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**SYNTHESIS AND STRUCTURE OF HETEROMETALLIC MULTILIGAND Ge(IV) - 3d-METALS COMPLEXES WITH 1-HYDROXYETHANE-1,1-DIPHOSPHONIC ACID AND 1,10-PHENANTHROLINE**

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# SYNTHESIS AND STRUCTURE OF HETEROMETALLIC MULTILIGAND Ge(IV) - 3d-METALS COMPLEXES WITH 1-HYDROXYETHANE-1,1-DIPHOSPHONIC ACID AND 1,10-PHENANTHROLINE

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**Abstract.** Synthesis methods were developed, five new coordination compounds were isolated and investigated:  $[M(\text{phen})_3]_4[\text{Ge}_6(\mu\text{-OH})_4(\mu\text{-O})_2(\mu\text{-hedp})_6] \cdot x\text{CH}_3\text{COOH} \cdot n\text{H}_2\text{O}$  (M= Fe (1),  $x=0$ ,  $n=20$ ; Co (2),  $x=2$ ,  $n=30$ ; Ni (3),  $x=2$ ,  $n=26$ ),  $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})]_2[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3]_2[\text{Ge}_6(\mu\text{-OH})_4(\mu\text{-O})_2(\mu\text{-hedp})_6] \cdot 16\text{H}_2\text{O}$  (4),  $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})_2]_2[\text{Zn}(\text{phen})(\text{H}_2\text{O})_4]_2[\text{Ge}_6(\mu\text{-OH})_4(\mu\text{-O})_2(\mu\text{-hedp})_6] \cdot 18\text{H}_2\text{O}$  (5), where  $\text{H}_4\text{hedp}$  – 1-hydroxyethane-1,1-diphosphonic acid, phen – 1,10-phenanthroline. It was found that the complexes belong to the cation-anion type, consisting of the hexanuclear complex anion, in which Ge atoms are connected by three types of bridging ligands (hydroxy-, oxo-, and 1-hydroxyethane-1,1-diphosphonate), and phenanthroline-containing cations of different compositions depending on the 3d-metal. Synthesized substances in crystals are organic-inorganic hybrid ensembles with three-dimensional networks formed by numerous intermolecular hydrogen bonds between complex cations, anions, and crystalline water molecules.

**Keywords:** 1-hydroxyethane-1,1-diphosphonic acid, 1,10-phenanthroline, germanium, 3d-metal, crystal structure.

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## Introduction

1-Hydroxyethane-1,1-phosphonic (1-hydroxyethylidenediphosphonic, etidronic) acid ( $\text{H}_4\text{hedp}$ ) is a well-known complexing agent of the phosphonic type that has various valuable properties and is used in different areas [1-4]. Thus, proton-conducting inorganic-organic hybrid membranes with high thermal stability and superior flexibility were developed based on  $\text{H}_4\text{hedp}$  and epoxyhexylethyltrimetoxysilane [1], and inhibitory protective films that reduce the corrosion rate of carbon steel in solutions with chloride ions [2]. In addition, 1-hydroxyethane-1,1-diphosphonic acid labelled with short-lived radionuclides suitable for therapeutic purposes ( $^{186}\text{Re}$ ,  $^{188}\text{Re}$ ,  $^{166}\text{Ho}$ ) is used in the radiopharmaceutical industry for the palliative treatment of bone metastases [3,4].

To date, complexes of metals with  $\text{H}_4\text{hedp}$  and additional nitrogen-containing compounds acting as exo-ligands are intensively studied. For example, hybrid metal-organic frameworks

with dielectric properties as new electrode materials for high-performance supercapacitors were obtained based on the complex  $[\text{H}_2\text{tepa}][\text{Zn}_6(\text{Hhedp})_2(\text{hedp})_2] \cdot 2\text{H}_2\text{O}$  (tepa – tetra ethylenepentamine) [5]. Fluorescent coordination polymers  $\{[\text{Zn}_6(\text{HL-H})_4(\text{bipy})_4] \cdot \frac{1}{4}\text{H}_2\text{O}\}_n$  and  $\{[\text{Zn}_3(\text{HL-H})_2(\text{H}_2\text{O})_4] \cdot 6\text{H}_2\text{O}\}_n$  with the  $\text{H}_4\text{hedp}$  derivative - 1-hydroxy-2-(3-pyridyl)ethylidene-1,1-diphosphonic acid ( $\text{H}_5\text{L}$ ) were synthesized by introducing 2,2'-bipyridine (bipy) as a second ligand [6].

As a result of systematic studies of coordination compounds of germanium(IV) in recent years, the authors showed the prospects of introducing an alcoholic solution of the 1,10-phenanthroline complex of the 3d-metal into the  $\text{GeO}_2$  - hydroxycarboxylic acid - water system for the crystallization of compounds with unique structures and interesting properties [7-9]. On the basis of 1-hydroxyethane-1,1-diphosphonic acid were obtained heterometallic complexes of germanium(IV) with  $\text{CoCl}_2$  and

2,2'-bipyridine [10], and with CuCl<sub>2</sub> and 1,10-phenanthroline [11].

The aim of this work is an investigation of systems GeO<sub>2</sub> – H<sub>4</sub>hedp – 3d-metal acetate – 1,10-phenanthroline, establishing the structure and properties of heterometallic multiligand complexes of Ge(IV) and divalent Fe, Co, Ni, Cu, Zn with 1-hydroxyethane-1,1-diphosphonic acid and 1,10-phenanthroline.

## Experimental

### Materials

Reagents used for the synthesis of compounds were purchased from Sigma-Aldrich and used without further purification: GeO<sub>2</sub>, FeSO<sub>4</sub>·7H<sub>2</sub>O, Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O, Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, 1-hydroxyethane-1,1-diphosphonic acid (C<sub>2</sub>H<sub>8</sub>O<sub>7</sub>P<sub>2</sub>, CAS 7414-83-7), 1,10-phenanthroline (phen, C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>, CAS 66-71-7).

**Synthesis of compounds 1-5.** A portion of GeO<sub>2</sub> (0.2092 g, 2 mmol) was added to a solution of H<sub>4</sub>hedp (0.412 g, 2 mmol) in 200 mL of water (100°C), heated to boiling and concentrated at 80°C for 6 h to 20 mL and cooled at room temperature (working solution). The solution was divided into 5 parts containing 0.4 mmol of complex 1-hydroxyethane-1,1-diphosphonategermanic acid [12]. Solutions containing 0.2 mmol of the corresponding metal salt and phen in a ratio of 1:2 and 1:3 were separately prepared in 10 mL of 95% ethanol. These solutions were added to part of the working solution and mixed. After 2 days, crystalline precipitates of yellow (complexes 1, 2), pink (3), blue (4), and white (5) colour were formed in the reaction medium. Yields were ranging between 64-72%. Single crystals of compounds 2, 4, and 5 for X-ray diffraction were grown by slow diffusion of acetonitrile vapours into a solution of the corresponding complex.

**Complex** [Fe(phen)<sub>3</sub>]<sub>4</sub>[Ge<sub>6</sub>(μ-OH)<sub>4</sub>(μ-O)<sub>2</sub>(μ-hedp)<sub>6</sub>]-20H<sub>2</sub>O (1). Calculated (%) for C<sub>156</sub>H<sub>164</sub>Fe<sub>4</sub>Ge<sub>6</sub>N<sub>24</sub>O<sub>68</sub>P<sub>12</sub>, (Mr= 4492) C 41.67, H 3.65, Fe 4.99, Ge 9.69, N 7.48, P 8.28. Found (%): C 41.29, H 3.57, Fe 4.82, Ge 9.72, N 7.39, P 8.19. IR (KBr, ν, cm<sup>-1</sup>): 3379 ν(OH), 2918 ν(C-H<sub>arom</sub>), 1598, 1518 ν(C-C<sub>arom</sub>), 1448, 1425 δ<sub>as</sub>(CH<sub>3</sub>), 1342 δ<sub>s</sub>(CH<sub>3</sub>), 1308 ν(C-N), 1176 ν(P=O), 1050 ν<sub>as</sub>(PO<sub>3</sub>), 973 ν<sub>s</sub>(PO<sub>3</sub>), 850 δ(C-H), 814 δ(Ge-OH), 674 ν(Ge-O<sub>phos</sub>).

**Complex** [Co(phen)<sub>3</sub>]<sub>4</sub>[Ge<sub>6</sub>(μ-OH)<sub>4</sub>(μ-O)<sub>2</sub>(μ-hedp)<sub>6</sub>]-2CH<sub>3</sub>COOH·30H<sub>2</sub>O (2). Calculated (%) for C<sub>160</sub>H<sub>192</sub>Co<sub>4</sub>Ge<sub>6</sub>N<sub>24</sub>O<sub>82</sub>P<sub>12</sub>, (Mr= 4806) C 39.95, H 3.40, Co 4.91, Ge 9.03, N 6.99, P 7.75.

Found (%): C 39.58, H 3.34, Co 4.85, Ge 9.03, N 6.87, P 7.66. IR (KBr, ν, cm<sup>-1</sup>): 3380 ν(OH), 2930 ν(C-H<sub>arom</sub>), 1720 ν(C=O<sub>COOH</sub>), 1598, 1517 ν(C-C<sub>arom</sub>), 1452, 1425 δ<sub>as</sub>(CH<sub>3</sub>), 1340 δ<sub>s</sub>(CH<sub>3</sub>), 1307 ν(C-N), 1199 ν(P=O), 1053 ν<sub>as</sub>(PO<sub>3</sub>), 970 ν<sub>s</sub>(PO<sub>3</sub>), 849 δ(C-H), 816 δ(Ge-OH), 677 ν(Ge-O<sub>phos</sub>).

**Complex** [Ni(phen)<sub>3</sub>]<sub>4</sub>[Ge<sub>6</sub>(μ-OH)<sub>4</sub>(μ-O)<sub>2</sub>(μ-hedp)<sub>6</sub>]-2CH<sub>3</sub>COOH·26H<sub>2</sub>O (3). Calculated (%) for C<sub>160</sub>H<sub>184</sub>Ge<sub>6</sub>N<sub>24</sub>Ni<sub>4</sub>O<sub>78</sub>P<sub>12</sub>, (Mr= 4734) C 40.56, H 3.89, Ni 4.99, Ge 9.20, N 7.10, P 7.86. Found (%): C 40.45, H 3.78, Ni 4.87, Ge 9.14, N 7.17, P 7.79. IR (KBr, ν, cm<sup>-1</sup>): 3399 ν(OH), 2929 ν(C-H<sub>arom</sub>), 1715 ν(C=O<sub>COOH</sub>), 1597, 1517 ν(C-C<sub>arom</sub>), 1450, 1426 δ<sub>as</sub>(CH<sub>3</sub>), 1341 δ<sub>s</sub>(CH<sub>3</sub>), 1307 ν(C-N), 1194 ν(P=O), 1051 ν<sub>as</sub>(PO<sub>3</sub>), 969 ν<sub>s</sub>(PO<sub>3</sub>), 849 δ(C-H), 815 δ(Ge-OH), 673 ν(Ge-O<sub>phos</sub>).

**Complex** [Cu(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>[Cu(phen)(H<sub>2</sub>O)<sub>3</sub>]<sub>2</sub>[Ge<sub>6</sub>(μ-OH)<sub>4</sub>(μ-O)<sub>2</sub>(μ-hedp)<sub>6</sub>]-16H<sub>2</sub>O (4). Calculated (%) for C<sub>84</sub>H<sub>124</sub>Cu<sub>4</sub>Ge<sub>6</sub>N<sub>12</sub>O<sub>72</sub>P<sub>12</sub>, (Mr= 3515) C 28.67, H 3.53, Cu 7.28, Ge 12.39, N 4.78. Found (%): C 28.45, H 3.44, Cu 7.38, Ge 12.40, N 4.69. IR (KBr, ν, cm<sup>-1</sup>): 3252 ν(OH), 3062 ν(C-H<sub>arom</sub>), 1627 δ(H<sub>2</sub>O), 1585, 1519 ν(C-C<sub>arom</sub>), 1428 δ<sub>as</sub>(CH<sub>3</sub>), 1341 δ<sub>s</sub>(CH<sub>3</sub>), 1310 ν(C-N), 1183 ν(P=O), 1053 ν<sub>as</sub>(PO<sub>3</sub>), 985 ν<sub>s</sub>(PO<sub>3</sub>), 851 δ(C-H), 813 δ(Ge-OH), 668 ν(Ge-O<sub>phos</sub>), 487 ν(Cu-O).

**Complex** [Zn(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>[Zn(phen)(H<sub>2</sub>O)<sub>4</sub>]<sub>2</sub>[Ge<sub>6</sub>(μ-OH)<sub>4</sub>(μ-O)<sub>2</sub>(μ-hedp)<sub>6</sub>]-18H<sub>2</sub>O (5). Calculated (%) for C<sub>84</sub>H<sub>136</sub>Ge<sub>6</sub>N<sub>12</sub>O<sub>78</sub>P<sub>12</sub>Zn<sub>4</sub>, (Mr= 3631) C 27.76, H 3.75, Zn 7.16, Ge 12.00, N 4.63. Found (%): C 27.69, H 3.78, Zn 7.23, Ge 12.04 N 4.56. IR (KBr, ν, cm<sup>-1</sup>): 3391 ν(OH), 2998 ν(C-H<sub>arom</sub>), 1625 δ(H<sub>2</sub>O), 1584, 1519 ν(C-C<sub>arom</sub>), 1449, 1428 δ<sub>as</sub>(CH<sub>3</sub>), 1343 δ<sub>s</sub>(CH<sub>3</sub>), 1307 ν(C-N), 1190 ν(P=O), 1054 ν<sub>as</sub>(PO<sub>3</sub>), 974 ν<sub>s</sub>(PO<sub>3</sub>), 851 δ(C-H), 815 δ(Ge-OH), 673 ν(Ge-O<sub>phos</sub>), 470 ν(Zn-O).

### Physical measurements

**Elemental analysis** was performed on C,N,H-analyzer Elemental Analyzer CE-440. The content of phosphorus, germanium and other metals was determined on an optical emission spectrometer with an inductively coupled plasma Optima 8000 PerkinElmer.

**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.

**IR spectroscopy.** IR absorption spectra of complexes and ligands (for comparison reasons) were recorded in KBr tablets on a Frontier PerkinElmer spectrophotometer in the range of

400–4000  $\text{cm}^{-1}$ , the bands were identified according to [7-13].

ESI-mass spectra were taken on TSQ Fortis Triple Quadrupole Mass Spectrometer (ThermoFisher Scientific, USA). Sample solutions in methanol were infused with a Chemyx Fusion 100T2 syringe pump with a 500  $\mu\text{L}$  Hamilton gas-tight syringe no 81265 (1750RNR) at a flow rate of 20  $\mu\text{L}/\text{min}$ . The electric potential used to initiate ESI was 3.0 to 3.5 kV in positive ionisation mode and 2.0 to 2.5 kV in negative ionisation mode. The ion transfer tube temperature was set at 300  $^{\circ}\text{C}$ , the vaporizer temperature was set at 150 $^{\circ}\text{C}$ , the sheath gas flow was 20 L/min, and the aux gas flow was 6 L/min. Mass spectra were collected in centroid mode in the  $m/z$  range of 50-500 Da using Q1 full scan mode with FWHM resolution set at 0.4 Da at a scan rate of 250 Da/sec. All spectra were measured in methanol-water (1/1, v/v) solutions with concentrations of complexes about 20-50  $\mu\text{g}/\text{mL}$ . Isotop distribution was calculated using [14].

Single crystal X-ray diffraction. X-ray diffraction data for compounds **2**, **4**, and **5** were measured on «Xcalibur-3» diffractometer (MoK $\alpha$  radiation, CCD-detector, graphite monochromator,  $\omega$ -scanning). The structure was solved using the SHELXT [15] and refined using

full-matrix least-squares based on F2 with the anisotropic approximation for non-hydrogen atoms using the SHELXL program [16], incorporated into the shell Olex2 [17]. The positions of hydrogen atoms were revealed from electron density maps and refined by “riding” model  $U_{\text{iso}} = nU_{\text{eq}}$  ( $n = 1.5$  for methyl and 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 Center, 12 Union Road, Cambridge, CB2 1EZ, UK (<https://www.ccdc.cam.ac.uk/structures/>) and are available on request quoting the deposition numbers. The crystal data and structure refinement are given in Table 1.

### Results and discussion

According to the data of the elemental analysis the products with constant composition corresponding to the molar ratio Ge : hedp : Fe (Co, Ni) : phen = 3:3:2:6 (**1**, **2**, **3**), Ge : hedp : Cu (Zn) : phen = 3:3:2:3 (**4**, **5**) were isolated from all synthetic systems regardless of the initial ratio of reagents. Solvate molecules of acetic acid were present in compounds **2** and **3** as the reaction with  $\text{K}_2\text{S}_2\text{O}_7$  confirmed that.

The crystal data and structure refinement for structures **2**, **4**, **5**

Table 1

Parameters	Structures		
	<b>2</b>	<b>4</b>	<b>5</b>
Empirical formula	$\text{C}_{160}\text{H}_{192}\text{Co}_4\text{Ge}_6\text{N}_{24}\text{O}_{82}\text{P}_{12}$	$\text{C}_{84}\text{H}_{124}\text{Cu}_4\text{Ge}_6\text{N}_{12}\text{O}_{72}\text{P}_{12}$	$\text{C}_{84}\text{H}_{136}\text{Ge}_6\text{N}_{12}\text{O}_{78}\text{P}_{12}\text{Zn}_4$
Formula weight	4806.26	3515.28	3630.7
Temperature/K	103	110	110
Crystal system	triclinic	triclinic	triclinic
Space group	$\text{P}\bar{1}$	$\text{P}\bar{1}$	$\text{P}\bar{1}$
$a/\text{\AA}$	17.2233(9)	14.9868(14)	15.1141(19)
$b/\text{\AA}$	17.9095(10)	15.8140(18)	15.8119(17)
$c/\text{\AA}$	19.3145(7)	17.7867(18)	19.842(3)
$\alpha/^\circ$	115.115(4)	115.549(10)	106.821(11)
$\beta/^\circ$	100.339(4)	94.136(8)	103.148(12)
$\gamma/^\circ$	91.448(4)	98.905(9)	97.728(10)
Volume/ $\text{\AA}^3$	5272.4(5)	3711.5(7)	4316.7(10)
Z	1	1	1
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.514	1.573	1.397
$\mu/\text{mm}^{-1}$	1.334	1.981	1.771
F(000)	2456	1776	1840
Reflections collected	48618	29835	34485
Independent reflections	20676 [ $R_{\text{int}} = 0.0775$ , $R_{\text{sigma}} = 0.1212$ ]	13031 [ $R_{\text{int}} = 0.1232$ , $R_{\text{sigma}} = 0.1888$ ]	15168 [ $R_{\text{int}} = 0.1061$ , $R_{\text{sigma}} = 0.1594$ ]
Data/restraints/parameters	20676/0/1313	13031/172/832	15168/235/842
Goodness-of-fit on $F^2$	1.019	0.971	0.972
Final R indexes [ $I \geq 2\sigma$ (I)]	$R_1 = 0.0790$ , $wR_2 = 0.1724$	$R_1 = 0.0875$ , $wR_2 = 0.1927$	$R_1 = 0.0876$ , $wR_2 = 0.2048$
Final R indexes [all data]	$R_1 = 0.1224$ , $wR_2 = 0.2010$	$R_1 = 0.1587$ , $wR_2 = 0.2441$	$R_1 = 0.1441$ , $wR_2 = 0.2386$
CCDC	2324734	2324735	2324736

The reaction of solvated acetic acid with potassium pyrosulfate produces potassium hydrogen sulphate and acetic anhydride. The reaction is carried out by thorough stirring, creating an intense smell of acetic anhydride.

Analysis of the IR spectra of the obtained compounds compared to initial ligands (H<sub>4</sub>hedp, phen) made it possible to obtain information about the forms of functional groups and the nature of bonds in **1-5**. The bands in the region of the valence vibrations of the bonds P=O 1176-1199 cm<sup>-1</sup>, P-O ~1050 and 970-985 cm<sup>-1</sup> point out the presence in the complexes of exclusively fully deprotonated phosphonic groups PO<sub>3</sub><sup>2-</sup>.

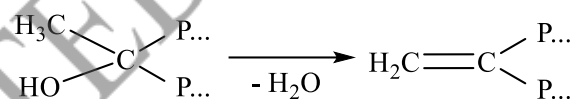
These groups are bonded to germanium thus the band ν(Ge-O<sub>phos</sub>) is observed in the spectra of all compounds at ~ 670 cm<sup>-1</sup>. In addition, germanium is in the complexes in the hydrolysed form of GeOH<sup>3+</sup>, since in spectra **1-5** there is a band of deformation vibrations δ(Ge-OH), which is typical for germanium complexonates [12].

The presence of coordinated phen molecules in the complexes is evidenced by the ν(C-N) and ν(C-C) bands of the heterocycle (at ~ 1310 and ~ 1590, 1517 cm<sup>-1</sup>, respectively), as well as δ(CH) at ~ 850 cm<sup>-1</sup> [7-9,11].

Intense and broad bands at 3390 cm<sup>-1</sup> in the IR spectra of the compounds are related to the presence of crystallization water molecules in their composition. That was also confirmed by

thermogravimetric analysis. Compounds **4** and **5** also contain water molecules coordinated to the *d*-metal, since the bands δ(H<sub>2</sub>O) at 1625 cm<sup>-1</sup> and ν(M-O) are noted in their spectra. The characteristic vibrational band of carboxyl groups at 1720 cm<sup>-1</sup> in the spectra of compounds **2** and **3** indicates the presence of solvated acetic acid molecules in their composition.

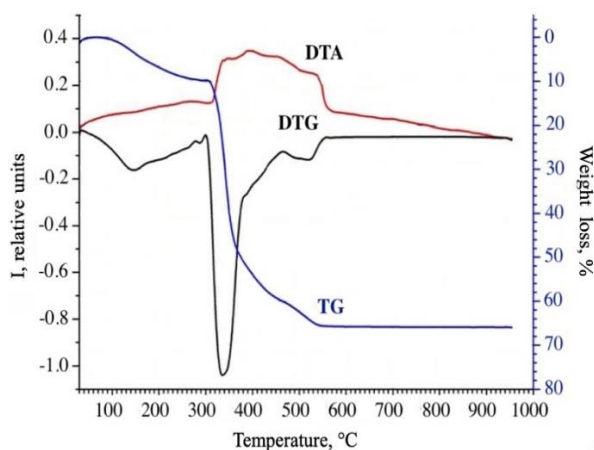
The thermal decomposition is similar for all the compounds (Table 2). Endo-effects on thermogravigrams profiles of **1-5** are observed in a wide temperature range of 80-220°C (up to 250°C for **4** and **5**), during which water molecules (crystallization water for **1-5** and coordinated water for **4, 5**) and acetic acid for **2** and **3** (Figure 1 shows the thermogravigram of complex **1**) are eliminated into the gas phase, which is consistent with the data of IR spectroscopy. In addition, endo-effects were recorded when heating all complexes in the temperature range of 250-310°C resulting in the formation of a vinylidenediphosphonium fragment and the removal of water molecules and are characteristic of germanium complexes with H<sub>4</sub>hedp [12] (Scheme 1).



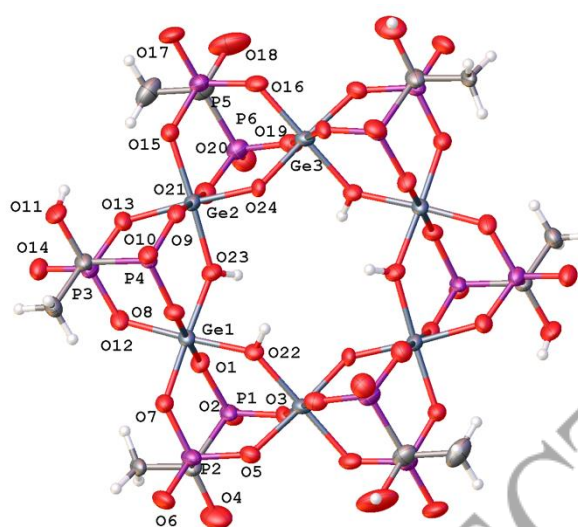
**Scheme 1. Process of the formation of a vinylidenediphosphonium fragment.**

Table 2

Thermal decomposition of complexes <b>1-5</b> .						
№	The character and temperature intervals of the processes					
	Δt (t <sub>max</sub> ) TGA, °C elimination product	Δm <sub>TG</sub> , %	Δm <sub>theor</sub> , %	Thermal destruction Δt (t <sub>max</sub> ) TGA, °C	Residue, % Δm <sub>TG</sub> / Δm <sub>theor</sub> final products	
<b>1</b>	100-220 (140↓) -20H <sub>2</sub> O	7.8	8.0	300-470 (400↑) 470-560 (520↑)	65.0 / 60.6 6GeP <sub>2</sub> O <sub>7</sub> +4FeO	
	270-300 (290↓) -6H <sub>2</sub> O	2.2	2.4			
<b>2</b>	70-200 (120↓) -30H <sub>2</sub> O, -2CH <sub>3</sub> COOH	14.0	13.7	460-610 (500↑) 680-800 (760↑)	64.0 / 62.3 6GeP <sub>2</sub> O <sub>7</sub> +2Co <sub>2</sub> O <sub>3</sub>	
	260-290 (280↓) -6H <sub>2</sub> O	2.1	2.3			
<b>3</b>	80-200 (125↓) -26H <sub>2</sub> O, -2CH <sub>3</sub> COOH	12.3	12.4	410-660 (555↑) 680-820 (780↑)	64.0 / 62.4 6GeP <sub>2</sub> O <sub>7</sub> +4NiO	
	250-300 (290↓) -6H <sub>2</sub> O	2.1	2.3			
<b>4</b>	100-250 (150↓) -18H <sub>2</sub> O	9.2	9.2	320-480 (410↑) 480-600 (540↑)	51.1 / 51.2 6GeP <sub>2</sub> O <sub>7</sub> +4CuO	
	270-310 (290↓) -6H <sub>2</sub> O	3.0	3.1			
<b>5</b>	100-260 (150↓) -22H <sub>2</sub> O	11.0	10.9	320-490 (400↑) 490-670 (540↑)	50.0 / 49.7 6GeP <sub>2</sub> O <sub>7</sub> +4ZnO	
	260-310 (280↓) -6H <sub>2</sub> O	3.0	3.0			



**Figure 1.** Thermogram of the complex **1**.



**Figure 2.** Molecular structure of anion  $[\text{Ge}_6(\mu\text{-OH})_4(\mu\text{-O})_2(\mu\text{-hedp})_6]^{8-}$  in **2**, **4**, **5**. Atom numbering is given for the symmetrically independent part.

Further heating of the samples is accompanied by several exo-effects, during which the oxidative thermal destruction of the organic part of the molecule and the formation of final products at 1000°C – a mixture of  $\text{GeP}_2\text{O}_7$  and the corresponding oxides occurs, which is consistent with calculations based on the thermogravimetric curve and previously obtained data for compounds of this type, including X-ray analysis of residues [12].

Anion  $[\text{Ge}_6(\mu\text{-OH})_4(\mu\text{-O})_2(\mu\text{-hedp})_6]^{8-}$  (Figure 2) in the structures of **2**, **4**, **5** is a centrosymmetric hexanuclear complex compound in which Ge atoms are pairwise bonded by hydroxo- (or oxo-) and 1-hydroxyethane-1,1-diphosphonate ligands. Coordination polyhedra of Ge atoms represent twisted octahedra. However, the structure of these polyhedra is slightly different for three symmetrically independent Ge atoms.

Each Ge atom is coordinated by four oxygen atoms of four phosphonate groups of two 1-hydroxyethane-1,1-diphosphonate ligands. The coordination of Ge atoms is supplemented to the octahedron by either two hydroxo-groups (for Ge1 atom), or hydroxo- and oxo-groups (for Ge2 and Ge3). The Ge–O bond lengths (hedp) in compounds **2**, **4**, **5** vary within the range 1.847(4)–1.912(5) Å, and in the range 1.872(6)–1.908(5) Å and 1.796(7)–1.829(7) Å for Ge–O (OH) and Ge–O (O), respectively (Table S1–S3). The O–Ge–O valence angles are within 86.06(17)–95.83(16)°. In general, the structure of the  $[\text{Ge}_6(\mu\text{-OH})_4(\mu\text{-O})_2(\mu\text{-hedp})_6]^{8-}$  anion is in good agreement with the data previously published in [12]. Cations in the structure of **2** are the complex of Co with three molecules of phen (Figure 3(a)). Coordination polyhedra of cobalt are twisted octahedra. The lengths of Co–N bonds vary within 2.122(5)–2.157(5) Å, and the valence angles N–Co–N are within 77.5(2)–100.0(2)° (Table S1).

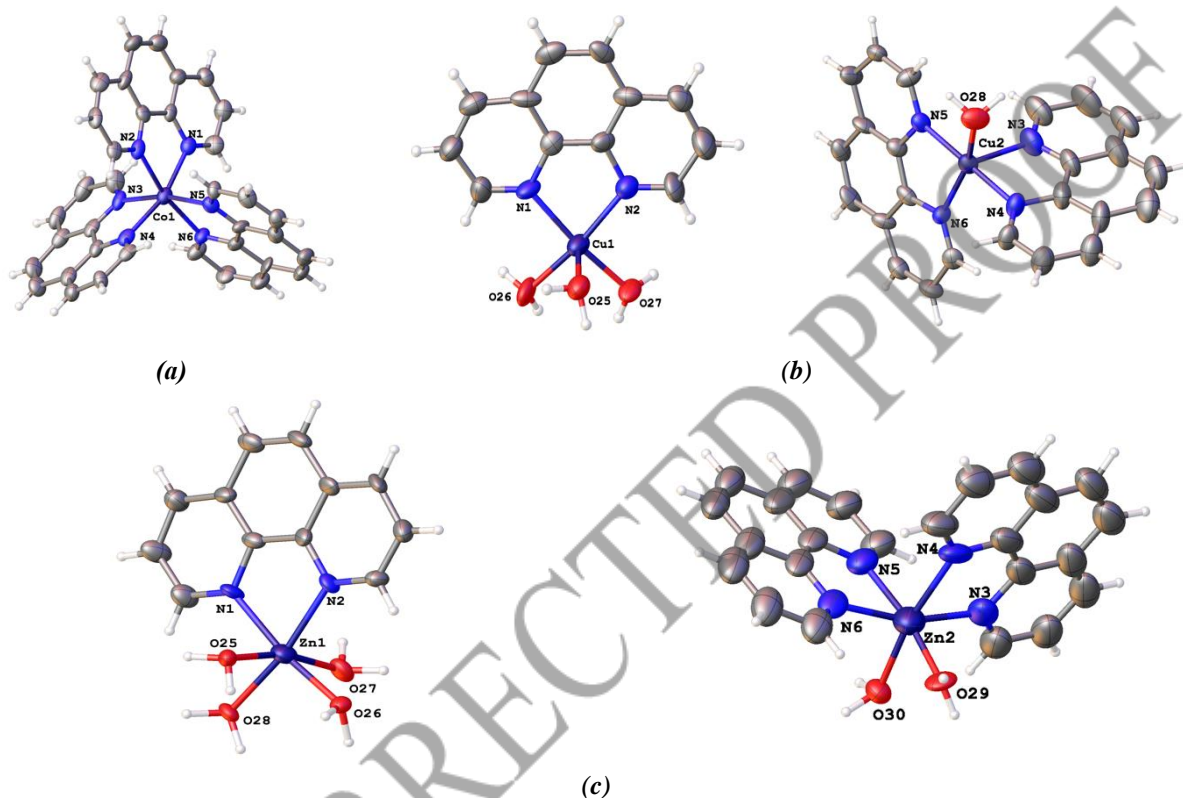
Two different cations containing different amounts of phenanthroline ligands and coordinating water molecules  $\text{Cu}(\text{phen})_2(\text{H}_2\text{O})$  and  $\text{Cu}(\text{phen})(\text{H}_2\text{O})_3$  were found in structure **4**. Thus, the Cu1 atom is coordinated by two nitrogen atoms of the phenanthroline molecule and three water molecules, while the Cu2 atom is coordinated by four nitrogen atoms of two phenanthroline molecules and one water molecule (Figure 3(b)). The coordination polyhedra of Cu atoms is a square pyramid. The base of the pyramid in the  $\text{Cu}(\text{phen})_2(\text{H}_2\text{O})$  cation is formed by the N4, N5, N6 atoms of the phenanthroline ligands and the O28 atom of the water molecule, and the top is the N3 atom of one of the ligands. Both nitrogen atoms of the phenanthroline ligand in the  $\text{Cu}(\text{phen})(\text{H}_2\text{O})_3$  cation and two coordinating water molecules (atoms O26, O27) are located at the base of the pyramid, and atom O25 of the third coordinating water molecule is located at the top. The lengths of the Cu–N, Cu–O bonds that lie at the base of the pyramid vary within 1.927(6)–1.982(4) Å, and the lengths of the Cu–O, Cu–N bonds with the atoms located in the tops of the pyramids, are much longer and equal to 2.217(8) Å and 2.142(11) Å, respectively (Table S2).

The cations in structure **5** also differ in composition. The Zn1 atom in the cation  $[\text{Zn}(\text{phen})(\text{H}_2\text{O})_4]^{2+}$  is coordinated by one ligand and four water molecules, while the Zn2 atom in the cation  $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$  is coordinated by two phenanthroline ligands and two water molecules. The coordination polyhedra of zinc atoms is a distorted octahedral structure. The Zn1

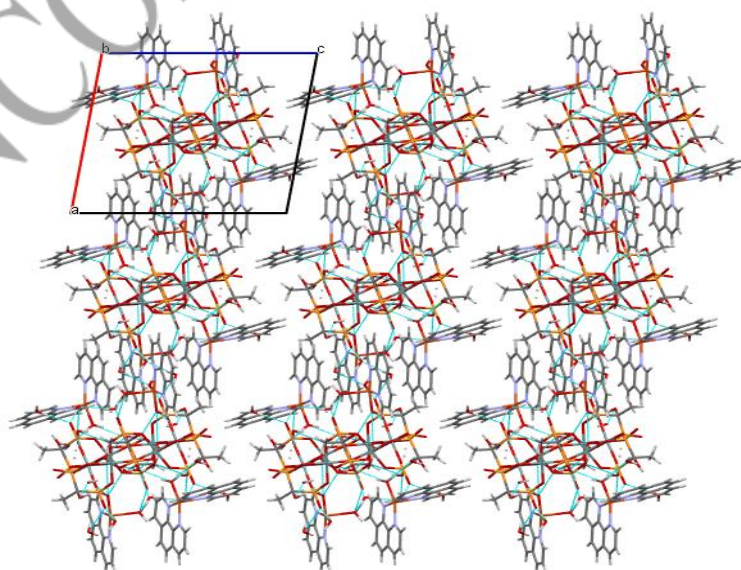
atom is coordinated in the equatorial directions by the nitrogen atoms N1, N2 of the phenanthroline ligand and the O26, O28 atoms, and in the axial directions by the O25, O27 atoms. The Zn2 atom is coordinated in the equatorial directions by three nitrogen atoms (N3, N4, N6) of the phenanthroline ligands and the O30 atom, and in the axial directions by the N5 and O29 atoms (Figure 3(c)). The bond lengths of Zn–N and Zn–O in the coordination polyhedron are within

2.075(7)–2.183(8) Å, and the valence angles O–Zn–O, N–Zn–N, and O–Zn–N vary in between 77.8(3)–98.4(3)° (Table S3).

The anions, cations and solvent molecules (acetic acid and water in **2**, or water in **4** and **5**) are connected in the crystal by numerous hydrogen bonds (Tables S4–S6) and form a three-dimensional network in the structure of **2**, or layers parallel crystallographic plane (001) in structures **4** and **5** (Figure 4).



**Figure 3.** Molecular structure of cations:  $[\text{Co}(\text{phen})_3]^{2+}$  in the complex **2** (a),  $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$  and  $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3]^{2+}$  in the complex **4** (b),  $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})_2]^{2+}$  and  $[\text{Zn}(\text{phen})(\text{H}_2\text{O})_4]^{2+}$  in the complex **5** (c).



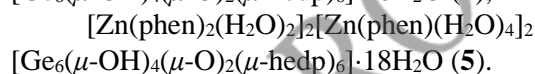
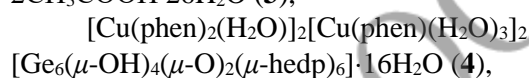
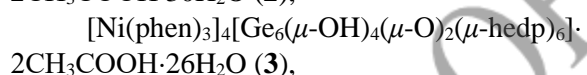
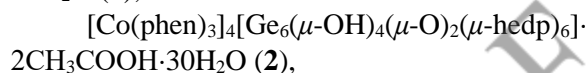
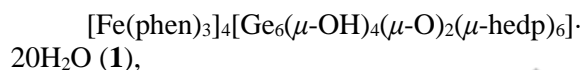
**Figure 4.** The crystal structure of compounds **4** and **5**. Projection along the crystallographic axis [010].

Mass spectrometry allows to study the behaviour of complex cations and anions in solution. The ESI(+) mass spectra of obtained compounds in positive polarity contain the signal of phenanthroline ( $M/z = 181$ ). The mass spectra of compounds Fe(II), Co(II), Ni(II) contain signals of doubly charged cations  $[\text{MePhen}_3]^{2+}$  (where Me - metal cation) with  $m/z = 298.18, 299.79, 299.08$  and less intense signals of  $[\text{Me}(\text{phen})_2]^{2+}$  ions with  $m/z = 208.15, 209.60, 209.05$  for compounds **1, 2, 3**, respectively (Figures S1-S3). The cations  $[\text{Me}(\text{phen})_2\text{Formate}]^+$  were also registered for compounds **2** and **3**. These cations are formed at electrospray ionisation upon the addition of the formate anion to the complex cation, formic acid was used at a concentration of 0.1% vol. as an agent to improve ESI ionization. Thus, the mass spectra indicate a similar structure of the cations of complexes **1, 2, 3**. It can be assumed that in the crystalline state for Fe(II), Co(II), Ni(II) the ratio Me:phen = 1:3 is realized, and the formation of particles of the composition Me:Phen = 1:2 occurs during dissociation in solution, which accompanied by the formation of free phenanthroline molecules. In the mass spectra of Cu(II) and Zn(II) compounds, particles  $[\text{Me}(\text{phen})\text{Formate}]^+$  and  $[\text{Me}(\text{phen})_2\text{Formate}]^+$  are detected in positive polarity (Figure S4, S5), the signals of these particles are comparable in intensity. The formation of cations with the composition Cu(Zn):phen = 1:3 was not observed. This behaviour corresponds to X-ray diffraction data for these compounds, according to which particles of the composition Me:phen = 1:2 and 1:1 are present in the crystals in equal quantities.

The ESI(-) mass spectra of all compounds in negative polarity are similar and contain the signal of the ethylenediphosphonic acid anion ( $m/z = 205$ ) and a large number of unidentified signals that can be formed during fragmentation of the complex eight-charged anion  $[\text{Ge}_6(\mu\text{-OH})_4(\mu\text{-O})_2(\mu\text{-hedp})_6]^{8-}$  or products of its dissociation in aqueous solution (Figure S6). The signal with  $m/z = 293$  corresponds to the charged anion  $[\text{Ge}(\text{OH})\text{C}(\text{CH}_3)(\text{OH})(\text{PO}_3)_2]^-$ , which is probably formed during the dissociation of  $[\text{Ge}_6(\mu\text{-OH})_4(\mu\text{-O})_2(\mu\text{-hedp})_6]^{8-}$  in the solution (Figure S7). The isotopic distribution of this signal corresponds to theoretically calculated particle with molecular formula  $\text{Ge}_2\text{H}_5\text{O}_8\text{P}_2$ .

The comparative analysis of the data obtained by the combination of the research methods described above regarding the composition and structure of the first synthesized complexes **1-5** was carried out. Special attention

was paid to the investigation of the structural characteristics of compounds **2, 4, 5**, which were considered as models, within the framework of which data correlation was observed for all described complexes. It was established that according to the type and structure of **1-5** are analogues, they represent heterometal multiligand coordination compounds of the cation-anion type, which correspond to the following molecular formulas:



## Conclusions

Thus, it can be stated that the same hexanuclear anion is present in five described complexes, the charge of which is compensated by complex cations consisting of phenanthroline and 3d-metal with composition depending on the nature of 3d-metal cation  $[\text{M}(\text{phen})_3]^{2-}$  (M = Fe, Co, Ni),  $[\text{Cu}(\text{phen})_2(\text{H}_2\text{O})]^{2-}$ ,  $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3]^{2-}$ ,  $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})_2]^{2-}$ ,  $[\text{Zn}(\text{phen})(\text{H}_2\text{O})_4]^{2-}$ . The replacement of bichelating phenanthroline with a monodentate water molecule in the cation contributes to the reduction of spatial complexities and tensions that arise during the formation of complexes with a large number of metallocycles, especially in the case of 3d-compression of the series (Cu, Zn - the end of a series of 3d-metals). The appearance of acetic acid in the composition of solvate molecules of complexes **2, 3** is a consequence of the side reaction of the interaction of  $\text{M}(\text{CH}_3\text{COO})_2$  with the complex acid  $\text{H}_8[\text{Ge}_6(\mu\text{-OH})_4(\mu\text{-O})_2(\mu\text{-hedp})_6]$ , the existence of which in the reaction medium is confirmed by the presence of such an anion in molecules **1-5**. In terms of structure and functional groups, it is like those existing in living nature.

## Supplementary information

Supplementary data are available free of charge at <http://cjm.ichem.md> as PDF file.

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