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Scientific paper

First Silver(I) – Complexes with Tetrazole Allyl Derivatives. Synthesis and Crystal Structure of $[Ag_2(C_{10}H_{10}N_4S)_2(H_2O)_2](BF_4)_2$ and $[Ag(C_{10}H_9ClN_4S)(NO_3)]$ π-Compounds ($C_{10}H_{10}N_4S$ and $C_{10}H_9ClN_4S$ – 5-(Allylthio)-1-phenyl- and 5-(Allylthio)-1-(4-chlorophenyl)-1*H*-tetrazole)

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Abstract

Crystalline silver(I) π-complexes $[Ag_2(atpt)_2(H_2O)_2](BF_4)_2$ (**1**) (*atpt* – 5-(allylthio)-1-phenyl-1*H*-tetrazole ($C_{10}H_{10}N_4S$)) and $[Ag(atcpt)(NO_3)]$ (**2**) (*atcpt* – 5-(allylthio)-1-(4-chlorophenyl)-1*H*-tetrazole ($C_{10}H_9ClN_4S$)) complexes have been obtained using silver salt and the organic ligands. Compounds were characterized by X-ray single crystal diffraction: for **1** space group $P2_1/n$, a = 10.4560(5), b = 11.4008(5), c = 12.7550(7) Å, β = 98.128(3)°, V = 1505.21(13) Å^3 at 200 K, Z = 2; for **2**: space group $P2_1/a$, a = 8.6790(8), b = 13.7324(10), c = 12.4597(13) Å, β = 102.288(5)°, V = 1451.0(2) Å^3 at 200 K, Z = 4. In both structures silver(I) atoms possess a trigonal pyramidal coordination environment with essentially different coordination modes of organic ligands. The Ag(I) arrangement in **1** involves the N3 and N4 atoms of two adjacent *atpt* molecules, an olefin C=C bond and a water molecule at the apical position. In crystal structure of **2** two O atoms from NO_3^- anions occupy two equatorial position of silver(I) coordination polyhedron, and *atcpt* is attached to the metal centre through the N4 atom of tetrazole core only. The weakly bound C=C bond is located at the apical position of Ag(I) environment.

Keywords: Tetrazole; Silver(I); π-Complex; Crystal structure

1. Introduction

Tetrazole derivatives may serve as suitable ligands for a design and self-organization of molecules through the coordination to transition metal ions by different nitrogen atoms of tetrazole ring and other donor atoms of substituents.[1] Use of the olefin-containing derivatives would improve specific coordination property of tetrazole moiety and therefore provide a formation of unexpected compounds.

Recently investigated [CuX(3*atpy*)] (3*atpy* – 3-(2-allyl-2*H*-tetrazole-5-yl)pyridine, X = Cl, Br),[2–3] $[Cu_2Cl_2(4atpy)_2]$ (4*atpy* – 4-(2-allyl-2*H*-tetrazole-5-yl)pyridine),[4] [CuBr(4*atpy*)],[5] $[Cu_2(atcpt)_2(H_2O)_2](NO_3)_2 \cdot C_2H_5OH$ and $[Cu_3(atcpt)Cl_3]$ (*atcpt* – $C_{10}H_9ClN_4S$ 5-(allylthio)-1-(4-chlorophenyl)-1*H*-tetrazole ($C_{10}H_9Cl\,N_4S$)),[6] are the only representatives among Cu(I) tetrazole π-compounds. The 5-allylthiosubstituted tetrazoles (*atcpt*) show a good affinity to Cu(I) and act as a topologically interesting coordination agent, being attached simultaneously to the metal with two N atoms of tetrazole core and through the olefin

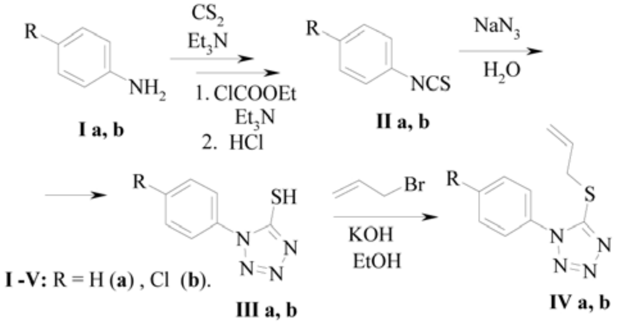
C=C bond from S-allyl group by chelating mode. N-allyl derivatives of tetrazoles (3*atpy* and 4*atpy*) do not promote participation of other nitrogen atoms of the ring in metal coordination and therefore they are bonded to Cu(I) by olefin C=C bond and pyridine type nitrogen atom only.

However, corresponding Ag(I) π-complexes with tertrazoles appeared to be unknown. In order to study 5-(allylthio)-1-phenyl tetrazoles coordination behavior regarding to silver(I) ion we have obtained crystalline $[Ag_2(atpt)_2(H_2O)_2](BF_4)_2$ (**1**) (*atpt* – 5-(allylthio)-1-phenyl-1*H*-tetrazole ($C_{10}H_{10}N_4S$)) and $[Ag(atcpt)(NO_3)]$ (**2**) π-complexes and performed their single crystal X-ray structure characterization.

2. Experimental Section

2. 1. Synthesis of $C_{10}H_{10}N_4S$ and $C_{10}H_9ClN_4S$

The target ligands **IV** ($C_{10}H_{10}N_4S$ (**a**) and $C_{10}H_9ClN_4S$ (**b**)) were synthesized from commercially available aniline (**I a**) and 4-chloroaniline (**I b**) by several procedures (Scheme 1). Appropriated 4-R-aniline **I** was converted into 4-R-isothiocyanatobenzene **II** by the reaction with dithioxomethane and the following treatment with ethyl chlorocarbonate and HCl according to the modified Kaluza method.[7] By 1,3-dipolar cycloaddition reaction of the obtained isothiocyanatobenzene **II** with azide ion, 1-(4-R-phenyl)-1H-tetrazole-5-thiol **III** was formed and readily reacted with 3-bromoprop-1-ene in the presence of KOH yielding corresponding ligand **IV**.[8,9]



Scheme 1. Synthesis of $C_{10}H_{10}N_4S$ and $C_{10}H_9ClN_4S$.

2. 2. Preparation of $[Ag_2(C_{10}H_{10}N_4S)_2(H_2O)_2](BF_4)_2$

To a solution of $C_{10}H_{10}N_4S$ (0.8 mmol) in 1.5 mL of methanol Ag_2CO_3 precipitate (0.3 mmol) was added at room temperature. The suspension acidity was adjusted to pH~3 using HBF_4 ($AgBF_4$ appeared *in situ*).[10] A white-red precipitate is formed. Keeping of the reactor at room temperature during 24 h led to colorless crystals of $[Ag_2(C_{10}H_{10}N_4S)_2(H_2O)_2](BF_4)_2$ which have appeared on the precipitate surface.

2. 3. Preparation of $[Ag(C_{10}H_9ClN_4S)(NO_3)]$

The solutions of $C_{10}H_9ClN_4S$ (0.8 mmol) in 0.5 mL of methanol and $AgNO_3$ (0.8 mmol) in 0.8 mL of water-methanol (0.5 mL of CH_3OH and 0.3 mL of H_2O) prepared at 60 °C were mixed and microcrystalline powder of **2** appeared after slow cooling to room temperature. A formation of colorless prismatic crystals of $[Ag(C_{10}H_9ClN_4S)(NO_3)]$ (**2**) was observed after keeping of the reactor at –6 °C over 48 h.

3. X–Ray Crystal Structure Determination

The crystallographic parameters and summaries of data collection for **1** and **2** are represented in Table 1. Single-crystal data were collected on a Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector, using graphite monochromatized MoKα radiation. Data were treated using the Rigaku CrystalClear software suite program package.[11] 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.[12–16] In both structures non-hydrogen atoms were found by direct methods. Full–matrix least–squares refinements based on F^2 were carried out for the positional and thermal parameters for all non-hydrogen atoms. For **1** and **2** structures positions of H atoms were treated as riding atoms and refined with C–H fixed distances and with $U_{iso}(H)$ values of $1.2U_{eq}(C)$. The figures were prepared using DIAMOND 3.1 software.[17]

4. Results and Discussion

In the crystal structure of $[Ag_2(atpt)_2(H_2O)_2](BF_4)_2$ (**1**) *atpt* molecule is coordinated to Ag(I) atom through a C=C-bond of the allyl group and two nucleophilic N

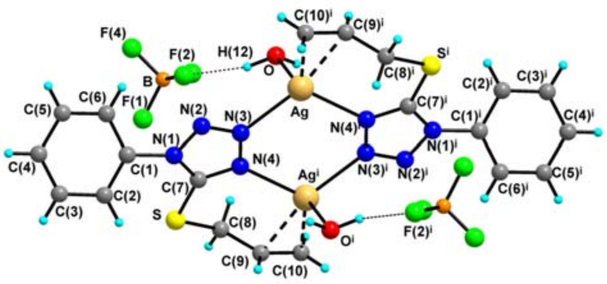


Figure 1. Fragment of crystal structure **1**. Symmetry code: (*i*) –x, –y, 2–z. Hydrogen O–H···F bonds are depicted as dot lines.

Table 1. Crystal data and structure refinement for the compounds 1–3[a].

	1	**2**
Empirical formula	$C_{20}H_{24}Ag_2N_8O_2S_2 \cdot 2(BF_4)$	$C_{10}H_9AgClN_5O_3S$
Formula weight	861.97 g/mol	422.60 g/mol
Temperature, K	200(2)	200(2)
Wavelength	0.71069 Å	0.71069 Å
Crystal system, space group	monoclinic, $P2_1/n$	monoclinic, $P2_1/a$
Unit cell dimensions, Å		
a, Å	10.4560(5)	8.6790(8)
b, Å	11.4008(5)	13.7324(10)
c, Å	12.7550(7)	12.4597(13)
α, °	90.00	90.00
β, °	98.128(3)	102.288(5)
γ, °	90.00	90.00
V, Å^3	1505.21(13)	1451.0(2)
Z	2	4
Calculated density, g/cm^3	1.90	1.94
Absorption coeff., mm^{-1}	1.53	1.73
F(000)	848	832
Crystal size, mm	0.1 × 0.08 × 0.07	0.1 × 0.1 × 0.08
Color	colorless	colorless
Theta range for data collection	2–29 deg	2–29 deg
Limiting indices	$-13 \le h \le 14$, $-14 \le k \le 14$, $-17 \le l \le 17$	$-11 \le h \le 8$, $-15 \le k \le 17$, $-9 \le l \le 16$
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Measured reflections	12077	6495
Used in refinement	3435	3370
Free parameters	199	190
Goodness-of-fit on F^2	1.17	1.049
R indices	$R_1 = 0.069$, $wR_1 = 0.1493$	$R_1 = 0.0995$, $wR_1 = 0.3362$
Largest diff. peak and hole	1.27 and –0.75 e Å^{-3}	1.54 and –1.11 e Å^{-3}

[a] CCDC 772787, 792001 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).

atoms of tetrazole ring (Fig. 1). As in the earlier studied $[Cu_2(\mathit{atcpt})_2(H_2O)_2](NO_3)_2 \cdot C_2H_5OH$ (**3**) and $[Cu_3(\mathit{atcpt})Cl_3]$ (**4**) π-complexes with Cu(I),[6] Ag(I) atoms in **1** possess trigonal pyramidal coordination environment arranged by two N3 and N4 atoms of adjacent tetrazole core and the C=C bond from the S-allyl group. The apical position of the metal coordination polyhedron is occupied by a water molecule (Figure 1, Table 2).

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

Ag–C(9)^i	2.385(5)	N(3)–Ag–*m*	138.9(2)
Ag–C(10)^i	2.340(6)	N(4)^i–Ag–*m*	101.8(2)
Ag–*m* [a]	2.265(6)	O–Ag–*m*	109.5(2)
Ag–N(3)	2.246(5)	N(3)–Ag–N(4)^i	114.1(2)
Ag–N(4)^i	2.298(5)	N(3)–Ag–O	85.1(2)
Ag–O	2.438(6)	N(4)^i–Ag–O	98.4(2)
C(9)=C(10)	1.346(8)	C(9)^i–Ag–C(10)^i	33.1(2)
C(8)–C(9)	1.491(9)	C(10)=C(9)–C(8)	124.0(6)

Symmetry code: (*i*) –x, –y, 2–z.
[a] *m* – middle point of C(9)=C(10) bond.

So, in the case of $AgBF_4$ (**1**) the organic ligand is attached to silver(I) atoms almost by its entire coordinating active sites similarly that in **3** and **4**. The *atpt* acts as a tridentate N,N,$(S\text{-}C_3H_5)$ chelate-bridging ligand connecting two Ag(I) atoms into centrosymmetric cationic $[Ag_2(\mathit{atpt})_2(H_2O)_2]^{2+}$ dimers with one almost planar six-membered $\{Ag_2N_4\}$ cycle and two seven-membered $\{AgNC_4S\}$ rings.

Essential role of coordinated water molecule in the structure stabilizing is also observed. The H_2O moiety acts as a bridge between Ag^+ cation and BF_4^- anion by means of H···F hydrogen contacts,[18,19] which occur between the water hydrogen atoms and fluorine atoms of BF_4^- anion ((Ow)H(11)···F(1) 1.95 Å, (Ow)H(12)···F(2) 1.92 Å). So, the H_2O molecule in **1** plays similar bridging role to that in earlier studied structure of $[Cu_2(\mathit{atcpt})_2(H_2O)_2](NO_3)_2 \cdot C_2H_5OH$ (**3**),[6] where the water bridge connects Cu^+ cation and NO_3^- anion.

Although Ag(I) atom is deviated by 0.29 Å from the base of the trigonal pyramid, and the distance Ag–*m* (*m* is a middle point of C=C bond) is equal to 2.265(6) Å, a noticeable difference between Ag–C(9) (2.385(5) Å) and Ag–C(10) (2.340(6) Å) bonds lengths, as well as rather

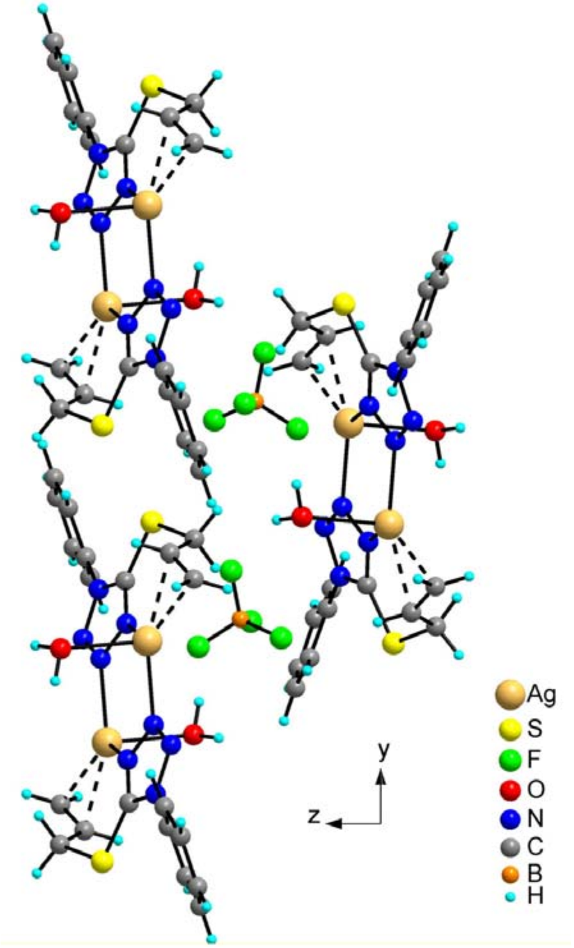


Figure 2. Mutual orientation of topological units in crystal structure of $[Ag_2(atpt)_2(H_2O)_2](BF_4)_2$.

large angle between olefin C=C bond and the base of the trigonal pyramid of 12.37, indicate the less effective Ag–(C=C) π-interaction comparatively to Cu(I)–(C=C) ones in **3** and **4**. Similar tendency was also observed among analogous Ag(I) and Cu(I) π-complexes.[20–23]

Use *atcpt* instead of *atcpt* in the presence of NO_3^- anion leads to a quite different structure of $[Ag(atcpt)(NO_3)]$ (**2**) π-complex. More covalent character of $Ag^+–O(NO_2^-)$ interaction in comparison to ionic $Ag^+\cdots BF_4^-$ one promotes participation of O atoms in the silver(I) coordination. Thus, in crystal structure of **2** Ag(I) possesses a trigonal-pyramidal coordination environment comprising the two O atoms from different NO_3^- anions, the only nitrogen atom from the ligand moiety and the C=C-bond from another ligand molecule at the apical position (Figure 3, Table 3). Nitrate anions play a role of pseudo-halide bridge connecting Ag^+ ions into infinite chains $\{AgNO_3\}_n$.

One may note that location of the olefin group at the apical position in the silver surrounding appears to be very unusual and indicates a weakness of Ag–(C=C) π-interaction. *Atcpt* molecule acts as a bidentate $N,(S–C_3H_5)$– bridging li-

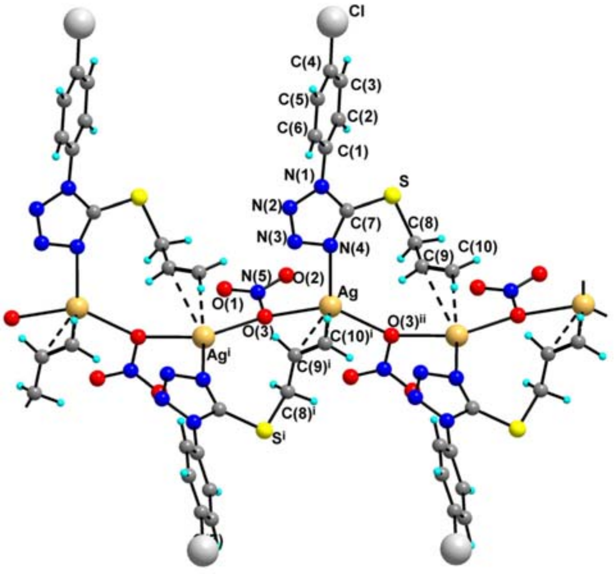


Figure 3. Fragment of structure **2**. Symmetry codes: (*i*) 0.5 + x, 0.5 – y, z; (*ii*) –0.5 + x, 0.5 – y, z.

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

Ag–C(9)^i	2.853(14)	N(4)–Ag–*m*	97.00(22)
Ag–C(10)^i	2.770(20)	O(3)–Ag–*m*	87.04(18)
Ag–*m* [a]	2.745(18)	N(4)–Ag–O(3)	117.7(3)
Ag–N(4)	2.311(9)	N(4)–Ag–O(3)^{ii}	106.0(3)
Ag–O(3)^{ii}	2.353(8)	O(3)–Ag–O(3)^{ii}	134.6(3)
Ag–O(3)	2.408(7)	C(9)^i–Ag–C(10)^i	25.0(5)
C(9)=C(10)	1.22(2)	C(10)=C(9)–C(8)	127.9(18)

Symmetry codes: (*i*) 0.5 + x, 0.5 – y, z; (*ii*) –0.5 + x, 0.5 – y, z.
[a] *m* – middle point of C(9)=C(10) bond.

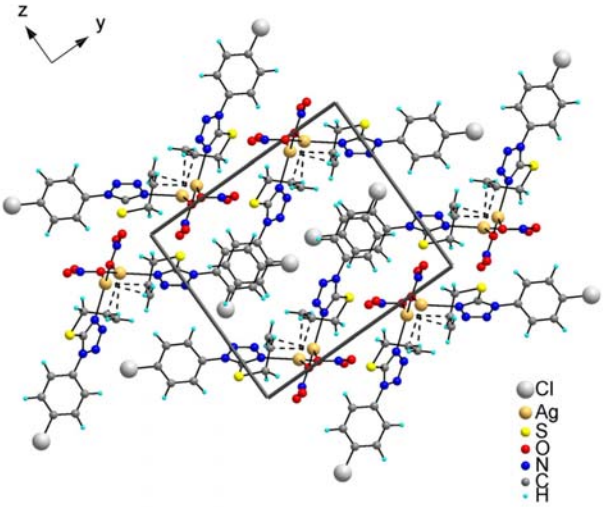


Figure 4. Projection of **2** crystal structure on yz plane.

gand, additionally connecting Ag(I) atoms in $\{AgNO_3\}_n$ chains. Crystal packing of **2** is shown in Figure 4.

5. Acknolegment

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Povzetek

Iz srebrovega karbonata in organskih ligandov smo pripravili kristalinična π-kompleksa srebra(I) $[Ag_2(atpt)_2(H_2O)_2](BF_4)_2$ (**1**) (*atpt* – 5-(aliltio)-1-fenil-1*H*-tetrazol ($C_{10}H_{10}N_4S$)) in $[Ag(atcpt)(NO_3)]$ (**2**) (*atcpt* – 5-(aliltio)-1-(4-klorofenil)-1*H*-tetrazol ($C_{10}H_9ClN_4S$)). Dobljeni spojini smo okarakterizirali z rentgensko strukturno analizo: za **1** je prostorska skupina $P2_1/n$, $a = 10.4560(5)$, $b = 11.4008(5)$, $c = 12.7550(7)$ A, $\beta = 98.128(3)°$, $V = 1505.21(13)$ A^3 pri 200 K, $Z = 2$; za **2**: prostorska skupina $P2_1/a$, $a = 8.6790(8)$, $b = 13.7324(10)$, $c = 12.4597(13)$ A, $\alpha = 102.288(5)°$, $V = 1451.0(2)$ A^3 pri 200 K, $Z = 4$. V obeh strukturah je koordinacijski polieder srebra(I) trikotna piramida, vendar je način koordinacije organskega liganda različen. V spojini **1** sta na vsak atom srebra koordinirana N3 in N4 atom iz dveh sosednjih *atpt* molekul, olefinska C=C vez in v apikalnem položaju molekula vode. V kristalni strukturi spojine **2** dva ekvatorialna položaja v koordinacijskem poliedru srebra(I) zavzemata kisikova atoma dveh različnih NO_3^- anionov, molekula *atcpt* pa je na kovinski atom koordinirana le preko N4 atoma tetrazolovega obroča. V apikalnem položaju je na Ag(I) šibko vezana C=C vez.