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The Reaction of Silver(I) Nitrate with 5-Phenyl-2-(2'-Pyridyl)-7,8-Benzo-6,5-Dihydro-1,3,6-Triazaindolizine

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Abstract—The complex of silver(I) with the condensation product of benzaldehyde and 3-(pyridin-2-yl)-5-(2-aminophenyl)-1*H*-1,2,4-triazole (L), $[AgL_2]NO_3$ (**I**), was synthesized. The reaction of L with silver(I) nitrate was found to afford 2-(2'-pyridyl)-1,4-dihydro-**5**H-1,3,4-benzotriazepin-5-one along with complex **I**. The compounds synthesized were characterized by X-ray diffraction analysis.

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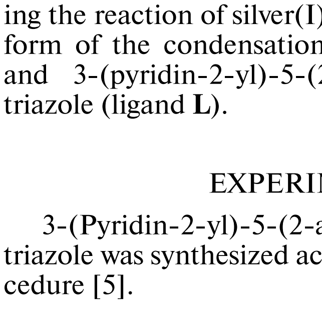
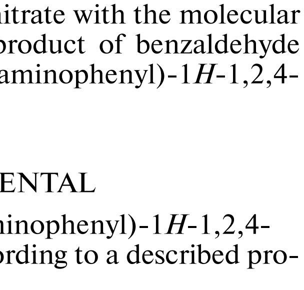
1,2,4-Triazole derivatives represent an interesting class of organic ligands used for the synthesis of various coordination compounds, which evoke increased interest as novel materials, first of all, magnetic and optical materials [1, 2]. The variation of substituents in the triazole ring makes it possible to change their spatial and electronic structures in a wide range, attaining the improvement of the physicochemical characteristics. The coordination compounds of zinc and cadmium with the condensation product of salicylaldehyde and 3-(pyridin-2-yl)-5-(2-aminophenyl)-1*H*-1,2,4-triazole exhibiting intense photo- and electroluminescence have been described recently [3]. It was shown that, depending on the complexing metal, the ligand can exist in two forms: linear azomethine (**A**) and cyclic dihydrotriazaindolizine (**B**) forms [4]



(A)



(B)

In the present work we describe the results of studying the reaction of silver(I) nitrate with the molecular form of the condensation product of benzaldehyde and 3-(pyridin-2-yl)-5-(2-aminophenyl)-1*H*-1,2,4-triazole (ligand **L**).

EXPERIMENTAL

3-(Pyridin-2-yl)-5-(2-aminophenyl)-1*H*-1,2,4-triazole was synthesized according to a described procedure [5].

Synthesis of L. Benzaldehyde (445 mg, 4.2 mmol) was added with stirring to a solution of 3-(pyridin-2-yl)-5-(2-aminophenyl)-1*H*-1,2,4-triazole (948 mg, 4 mmol) in 96% ethanol (20 ml) heated to 60–70°C. The reaction mixture was stirred on heating with a reflux condenser for 1 h. The solution was cooled, and the precipitate formed was filtered off, washed with cold ethanol, and dried in air. Colorless crystals were obtained. The yield was 988 mg (76%), mp = 216°C.

^1H NMR, δ, ppm: 8.62 d ($1H_{arom}$), 8.07 d ($1H_{arom}$), 7.89 dt ($1H_{arom}$), 7.79 d ($1H_{arom}$), 7.69 s ($1H_{arom}$), 7.44–7.36 m ($5H_{arom}$ + (C^2–H), 7.29 dt ($1H_{arom}$), 6.99 d (N–H), 6.92 d ($1H_{arom}$), 6.86 t ($1H_{arom}$).

IR, ν, cm^{-1}: 3296 ν(NH), 3034 ν(C–H), 1624 ν(N–C–N), 1528, 1480.

Synthesis of bis[5-phenyl-2-(2'-pyridiyl)-7,8-benzo-6,5-dihydro-1,3,6-triazaindolizine]silver(I) nitrate, $[AgL_2]NO_3$ (I). Silver nitrate (253 mg, 1.5 mmol) was added to a suspension of L (975 mg, 3 mmol) in MeOH (10 ml), and the mixture was stirred for 2 h on heating with a reflux condenser. The resulting solution was evaporated to half a volume. The precipitate formed was left overnight under the mother liquor, then filtered off, washed with methanol, and dried in air. The yield of complex **I** was 836 mg (68%).

For $C_{40}H_{32}N_{11}O_3Ag$

anal. calcd., %:	C, 56.54;	H, 3.90;	N, 18.78.
Found, %:	C, 56.32;	H, 4.03;	N, 18.51.

IR, ν, cm^{-1}: 3262 ν(NH), 3060 ν($C–H_{arom}$), 1622 ν(N–C–N), 1550, 1500, 1392, 1308.

Synthesis of 2-(2'-pyridyl)-1,4-dihydro-5*H*-1,3,4-benzotriazepin-5-one (II). A methanolic solution obtained in the synthesis of **I** was evaporated to dry-

Selected crystallographic data and characteristics of X-ray diffraction experiment for compounds **I** and **II**

Parameter	Value	
	I	**II**
Formula	$C_{40}H_{32}AgN_{11}O_3$	$C_{13}H_{10}N_4O$
Molecular weight	822.64	238.25
Crystal size, mm	0.30 × 0.30 × 0.15	0.30 × 0.10 × 0.10
Temperature, K	173(2)	150(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Cell parameters:		
a, Å	9.8983(7)	11.9763(11)
b, Å	13.3266(9)	5.4108(5)
c, Å	15.2977(11)	16.8193(15)
α, deg	66.656(1)	90
β, deg	80.081(1)	96.933(2)
γ, deg	70.051(1)	90
V, Å^3	1740.0(2)	1081.94(17)
Z	2	4
ρ_{calcd}, g/cm^3	1.570	1.463
μ, cm^{-1}	63.8	9.9
$F(000)$	840	496
θ Range, deg	1.45–28.44	1.98–30.62
Ranges of indices	$13 \le h \le 13, -17 \le k \le 17, -20 \le l \le 20$	$-17 \le h \le 17, -7 \le k \le 7, -24 \le l \le 21$
Total number of reflections/independent reflections with $I \ge 2\sigma(I)$	18469/8728 ($R_{int} = 0.0208$)	8288/3299 ($R_{int} = 0.0427$)
T_{min}/T_{max}	0.8316/0.9103	0.9710/0.9902
Number of refined parameters	496	171
Goodness-of-fit	1.058	1.009
R ($I \ge 2\sigma(I)$)	$R_1 = 0.0432$, $wR_2 = 0.1287$	$R_1 = 0.0524$, $wR_2 = 0.1267$
R (all data)	$R_1 = 0.0518$, $wR_2 = 0.1381$	$R_1 = 0.0832$, $wR_2 = 0.1443$
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	–0.926/2.945	–0.309/0.342

ness. The dry residue was recrystallized from pyridine. Yellow needle-like crystals of compound **II** were isolated. The yield was 45 mg (6%), mp = 245°C (mp = 248°C [6]).

^{1}H NMR, δ, ppm: 10.22 s (N–H), 8.79 s (N–H), 8.65 d (1H_{arom}), 8.01 d (1H_{arom}), 7.93 t (1H_{arom}), 7.73 d (1H_{arom}), 7.54 t (1H_{arom}), 7.39 t (1H_{arom}), 7.09 d (1H_{arom}), 6.95 t (1H_{arom}).

IR spectra were recorded in the range from 4000 to 400 cm^{-1} on a Nicolet Nexus 470 FT-IR spectrometer using a standard procedure of pressing a sample with KBr. NMR spectra were measured on a Bruker VXR-400 spectrometer (400 MHz) using Me_4Si as an internal standard and DMSO-d_6 as a solvent.

X-ray diffraction analysis. Experimental sets of reflections for compounds **I** and **II** were obtained by a standard method [7] on a Bruker SMART APEX II diffractometer equipped with a CCD detector and a monochromatic radiation source (MoK_α, λ = 0.71073 Å). Structures **I** and **II** were solved by a direct method and refined in the full-matrix anisotropic approximation for all non-hydrogen atoms. Hydrogen

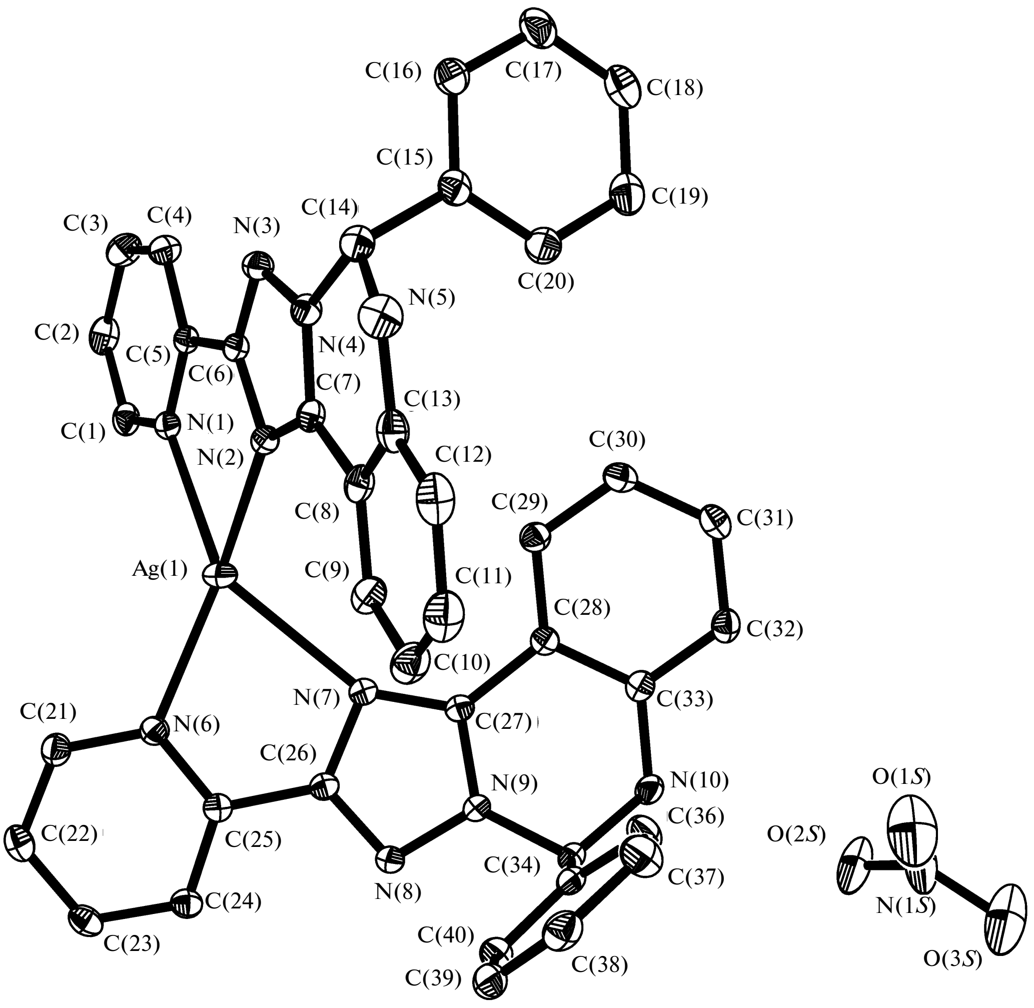


Fig. 1. Molecular structure of complex **I** (hydrogen atoms are not shown, thermal ellipsoids with 30% probability). Selected bond lengths Ag(1)–N(6) 2.260(2), Ag(1)–N(2) 2.320(2), Ag(1)–N(1) 2.404(2), Ag(1)–N(7) 2.478(2), N(1*S*)–O(1*S*) 1.169(4), N(1*S*)–O(2*S*) 1.216(4), N(1*S*)–O(3*S*) 1.303(5) Å and bond angles N(6)Ag(1)N(2) 144.73(8)°, N(6)Ag(1)N(1) 130.77(7)°, N(2)Ag(1)N(1) 72.00(7)°, N(6)Ag(1)N(7) 73.57(7)°, N(2)Ag(1)N(7) 105.36(7)°, N(1)Ag(1)N(7) 141.68(7)°.

atoms were calculated geometrically and refined in the riding model. The calculations were performed using the SHELX-97 program package [8]. The crystallographic parameters and X-ray diffraction details are given in the table. The full sets of X-ray structural data for compounds **I** and **II** were deposited with the Cambridge Crystallographic Data Centre (nos. 798563 (**I**) and 798564 (**II**)).

RESULTS AND DISCUSSION

The results of studies of the condensation product of benzaldehyde with 3-(pyridin-2-yl)-5-(2-aminophenyl)-1*H*-1,2,4-triazole (L) show that the compound exists in the cyclic dihydrotriazaindolizine form **B**. The ^{1}H NMR spectrum of the compound contains no signal of the hydrogen atom of the triazole cycle, which usually appears at 13–14 ppm, and exhibits the signal of the hydrogen atom of secondary amine at 6.99 ppm. In addition, the singlet signal of the C^2–H proton of dihydrotriazaindolizine is observed at 7.35 ppm, which lies in the range of chemical shifts characteristic of related heterocyclic systems [9].

The reaction of studied ligand L with silver(I) nitrate in anhydrous methanol affords the cationic complex $[AgL_2]NO_3$ (**I**). According to the data of IR spectroscopy, the coordination of dihydrotriazaindolizine is not accompanied by the transition to the azomethine form. The most part of bands assigned to vibrations of the groups of ligand L undergo an insignificant shift.

The structure of complex **I** was established by X-ray diffraction analysis. The complex has the cationic structure. The coordination sphere of the silver(I) atom formed by the nitrogen atoms of the pyridyl rings (N(1), N(6)) and triazole fragments (N(2), N(7)) has the geometry of a distorted tetrahedron (Fig. 1). The

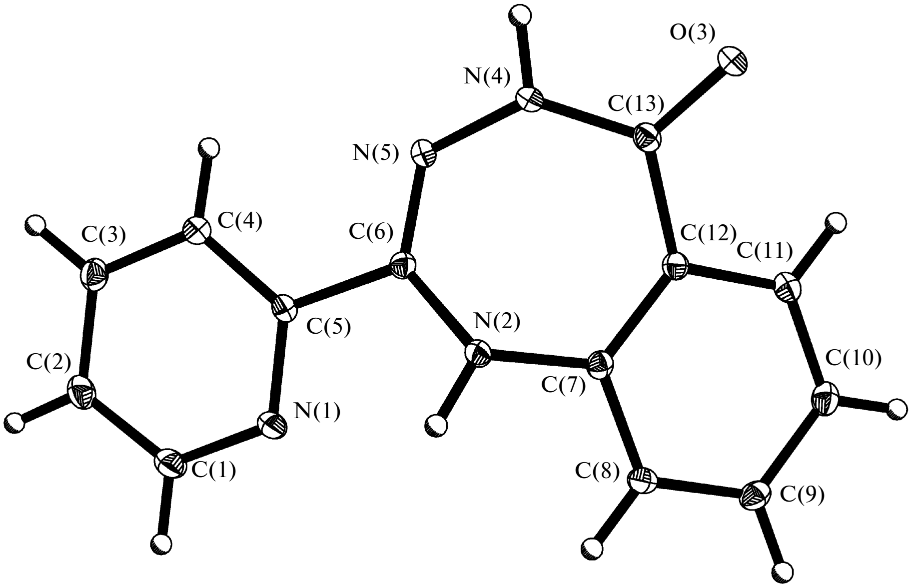


Fig. 2. Molecular structure of compound **II** (thermal ellipsoids with 30% probability). Selected bond lengths N(1)–C(5) 1.3410(19), N(1)–C(1) 1.345(2), N(2)–C(6) 1.3827(19), N(2)–C(7) 1.4100(18), O(3)–C(13) 1.2357918), N(4)–C(13) 1.355(2), N(4)–N(5) 1.4008(17), N(5)–C(6) 1.2831(19) Åand bond angles C(6)N(2)C(7) 122.66(12)°, C(13)N(4)N(5) 130.25(13)°, C(6)N(5)N(4) 119.55(13)°, N(5)C(6)N(2) 128.15.15(13)°, N(4)C(13)C(12) 121.72(13)°.

Ag–N(1) and Ag–N(6) bonds (2.404(2) and 2.478(2) Å) are substantially longer than the Ag–N(2) and Ag–N(7) bonds (2.320(2) and 2.260(2) Å), respectively).

The triazole, iminophenyl, and pyridyl cycles lie almost in the same plane, and the phenyl fragment is turned relatively to the iminophenyl ring by 89.29°. The N(2)–N(3) bond (1.355(3) Å) is somewhat shorter than the standard ordinary bond N–N (1.451 Å), which can be due to the delocalization of the double bond in the triazole fragment.

The C(14)–N(4) bond (1.476(3) Å) is noticeably elongated, and other bonds in the organic ligand have usual values [10].

The outer-sphere nitrate anion in complex **I** is asymmetric. The N–O bonds differ noticeably in length (1.169(4), 1.216(4), 1.303(5) Å) due to the formation of hydrogen bonds between the oxygen atoms and the hydrogen atoms of the NH groups of two adjacent molecules: O(2S)···N(10) (*x*, *y*, *z*) 2.893, O(3S)···N(5) (*x*, *y* – 1, *z*) 2.917 Å. Owing to a decrease in symmetry of the NO_3^- anion due to the formation of strong hydrogen bonds, no intense band with an absorption maximum at 1380 cm^{-1} is observed, which is characteristic of outer-sphere nitrate anions.

An interesting result was obtained by the study of the mother liquor after the synthesis of complex **I**. 2(2'-Pyridyl)-1,4-dihydro-5*H*-1,3,4-benzotriazepin-5-one (**II**) was isolated, and its structure was confirmed by direct X-ray diffraction analysis. It was found that the seven-membered nitrogen-containing heterocycle has the conformation of a distorted envelope (Fig. 2). The dihedral angle between the hydrazone fragment and the base of the envelope is 47.66°. The bond lengths and bond angles in molecule **II** are close to standard values [10].

The data on the synthesis of dihydro-5*H*-1,3,4-benzotriazepin-5-ones were published; however, the structures of similar compounds were established only by spectral methods. The authors [5, 9] ascribe the structure of 3,4-dihydro-5*H*-1,3,4-benzotriazepin-5-ones to compounds of this type. In studied compound **II**, the C(6)–N(2) bond lengths (1.3827(19) Å) is characteristic of the carbon–nitrogen ordinary bond, whereas C(6)–N(5) (1.2831(19) Å) is typical of the azomethine bond. Thus, the X-ray diffraction data indicate that compound **II** has the 1,4-dihydrobenzotriazepinone form.

An attempt to synthesize compound **II** by the recrystallization of L from a pyridine–ethanol mixture did not give the desired result. Perhaps, the coordination of the nitrogen atom by the silver cation favors the primary hydrolytic cleavage of the triazole cycle followed by the closure of the seven-membered cycle of triazepinone. Similar rearrangements of azomethine systems in coordination compounds were described in the literature but are met rather rarely [11].

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