UDC 548.736:546.571

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SYNTHESIS AND CRYSTAL STRUCTURE OF Ag(I) *p*-TOLUENESULPHONATE COMPLEX WITH 5-METHYL-3-ALLYL-2-THIOHYDANTOIN

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New silver(I) toluenesulphonate coordination compound $[Ag_2(amth)_4(TsO)_2]$ (I) (where *amth*=3-allyl-5-methyl-2-thiohydantoin, TsO^-=*p*-toluenesulphonate anion) has been synthesized by direct interaction between *amth* ligand, Ag_2CO_3 and *p*-$CH_3C_6H_4SO_3H$ in *n*-propanol and studied by X-ray single crystal diffraction method. Complex I crystallizes in the triclinic centrosymmetric space group *P-1* with one silver(I) atom, one TsO^- anion and two *amth* molecules in the asymmetric unit, with the following cell parameters: a=10.411(4) Å, b=11.516(4) Å, c=12.772(4) Å, α=109.15(3)⁰, β=107.75(3)⁰, γ=105.27(3)⁰, V=1260.3(8) $Å^3$. The structure of compound I is built of dimeric binuclear $[Ag_2(amth)_4(TsO)_2]$ fragments within which a weak $Ag-Ag^i$ interaction was observed ($Ag-Ag^i$ bond distance is equal to 3.0897(13) Å). Ag atom in I has a distorted tetrahedral environment (τ_4=0.92), formed by three *amth* ligand's S atoms and one O atom of TsO^- anion. Both crystallographically independent *amth* molecules are coordinated to the metal centers only through their thiogroup's S atoms. In order to analyze weak interactions in I, Hirshfeld surface for some structural fragments were built and discussed. Unexpected interaction between oxogroup's O atom of one *amth* molecule and the ring of another one *amth* molecule was observed.

Keywords: silver(I), toluenesulphonate, coordination compound, 2-thiohydantoin, crystal structure.

DOI: 10.32434/0321-4095-2019-125-4-172-178

Introduction

Heterocyclic compounds based on 2-thiohydantoin (2-thioxoimidazolidin-4-one) fragment are well known in analytical chemistry, in particular as reagents for the determination of *d*-metals (such as Pd(II), Cu(I), Cu(II), Ag(I) and Hg(II)) due to the strong complexes formation [1] in which ligand coordination behavior is realized thanks to a simultaneous presence of thiocarbamide >C=S, carbonyl >C=O as well as >N–H donor groups. 2-Thiohydantoin derivatives have been reported to exhibit anticancer, antimalarial, anti-diabetic treatment as well as other valuable biological properties [2]. One of the methods to increase mentioned properties is a formation of corresponding coordination compounds which are also reported to have antimicrobial activity [3]. Moreover, 2-thiohydantoin derivatives exhibit fluorescence sensing properties towards Cu^+ in corresponding complexes [4].

In our previous works, a series of silver complexes of 3-allyl-2-thiohydantoin in the presence of benzenesulphonate and toluenesulphonate anions was studied and unexpected coordination behavior of this organic ligand in the reaction with Ag(I) was shown [5,6]. In the course of these studies, in order to investigate the coordination features of the another 2-thiohydantoin allyl derivative, namely 3-allyl-5-methyl-2-thiohydantoin (*amth*) towards silver(I) *p*-toluensulfonate, we carried out a synthesis and X-ray diffraction analysis with further detailed structure description of new complex $[Ag_2(amth)_4(TsO)_2]$ (I).

Experimental

General consideration

Unless mentioned otherwise, all chemicals were obtained from commercial sources and used without further purification. The NMR experiments: ^{1}H NMR (500 MHz), ^{13}C{1H} NMR (125 MHz) were recorded using a Bruker Avance 500 MHz NMR spectrometer. The chemical shifts are reported in ppm relative to the residual peak of the deuterated

$CDCl_3$ for the [1]H and [13]C{1H} NMR spectra. Diffraction data for I was collected by means of a Kuma KM4CCD diffractometer with MoK_α radiation (λ=0.71073 Å). Hirshfeld surfaces of discussed fragments in complex I were produced by CrystalExplorer software [7]. Ligand *amth* (3-allyl-5-methyl-2-thiohydantoin) was synthesized from allylisothiocyanate and alanine in the presence of triethylamine and pyridine, in accordance with the known procedure (Scheme) [5]. [1]H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 5.85 (ddt, J=16.9, 10.3, 5.7 Hz, 1H), 5.27–5.19 (m, 2H), 4.47–4.37 (m, 2H), 4.17 (qd, J=7.0, 1.0 Hz, 1H), 1.49 (d, J=7.1 Hz, 3H). [13]C NMR (126 MHz, $CDCl_3$) δ 183.59 (s), 174.49 (s), 130.72 (s), 118.60 (s), 55.11 (s), 43.33 (s), 17.01 (s).

Preparation of [Ag_2(amth)$_4$(TsO)$_2$] (I)

To the mixture of *amth* (204 mg, 1.20 mmol) and Ag_2CO_3 (92 mg, 0.33 mmol) 1 mL of *n*-propanol was added and stirred for 1 min. Then *p*-$CH_3C_6H_4SO_3H$ (292 mg, 1.70 mmol) was added, obtained mixture was carefully mixed and brown solution with grey precipitate was obtained. Keeping the reactor at room temperature in a dark place during 24 h led to the preparation of colorless [Ag_2(*amth*)$_4$(TsO)$_2$] crystals, which have appeared on the precipitate surface. The yield was about 35%.

X–ray crystal structure determination

The crystallographic parameters and summary of data collection for I are presented in Table 1. The collected diffraction data array for I was processed with the CrysAlis PRO program [8]. The structure was solved by ShelXT and refined by least squares method on F^2 by ShelXL software with the following graphical user interfaces of $OLEX^2$ [9]. Atomic displacements for non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms were placed on geometrically calculated positions and refined as riding atoms with relative isotropic displacement parameters.

CCDC number (1871030) 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).

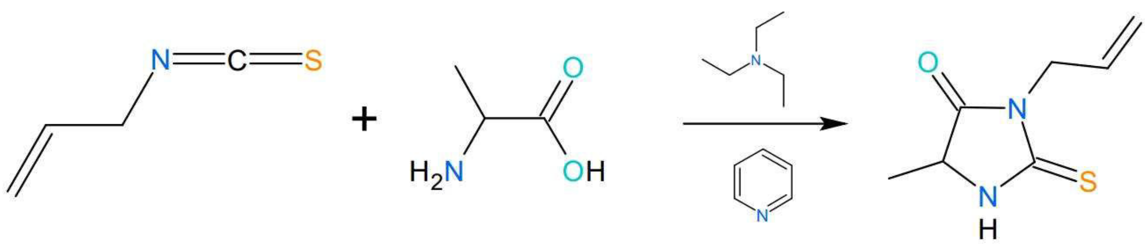
Table 1

Selected crystal data and structure refinement parameters of I

Empirical formula	$C_{42}H_{54}Ag_2N_8O_{10}S_6$
CCDC number	1871030
Formula weight (g·mol^{-1})	1239.03
Crystal system	Triclinic
Space group	P–1
a (Å)	10.411(4)
b (Å)	11.516(4)
c (Å)	12.772(4)
α (^{0})	109.15(3)
β (^{0})	107.75(3)
λ (^{0})	105.27(3)
V (Å^3)	1260.3(8)
Z	1
μ (mm^{-1})	1.09
F(000)	632
Calculated density (g cm^{-3})	1.633
Crystal size (mm)	0.33×0.12×0.06
Crystal color and shape	Clear colorless prism
Diffractometer and detector type	Kuma KM4CCD
Radiation type, wavelength, λ (Å)	MoK_α, 0.71073
Temperature, K	120
θ range for data collection (^{0})	3.0–28.8
Index ranges	–13≤h≤10
	–14≤k≤15
	–17≤l≤16
Measured reflections	8524
Independent reflections	5816
Observed refl. (I>2σ(I))	4582
Refined parameters	310
R_{int}	0.052
R[F^2>2σ(F^2)]	0.063
wR(F^2)	0.172
Goodness of fit	1.09

Results and discussion

Complex I crystallizes in the triclinic centro-symmetric space group *P–1* with one silver(I) atom,



Scheme. Synthesis of *amth*

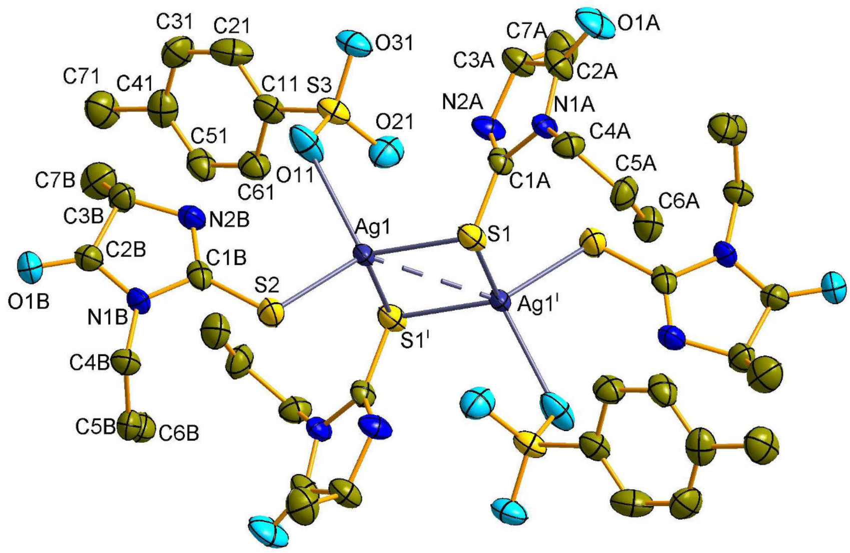


Fig. 1. Dimeric $[Ag_2(amth)_4(TsO)_2]$ fragment in the crystal structure I. Hydrogen atoms are removed for better visualization. Symmetry code: (i) 2–x, 1–y, 1–z

one TsO^- anion and two *amth* molecules in the asymmetric unit. The structure of compound I is built of dimeric binuclear $[Ag_2(amth)_4(TsO)_2]$ fragments (Fig. 1). Both silver atoms are bonded among themselves through two S atoms of two *amth* ligand molecules (Fig. 2). As a result, flat four-membered $\{Ag_2S_2\}$ ring is formed (S1–Ag1–S1^i angle is equal to 108.28(6)^0). Ag–Ag^i distance within it is equal to 3.0897(13) Å (Table 2), that is shorter than the doubled van der Waals radii of Ag (3.44 Å) reported by Bondi and significantly shorter than the corresponding sum according to Batsanov and Alvarez [10] (4.2 and 4.06 Å, respectively) that shows availability of weak Ag–Ag^i interaction. Coordination environment of each silver atom also includes one exocyclic S2 atom of second *amth* ligand molecule and O11 atom of TsO^- anion forming distorted tetrahedral arrangement (τ_4=0.92) [11]. Within this coordination polyhedron two Ag–S distances between silver atom and S atoms are very close (2.5491(18) and 2.5049(16) Å) and are significantly shorter then to the third one (2.720(2) Å).

Table 2

Selected bond lengths and angle values in I

Bond	d, Å	Angle	ω, °
Ag1–Ag1^i	3.0897(13)	S1–Ag1–S1^i	108.28(6)
Ag1–S1^i	2.720(2)	S2–Ag1–S1^i	110.20(6)
Ag1–S1	2.5491(18)	S2–Ag1–S1	118.16(5)
Ag1–S2	2.5049(16)	S2–Ag1–O11	97.82(10)
Ag1–O11	2.543(4)		

Note: – Symmetry code: (i) 2–x, 1–y, 1–z.

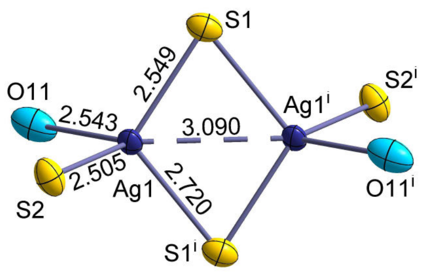


Fig. 2. Silver atoms and their closest surrounding with depicted bond length in the structure I. Symmetry code: (i) 2–x, 1–y, 1–z

Accordingly, both *amth* molecules are coordinated to the metal centers only through their exocyclic S atoms. Neither carbonyl O atom nor C=C double bond of allyl group participates in coordination to the Ag(I) atom. It could be explained by larger thermodynamic stability of a complex, where, corresponding to the Pearson hard-soft acid-base theory, typical soft Lewis acid such as Ag^+ is interconnected with a soft base as S atom in C=S group instead of O atom of C=O group. Although allylic C=C bond (as a soft base) is suitable for formation of stable Ag(I) π-complexes [12], thiogroup in I remains more preferable. Similar situation is also obtained with analogous *p*-toluenesulphonate $[Ag_2(L)_4(CH_3C_6H_4SO_3)_2]$ and benzenesulphonate $[Ag_2(L)_4(C_6H_5SO_3)_2]\cdot 0.5C_3H_7OH$ complexes with homologous 3-allyl-2-thiohydantoin ligand. In both this structures, there are three different coordination modes of silver atom (tetragonal pyramidal, seesaw and distorted octahedral) and four crystallographically independent ligand molecules, all of which were coordinated through their thiogroup's S atoms only [5,6].

In $[Ag_2(amth)_4(TsO)_2]$ (I), dimeric fragment toluenesulphonate anion is not only bonded to the Ag atom through the O11 atom, but is also involved in a wide system of weak bonding. In order to analyze these interactions, Hirshfeld surface was built for structural $\{Ag_2(amth)_4\}^{2+}$ fragment using CrystalExplorer software. Areas, where the most prominent interactions among atoms are, can be seen in the Hirshfeld surface plots as the red ones (Fig. 3). One can see a presence of two red areas corresponding to the N–H···O hydrogen bonding between *amth* ligand iminogroups and toluenesulphonate anion's O atoms (Table 3). This system of hydrogen bonds stabilizes mentioned $[Ag_2(amth)_4(TsO)_2]$ dimer. Another big red area, corresponding to the already discussed Ag1–O11 bond, is heavily painted in red, but there is other one smaller area near it slightly marked in red that responds to another one Ag1–O interaction, namely Ag1–O21 weak bonding (Ag1–O21 distance is equal to 3.015(4) Å).

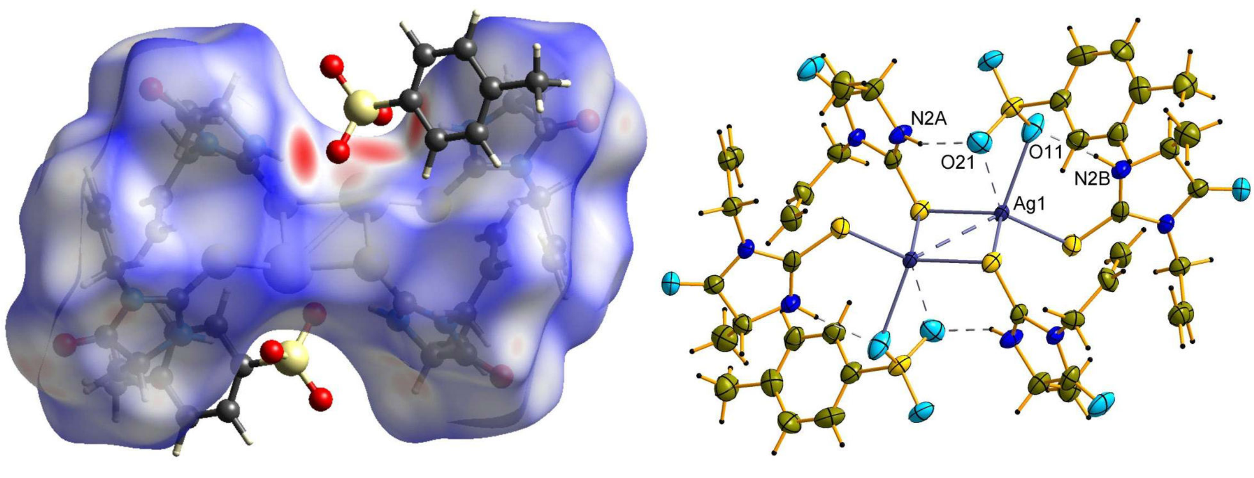
In order to analyze weak interactions via $[Ag_2(amth)_4(TsO)_2]$ dimers in I, packing Hirshfeld surface for the above dimer was built (Fig. 4). There are two main interdimeric interactions. One of them corresponds to weak C–H···O interaction, and another one, which at the Hirshfeld surface is represented as a group of three red areas, corresponds to the interaction between oxogroup's O atom of one *amth* molecule and the ring of another one *amth* molecule. This interaction could be described as both electrostatic and VdW interaction. Since 2-thiohydantoin (2-sulfanylideneimidazolidin-4-one) ring contains thio- and oxogroup, which possess high electronegativity and pull electron density on S and O atom respectively, there is partial positive charge and lack of electron density on imidazolidin ring. In order to visualize the distribution of electron density, the 2-thiohydantoine molecule was optimized using DFT method with B3LYP functional supplemented and standard 6-31G(d) basis set using Gaussian W09 package [13] and electron density surface was built (Fig. 5). This plot shows that a negative charge is generally localized near ligand's C=O and C=S groups (marked in yellow) at the time when the ring possesses generally positive charge (marked in blue).

Distance from O atom to the center of imidazolidin ring (Q) is equal to 2.831(8) Å and C–O–Q angle equals to 133.8(2)^0. Analyzing distances from O atom to all atoms of the ring, one can notice that these distances are mainly shorter than the sum of the corresponding VdW radii, which

Table 3

Geometry of selected hydrogen bonds in I

Atoms involved D–H···A	Symmetry	Distances, Å			Angle, deg D–H···A
		D···H	H···A	D···A	
N2B–H2B···O11		0.88	1.94	2.7961(1)	162
N2A–H2A···O21	–*x*, 1–*y*, 1–*z*	0.88	1.99	2.8208(1)	156



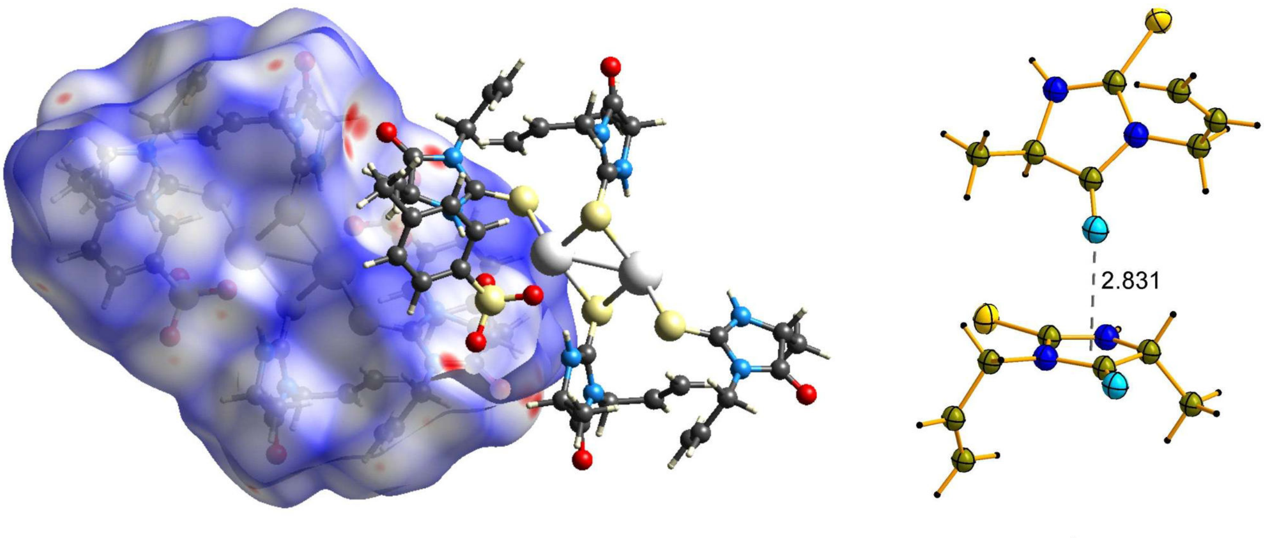
a *b*

Fig. 3. a – Hirshfeld surface analysis of structural $\{Ag_2(amth)_4\}^{2+}$ fragment in I. Hirshfeld surface is mapped with d_{norm} which highlights both donor and acceptor ability. b – Hydrogen bonds in I

Table 4

Geometry of C=O···ring interaction in I

Atoms involved C–O···X	O···X distance, Å	Sum of VdW radii of O and X (Bondi)	Sum of VdW radii of O and X (Alvarez)	Angle, deg C=O···X
C2B–O1B···N2A	3.159(8)	3.07	3.16	114.1(5)
C2B–O1B···C1A	3.083(8)	3.22	3.27	115.9(5)
C2B–O1B···N1A	3.027(8)	3.07	3.16	138.8(5)
C2B–O1B···C2A	3.026(8)	3.22	3.27	157.5(5)
C2B–O1B···C3A	3.082(8)	3.22	3.27	132.9(5)
C2B–O1B···H3A	2.63(2)	2.72	2.70	125(2)



a *b*

Fig. 4. a – Hirshfeld surface analysis of $[Ag_2(amth)_4(TsO)_2]$ fragment in I. Hirshfeld surface is mapped with d_{norm} which highlights both donor and acceptor ability. b – C=O···ring interaction in I

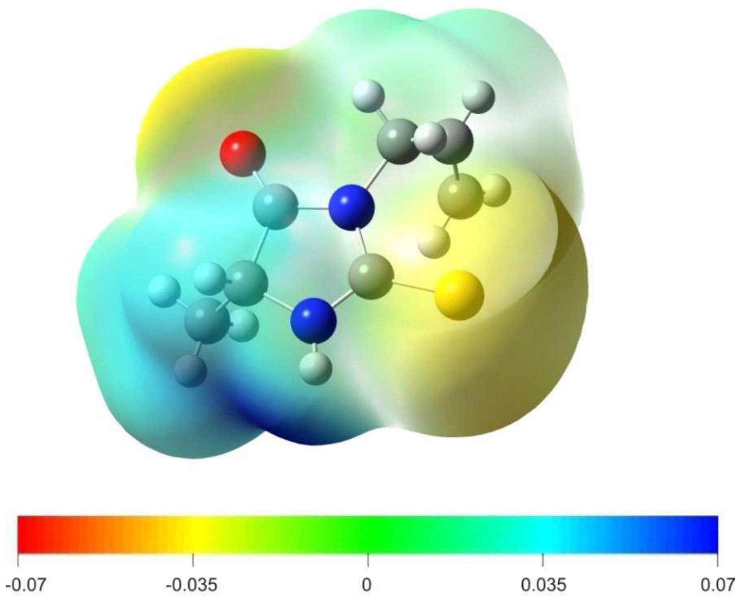


Fig. 5. Electron density surface mapped with electrostatic potential for *amth* molecule

indicates the presence of interaction between O atom and the ring (Table 4.). Nature of this interaction is quite debatable, but it could be treated as example of nonaromatic analog of lone pair-π interaction (lp–π), which is bonding association between a neutral electron-rich molecule and an electron-poor ring [14]. As a rule, the ring has to be aromatic one but lp–π interactions could be expanded to nonaromatic systems too [15].

Conclusions

New silver(I) toluenesulphonate complex of $[Ag_2(amth)_4(TsO)_2]$ (where *amth*=3-allyl-5-methyl-2-thiohydantoin, TsO^-=*p*-toluenesulphonate anion) was obtained and its structure was determined and studied by X-ray single crystal diffraction. The structure of this complex is built of binuclear $[Ag_2(amth)_4(TsO)_2]$ dimers in which Ag atom has a distorted tetrahedral environment (τ_4=0.92), formed by three *amth* ligand's S atoms and one O atom of TsO^- anion. Also within this fragments, a weak Ag–Ag^i interaction (Ag–Ag^i distance is equal to 3.0897(13) Å) was observed. Both crystallographically independent *amth* molecules are coordinated to the metal centers through their thiogroup's S atoms only. Unexpected interaction between oxogroup's O atom of one *amth* molecule and the ring of another one *amth* molecule was discussed.

REFERENCES

1. *Montana Gonzalez M.T., Sanchez Martin A., Gomez Ariza J.L.* Derivatives of 2-thiohydantoin as spectrophotometric analytical reagents. III // Microchim. Acta. – 1982. – Vol.78. – P.363-369.

2. *Savjani J.K., Gajjar A.K.* Pharmaceutical importance and synthetic strategies for imidazolidine-2-thione and imidazole-2-thione derivatives // Pakistan J. Bio. Sci. – 2011. – Vol.14. – No. 24. – P.1076-1089.

3. *Wazeer M.I.M.,, Isab A.A., Fettouhi M.* New cadmium chloride complexes with imidazolidine-2-thione and its derivatives: X-ray structures, solid state and solution NMR and antimicrobial activity studies // Polyhedron. – 2007. – Vol.26. – P.1725-1730.

4. *Conjugated* polymers containing 2-thiohydantoin: detection of cuprous ion, hydrogen peroxide and glucose / Zeng W., Yang X., Chen X., Yan Y., Lu X., Qu J., Liu R. // Eur. Polym. J. – 2014. – Vol.61. – P.309-315.

5. *An unusual* diverse coordination of silver(I) with N-allylthiohydantoin ligand in the presence of benzene- and *p*-toluenesulfonate anions / Fedorchuk A.A., Slyvka Yu.I., Kinzhybalo V., Lis T., Mys'kiv M.G. // Inorg. Chim. Acta. – 2019. – Vol.484. – P.79-86.

6. *Crystal* structure peculiarities of silver(I) *p*-toluenesulphonate complex with 3-allyl-2-sulfanylideneimidazolidin-4-one of $[Ag_2(L)_4(CH_3C_6H_4SO_3)_2]$ composition / Fedorchuk A., Kinzhybalo V., Slyvka Y., Mys'kiv M. // Visnyk of the Lviv University. Series Chemistry. – 2018. – Vol.59. – No. 1. – P.140-147.

7. *CrystalExplorer* (Version 3.1) / Wolff S.K., Grimwood D.J., McKinnon J.J., Turner M.J., Jayatilaka D., Spackman M.A. – University of Western Australia, 2012.

8. *Rigaku* Oxford Diffraction CrysAlis PRO. – Yarnton, Oxfordshire, England: Rigaku Oxford Diffraction, 2015.

9. *Sheldrick G.M.* Crystal structure refinement with SHELXL // Acta Cryst. C. – 2015. – Vol.C71. –P.3-8.

10. *Alvarez S.* A cartography of the van der Waals territories // Dalton Trans. – 2013. – Vol.42. – P.8617-8636.

11. *Yang L., Powell D.R., Houser R.P.* Structural variation in copper(I) complexes with pyridylmethylamide ligands: structural analysis with a new four-coordinate geometry index, τ_4 // Dalton Trans. – 2007. – Vol.9. – P.955-964.

12. *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)-1H-tetrazole) / Slyvka Yu., Pavlyuk O., Pokhodylo N., Ardan B., Mazej Z., Goreshnik E. // Acta Chim. Slov. – 2011. – Vol.58. – No. 1. – P.134-138.

13. *Gaussian 09*, Revision A. 02 / Frisch M., Trucks G.W., Schlegel H.B. et al. // Inc, Wallingford, CT, 2009.

14. *Mooibroek T.J., Gamez P., Reedijk J.* Lone pair–π interactions: a new supramolecular bond? // CrystEngComm. – 2008. – Vol.10. – P.1501-1515.

15. *Geboes Y., De Proft F., Herrebout W.A.* Expanding lone pair···π interactions to nonaromatic systems and nitrogen bases: complexes of C_2F_3X (X = F, Cl, Br, I) and TMA-d_9 // J. Phys. Chem. A. – 2015. – Vol.119. – No. 22. – P.5597-5606.

Received 22.01.2019

СИНТЕЗ І КРИСТАЛІЧНА СТРУКТУРА *п*-ТОЛУЕНСУЛЬФОНАТНОГО КОМПЛЕКСУ Ag(I) З 5-МЕТИЛ-3-АЛІЛ-2-ТІОГІДАНТОЇНОМ

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Новий п-толуенсульфонатний комплекс Ag(I) складу $[Ag_2(amth)_4(TsO)_2]$ (I) (amth=3-аліл-5-метил-2-тіогідантоїн, TsO^-=п-толуенсульфонат аніон) було одержано безпосередньою взаємодією між лігандом amth, Ag_2CO_3 та р-$CH_3C_6H_4SO_3H$ у н-пропанолі та досліджено методом рентгенівської монокристалічної дифракції. Комплекс I кристалізується в триклінній центросиметричній просторовій групі P-1 з одним атомом аргентуму (I), одним TsO-аніоном і двома молекулами ліганду amth в асиметричній частині з параметрами комірки: a=10,411(4) Å, b=11,516(4) Å, c=12,772(4) Å, α=109,15(3)°, β=107,75(3)°, γ=105,27(3)°, V=1260,3(8) Å³. Структура сполуки I побудована з димерних двоядерних фрагментів $[Ag_2(amth)_4(TsO)_2]$, в яких наявна слабка взаємодія Ag–Ag^i (відстань Ag–Ag^i становить 3,0897(13) Å). Атом Ag в I має деформоване тетраедричне координаційне оточення (τ_4=0,92), утворене трьома атомами S ліганду amth та одним атомом O

TsO-аніона. Обидві кристалографічно незалежні молекули amth координуються до металічних центрів лише через атоми S своїх тіогруп. З метою проаналізувати слабкі взаємодії у сполуці I були побудовані та проаналізовані поверхні Хіршфельда для деяких структурних фрагментів. Також в I помічено несподівану взаємодію між атомом O оксогрупи однієї молекули ліганду amth та кільцем іншої.

Ключові слова: аргентум(I), толуенсульфонат, координаційна сполука, 2-тіогідантоїн, кристалічна структура.

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Keywords: silver(I); toluenesulphonate; coordination compound; 2-thiohydantoin; crystal structure.

REFERENCES

1. Montana Gonzalez M.T., Sanchez Martin A., Gomez Ariza J.L. Derivatives of 2-thiohydantoin as spectrophotometric analytical reagents. III. *Microchimica Acta*, 1982, vol. 78, pp. 363-369.

2. Savjani J.K., Gajjar A.K. Pharmaceutical importance and synthetic strategies for imidazolidine-2-thione and imidazole-2-thione derivatives. *Pakistan Journal of Biological Sciences*, 2011, vol. 14, pp. 1076-1089.

3. Wazeer M.I.M., Isab A.A., Fettouhi M. New cadmium chloride complexes with imidazolidine-2-thione and its derivatives: X-ray structures, solid state and solution NMR and antimicrobial activity studies. *Polyhedron*, 2007, vol. 26, pp. 1725-1730.

4. Zeng W., Yang X., Chen X., Yan Y., Lu X., Qu J., Liu R. Conjugated polymers containing 2-thiohydantoin: detection of cuprous ion, hydrogen peroxide and glucose. *European Polymer Journal*, 2014, vol. 61, pp. 309-315.

5. Fedorchuk A.A., Slyvka Yu.I., Kinzhybalo V., Lis T., Mys'kiv M.G. An unusual diverse coordination of silver(I) with N-allylthiohydantoin ligand in the presence of benzene- and p-toluenesulfonate anions. *Inorganica Chimica Acta*, 2019, vol. 484, pp. 79-86.

6. Fedorchuk A., Kinzhybalo V., Slyvka Y., Mys'kiv M. Crystal structure peculiarities of silver(I) *p*-toluenesulphonate complex with 3-allyl-2-sulfanylideneimidazolidin-4-one of $[Ag_2(L)_4(CH_3C_6H_4SO_3)_2]$ composition. *Visnyk of the Lviv University. Series Chemistry*, 2018, vol. 59, no. 1, pp. 140-147.

7. Wolff S.K., Grimwood D.J., McKinnon J.J., Turner M.J., Jayatilaka D., Spackman M.A., *CrystalExplorer (Version 3.1)*. University of Western Australia, 2012.

8. *Rigaku Oxford Diffraction. CrysAlis PRO.* Yarnton, Oxfordshire, England, 2015.

9. Sheldrick G.M. Crystal structure refinement with SHELXL. *Acta Crystallographica, Section C: Crystal Structure Communications*, 2015, vol. C71, pp. 3-8.

10. Alvarez S. A cartography of the van der Waals territories. *Dalton Transactions*, 2013, vol. 42, pp. 8617-8636.

11. Yang L. Powell D.R., Houser R.P. Structural variation in copper(I) complexes with pyridylmethylamide ligands: structural analysis with a new four-coordinate geometry index, τ_4. *Dalton Transactions*, 2007, pp. 955-964.

12. Slyvka Yu., Pavlyuk O., Pokhodylo N., Ardan B., Mazej Z., Goreshnik E. 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)-1H-tetrazole). *Acta Chimica Slovenica*, 2011, vol. 58, pp. 134-138.

13. Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Scalmani G., Barone V., Mennucci B., Petersson G.A., Nakatsuji H., Caricato M., Li X., Hratchian H.P., Izmaylov A.F., Bloino J., Zheng G., Sonnenberg J.L., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Vreven T., Montgomery J.A., Peralta J.E., Ogliaro F., Bearpark M., Heyd J.J., Brothers E., Kudin K.N., Staroverov V.N., Kobayashi R., Normand J., Raghavachari K., Rendell A., Burant J.C., Iyengar S.S., Tomasi J., Cossi M., Rega N., Millam J.M., Klene M., Knox J.E., Cross J.B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Ochterski J.W., Martin R.L., Morokuma K., Zakrzewski V.G., Voth G.A., Salvador P., Dannenberg J.J., Dapprich S., Daniels A.D., Farkas O., Foresman J.B., Ortiz J.V., Cioslowski J., Fox D.J., *Gaussian 09, Revision A. 02.* Gaussian, Inc., Wallingford CT, 2009.

14. Mooibroek T.J., Gamez P., Reedijk J. Lone pair–π interactions: a new supramolecular bond? *CrystEngComm*, 2008, vol. 10, pp. 1501-1515.

15. Geboes Y., De Proft F., Herrebout W.A. Expanding lone pair···π interactions to nonaromatic systems and nitrogen bases: complexes of C_2F_3X (X = F, Cl, Br, I) and TMA-d_9. *The Journal of Physical Chemistry A*, 2015, vol. 119, pp. 5597-5606.