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**O. E. Martsynko<sup>1</sup>, O. A. Finik<sup>2</sup>, I. I. Seifullina<sup>1</sup>, V. V. Dyakonenko<sup>3</sup>,  
S. V. Shishkina<sup>3,4</sup>, A. M. Morozov<sup>1</sup>**<sup>1</sup>Odesa I. I. Mechnikov National University, Department of Inorganic Chemistry and Chemical Education, 2 Dvorianska St, Odesa, 65082, Ukraine; e-mail: [lborn@ukr.net](mailto:lborn@ukr.net)<sup>2</sup>LLC "INSPECTORAT UKRAINE", ave. Udilny, 1, Odesa, 65044, Ukraine<sup>3</sup>SSI "Institute for Single Crystals", National Academy of Sciences of Ukraine, Nauki Ave 60, Kharkov, 61001, Ukraine<sup>4</sup>Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Academician Kukhar str., 5, Kyiv-94, 02660, Ukraine

## SYNTHESIS AND STRUCTURE OF SUPRAMOLECULAR GLUCONATOGERMANATES(IV) WITH NITROGEN-CONTAINING ORGANIC CATIONS

Optimal methods of synthesis of germanium(IV) complexes with gluconic acid ( $H_6\text{Gluc}$ ) and exo-ligands niacin (Nic), niamide (Nad) and isoniazid (Ind) in aqueous solution were developed. The structure and stereochemistry of the presented complexes were stated by elemental analyses, thermal analysis, IR spectroscopy and single crystal X-ray analysis. It was shown the formation of supramolecular salts of the composition  $(\text{NicH})_2[\text{Ge}_2(\text{OH})_2(\mu\text{-H}_2\text{Gluc})_2] \cdot 3\text{H}_2\text{O}$  (**1**),  $(\text{NadH})_2[\text{Ge}_2(\text{OH})_2(\mu\text{-H}_2\text{Gluc})_2] \cdot 3\text{H}_2\text{O}$  (**2**),  $(\text{IndH})_2[\text{Ge}_2(\text{OH})_2(\mu\text{-H}_2\text{Gluc})_2]$  (**3**). It was established that complex **2** consists of two protonated niamide molecules and a complex anion in which two germanium atoms are coordinated by two bridging ligands of deprotonated gluconic acid  $H_5\text{Gluc}^-$ . The trigonal-bipyramidal polyhedron of Ge(IV) is additionally formed by the coordination of the hydroxyl group. In the crystalline phase, the complex exists as a trihydrate.

**Key words:** germanium, gluconic acid, coordination compounds, niacin, niamide, isoniazid, IR spectroscopy, X-ray analysis.

Gluconic (pentahydroxyhexanoic,  $H_6\text{Gluc}$ ) acid occurs naturally in plants, fruits, wine, honey, rice and other natural sources. Its physiologically active D-form, formed at microbial oxidation of glucose, is a non-toxic organic compound that readily decomposes in soil (98% within 2 days) [1].

The interaction of this acid with alkaline earth and 3d-metals is actively studied, as its salts and coordination compounds exhibit pharmacological properties. Thus, calcium gluconate normalizes the disturbed balance of potassium and sodium in the myocardium in coronary insufficiency and exhibits an antiarrhythmic effect in heart ischemia [2], and also has a positive effect on the activity of enzymes of the brush border of the intestines of animals [3]. The copper(II) complex  $[\text{Cu}(\text{DPQ})(\text{H}_4\text{Gluc})] \cdot 2\text{H}_2\text{O}$  (DPQ – pyrazino-[2,3-f][1,10]-phenanthroline) is able to bind to DNA by intercalation and exhibits better antitumor activity against liver cancer cells than cisplatin *in vitro* [4].

A number of complex compounds of gluconic acid with f-elements have been obtained and investigated by potentiometry, mass-spectrometry, UV-Vis spectrophotometry, Raman and  $^1\text{H}$  and  $^{13}\text{C}$  NMR [5, 6]. It has been proved that the ligand is coordinated to Pr(III) and Nd(III) by deprotonated carboxyl and two hydroxyl groups at C2 and C3. At the same time, neodymium forms compounds with bi-  $([\text{Nd}_2(\text{H}_4\text{Gluc})_4]^{2-}, [\text{Nd}_2(\text{H}_4\text{Gluc})_3(\text{H}_3\text{Gluc})]^{3-},$

$[\text{Nd}_2(\text{H}_4\text{Gluc})_2(\text{H}_3\text{Gluc})_2]^{4+}$  and mononuclear  $([\text{Nd}(\text{H}_4\text{Gluc})_2(\text{H}_3\text{Gluc})]^{4+}, [\text{Nd}(\text{H}_4\text{Gluc})(\text{H}_3\text{Gluc})]^{4+})$  anions [6].

The existence of 2 to 10 forms of aluminum(III) complexes with D-gluconic acid in solution has been demonstrated, and the compound  $[\text{Al}(\text{H}_4\text{Gluc})(\text{H}_3\text{Gluc})] \cdot 2\text{H}_2\text{O}$  with tridentate coordination of ligand molecules has been characterized in the solid state [7]. Potentiometric and voltammetric measurements in the  $\text{Sn}^{2+} - \text{H}_6\text{Gluc}$  system have been determined the existence of complexes of the composition  $[\text{SnH}_5\text{Gluc}]^+ [\text{Sn}(\text{H}_5\text{Gluc})_2]$  and  $[\text{Sn}(\text{OH})(\text{H}_5\text{Gluc})]$  with the highest formation constant for the first [8].

Based on the above data, it can be concluded that the advantages of gluconic acid are not only high biological activity, low toxicity, but also its features as a polydentate chelating ligand. The presence of many donor centers in the molecule and their spatial organization selective for each metal ion, contribute to the formation of complexes of various forms and structures, in particular, mono- and binuclear complexes.

However, at present, the number of investigated metalochelates with gluconic acid is not large. There is no information about essential germanium, whose biocoordination compounds with polyhydropolycarboxylic acids (tartaric, malic, xylic, citric) the authors have been engaged in for many years [9–11].

The presented work is a logical continuation of these studies, its goal is to develop methods and obtain coordination compounds of germanium(IV) with gluconic acid and exo-ligands, to determine their composition, structure and properties.

#### Materials and methods

The starting reagents for the synthesis – germanium(IV) oxide ( $\text{GeO}_2$ , CAS1310–53–8, 99.99%), gluconic acid (50% aqueous solution, CAS527–07–1), niacin (nicotinic acid,  $\text{C}_6\text{H}_5\text{NO}_2$ , CAS59–67–6, 99%), niamide (nicotinamide,  $\text{C}_6\text{H}_6\text{N}_2\text{O}$ , CAS98–92–0, 99.5%), isoniazid ( $\text{C}_6\text{H}_7\text{N}_3\text{O}$ , CAS54–85–3, 99%) (all were purchased from Sigma Aldrich).

*Synthesis.* A portion of  $\text{GeO}_2$  (6.2 mmol, 0.65 g) was dissolved in 200 ml of distilled water (90 °C), then 2.05 ml (6.2 mmol) of a 50% aqueous solution of gluconic acid was added, stirred and slowly evaporated at 80 °C to volume 20 ml. After cooling to 25 °C (pH = 2.5–3), an equimolar amount of Nic (Nad, Ind) was added and stirred till the reagent was completely dissolved. Precipitates of complex compounds were formed a day after the addition of 10 ml of ethanol, they were separated on a glass Schott filter and dried in air at 20–25 °C. Yield: 62–70%.

Single crystals of compound **2** for X-ray analysis were grown by the method of slow diffusion of ethanol vapors into an aqueous solution of the complex.

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

Calculated for  $\text{C}_{24}\text{H}_{36}\text{Ge}_2\text{N}_2\text{O}_{23}$  (**1**) (%): C – 33.28, H – 4.16, Ge – 16.78, N – 3.24. Found (%): C – 33.65, H – 4.24, Ge – 16.60, N – 3.16.

Calculated for  $\text{C}_{24}\text{H}_{38}\text{Ge}_2\text{N}_4\text{O}_{21}$  (**2**) (%): C – 33.34, H – 4.40, Ge – 16.81, N – 6.48. Found (%): C – 33.23, H – 4.34, Ge – 16.75, N – 6.33.

Calculated for  $\text{C}_{24}\text{H}_{34}\text{Ge}_2\text{N}_6\text{O}_{18}$  (**3**) (%): C – 34.31, H – 4.05, Ge – 17.30, N – 10.01. Found (%): C – 34.21, H – 4.00, Ge – 16.99, N – 9.92.

*Thermoanalytical curves* (DTA, DTG, TG) were obtained on the Q-1500 D derivatograph of the Paulik-Paulik-Erdey system. Sample heating rate – 10 degrees/min, sample loading –

150 mg, standard – calcined aluminum oxide, platinum crucible, static air atmosphere, temperature range 20–1000 °C.

The IR spectra in the range of 4000–400 cm<sup>-1</sup> 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 and complex compounds of germanium(IV) [9–12].

IR spectrum **1** (ν, cm<sup>-1</sup>): 3409 ν(OH), 1689 ν<sub>as</sub>(COO<sup>-</sup>), 1589 ν(C-N), 1440 ν<sub>s</sub>(COO<sup>-</sup>), 1260 δ(C-OH), 1135 δ(C-O), 1080 ν(C-O), 822 δ(Ge-OH), 669 ν(Ge-O).

IR spectrum **2** (ν, cm<sup>-1</sup>): 3443 ν(OH), 1687 ν<sub>as</sub>(COO<sup>-</sup>), 1641 δ(NH<sub>2</sub>), 1604 ν(C-N), 1459 ν<sub>s</sub>(COO<sup>-</sup>), 1263 δ(C-OH), 1132 δ(C-O), 1075 ν(C-O), 819 δ(Ge-OH), 680 ν(Ge-O).

IR spectrum **3** (ν, cm<sup>-1</sup>): 1693 ν<sub>as</sub>(COO<sup>-</sup>), 1640 δ(NH<sub>2</sub>), 1579 ν(C-N), 1438 ν<sub>s</sub>(COO<sup>-</sup>), 1262 δ(C-OH), 1130 δ(C-O), 1078 ν(C-O), 820 δ(Ge-OH), 672 ν(Ge-O).

*X-ray structural analysis.* Crystals of compound **2** (C<sub>12</sub>H<sub>18</sub>Ge<sub>2</sub>O<sub>16</sub>·2C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>O<sup>+1</sup>, 3H<sub>2</sub>O) are monoclinic, at 294 K, *a* = 8.1501(18), *b* = 20.098(5), *c* = 11.021(2) Å, β = 94.19(2)°, *V* = 1800.4(7) Å<sup>3</sup>, *M<sub>r</sub>* = 863.76, *Z* = 2, space group *P2*<sub>1</sub>, *d*<sub>calc</sub> = 1.593 g/cm<sup>3</sup>, μ(MoKα) = 1.757 mm<sup>-1</sup>, *F*(000) = 884. The unit cell parameters and intensity of 15440 reflections (7792 independent, *R*<sub>int</sub> = 0.0942) were measured on an Xcalibur-3 diffractometer (graphite monochromated MoKα radiation, CCD detector, ω-scanning, 2θ<sub>max</sub> = 55°).

The structure was deciphered by the direct method using the SHELXTL complex of programs [13]. Full-matrix least-squares refinement against *F*<sup>2</sup> in anisotropic approximation was used for the non-hydrogen atoms to *wR*<sub>2</sub> = 0.191 to 7792 reflection (*R*<sub>1</sub> = 0.074 to 6025 reflection with *F* > 4 σ(*F*), *S* = 1.061). Positions of the hydrogen atoms were located from electron density difference maps and refined by the “riding” model with *U*<sub>iso</sub> = *nU*<sub>eq</sub> of the carrier atom (*n* = 1.5 for hydroxyl groups and water molecules and *n* = 1.2 for other hydrogen atoms). Atomic coordinates as well as complete tables of bond lengths and valence angles have been deposited with the Cambridge Crystallographic Data Bank (e-mail: deposit@ccdc.cam.ac.uk) and are available under reference number CCDC 2324990.

## RESULTS AND DISCUSSION

According to the results of the elemental analysis, the molar ratio of the elements in the compounds is Ge : N = 1:1 (**1**), 1:2 (**2**), 1:3 (**3**), so they have the same molar ratio of Ge : gluconate : Nic (Nad, Ind) = 1:1:1.

Thermal decomposition of compounds **1** and **2** (fig. 1a) begins with an endothermic effect in the temperature range of 80–150 °C at which three molecules of water of crystallization are eliminated into the gas phase (Δ*m* = 6.50%, Δ*m* = 6.24% (**1**), (Δ*m* = 6.50%, Δ*m* = 6.25% (**2**)), the presence of which is confirmed by IR spectroscopy data (bands ν(H O) at 3409 and 3443 cm<sup>-1</sup>, for **1** and **2**, respectively). Compound **3** (fig. 1b) is not a crystal hydrate, as evidenced by the absence of effects on thermogravimogram of the complex up to 220 °C.

Subsequently, the thermal decomposition of the complexes occurs in the same way: an endo-effect is observed in the range of 200–300 °C, accompanied by the removal of Nic, Nad, Ind molecules, which turns into a number of exo-effects corresponding to the

oxidative thermal destruction of the organic part of the molecules of the complexes. The final product at 1000°C is GeO ( $\Delta m = 78.00\%$ ,  $\Delta m = 75.83\%$  (1),  $\Delta m = 77.00\%$ ,  $\Delta m = 75.77\%$  (2),  $\Delta m = 75.00\%$ ,  $\Delta m = 75.08\%$  (3)).

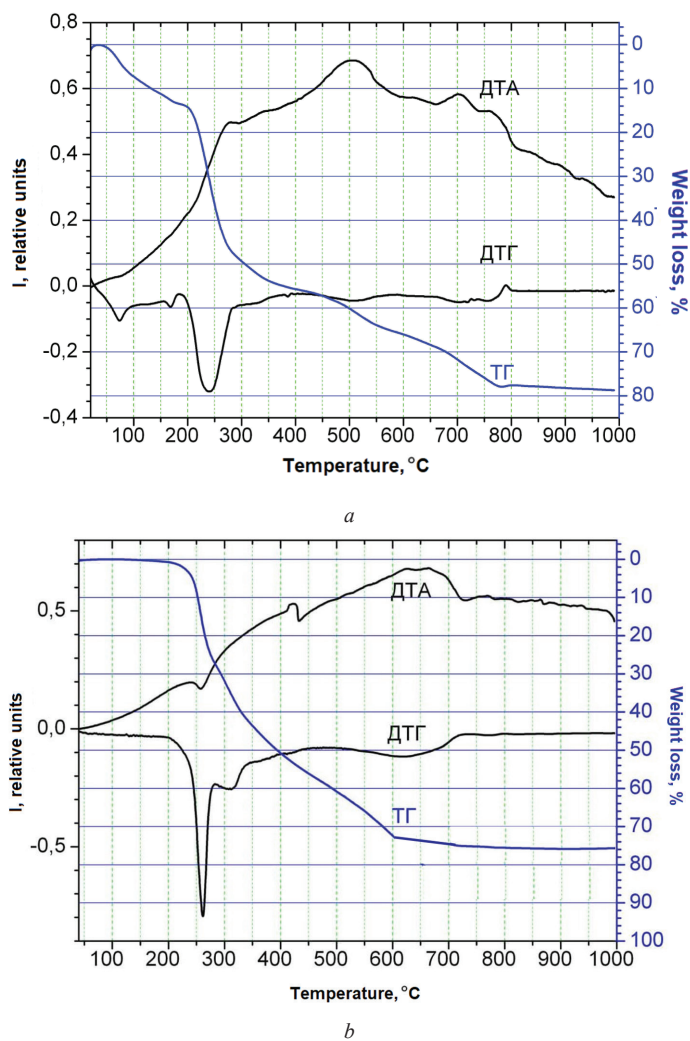


Fig. 1. Thermogravigrams of complexes 1 (a) and 3 (b)

IR spectra of compounds 1-3 are similar in the area of the bands corresponding to bond vibrations in the germanium coordination polyhedron. The presence of  $\nu_{as}(\text{COO}^-)$  and  $\nu_s(\text{COO}^-)$  bands, typical for carboxylate ions, indicates the deprotonation of the COOH group of gluconic acid and its binding to Ge, which is confirmed by the appearance of the  $\nu(\text{Ge-O})$  band. The presence of bands  $\delta(\text{C-O})$ ,  $\nu(\text{C-O})$  of

alcoholate type and preservation  $\delta(\text{C-OH})$  indicate the non-equivalence of hydroxyl groups in the complexes – free and coordinated to germanium. In the compounds the hydrolyzed form of Ge is realized, which correlates with the presence of deformation vibrations  $\delta(\text{Ge-OH})$ . A comparative analysis of the IR spectra of complexes **1-3** and the original nitrogen-containing molecules Nic, Nad, Ind showed that the formation of supramolecular salts occurs due to the protonation of the nitrogen atom of the pyridine ring. There is an increase in the frequencies of its vibrations  $\nu(\text{CN})$  by 19-24  $\text{cm}^{-1}$  (1570, 1580, 1555  $\text{cm}^{-1}$  for Nic, Nad, Ind and 1589, 1604, 1579  $\text{cm}^{-1}$  for **1**, **2**, **3**, respectively), at the same time, there are no changes in the region of the band of deformation oscillations  $\delta(\text{NH}_2)$  at 1640  $\text{cm}^{-1}$  for complexes **2** and **3**.

According to X-ray structural analysis, the complex  $(\text{NadH})_2[\text{Ge}_2(\text{OH})_2(\mu\text{-H}_2\text{Gluc})_2]\cdot 3\text{H}_2\text{O}$  (**2**) is a supramolecular salt with a complex anion  $[\text{Ge}_2(\text{OH})_2(\mu\text{-H}_2\text{Gluc})_2]^{2-}$  and two protonated molecules of nicotinamide  $\text{NadH}^+$  as cations (fig. 2). In the crystal, the complex exists in the form of a trihydrate.

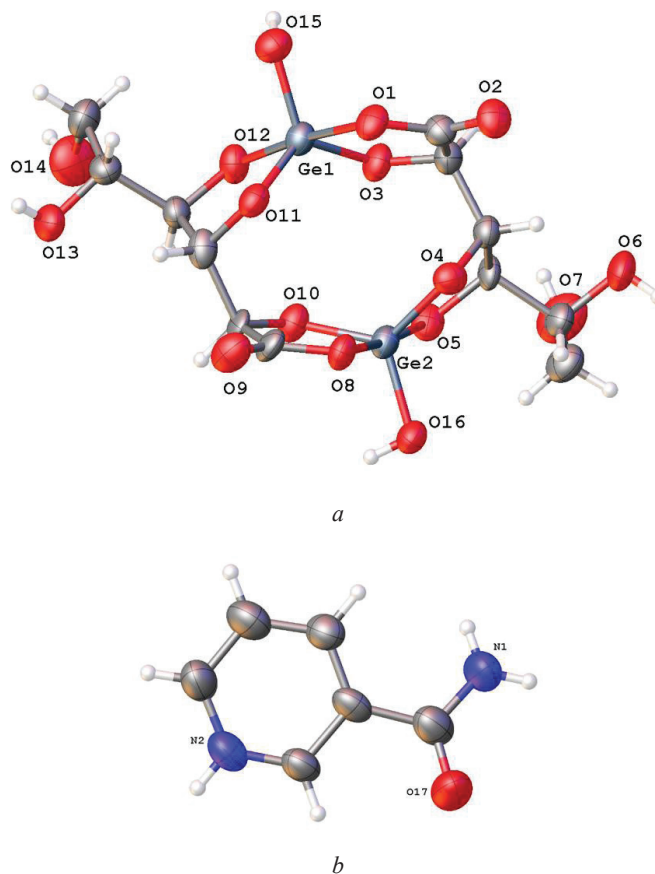


Fig. 2. Molecular structure of the anion  $[\text{Ge}_2(\text{OH})_2(\mu\text{-H}_2\text{Gluc})_2]^{2-}$  (a) and the cation  $\text{NadH}^+$  (b) in structure **2**

In the complex anion each of the two partially deprotonated gluconic acid molecules is coordinated to two Ge atoms. The coordination polyhedrons of Ge1 and Ge2 atoms are distorted trigonal bipyramid, which formed in the equatorial position by atoms O3, O11, O15 (atom Ge1) or atoms O4, O10, O16 (atom Ge2). In the axial position in the coordination polyhedron of Ge1 there are atoms O1 and O12, and atoms O5 and O8 of Ge2. Thus, each Ge atom connects with two deprotonated hydroxyl groups of one ligand and deprotonated hydroxyl and carboxyl groups of the second ligand, as well as a hydroxo-group (fig. 2). Bond lengths Ge–O vary within 1.813(8)÷1.851(8) Å and 1.911(7)÷2.003(7) Å for the equatorial and axial positions respectively (tab. 1).

It should be noted that the described dimeric the gluconatogermanate anion is similar to the complex tartrate and xylaratogermanate anions were characterized earlier [12].

Table 1

Selected bond lengths (Å) in structure 2

Connection	Length, Å	Connection	Length, Å
Ge1—O1	2.003(7)	Ge2—O4	1.848(7)
Ge1—O3	1.836(8)	Ge2—O5	1.911(7)
Ge1—O11	1.822(8)	Ge2—O8	1.977(7)
Ge1—O12	1.912(7)	Ge2—O10	1.851(8)
Ge1—O15	1.813(8)	Ge2—O16	1.833(8)

In the crystalline phase, anions, cations, and water molecules are connected by numerous hydrogen bonds (tab. 2) and form a three-dimensional network.

Table 2

Geometric characteristics of hydrogen bonds in structure 2 (symmetry operations (i)  $-x+1, y+1/2, -z+1$ ; (ii)  $-x+2, y+1/2, -z$ ; (iii)  $x-1, y, z$ ; (iv)  $x, y, z-1$ )

$D-H\cdots A$	$H\cdots A, \text{Å}$	$D\cdots A, \text{Å}$	$D-H\cdots A, \text{deg}$
O13—H13 $\cdots$ O16 <sup>i</sup>	1.98	2.800(12)	177
O14—H14 $\cdots$ O19 <sup>ii</sup>	2.14	2.870(15)	148
O16—H16 $\cdots$ O2 <sup>iii</sup>	2.20	2.807(11)	128
O19—H19A $\cdots$ O17	2.04	2.867(18)	140
O19—H19B $\cdots$ O20	2.05	2.789(15)	143
O20—H20B $\cdots$ O6	2.14	2.861(16)	142
O21—H21A $\cdots$ O18	2.02	2.805(14)	152
N2—H2A $\cdots$ O12	1.89	2.741(12)	172
N3—H3B $\cdots$ O9 <sup>iv</sup>	2.02	2.863(13)	167
N4—H4A $\cdots$ O5	1.87	2.713(12)	168

Thus, based on the results of a set of research methods, including X-ray diffraction, it can be concluded that complexes **1-3** are supramolecular salts of the stable complex acid  $H_2[Ge_2(OH)_2(\mu-H_2Gluc)_2]$  existing in solution. This opens up the prospects of obtaining on its basis coordination compounds with cations of various biometals, researching their pharmacological action and determining directions of medical application.

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О. Е. Марцинко<sup>1</sup>, О. А. Фінік<sup>2</sup>, І. Й. Сейфулліна<sup>1</sup>, В. В. Дьяконенко<sup>3</sup>,  
С. В. Шишкіна<sup>3,4</sup>, А. М. Морозов<sup>1</sup>

<sup>1</sup>Одеський національний університет імені І.І. Мечникова, кафедра неорганічної хімії та хімічної освіти, вул. Дворянська 2, Одеса, 65082, Україна; e-mail: lborn@ukr.net

<sup>2</sup>Випробувальний центр ТОВ «ІНСПЕКТОРАТ УКРАЇНА», Удільний провулок, 1, Одеса, 65044, Україна

<sup>3</sup>ДНУ НТК «Інститут монокристалів» НАН України, пр. Науки 60, 61001, Харків, Україна

<sup>4</sup>Інститут органічної хімії НАН України, вул. Академіка Кухаря, 5, Київ, 02660, Україна

## СИНТЕЗ ТА БУДОВА СУПРАМОЛЕКУЛЯРНИХ ГЛЮКОНАТОГЕРМАНАТІВ(IV) З НІТРОГЕНВМІСНИМИ ОРГАНІЧНИМИ КАТІОНАМИ

Розроблено оптимальні методики синтезу комплексів германію(IV) з глюконою кислотою ( $H_6\text{Gluc}$ ) та екзо-лігандами ніотиною кислотою ( $\text{Nic}$ ), нікотинамідом ( $\text{Nad}$ ) та ізоніазидом ( $\text{Ind}$ ) у водному розчині. Показано, що утворюються супрамолекулярні солі складу  $(\text{NicH})_2[\text{Ge}_2(\text{OH})_2(\mu\text{-H}_2\text{Gluc})_2]\cdot 3\text{H}_2\text{O}$  (**1**),  $(\text{NadH})_2[\text{Ge}_2(\text{OH})_2(\mu\text{-H}_2\text{Gluc})_2]\cdot 3\text{H}_2\text{O}$  (**2**),  $(\text{IndH})_2[\text{Ge}_2(\text{OH})_2(\mu\text{-H}_2\text{Gluc})_2]$  (**3**).

Термічний розклад сполук **1** і **2** розпочинається з ендотермічного ефекту в інтервалі температур 80-150 °С, при якому відбувається елімінація в газову фазу трьох молекул кристалізаційної води. Сполука **3** не є кристалогідратом, про що свідчить відсутність ефектів на термограмі комплексу до 220 °С. В подальшому терморозклад комплексів відбувається однотипно: спостерігається ендоефект в інтервалі 200-300 °С, що супроводжується видаленням молекул  $\text{Nic}$ ,  $\text{Nad}$ ,  $\text{Ind}$ , який переходить в ряд екзоєфектів з окисною термодекструкцією органічної частини молекул комплексів. ІЧ-спектри сполук **1-3** аналогічні в області смуг, що відповідають коливанням зв'язків в координаційному полієдрі Германію. Наявність смуг  $\nu_{\text{as}}(\text{COO}^-)$  та  $\nu_{\text{s}}(\text{COO}^-)$ , типових для карбоксилатних іонів, вказує на депротонування  $\text{COOH}$ -групи глюконової кислоти та її зв'язування з Германієм, що підтверджується появою смуги  $\nu(\text{Ge-O})$ . Присутність смуг  $\delta(\text{C-O})$ ,  $\nu(\text{C-O})$  алкоголятного типу та збереження  $\delta(\text{C-OH})$  свідчать про нерівноцінність гідроксильних груп в комплексах – вільних та зв'язаних з Германієм. У сполуках реалізується гідролізована форма Германію, що корелює з наявністю деформаційних коливань  $\delta(\text{Ge-OH})$ . Порівняльний аналіз ІЧ-спектрів комплексів **1-3** та вихідних екзо-лігандів показав, що утворення супрамолекулярних солей відбувається за рахунок протонування атому нітрогену піридинового кільця.

В результаті рентгеноструктурного аналізу встановлено, що комплекс **2** складається з двох протонованих молекул нікотинаміду та комплексного аніону, в якому два атоми Германію координовані двома містковими лігандами депротонованої глюконової кислоти  $\text{H}_2\text{Gluc}^{4-}$  і гідроксо-групою. В кристалічній фазі комплекс існує у вигляді тригідрату.

**Ключові слова:** германій, глюконова кислота, координаційні сполуки, нікотинамова кислота, нікотинамід, ізоніазид, ІЧ спектроскопія, рентгеноструктурний аналіз.

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