

СИНТЕЗ И СТРУКТУРА ТЕТРАХЛОР-ГАЛЛАТ 3,5-ДИАМИНО-1,2,4-ТРИАЗОЛИЯ**Т.В. Кудаярова, Е.А. Данилова, Ю.А. Питева, К.Е. Мочалина, М.В. Дмитриев**

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В работе обсуждается синтез и структура комплексного соединения на основе 3,5-диамино-1H-1,2,4-триазола (гуаназола) с ионами галлия, образующегося при взаимодействии безводного хлорида галлия (III) и гуаназола в среде осушенного метанола. После отгонки растворителя под вакуумом образовавшийся продукт промывали гексаном, ацетоном, целевое соединение экстрагировали ацетонитрилом, и медленным испарением последнего при комнатной температуре в течение трех дней получили кристаллы бежевого цвета, которые были охарактеризованы методами ИК спектроскопии, элементного анализа, масс-спектрометрии и данными рентгеноструктурного анализа. Комплексный галлат состава $C_2H_6N_5^+ [GaCl_4]^-$ существует в виде двух кристаллографически независимых катионов и двух анионов. Комплексное соединение кристаллизуется в центросимметричной пространственной группе моноклинной сингонии. Тетрахлорогаллат-анион представляет собой слегка искаженный тетраэдр, что характерно для структур этого типа. Катионы 1,2,4-триазолия селективно протонированы по атомам N^4 и N^4A , однако местом преимущественной локализации положительного заряда являются атомы N^2 и N^2A . Помимо электростатического взаимодействия разноименно заряженных ионов важную роль в стабилизации кристаллической упаковки играет развитая система водородных связей: практически все атомы водорода и хлора задействованы в ее образовании. Каждый из кристаллографически независимых катионов образует центросимметричный димер за счет межмолекулярной водородной связи $N^2 \cdots N^3$ и $N^2A \cdots N^3A$. Полный набор рентгеноструктурных данных депонирован в Кембриджский банк структурных данных соединений - Cambridge Structural Database (депонент CCDC 1894815) и может быть свободно получен по запросу на сайте www.ccdc.cam.ac.uk/data_request/cif.

Ключевые слова: 3,5-диамино-1H-1,2,4-триазол, гуаназол, хлорид галлия, комплексное соединение, рентгеноструктурный анализ

SYNTHESIS AND STRUCTURE OF 3,5-DIAMINO-1,2,4-TRIAZOLIUM TETRACHLORO-GALLATE**T.V. Kudayarova, E.A. Danilova, Yu.A. Piteva, K.E. Mochalina, M.V. Dmitriev**

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This paper discusses the synthesis and structure of a complex compound based on 3,5-diamino-1H-1,2,4-triazole (guanazole) with gallium ions, formed by the interaction of anhydrous gallium (III) chloride and guanazole in dried methanol. After distilling off the solvent under vacuum, the resulting product was washed with hexane, acetone. The target compound was extracted with acetonitrile, and slow evaporation of the latter at room temperature for three days resulted in beige-colored crystals, which were characterized by IR spectroscopy, elemental analysis, mass-spectrometry and X-ray diffraction analysis. The complex composition of gallate, $C_2H_6N_5^+ \cdot [GaCl_4]$, exists as two crystallographically independent cations and two anions. The complex compound crystallizes in the centrosymmetric space group of the monoclinic syngony. The tetrachlorogallate anion is a slightly distorted tetrahedron, which is typical of structures of this type. 1,2,4-triazolium cations are selectively protonated on the N^4 and N^4A atoms, however, the site of the preferential localization of the positive charge is the N^2 and N^2A atoms. In addition to the electrostatic interaction of oppositely charged ions, a developed system of hydrogen bonds plays an important role in the stabilization of the crystal packing: almost all hydrogen and chlorine atoms are involved in its formation. Each of the crystallographically independent cations forms a centrosymmetric dimer due to the intermolecular hydrogen bond $N^2 - H^2 \cdots N^3$ and $N^2A - H^2A \cdots N^3A$. A full set of X-ray data is deposited into the Cambridge Structural Database of Compounds - the Cambridge Structural Database (Contributor CCDC 1894815) and it can be gotten from the site www.ccdc.cam.ac.uk/data_request/cif.

Key words: 3,5-diamino-1H-1,2,4-triazole, guanazole, gallium chloride, complex compound, X-ray diffraction analysis

Для цитирования:

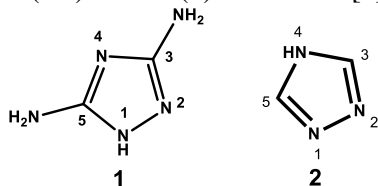
Кудаярова Т.В., Данилова Е.А., Питева Ю.А., Мочалина К.Е., Дмитриев М.В. Синтез и структура тетрахлор-галлат 3,5-диамино-1,2,4-триазолия. *Изв. вузов. Химия и хим. технология.* 2019. Т. 62. Вып. 4. С. 121–127

For citation:

Kudayarova T.V., Danilova E.A., Piteva Yu.A., Mochalina K.E., Dmitriev M.V. Synthesis and structure of 3,5-diamino-1,2,4-triazolium tetrachloro-gallate. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2019. V. 62. N 4. P. 121–127

INTRODUCTION

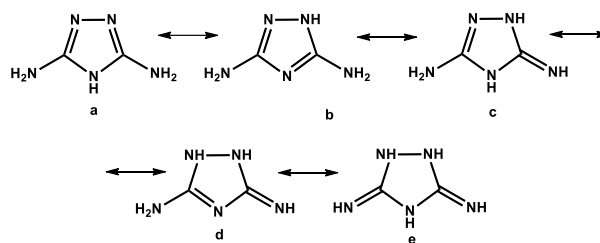
For 1,2,4-triazole two tautomeric forms (1H) – form **(1)** and (4H) – form **(2)** are known [1]:



Due to the rapid movement of the proton between N^1 and N^2 , positions 3 and 5 become equivalent in the form **1**.

Measuring dipole moments has shown that the preferred tautomeric form is **1** [1].

1,2,4-triazoles unsubstituted at the nitrogen atom exhibit amphoteric properties and, depending on the pH of the medium, can donate or attach a proton. In N-unsubstituted triazoles, when interacting with metals, substitution of both hydrogen and the formation of complexes can occur. The latter largely depends on the reaction conditions and the ratio of reagents. It is known that guanazole derivatives exist in several tautomeric forms (**a-d**), the state of which in crystalline form often differs from that in solution.



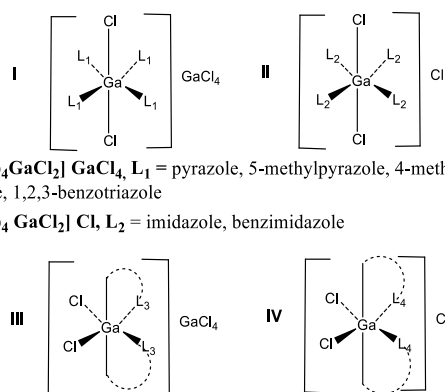
An analysis of foreign and domestic literature data [2-9] shows that guanazole contains several reaction centers in its structure that can be used to introduce additional groups (substitutes or metal ions) into the guanazole structure, which offer the prospect of increasing bioavailability, selectivity of accumulation and increase the effectiveness of chemotherapy. In addition, guanazole, as a ligand, binds to inorganic or organic anions, forming complexes of various structures, which leads to interesting physical properties, such as photoluminescence and magnetic ones [9, 10].

It should be noted that among coordination compounds, a special place is occupied by complexes obtained on the basis of biogenic metals. This is due to the fact that they play an important role in many biochemical processes and therefore are widely used in plant growing, animal husbandry and pharmacology [11, 12].

On the other hand, complex compounds of many transition elements, including gallium or manganese, can have a wide range of useful properties for which the chemistry of complex compounds is not well understood [13, 14].

So, the author [14] considers the synthesis, structural characteristics and antimicrobial activity of azo dye-based complexes of triazole with Mn (II), Co (II), Ni (II), Cu (II) и Zn (II). Five, of the ten obtained complexes, established biological activity against gram-positive and gram-negative bacteria.

At present, the gallium (III) complexes of N-heterocycles (Fig. 1) are presented in the literature, the structure of which was established only on the basis of the data of IR, UV-spectroscopy and elemental analysis data [15].



I. $[(L_1)_4GaCl_2] GaCl_4$, L_1 = pyrazole, 5-methylpyrazole, 4-methylpyrazole, indazole, 1,2,3-benzotriazole

II. $[(L_2)_4 GaCl_2] Cl$, L_2 = imidazole, benzimidazole

III. $[(L_3)_2 GaCl_2] GaCl_4$, L_3 = 1,10-phenanthroline, 2,2-dipyridyl

IV. $[(L_4)_2 GaCl_2] Cl$, L_4 = 1,10-phenanthroline

Fig. 1. Possible structures of gallium (III) complexes with N-heterocycles [15]

Рис. 1. Возможное строение комплексов галлия (III) с N-гетероциклами [15]

In [16], it was shown that gallium (III) salts have pronounced toxicity with respect to a number of tumor cells. For gallium chloride and nitrate [17, 18], the first and second stages of clinical trials were conducted, where they in one degree or another retarded the growth of bladder, liver, and lymphatic tumors. Studies have shown, however, that the effectiveness of drugs is not high enough due to the loss of toxicity due to hydrolysis and the difficulties of transmembrane transport inside tumor cells due to high hydrophilicity [19]. It is obvious that the solution of the above problems can significantly enhance the antitumor activity of gallium salts, which should have a good clinical perspective.

The search for new effective drugs for chemotherapy of tumors is extremely relevant and is conducted in different directions [20-24]. In this regard, studies aimed at the development of methods for the

synthesis of gallium complexes with guanazole, which itself has an antitumor effect [25] are scientifically based. The use of such complexes will increase the solubility of guanazole due to complexation, reduce the tendency to associate the metal complex and increase the selectivity of its accumulation in tumor cells through the formation of a molecular complex with polyvinylpyrrolidone, by analogy with how this is achieved with the targeted delivery of the «Fotolon» photosensitizer [26].

EXPERIMENTAL PART

The synthesis of guanazole 1 was carried out according to the method [27] by the cyclization reaction of dicyandiamide and hydrazine hydrate.

IR spectra were measured using the AVATAR 360 FT-IR spectrometer. X-ray diffraction analysis (XRD) was performed on a single-crystal Xcalibur Ruby diffractometer with a CCD detector using the standard procedure (MoK α -radiation, 295(2) K, ω -scanning step 1 $^\circ$). Absorption is taken into account empirically using an algorithm SCALE3 ABSPACK [28]. Crystal syngony (C₂H₆N₅·Cl₄Ga, MM = 311.64) monoclinic, space group P21/n, a 17.358(3), b 6.4407(11), c 18.421(3) Å, β 92.119(18) $^\circ$, V 2058.1(7) Å³, Z 8, dcalc 2.012 g/cm³; μ 3.668 mm⁻¹. The structure was deciphered using the SHELXS [29] program and refined with the full-matrix MNK by F2 in the anisotropic approximation for all non-hydrogen atoms using the program SHELXL [30] with graphic interface OLEX2 [31]. Hydrogen atoms were refined independently in the isotropic approximation with normalization of the N–H bond lengths by soft constraints DFIX. Final refinement parameters: R1 0.0376, wR2 0.0682 [for 3574 reflections with I > 2 σ (I)], R1 0.0613, wR2 0.0769 (for all 4829 independent reflections), S 1.025.

Complex compound with gallium was synthesized by the method [13].

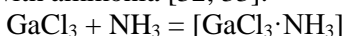
A mixture consisting of guanazole 1 (1 g, 2.52 mmol) and gallium (III) chloride (0.89 g, 2.52 mmol) in dried methanol (30 ml) was stirred under heating to 60 $^\circ$ C for 2 h. The solvent was distilled off in vacuum, the precipitate formed was washed with hexane, acetone, and the target compound was extracted with acetonitrile. Slow evaporation of the solvent at room temperature for three days gave beige crystals, well soluble in water, in alcohols, DMSO.

Yield = 0.58 g (74%). $T_{melt.}$ = 190-192 $^\circ$ C. IR: ν (KBr)/cm⁻¹: 3455 (NH₂, vas), 3357 (NH₂, vs), 2920, 2853, 1691 (C=N), 1658 (NH₂, d), 1527, 1464, 1332, 1159. (C–N, alif), 1065, 1010, 798, 687, 632. Found, %: C 7.68, H 1.98, N 22.44, Cl 45.48, Ga 22.34 C₂H₆N₅GaCl₄. Calculated, %: C 7.71, H 1.94, N 22.47, Ga 22.37, Cl 45.51. MM 308.86.

RESULTS AND DISCUSSION

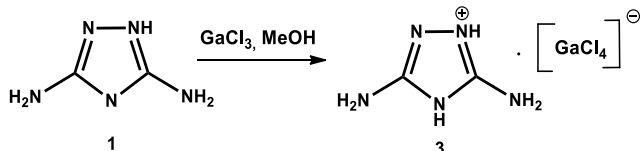
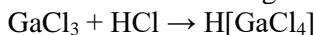
The single crystal obtained as a result of slow evaporation from a solution of acetonitrile single crystal represents XRD the complex compound **3** of tetrachlorogallate with an organic ligand 3,5-diamino-1,2,4-triazolium cation of composition – $C_2H_6N_5^+ [GaCl_4]^-$.

Gallium (III) chloride, which was used in the synthesis, is a typical molecular compound resembling aluminum chloride in properties. It is well soluble in organic solvents and water, while it is hydrolyzed. Gallium is not a typical complexing agent, however, many organometallic complex compounds of gallium chloride with various ligands have been obtained. Thus, the simplest complex can be obtained by direct interaction of chloride with ammonia [32, 33]:



It is known that gallium chloride forms adducts with other nitrogen-containing compounds: pyridine, dipyridyl, trimentylamine, etc. The compound $[GaCl_3 \cdot PPh_3]$, which is obtained by interaction with triphenylphosphine, similar in structure can be obtained with trimethylarsine [34].

Based on the literature data [32-34], it can be assumed that the residual water in the reaction mass contributed to the partial hydrolysis of gallium chloride and the formation of HCl, resulting in protonation **1** with the formation of the triazolium cation, the counter-ion of which was the tetrachlorogallate anion.



Scheme. Synthesis of 3,5-diamino-1,2,4-triazolium tetrachlorogallate
Схема. Синтез тетрачлор-галлата 3,5-диамино-1,2,4-триазолия

According to the data of X-ray structural analysis, two crystallographically independent cations and two anions in compound **3** crystallize in the centrosymmetric space group of the monoclinic syngony (Fig. 2).

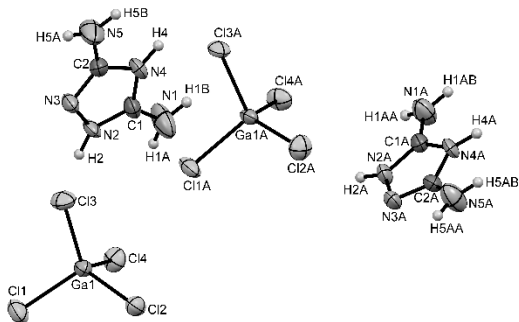


Fig. 2. Independent element of the unit cell **3**
Рис. 2. Независимый элемент элементарной ячейки **3**

The unit cell of the crystal of compound **3** is shown in Fig. 3. The tetrachloro-gallate anion is a slightly distorted tetrahedron, which is typical of structures of this type.

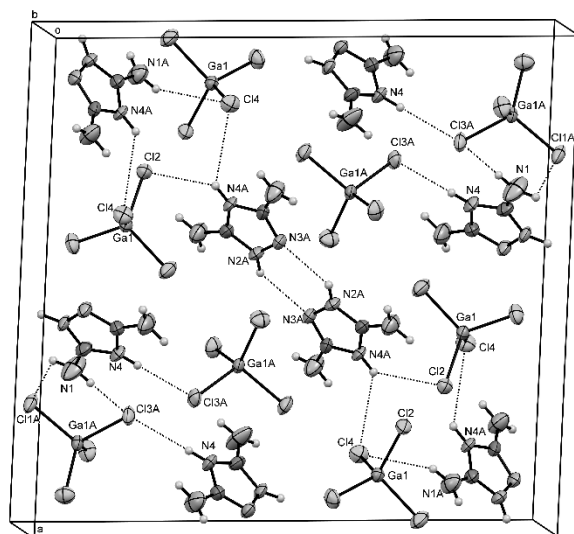


Fig. 3. Unit cell in crystal **3**
Рис. 3. Элементарная ячейка в кристалле **3**

Triazolium cations are selectively protonated on the N⁴ and N^{4A} atoms, however, the site of the predominant positive charge localization is the N² and N^{2A} atoms. The latter fact is confirmed by the distribution of bond lengths in the triazole cycle (Table). So, communication C¹=N², C^{1A}=N^{2A}, C²=N³ and C^{2A}=N^{3A} can only be considered partially delocalized doubles, and C¹-N⁴, C^{1A}-N^{4A}, C²-N⁴ and C^{2A}-N^{4A} – single bond. A similar distribution of bond lengths in the triazole cycle was observed in other triazole salts [35, 36].

Table

Selected bond lengths for **3**

Таблица. Некоторые длины связей для **3**

Bond	length, Å	bond	length, Å
C ¹ -N ¹	1.330(5)	C ^{1A} -N ^{1A}	1.323(5)
C ¹ -N ²	1.290(4)	C ^{1A} -N ^{2A}	1.298(4)
C ¹ -N ⁴	1.356(4)	C ^{1A} -N ^{4A}	1.351(4)
C ² -N ³	1.293(4)	C ^{2A} -N ^{3A}	1.293(4)
C ² -N ⁴	1.361(4)	C ^{2A} -N ^{4A}	1.362(4)
C ² -N ⁵	1.335(5)	C ^{2A} -N ^{5A}	1.337(4)
N ² -N ³	1.390(3)	N ^{2A} -N ^{3A}	1.388(3)

In addition to the electrostatic interaction of oppositely charged ions, an developed system of hydrogen bonds plays an important role in the stabilization of the crystal packing: almost all hydrogen and chlorine atoms are involved in its formation. Each of the crystallographically independent cations forms a

centrosymmetric dimer due to the intermolecular hydrogen bond $N^2-H^2 \cdots N^3$ and $N^2A-H^2A \cdots N^3A$.

Crystal data were obtained using computer programs: CrysAlis PRO [17], SHELXS97 [18, 19], Mercury [37], pubCIF [38]. A complete set of X-ray diffraction data has been placed in the database Cambridge Structural Database (Deposit CCDC 1894815).

CONCLUSIONS

Thus, we obtained a new complex compound with gallium – tetrachloro-gallate of 3,5-diamino-1,2,4-triazolium, which is characterized by physico-chemical methods of analysis. The obtained results of X-ray

crystallographic analysis of a complex compound crystal are deposited in the Cambridge Structural Database of Compounds and can be freely obtained on request at the site www.ccdc.cam.ac.uk/data_request/cif.

ACKNOWLEDGEMENTS

The research was performed using resources of the Center for Collective Use, Ivanovo State University of Chemical Technology "ISUCT".

This work has been made by Financial support from Russian Scientific Foundation, grant No. 18-73-00217.

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Поступила в редакцию 11.02.2019

Принята к опубликованию 04.03.2019

Received 11.02.2019

Accepted 04.03.2019