

Synthesis and crystal structure of the [Ag(2-allyl-5-phenyl-2H-tetrazole)ClO₄] π,σ -complex

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The crystalline silver(I) π,σ -complex [Ag(2-*aphtr*)ClO₄] (I) (2-*aphtr* = 2-allyl-5-phenyl-2H-tetrazole, C₁₀H₁₀N₄) was obtained starting from Ag₂CO₃, HClO₄ and the organic ligand 2-*aphtr* in ethanol, and studied by single crystal X-ray diffraction. The crystal structure is triclinic, space group *P*-1, *a* = 6.3078(12), *b* = 7.0690(15), *c* = 14.566(3) Å, α = 80.780(12), β = 88.148(12), γ = 79.759(13)°, *V* = 630.9(2) Å³ at 200 K, *Z* = 2. The Ag(I) atom possesses a trigonal pyramidal coordination environment involving the C=C bond of an allyl group, two N atoms from two adjacent tetrazole molecules and one perchlorate O atom, which occupies the apical position of the coordination polyhedron. Bridging Ag(I) atoms connect the 2-*aphtr* molecules into infinite {Ag(2-*aphtr*)ClO₄}_n chains. $\pi\cdots\pi$ -Stacking of aromatic rings of neighboring chains is observed.

Tetrazole / Silver(I) / π -Complex / Crystal structure

1. Introduction

The advance in the preparation of different tetrazole derivatives has provided an opportunity to evaluate the key role of this class of heterocycles in organo-metallic chemistry. Coordination compounds of tetrazoles are found to be important as precursors and catalysts in organic syntheses, as very effective corrosion inhibitors, luminophores, and as substances possessing other useful properties [1,2]. Due to the simultaneous presence of four nitrogen atoms in the same heterocyclic ring, the behavior of tetrazole ligands in the self-organization of particles through coordination to different transition metal ions is strongly sensitive to the presence of other donor centers. Addition of allyl substituents to the tetrazole ring are expected to improve the specific coordination properties of such heterocyclic derivatives and may result in the formation of unusual organo-metallic compounds. On the other hand, the coordination chemistry of allyl derivatives of tetrazole with Ib group ions is relatively poorly studied from the structural point of view [3]. For example, only a few π -complexes of Cu(I) with allyl derivatives of tetrazole have been studied hitherto [4-9], and only four Ag(I) compounds of the same type are known [10-12]. In order to evaluate the role of different inorganic anions on the coordination behavior of 5-substituted tetrazole, the synthesis and structure

characterization of the new silver(I) π,σ -complex [Ag(2-*aphtr*)ClO₄] (I) with 2-allyl-5-phenyl-2H-tetrazole (2-*aphtr*) were undertaken.

2. Experimental section

5-Phenyl-2H-tetrazole was prepared from commercially available benzonitrile and sodium azide, in accordance to the procedure described by Finnegan *et al.* [13].

2.1 Preparation of N-allyl-5-phenyl-2H-tetrazole (C₁₀H₁₀N₄)

N-Allyl-5-phenyl-2H-tetrazole C₁₀H₁₀N₄ was obtained by refluxing on an oil bath under magnetic stirring a mixture of 2.19 g (15.0 mmol) 5-phenyl-2H-tetrazole, 1.26 g (16.5 mmol) freshly distilled allyl chloride and 1.26 g (15.0 mmol) NaHCO₃ in 30 mL of 95 % ethanol for 15 h. After that, the reaction mixture was cooled to room temperature, precipitated NaCl was filtered off and ethanol was evaporated from the filtrate to give N-allyl-5-phenyl-2H-tetrazole (yield 93 %).

2.2 Preparation of [Ag(C₁₀H₁₀N₄)ClO₄] (I)

Freshly precipitated Ag₂CO₃ (0.22 g, 0.8 mmol) was added at room temperature to a solution of N-allyl-5-phenyl-2H-tetrazole C₁₀H₁₀N₄ (0.15 g, 0.8 mmol)

in 1.5 mL of ethanol. The acidity of the suspension was adjusted to pH = 3 using HClO₄ (AgClO₄ appeared *in situ*). A white-yellow precipitate formed. Keeping the reactor at room temperature for 54 h led to the formation of colorless crystals of the [Ag(C₁₀H₁₀N₄)ClO₄] complex, which appeared on the surface of the precipitate.

2.3 X-ray crystal structure determination

The crystallographic parameters and summaries of the data collection for **I** 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 MoK α radiation. The data were treated using the Rigaku CrystalClear software suite [14]. The structure was solved by direct methods with the use of SIR-92 and SHELXS-97 programs (TeXan crystallographic software package) and refined with SHELXL-97 software, implemented in the program package WinGX [15-19]. The non-hydrogen atoms were found by direct methods and the positions of the hydrogen atoms were derived geometrically. Full-matrix least-squares refinements based on F^2 were carried out for the positional and thermal parameters of all the non-hydrogen atoms in the anisotropic mode. The H atoms were treated as riding atoms and refined with fixed C-H distances and with the constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

3. Results and discussion

The crystal structure of **I** is similar to the recently studied [Ag(C₁₀H₁₀N₄)BF₄] (**II**) π -complex [12]. Both **I** and **II** are built up of linear ($\{\text{Ag}(2\text{-aphtr})\}^+_n$

metalorganic polymers, in which the organic molecule 2-allyl-5-phenyl-2*H*-tetrazole (2-*aphtr*) acts as a chelate bridging ligand (Fig. 1). 2-*aphtr* is coordinated to the Ag(I) atoms through an allylic C=C bond and two N atoms (N1 and N3) of the tetrazole ring, while another N4 atom of the tetrazole ring is completely excluded from the metal surrounding (Tables 2,3). It is interesting to note that in the structure of the previously studied π,σ -complex [Ag(*atcpt*)(NO₃)] (**III**) (*atcpt* = 5-(allylthio)-1-(4-chlorophenyl)-1*H*-tetrazole) only one N tetrazole atom (N4), together with the olefinic C=C bond of the S-allyl group, is bound to silver(I) [10]. The presence of an allylic group attached to a second N tetrazole atom in 2-allyl-5-phenyl-2*H*-tetrazole (2-*aphtr*) promotes a significant electron density shift to the N1 and N3 atoms, in comparison with the substituted 1*H*-tetrazoles, in which the nucleophilic activity of the N-atoms decreases from N4 to N3, and then to N2. For example, in the copper(I) crystalline π -complexes with 1-aryl substituted 5-(allylthio)-1*H*-tetrazole, the heterocyclic ring is attached to Cu(I) by the N4 and N3 centers [8,9] to form {Cu₂N₄} cycles. One more interesting example is the structure of [Ag₂(1-*apytr*)₂](ClO₄)₂ (**IV**) (where 1-*apytr* = 1-allyl-5-(2-pyridyl)-1*H*-tetrazole) π -complex [11]. As shown in Fig. 2, the presence of a pyridyl ring in the complex **IV** (instead of phenyl in **I**) leads to the appearance of two independent Ag(I) atoms, one of which is π,σ -attached to 1-*apytr* (two allylic C=C bonds and two pyridyl N atoms of neighboring 1-*apytr* are involved in the coordination). The other silver(I) atom, through σ -attachment to N3 and N4 tetrazole centers, connects individual globular {Ag(1-*apytr*)₂} fragments into a polymeric {Ag₂(1-*apytr*)₂}_n²ⁿ⁺ cation.

Table 1 Crystallographic data and details of the structure refinement for **I**.

Empirical formula	C ₁₀ H ₁₀ AgClN ₄ O ₄	Color, shape	colorless, prism
Formula weight, g mol ⁻¹	393.54	Theta range for data collection, °	1.4-24.2
Temperature, K	200(2)	Limiting indices	-6 ≤ h ≤ 6, -8 ≤ k ≤ 8, -15 ≤ l ≤ 15
Wavelength, Å	0.71069	Refinement method	Full-matrix least-squares on F^2
Crystal system, space group	triclinic, <i>P</i> -1	Measured reflections	2226
Unit cell dimensions: <i>a</i> , Å	6.3078(12)	Unique reflections	1306
<i>b</i> , Å	7.0690(15)	R_{int} value	0.0444
<i>c</i> , Å	14.566(3)	Reflections used	1306
α , °	80.780(12)	Free parameters	189
β , °	88.148(12)	Goodness-of-fit on F^2	1.22
γ , °	79.759(13)	R values: R_1	0.085
Unit cell volume V , Å ³	630.9(2)	wR_2	0.195
Z	2	Largest difference peak and hole, e ⁻ ·Å ⁻³	0.78 and -0.72
Absorption coefficient, mm ⁻¹	1.829	Measured density, g cm ⁻³	2.06
Calculated density, g cm ⁻³	2.077		
$F(000)$	388.0		

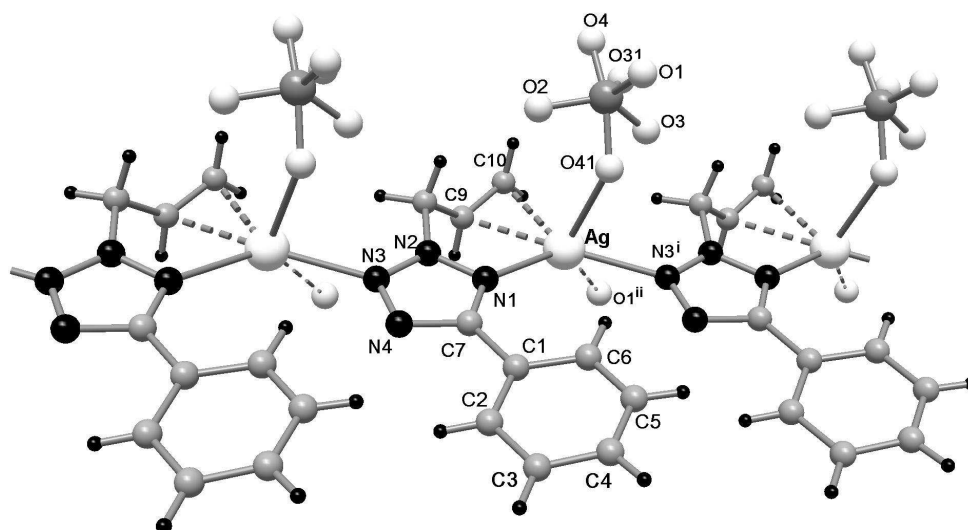


Fig. 1 Part of an infinite chain in the crystal structure of **I**. Symmetry codes: (i) $x+1, y, z$; (ii) $x, 1+y, z$.

Table 2 Fractional atomic coordinates and (equivalent) isotropic displacement parameters (in \AA^2) for **I**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U_{iso}^a	Occ. ^b
Ag1	0.75985(19)	0.7960(2)	0.77320(9)	0.0434(6)	
C11	0.8909(7)	0.2961(7)	0.8610(3)	0.0461(12)	
O1	0.962(2)	0.1249(19)	0.8201(11)	0.070(4)	
O2	0.666(3)	0.345(3)	0.859(2)	0.144(9)	
O3	1.044(5)	0.413(4)	0.851(3)	0.150(15)	0.77(3)
O31	0.99(2)	0.331(16)	0.924(11)	0.150(15)	0.23(3)
O4	0.891(7)	0.234(6)	0.9571(16)	0.112(10)	0.58(3)
O41	0.872(9)	0.442(8)	0.778(2)	0.112(10)	0.42(3)
N1	0.4396(19)	0.7603(18)	0.6933(9)	0.030(3)	
N2	0.2777(19)	0.7740(18)	0.7536(8)	0.029(3)	
N3	0.0897(19)	0.794(2)	0.7097(10)	0.037(3)	
N4	0.128(2)	0.7977(19)	0.6220(9)	0.032(3)	
C1	0.453(2)	0.765(2)	0.5226(10)	0.023(3)	
C2	0.331(3)	0.809(2)	0.4422(12)	0.038(4)	
C3	0.430(3)	0.786(3)	0.3544(11)	0.043(4)	
C4	0.646(3)	0.719(3)	0.3521(12)	0.047(5)	
C5	0.768(3)	0.687(3)	0.4309(13)	0.046(5)	
C6	0.675(2)	0.704(2)	0.5148(11)	0.034(4)	
C7	0.348(2)	0.773(2)	0.6116(10)	0.027(4)	
C8	0.309(2)	0.751(2)	0.8536(11)	0.034(4)	
C9	0.459(2)	0.873(2)	0.8785(10)	0.031(4)	
C10	0.630(3)	0.813(3)	0.9316(11)	0.042(4)	
H2	0.1839	0.8541	0.4455	0.045	
H3	0.3497	0.8164	0.3001	0.051	
H4	0.7111	0.6949	0.2960	0.056	
H5	0.9168	0.6520	0.4268	0.055	
H6	0.7594	0.6757	0.5679	0.041	
H8A	0.3647	0.6153	0.8769	0.041	
H8B	0.1707	0.7854	0.8834	0.041	
H9	0.4292	1.0046	0.8543	0.037	
H10A	0.6658	0.6819	0.9574	0.051	
H10B	0.7149	0.9007	0.9434	0.051	

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

^b Occ. – occupation parameter.

The silver(I) atom possesses trigonal pyramidal coordination environment formed by the olefinic C=C bond of an allyl group, two N1 and N3 atoms of a tetrazole ring and one perchlorate O atom. The latter is located at the apical position of the coordination pyramid and the distance Ag–O41 is equal to 2.47(5) Å (this distance is within the range of earlier observed Ag–O distances in other silver(I) π -compounds [20]). It should be noted that

an additional Ag...O1 contact at a distance of 3.02(2) Å exists between silver(I) and an opposite ClO₄[−] anion. A phenyl group of the ligand 2-*aphtr* in the complex **I** is positioned at an angle of about 11.8° with respect to the tetrazole ring. As a result, in the structure of **I** face-to-face $\pi\cdots\pi$ -stacking, with a distance of 3.41 Å between aromatic rings of neighboring {Ag(2-*aphtr*)ClO₄}_n chains, is also observed (Fig. 3).

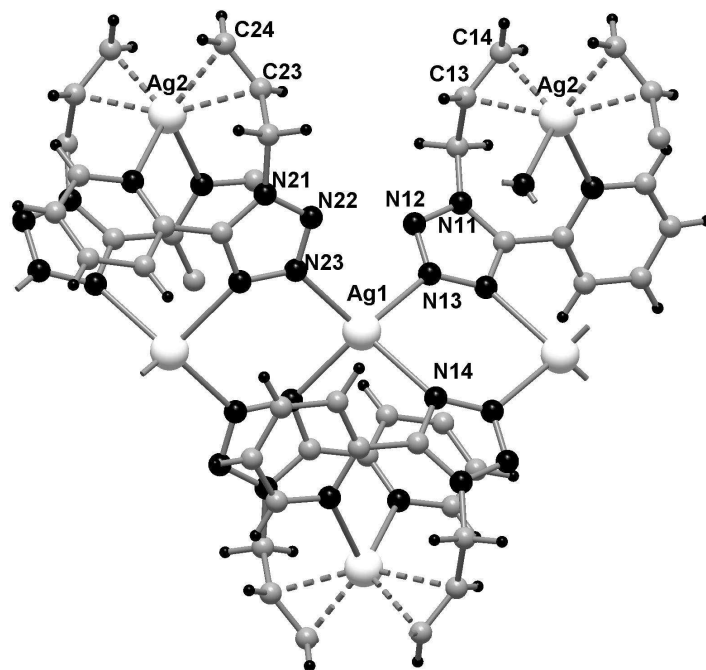


Fig. 2 Fragment of the crystal structure of **IV**.

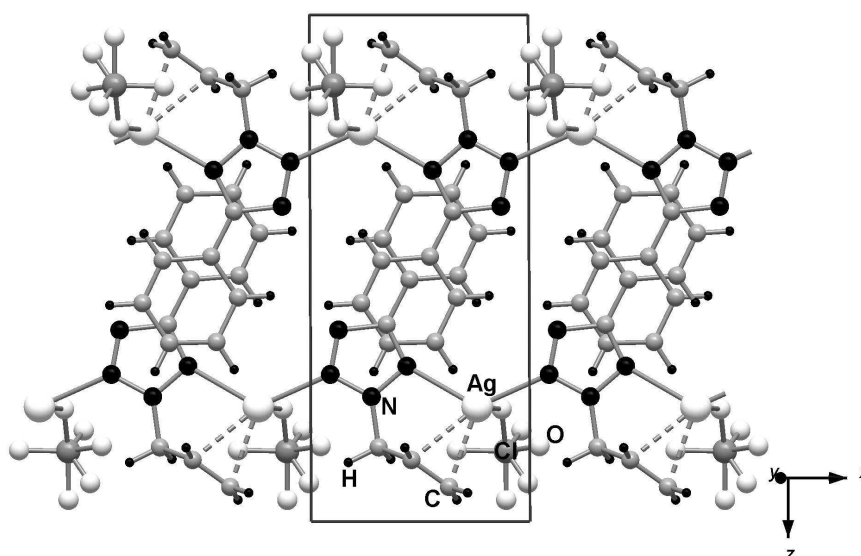


Fig. 3 Crystal structure of **I** in a projection onto the *xz* plane.

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

Bond	Value	Angle	Value
Ag—N3 ⁱ ^a	2.248(13)	N3 ⁱ —Ag—N1 ^a	125.6(4)
Ag—N1	2.435(13)	N3 ⁱ —Ag—C10 ^a	131.6(5)
Ag—C10	2.437(15)	N1—Ag—C10	102.7(5)
Ag—C9	2.443(15)	N1—Ag—C9	74.2(4)
Ag— <i>m</i> ^b	2.349(15)	C10—Ag—C9	31.3(5)
Ag—O41	2.47(5)	N1—Ag—O41	86.0(13)
C9—C10	1.32(2)	C10—Ag—O41	101.6(9)

^a symmetry code: (i) $x+1, y, z$; ^b middle point of the C9=C10 bond.

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