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GROWTH-STIMULATING ACTIVITY OF NEW BIOCOORDINATION HETEROMETALLIC BIS(CITRATO)GERMANATES(IV) OF WINTER WHEAT

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Introduction. Formulation of the problem

Modern research conducted in Ukraine and globally has demonstrated that a deficiency of micronutrients – key participants in plant metabolic processes – leads to reduced crop yields, increased susceptibility to diseases, and even plant death. As a result, there is a decline in both the quantity and quality

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Abstract. The results of using synthesized and characterized heterometallic chelates using a combination of modern physicochemical methods for studying them are presented for the first time of bis(citrato)germanates(IV): $[M(H_2O)_6][Ge(HCit)_2] \cdot nH_2O$, where $M=Mn$, $n=4$ (1); Fe , $n=4$ (2); Cu , $n=1$ (3); Zn , $n=3$ (4) ($HCit^{3-}$ is anion of citric acid) for pre-sowing treatment of winter wheat seeds in field conditions are presented for the first time. It was found that their addition to the mixture with the fungicide increases plants' germination and growth rates at the initial stage of autumn development when wheat especially needs the microelements necessary for biofortification and further crop formation. An increase in yield was recorded compared to the control, which is evidence of the creation of favourable conditions under which the studied bis(citrato)germanates (1-4) are well absorbed as chelate microfertilizers. They contribute to the disclosure of the genetic potential of winter wheat, effectively affect its growth and development, and increase the yield and quality of grain. At certain stages of winter wheat growth, the degree of manifestation of the growth-stimulating activity of compounds (1-4) varies depending on the composition of the complex cation. In the variant of application of $[Fe(H_2O)_6][Ge(HCit)_2] \cdot 4H_2O$ (2), field seed germination increased by 10.7%, an increase in the above-ground mass of plants up to 18 cm and the development of the primary root system up to 8.0 cm were recorded. The increase in yield also significantly depended on the variant of seed treatment. The best indicator was characterized by $[Cu(H_2O)_6][Ge(HCit)_2] \cdot H_2O$ (3), which subsequently significantly influenced the formation of winter wheat grain and increased yield by 19.32%. It has been shown that the chemical design of such heterometallic compounds, built from bioactive, non-toxic complex cations and anions, which do not compete with each other for binding to the plant biosystem and jointly contribute to the overall growth-stimulating effect, opens up prospects for the creation of effective new generation drugs that are capable of providing a significant increase in the yield of grain crops.

Keywords: heterometallic bis(citrato)germanates, chelated micronutrient fertilizers, pre-sowing seed treatment, growth-stimulating activity, winter wheat yield, national food security.

of environmentally friendly products with a high content of nutritional components. The issue of supplying plants with essential micronutrients has become a general biological concern, particularly relevant to agricultural production and the food industry [1,2].

Analysis of recent research and publications

In recent years, the methodology of plant micronutrient supplementation has undergone significant changes. Chelated micronutrient fertilizers have become the most in-demand, as they supply plants with essential elements, promote active growth, and enhance immunity. Numerous studies have shown that the chelating agents that ultimately determine the effectiveness of the fertilizer and the extent to which plants absorb micronutrients from them [3,4].

Today, the Ukrainian market offers a range of such products, including Novalon Seed Treatment, Nano-Mineralis, and Quantum Zinc, among others. However, selecting the most effective product for a particular crop remains challenging, as each crop requires a set of nutrients depending on its growing conditions. This issue is especially pressing for cereal crops, particularly wheat, which is highly sensitive to micronutrient deficiency during the early stages of development.

Winter wheat accounts for the largest share of cereal crops in Ukraine and worldwide. Unlike other agricultural crops, it holds immense agrotechnical, economic, and strategic importance for the agro-industrial sector [5-9]. Its yield and total production volumes not only ensure the stable development of agricultural production but also play a critical role in ensuring food security for many countries [10-12].

Modern technology for cultivating winter wheat involves using a broad range of agrotechnical measures, with pre-sowing seed treatment being a key component [13]. This practice significantly mitigates the adverse effects on field germination, plant growth, and development at early stages, which is why it is now considered an essential part of contemporary cultivation strategies. This underscores the urgency of developing a new generation of formulations characterized by higher efficiency and environmental safety.

Within the framework of bioinorganic chemistry research focused on the essential element germanium, conducted at the Faculty of Chemistry and Pharmacy of I.I. Mechnikov Odesa National University, the authors were the first to implement the idea of synthesizing a wide series of heterometallic bis(citrato)germanates(IV) of the type $[M(H_2O)_6][Ge(HCit)_2] \cdot nH_2O$ with divalent metals. A method for their eco-friendly synthesis in aqueous solution was developed. A complete physicochemical characterization of the complexes was performed using modern analytical techniques [14]. The crystal structures of the metal complexes have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under numbers 768370 (2) and 910286 (3). It has been proven that the synthesized coordination compounds are of the cation-anion type, exhibit low toxicity, possess a broad spectrum of pharmacological activity [15-17], and can act as enzyme effectors [18].

In preliminary laboratory studies on the pre-sowing treatment of winter wheat seeds, the complex $[Fe(H_2O)_6][Ge(HCit)_2] \cdot 4H_2O$ demonstrated significant growth-promoting activity (Patent No. 131091: Plant

Growth Stimulator–ferrum(II) bis(citrato)germanate(IV). This finding has served as a foundation for continuing research in this area.

The purpose and objectives of the research.

Thus, the purpose of this research was defined as a field investigation of the bio-coordination heterometallic bis(citrato)germanates(IV): $[Mn(H_2O)_6][Ge(HCit)_2] \cdot 4H_2O$ (1), $[Fe(H_2O)_6][Ge(HCit)_2] \cdot 4H_2O$ (2), $[Cu(H_2O)_6][Ge(HCit)_2] \cdot H_2O$ (3), and $[Zn(H_2O)_6][Ge(HCit)_2] \cdot 3H_2O$ (4), as plant growth regulators for pre-sowing seed treatment of winter wheat. The research aimed to determine the patterns of influence of compounds' nature, composition, and structure (1-4) on the degree of their growth-stimulating activity.

To achieve the stated purpose, the following objectives were undertaken:

1. To synthesize experimental samples of chelated bis(citrato)germanates(IV) (compounds 1–4) and to perform their identification using a combination of modern physicochemical analytical methods.
2. To carry out pre-sowing treatment of winter wheat seeds with the synthesized compounds (1–4) in combination with a seed dressing agent and to study their effects on field germination, plant growth and development at early stages, as well as on grain yield and quality.
3. To evaluate the effectiveness of compounds (1–4) as chelated micronutrient fertilizers for the pre-sowing treatment of winter wheat seeds.

Research materials and methods

For the synthesis of novel heterometallic bis(citrato)germanates(IV) (1–4), the following reagents from ©Sigma Aldrich were used as starting materials: germanium(IV) oxide (GeO_2 , 99.99%), citric acid monohydrate ($H_4Cit \cdot H_2O$, $\geq 99\%$), manganese(II) acetate tetrahydrate ($Mn(CH_3COO)_2 \cdot 4H_2O$, $\geq 99\%$), iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, $\geq 99\%$), copper(II) acetate monohydrate ($Cu(CH_3COO)_2 \cdot H_2O$, $\geq 99\%$), and zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, 99%).

At the first stage, a saturated bis(citrato)germanic acid solution was prepared. Precisely weighed amounts of 1.046 g (0.01 mol) of GeO_2 and 4.2 g (0.02 mol) of citric acid monohydrate were added to 400 ml of hot water. The mixture was heated to 80–90 °C with constant stirring until the reagents were dissolved entirely. The resulting clear solution (pH 1.5–2) was evaporated in a water bath to a final volume of 100 ml (approximately 2 hours) and then cooled.

At the second stage, 20 ml (0.002 mol) of the prepared solution was combined with weighed portions of the respective metal salts: $Mn(CH_3COO)_2 \cdot 4H_2O$ (1), $FeSO_4 \cdot 7H_2O$ (2), $Cu(CH_3COO)_2 \cdot H_2O$ (3), and $Zn(CH_3COO)_2 \cdot 2H_2O$ (4), maintaining a molar ratio of $Ge : M$ (Mn, Fe, Cu, Zn) = 1 : 1. The mixtures were stirred at room temperature for 5 minutes without

heating. The resulting solutions (pH 4-5) were left to crystallize at 20 °C. After 1–2 days, crystalline precipitates of the target compounds formed, which were separated using a Schott filter, washed with cold water and dried at ambient temperature. The yields of the products were 80–85%.

Elemental analysis of the synthesized heterometallic bis(citrato)germanates(IV) (1–4) was performed using a semi-automatic C, N, H analyzer. The germanium and corresponding metal contents in the presence of other elements were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an Optima 2000 DV spectrometer (Perkin Elmer). X-ray phase analysis (XRD) was conducted using a DRON-0.5 diffractometer with a copper anode and nickel filter. The hydration state of the compounds was established based on calculations derived from thermogravimetric (TG) curves. Thermal analysis (DTA, DTG, TG) was performed using a Q-1500 D derivatograph (Paulik–Paulik–Erdey system). Thermal stability was assessed under air atmosphere over the 20–1000 °C temperature range with a heating rate of 10 °C/min. IR spectroscopy was carried out using a “Frontier” spectrophotometer of the company “Perkin Elmer”.

The material used for field experiments was a certified seed of soft winter wheat of “Garantia Odeska” variety. The field trials were conducted under steppe zone conditions in Ukraine at the experimental station “Pokrovske” of the Plant Breeding and Genetics Institute – National Center for Seed Science and Variety Studies. Experimental plots were 10 m² in size, with three replications. The previous crop was soybean. The seeding rate was 5.2 million seeds per hectare, row spacing was 15 cm, and sowing depth was 4–6 cm. The basic fertilization background was N₂₄P₄₈K₂₄S₁₂.

Biometric parameters were assessed using morphophysiological evaluation of the seedlings. Harvesting was performed plot-wise using a Sampo-500 combine harvester. Grain yield was measured through individual plot threshing, followed by grain cleaning and recalculation to 100% purity and 14% moisture content, by the Methodology of State Variety Testing of Agricultural Crops [19]. Experimental data was processed using variance analysis methods using the software package Statistica 10.0 [20].

Results of the research and their discussion

Based on the results of elemental analysis (Table 1), it was established that in all cases the experimental samples (1–4) form compounds with the stoichiometric composition M (Mn, Fe, Cu, Zn) : Ge : ligand = 1 : 1 : 2.

The individuality of the synthesized compounds (1–4) was confirmed by X-ray phase analysis (XRD). Their powder diffraction patterns are characterized by a unique set of interplanar spacings, which rule out the presence of impurities from starting materials.

The hydration composition was determined using thermogravimetric analysis (TGA): within the temperature range of approximately 60–270 °C, a mass loss occurs, corresponding to the release of all crystallization water molecules as well as the coordinated water in the hexaaqua cation [M(H₂O)₆]²⁺. The synthesized compounds (1–4) are thermally stable and do not undergo hydrolysis in air. The uniform nature of their thermal decomposition suggests that compounds (1–4) possess analogous structural frameworks.

Special attention was paid to identifying similarities among the compounds in the comparative analysis of their IR spectra (Table 2). It was found that the set of characteristic absorption band frequencies in the IR spectra of compounds (1–4) is virtually identical. Notable are the bands corresponding to the stretching vibrations $\nu(\text{C}=\text{O})$, $\nu_{\text{as}}(\text{COO}^-)$, $\nu_{\text{s}}(\text{COO}^-)$, $\nu(\text{C}-\text{O})$ of alkoxide-type, and $\nu(\text{Ge}-\text{O})$, indicating the involvement of oxygen atoms from deprotonated hydroxyl and carboxyl groups in coordination with the complex-forming center. As a result, chelation occurs with the formation of two five-membered metallacycles. The IR spectra also exhibit water bending and libration modes, $\delta(\text{H}_2\text{O}) = 1636\text{--}1641\text{ cm}^{-1}$ and $\rho(\text{H}_2\text{O}) = 729\text{--}735\text{ cm}^{-1}$, characteristic of hexaaqua metal complexes.

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Based on the entirety of the obtained data, the synthesized compounds (1–4) correspond to the following structural scheme (Fig. 1):

Pre-sowing treatment of winter wheat seeds was performed using the fungicidal-type seed dressing agent Galeon (0.6 l/t) (“Manufacturer: Agrosfera”), the synthesized chelated bis(citrato)germanates(IV) (compounds 1–4) (0.2 l/t), and the reference seed treatment agent Novalon Seed Treatment (0.6 kg/t) (“Manufacturer: TerraTarsa”), which is widely used for seed pre-treatment in various countries, including Ukraine. Water was used in the control variant.

Table 1 – Composition of heterometallic bis(citrato)germanates(IV) (1-4) according to elemental analysis results

No	Molecular formula of the compounds	Found, %				Calculated, %			
		Ge	M	C	H	Ge	M	C	H
1	C ₁₂ H ₃₀ MnGeO ₂₄	10.59	8.00	20.99	4.37	10.53	7.93	20.91	4.41
2	C ₁₂ H ₃₀ FeGeO ₂₄	10.50	8.10	20.89	4.35	10.57	8.16	20.97	4.37
3	C ₁₂ H ₂₄ CuGeO ₂₁	11.31	9.90	22.43	3.69	11.33	9.99	22.48	3.75
4	C ₁₂ H ₂₈ ZnGeO ₂₃	10.65	9.51	21.20	4.09	10.71	9.59	21.25	4.13

Table 2 – Characteristic absorption band frequencies in the IR spectra of heterometallic bis(citrato)germanates(IV) (1-4)

Assignment of ν , cm ⁻¹	Experimental compounds			
	Mn (1)	Fe (2)	Cu (3)	Zn (4)
$\nu(\text{OH}) (\text{H}_2\text{O})$	3510	3523	3528	3529
$\nu(\text{OH}) (\text{COOH})$	3262	3264	3280	3270
$\nu(\text{C}=\text{O})$ (free carboxylic groups, COOH)	1701	1705	1704	1710
$\nu_{\text{as}}(\text{COO}-)$	1670	1677	1679	1676
	1601	1601	1597	1600
$\nu_{\text{s}}(\text{COO}-)$	1410	1421	1416	1418
	1362	1359	1361	1357
$\nu(\text{C}-\text{O}) (\text{COOH})$	1258	1255	1249	1253
$\nu(\text{C}-\text{O}) (\text{OH})$	1092	1072	1069	1073
$\delta(\text{H}_2\text{O})$	1639	1641	1638	1636
$\rho(\text{H}_2\text{O})$ rocking	729	731	735	731
$\omega(\text{H}_2\text{O})$ wagging	460	471	531	541
$\nu(\text{Ge}-\text{O})$	702	695	697	697
	663	665	668	669
	636	633	631	628

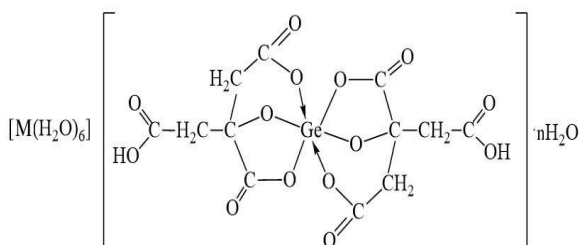


Fig. 1. Structural scheme of heterometallic bis(citrato)germanates(IV), where M = Mn, n = 4 (1); Fe, n = 4 (2); Cu, n = 1 (3); Zn, n = 3 (4)

Following treatment, the seeds were air-dried in the absence of direct sunlight. Sowing was carried out during the first ten days of October 2018-2020. During the experimental period, meteorological conditions were variable but overall favorable for cultivating winter wheat. In the spring, nitrogen fertilizer was applied at N₂₅, N₅₀, and N₇₅ rates on frozen-thawed soil at the beginning of vegetation renewal.

Field germination was calculated as the ratio of the number of emerged seedlings to the total number of sown viable seeds.

It is generally acknowledged that pre-sowing seed treatment with a fungicidal dressing agent slightly reduces field germination; however, this effect is subsequently compensated by enhanced protection of plants against fungal diseases. As a result of the conducted studies, it was observed that the application of the reference preparation Novalon Seed Treatment and the synthesized chelated heterometallic bis(citrato)germanates(IV) (1-4) for pre-sowing seed treatment neutralizes the adverse effects of the fungicidal agent and contributes to a more regulated process of plant growth and development, starting from the initial phase of vegetation.

It was established (Figs. 2, 3) that, in comparison with the control variant, the fungicidal seed treatment Galeon and the reference preparation Novalon Seed Treatment, compounds (1-4) increase the field germination rate of soft winter wheat of "Garantia Odeska" variety by 4.2-10.7%.

Biometric parameters of winter wheat were determined on the 20th day after seedling emergence. It was found that pre-sowing treatment of seeds in variants (1-5) positively influenced the growth of the aerial part of the plants and the development of the primary root system during the initial stage of autumn growth, in comparison with the control variants (6-7) (Table 3).



Fig. 2. Field germination of soft winter wheat of “Garantia Odeska” variety

During the analysis of the parameters (Table 3) at the initial stage of plant growth and development, the most significant positive effect was observed upon application of $[\text{Fe}(\text{H}_2\text{O})_6][\text{Ge}(\text{HCit})_2] \cdot 4\text{H}_2\text{O}$ (compound 2) in combination with the fungicidal seed treatment agent. This treatment resulted in the highest field germination rate of 82%, enhanced development of the aerial plant parts (18 cm), and intensive formation of the primary root system (8.0 cm).

Grain yield assessment was based on aggregated data, including the number of grains per ear and the weight of 1000 grains. The experimental results (Table 4) indicate that the maximum yield increase depends on the composition of the mineral nutrient treatment applied.

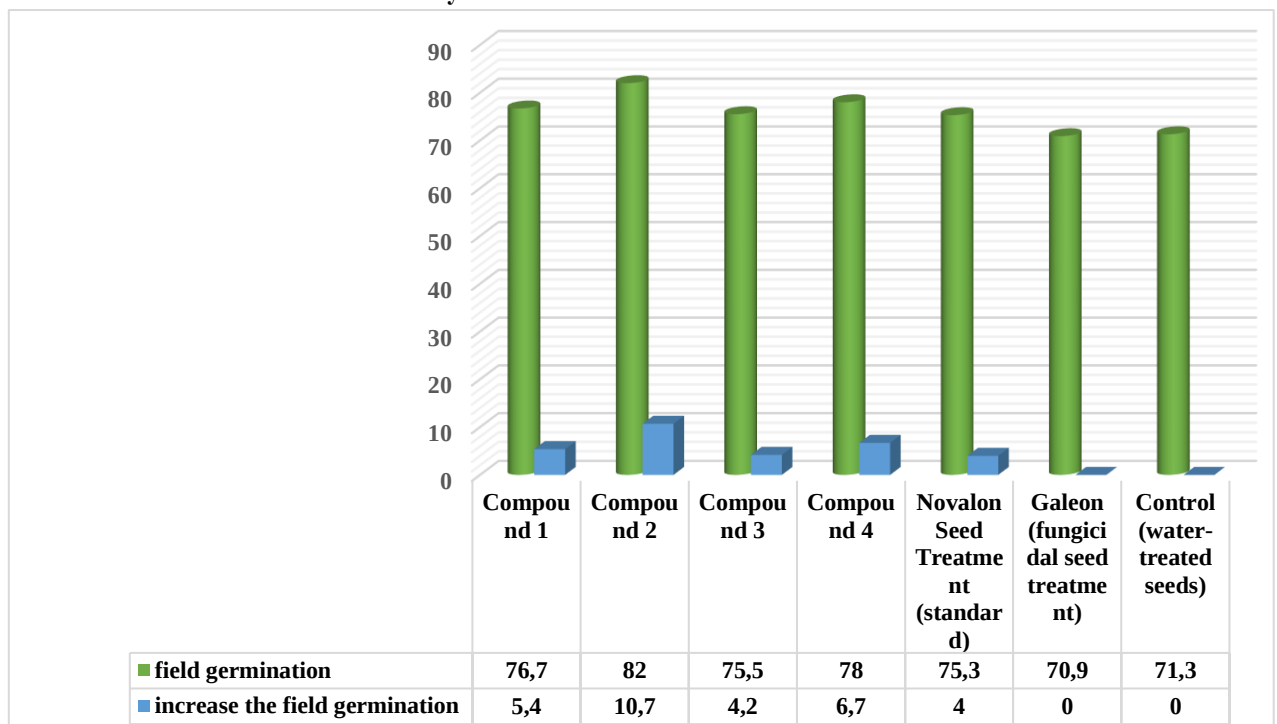


Fig. 3. Field germination of soft winter wheat of “Garantia Odeska” variety depending on the pre-sowing seed treatment agent used (mean values for 2018-2020)

Table 3 – Biometric parameters of soft winter wheat of “Garantia Odeska” variety depending on the pre-sowing seed treatment agent used (mean values for 2018-2020)

No	Variant	Plant stem height, cm	Depth of tillering node, cm	Number of seminal roots, pcs	Root length, cm
1	$[\text{Mn}(\text{H}_2\text{O})_6][\text{Ge}(\text{HCit})_2] \cdot 4\text{H}_2\text{O}$	16,8	3,5	5,5	7,4
2	$[\text{Fe}(\text{H}_2\text{O})_6][\text{Ge}(\text{HCit})_2] \cdot 4\text{H}_2\text{O}$	18,0	3,6	5,2	8,0
3	$[\text{Cu}(\text{H}_2\text{O})_6][\text{Ge}(\text{HCit})_2] \cdot \text{H}_2\text{O}$	15,8	4,2	4,4	7,2
4	$[\text{Zn}(\text{H}_2\text{O})_6][\text{Ge}(\text{HCit})_2] \cdot 3\text{H}_2\text{O}$	16,0	3,5	5,5	7,3
5	Novalon Seed Treatment (standard)	15,5	3,5	4,3	6,8
6	Galeon (fungicidal seed treatment)	15,0	3,2	3,4	5,6
7	Control (water-treated seeds)	15,1	3,1	3,7	6,0

Table 4 – Grain yield of soft winter wheat of “Garantia Odeska” variety depending on the pre-sowing seed treatment agent used (mean values for 2018-2020)

No	Variant	Number of grains per ear, pcs	Weight of 1000 grains, g	Grain yield, t/ha	Yield increase, t/ha	Yield increase, %
1	$[\text{Mn}(\text{H}_2\text{O})_6][\text{Ge}(\text{HCit})_2] \cdot 4\text{H}_2\text{O}$	40,8	41,36	5,13	+0,42	8,92
2	$[\text{Fe}(\text{H}_2\text{O})_6][\text{Ge}(\text{HCit})_2] \cdot 4\text{H}_2\text{O}$	41,2	41,84	5,17	+0,46	9,77
3	$[\text{Cu}(\text{H}_2\text{O})_6][\text{Ge}(\text{HCit})_2] \cdot \text{H}_2\text{O}$	41,8	44,21	5,62	+0,91	19,32
4	$[\text{Zn}(\text{H}_2\text{O})_6][\text{Ge}(\text{HCit})_2] \cdot 3\text{H}_2\text{O}$	41,6	42,49	5,24	+0,53	11,25
5	Novalon Seed Treatment (standard)	39,8	41,25	5,10	+0,39	8,28
6	Galeon (fungicidal seed treatment)	38,6	40,65	4,85	+0,14	2,97
7	Control (water-treated seeds)	38,4	40,24	4,71	-	-

As shown in Table 4, pre-sowing seed treatment in all experimental variants increased grain yield compared to the control. The highest yield increase – 0.91 t/ha – was observed with the use of $[\text{Cu}(\text{H}_2\text{O})_6][\text{Ge}(\text{HCit})_2] \cdot \text{H}_2\text{O}$ (3), which significantly influenced both the number and weight of grains in the ear of soft winter wheat (cv. Garantia Odeska), ultimately enhancing overall yield by 19.32%.

It was noted that the application of compounds (1-4) for the pre-sowing treatment of winter wheat exhibited plant growth-stimulating activity comparable to that of the reference preparation Novalon Seed Treatment, with $[\text{Cu}(\text{H}_2\text{O})_6][\text{Ge}(\text{HCit})_2] \cdot \text{H}_2\text{O}$ (3) demonstrating significantly superior efficacy.

The observed biostimulatory activity of compounds (1-4) is primarily attributed to the presence of a common bis(citrato)germanate(IV) anion $[\text{Ge}(\text{HCit})_2]^{2-}$ in their molecular structure. This anion is formed due to the chelation of the bioessential element germanium with food-grade citric acid, which, due to its chemical structure, is identical to the natural constituents of living cells.

Germanium is a trace bioelement and antioxidant that strengthens the plant immune system enhances resistance to various diseases, bacteria, fungi, and adverse environmental conditions, and participates in the regulation of physiological processes essential for crop formation [21, 22].

The presence of a chelated bis(citrato)germanate(IV) anion in complexes (1-4) facilitates more efficient uptake of germanium by plants, enabling it to act both as a nutrient element and an additional source of energy.

A correlation was observed between the growth-stimulating activity of compounds (1-4) and the nature of the hexaaquacationic metal (Mn^{2+} , Fe^{2+} , Cu^{2+} , Zn^{2+}) since all complexes share the same chelating bis(citrato)germanate(IV) anion, $[\text{Ge}(\text{HCit})_2]^{2-}$. These differences indicate the biological contribution of all active components within the investigated compounds.

Based on a detailed analysis of the individual parameters of the effectiveness of compounds (1-4), activity ranking sequences were constructed (Table 5).

It has been established that the activity series of compounds (1-4) vary depending on the metal forming the complex hexaaquacation. This is explained by trace elements' different effects on specific growth and development stages in winter wheat.

For instance, $[\text{Fe}(\text{H}_2\text{O})_6][\text{Ge}(\text{HCit})_2] \cdot 4\text{H}_2\text{O}$ (2) most significantly increases the field germination of the seeds. It promotes more significant growth of both the above-ground biomass and the root system of winter wheat. This is related to the fact that Fe^{2+} plays a key role in chlorophyll synthesis, enhances immunity, improves photosynthesis and respiratory processes, normalizes metabolism, and stimulates growth and development.

The compound $[\text{Zn}(\text{H}_2\text{O})_6][\text{Ge}(\text{HCit})_2] \cdot 3\text{H}_2\text{O}$ (3) showed the best results during the formation of seminal roots in winter wheat due to the ability of Zn^{2+} to accelerate metabolism, improve the internal structure of cells, and enhance the growth of the root system.

The compound $[\text{Cu}(\text{H}_2\text{O})_6][\text{Ge}(\text{HCit})_2] \cdot \text{H}_2\text{O}$ (4) is particularly notable for its most potent effect on the depth of the tillering node placement and the formation of wheat yield, as copper is highly sensitive in the formation of generative organs. Cu^{2+} is part of many enzymes, enhances resistance to temperature stresses, infectious diseases, and fungal infections, promotes more efficient nitrogen uptake by the plant, improves seed formation, and helps prevent lodging in cereal crops. Thus, through a stereochemical approach to studying the growth-stimulating effects of similar heterometallic bis(citrato)germanates(IV) (1-4) in the sequence: composition, structure, properties, and function, factors influencing their effectiveness as chelated micronutrient fertilizers have been identified.

Using an original methodology, heterometallic chelates of bis(citrato)germanates(IV) (1-4) were synthesized and identified by modern physicochemical methods to study their growth-stimulating activity under field conditions in winter wheat.

Table 5 – Analysis of the effectiveness of chelated bis(citrato)germanates(IV) (1-4)

No	Indicators	Activity Series of Compounds (1-4)
1	Field germination, %	Fe(2) > Zn(4) > Mn(1) > Cu(3)
2	Plant stem height, cm	Fe(2) > Mn(1) > Zn(4) > Cu(3)
3	Depth of tillering node, cm	Cu(3) > Fe(2) > Zn(4) = Mn(1)
4	Number of seminal roots, pcs	Zn(4) = Mn(1) > Fe(2) > Cu(3)
5	Root length, cm	Fe(2) > Mn(1) > Zn(4) > Cu(3)
6	Number of grains per ear, pcs	Cu(3) > Zn(4) > Fe(2) > Mn(1)
7	Thousand grain weight, g	Cu(3) > Zn(4) > Fe(2) > Mn(1)
8	Grain yield, t/ha	Cu(3) > Zn(4) > Fe(2) > Mn(1)

Conclusion

Activity series for compounds (1-4) were constructed based on various biological indicators of plant growth and development, which revealed the influence of different compositions of hexaaquacations $[M(H_2O)_6]^{2+}$, where $M = Mn^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}$, on the degree of manifestation of their growth-stimulating effect.

It has been proven that the application of compounds (1-4) for seed treatment in combination with a fungicide significantly increases the field germination of seeds, promotes the development of uniform and well-developed seedlings, and activates growth processes, which subsequently ensures the winter hardiness of crops and a significant increase in the yield of winter soft wheat variety “Garantia Odeska”.

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РІСТСТИМУЛОВАЛЬНА АКТИВНІСТЬ НОВИХ БІОКООРДИНАЦІЙНИХ ГЕТЕРОМЕТАЛЬНИХ БІС(ЦИТРАТО)ГЕРМАНАТІВ(IV) НА ПШЕНИЦІ ОЗИМІЙ

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Анотація Вперше наведено результати використання синтезованих та охарактеризованих сукупністю сучасних фізико-хімічних методів дослідження гетерометальних хелатів біс(цитрато)германатів (IV): $[M(H_2O)_6][Ge(HCit)_2] \cdot nH_2O$, де $M=Mn$, $n=4$ (1); Fe , $n=4$ (2); Cu , $n=1$ (3); Zn , $n=3$ (4) (де $HCit^{3-}$ – аніон лимонної кислоти) для передпосівної обробки насіння пшениці озимої в польових умовах. Встановлено, що їх додавання у суміш з протруйником підвищує показники сходів і росту рослин на початковому етапі осіннього розвитку, коли пшениця особливо потребує мікроелементи, необхідні їй для біоукріплення та подальшого формування врожаю. Збільшення урожайності зафіксовано в порівнянні з контролем, що є доказом створення сприятливих умов, при яких досліджені біс(цитрато)германати (1-4) добре засвоюються як хелатні мікродобрива. Вони сприяють розкриттю генетичного потенціалу пшениці озимої, ефективно впливають на її ріст і розвиток, підвищують урожайність та якість зерна. Виявлено, що на окремих етапах зростання пшениці озимої ступінь прояву рістстимулювальної активності сполук (1-4) змінюється в залежності від складу комплексного катіону. У варіанті застосування $[Fe(H_2O)_6][Ge(HCit)_2] \cdot 4H_2O$ (2) польова схожість насіння зросла на 10,7 %, зафіксовано наростання наземної маси рослин до 18 см та розвиток первинної кореневої системи до 8,0 см. Прибавка врожаю також істотно залежала від варіанту обробки насіння. Найкращим показником характеризувався $[Cu(H_2O)_6][Ge(HCit)_2] \cdot H_2O$ (3), що в подальшому значною мірою вплинув на формування зерна пшениці озимої та підвищення урожайності на 19,32%. Показано, що хімічне конструювання подібних гетерометальних сполук, побудованих з біоактивних нетоксичних комплексних катіону і аніону, що не конкурують між собою за зв'язування з біосистемою рослини та сумісно вносять вклад у загальну рістстимулювальну дію, відкриває перспективи створення ефективних препаратів нового покоління, які здатні забезпечити значний приріст урожайності зернових культур.

Ключові слова: гетерометальні біс(цитрато)германати, хелатні мікродобрива, передпосівна обробка насіння, рістстимулювальна активність, урожайність пшениці озимої, продовольча безпека держави.