619(12)	0.9978(8)	0.065(3)
S(1)	0.8942(3)	-0.2038(3)	0.3890(2)	0.0606(9)	C(16)	0.2926(13)	-0.3786(12)	0.9759(8)	0.066(4)
S(2)	0.1541(3)	-0.0507(3)	0.9162(2)	0.0579(9)	C(17)	0.3128(9)	-0.1187(10)	0.9740(7)	0.039(3)
F(1)	0.3954(11)	0.2774(9)	0.2869(7)	0.130(3)	C(18)	0.0909(10)	0.1144(10)	0.9258(8)	0.055(3)
F(2)	0.5789(15)	0.2959(14)	0.2433(13)	0.226(8)	C(19)	0.1574(10)	0.1887(10)	0.8717(8)	0.053(3)
F(3)	0.5808(12)	0.1081(10)	0.2676(9)	0.158(4)	C(20)	0.1757(10)	0.2814(10)	0.8951(8)	0.051(3)
F(4)	0.4797(13)	0.2525(14)	0.1565(9)	0.194(6)	C(1S)	0.378(2)	0.516(2)	0.4023(16)	0.184(11)
F(51) ^b	0.8489(16)	0.0578(15)	0.8564(13)	0.073(7)	C(2S)	0.230(2)	0.5594(13)	0.4008(19)	0.29(3)
F(52) ^b	0.879(2)	0.151(3)	0.745(2)	0.076(11)	B(1)	0.5155(15)	0.2342(15)	0.2418(12)	0.061(4)
F(53) ^b	0.889(3)	0.097(3)	0.804(2)	0.042(14)	B(2)	0.7968(18)	0.0726(17)	0.7767(12)	0.076(5)
F(6)	0.6671(7)	0.1598(8)	0.7702(7)	0.108(3)	H(2)	0.57030	-0.34500	0.29350	0.0600*
F(7)	0.8428(11)	0.0284(13)	0.7072(8)	0.162(5)	H(3)	0.65850	-0.53020	0.24330	0.0650*
F(8)	0.784(2)	-0.0415(16)	0.8204(15)	0.287(12)	H(5)	1.02210	-0.63020	0.35540	0.0740*
Ow(1)	0.7315(8)	-0.1259(8)	0.6452(6)	0.078(3)	H(6)	0.93500	-0.45020	0.41230	0.0680*
Ow(2)	0.4571(7)	0.0770(7)	0.7901(5)	0.063(2)	H(9)	0.88790	-0.06640	0.52280	0.0720*
O(2S)	0.2445(12)	0.4340(11)	0.4051(8)	0.106(4)	H(12)	0.30130	-0.33500	1.17580	0.0700*
N(1)	0.6832(8)	-0.2692(7)	0.3973(5)	0.041(2)	H(13)	0.19480	-0.47040	1.20890	0.0670*
N(2)	0.5533(8)	-0.2302(8)	0.4242(6)	0.046(2)	H(15)	0.21260	-0.49510	0.95320	0.0780*
N(3)	0.5276(8)	-0.1329(8)	0.4556(6)	0.046(2)	H(16)	0.31710	-0.35570	0.91670	0.0790*
N(4)	0.6371(8)	-0.1071(8)	0.4521(6)	0.042(2)	H(19)	0.18980	0.17010	0.81630	0.0630*
N(5)	0.3710(7)	-0.2396(8)	1.0217(6)	0.038(2)	H(8A)	0.94990	-0.03200	0.35630	0.0700*
N(6)	0.4903(8)	-0.2613(8)	1.0600(6)	0.045(2)	H(8B)	0.79280	0.01800	0.34110	0.0700*
N(7)	0.5009(8)	-0.1557(8)	1.0339(6)	0.042(2)	H(20A)	0.14480	0.30290	0.95000	0.0610*
N(8)	0.3912(7)	-0.0609(7)	0.9780(5)	0.039(2)	H(20B)	0.21940	0.32440	0.85650	0.0610*
C(1)	0.7424(10)	-0.3806(10)	0.3606(7)	0.043(3)	H(10A)	0.73070	0.18660	0.42580	0.0820*
C(2)	0.6608(11)	-0.4037(10)	0.3076(8)	0.050(3)	H(10B)	0.76080	0.14020	0.53440	0.0820*
C(3)	0.7138(11)	-0.5126(10)	0.2765(8)	0.054(3)	H(18B)	-0.00550	0.15840	0.90860	0.0670*
C(4)	0.8469(11)	-0.595(1)	0.2940(8)	0.052(3)	H(18A)	0.10020	0.11320	0.98930	0.0670*
C(5)	0.9307(12)	-0.5726(11)	0.3444(8)	0.061(3)	H(2S)	0.28910	0.38480	0.45150	0.1590*
C(6)	0.8793(11)	-0.4658(11)	0.3780(8)	0.057(3)	H(1S1)	0.39750	0.58790	0.39930	0.2760*
C(7)	0.7341(10)	-0.1927(10)	0.4149(7)	0.039(2)	H(1S2)	0.41420	0.48030	0.35110	0.2760*
C(8)	0.8703(11)	-0.0411(11)	0.3824(8)	0.059(3)	H(1S3)	0.41810	0.45250	0.45760	0.2760*
C(9)	0.8482(11)	-0.0032(12)	0.4700(9)	0.060(3)	H(2S1)	0.18760	0.59130	0.45340	0.3490*
C(10)	0.7715(12)	0.1215(13)	0.4776(10)	0.068(4)	H(2S2)	0.18350	0.62090	0.34500	0.3490*
C(11)	0.3168(10)	-0.3322(9)	1.0426(8)	0.042(3)					

^a For non-hydrogen atoms U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor, for hydrogen U_{iso} .^b Fluorine atoms are disordered and fill three sites with 0.46, 0.31 and 0.23 occupation.**Table 4** Selected bond lengths (in Å) and angles (in deg) in structure **1**.

1			
Cu–C(9) ⁱ ^a	2.052(4)	N(3)–Cu– <i>m</i> (1)	130.1(2)
Cu–C(10) ⁱ	2.052(4)	N(4) ⁱ –Cu– <i>m</i> (1)	114.0(2)
Cu– <i>m</i> (1) ^b	1.945(4)	N(3)–Cu–N(4) ⁱ	110.5(1)
Cu–N(3)	1.995(3)	<i>m</i> (1)–Cu–O(1)	110.0(2)
Cu–N(4) ⁱ	2.005(3)	N(3)–Cu–O(1)	87.8(1)
Cu–O(1)	2.252(4)	N(4) ⁱ –Cu–O(1)	94.3(2)
C(9)=C(10)	1.368(6)	C(9)–Cu–C(10)	38.9(2)
C(8)–C(9)	1.512(6)	C(10)=C(9)–C(8)	122.1(4)

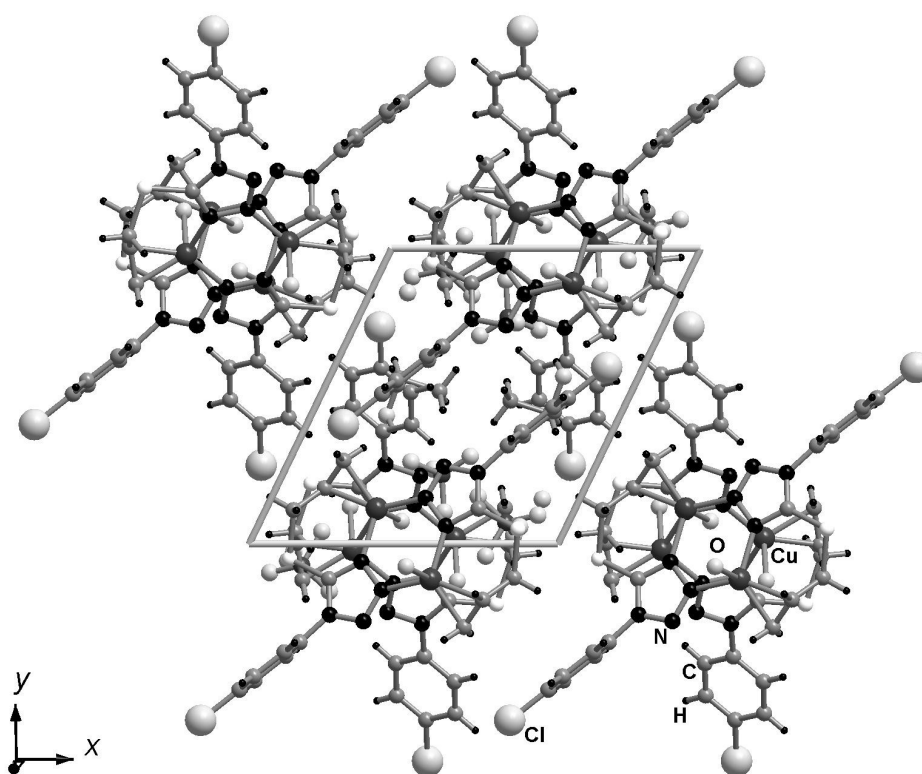
^a symmetry code: (*i*) 1–*x*, –*y*, –*z*;^b *m*(1) is the midpoint of the C(9)=C(10) bond.

Table 5 Selected bond lengths (in Å) and angles (in deg) in structure **2**.

Cu(1)–C(9)	2.07(1)	N(3) ⁱ –Cu(1)– <i>m</i> (1)	129.1(4)
Cu(1)–C(10)	2.07(1)	N(4)–Cu(1)– <i>m</i> (1)	115.7(4)
Cu(1)– <i>m</i> (1) ^a	1.95(1)	N(3) ⁱ –Cu(1)–N(4)	108.2(3)
Cu(1)–N(3) ⁱ ^b	1.987(8)	<i>m</i> (1)–Cu(1)–Ow(1)	103.3(4)
Cu(1)–N(4)	2.020(8)	N(3) ⁱ –Cu(1)–Ow(1)	99.4(3)
Cu(1)–Ow(1)	2.262(8)	N(4)–Cu(1)–Ow(1)	92.3(3)
C(9)=C(10)	1.38(2)	C(9)–Cu(1)–C(10)	39.1(4)
C(8)–C(9)	1.48(2)	C(10)=C(9)–C(8)	124(1)
Cu(2)–C(19)	2.08(1)	N(7) ⁱⁱ –Cu(2)– <i>m</i> (2)	129.1(4)
Cu(2)–C(20)	2.05(1)	N(8)–Cu(2)– <i>m</i> (2)	114.1(4)
Cu(2)– <i>m</i> (2) ^a	1.96(1)	N(7) ⁱⁱ –Cu(2)–N(8)	108.9(3)
Cu(2)–N(7) ⁱⁱ ^b	1.989(8)	<i>m</i> (2)–Cu(2)–Ow(2)	105.2(4)
Cu(2)–N(8)	1.998(8)	N(7) ⁱⁱ –Cu(2)–Ow(2)	96.5(3)
Cu(2)–Ow(2)	2.239(8)	N(8)–Cu(2)–Ow(2)	95.3(3)
C(19)=C(20)	1.34(1)	C(19)–Cu(2)–C(20)	37.8(4)
C(18)–C(19)	1.46(2)	C(20)=C(19)–C(18)	125(1)

^a *m*(1) and *m*(2) are the midpoints of the C(9)=C(10) and C(19)=C(20) bonds respectively;

^b symmetry codes: (i) 1-*x*, -*y*, 1-*z*; (ii) 1-*x*, -*y*, 2-*z*.

**Fig. 3** Projection of structure **2** on the *xy* plane.

by a variety of hydrogen contacts H...F [20,21], which occur predominately between hydrogen atoms of coordinated water molecules and fluorine atoms (with O...F distance of 2.77–3.28 Å for **1** and 2.71–2.95 Å for **2**) of the BF₄[−] anion in a bridging mode. Thus, the BF₄[−] anions in the π-complexes **1** and **2** play the same bridging role as the NO₃[−] anions in the previously studied structure of

[Cu₂(*atcpt*)₂(H₂O)₂](NO₃)₂·C₂H₅OH (**3**) [6]. In addition, it should be noticed that weak C–H...π interaction [22] is observed in both **1** and **2**; the corresponding distances between phenyl rings and olefin hydrogen atoms of adjacent [Cu₂(*L*)₂(H₂O)₂]²⁺ (*L* = *atpt* or *atcpt*) π-complex cations are equal to 2.62 Å (**1**) and 2.75 Å (**2**).

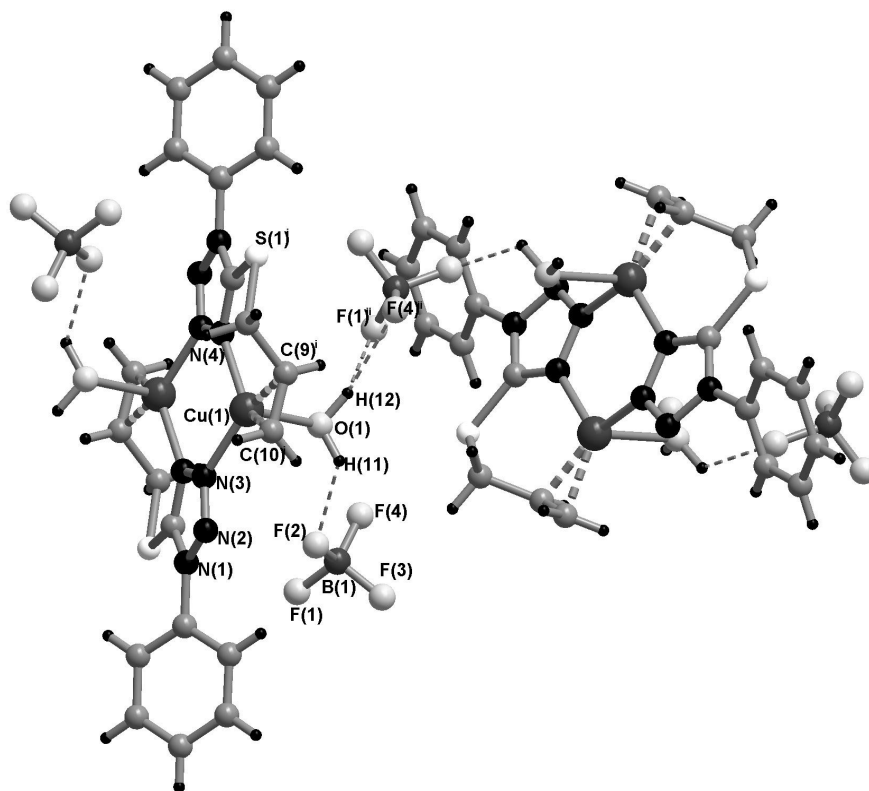


Fig. 4 Fragment of structure **1**. Hydrogen O-H...F bonds are depicted as dashed lines. Symmetry codes: (i) $1-x, -y, -z$; (ii) $0.5-x, 0.5+y, -0.5-z$.

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