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SYNTHESIS AND COMPREHENSIVE STUDY OF HETERONUCLEAR Ge(IV) – 3d METAL COMPLEXES WITH ETHYLENEDIAMINE-TETRAACETIC ACID AND 2,2'-BIPYRIDINE.

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Synthetic approach have been developed, and different-metal coordination compounds $[M(bipy)_2\{Ge(OH)(\mu\text{-}Edta)\}_2]\times nH_2O$ (H_4Edta is ethylenediaminetetraacetic acid, bipy is 2,2'-bipyridine, M = Mn(II), n=5 (**1**); Co(II), n=7 (**2**); Ni(II), n=7 (**3**); Cu(II), n=4 (**4**); Zn(II), n=5 (**5**)) have been prepared, their comprehensive characterization has been carried out using modern physicochemical methods (elemental analysis, IR spectroscopy, mass spectrometry, and thermogravimetry), and structural features of new complexes have been determined. The synthesised complexes were found to be heteronuclear. The coordination polyhedron of the germanium(IV) remains analogous to that in the structurally characterized ethylenediaminetetraacetatogermanic acid, $[Ge(OH)(HEdta)]\cdot H_2O$, adopting a distorted octahedral geometry formed by coordination to one hydroxyl group, three carboxylate oxygen atoms, and two nitrogen atoms of the Edta-ligand. The 3d metal center exhibits a coordination number of six, and it is bonded to two oxygen atoms of the carboxylate groups from two germanium-containing complex anions and four nitrogen atoms from two bipyridine molecules.

Keywords: germanium(IV), ethylenediaminetetraacetic acid, heterocyclic amines, coordination compounds, IR spectroscopy, thermogravimetry, mass spectrometry.

INTRODUCTION. Metal compounds with aminopolycarboxylate complexones have long been the subject of intensive research and practical application in agriculture, analytical chemistry, materials science, and environmental chemistry due to their unique structural, spectroscopic, catalytic, and biological properties [1, 2]. The most extensively studied systems are complexes based on ethylenediaminetetraacetic acid (H_4Edta) and its structural analogues, including heterometallic complexes [3–9]. Significant attention has been paid to the widespread application of such coordination compounds in crop production. In particular, soil amendment or foliar fertilization with solutions of ethylenediaminetetraacetates of 3d metals has been shown to increase the yield of grain crops (buckwheat, oats, barley, rye, flax) and to accelerate seed germination and vegetative growth processes [1].

Anions of polyaminopolycarboxylic acids, acting as bridging ligands, can form one-, two-,

and three-dimensional polymeric chains and networks, in some cases featuring large cavities. Such structures are classified as metal-organic frameworks (MOFs) and are characterized by high thermal stability and durability. An illustrative example is the mesoporous three-dimensional polymeric complex $\{[Zr^{IV}O\text{-}\mu_3\text{-}(Edta)Fe^{III}OH]\cdot H_2O\}_n$ [5]. The incorporation of heteroaromatic amines, such as 2,2'-bipyridine (bipy), into carboxylate complexes contributes to their stabilization through noncovalent interactions, including hydrogen bonding, π–π stacking, and C–H···π interactions [10].

It has been demonstrated that Cu(II) complexes with amino acids and 2,2′-bipyridine can promote the generation of reactive oxygen species and induce DNA and RNA degradation. The heterocyclic amine intercalates into the DNA helix, while copper ions catalyze the in situ formation of hydroxyl radicals, which subsequently cause oxidative DNA damage. This property is of interest for therapeutic and biotechnological research [10]. Moreover, copper(II)-bipyridine complexes with amino acids exhibit cytotoxic activity even against cisplatin-resistant tumor cell lines [11].

Among the least studied systems are heterometallic multiligand complexes of p- and d-block metals. Representative examples include Co(II)–Bi(III) cation–anion compounds such as $[Co(NH_3)_5NCS](Bi(Edta)]_2\cdot 4H_2O$, $[Co(NH_3)_4(NO_2)_2][Bi(Edta)(H_2O)]\cdot 2H_2O$, $[Co(NH_3)_4(CO_3)][Bi(Edta)]\cdot 3H_2O$ [6], and $[Co(NxH)_2(An)_2]_2[Bi(Edta)(H_2O)]_2\cdot 7H_2O$, $[Co(NxH)_2(p\text{-}Tol)_2][Bi(Edta)]\cdot 4H_2O$ (where An is aniline, *p*-Tol is *p*-toluidine, NxH is 1,2-cyclohexanedione dioximate) [7].

Aminopolycarboxylate complexes of germanium(IV) have attracted considerable interest due to their intriguing structural features and plant growth-stimulating properties. These compounds have been systematically investigated for many years at the Faculty of Chemistry and Pharmacy of Odesa I.I. Mechnikov National University within the scientific school led by I.I. Seifullina [12–14]. The complex acid $[Ge(OH)(HEdta)]\times H_2O$ was synthesized, and heteronuclear complexes with various 3d metals were obtained using this compound as a structural building block. It was shown that, in the presence of Cu^{2+} ions, a heteronuclear complex $[Cu(H_2O)_4\{Ge(OH)(\mu\text{-}Edta)\}_2]$ is formed, in which the copper ion is coordinated by two nitrogen atoms of the fully deprotonated ligand and four water molecules [12]. A polymeric heteronuclear Ge(IV)-Cu(II) compound based on the H_4Edta derivative 3-diamino-2-hydroxypropanetetraacetic acid (H_5Hpdta) and 2,2'-bipyridine, $\{[Ge_2(OH)_2(\mu_3\text{-}hpdta)_2Cu_2(bipy)_2]\times 2H_2O\}_n$, was also obtained [15]. However, mixed-ligand complexes of Ge(IV) – 3d metals with H_4Edta and heterocyclic amines have not yet been systematically investigated.

The aim of this work is to develop synthetic approaches for coordination compounds of Ge(IV)–Mn(II)/Co(II), Ni(II), Cu(II), and Zn(II) with ethylenediaminetetraacetic acid and 2,2′-bipyridine, to perform their comprehensive characterization using modern physicochemical methods, and to establish their structural features.

EXPERIMENT AND DISCUSSION OF THE RESULTS. As starting reagents for the synthesis of new complexes, were used ready-made reagents (Sigma-Aldrich) without additional purification: germanium(IV) oxide (GeO_2, 99.99%), ethylenediaminetetraacetic acid (H_4Edta, CAS 60-00-4, ³98%), 2,2'-bipyridine

(bipy, CAS 366-18-7, 99.5%), and metal salts $Mn(CH_3COO)_2 \cdot 4H_2O$, $Co(CH_3COO)_2 \cdot 4H_2O$, $Ni(CH_3COO)_2 \cdot 4H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, $Zn(CH_3COO)_2 \cdot 2H_2O$ (98-99%).

Synthesis of compounds **1**–**5**. An equimolar amount of GeO_2 (0.05 mol, 5.23 g) was added to an aqueous solution of H_4Edta (0.05 mol, 14.6 g in 1 L of water at 100°C), and the mixture was evaporated for 2 hours at 80 °C to a volume of 500 mL and cooled at room temperature 20–25 °C (working solution). The working solution was divided into 5 parts. Solutions containing 0.005 mol of the corresponding metal salt and bipy, in a 1:2 ratio, were separately prepared in 10 mL of 95% ethanol. These solutions were added to part of the working solution and mixed. After 24 h, crystalline precipitates of light pink (complexes **1** – with Mn, **5** – with Zn), yellow (complex **2** – with Co), burgundy (complex **3** – with Ni), and blue (complex **4** – with Cu) were formed in the reaction medium. Yields ranged between 63–70%.

Elemental analysis was performed on C,N,H-analyzer Elemental Analyzer CE-440. The metal content in the complexes was measured by inductively coupled plasma atomic emission spectroscopy using a PerkinElmer Optima 8000.

Thermogravimetric analysis (TGA) was performed on a Q-1500D device at a heating rate of 10°C/min in air, over the temperature range 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 and complex compounds of germanium(IV) and other metals [12, 16, 17].

ESI-mass spectra were taken on a TSQ Fortis Triple Quadrupole Mass Spectrometer (ThermoFisher Scientific, USA). The sample was infused with a Chemyx Fusion 100T2 syringe pump at a flow rate of 20 mL/min. Water-methanol solutions of the complexes (at about 10 μg/mL) were introduced using a 500 μL Hamilton gas-tight syringe. 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. Mass spectra were collected in centroid mode over the m/z range of 50–1500 Da.

The main results of the study of complexes are presented below.

Elem. Anal. Calculated (%) for $C_{40}H_{52}Ge_2MnN_8O_{23}$ (**1**, M_r = 1212): C 39.60, H 4.29, Ge 11.96, Mn 4.54, N 9.24; found (%): C 39.37, H 4.20, Ge 11.87, Mn 4.48, N 9.16. *IR spectrum* (KBr, ν cm^{-1}): 3422 ν(OH), 3058 $\nu(C–H_{bipy})$, 2996 ν(C–H), 1712 $\nu_{as}(COO)$, 1592, 1173 $\nu(C–C_{bipy})$, 1472 $\delta_{as}(CH_2)$, 1437 $\nu_s(COO)$, 1402 $\delta_s(CH_2)$, 1312 $\nu(C–N_{bipy})$, 1079 ν(C–N), 1012 ν(C–O), 934, 873 $\delta(C–H_{bipy})$, 773, 736 $\gamma(C–H_{bipy})$, 818 δ(GeOH), 652 ν(Ge–O), 509 ν(Mn–N), 428 ν(Mn–O). *TGA data* (weight losses): 50-170 °C (7.5%); 170–320 °C (25.5%); 320–700 °C (46.0%); residue 21.0%. *ESI-mass spectrum* ESI(-): $[Ge(OH)(Edta)]^-$ (m/z = 375.16, 376.88, 379.08); ESI(+): $Hbipy^+$ (m/z = 157.10), $[Mn(bipy)_2]^{2+}$ (m/z = 183.61).

Elem. Anal. Calculated (%) for $C_{40}H_{56}CoGe_2N_8O_{25}$ (**2**, M_r = 1252): C 38.34, H 4.47, Co 4.71, Ge 11.58, N 8.85; found (%): C 38.21, H 4.30, Co 4.58, Ge 11.45, N 8.72. *IR spectrum* (KBr, ν, cm^{-1}): 3421 ν(OH), 3079 $\nu(C–H_{bipy})$, 2990 ν(C–H), 1713 $\nu_{as}(COO)$, 1598, 1158 $\nu(C–C_{bipy})$, 1473 $\delta_{as}(CH_2)$, 1442 $\nu_s(COO)$, 1399 $\delta_s(CH_2)$, 1314 $\nu(C–N_{bipy})$, 1078 ν(C–N), 1018 ν(C–O), 935, 872 $\delta(C–H_{bipy})$,

776, 737 γ(C–H_{bipy}), 816 δ(GeOH), 652 ν(Ge–O), 510 ν(Co–N), 419 ν(Co–O). *TGA data* (weight losses): 50-190 °C (10.0%); 190–340 °C (24.0%); 340–550 °C (44.0%); residue 22.0%. *ESI-mass spectrum* ESI(-): $[Ge(OH)(Edta)]^-$ (m/z = 375.23, 376.87, 379.07), other fragments (m/z = 393.36, 403.39); ESI(+): $Hbipy^+$ (m/z = 157.10), $[Co(bipy)_2]^{2+}$ (m/z = 185.59, 186.33).

Elem. Anal. Calculated (%) for $C_{40}H_{56}Ge_2N_8NiO_{25}$ (**3**, M_r = 1252): C 38.34, H 4.47, Ge 11.58, N 8.85, Ni 4.71; found (%): C 38.09, H 4.36, Ge 11.50, N 8.79, Ni 4.67. *IR spectrum* (KBr, ν, cm^{-1}): 3416 ν(OH), 3076 ν(C–H_{bipy}), 2986 ν(C–H), 1711 ν_{as}(COO), 1599, 1159 ν(C–C_{bipy}), 1473 $\delta_{as}(CH_2)$, 1444 ν_s(COO), 1396 $\delta_s(CH_2)$, 1312 ν(C–N_{bipy}), 1078 ν(C–N), 1021 ν(C–O), 933, 871 δ(C–H_{bipy}), 776, 738 γ(C–H_{bipy}), 818 δ(GeOH), 654 ν(Ge–O), 536 ν(Ni–N), 427 ν(Ni–O). *TGA data* (weight losses): 50-180 °C (10.0%); 180–340 °C (24.0%); 340–550 °C (47.5%); residue 18.5%. *ESI-mass spectrum* ESI(-): $[Ge(OH)(Edta)]^-$ (m/z = 375.00, 376.97, 378.95); ESI(+): $Hbipy^+$ (m/z = 157.09), $[Ni(bipy)_2]^{2+}$ (m/z = 185.08, 186.03).

Elem. Anal. Calculated (%) for $C_{40}H_{50}CuGe_2N_8O_{22}$ (**4**, M_r = 1203): C 39.90, H 4.16, Cu 5.32, Ge 12.05, N 9.31; found (%): C 39.81, H 4.10, Cu 5.24, Ge 12.15, N 9.26. *IR spectrum* (KBr, ν, cm^{-1}): 3415 ν(OH), 3095 ν(C–H_{bipy}), 2993 ν(C–H), 1714 ν_{as}(COO), 1600, 1159 ν(C–C_{bipy}), 1473 $\delta_{as}(CH_2)$, 1444 ν_s(COO), 1394 $\delta_s(CH_2)$, 1312 ν(C–N_{bipy}), 1079 ν(C–N), 1014 ν(C–O), 964, 872 δ(C–H_{bipy}), 773, 732 γ(C–H_{bipy}), 816 δ(GeOH), 658 ν(Ge–O), 512 ν(Cu–N), 425 ν(Cu–O). *TGA data* (weight losses): 50-170 °C (6.0%); 170–280 °C (26.0%); 280–550 °C (46.0%); residue 22.0%. *ESI-mass spectrum* ESI(-): $[Ge(OH)(Edta)]^-$ (m/z = 375.19, 376.76, 379.12), other fragments (m/z = 393.42, 403.43); ESI(+): $Hbipy^+$ (m/z = 157.14), $[Cu(bipy)_2]^{2+}$ (m/z = 187.63, 188.55).

Elem. Anal. Calculated (%) for $C_{40}H_{52}Ge_2N_8O_{23}Zn$ (**5**, M_r = 1222): C 39.28, H 4.26, Ge 11.87, N 9.17, Zn 5.32; found (%): C 39.19, H 4.30, Ge 11.78, N 9.10, Zn 5.37. *IR spectrum* (KBr, ν, cm^{-1}): 3420 ν(OH), 3075 ν(C–H_{bipy}), 2994 ν(C–H), 1711 ν_{as}(COO), 1589, 1160 ν(C–C_{bipy}), 1472 $\delta_{as}(CH_2)$, 1440 ν_s(COO), 1395 $\delta_s(CH_2)$, 1313 ν(C–N_{bipy}), 1078 ν(C–N), 1020 ν(C–O), 932, 873 δ(C–H_{bipy}), 775, 736 γ(C–H_{bipy}), 814 δ(GeOH), 651 ν(Ge–O), 515 ν(Zn–N), 434 ν(Zn–O). *TGA data* (weight losses): 60-190 °C (7.0%); 190-330 °C (26.0%); 330–800 °C (46.0%); residue 21.0%. *ESI-mass spectrum* ESI(-): $[Ge(OH)(Edta)]^-$ (m/z = 375.05, 376.76, 379.01), other fragment (m/z = 393.33); ESI(+): $Hbipy^+$ (m/z = 157.09), $[Zn(bipy)_2]^{2+}$ (m/z = 188.56, 189.09).

IR spectra of **1**–**5** are similar in the region of vibrational bands (as an example, fig. 1 shows the spectra of complexes Co(II), and Ni(II)) characteristic of the coordination polyhedron of germanium. The presence of asymmetric and symmetric stretching vibrations of the carboxylate groups ν_{as}(COO) and ν_s(COO), clearly indicates coordination of the carboxylate moieties to the Ge(IV) center. The value of the Deacon–Phillips criterion $\Delta\nu = \nu_{as}(COO) - \nu_s(COO) \sim 267–275$ cm^{-1} indicates monodentate coordination of all carboxylate groups of the ligand. In addition, bands assigned to Ge–O and Ge–N stretching vibrations, as well as deformation vibrations δ(GeOH), are observed. The absence of bands in the region around 1730 cm^{-1} confirms that protonated carboxylic groups are not present. In general, the spectra **1**–**5** in this region are similar to the spectrum of complex ethylenediaminetetraacetategermanic acid.

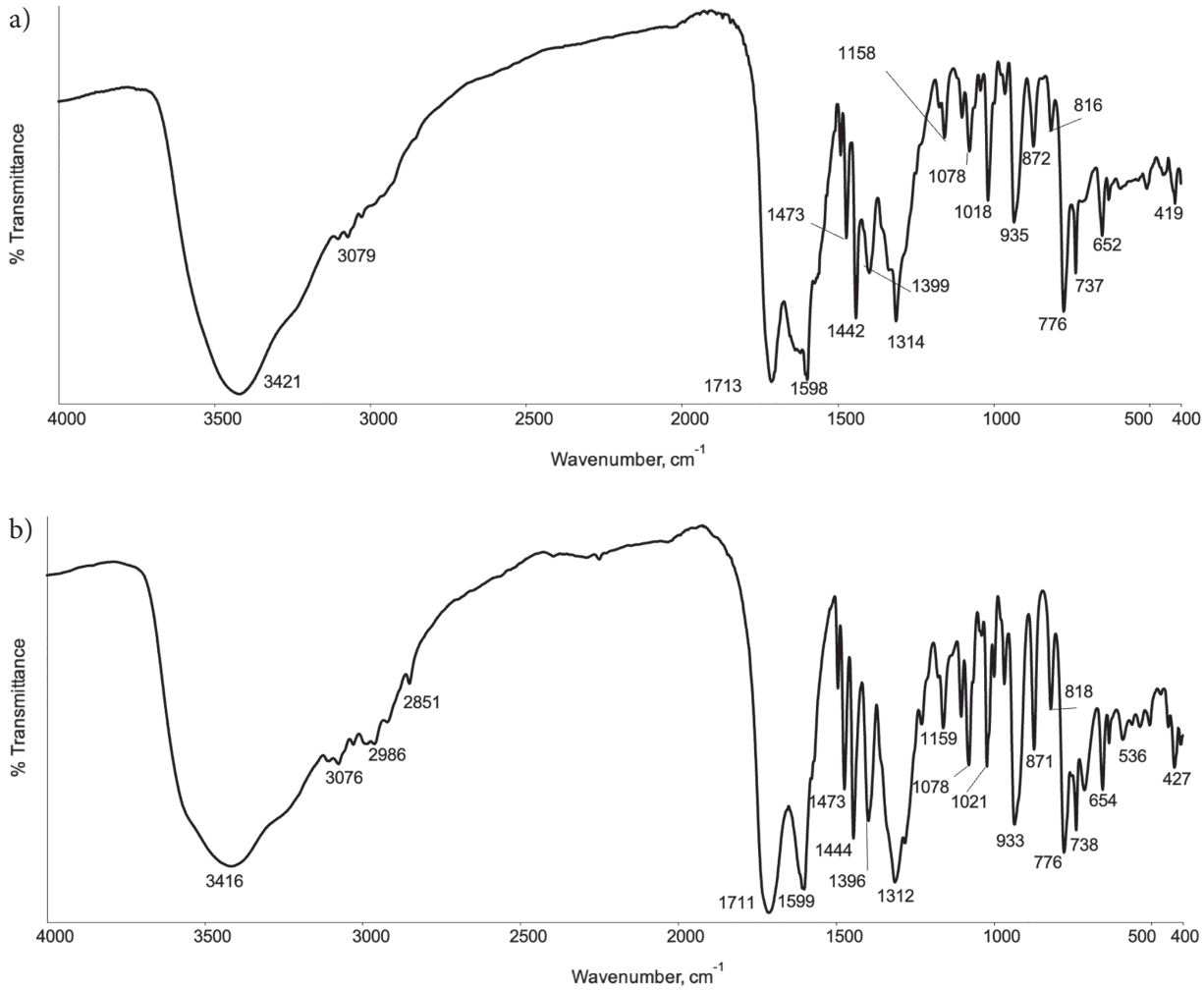


Fig. 1. IR spectra of the complexes **2** (a) and **3** (b).

Overall, the spectra of complexes **1**–**5** in this region closely resemble that of ethylenediaminetetraacetatogermanic acid. This indicates that the coordination environment of germanium remains analogous to that in [Ge(OH)(HEdta)]×H_2O [12], adopting a distorted octahedral polyhedron. The coordination number of six is achieved through coordination with one hydroxyl group, three oxygen atoms of three carboxylate groups, and two nitrogen atoms of the Edta-ligand.

A set of characteristic bands assigned to $\nu(C–H_{bipy})$, $\nu(C–N_{bipy})$, $\delta(C–H_{bipy})$, $\gamma(C–H_{bipy})$ confirms the presence of 2,2'-bipyridine in the complexes and its coordination to the 3d metal ions. This is further supported by the appearance of a band corresponding to M–N stretching vibrations. The absorption band attributed to ν(M–O) stretching vibrations indicates the coordination of the fourth carboxylate group of Edta to the 3d metal ion. Based on the IR spectral data and considering the +2 oxidation

state of the 3d metal ions, an octahedral coordination polyhedron can be proposed for these metal centers. It is formed due to valence bonds with oxygen atoms of two carboxylate groups of two fragments [Ge(OH)(Edta)] and four coordination bonds with nitrogen atoms of two bipyridine molecules.

Broad and intense absorption bands observed at approximately ~3400 cm^{-1} in the IR spectra of complexes **1**–**5** are assigned to O–H stretching vibrations of crystallization water molecules, which is consistent with the thermogravimetric analysis data (fig. 2).

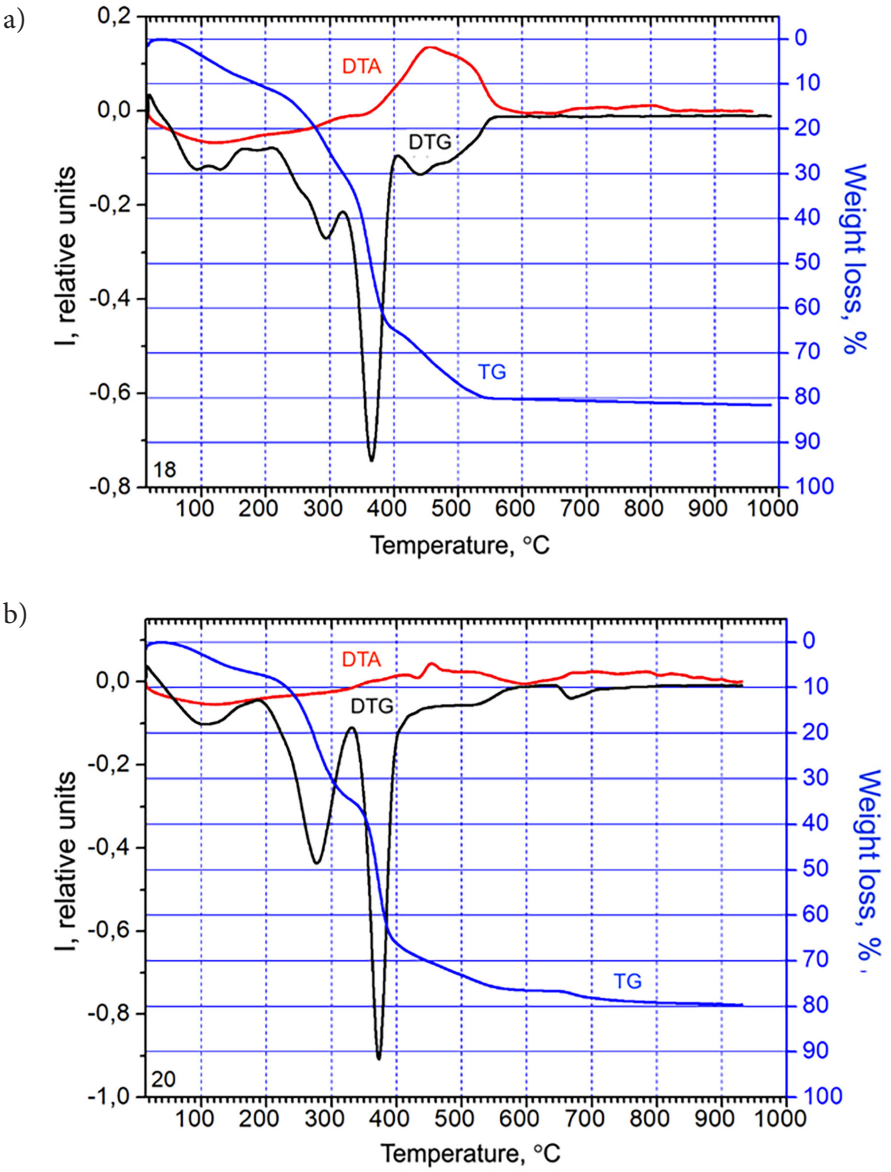
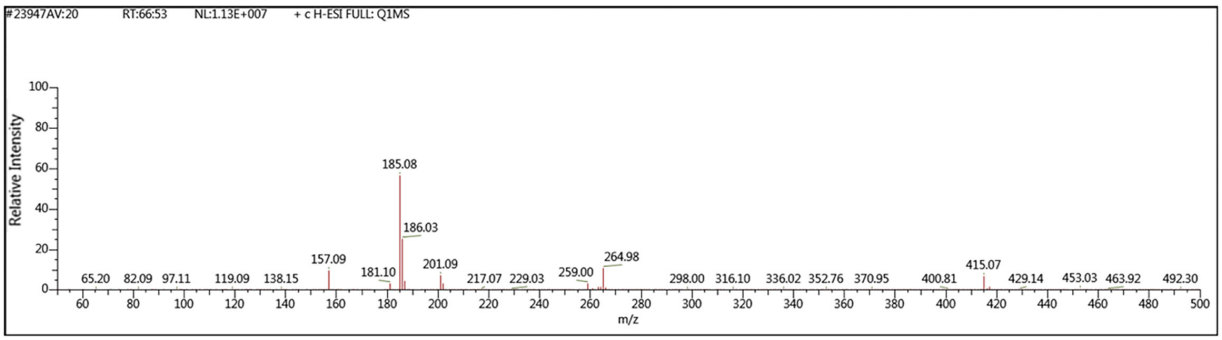


Fig. 2. Thermogravigrams of the complexes **2** (a) and **5** (b).

The thermal decomposition behavior of the studied compounds is generally similar (as an example, fig. 2 shows the thermogravimetric curves of complexes Co(II), and Zn(II)). Thermogravimetric analysis confirms that they are crystalline hydrates. In the temperature range of 50–180 °C, the corresponding number of crystallization water molecules is released into the gas phase (5 for complexes **1** and **5**, 7 for complexes **2** and **3**, and 4 for complex **4**). Upon further heating, in the interval of 180-340 °C, the removal of two bipyridine molecules occurs, as evidenced by the mass losses calculated from the TG curves. Evaluation of the mass loss from the thermogravimetric data at 800 °C confirms that the final decomposition product of compounds **1**–**5** is a mixture of GeO_2 and the oxide of the corresponding 3d metal.

Analysis of the mass spectra of the newly synthesized complexes revealed that the ESI(+) mass spectra recorded in positive ion mode exhibit a low-intensity signal corresponding to protonated 2,2'-bipyridine $Hbipy^+$, along with signals attributable to doubly charged cations $[M(bipy)_2]^{2+}$ (where M denotes a 3d metal ion). The presence of multiple peaks in this region arises from the natural isotopic distribution of the constituent elements that form these cations (as an example, fig. 3 shows the spectra of heterometallic complexes Co(II), Cu(II)).

a)



b)

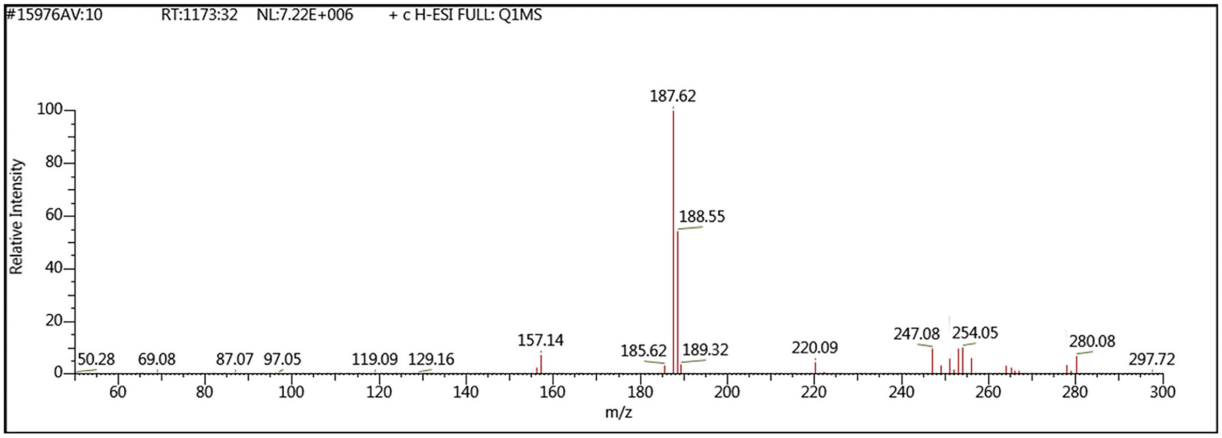
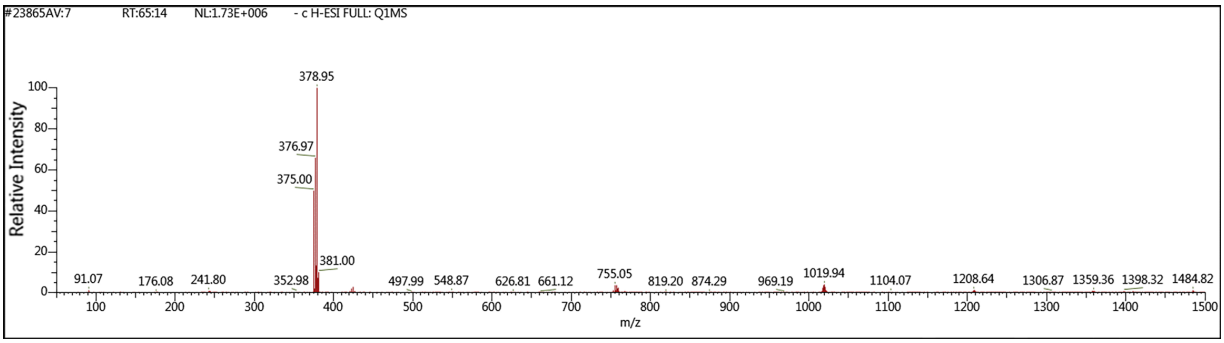


Fig. 3. ESI(+) mass spectra of a water-methanol solution of complex **2** (*a*) and **4** (b).

a)



b)

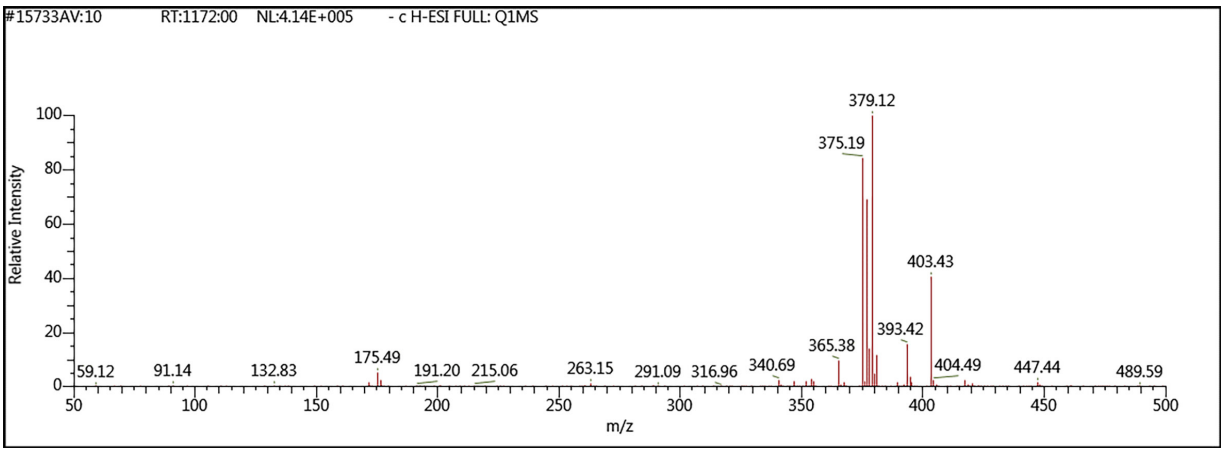


Fig. 4. ESI(-) mass spectra of a water-methanol solution of complex **2** (*a*) and **4** (b).

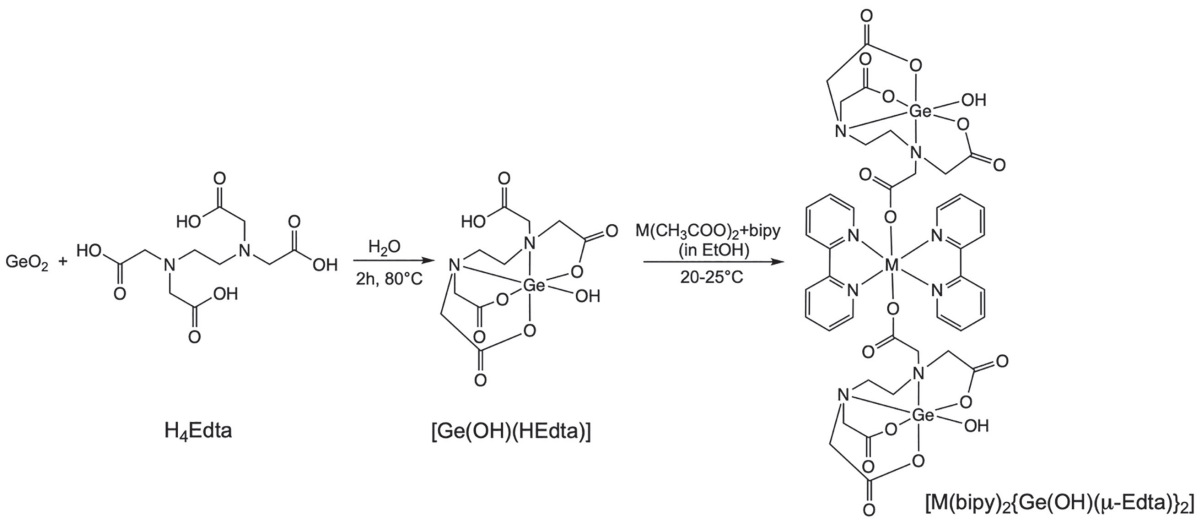


Fig. 5. The synthesis scheme and the supposed structure of the compounds **1**–**5** (M = Mn, Co, Ni, Cu, Zn).

In the negative ion mode (fig. 4), the mass spectra display an intense signal at m/z ~ 379, belonging to anion $[Ge(OH)(Edta)]^-$, along with several additional, unassigned signals that are likely formed as a result of fragmentation processes occurring for complexes **4**, and **5**.

On the basis of a comprehensive analysis of the elemental composition, thermogravimetric data, infrared spectral features, and mass spectrometric results, together with consideration of the characteristic coordination number of six for Ge(IV) and comparison with previously structurally characterized germanium compounds, formulas for the synthesized complexes were proposed: $[M(bipy)_2\{Ge(OH)(\mu\text{-}Edta)\}_2]\times nH_2O$ (M = Mn(II), n=5 (**1**); Co(II), n=7 (**2**); Ni(II), n=7 (**3**); Cu(II), n=4 (**4**); Zn(II), n=5 (**5**)).

The synthesis scheme and the supposed structure of the compounds, excluding crystallization water molecules, can be presented as follows (fig. 5).

CONCLUSIONS. Thus, five new different-metall mixed-ligand coordination compounds were synthesized. It was shown that the ligand-complexon is a bridge between the Ge and Cu atoms. The octahedral coordination polyhedron of Ge(IV) is formed through coordination with one hydroxyl group, three oxygen atoms of three carboxylate groups, and two nitrogen atoms of the Edta. An octahedral polyhedron of 3d-metal is realized due to two bonds with oxygen atoms of carboxylate groups of two fragments [Ge(OH)(Edta)] and four bonds with nitrogen atoms of two 2,2'-bipyridine molecules.

This work was performed within the theme "Chemical construction of organo-inorganic ensembles of coordinating, supramolecular, polymeric nature for use as new materials and pharmaceuticals", state registration number: 0122U201403.

СИНТЕЗ ТА КОМПЛЕКСНЕ ДОСЛІДЖЕННЯ ГЕТЕРОЯДЕРНИХ Ge(IV) – 3d-МЕТАЛОКОМПЛЕКСІВ З ЕТИЛЕНДІАМІНТЕТРАОЦТОВОЮ КИСЛОТОЮ ТА 2,2'-БІПІРИДИНОМ

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Розроблено синтетичний підхід та отримано різнометальні координаційні сполуки $[M(bipy)_2\{Ge(OH)(\mu\text{-}Edta)\}_2]\times nH_2O$ (H_4Edta – етилендіамінтетраоцтова кислота, bipy – 2,2'-біпіридин, M = Mn(II), n=5 (1); Co(II), n=7 (2); Ni(II), n=7 (3); Cu(II), n=4 (4); Zn(II), n=5 (5)). Проведено їхнє комплексне дослідження з використанням сучасних фізико-хімічних методів (елементний аналіз, ІЧ-спектрометрія, мас-спектрометрія, термогравіметрія) та встановлено структурні особливості. Показано, що всі синтезовані комплекси є гетероядерними. Координаційний поліедр германію(IV) є аналогічним до такого в раніше структурно охарактеризованій етилендіамінтетраацетатогерманатній кислоті $[Ge(OH)(HEdta)]\cdot H_2O$: несиметричний октаедр, що утворений в результаті координації гідроксильної групи, трьох атомів Оксигену трьох карбоксилатних груп та

двома атомами Нітрогену Edta-ліганду. Координаційне число 3d-металу дорівнює шести та реалізується за рахунок двох зв'язків з Оксигенами карбоксилатних груп двох германієвмісних комплексних аніонів та чотирьох зв'язків з атомами Нітрогену двох молекул 2,2'-біпіридину.

Ключові слова: германій(IV), етилендіамінтетраоцтова кислота, гетероциклічний амін, координаційні сполуки, ІЧ-спектроскопія, термогравіметрія, мас-спектрометрія.

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