

Scientific paper

Two Related Copper(I) π -Complexes Based on 2-Allyl-5-(2-pyridyl)-2H-tetrazole Ligand: Synthesis and Structure of [Cu(2-apyt)NO₃] and [Cu(2-apyt)(H₂O)](BF₄) Compounds

Yurii Slyvka,^{1,*} Evgeny Goreshnik,² Nazariy Pokhodylo,¹ Oleksiy Pavlyuk¹ and Marian Mys'kiv¹

¹ Ivan Franko National University of Lviv, Kyryla i Mefodiya Str., 6, 79005, Lviv, Ukraine

² Department of Inorganic Chemistry and Technology, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

* Corresponding author: E-mail: y_slyvka@franko.lviv.ua

Tel.: +380 32 23 94 506

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Abstract

By means of the alternating current electrochemical technique two new π -compounds [Cu(2-apyt)NO₃] (**1**) and [Cu(2-apyt)(H₂O)](BF₄) (**2**) have been obtained starting from the mixture of 1-allyl-5-(2-pyridyl)-2H-tetrazole (1-apyt), 2-allyl-5-(2-pyridyl)-2H-tetrazole (2-apyt) and corresponding copper(II) salts, and have been structurally studied. Selective complexation towards 2-allyl- isomer results in a formation of 2-apyt complexes. Copper(I) ion in both **1** and **2** complexes coordinates the allylic C=C bond, one pyridyl and one tetrazole N atoms. In both structures Cu⁺ center adopts distorted tetrahedral surrounding which additionally includes oxygen of NO₃⁻ in **1** and H₂O moiety in **2**. Structure **1** is built from [Cu(2-apyt)NO₃]₂ dimeric fragments. Contrary, participation of H₂O in the metal coordination in **2** leads to the infinite {[Cu(2-apyt)(H₂O)]⁺}_n chain construction. To analyze interactions between the particles in **1** and **2** Hirshfeld surface analysis was performed.

Keywords: Copper(I); tetrazole; π -complex; Hirshfeld surface analysis; crystal structure

1. Introduction

Tetrazoles are well known heterocyclic compounds that have found wide application in pharmaceutical chemistry (showing antibacterial, anticancer, anti-convulsant, anti-tuberculosis activity *etc.*), in the agricultural sector (pesticides, plant growth regulators), as well as corrosion inhibitors, luminophores and the effective precursors for transition metal complex preparation.^{1–5} Different tetrazole derivatives serve as suitable ligands for a design and self-organization of molecules through the selective attachment to metal ions by one, two, three or four nitrogen atoms of tetrazole ring and other donor atoms of substituents. An appearance of olefine C=C bond in a skeleton of the above substituents may serve as actual key for the selected coordination of transition metal ions due to metal-olefin π -bonding.⁶

Despite the huge advances in tetrazole chemistry, the metal-olefine π -coordination in the presence of tetrazole moiety is scarcely studied (Cambridge Crystallographic Database).⁷

In recent years a considerable attention have been paid for investigation of Cu(I) π -complexes with allyl derivatives of organic heterocyclic compounds since the combination of allylic radical and heterocyclic cores (both of which according to HSAB theory act as “soft bases”) efficiently contributes to the isolation of the compounds with extremely rare occurred inorganic fragments.⁸ Using special *ac*-electrochemical technique we have recently succeeded to obtain in a crystalline form few copper(I) π -complexes with 5-allylsulfanyl-1-aryl-substituted tetrazoles in which tetrazole moiety reveals a strong tendency to the dimeric [Cu₂(L)₂]²⁺ tectones formation, regardless of aryl-substituent's and anion type or somewhat different

reaction condition.^{9,10} In contrast, π -coordination of N-allyltetrazoles regarding transition metal ions was studied only in the case of four CuCl and CuBr compounds, obtained under solvothermal conditions.^{11–14} To fill the gap mentioned above we present herein synthesis and structural characterization of two new [Cu(2-apyt)NO₃] (**1**) and [Cu(2-apyt)(H₂O)](BF₄) (**2**) π -compounds with 2-allyl-5-(2-pyridyl)-2H-tetrazole (2-apyt), emphasizing the isomer-selective complexation of Cu⁺ by 2-allyl-5-(2-pyridyl)-2H-tetrazole under *ac*-electrochemical technique.

2. Experimental

2.1. Materials and Instrumentation

Unless otherwise mentioned, all chemicals were obtained from commercial sources and used without further purification. ¹H NMR spectrum of the 1-apyt and 2-apyt mixture was recorded on a Bruker 500 instrument (500 MHz for ¹H) with deuterated CDCl₃ solvent as an internal reference. Diffraction data for **1** and **2** crystals were collected on a Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector, graphite monochromatized MoK α radiation. Hirshfeld surface of the fragment in **1** complex and fingerprint plots were produced by Crystal-Explorer software.^{15,16}

2.2. Preparation of N-allyl-5-(2-pyridyl)-2H-tetrazole (apyt)

5-(2-Pyridyl)-1H-tetrazole (Hpyt) was synthesized from 2-cyanopyridine and sodium azide in accordance with the reported method.¹⁷ The reaction of 5-(2-pyridyl)-1H-tetrazole with 3-bromoprop-1-ene in the presence of NaOH in ethanol solution yields corresponding mixture of 1-allyl-5-(2-pyridyl)-1H-tetrazole (1-apyt) and 2-allyl-5-(2-pyridyl)-2H-tetrazole (2-apyt) in approximately 2:3 molar ratio. Total yield ~93%. NMR ¹H (500 MHz, CDCl₃), δ , ppm.: 1-allyl-5-(2-pyridyl)-1H-tetrazole (1-apyt), 8.76 (d, $J = 4.5$, 1H, H_{Py-6}), 8.27 (d, $J = 7.9$, 1H, H_{Py-3}), 8.10 (t, $J = 7.8$, 1H, H_{Py-4}), 7.66 (dd, $J = 7.5$, 4.8, 1H, H_{Py-5}), 6.12–6.06 (m, 1H, H^X_{CH=CH2}), 5.59 (dd, $J = 5.5$, 1.3, 2H, H_{CH2}), 5.24 (d, $J = 10.3$, 1H, H^B_{CH=CH2}), 5.11 (d, $J = 17.1$, 1H, H^A_{CH=CH2}); 2-allyl-5-(2-pyridyl)-2H-tetrazole (2-apyt), 8.82 (d, $J = 4.5$, 1H, H_{Py-6}), 8.15 (d, $J = 7.0$, 1H, H_{Py-3}), 8.02 (t, $J = 7.7$, 1H, H_{Py-4}), 7.57 (dd, $J = 7.5$, 4.8, 1H, H_{Py-5}), 6.22–6.12 (m, 1H, H^X_{CH=CH2}), 5.46 (dd, $J = 5.9$, 1.3, 2H, H_{CH2}), 5.39 (d, $J = 9.2$, 1H, H^B_{CH=CH2}), 5.37 (d, $J = 16.0$, 1H, H^A_{CH=CH2}).

2.3. Synthesis of Copper(I) π -complexes

Crystals of the π -complexes were obtained under conditions of the alternating-current electrochemical synthesis,¹⁸ starting from the alcohol solution of the 1-apyt/2-apyt mixture and the corresponding copper(II) salt.

Table 1. Selected crystal data and structure refinement parameters of **1** and **2**.

Crystal data	1	2
CCDC number	1471651	1471664
Empirical formula	C ₉ H ₉ CuN ₆ O ₃	C ₉ H ₁₁ BCuF ₄ N ₅ O
Formula weight (g mol ⁻¹)	312.76	355.58
Crystal system, space group	Monoclinic, <i>P2₁/c</i>	Monoclinic, <i>P2₁/n</i>
<i>a</i> (Å)	9.247(3)	12.497(4)
<i>b</i> (Å)	12.543(4)	8.055(3)
<i>c</i> (Å)	11.197(4)	13.828(4)
β (°)	113.54(3)	106.86(3)
<i>V</i> (Å ³)	1190.6(7)	1332.1(8)
<i>Z</i>	4	4
μ (mm ⁻¹)	1.849	1.692
F(000)	632	712
Crystal size (mm)	0.20 × 0.20 × 0.20	0.12 × 0.11 × 0.04
Crystal color	colourless	colourless
Calculated density, g/cm ³	1.745	1.773
Radiation type, wavelength, λ (Å)	Mo <i>Ka</i> , 0.71073	Mo <i>Ka</i> , 0.71073
Temperature, <i>K</i>	200(2)	200(2)
Measured reflections	3373	10463
Independent reflections	2472	3088
Observed refl. ($I > 2\sigma(I)$)	2219	2679
<i>R</i> _{int}	0.028	0.026
Data/restraints/parameters	2472/0/176	3088/6/228
$R[F^2 > 2\sigma(F^2)]$	0.087	0.056
$wR(F^2)$	0.168	0.184
GooF = <i>S</i>	1.06	1.10
$\Delta\rho_{\max}/\Delta\rho_{\min}$ (e Å ⁻³)	0.77 and -0.64 e Å ⁻³	1.20 and -0.82 e Å ⁻³

2. 2. 1 Preparation of [Cu(2-apyt)NO₃]₂ (1)

To 4.5 mL of ethanol/benzene solution (3.6 mL of C₂H₅OH and 0.9 mL of C₆H₆) of Cu(NO₃)₂ · 3H₂O (0.90 mmol, 0.217 g) 0.170 g (0.91 mmol) of 1-apyt/2-apyt mixture was added dropwise with stirring. The prepared suspension was placed into a 5 mL test-tube and then copper-wire electrodes in cork were inserted. By the application of alternating-current tension (frequency 50 Hz) of 0.48 V for 15 days a very small amount of colorless crystals of **1** appeared on copper electrodes.

2. 2. 2 Preparation of [Cu(2-apyt)(H₂O)](BF₄) (2)

To 4.5 mL of ethanol/benzene solution (3.2 mL of C₂H₅OH and 1.3 mL of C₆H₆) of Cu(BF₄)₂ · 6H₂O (0.90 mmol, 0.311 g) 0.170 g (0.91 mmol) of 1-apyt/2-apyt mixture was added dropwise with stirring. The prepared light-blue suspension immediately was prone to the alternating-current reduction (frequency 50 Hz) of 0.43 V. After 16 days a few suitable for single X-ray studying crystals of **2** were found on the electrode surface.

2. 4. Single Crystal X-ray Diffraction Studies

The collected diffraction data for **1** and **2** were processed with the Rigaku CrystalClear software suite program package.¹⁹ The structures were solved by direct methods using SHELXS-97 and refined by least squares method on *F*² by SHELXL-2014 with the following graphical user interfaces of OLEX2.^{20,21} Metal atom in **1** is split into two positions (s.o.f. 90% and 10%). Fluorine atoms of BF₄⁻ anion in **2** were refined over two disordered positions (s.o.f. 59% and 41%) applying the same geometry restraints for disordered units. Atomic displacements for

non-hydrogen atoms were refined using an anisotropic model; the only exception is Cu2B (with s.o.f. 10%) atomic displacement in **1** that was refined in the isotropic mode. Hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The crystal data parameters, data collection and the refinement details are summarized in Table 1.

3. Results and Discussion

The structures **1** and **2** demonstrate the first examples of N-allyltetrazoles allyl derivatives π -complexes with ionic copper(I) salts. In both compounds 2-apyt molecule acts as chelate-bridging π , σ -ligand being attached to the metal center by C=C bond of allyl group, pyridyl N atom and the most nucleophilic N atom of tetrazole ring (Figs. 1 and 2). Copper(I) atom adopts distorted tetrahedral ($\tau_4 = 0.71$ for **1**, $\tau_4 = 0.67$ for **2**) surrounding (τ_4 – four-coordinate geometry index)²², including two mentioned N atoms of the same 2-apyt moiety, C=C bond of the neighbouring organic molecule and one O atom of the anion in **1** and water molecule in **2** (Table 2). Taking into account that the sum of van der Waals radii of Cu and O according to the recent results reported by Batsanov²³ and Alvarez²⁴ is much higher than Cu1A–O3 distance value of 2.918(5) Å, copper(I) surrounding in **1** may be completed to five including one more O atom of the same nitrate anion. It is interesting to note that [Cu(2-apyt)NO₃]₂ (**1**) is topologically reminiscent of {[Cu(1-abtr)NO₃]}_n π -complex with 1-allylbenzotriazole (1-abtr),²⁵ in which 1-abtr molecule connects two Cu⁺ ions through μ_2 -C₃N₄-bridge into an infinite {[Cu(1-abtr)]⁺}_n chain, while the last ones are coupled by two bridging NO₃⁻ anions in the geminated chain. An additional coordination of pyridyl N atom to

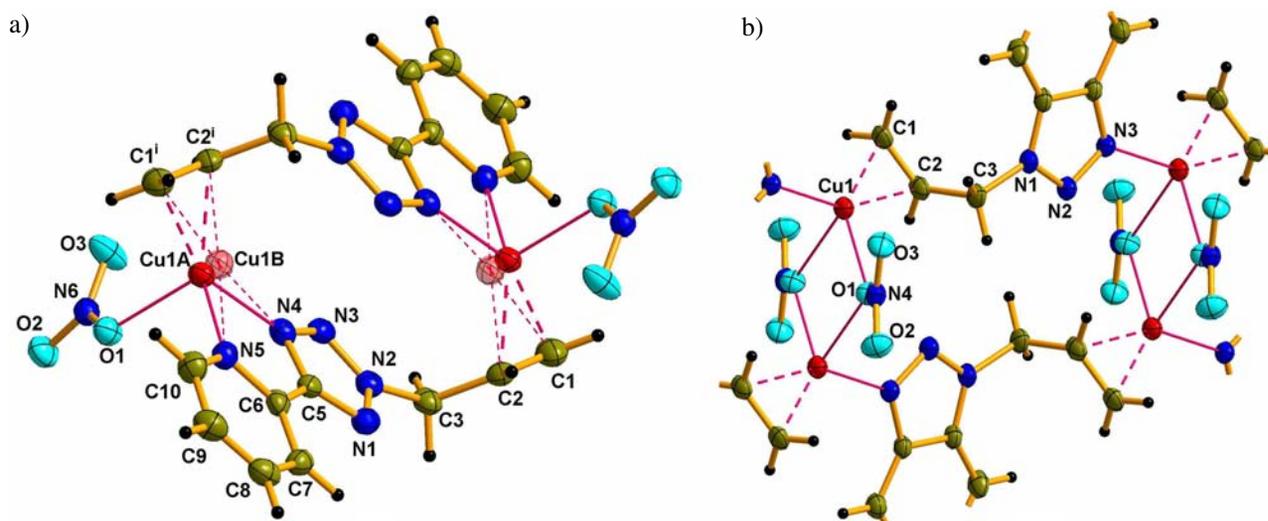


Figure 1. Centrosymmetric [Cu(2-apyt)NO₃]₂ dimer in **1** (a) and double {[Cu(1-abtr)NO₃]}_n chain (b).²⁵ (a) One of the disordered copper(I) positions with s.o.f. 10% in **1** is shown in semidashed mode. Symmetry codes: (i) 2 - x, -y, 1 - z.

Cu⁺ in **1** prevents the second nitrate ion binding to the metal, resulting in the finite macrocyclic [Cu(2-apyt)NO₃]₂ fragment with two five-membered {CuN₂C₂} rings (Fig. 1). Due to a coordination to Cu(I), pyridyl ring of the 2-apyt in the structure of complex **1** is tilted by nearly 5° with respect to tetrazole ring. Both the above angle value and the distance of 1.437(5) Å for C5–C6 between carbon atoms of tetrazole and pyridyl rings indicate the noticeable contribution of π -component of the bond.

Marked hardness of fluorine in BF₄⁻ anion is not conducive for its coordination to such “soft acid” as Cu⁺, therefore in **2** water O atom completes metal surrounding. In general, Cu⁺–F(BF₄⁻) contacts in the structures of substituted olefins π -complexes occur rarely and, in particu-

lar, they were previously found in Cu(I) π -complexes with diallylsulfide,²⁶ diallylamine or ethylene in co-presence of 3,6-bis(byrudin-2-yl)-4,5-dihydropyridazine.^{27,28} Thus, Cu⁺ ions in **2** connect 2-apyt molecules in the infinite undulated {[Cu(2-apyt)(H₂O)]⁺}_n chain while tetrafluoroborate anion is bound with the metal center only through water bridge by O–H...F contacts (Table 3). As a result complex **2** is constructed in such a way, that BF₄⁻ becomes a specific H-bonded linker between two neighbouring {[Cu(2-apyt)(H₂O)]⁺}_n chains, binding them together into double chain. Pyridyl ring of the 2-apyt in complex **2** is tilted by 6° with respect to tetrazole ring.

The presence of N-allylic group in 2-apyt with more “softer” C=C bond brings a considerable difficulties to neighbouring N atoms (possessing border line basicity) to be bound with “soft” Cu⁺ center. Instead, pyridyl N atom of 2-apyt in **1** and **2** becomes more favourable to compete with tetrazole moiety in metal coordination for two reasons: due to greater nucleophilicity of pyridyl N atom and due to a formation of a five-membered {Cu–N₂C₂} ring. It is well known, that chelate effect strongly increases complex stability. In comparison to **1** and **2**, there are a number of Cu(II) complexes with 2-substituted 5-(2-pyridyl)tetrazoles in which organic ligand, being attached to the metal center in the same way, produces similar five-membered rings.^{29,30} Most likely an appearance of {CuN₂C₂} ring is the main reason of selective complexation of 2-apyt from starting mixture of 1-apyt and 2-apyt under electrochemical condition to form thermodynamically stable **1** and **2** in crystalline form. Otherwise, the presence of three nitrogen atoms with decreasing nucleophilicity in the order N₄>N₃>N₂ and possessing higher spatial accessibility in 1-apyt should promote a considerable increase of tetrazole moiety participation in metal coordination, thus significantly reducing the contribution of chelating {CuN₂C₂} function. Similar isomer-selective

Table 2. Selected bond distances and angles for complex **1** and **2**.

Distance	(Å)	Angle	(deg)
1			
Cu1A–N4	2.071(5)	N4–Cu1A–O1	100.6(2)
Cu1A–O1	2.120(5)	N4–Cu1A–N5	80.3(2)
Cu1A–N5	2.072(6)	N5–Cu1A–O1	93.0(2)
Cu1A– <i>m</i> ⁱ	1.938(6)	<i>m</i> ⁱ –Cu1A–N4	134.6(2)
Cu1B– <i>m</i> ⁱ	1.929(7)	<i>m</i> ⁱ –Cu1A–O1	113.0(2)
C2–C1	1.349(10)	<i>m</i> ⁱ –Cu1A–N5	125.3(3)
C5–C6	1.437(9)	C1 ⁱ –Cu1A–C2 ⁱ	38.4(3)
2			
Cu1–N4	2.021(3)	N4–Cu1–O1	95.6(1)
Cu1–N5	2.060(3)	N4–Cu1–N5	81.8(1)
Cu1–O1	2.236(3)	N5–Cu1–O1	100.6(1)
Cu1– <i>m</i> ⁱⁱ	1.921(4)	<i>m</i> ⁱⁱ –Cu1–N4	139.1(1)
C1–C2	1.360(5)	<i>m</i> ⁱⁱ –Cu1–O1	105.1(1)
C5–C6	1.462(4)	<i>m</i> ⁱⁱ –Cu1–N5	126.8(1)

Symmetry codes: (i) 2 - x, -y, 1 - z; (ii) 1.5 - x, -0.5 + y, 1.5 - z. *m* – middle point of C1=C2 double bond.

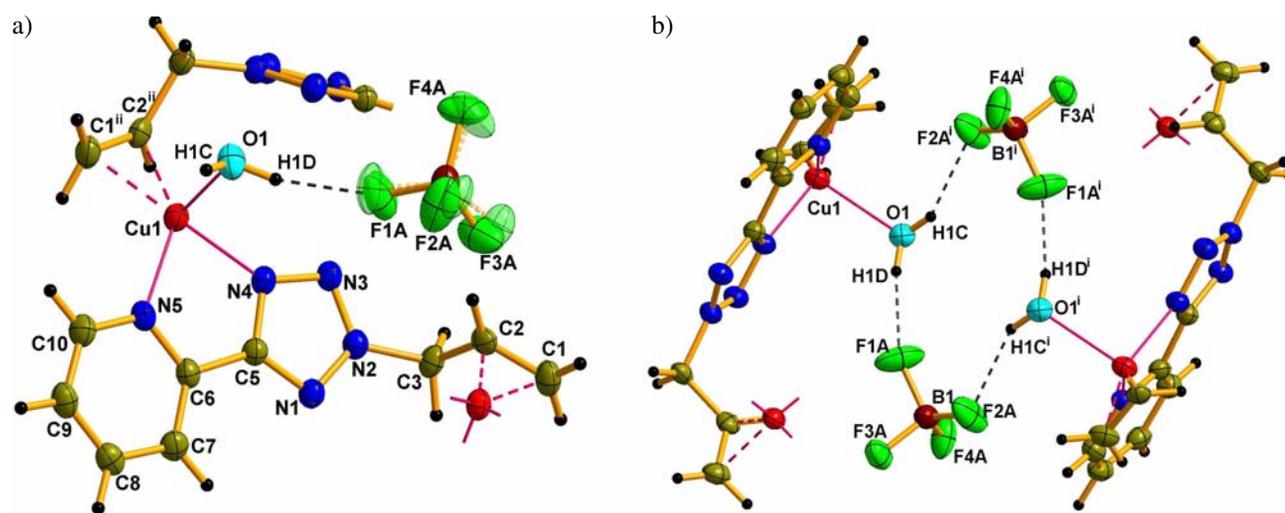
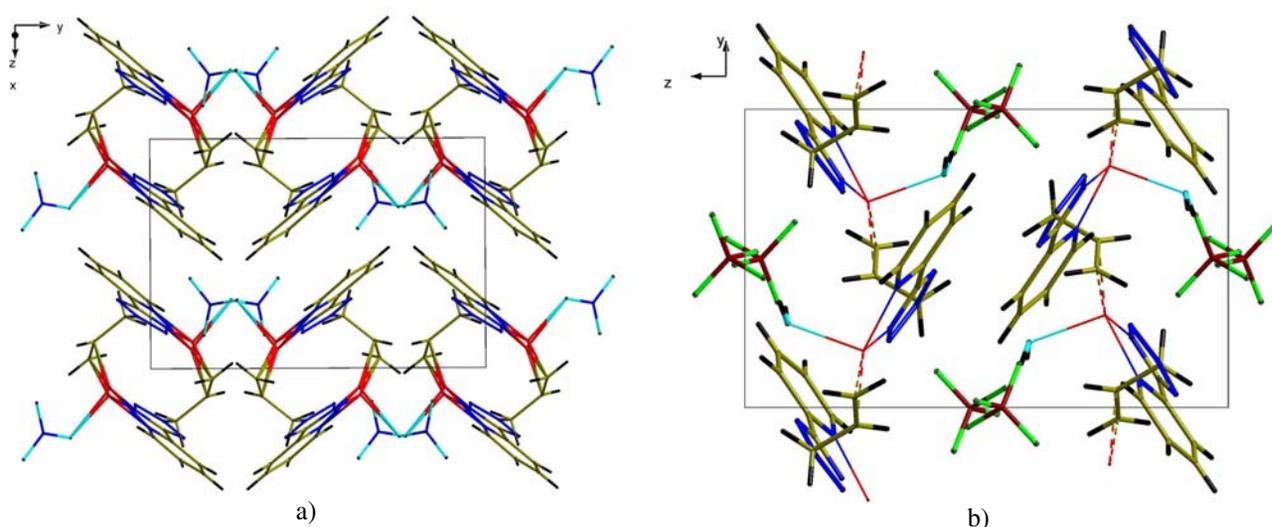
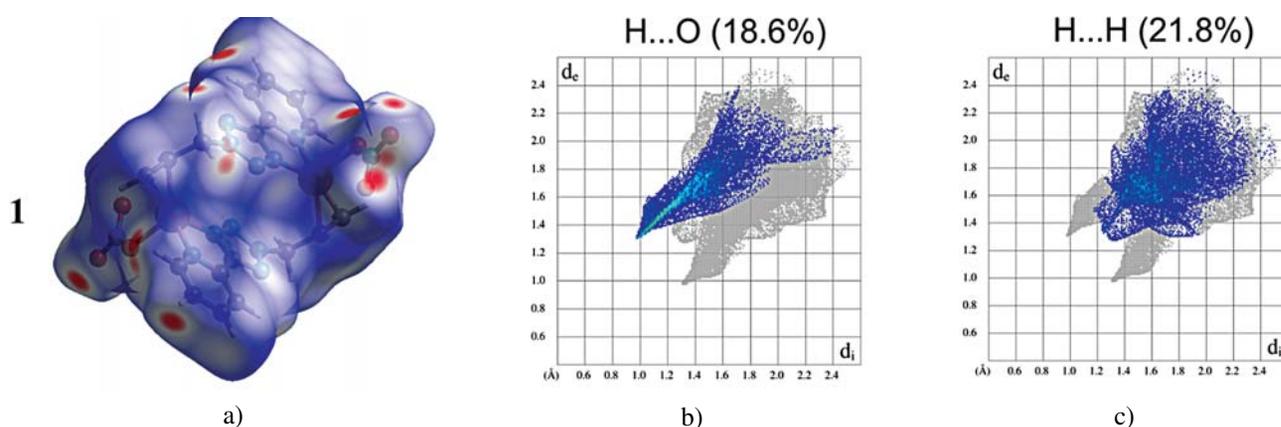


Figure 2. Coordination environment of copper (a) and H-bonded array (b) of double chain in **2**. One of the two disordered positions of BF₄⁻ with s.o.f. 41% is shown in semidashed mode. Symmetry codes: (i) 1 - x, -y, 1 - z; (ii) 1.5 - x, -0.5 + y, 1.5 - z.

Table 3. Geometry of selected hydrogen bonds in **1** and **2**.

Atoms involved D–H...A	Symmetry	Distances, Å			Angle, deg D–H...A
		D...H	H...A	D...A	
1					
C7–H7...O1	$1 - x, -y, 1 - z$	0.95	2.37	3.160(8)	140
C9–H9...O2	$1 - x, -0.5 + y, 1.5 - z$	0.95	2.40	3.280(10)	154
C10–H10...O3	$x, 0.5 - y, 0.5 + z$	0.95	2.49	3.434(10)	179
2					
O1–H1C...F2A	$1 - x, -y, 1 - z$	0.87	2.07	2.76(2)	137
O1–H1D...F1A		0.87	1.99	2.84(2)	166
O1–H1C...F2B	$1 - x, -y, 1 - z$	0.87	2.32	2.97(2)	132
O1–H1D...F1B		0.87	2.05	2.85(1)	152
C7–H7...F4A	$-0.5 + x, -0.5 - y, -0.5 + z$	0.95	2.53	3.320(11)	141

**Figure 3.** Diverse crystal packing of **1** (a) and **2** (b) along [100] direction.**Figure 4.** Hirshfeld surface analysis of $[\text{Cu}(2\text{-apyt})\text{NO}_3]_2$ dimer in **1** structure. (a) Hirshfeld surface mapped with d_{norm} which highlights both donor and acceptor ability. (b) Fingerprint plots of crystal fragments resolved into H...O contacts. (c) Fingerprint plots of crystal fragments resolved into H...H contacts. The full fingerprint appears beneath each decomposed plot in grey.

complexation of copper(I) ionic salts towards 1- and 2-allylbenzotriazoles was described few years ago.^{31,32} The chelating effect of 2-allylbenzotriazole was found to be a

crucial factor in the construction of the π -compounds with copper(I) tetrafluoroborate, perchlorate and hydro-sulfate. One may compare $[\text{Ag}_2(1\text{-apyt})_2](\text{ClO}_4)_2$ π -com-

plex (prepared also from a mixture of 1-apyt and 2-apyt), in which 1-apyt molecule is attached to one silver(I) atom by means of C=C bond and pyridyl N atom, forming less stable eight-member {CuN₂C₅} ring, while two tetrazole N atoms are μ_2 -bonded to crystallographically another Ag(I) atoms.³³

To analyze interactions between the particles the Hirshfeld surface was built for [Cu(2-apyt)NO₃]₂ dimer in **1**. The most prominent C–H...O interactions between the dimers can be seen in the Hirshfeld surface plot as the red areas (Fig. 4). Fingerprint plots were produced to show the intermolecular surface bond distances with the regions highlighted for (C)H...O(N) and residual H...H interactions. The C...C contacts belong to π ... π -interactions between heterocyclic nuclei and contribute only 3.6% to the surface area. The contribution to the surface area for H...H contacts is 21.8%.

4. Conclusion

The synthesis and crystal structures of the two new π -compounds [Cu(2-apyt)NO₃] (**1**) and [Cu(2-apyt)(H₂O)](BF₄) (**2**) with 2-allyl-5-(2-pyridyl)-2H-tetrazole (2-apyt) have been performed. Due to significant ligand chelating effect the isomer-selective complexation of 2-apyt with Cu⁺ under *ac*-electrochemical condition was found. The ligand 2-apyt acts in **1** and **2** as a chelate-bridging π , σ -ligand, being attached to the Cu(I) by means of allylic C=C bond, by pyridyl N atom and one tetrazole N atom. In complex **1** a centrosymmetric [Cu(2-apyt)NO₃]₂ dimer is formed due to a bridging organic ligand. Participation of H₂O in metal coordination in **2** leads to linking of organometallic fragment into infinite {[Cu(2-apyt)(H₂O)]⁺]_n chain, interconnected by O–H...F hydrogen bonds among water and tetrafluoroborate anions into double chain. To depict interactions between the particles in **1** Hirshfeld surface analysis has been performed.

5. Supplementary Material

CCDC number contains 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).

6. Acknowledgments

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Povzetek

Dva nova bakrova(I) π -kompleksa [Cu(2-apyt)NO₃] (**1**) in [Cu(2-apyt)(H₂O)](BF₄) (**2**) sta bila sintetizirana iz mešanice izomerov 1-alil-5-(2-piridil)-2H-tetrazola (1-apyt) in 2-alil-5-(2-piridil)-2H-tetrazola (2-apyt) ter ustreznih bakrovih soli z elektrokemijskim postopkom in sta bila strukturno okarakterizirana. Selektivno kompleksiranje omogoča tvorbo kompleksov, ki vsebujejo 2-apyt izomer. V obeh spojinah je bakrov kation koordiniran z C=C vezjo alilne skupine, dušikovem atomom piridilnega obroča ter dušikovem atomom tetrazolnega obroča. V obeh spojinah ima Cu⁺ center tetraedrično koordinacijsko sfero, ki vsebuje tudi kisikov atom NO₃⁻ aniona v **1** ter koordinirano molekulo vode v **2**. Struktura **1** vsebuje [Cu(2-apyt)NO₃]₂ dimer. Prisotnost molekule vode v koordinacijskem okolju bakrovega iona v **2** omogoča tvorbo neskončnih {[Cu(2-apyt)(H₂O)]²⁺}_n verig. Interakcije med gradniki so bile proučevane s pomočjo Hirshfeldove analize.