UDC 541.49:661.693:547.587.26

M. A. Martyniuk, O. E. Martsynko
Odesa I. I. Mechnikov National University, Department of Inorganic Chemistry and Chemical Education, 2 Dvorianska St, Odesa, 65082, Ukraine; e-mail: lborn@ukr.net

SYNTHESIS AND RESEARCH OF COORDINATION COMPOUNDS OF GERMANIUM(IV) WITH GALLIC ACID AND ETHYL GALLATE

Optimal methods of synthesis of germanium(IV) complexes with gallic acid (H_4Gal) and ethyl gallate (H_3EtGal) in aqueous solution have been developed. The compounds have been characterized by research methods: elemental analysis, thermogravimetry, infrared spectroscopy, and mass spectrometry. The composition and structure of the studied compounds have been determined. It has been shown that the complexes $[Ge(H_2Gal)(H_3Gal)_2]\cdot H_2O$ (1) $[Ge(HEtGal)(H_2EtGal)_2]\cdot 2H_2O$ (2) have a germanium : H_4Gal (H_3EtGal) ratio of 1:3, in coordination with Germanium(IV) involved two hydroxyl groups from each ligand, forming an octahedral coordination polyhedron of this metal.

Key words: germanium, gallic acid, ethyl gallate, coordination compounds, IR spectroscopy, thermogravimetric analysis, ESI mass spectrometry.

Gallic acid (**H_4Gal**) has been used in the production of blue ink and photographic developers, but it has recently emerged as a high-value compound with important biological activities such as antioxidant [1-3], anti-inflammatory [4], anticancer [5-7], and antimutagenicity [8].

According to the authors [9], aliphatic gallic acid esters were prepared, and their anti-thrombotic effects were evaluated in the mouse thrombosis model. It has been shown that ethyl ester (**H_3EtGal**) treatment significantly lowered the death rate and increased the recovery from paralysis due to the thrombotic challenge. The gallic acid's methyl, ethyl, and propyl esters were examined for their antimicrobial potential, preservative efficacy and antioxidant potential. They can be used as lead compounds to further explore their application as preservative agents in pharmaceuticals and the food industry [10].

It was found that the cytotoxicity of a drug based on *Paeonia lactiflora* roots against human breast cancer cells is primarily related to the presence of gallic acid and methyl gallate as an essential backbone of pentahaloylglucose in its composition. By studying the relationship between the structure and activity of gallic acid, it was found that three hydroxy groups are important for its cytotoxicity. In addition, the drug's efficacy was confirmed by increasing its lipid affinity by synthesizing various ester derivatives of gallic acid [11].

In recent years, at the Department of Inorganic Chemistry and Chemical Education of the Odesa I.I. Mechnikov National University various metal and various ligand coordination compounds of germanium(IV) with aliphatic hydroxycarboxylic acids (tartaric, malic, citric, gluconic) were studied [12-15]. The least studied are the complexes of this element with carboxylic acids containing aromatic fragments. The optimal synthesis method of Ge(IV) coordination compound with H_4Gal and

DOI: https://doi.org/10.18524/2304-0947.2024.2(88).322127

1,10-phenanthroline (phen) in a water solution was developed. During the X-ray analytics, it was established that [Ge(H_2Gal)$_2$(phen)] is a different-ligand complex with a distorted octahedral polyhedron formed with four oxygen atoms of two gallic acid molecules and two nitrogen atoms of 1,10-phenanthroline. In the crystal, three molecules are bonded between each other through hydrogen bonds and form a three-dimensional net [16].

This work continues these studies; its goal is to synthesize germanium(IV) coordination compounds with gallic acid and ethyl gallate and to research their composition, structure, and properties.

MATERIALS AND METHODS

The starting reagents (all were purchased from Sigma Aldrich) for the synthesis – germanium(IV) oxide (GeO_2, CAS 1310-53-8, 99.99%), gallic acid (**H$_4$Gal**, CAS 149-91-7), ethyl gallate (**H$_3$EtGal,** CAS 831-61-8).

Synthesis. In the synthesis of the compounds various molar ratios Ge : ligand = 1 : 2 and 1 : 3 were tested. A mixture of GeO_2 (10 mmol, 1.046 g), H$_4$Gal (20 mmol, 3,40 g – variant ***a*** and 30 mmol, 5,10 g - – variant ***b***) or **H$_3$EtGal** (20 mmol, mmol, 3,96 g – variant ***a*** and 30 mmol, 5,94 g - – variant ***b***) was dissolved in 500 mL of water under heating and evaporated to a volume of 150 mL. When the solutions were cooled to room temperature, white precipitates of substances **1*a*, 1*a*, 2*b*, 2*b*** formed. They were separated on a Schott filter, washed with water and dried at room temperature.

Elemental analysis was performed in the C,N,H-analyzer Elemental Analyzer CE-440. Germanium content was determined by inductively coupled plasma atomic emission spectroscopy with an Optima 8000 PerkinElmer.

The elemental analysis results of sediments obtained in options ***a*** and ***b*** were identical.

Calculated for $C_{21}H_{16}GeO_{16}$ (**1**) (%): C – 42.24, H – 2.68, Ge – 12.17. Found (%): C – 41.78, H – 2.39, Ge – 12.67.

Calculated for $C_{27}H_{30}GeO_{17}$ (**2**) (%): C – 46.38, H – 4.29, Ge – 10.39. Found (%): C – 45.69, H – 4.31, Ge – 10.55.

Thermogravimetric analysis was performed on a Q-1500D device with a heating rate of 10°C/min in an air atmosphere in the temperature range of 20-1000°C.

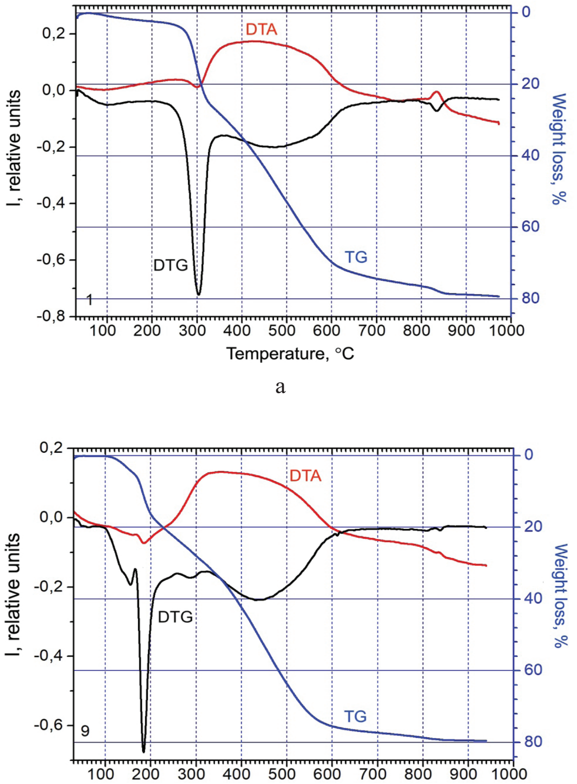
The IR spectra in the range of 4000-400 cm^{-1} were recorded as potassium bromide pellets on a Frontier spectrometer (PerkinElmer). IR spectra were interpreted based on literature data on the characteristic absorption bands of organic molecules [17-19] and complex compounds of germanium(IV) and other metals [12-16, 20].

The ESI mass spectra were taken on TSQ Fortis Triple Quadrupole Mass Spectrometer (ThermoFisher Scientific, USA). Sample solutions in methanol were infused with a Chemyx Fusion 100T2 syringe pump with a 500 µL Hamilton gas-tight syringe no 81265 (1750RNR) at a 20 µL/min flow rate. The electric potential to initiate ESI was 3.0 to 3.5 kV in positive ionisation mode and 2.0 to 2.5 kV in negative ionization mode. The ion transfer tube temperature was set at 300 °C, the vaporiser temperature was set at 150 °C, the sheath gas flow was 20 L/min, and the aux gas flow was 6 L/min. Mass spectra were collected in centroid mode in the m/z range of 50-500 Da using Q1 full scan mode with FWHM resolution set at 0.4 Da at a scan rate of 250 Da/sec. All spectra were measured in methanol-water (1/1, v/v) solutions with complexes about 20-50 μg/mL concentrations. Isotope distribution was calculated using [21].

RESULTS AND DISCUSSION

The complexes **1** and **2** are white homogeneous substances stable in air. The elemental analysis revealed that the complexes have a molar ratio of Germanium : gallic acid (ethyl gallat) = 1:3, regardless of the initial ratio of reactants.

The thermogravimetric study of coordination compounds 1 and 2 showed that the complexes are hydrates. The thermodecomposition of both compounds is similar (fig. 1): in the temperature range of 80-200 °C (for **1**) and 100-170 °C (for **2**), an endothermic effect with a maximum at 100 °C and 150 °C, respectively, is observed (fig. 1). This effect is accompanied by a decrease in mass by 3.10% (Δm_{theor} = 3.02%) for complex **1** and 5.10% (Δm_{theor} = 5.15%) for **2**, which corresponds to one and two molecules of crystallisation water, respectively. The final product at 1000°C is GeO_2 (Δm_{TG} = 79.50%, Δm_{theor} = 82.46% (**1**), Δm_{TG} = 80.0%, Δm_{theor} = 85.00% (**2**)).



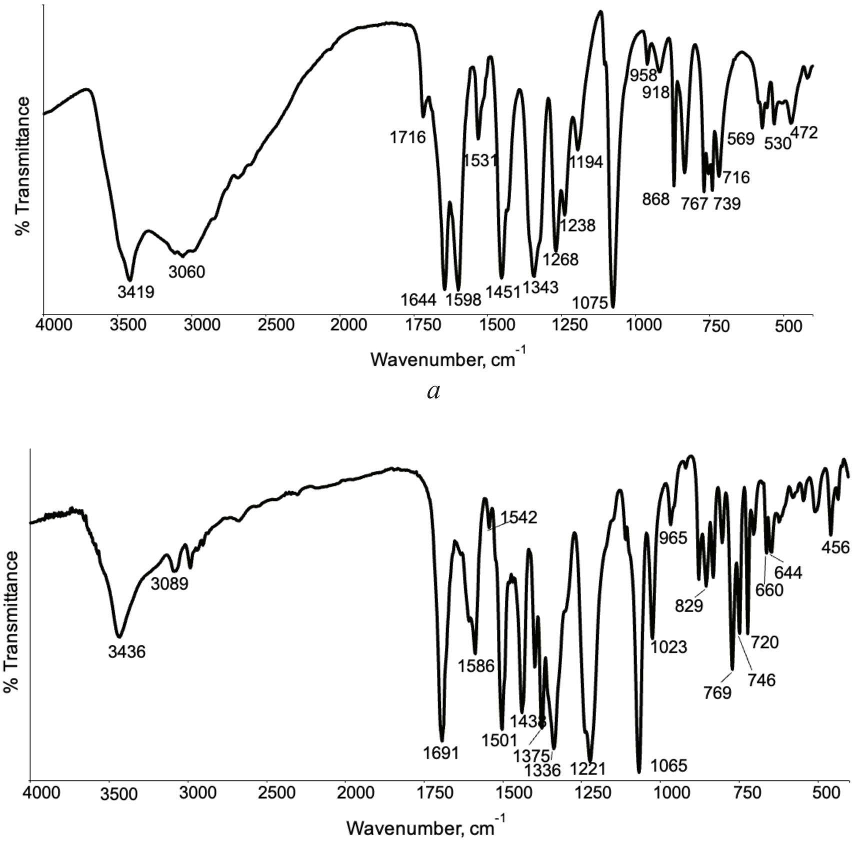
a

b

Fig. 1. Thermogravigrams of complexes **1** (*a*) and **2** (*b*)

When analyzing the IR spectra of **1**, **2** (fig. 2) it was noted that the existence of bound OH groups in the molecules of the complexes is unambiguously determined by the presence of a broad band at 3419 and 3436 cm^{-1}, as well as the Ge-O valence vibrations at 833 (for **1**) and 829 cm^{-1} (for **3**).

The coordination of phenoxy oxygen atoms is accompanied by a split of the C_{ph}-O-H strain vibration band from 1266 cm^{-1} in gallic acid to 1268 and 1238 cm^{-1} in complex **1** and by a low-frequency shift of the bending vibration band from 1257 cm^{-1} in ethyl gallate to 1221 cm^{-1} in complex **2**. The carboxylic group of the gallic acid is uncoordinated because there are no changes in this area (ν(COOH) = 1716 cm^{-1}).



a

b

Fig. 2. IR spectra of complexes **1** (*a*) and **2** (*b*)

The ESI(-) mass spectrum of compound 1 (fig. 3a) in negative polarity contains the signal of the gallic acid anion H_3Gal^- (m/z=169), two signals of the complex anions $[Ge(H_2Gal)_3]^{2-}$ (m/z=289), $[Ge(H_3Gal)(H_2Gal)_2]^-$ (m/z=579) and several signals that can be formed during fragmentation of the complex anion, e.g. m/z=437, 439, 441.

In ESI(-) mass spectrum of complex 2 (fig. 3b) also found the signal of the ligand anion H_2EtGal^- (m/z= 197). The signal with m/z= 330 corresponds to the two-charged anion $[Ge(HEtGal)_3]^{2-}$, with m/z=663 – to the anion $[Ge(H_2EtGal)(HEtGal)_2]^-$. Particles with signals m/z=481, 483, 495 497 are formed due to the fragmentation of the molecule 2.

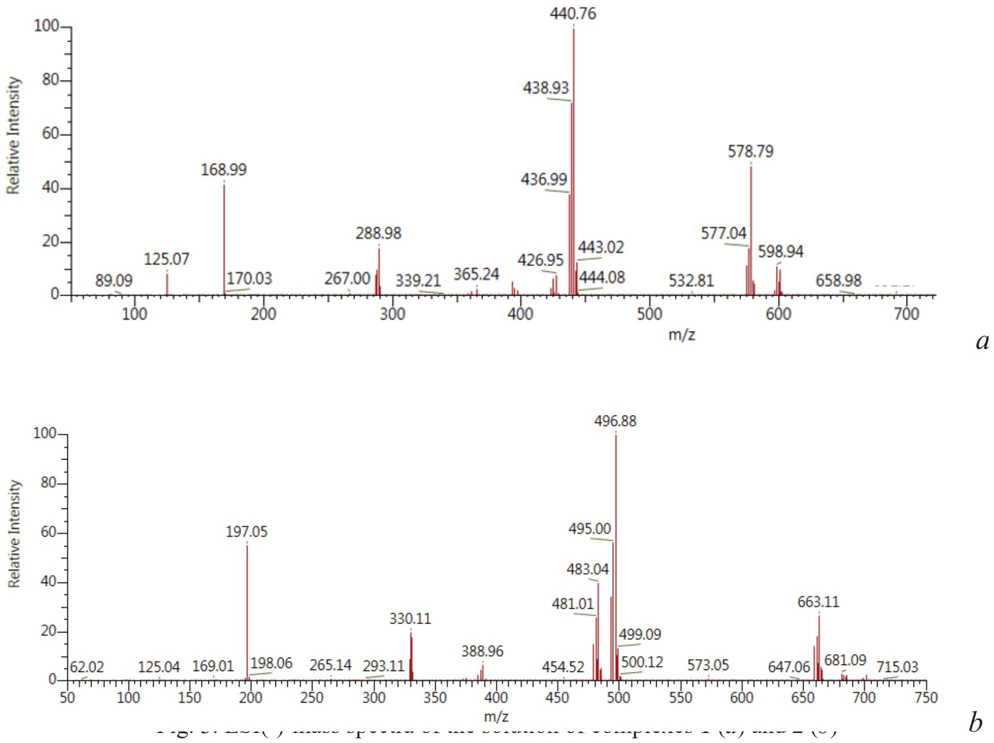


Fig. 3. ESI(-) mass spectra of the solution of complexes 1 (*a*) and 2 (*b*)

Based on the combined results of elemental analysis, thermogravimetry, infrared spectroscopy, and mass spectrometry, considering the coordination number 6 characteristic of Ge(IV), the structure schemes for the synthesized complexes were proposed (Fig. 4).

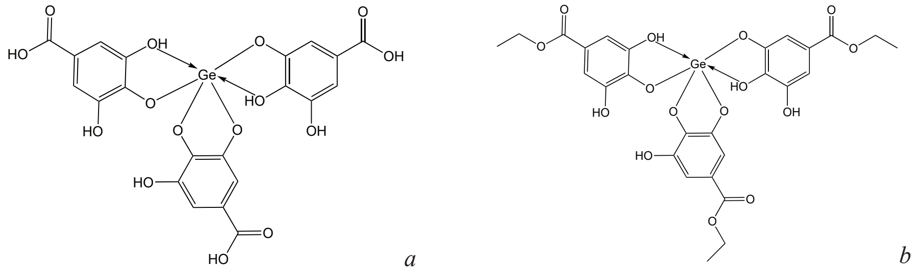


Fig. 4. Schemes of the structures of complexes **1** (*a*) and **2** (*b*)

Thus, the complexes $[[Ge(H_2Gal)(H_3Gal)_2]{\cdot}H_2O$ (1) $[Ge(HEtGal)(H_2EtGal)_2]{\cdot}2H_2O$ (2) have a germanium : H_4Gal (H_3EtGal) ratio of 1:3, in coordination with Germanium(IV) involved two hydroxyl groups from each ligand, forming an octahedral coordination polyhedron of this metal.

REFERENCES

1. *Yen G.-C., Duh P.-D., Tsai H.-L.* Antioxidant and pro-oxidant properties of ascorbic acid and gallic acid // Food Chem. – 2002. – Vol. 79. – P. 307–313. https://doi.org/10.1016/S0308-8146(02)00145-0
2. *Lu Z., Nie G., Belton P.S., Tang H., Zhao B.* Structure-activity relationship analysis of antioxidant ability and neuroprotective effect of gallic acid derivatives // Neurochem. Int. – 2006. – Vol. 48. – P. 263–274. https://doi.org/10.1016/j.neuint.2005.10.010
3. *Kim Y.-J.* Antimelanogenic and Antioxidant Properties of Gallic Acid // Biol. Pharm. Bull. – 2007. – Vol. 30. – P. 1052–1055. https://doi.org/10.1248/bpb.30.1052
4. *Bai J., Zhang Y., Tang C., Hou Y., Ai X., Chen X., Zhang Y., Wang X., Meng X.* Gallic acid: Pharmacological activities and molecular mechanisms involved in inflammation-related diseases // Biomed. Pharmacother. – 2021. – Vol. 133. – P. 110985. https://doi.org/10.1016/j.biopha.2020.110985
5. *Maurya D.K., Nandakumar N., Devasagayam T.P.A.* Anticancer property of gallic acid in A549, a human lung adenocarcinoma cell line, and possible mechanisms // J. Clin. Biochem. Nutr. – 2011. – Vol. 48. – P. 85–90. https://doi.org/10.3164/jcbn.11-004FR
6. *Zhang T., Ma L., Wu P., Li W., Li T., Gu R., Dan X., Li Z., Fan X., Xiao Z.* Gallic acid has anticancer activity and enhances the anticancer effects of cisplatin in non-small cell lung cancer A549 cells via the JAK/STAT3 signaling pathway // Oncol. Rep. – 2019. – Vol. 41. – P. 1779–1788. https://doi.org/10.3892/or.2019.6976
7. *Khorsandi K., Kianmehr Z., Hosseinmardi Z., Hosseinzadeh R.* Anti-cancer effect of gallic acid in presence of low level laser irradiation: ROS production and induction of apoptosis and ferroptosis // Cancer Cell Int. – 2020. – Vol 20, N18. https://doi.org/10.1186/s12935-020-1100-y
8. *Birosova L., Mikulasova M., Vaverkova S.* Antimutagenic effect of phenolic acids // Biomed. Pap. Med. Fac. Univ. Palacky. Olomouc Czech Repub. – 2005. – Vol. 149. – P. 489–491. https://doi.org/10.5507/bp.2005.087
9. *Yun-Choi H., Kim M., Jung Ki.* Esters of substituted benzoic acids as anti-thrombotic agents // Arch. Pharmacal Res. – 1996. – Vol. 19. – P. 66–70. https://doi.org/10.1007/BF02976823
10. *Sigroha S., Lather A., Khatkar A.* Phenolic acid derivatives as preservatives: synthesis, antioxidant, antimicrobial potential and their preservative effectiveness // Int. J. Pharm. Sci. and Res. – 2021. – Vol. 12, N10. – P. 5526–5537. https://doi.org/10.13040/IJPSR.0975-8232.12(10).5526-37
11. *Yoon G., Shim J.-H., Kim H. J., Kim S.-N., Bae M.-S., Cho S., Kim E.* Structure–activity relationship of gallic acid from *Paeonia lactiflora* and its synthetic analogs against human breast cancer cells // Bull. Korean Chem. Soc. – 2022. – Vol. 44, N3. – P. 222–229. https://doi.org/10.1002/bkcs.12657
12. *Martsinko E., Buchko O., Chebanenko E., Seifullina I., Dyakonenko V., Shishkina S.* Different structural types of hetero-metal bis(citrato)germanates with 1,10-phenanthroline: Targeted synthesis, spectral, thermal properties and Hirshfeld surface // J. Mol. Struct. – 2021. – Vol. 1237. – P. 130297. https://doi.org/10.1016/j.molstruc.2021.130297
13. *Seifullina I., Martsinko E., Afanasenko E.* Biocoordination compounds of Germanium(IV): formation of supramolecular salts with tartratogermanate anions. Chapter in book: «Selected Topics in Germanium». – New York: Nova Science Publishers Inc., 2022. – P. 93–126.
14. *Afanasenko E., Seifullina I., Martsinko E., Dyakonenko V., Shishkina S., Gudzenko O., Varbanets L.* Supramolecular organization and enzyme-effector properties of double coordination salts with malatostannate/germanate(IV) anions and Fe(II), Co(II), Ni(II), Cu(II) 1,10-phenanthroline cations // J. Mol. Struct. – 2023. – Vol. 1271. – P. 133996. https://doi.org/10.1016/j.molstruc.2022.133996
15. *Gudzenko O.V., Borzova N.V., Varbanets L.D., Seifullina I.I., Martsinko O.E., Chebanenko O.A.* Germanium(IV) Complexes with Gluconic Acid as Effectors of Penicillium tardum and Eupenicillium erubescens α-LRhamnosidases // Microbiol. J. – 2023. – Vol. 85, N4. – P. 58–65. https://doi.org/10.15407/microbiolj85.04.058
16. *Марцинко О.Е., Чебаненко О.А., Сейфулліна І.Й., Дьяконенко В.В., Шишкіна С.В., Кім Ю.Р., Громова М.І.* Різнолігандні комплекси германію(IV) з мигдальною, галовою кислотами та гетероциклічними амінами // Вісник ОНУ. Хімія. – 2018. – Т. 23, № 3. – С. 86–95. http://dx.doi.org/10.18524/2304-0947.2018.3(67).140803

17. *Bellamy L.J.* The Infra-red spectra of complex molecules. London: Chapman and Hall, 1975. – 433 p. https://doi.org/10.1007/978-94-011-6017-9
18. *ІЧ-спектр* галової кислоти https://www.chemicalbook.com/SpectrumEN_149-91-7_IR1.htm
19. *ІЧ-спектр* етилгалату https://www.chemicalbook.com/SpectrumEN_831-61-8_IR1.htm
20. *Motloung D., Mashele S., Matowane R., Swain S., Bonnet S., Noreljaleel A., Oyedemi S., Chukwuma C.* Synthesis, characterization, antidiabetic and antioxidative evaluation of a novel Zn(II)-gallic acid complex with multi-facet activity: Antidiabetic effect of Zn(II)-gallic acid complex // J. Pharm. Pharmacol. – 2020. – Vol. 72, N 10. – P. 1412–1426. https://doi.org/10.1111/jphp.13322
21. *Isotope* Distribution Calculator and Mass Spec Plotter https://www.sisweb.com/mstools/isotope.htm

Стаття надійшла до редакції 23.10.2024

М. А. Мартинюк, О. Е. Марцинко
Одеський національний університет імені І. І. Мечникова, кафедра неорганічної хімії та хімічної освіти, вул. Дворянська, 2, м. Одеса, 65082, Україна; e-mail: lborn@ukr.net

СИНТЕЗ ТА ДОСЛІДЖЕННЯ КООРДИНАЦІЙНИХ СПОЛУК ГЕРМАНІЮ(IV) З ГАЛОВОЮ КИСЛОТОЮ ТА ЕТИЛГАЛАТОМ

Розроблено оптимальні методи синтезу комплексів Германію(IV) з галовою кислотою (H_4Gal) та етилгалатом (H_3EtGal) у водному розчині. Сполуки охарактеризовано сучасними методами дослідження: елементним аналізом, термогравіметрією, інфрачервоною спектроскопією, мас-спектрометрією. Комплекси $[Ge(H_2Gal)(H_3Gal)_2]\cdot H_2O$ (**1**) $[Ge(HEtGal)(H_2EtGal)_2]\cdot 2H_2O$ (**2**) є білими однорідними речовинами, стійкими на повітрі. Встановлено, що в сполуках реалізується мольне співвідношення германій : галова кислота (етилгалат) = 1:3 незалежно від вихідного співвідношення реагентів. Термогравіметричне дослідження координаційних сполук показало, що комплекси є гідратами. Терморозпад обох сполук подібний, в інтервалі температур 80-200 °C спостерігається ендотермічний ефект, який супроводжується зменшенням маси на 3,10% для комплексу 1 і на 5,10% для 2, що відповідає одній і двом молекулам кристалізаційної води. При аналізі ІЧ-спектрів комплексів доведена наявність зв’язаних ОН-груп в їх молекулах, їх координація до Германію визначається як смугою валентних коливань ν(Ge-O), так і розщепленням смуги деформаційних коливань $\delta(C_{ph}\text{-O-H}) = 1266$ см$^{-1}$ у галовій кислоті до 1268 і 1238 см$^{-1}$ у комплексі 1 та низькочастотним зміщенням смуги коливань деформацій від 1257 см$^{-1}$ в етилгалаті до 1221 см$^{-1}$ в комплексі 2. Карбоксильна група галової кислоти некоординована, про що свідчить смуга ν(COOH) = 1716 см$^{-1}$. Мас-спектр ESI(-) сполуки 1 містить сигнал аніону галової кислоти H_3Gal^- (m/z = 169), два сигнали комплексних аніонів $[Ge(H_2Gal)_3]^{2-}$ (m/z = 289), $[Ge(H_3Gal)(H_2Gal)_2]^-$ (m/z = 579) та кілька сигналів, які можуть формуватися під час фрагментації комплексного аніону. У мас-спектрі ESI(-) комплексу 2 також виявлено сигнал аніону ліганду H_2EtGal^- (m/z = 197). Сигнал з m/z = 330 відповідає двозарядному аніону $Ge(HEtGal)_3]^{2-}$, з m/z = 663 – аніону $[Ge(H_2EtGal)(HEtGal)_2]^-$. Частинки з сигналами m/z = 481, 483, 495 497 утворюються внаслідок фрагментації молекули 2. Показано, що у сполуках в координації з Германієм(IV) беруть участь дві гідроксильні групи від кожного ліганду, утворюючи октаедричний координаційний поліедр.

Ключові слова: Германій, галова кислота, етилгалат, координаційні сполуки, ІЧ спектроскопія, термогравіметричний аналіз, ESI мас-спектрометрія.

REFERENCES

1. Yen G.-C., Duh P.-D., Tsai H.-L. *Antioxidant and pro-oxidant properties of ascorbic acid and gallic acid*. Food Chem. 2002, vol. 79, pp. 307–313. https://doi.org/10.1016/S0308-8146(02)00145-0
2. Lu Z., Nie G., Belton P.S., Tang H., Zhao B. *Structure-activity relationship analysis of antioxidant ability and neuroprotective effect of gallic acid derivatives.* Neurochem. Int. 2006, vol. 48, pp. 263–274. https://doi.org/10.1016/j.neuint.2005.10.010
3. Kim Y.-J. *Antimelanogenic and Antioxidant Properties of Gallic Acid*. Biol. Pharm. Bull. 2007, vol. 30, pp. 1052–1055. https://doi.org/10.1248/bpb.30.1052
4. Bai J., Zhang Y., Tang C., Hou Y., Ai X., Chen X., Zhang Y., Wang X., Meng X. *Gallic acid: Pharmacological activities and molecular mechanisms involved in inflammation-related diseases*. Biomed. Pharmacother. 2021, vol. 133, pp. 110985. https://doi.org/10.1016/j.biopha.2020.110985
5. Maurya D.K., Nandakumar N., Devasagayam T.P.A. *Anticancer property of gallic acid in A*549*, a human lung adenocarcinoma cell line, and possible mechanisms*. J. Clin. Biochem. Nutr. 2011, vol. 48, pp. 85–90. https://doi.org/10.3164/jcbn.11-004FR
6. Zhang T., Ma L., Wu P., Li W., Li T., Gu R., Dan X., Li Z., Fan X., Xiao Z. *Gallic acid has anticancer activity and enhances the anticancer effects of cisplatin in non-small cell lung cancer A*549 *cells via the JAK/STAT*3 *signaling pathway*. Oncol. Rep. 2019, vol. 41, pp. 1779–1788. https://doi.org/10.3892/or.2019.6976
7. Khorsandi K., Kianmehr Z., Hosseinmardi Z., Hosseinzadeh R. *Anti-cancer effect of gallic acid in presence of low level laser irradiation: ROS production and induction of apoptosis and ferroptosis*. Cancer Cell Int. 2020, vol. 20, no 18. https://doi.org/10.1186/s12935-020-1100-y
8. Birosova L., Mikulasova M., Vaverkova S. *Antimutagenic effect of phenolic acids.* Biomed. Pap. Med. Fac. Univ. Palacky. Olomouc Czech Repub. 2005, vol. 149, pp. 489–491. https://doi.org/10.5507/bp.2005.087
9. Yun-Choi H., Kim M., Jung Ki. *Esters of substituted benzoic acids as anti-thrombotic agents*. Arch. Pharmacal Res. 1996, vol. 19, pp. 66–70. https://doi.org/10.1007/BF02976823
10. Sigroha S., Lather A., Khatkar A. *Phenolic acid derivatives as preservatives: synthesis, antioxidant, antimicrobial potential and their preservative effectiveness.* Int. J. Pharm. Sci. and Res. 2021, vol. 12, no 10, pp. 5526–5537. https://doi.org/10.13040/IJPSR.0975-8232.12(10).5526-37
11. Yoon G., Shim J.-H., Kim H. J., Kim S.-N., Bae M.-S., Cho S., Kim E. *Structure–activity relationship of gallic acid from Paeonia lactiflora and its synthetic analogs against human breast cancer cells*. Bull. Korean Chem. Soc. 2022, vol. 44, no 3, pp. 222–229. https://doi.org/10.1002/bkcs.12657
12. Martsinko E., Buchko O., Chebanenko E., Seifullina I., Dyakonenko V., Shishkina S. *Different structural types of hetero-metal bis(citrato)germanates with* 1,10-*phenanthroline: Targeted synthesis, spectral, thermal properties and Hirshfeld surface*. J. Mol. Struct. 2021, vol. 1237. pp. 130297. https://doi.org/10.1016/j.molstruc.2021.130297
13. Seifullina I., Martsinko E., Afanasenko E. *Biocoordination compounds of Germanium(IV): formation of supramolecular salts with tartratogermanate anions.* Chapter in book: «Selected Topics in Germanium». New York: Nova Science Publishers Inc., 2022, pp. 93–126.
14. Afanasenko E., Seifullina I., Martsinko E., Dyakonenko V., Shishkina S., Gudzenko O., Varbanets L. *Supramolecular organization and enzyme-effector properties of double coordination salts with malatostannate/germanate(IV) anions and Fe(II), Co(II), Ni(II), Cu(II)* 1,10-*phenanthroline cations*. J. Mol. Struct. 2023, vol. 1271, pp. 133996. https://doi.org/10.1016/j.molstruc.2022.133996
15. Gudzenko O.V., Borzova N.V., Varbanets L.D., Seifullina I.I., Martsinko O.E., Chebanenko O.A. *Germanium(IV) Complexes with Gluconic Acid as Effectors of Penicillium tardum and Eupenicillium erubescens α-LRhamnosidases*. Microbiol. J. 2023, vol. 85, no 4. pp. 58–65. https://doi.org/10.15407/microbiolj85.04.058
16. Martsinko O.E., Chebanenko O.A., Seifullina I.I., Dyakonenko V.V., Shishkina S.V. *Different-ligand complexes of Germanium(IV) with mandelic, gallic acids and heterocyclic amines*. Visn. Odes. nac. univ., Him. 2018, vol. 23, no 3, pp. 86–95. http://dx.doi.org/10.18524/2304-0947.2018.3(67).140803
17. Bellamy L.J. *The Infra-red spectra of complex molecules.* London: Chapman and Hall, 1975. 433 p. https://doi.org/10.1007/978-94-011-6017-9
18. *IR spectrum of gallic acid* https://www.chemicalbook.com/SpectrumEN_149-91-7_IR1.htm
19. *IR spectrum of ethyl gallate* https://www.chemicalbook.com/SpectrumEN_831-61-8_IR1.htm
20. Motloung D., Mashele S., Matowane R., Swain S., Bonnet S., Noreljaleel A., Oyedemi S., Chukwuma C. *Synthesis, characterization, antidiabetic and antioxidative evaluation of a novel Zn(II)-gallic acid complex with multi-facet activity: Antidiabetic effect of Zn(II)-gallic acid complex*. Journal of Pharm. Pharmacol., 2020, vol. 72, no 10, pp. 1412–1426. https://doi.org/10.1111/jphp.13322
21. *Isotope Distribution Calculator and Mass Spec Plotter* https://www.sisweb.com/mstools/isotope.htm