УДК 541.49:661.693:547.463:631.811

D. M. Pechinka[1], O. A. Finik[2], O. G. Pesaroglo[3], Y. M. Fadieiev[2], I. I. Seifullina[1], O. E. Martsynko[1]

[1]Odesa I. I. Mechnikov National University, Department of Inorganic Chemistry and Chemical Education, 2 Dvorianska St, Odesa, 65082, Ukraine; e-mail: lborn@ukr.net

[2]LLC “INSPECTORAT UKRAINE”, 1 Udilnyi Ln, Odesa, 65044, Ukraine

[3]Odesa State Agrarian University, 99 Kanatna St, Odesa, 65039, Ukraine

ONIUM DIAMINOTETRACARBOXYLATES OF GERMANIUM(IV): SYNTHESIS, STRUCTURE, APPLICATIONS

Coordination compounds of grmanium(IV) have been obtained through an interaction of GeO_2 in aqueous solutions with ethylenediaminetetraacetic (H_4Edta) or 1,3-diamino-2-hydroxypropanetetraacetic (H_5Hpdta) acid followed by addition nicotinamide (Nad) in different molar ratios. The composition and structure of obtained compounds have been determined by elemental analysis, IR spectroscopy, mass spectrometry, and thermogravimetry. Taking into account the data obtained by mass spectrometry regarding the existence of the protonated form of $HNad^+$ and complex acid-germanate(IV) anions in methanol-aqueous solution, the following formulas were assigned to the new compounds: $(HNad)[Ge(OH)(Edta)]\cdot H_2O$ (**1**), $(HNad)[Ge(OH)(HHpdta)(H_2O)]$ (**2**). It has been shown that seed treatment of winter pea variety Balltrap with aqueous solutions of compounds **1**, **2** (Ge content in substance 0.05 g/l) led to increasing content in microgreens the protein (complex **1** – 6.40%; complex **2** – 6.65%; control (H_2O) – 5.22%; complex fertilizer – 5.26%) and germanium (25.89, 21.13 ppm for **1** and **2**, respectively; control (H_2O) – 0.46 ppm; complex fertilizer – 0.32 ppm). In addition, it has been noted that the growth-stimulating effect of the complex $(HNad)[Ge(OH)(Edta)]\cdot H_2O$ at the initial stages of growth and development of pea microgreen sprouts and increasing its raw biomass by 6% compared to the control.

Keywords: germanium, ethylenediaminetetraacetic acid, 1,3-diamino-2-hydroxypropanetetraacetic acid, coordination compounds, biological activity, pea microgreens.

Synthesis of safe and effective compounds capable of stimulating growth and enriching cultivated plants intended for healthy nutrition, like microgreens with valuable substances, is an actual task of modern agrochemistry. Microgreens are tender, immature seedlings of greens, vegetables and herbs widely used in contemporary food culture and positively affect human health [1-4].

Metal complexates are often used as effective fertilisers [5]. To enrich the zinc of pea, radish, and sunflower microgreens grown in a soilless cultivation system, a zinc complex with ethylenediaminetetraacetic acid was the most helpful [6, 7]. At the same time, authors [8], as a result of field experiments in Egypt, showed that nicotinamide at 5, 10, and 20 mg/l has a positive effect on growth parameters, photosynthetic pigments, seed yield, and yield components as well as some biochemical constituents of the yielded bean seeds.

Previous studies [9, 10] have shown the positive effect on the living organisms of some plant consumption (e.g., garlic, tea, aloe, ginseng), which is associated with a high composition of germanium compounds with immunomodulator and antioxidant properties.

DOI: https://doi.org/10.18524/2304-0947.2024.2(88).322128

According to the authors' previous systematic research [11-13], homo- and heterometallic complexes of germanium(IV) with polybasic organic acids are of great interest as plant growth stimulators. In particular, ammonium ethylenediaminetetraacetategerm anate(IV) was patented as a compound that positively affects the growth and development of winter wheat [14].

Thus, the data accumulated so far confirm the relevance of the creation and research of agrochemical preparations based on coordination compounds of germanium(IV) as stimulators of the physiological processes in plants in a natural way. Therefore, this work aimed to synthesize onium compounds of germanium with ethylenediaminetetraacetic (H_4Edta), 1,3-diamino-2-hydroxypropanetetraacetic acid (H_5Hpdta) acids and nicotinamide, determine their structure and identify impact on growth, development and composition of pea microgreens.

MATERIALS AND RESEARCH METHODS

As starting materials for the synthesis of new complexes, we used ready-made reagents ©Sigma Aldrich without additional purification: germanium(IV) oxide (GeO_2, 99,99%), ethylenediaminetetraacetic acid (H_4Edta, CAS 60-00-4, ≥98%), 1,3-diamino-2-hydroxypropanetetraacetic acid (H_5Hpdta, CAS 3148-72-9, 99%), nicotinamide (Nad, CAS 98-92-0, 99.5%).

Synthesis of **(HNad)[Ge(OH)(Edta)]·H_2O** (**1**). An equimolar amount of GeO2 (5 mmol, 0.523 g) was added to an aqueous solution of H_4Edta (5 mmol, 1.46 g in 300 ml of water), evaporated for two h to a volume of 200 ml and 0.61 g (5 mmol) of nicotinamide was added without cooling. Evaporation was continued to 50 ml (40 min). After an hour, a precipitate formed, which was separated on a Schott filter, washed with a water-ethanol mixture and dried to constant weight at 20-25 °C in a desiccator over $CaCl_2$. The product yield was 72% of the theoretical.

Synthesis of **(HNad)[Ge(OH)(HHpdta)(H_2O)]·2H_2O (2)** was carried out according to the above procedure for complex 1, adding 1.61 g of H_5Hpdta (5 mmol) instead of H_4Edta. The product yield was 68% of the theoretical.

Elemental analysis. The Carbon content in the complexes was performed with a Carbon and Sulphur Analyzer Combustion Master CS, NCS Testing. Nitrogen in complexes and microgreens were determined according to Kjeldahl with an automatic system KjeLROC Analyzer KD-310-B. The protein content of foods has been determined on the basis of total nitrogen content [15]. The Germanium content in complexes and microgreens was performed inductively by coupled plasma atomic emission spectroscopy with an Optima 8000 PerkinElmer.

When preparing samples of microgreens for analysis, they were dried to constant weight at 105 °C for 3 hours and calculated the water content.

Calculated for $C_{16}H_{22}GeN_4O_{11}$ (**1**) (%): C – 37.02, N – 10.80, Ge – 14.00. Found (%): C – 37.11, N – 10.72, Ge – 13.89.

Calculated for $C_{17}H_{28}GeN_4O_{14}$ (**2**) (%): C – 34.90, N – 9.58, Ge – 12.42. Found (%): C – 35.09, N – 9.51, Ge – 12.55.

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 [16-19] and complex compounds of germanium(IV) and other metals [11-14].

ESI-mass spectra were taken on TSQ Fortis Triple Quadrupole Mass Spectrometer (ThermoFisher Scientific, USA). Sample was infused with a Chemyx Fusion 100T2 syringe pump at a flow rate 20 mL/min. Sample solutions were introduced with a 500 µL Hamilton gas-tight syringe no 81265 (1750RNR). The syringe was connected with ESI camera by 75 cm of 1/16 in. o.d. and 0.005 in. i.d. polyetheretherketone tubing. The electric potential used to initiate ESI was 3.0 to 3.5 kV in positive ionization mode and 2.0 to 2.5 kV in negative ionization mode. The ion transfer tube temperature was set as 300 °C, the vaporizer temperature was set as 150 °C, the sheath gas flow was 20 L/min, 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 scan rate of 250 Da/sec. All spectra were measured for water-methanol solutions with concentration of complexes about 10 µg/ml. Isotop distribution patterns were calculated using [20].

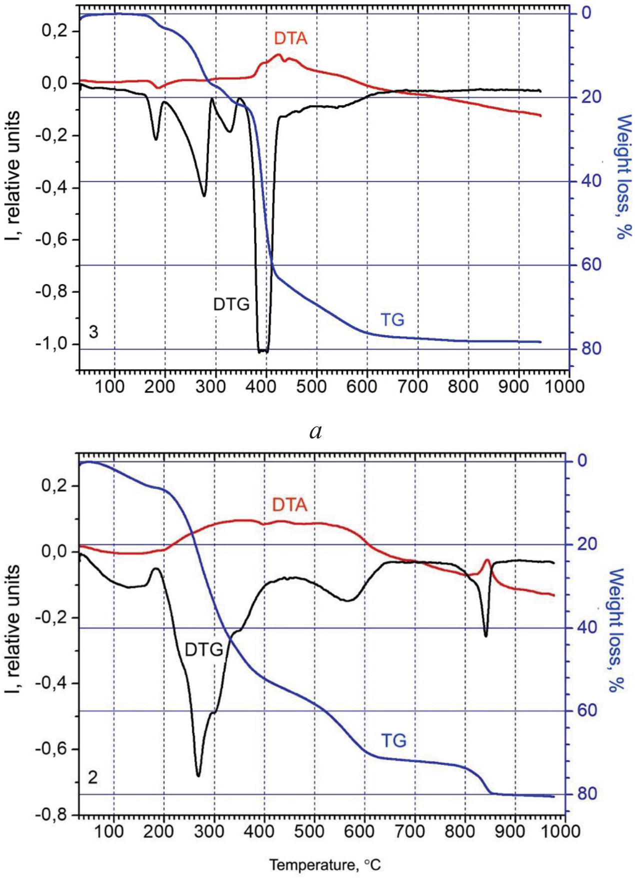
Research on the effects of compounds on the growth and development of sprouts and the qualitative composition of microgreens. Microgreens of winter pea of the Balltrap variety from Florimond Desprez (France) were grown in the laboratory of the Odesa State Agrarian University. First, pea seeds were sterilized with a 30% solution of H_2O_2 for 3 min, then washed with distilled water and soaked in water for 10 hours. In experimental samples, pea seeds were treated with aqueous solutions of compounds **1**, **2** (Ge content 0.05 g/l); in control samples, pea seeds were treated with distilled water and complex fertilizer for growing peas. After treatment, pea seeds were placed in trays with moistened agrofibre (50 seeds each) and incubated in a thermostat in the dark at 22-24°C for 48 hours. After the incubation period, pea microgreens were grown in laboratory climatic conditions for 14 days, periodically moistening the agrofibre, with a light/dark regime of 16/8 hours, temperature of 22-24°C, illumination of 3000 lux and air humidity of 70-80%.

RESULTS AND DISCUSSION

According to the elemental analysis results, the molar ratio of elements in the compounds is Ge : N = 1:4, therefore, they have the same molar ratio Ge : complexone : Nad = 1:1:1.

The thermal decomposition of the complexes (Fig. 1) begins with an endothermic effect at 150-200 °C (complex **1**) and 80-200 °C (complex **2**), at which one and two molecules of water of crystallization are released, respectively (Δm_{theor} = 3.47% for **1** and 6.16% for **2**). The presence of crystallization water in the compounds confirms the presence of stretching vibration bands in their IR spectra ν(OH) = 3371 (**1**), 3353 (**2**) cm^{-1}.

With increasing temperature, the thermal decomposition of the compounds differs. Two exothermic effects are recorded on the thermogravigram of complex **1** (Fig. 1*a*). At a temperature of 200-300 °C (Δm_{theor} = 11.96%, Δm_{pract} = 12.00%), a water molecule is removed, which is formed as a result of the separation of the OH group and proton bound



a

b

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

to germanium from the exo-ligand, as well as one CO_2 molecule. Then, in the range of 300-350 °C ($\Delta m_{theor} = 8.48\%$, $\Delta m_{pract} = 8.50\%$), another CO_2 molecule is removed. When complex **2** is heated in a wide temperature range of 200-340 °C ($\Delta m_{theor} = 36.26\%$, $\Delta m_{pract} = 36.00\%$), two water molecules and four CO_2 molecules are removed (Fig. 1*b*).

Further decomposition is accompanied by exo-effects, in which the organic part of the molecules is destroyed. The final product at 1000 °C is GeO_2 ($\Delta m_{TG} = 78{,}50\%$, $\Delta m_{theor} = 79.83\%$ (**1**), $\Delta m_{TG} = 80.5\%$, $\Delta m_{theor} = 82.10\%$ (**2**))

IR spectra of **1** and **2** are similar in the region of vibrational bands (Fig. 2), which characterize bonds in the coordination polyhedron of Germanium. The bands ν_{as}(C-O) = 1683 (**1**), 1695 (**2**) cm^{-1} and ν_s(C-O) = 1396 (**1**), 1388 (**2**) cm^{-1}, characteristic of COO^-, clearly indicate the presence of carboxylate groups bound to germanium in the molecules, as well as the presence of the band of stretching vibrations of the Ge-O bond in the region of 604 (**1**), 608 (**2**) cm^{-1}. In both complexes, there are no protonated carboxyl groups in the region of 1715 cm^{-1} [17, 18]. There are also bands of stretching vibrations ν(Ge-N) = 641 (**1**), 652 (**2**) cm^{-1} and deformation vibrations δ(GeOH) = 830 (**1**), 823 (**2**) cm^{-1}.

The spectrum of complex **2** (Fig. 2*b*) also contains a band at 1641 cm^{-1}, corresponding to vibrations of coordinating water molecules. In IR spectrum **2**, a ν(C-O) band of the alcoholate type at 1075 cm^{-1} is also noted in the absence of deformation vibrations of C-OH at 1227 and 1209 cm^{-1} [18], which indicates the coordination of the deprotonated hydroxyl group to the ligand.

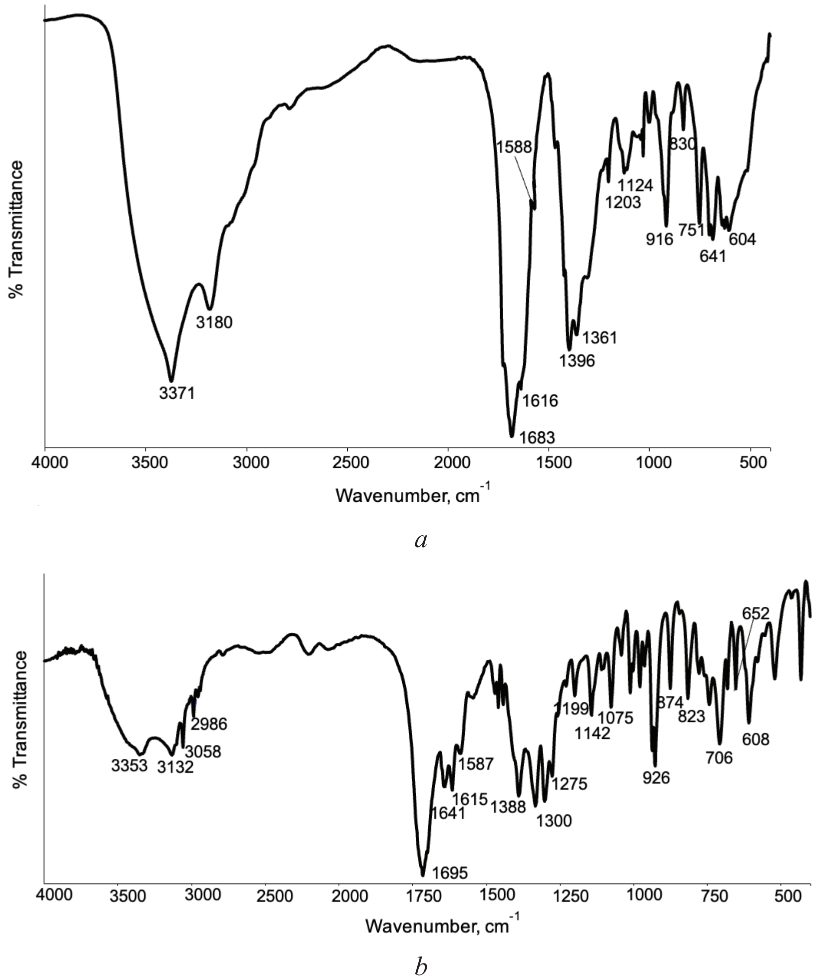
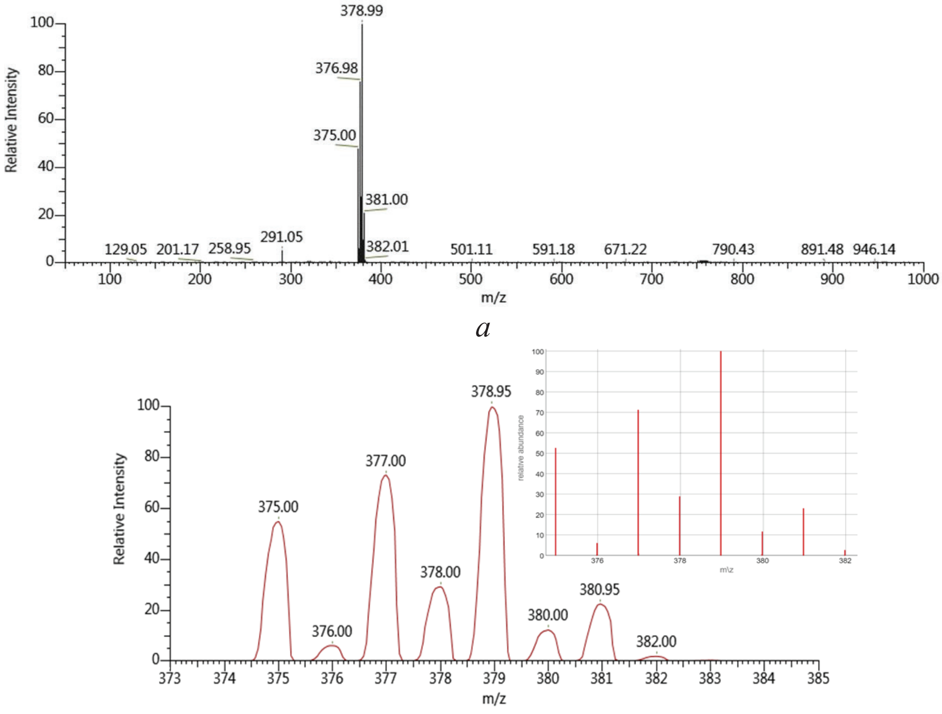


Fig. 2. IR spectra of complexes **1** (*a*) and **2** (*b*)

It should be noted that the IR spectra of **1**, **2** and the initial complex acids [11] are characterized by the same set of absorption bands ν(Ge-N), δ(GeOH), ν_{as}(C-O) and ν_s(C-O), which characterize the bonds in the coordination polyhedron of Germanium.

A comparative analysis of the IR spectrum of complexes **1**, **2** and Nad [19] showed that the formation of onion compounds occurs due to the protonation of the nitrogen atom of the pyridine ring. There is an increase in the frequencies of its vibrations ν(CN) by 11-15 cm^{-1} (1576 cm^{-1} for Nad and 1591, 1587 cm^{-1} for **1**, **2**, respectively). At the same time, there are no changes in the region of the band of deformation oscillations $\delta(NH_2)$ in the area 1615 cm^{-1}.

The mass spectrum of compound **1** in negative polarity (Fig. 3*a*) contains an intense signal with m/z = 379, corresponding to the singly charged complex anion $[Ge(OH)Edta]^{-}$. The isotopic distribution of these signals coincides with that theoretically calculated for the corresponding particles (Fig. 3*b*).



a

b

Fig. 3. ESI(-) mass spectrum of a water-methanol solution of complex **1** (*a*); experimentally obtained and calculated (insert) isotopic distribution of the signal m/z = 379 for the particle $[Ge(OH)Edta]^{-}$ (*b*)

The mass spectrum of compound **2** in negative polarity (Fig. 4*a*) contains an intense signal with m/z = 321, belonging to deprotonated H_4Hpdta^{-}. The signal with m/z = 409 corresponds to the singly charged complex anion $[Ge(OH)(HHpdta)]^{-}$, and the signal with m/z = 213 belongs to the divalent anion $[Ge(OH)(Hpdta)(H_2O)]^{2-}$. The isotopic distribution of these signals coincides with that theoretically calculated for the corresponding particles (Fig. 4*b*, *c*).

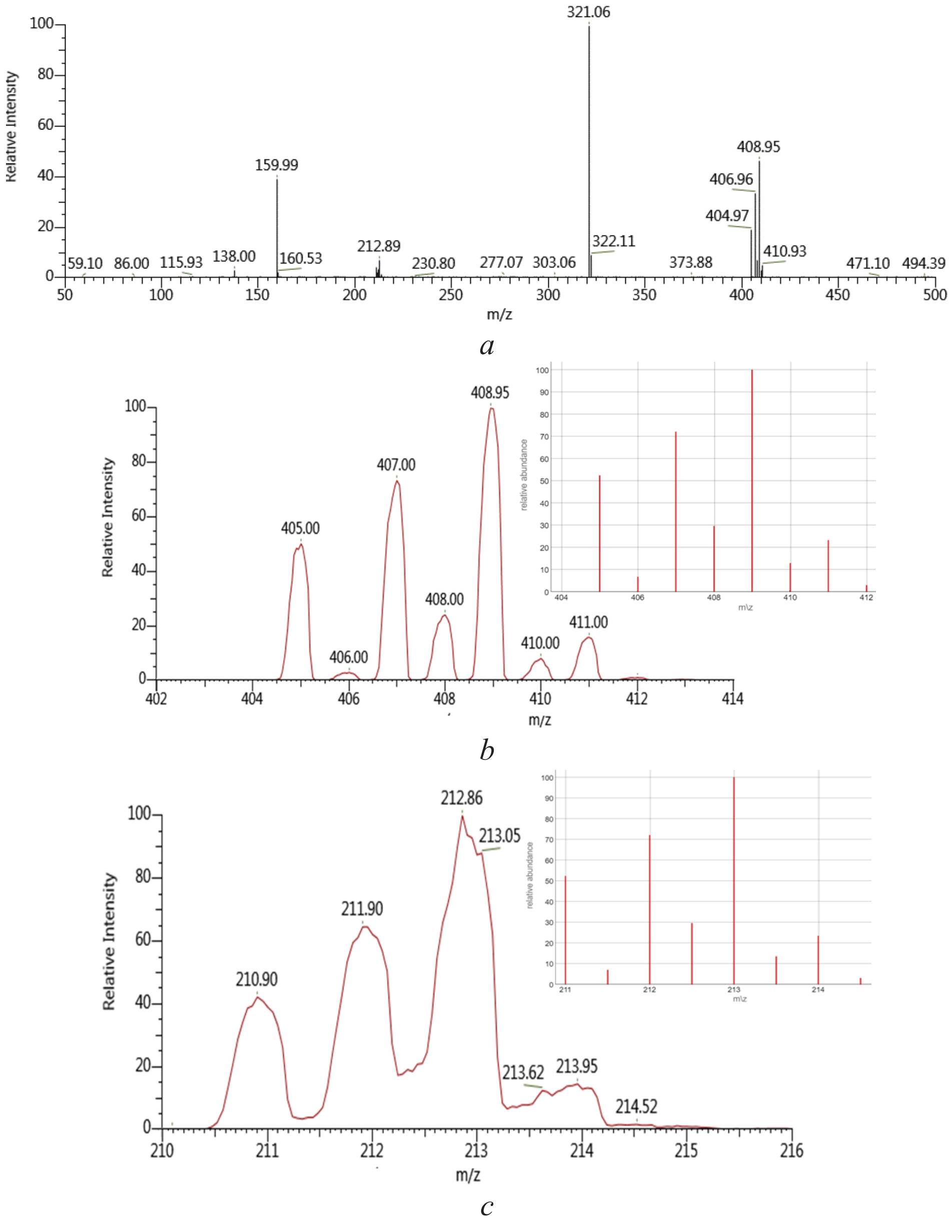


Fig. 4. ESI(-) mass spectrum of a water-methanol solution of complex **2** (*a*); experimentally obtained and calculated (insert) isotopic distribution of the signal for the particle $[Ge(OH)(HHpdta)]^-$ (*b*) and $[Ge(OH)(Hpdta)(H_2O)]^{2-}$ (*c*)

The mass spectre **1** and **2** in positive polarity (e.g. Fig. 5) contains a signal of protonated nicotinamide (m/z = 123).

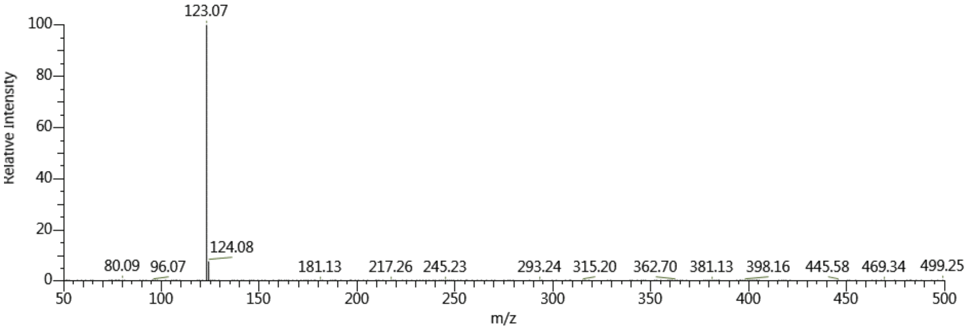
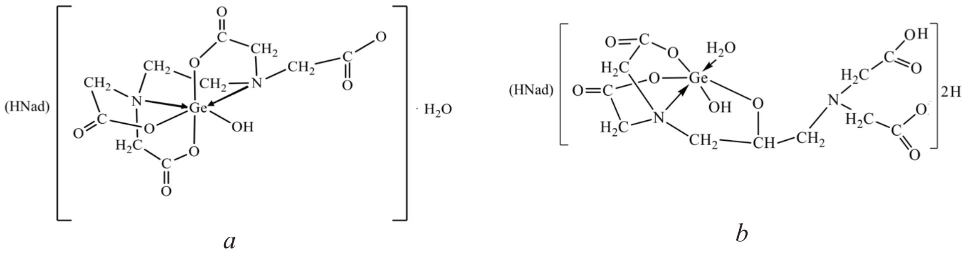


Fig. 5. ESI(+) mass spectrum of a water-methanol solution of complex **1**

Thus, it can be concluded that in complexes **1** and **2**, the structure of the complex anion remains the same as that of the corresponding complex acids [11]. In (HNad)[Ge(OH)(Edta)]·H_2O (**1**), the coordination polyhedron of Germanium is a distorted octahedron; the saturation of the coordination number to 6 occurs due to bonds with the hydroxyl group, three carboxylate groups and two nitrogen atoms of the ligand (Fig. 6 a). In (HNad)[Ge(OH)(HHpdta)(H_2O)]·$2H_2O$ (**2**) the octahedral polyhedron of Germanium is formed due to bonds with two carboxylates, a deprotonated hydroxyl group and a nitrogen atom of the ligand, as well as a hydroxyl group and a coordinated water molecule (fig. 6 b). The absence of the band of valence vibrations of the carboxyl group in the IR spectrum of complex **2** is explained by its participation in the system of hydrogen bonds.



a

b

Fig. 6. Schemes of the structures of complexes **1** (*a*) and **2** (*b*)

It was noted that treating winter pea seeds of the Balltrap variety with aqueous solutions of compounds **1, 2** led to increased protein content in microgreens. Complex **2** increases protein content in microgreens by 1.4% compared to control and complex fertilizer (tabl. 1).

Table 1

The effect of treating winter pea seeds of the Balltrap variety with aqueous solutions of complexes 1 and 2 on the qualitative composition and increase in its raw biomass compared to the control (water) and complex fertilizer

Processing / Option	**Water, %**	**Protein, g/100g**	**Germanium, ppm**	**Productivity raw biomass, %**
Complex **1**	88.08	6.40	25.89	106
Complex **2**	88.25	6.65	21.13	97
Control (H_2O)	89.05	5.22	0.46	100
Complex fertilizer	88.40	5.26	0.32	107

It is noted that the growth-stimulating effect of the complex (HNad)[Ge(OH)(Edta)]·H_2O (**1**) at the initial stages of growth and development of microgreen sprouts of winter pea variety Baltrap and increasing its raw biomass by 6% compared to the control (Fig. 7).

Fig. 7. Effect of aqueous solutions of complexes **1** and **2** on the growth and development of microgreen sprouts of winter pea variety Balltrap compared to the control (water) and complex fertilizer

The result regarding the germanium content in the grown microgreen is interesting, which increases significantly compared to the control and complex fertilizer (tabl. 1). From the literature it is known that the germanium content in plants is low (from 0.01 to 1 ppm). This element has higher levels in garlic, cereal seeds, mushrooms, and ginseng [21]. The high concentrations of germanium were found in garlic grown in China and Ukraine of 2.79 and 3.2 ppm [22, 23]. The highest Ge content was found in mushrooms [24]. In mushroom varieties from which pharmacological preparations are made, grown in experimental conditions with the addition of Ge, the content of this trace element in the fruiting body increased to 70–80 ppm. Thus, the use of these complexes can be recommended to increase germanium content in microgreens in order to give them pharmacological properties.

The results indicate the prospect of further study on the treatment effect of seeds with germanium(IV) acidocomplexes on increasing productivity, antioxidant and immunostimulating properties, and stress resistance of plants.

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Стаття надійшла до редакції 24.11.2024

Д. М. Печінка[1], О. А. Фінік[2], О. Г. Пєсарогло[3], Є. М. Фадєєв[2], І. Й. Сейфулліна[1], О. Е. Марцинко[1]
[1]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
[2]Випробувальний центр ТОВ «ІНСПЕКТОРАТ УКРАЇНА», Удільний пров., 1, м. Одеса, 65044, Україна
[3]Одеський державний аграрний університет, вул. Канатна, 99, м. Одеса, 65039, Україна

ОНІЄВІ ДІАМІНОТЕТРАКАРБОКСИЛАТИ ГЕРМАНІЮ(IV): СИНТЕЗ, БУДОВА, ЗАСТОСУВАННЯ

Координаційні сполуки Германію(IV) отримано шляхом взаємодії GeO_2 у водних розчинах з етилендіамінтетраоцтовою (H_4Edta) або 1,3-діаміно-2-гідроксипропантетраоцтовою (H_5Hpdta) кислотою з наступним додаванням нікотинаміду (Nad) у різних молярних співвідношеннях. Склад і структуру отриманих сполук визначено методами елементного аналізу, ІЧ-спектроскопії, мас-спектрометрії та термогравіметрії. За результатами елементного аналізу у сполуках мольне співвідношення Ge : комплексон : Nad = 1:1:1. Термічний розпад комплексів з ендотермічного ефекту при 150-200 °C (**1**) і 80–200 °C (**2**), при якому вивільняються одна і дві молекули кристалізаційної води, відповідно. ІЧ-спектри сполук подібні в області смуг коливання, які характеризують зв'язки в координаційному поліедрі германію. Смуги коливань ν_{as}(C-O), ν_s(C-O), що характерні для груп COO^-, вказують на наявність в молекулах комплексів карбоксилатних груп, зв'язаних з Германієм, як і смуга валентних коливань ν(Ge-O). Також зафіксовано смуги валентних коливань ν(Ge-N) і деформаційних коливань δ(GeOH). Спектр комплексу з H_5Hpdta одночасно містить смугу при 1641 см$^{-1}$, що відповідає коливанням координованих молекул води. Враховуючи дані мас-спектрометрії щодо існування протонованої форми $HNad^+$ та комплексних діамінотетракарбоксилатогерманатних(IV) аніонів у метанольно-водному розчині, запропоновано наступні формули нових сполук: (HNad)[Ge(OH)(Edta)]·H_2O (**1**), (HNad)[Ge(OH)(HHpdta)(H_2O)] (**2**). Показано, що обробка насіння озимого гороху Баллтрап водними розчинами сполук **1**, **2** (вміст Ge в речовині 0,05 г/л) призводить до підвищення вмісту в мікрозелені гороху білку (комплекс **1** –

6,40%, комплекс **2** – 6,65%, контроль (H_2O) – 5,22% комплексне добриво – 5,26%) та германію (25,89, 21,13 ppm для **1** і **2** відповідно; контроль – 0,46 ppm; комплексне добриво – 0,32 ppm). Крім того, відзначено ріістстимулюючу дію комплексу (HNad)[Ge(OH)(Edta)]·H_2O (**1**) на початкових етапах росту та розвитку паростків мікрозелені гороху та збільшення його біомаси на 6% порівняно з контролем.

Ключові слова: Германій, етилендіамінтетраоцтова кислота, 1,3-діаміно-2-гідроксипропантетраоцтова кислота, координаційні сполуки, біологічна активність, мікрозелень гороху.

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