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# An unusual diverse coordination of silver(I) with N-allylthiohydantoin ligand in the presence of benzene- and *p*-toluenesulfonate anions

A. A. Fedorchuk<sup>a</sup>, Yu. I. Slyvka<sup>a,\*</sup>, V. Kinzhybalo<sup>b</sup>, T. Lis<sup>c</sup>, M. G. Mys'kiv<sup>a</sup>

<sup>a</sup> Faculty of Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya 6, 79005 Lviv, Ukraine

<sup>b</sup> Institute of Low Temperature and Structure Research, Okólna 2, 50-422 Wrocław, Poland <sup>c</sup> Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland

\*Corresponding author. Tel.: +380322394506; e-mail: yurii.slyvka@lnu.edu.ua (Yu. I. Slyvka)

### **Highlights:**

- Two novel complexes with unusual diverse coordination of Ag(I) with N-allylthiohydantoin were studied
- Different Ag(I) arrangements are determined by variable thiohydantoin coordination modes
- Simulations presence of molecular ligand and its ionic form were observed

Abstract: Crystalline coordination compounds silver(I)  $[Ag_{2}(HL)_{4}(C_{6}H_{5}SO_{3})_{2}] \cdot 0.5C_{3}H_{7}OH$  (1) and  $[Ag_{2}(HL)(L)(CH_{3}C_{6}H_{4}SO_{3})]$  (2) (HL = 3-(prop-2-en-1-yl)-2-thioxoimidazolidin-4-one) have been obtained using silver(I) salts and the organic ligand HL. Three independent Ag(I) atoms in crystal 1 adopt exclusively different coordination environment: tetragonal pyramidal, seesaw and distorted tetrahedral. In crystal 2 metal ions coordination polyhedra are characterized by seesaw and distorted tetrahedral arrangements. Thiohydantoin molecules in both structures are attached to Ag(I) only through thiohydantoin S-atom, while its anionic form in 2 plays a role of N,S-linker.  $C_6H_5SO_3^-$  anions in 1 are bound to the Ag(I) ions in a bridging mode, connecting silver ions into serpentine-like  $\{Ag_4(C_6H_5SO_3)_4\}_n$ chains, within which silver ions are additionally bind with  $\mu_2$ -S atoms of HL. Simultaneous coordination of HL and  $L^-$  moieties in polymeric chains of 2 allow the formation of Ag....Ag metallophilic interactions with the distance range of 2.99 -3.13 Å.

**Keywords**: silver(I); benzenesulfonate anion; toluenesulfonate anion; thiohydantoin; crystal structure.

#### 1. Introduction

Heterocyclic compounds containing 2-thioxoimidazolidin-4-ones (namely 2thiohydantoin) fragment possess valuable pharmaceutical properties such as anticarcinogenic, antimutagenic, antimicrobial, anticonvulsant, etc [1-7]. They also exhibit fluorescence sensing properties towards Cu<sup>2+</sup> and Cu<sup>+</sup> [8] and may by successfully used in crystal engineering of organometallics. Due to simultaneous presence of thiocarbamide and carbonyl as well as N–H donor groups, 2-thiohydantoins take part in the controlled formation of hydrogen bonded arrays determining a special condition of target supramolecular assemblies formation [9]. Despite the huge advances in synthesis and possible application of 2-thiohydantoin derivatives, the data concerning its use as ligands in coordination compounds still remains quite limited, only 28 corresponding entries have been found in Cambridge Crystallographic Database [10]. Among these some of copper containing complexes were found to be cytotoxic for a variety of cancer cell lines. The presence of N-allyl radical at imidazolin-4-one core significantly reduces the toxicity of copper (mixed valence) chloride complexes in comparison with the well-known drug cisplatin [11].

In contrast to copper, coordination chemistry of 3,5-dihydroimidazol-4-ones regarding to silver(I) salts is represented by only one AgNO<sub>3</sub> derivative, containing 2-(methylthio)-3-phenyl-5-(pyridine-3-ylmethylene)-3,5-dihydro-4*H*-imidazol-4-one as a ligand [12]. The ligand molecule is connected to silver ion in a bridging mode by means of pyridine nitrogen atom and *S*-methyl sulfur one, while N atom of imidazol-4-one ring remains unbound to the metal centre. In this aspect coordination activity of imidazol-4-one fragment in regard to copper and silver is significantly different, since Cu<sup>+</sup> ions in all the cases are attached to heterocyclic N atom of 2-*S*-alkyl-imidazol-4-ones, leaving sulfur atom uncoordinated [13]. Contrary to the above, 2-thioxoimidazolidin-4-ones (non *S*-substituted 2-thiohydantoin) tend to be bound to "soft" Cu<sup>+</sup> ions by means of the only exocyclic sulfur atom [14].

Taking into account that according to HSAB theory [15] olefinic C=C bond acts as a "soft" base, a comprehensive investigation of thiohydantoin allyl derivatives coordination with Ag(I) becomes very attractive. Allylic C=C bond may successfully

compete with exocyclic sulfur in metal coordination, causing an exclusive inorganic fragment formation, like it was observed for copper(I)  $\pi$ -complexes with allyl derivatives of heterocycles [16]. To study coordination behaviour of N-allyl-2-thiohydantoin in regard to silver(I) herein we present synthesis and structural characterization of [Ag<sub>2</sub>(HL)<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>)<sub>2</sub>]·0.5C<sub>3</sub>H<sub>7</sub>OH (1) complex with an unusually diverse Ag(C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>) coordination mode and [Ag<sub>2</sub>(HL)(L)(CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>)] (2) coordination compound, emphasizing the influence of thiohydantoin ligand on exclusively different environments of Ag<sup>+</sup>.

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#### 2. Experimental section

#### 2.1. Materials and instrumentation

Unless mentioned otherwise, all chemicals were obtained from commercial sources and used without further purification. The NMR experiments: <sup>1</sup>H NMR (500 MHz), <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz) were recorded on a Bruker Avance 500 MHz NMR spectrometer. The chemical shifts are reported in ppm relative to the residual peak of the deuterated CD<sub>3</sub>OD for the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra. The infrared (IR) spectra were recorded on the Bruker IFS-88 spectrometer for 1 and on FT-IR Spectrum BX-II (Perkin Elmer) for 2 as nujol mulls. Diffraction data for 1 and 2 crystals were collected on an Agilent Xcalibur four-circle diffractometer with Mo  $K_a$ radiation ( $\lambda = 0.71073$  Å) and a Ruby and Atlas CCD detectors, respectively [17]. Hirshfeld surfaces of the molecules in complex 1 and fingerprint plots were produced by CrystalExplorer software [18, 19]. Ligand HL was synthesized from allylisothiocyanate and glycine in the presence of triethylamine and pyridine, in accordance with the reported method [20]. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD)  $\delta$ , 5.84 p.p.m. (ddt, J = 17.1, 10.4, 5.6 1H, =CH), 5.18 p.p.m. (ddd, J = 17.1, 2.9, 1.5 Hz, 1H, CH<sub>2</sub>=), 5.14 p.p.m. (ddd, J = 10.5, 2.5, 1.0 Hz, 1H, -CH<sub>2</sub>=), 4.38 p.p.m. (dt, J = 5.6Hz, 1.5 2H, CH<sub>2</sub>), 4.14 (s, 2H, CH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CD<sub>3</sub>OD)  $\delta$ , p.p.m. 185.74 p.p.m. (-C=S), 174.17 p.p.m. (-C=O), 132.62 p.p.m. (=CH), 117.94 p.p.m. (CH<sub>2</sub>=), 49.48 p.p.m. (CH<sub>2</sub>), 43.80 p.p.m. (CH<sub>2</sub>). IR (nujol, cm<sup>-1</sup>): 3488 (w), 3225 (s), 3091 (w), 3011 (vw), 1864 (vw), 1751 (vs), 1650 (m), 1524 (vs), 1431 (vs), 1367 (w), 1344 (vs), 1306 (s), 1289 (w), 1260 (s), 1176 (vs), 1106 (m), 1048 (m), 1029 (m),

994 (m), 977 (w), 930 (s), 893 (m), 755 (vw), 719 (w), 700 (vs), 610 (m), 581 (m), 563 (m), 541 (m), 515 (m), 474 (m), 440 (vw).

### 2.2. Synthesis of the $[Ag_2(HL)_4(C_6H_5SO_3)_2] \cdot 0.5C_3H_7OH(1)$

To the mixture of HL (50 mg, 0.32 mmol) and Ag<sub>2</sub>CO<sub>3</sub> (45 mg, 0.16 mmol) 1 mL of *n*-propanol was added. After careful stirring of the obtained suspension, followed by upholding it for one minute, a yellow clear solution (with furry graybrown precipitate) was obtained. The mixture acidity was adjusted by 0.25 ml of 40% aqueous benzenesulfonic acid solution. After the evolution of gas stopped, reddishbrown solution containing some amount of gray-brown precipitate was obtained. Keeping the reactor at room temperature in a dark place during 48 h led to yellowish crystals of [Ag2(HL)4(C6H5SO3)2]·0.5C3H7OH, which have appeared on the precipitate surface. Yield about 55%. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD)  $\delta$ , 7.86 p.p.m. (d, J = 7.6 8H, HPh-2,6), 7.46 p.p.m. (d, J = 6.3 12H, HPh-3-5), 5.93 p.p.m. (ddd, J = 22.3, 10.5, 5.4 8H, =CH), 5.42-5.17 p.p.m. (m, 16H, CH<sub>2</sub>=), 4.46 p.p.m. (d, J = 5.3 Hz, 16H, -CH<sub>2</sub>), 4.28 p.p.m. (s, 8H, CH<sub>2</sub>), 3.50 p.p.m. (t, J = 6.6 Hz, 2H, CH<sub>2</sub>), 1.51-1.56 p.p.m. (m, 2H, CH<sub>2</sub>), 0.93 p.p.m. (t, J = 7.4 Hz, 3H, CH<sub>3</sub>).<sup>13</sup>C{<sup>1</sup>H} NMR (125) MHz, CD<sub>3</sub>OD) δ, p.p.m. 185.00 p.p.m. (-C=S), 173.15 p.p.m. (-C=O), 132.08 p.p.m. (=CH), 131.37 p.p.m. (CPh-4), 129.35 p.p.m. (CPh-3,5), 126.97 p.p.m. (CPh-2,6), 117.85 p.p.m. (CH<sub>2</sub>=), 50.18 p.p.m. (CH<sub>2</sub>), 44.26 p.p.m. (CH<sub>2</sub>). IR (nujol, cm<sup>-1</sup>): 3561 (w), 3509 (w), 3127 (m), 3084 (m), 3046 (m), 1758 (vs), 1658 (vw), 1644 (w), 1536 (vs), 1447 (vs), 1423 (m), 1409 (m), 1365 (v), 1334 (vs), 1262 (m), 1224 (s), 1176 (vs), 1152 (vs), 1120 (vs), 1068 (m), 1058 (m), 1030 (m), 1012 (s), 995 (m), 986 (w), 923 (m), 910 (m), 878 (m), 758 (m), 694 (s), 652 (m), 611 (s), 580 (m), 565 (m), 544 (m), 521 (w), 484 (v), 437 (vw).

### 2.3. Synthesis of the $[Ag_2(HL)(L)(CH_3C_6H_4SO_3)]$ (2)

To the mixture of p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H (125 mg, 0.73 mmol) and Ag<sub>2</sub>CO<sub>3</sub> (100 mg, 0.36 mmol) 1 mL of *n*-propanol and 1 mL of water was added. After the evolution of gas stopped, 125 mg of HL (0.80 mmol) was added and orange-brown suspension with yellow-grey precipitate was obtained. Keeping the reactor at room temperature

in a dark place during 100 h led to colourless crystals of  $[Ag_2(HL)(L)(CH_3C_6H_4SO_3)]$ , which have appeared on the precipitate surface. Yield was about 36%.

IR (nujol, cm<sup>-1</sup>): 2724 (w), 2682 (vw), 2361 (w), 2340 (w), 1760 (m), 1739 (m), 1647(vw), 1623 (m), 1539 (w), 1516 (s), 1456 (s), 1410 (vw), 1339 (w), 1328 (w), 1299 (w), 1248 (w), 1194 (m), 1171 (v), 1159 (vw), 1130 (m), 1045 (w), 1014 (vw), 926 (w), 919 (w), 882 (w), 816 (v), 776 (vw), 772 (m), 694 (m), 660 (w), 598 (vw), 565 (w).

#### 2.4. Single crystal X-ray diffraction studies.

The collected diffraction data for **1** and **2** were processed with the CrysAlis PRO program [21]. The structures were solved by direct methods and refined by least squares method on  $F^2$  by SHELXL-2014 with the following graphical user interfaces of OLEX2 [22, 23]. Atomic displacements for non-hydrogen atoms in both structures were refined using an anisotropic model. Solvent *n*-propanol carbon atoms in **1** were refined with fixed at 0.5 atom site occupancy factors, the molecule is disordered around the center of inversion. One of metal atoms (Ag2) in **1** is splitted into two equivalent positions (s.o.f. 50%). All hydrogen atoms in **1** and **2** were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The crystal parameters, data collection and the refinement are summarized in Table 1.

Crystal data	1	2
CCDC number <sup>[a]</sup>	1842308	1842309
Empirical formula	$\begin{array}{c} C_{36}H_{42}Ag_2N_8O_{10}S_6\\ \cdot 0.5C_3H_7OH \end{array}$	$C_{19}H_{22}Ag_2N_4O_5S_3$
Formula weight (g·mol <sup>-1</sup> )	1184.92	698.32
Crystal system, space group	Triclinic, <i>p</i> ī	Triclinic, <i>p</i> ī
<i>a</i> (Å)	12.301(3)	7.255 (2)
<i>b</i> (Å)	14.334(4)	12.532 (3)
<i>c</i> (Å)	14.377(4)	14.211 (4)
α (°)	106.77(5)	67.41 (5)
β (°)	92.90(5)	84.69 (5)

<b>Fable</b>	1. Selected	crystal data	and structure	refinement	parameters	of <b>1</b>	and <b>2</b> . <sup>[a]</sup>
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γ (°)	102.81(5)	89.70 (5)
$V(\text{\AA}^3)$	2348.9(13)	1187.2 (7)
Z	2	2
$\mu (\text{mm}^{-1})$	1.16	1.95
F(000)	1202	692
Crystal size (mm)	$0.40 \times 0.12 \times 0.07$	0.48×0.20×0.13
Crystal color	yellow	clear colourless
Calculated density, g/cm <sup>3</sup>	1.675	1.176
Data collection		
Radiation type, wavelength, $\lambda(A)$	Mo <i>Ka</i> , 0.71073	Mo Ka, 0.71073
Temperature, K	80(2)	100(2)
$\theta$ range for data collection (°)	2.0 - 30.8	2.8 - 29.3
Index ranges	$-17 \le h \le 17, -16 \le k \le 20, \\ -18 \le l \le 20$	$-9 \le h \le 9, -16 \le k \le 17, \\ -18 \le l \le 19$
Measured reflections	22124	25660
Independent reflections	13183	5919
Observed refl. $(I > 2\sigma(I))$	7031	5206
R <sub>int</sub>	0.052	0.029
Completeness to $\theta = 25.49$	99.86 %	99.94%
Refinement on	$F^2$	$F^2$
Data/restraints/parameters	13183/3/602	5919/0/299
$R[F^2 > 2\sigma(F^2)]$	0.062	0.029
$wR(F^2)$	0.120	0.071
GooF = S	1.00	1.05
$\Delta \rho_{\rm max} / \Delta \rho_{\rm min}  ({\rm e}  {\rm \AA}^3)$	0.74 and -1.27	1.09 and -1.32

[a] CCDC number 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).

### 3. Results and discussion

#### 3.1 Crystal structure descriptions.

Asymmetric part of  $[Ag_2(HL)_4(C_6H_5SO_3)_2] \cdot 0.5C_3H_7OH$  (1) crystal is represented by three independent silver(I) atoms, each of which possess different coordination (Fig. 1). A closest Ag1 environment includes three bridging exocyclic sulfur atoms (S1, S2 and S3) of the three neighbouring thiohydantoin molecules (correspondingly

named HL<sup>1</sup>, HL<sup>2</sup> and HL<sup>3</sup>) and one oxygen (O25) atom of benzenesulfonate anion (Fig. 1). Due to some steric hindrance (caused by C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub><sup>-</sup> anion) Ag1—S3 bond distance is significantly longer (2.808(2) Å) in comparison with the other two Ag1—S1 (2.443(2) Å) and Ag1—S2 (2.450(2) Å). The nearest to Ag1 atom – O36 of the adjacent C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub><sup>-</sup> anion is placed at quite long distance from Ag1 of 3.067(3) Å, although this distance is shorter than the sum of corresponding VdW radii (3.24 Å) [24, 25]. Therefore, according to geometric index, proposed by Addison [26] geometrical environment of Ag1 metal center can be treated as tetragonal pyramid ( $\tau_5$ =0.23).



Figure 1. Asymmetric part of crystal **1** along with the numbering scheme. Symmetry codes: (i) -x, -y, -z+1; (ii) -x+1, -y+1, -z+1.

#### Table 2

Selected interatomic distances and angles for crystal 1.

Distance	(Å)	Distance	(Å)
Ag1—S1	2.443(2)	Ag2—S3	2.394(4)
Ag1—S2	2.450(2)	$Ag2 - S3^{ia}$	2.456(4)
Ag1—S3	2.809(2)	Ag2—S2	3.191(3)
Ag1—025	2.675(3)	Ag2—O26	2.728(4)

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A	g1—O36	3.067(3)	Ag2—O26 $^i$	3.197(4)
A	g3—S4	2.475(2)	S1S2	4.659(4)
A	g3—015	2.634(4)	S3S3 <sup><i>i</i></sup>	4.817(4)
A	g3—S1	3.085(2)		
				(0)
A	ngle	(°)	Angle	(*)
<b>S</b> 1	l—Ag1—O25	98.83(8)	S3—Ag2—O26	79.40(11)
<b>S</b> 2	2—Ag1—O25	102.67(9)	$S3-Ag2-S3^i$	166.61(6)
SE	3—Ag1—O25	85.46(8)	S3 <sup><i>i</i></sup> —Ag2—O26	111.23(13)
<b>S</b> 1	I—Ag1—S2	144.43(6)	O26—Ag2—S2	83.73(9)
<b>S</b> 1	I—Ag1—S3	111.06(6)	S3—Ag2—S2	90.18(10)
<b>S</b> 2	2—Ag1—S3	98.67(6)	S3 <sup><i>i</i></sup> —Ag2—S2	111.23(13)
O2	25—Ag1—O36	158.21(10)	$S2$ — $Ag2$ — $S2^i$	173.35(8)
S4	4—Ag3—O15	94.78(9)	Ag1—S3—Ag2	89.71(9)
<b>S</b> 4	4—Ag3—O15 <sup><i>ii</i></sup>	85.22(9)	Ag1—S2—Ag2	80.30(8)
<b>S</b> 1	l—Ag3—O15	79.86(9)	Ag1—S1—Ag3	119.48(6)
<b>S</b> 1	$I = Ag3 = O15^{ii}$	85.22(9)		
	F 7 0	1 (1)	A (11) A (4	

[a] Symmetry codes: (i) -x, -y, -z+1; (ii) -x+1, -y+1, -z+1.

The Ag3 atom lies on the center of symmetry and is surrounded by four S atoms (two terminal and two bridging) of four symmetry related HL<sup>1</sup> and HL<sup>4</sup> molecules and by two O atoms of the two bridging C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub><sup>-</sup> anions (Fig. 2). Two terminal sulfur atoms of two centrosymmetrically related HL moieties are closer to the metal center (Ag3—S4 2.475(2) Å) than the other bridging two (Ag3—S1 3.085(2) Å) and together with two O15 form square surrounding of the metal ion. Both Ag3—S4 and Ag3—O15 bond distance values are comparable with Ag1—S1, Ag1—S2 and Ag1—O25 (Table 2) ones. It is worth to note, that Ag3—S1 bond distance value is significantly shorter than its corresponding VdW radii sum (3.52 Å). Therefore symmetry related S1 atoms complete Ag3 surrounding to distorted octahedral with three different atom pairs.



Figure 2. Coordination environment of Ag3 in **1**. Symmetry codes: (ii) -x+1, -y+1, -z+1.

Somewhat similar coordination environment may be attributed to Ag2 atom: two O atoms and four thiohydantoin S atoms (of HL<sup>2</sup> and HL<sup>3</sup>) form distorted tetrahedron. But significant removal of centrosymmetrically related S2 and S2<sup>i</sup> atoms from the octahedron middle point by 3.391(4) Å allows Ag2 atom to be split with two centrosymmetrically related sites (Fig. 3), enabling seesaw arrangement of the metal. The distance from Ag2 to opposite thiohydantoin S3<sup>i</sup> of 3.602(4) Å somewhat exceeds the sum of corresponding VdW radii (3.52 Å) and also confirms the seesaw geometry of Ag2 arrangement. S3—Ag2—S3<sup>i</sup> bond angle of  $166.61(6)^{\circ}$  indicates closer to linear atoms arrangement, while the remaining atoms pair forms O26—Ag2—S2 angle of  $83.73(9)^{\circ}$ . Ag2—S2 bond value of 3.191(3) Å is comparable with Ag3—S1 of 3.085(2) Å. The nearest to silver(I) S3 and S3<sup>i</sup> atoms are separated from each other at the distance of 4.817(5) Å, that is closer than analogous S4…S4<sup>i</sup> 4.950(5) Å and S1…S2 4.659(4) Å distances. In contrast, due to significant packaging hindrance of C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub><sup>-</sup> anion Ag2—O26 distance is somewhat longer (Ag2—O26 2.728(4) Å) in comparison with the other observed.



Figure 3. Coordination environment of disordered Ag2 in 1. Symmetry codes: (*i*) -x, -y, -z+1. Hydrogen atoms are omitted for clarity.

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All four  $HL^1$  -  $HL^4$  moieties have similar geometrical parameters except for the conformation of non-coordinated allyl groups, which are involved into C–H...O and C–H... $\pi$  types of intermolecular interactions (Fig. 5).  $HL^1$  –  $HL^4$  moieties according to Klyne-Prelog system are characterized by synclinal conformation (+96.19(5)° (HL<sup>1</sup>), -64.69(5)° (HL<sup>2</sup>), -64.86(6)° (HL<sup>3</sup>), -66.38(6)° (HL<sup>4</sup>)) relative N1–C4 bond and synperiplanar (-5.8(7)° (HL<sup>1</sup>), -2.8(7)° (HL<sup>2</sup>)) and anticlinal (+119.8(6)°(HL<sup>3</sup>), -

121.4(6)° (HL<sup>4</sup>)) conformation relative to C4—C5 bond. The distance value changes in the range of 1.451 - 1.459(6) Å for C3—N2 between methylene carbon atom and unsubstituted nitrogen of HL<sup>1</sup> - HL<sup>4</sup> thiohydantoin rings, what indicates the presence of dominant  $\sigma$ -component of the bond. Due to the effect of conjugation between heterocyclic nitrogen atoms and S=C and C=O bonds in thiohydantoin the bond lengths of C1—N1 and C2—N1 are al most identical and range from 1.375 to 1.396(6) Å correspondingly for all four molecules. The C1—N2 bond value is significantly shorter and decreases in the order: 1.324(5) Å (HL<sup>4</sup>), 1.314(6) Å (HL<sup>1</sup>), 1.311(6) Å (HL<sup>2</sup>) and 1.308(6) Å (HL<sup>3</sup>).



Figure 5. (a) Overlay of N-allylthiohydantoin molecules in (a) **1** and (b) **2**. Molecule A in **1** is inverted. Atoms used for overlay fit are labeled.

Two independent  $C_6H_5SO_3^-$  anions are bound to the Ag(I) atoms in a bridging mode, connecting silver ions into serpentine-like  $\{Ag_4(C_6H_5SO_3)_4\}_n$  chain (Fig. 6). Additionally S atoms of thiohydantoin molecules bind neighboring Ag<sup>+</sup> ions. Organic HL molecules are additionally fixed to the organometallic chain with N–H…O hydrogen bonds (Table 3) and both anions are involved in hydrogen bonding simultaneously with two thiohydantoin molecules.



Figure 6. Organometallic chains with  $\{Ag_4(C_6H_5SO_3)_4\}_n$  fragments in 1. Symmetry codes: (*i*) -x, -y, -z+1; (*ii*) -x+1, -y+1, -z+1.

Atoms involved	Symmetry	Distances, Å			Angle
D−H···A		D···H	H···A	D···A	D−H···A
		1	~		
N2A-H2AO36		0.88	1.93	2.778(6)	161.6
N2B-H2B····O25		0.88	1.95	2.827(5)	172.5
N2C-H2C···O26	-x, -y, -z+1	0.88	2.13	2.962(6)	157.4
N2D-H2D015		0.88	2.05	2.821(5)	145.7
2					
N2B-H2B···O33	-x+2, -y+2, -z+1	0.88	1.86	2.712(3)	162.1

Table 3. Geometry of N–H..O hydrogen bonds in the crystals of 1 and 2.

In contrast to other coordination compounds of ionic silver(I) salts with N-allyl derivatives of heterocycles [27-29], in which allylic C=C bond is involved in metal coordination, N-allyl residue of thiohydantoin in **1** prefers to be unattached to the metal. The planes of neighboring independent thiohydantoin rings are wrapped relative to each other by  $49.1(3)^\circ$ , so that the O atom of one HL is oriented very close (~3.1 Å) to the center of the second thiohydantoin ring.

It should be noted, that **1** may be considered as a new example of coordination mode of  $Ag^+$  and  $C_6H_5SO_3^-$ , since only one entry (corresponding to silver(I) benzenesulfonate) in Cambridge Structural Database was deposited up-to-date and shows a tridentate coordination of the anion [30]. In the last structure nine-coordinated Ag(I) is occupied by six O atoms of the tridentate-bridging  $C_6H_5SO_3^-$  anions and by three neighboring Ag atoms (Ag – Ag 2.915(1) Å), forming a two-

dimensional infinite array incorporating a first known six-fold metal-bridging mode for the sulfonate ion.

The comparison of <sup>1</sup>H NMR-spectra of **HL** and **1** in deuterated CD<sub>3</sub>OD solvent indicates the inactivity of the allyl group with respect to Ag(I)-(C=C)  $\pi$ -interaction. This fact agrees with HSAB rule as well as with a large affinity of Ag(I) to O and S atoms. In contrast to **1**, there are a number of earlier studied crystalline coordination compounds of Ag(I) with allyl derivatives of heterocycles, in which metal ion is  $\pi$ , $\sigma$ bonded to the organic ligand through  $\eta^2$ -coordination of the allylic C=C bond [31-35].

During a formation of  $[Ag_2(HL)(L)(CH_3C_6H_4SO_3)]$  (2) complex HL ligands undergo partial deprotonation, resulting in coordination to the metal of simultaneously neutral HL and anionic L<sup>-</sup> forms of the N-allylthiohydantoin ligand. Independent part of crystal 2 is represented by two different four-coordinated silver(I) atoms (Fig. 7). Ag1 surrounding in structure 2 is close to seesaw arrangement ( $\tau_{4}$ = 0.63) and includes one heterocyclic N atom of the L<sup>-</sup> anion, one O atom of the CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup> anion and two bridging exocyclic sulfur atoms (S1 and S2) from two different HL and L<sup>-</sup> ligand moieties (Fig. 8). Ag2 atoms have distorted tetrahedral surrounding ( $\tau_{4}=0.82$ ) formed by O atom of the bridging CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup> anion and three bridging S atoms of allylthiohydantoin ligands, one of which is from HL (S2) molecule and two – from L<sup>-</sup> anions (S1<sup>*i*</sup> and S1<sup>*i*</sup>). As the result, Ag(I) atoms in 2 stitch allylthiohydantoin ligands together with CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup> anions into polymer chain. Ag2—S2 and Ag2—S1<sup>*i*</sup> distances are comparable and equal to 2.5650(13) Å and 2.5611(11) Å, respectively, but they are significantly shorter than Ag2–S1<sup> $\ddot{u}$ </sup> (2.7199(12) Å). Each L<sup>-</sup> fragment is involved in coordination with four different Ag ions: one Ag ion is attached through Ag1-N2A bond (2.208(3) Å) and the other three Ag ions through Ag-S1 interactions. Due to geometrical reasons all three Ag—S1 bonds are not equal in this structure (Table 4). Unlike L<sup>-</sup>, HL is bonded only with two Ag ions through bridging S2 atom (Ag1—S2<sup>i</sup>, 2.6192(13) Å, Ag2—S2 2.5650(13) Å). Neutral HL ligands are additionally involved in N-H...O hydrogen bonds with neighbouring toluenesulfonate anions (Table 3).



Figure 7. Part of crystal **2** along with the numbering scheme. Symmetry codes: (*i*) -x+1, -y+2, -z+1; (*ii*) x+1, y, z.



Figure 8. Coordination environments of Ag1 (*a*) and Ag2 (*b*) in crystal 2.

Table 4

Selected interatomic distances and angles for crystal 2.

Distance	(Å)	Distance	(Å)
Ag1—N2A	2.208(3)	Ag2—S2	2.5650(13)
Ag1-013	2.568(3)	Ag2—O23	2.489(3)
$Ag1$ — $S2^{ia}$	2.6192(13)	$Ag2 - S1^{ii}$	2.7199(12)
$Ag1 - S1^i$	2.6437(16)	$Ag2 - S1^i$	2.5611(11)
Ag2 — Ag2 <sup>iii</sup>	3.1295(14)	Ag2 - Ag1	2.9899(15)
Ag2 — Ag1 <sup>ii</sup>	3.0126(17)	Ag1 — Ag1 <sup><i>ii</i></sup>	3.0497(15)
Angle	(°)	Angle	(°)
N2A—Ag1—O13	94.80(9)	S2—Ag2—O23	101.57(6)

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N2A—Ag1—S1 <sup><i>i</i></sup>	142.14(7)	$S2-Ag2-S1^i$	136.93(4)
N2A—Ag1—S2 <sup><math>i</math></sup>	128.46(7)	S2—Ag2— S1 <sup><i>ii</i></sup>	102.90(4)
$S1^i$ —Ag1— $S2^i$	86.84(4)	O23—Ag2—S1 <sup><i>ii</i></sup>	96.35(8)
S1 <sup><i>i</i></sup> —Ag1—O13	77.43(7)	O23—Ag2—S1 <sup><math>i</math></sup>	104.67(6)
S2 <sup><i>i</i></sup> —Ag1—O13	116.23(6)	$S1^{ii}$ —Ag2— $S1^{i}$	107.39(5)
[a] Symme	etry codes: (i) $-x+$	-1, -y+2, -z+1; ( <i>ii</i> ) $x+1$	1, y, z.; ( <i>iii</i> ) $-x+2$ , $-y+2$ .

-z+1

It should be noted, that dehydrogenation of thiohydantoin molecule during transition metal ion complexation is not a unique phenomenon and recently was encountered in the reaction of 5-(pyridine-2-yl-methyl)-2-thioxo-4-imidazolidinones and copper(II) chloride [36]. Simultaneous coordination of HL and L<sup>-</sup> moieties in polymeric chain of **2** makes possible Ag ... Ag metallophilic interactions (Fig. 9) with the distance range of 2.99 - 3.13 Å. All marked Ag(I)....Ag(I) distances are significantly shorter than the sum of corresponding metal VdW radii (3.44 Å). Taking into account general geometry of the {[Ag<sub>2</sub>(HL)(L)(CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>)]}<sub>n</sub> chain, two types of fragments ({Ag<sub>4</sub>S<sub>4</sub>} and {Ag<sub>2</sub>S<sub>2</sub>}) may be marked. In {Ag<sub>4</sub>S<sub>4</sub>} fragment Ag....Ag distances are relatively close (2.99 - 3.01 Å) and are somewhat shorter than Ag2....Ag2 distance (3.13 Å) in {Ag<sub>2</sub>S<sub>2</sub>} (Fig. 9).



Figure 9. Ag—S bonded chain with metallophilic interactions in 2.

#### 3.2 Vibrational spectra of compounds 1 and 2.

Although the spectra of coordination compounds **1** and **2** are complex, their comparison with IR-spectrum of respective ligands leads to certain conclusions. The bands at 1152, 1120, 1012, 652 cm<sup>-1</sup> in IR-spectrum of complex **1** and 1159, 1130, 1014, 660 cm<sup>-1</sup> in **2** are not present in the spectrum of free HL, and in accordance with literature data [37] can be assigned to benzenesulfonate and toluenesulfonate

anions as  $v_{as}(SO_3)$ ,  $v(SO_3)$ ,  $v_s(SO_3)$  and  $\delta_s(SO_3)$  modes, respectively. The bands at 1068 and 878 cm<sup>-1</sup> in **1** as well as at 1045 and 882 cm<sup>-1</sup> in **2** also can be assigned to C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub><sup>-</sup> and CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup> anions *as*  $v(C-C)_{ring}+v(C-S)$  and  $\gamma(CH) + \delta(CS)$  modes. The bands at 1751, 1650 and 1524 cm<sup>-1</sup> in spectrum of free ligand and 1758, 1658 and 1524 cm<sup>-1</sup> in spectrum of complex **1** and 1760, 1647, 1516 of complex **2** arise from HL thiohydantoin C=O vibration, allyl C=C stretching and ring motions [38, 39].

### 3.3 Hirshfeld surfaces of the ligand in 1.

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The Hirshfeld surfaces were built for all independent thiohidantoin moieties to analyze interactions between the ligands. The most prominent interactions between hydantoin N-H and anion O atoms as well as between hydantoin O and other H atoms can be seen in the Hirshfeld surface plots as the middle and poorly red areas (Fig. 10A). Fingerprint plots were produced to show the intermolecular surface bond distances with the regions highlighted for (N)H…O and (HL)O…H interactions. From Fig. 10 one can derive the most significant (HL)O…H interaction of HL in comparison with the other three ligands, that may be explained by participation of HL in hydrogen bonding with hydroxyl group of the solvent propanol molecule. C–H… $\pi$ -interactions between hydrogen atoms of allyl group or thiohydantoin methyl groups and benzensulfonate phenyl rings make up 2.4 - 12.6% of the surface area. The contribution to the surface area for S…H contacts is in the range of 3.7 to 8.4%.



Figure 10. Hirshfeld surface analysis of thiohydantoin  $HL^1 - HL^4$  molecules (corresponding to S1 – S4 atoms) in complex **1**. (A) Hirshfeld surfaces mapped with d<sub>norm</sub> which highlights both donor and acceptor ability. (B) Fingerprint plots for  $HL^1 - HL^4$  molecules resolved into (HL)O····H contacts. The full fingerprint appears beneath each decomposed plot in grey. (C) Fingerprint plots for four  $HL^1 - HL^4$  resolved into (N)H···O contacts. The full fingerprint appears beneath each decomposed plot in grey.

### 4. Conclusions

reaction By the of N-allylthiohydantoin with  $Ag(C_6H_5SO_3)$ and Ag(CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>) the two new  $\sigma$ -complexes (1 and 2) with an interestingly diverse Ag(I) coordination environments were synthesized. The structure 1 represents the second known (and completely different from earlier studied) example of AgC<sub>6</sub>H<sub>5</sub>SO<sub>3</sub> coordination mode. Different silver(I) arrangements are determined by variable thiohydantoin coordination modes due to steric hindrances, caused in 1 by both an efficient (N)H...O (1.93 - 2.13 Å) bonding with the anions and allyl group mobility and partial deprotonation of HL in complex 2. Ag(I) environments in 1 appear to be tetragonal pyramidal, seesaw and distorted octahedral, while in 2 metal atoms are characterized by seesaw and distorted tetrahedral arrangements.

Independent C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub><sup>-</sup> anions in **1** are bound to the Ag(I) ions in a bridging mode, connecting silver ions into serpentine-like {Ag<sub>4</sub>(C<sub>6</sub>H<sub>5</sub>SO<sub>3</sub>)<sub>4</sub>}<sub>n</sub> fragment. The last ones are sewn by bridging S atoms of thiohydantoin into infinite chains. Simultaneous coordination of HL and L<sup>-</sup> moieties in polymeric chains in **2** makes possible Ag....Ag metallophilic interactions with the distance range of 2.99 - 3.13 Å. Due to HSAB theory rule as well as a large affinity of Ag(I) to O atoms Ag(I)-(C=C)  $\pi$ -bonding does not occur in the studied compounds.

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### **Highlights:**

- Two novel complexes with unusual diverse coordination of Ag(I) with Nallylthiohydantoin were studied
- Different Ag(I) arrangements are determined by variable thiohydantoin coordination modes
- Simultaneous presence of molecular ligand and its ionic form was observed \_

