

## SYNTHESIS AND CRYSTAL STRUCTURE OF BIS(CITRATO)GERMANATE AND STANNATE WITH TRIS(PHENANTHROLINE)NICKEL(II) CATION

Elena Martsinko <sup>a\*</sup>, Inna Seifullina <sup>a</sup>, Elena Chebanenko <sup>a</sup>, Olha Pirozhok <sup>a</sup>,  
Viktoriya Dyakonenko <sup>b</sup>, Svitlana Shishkina <sup>b,c</sup>

<sup>a</sup>I.I. Mechnikov Odessa National University, 2, Dvoryanskaya str., Odessa 65082, Ukraine

<sup>b</sup>SSI "Institute for Single Crystals", National Academy of Sciences of Ukraine,  
60, Nauki ave., Kharkiv 61001, Ukraine

<sup>c</sup>V.N. Karazin Kharkiv National University, 4, Svobody sq., Kharkiv 61077, Ukraine

\*e-mail: lborn@ukr.net

**Abstract.** The new complexes [Ni(phen)<sub>3</sub>][Ge(HCit)<sub>2</sub>]-2H<sub>2</sub>O (**1**), [Ni(phen)<sub>3</sub>][Sn(HCit)<sub>2</sub>]-3H<sub>2</sub>O (**2**) (where phen is 1,10-phenanthroline, H<sub>4</sub>Cit is citric acid) were synthesized. The identity, composition, and thermal stability of the complexes were established by elemental analysis, thermogravimetry, and IR spectroscopy. According to the data of X-ray diffraction, the bis(citrate)germanate/bis(citrate)stannate [Ge/Sn(HCit)<sub>2</sub>]<sup>2-</sup> is the anion, while [Ni(phen)<sub>3</sub>]<sup>2+</sup> is the cation in the studied complexes. The coordination polyhedrons of Ge, Sn and Ni atoms are octahedral and are formed by three pairs of oxygen atoms of different types of two HCit<sup>3-</sup> ligands or by three 1,10-phenanthroline molecules.

**Keywords:** citric acid, 1,10-phenanthroline, germanium(IV), tin(IV), nickel(II) complex.

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### Introduction

Obtaining and determining of the structure of coordination compounds formed with biometals and hydroxycarbonic acids is of great interest nowadays because of the creation of new medicines on their basis. Citric acid is the direct participant of a cycle of three carbonic acids (the Krebs cycle) and is present in blood plasma [1]; germanium lactate-citrate possesses radioprotective properties [2].

In the past few years, authors have shown that germanium(IV) and tin(IV) in water solution are able to form cation–anion coordination compounds with bis(citrate)germanate [Ge(HCit)<sub>2</sub>]<sup>2-</sup> or bis(citrate)stannate [Sn(HCit)<sub>2</sub>]<sup>2-</sup> anions and octahedral [M(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> cations (M= Mg, Mn, Fe, Co, Ni, Cu, Zn) [3,4]. Such a type of coordination compounds show antihypoxic, cerebroprotective and antiviral properties [5]. Subsequently, new complexes with similar bis(citrate)germanate anions and cations [M(phen)<sub>3</sub>]<sup>2+</sup> (phen - 1,10-phenanthroline, M= Fe(II), Co(II)) and [CuCl(phen)<sub>2</sub>]<sup>+</sup> have been synthesized and described by the authors [6,7]. A group of British and Portuguese scientists also have synthesized a number of complex compounds, which contain tris(oxalato-

O,O')germanate anion [Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>2-</sup> and transition-metal cationic complexes [M(phen)<sub>3</sub>][Ge(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>2-</sup>·xH<sub>2</sub>O (where M<sup>2+</sup> = Cu<sup>2+</sup>, Fe<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>) [8]. Synthesis of new analogical bis(citrato)stannates is also of particular interest. These complexes can not be prepared from SnO<sub>2</sub> because of its poor solubility in water and acids.

This work is dedicated to the development of new synthesis methods and study of structure of new heterometal-different-ligand complexes of germanium(IV) or tin(IV) and nickel(II) with citric acid and 1,10-phenanthroline as promising biologically active compounds.

### Experimental

#### Materials

Germanium(IV) oxide (GeO<sub>2</sub>, 99.99%), tin(IV) chloride (SnCl<sub>4</sub>, 98%), citric acid (H<sub>4</sub>Cit·H<sub>2</sub>O, 99%), 1,10-phenanthroline (phen, 99%), nickel(II) salts NiCl<sub>2</sub>·6H<sub>2</sub>O (99%) and Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (98%) were used as initial reagents for the synthesis of new complexes.

#### Methods

*Elemental analysis* for germanium, tin and nickel was performed using inductively coupled plasma atomic emission spectroscopy with an Optima 2000 DV instrument (PerkinElmer).

Analysis for C, H, and N was performed using a CE-440 Elemental Analyzer.

*Thermogravimetric analysis* (TGA) was carried out using a Q-1500D with a heating rate of 10°C/min on air in the temperature range 20-1000°C.

The IR spectra in the range of 4000-400 cm<sup>-1</sup> were recorded as potassium bromide pellets on a Frontier spectrometer (PerkinElmer). The absorption bands were attributed according to the reference data for citric acid and our earlier obtained germanium(IV) coordination compounds with hydroxycarboxylic acids [3,4,6,7].

*X-ray crystallography.* Crystal data for structures **1** and **2** were measured on a Xcalibur-3 diffractometer (graphite monochromated MoK $\alpha$  radiation, CCD detector,  $\omega$ -scanning). The structures were solved by the direct method using the SHELXTL package [9]. Full-matrix least-squares refinement against F<sup>2</sup> in anisotropic approximation was used for non-hydrogen atoms. Positions of hydrogen atoms were determined from electron density difference maps and refined by "riding" model with U<sub>iso</sub> = *n*U<sub>eq</sub> of the carrier atom (*n* = 1.5 for hydroxyl groups and *n* = 1.2 for other hydrogen atoms). CCDC 1854034 and 1854035 contains the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). Full use of the CCDC package was also made for searching in the CSD Database.

### Synthesis

#### [Ni(phen)<sub>3</sub>][Ge(HCit)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O (**1**)

A suspension of germanium(IV) oxide (0.0523 g, 0.5 mmol) and citric acid (0.21 g, 1 mmol) in 100 mL of hot distilled water was stirred to dissolve reagents completely and slowly evaporated at 50°C to a 20 mL volume. After cooling the solution to the room temperature, 20 mL of a 95% ethanol solution containing 1,10-phenanthroline (0.27 g, 1.5 mmol) and NiCl<sub>2</sub> $\cdot$ 6H<sub>2</sub>O (0.119 g, 0.5 mmol) were added. After 3 days, a pink-colored crystalline solid precipitated. Single crystals suitable for X-ray diffraction were collected from the reaction medium.

Elemental composition, based on single-crystal data for C<sub>48</sub>H<sub>38</sub>GeN<sub>6</sub>NiO<sub>16</sub> (1086.14), analytically calculated in %: C 53.03, H 3.50, Ge 6.68, N 7.73, Ni 5.43; found for the

as-synthesized bulk material (in %): C 52.78, H 3.29, Ge 6.57, N 7.63, Ni 5.38.

The thermal destruction of **1** (weight losses,  $\Delta m$ ): 80-140°C, endothermic peak 100°C (-3.3%); 290-360°C, endothermic peak 350°C (-24.7%); 420-580°C, exothermic peak 530°C (-54.0%).

Selected IR data for **1** (in cm<sup>-1</sup>): 3396  $\nu$ (OH), 1722  $\nu$ (C=O), 1626  $\nu_{as}$ (COO<sup>-</sup>), 1588, 1518  $\nu$ (C-C<sub>Ar</sub>), 1393  $\nu_s$ (COO<sup>-</sup>), 1349  $\nu$ (C-N), 1086  $\nu$ (C-O), 1151, 905, 855  $\delta$ (CH), 641  $\nu$ (Ge-O).

The [Ni(phen)<sub>3</sub>][Ge(HCit)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O (**1**) crystal data (M = 1086.14 g/mol): monoclinic, space group *P2/c*, *a* = 23.012(2), *b* = 11.3384(6), *c* = 18.5747(8) Å,  $\beta$  = 94.660(5)°, *V* = 4830.4(5) Å<sup>3</sup>, *Z* = 4, *T* = 294 K,  $\mu$ (MoK $\alpha$ ) = 1.090 mm<sup>-1</sup>, *D*<sub>calc</sub> = 1.494 g/cm<sup>3</sup>, 41649 reflections measured, 9454 unique (*R*<sub>int</sub> = 0.221, *R*<sub>sigma</sub> = 0.214), which were used in all calculations. The final *R*<sub>1</sub> was 0.086 for 3980 reflections with *I* > 2 $\sigma$ (*I*) and *wR*<sub>2</sub> was 0.213 (all data), *S* = 0.936.

#### [Ni(phen)<sub>3</sub>][Sn(HCit)<sub>2</sub>] $\cdot$ 3H<sub>2</sub>O (**2**)

It was prepared by dissolving citric acid (0.01 mol, 4.2 g) in water (20 mL), further, this solution was brought to boiling, SnCl<sub>4</sub> (0.005 mol, 0.625 mL) was added, heated for 10 min and cooled. After addition of tin tetrachloride to the acid solution, pH was brought to 1 by adding ammonium hydroxide. This was done because the complexation does not take place in a highly acidic medium, while further increase in the pH results in hydrolysis.

In the second step, the solution of Ni(CH<sub>3</sub>COO)<sub>2</sub> $\cdot$ 4H<sub>2</sub>O in water (5 mL) was added, the mixture was stirred and the complex [Ni(H<sub>2</sub>O)<sub>6</sub>][Sn(HCit)<sub>2</sub>] $\cdot$ 4H<sub>2</sub>O [**3**] crystallized at room temperature. The blue precipitate was filtered off on a Schott glass filter, washed with cold water, and dried at room temperature (20°C).

In the third step, a suspension of [Ni(H<sub>2</sub>O)<sub>6</sub>][Sn(HCit)<sub>2</sub>] $\cdot$ 4H<sub>2</sub>O (0.0523 g, 0.5 mmol) and 1,10-phenanthroline (0.27 g, 1.5 mmol) was stirred in 20 mL of warm distilled water. On the next day, a red crystalline solid precipitated, from which single crystals were collected mechanically and analyzed by X-ray crystallography.

Elemental composition, based on single-crystal data for C<sub>48</sub>H<sub>40</sub>N<sub>6</sub>NiO<sub>17</sub>Sn (1150.25), analytically calculated in %: C 50.12, H 3.39, N 7.31, Ni 5.13, Sn 10.35; found for the as-synthesized bulk material (in %): C 50.00, H 3.11, N 7.58, Ni 5.10, Sn 10.24.

The thermal destruction of **2** (weight losses,  $\Delta m$ ): 80-160°C, endothermic peak 150°C (-4.7%); 270-320°C, endothermic peak 280°C (-15.7%);

320-360°C, endothermic peak 330°C (-7.7%); 360-680°C, exothermic peak 570°C (-50.2%).

Selected IR data for **2** (in  $\text{cm}^{-1}$ ): 3417  $\nu(\text{OH})$ , 1723  $\nu(\text{C}=\text{O})$ , 1625  $\nu_{\text{as}}(\text{COO}^-)$ , 1589, 1518  $\nu(\text{C}-\text{C}_{\text{Ar}})$ , 1427  $\nu_{\text{s}}(\text{COO}^-)$ , 1341  $\nu(\text{C}-\text{N})$ , 1077  $\nu(\text{C}-\text{O})$ , 1144, 940, 869  $\delta(\text{CH})$ , 537  $\nu(\text{Sn}-\text{O})$ .

The  $[\text{Ni}(\text{phen})_3][\text{Sn}(\text{HCit})_2] \cdot 3\text{H}_2\text{O}$  (**2**) crystal data ( $M = 1150.26$  g/mol): monoclinic, space group  $P2_1/c$ ,  $a = 23.026(1)$ ,  $b = 11.2346(7)$ ,  $c = 18.5169(8)$  Å,  $\beta = 93.917(3)^\circ$ ,  $V = 4778.8(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 294$  K,  $\mu(\text{MoK}\alpha) = 0.998$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.599$  g/cm<sup>3</sup>, 41535 reflections measured, 9367 unique ( $R_{\text{int}} = 0.096$ ,  $R_{\text{sigma}} = 0.082$ ) which were used in all calculations. The final  $R_1$  was 0.066 for 6794 reflections with  $I > 2\sigma(I)$  and  $wR_2$  was 0.164 (all data),  $S = 1.073$ .

## Results and discussion

Complexes **1** and **2** are crystalline solids which are stable on air with the similar molar ratio  $\text{Ge}(\text{Sn})\text{:citrate}\text{:Ni}\text{:phen} = 1\text{:2}\text{:1}\text{:3}$ , molecular structures are presented in Figure 1. The crystal packing of  $[\text{Ni}(\text{phen})_3][\text{Ge}/\text{Sn}(\text{HCit})_2] \cdot n\text{H}_2\text{O}$  is presented in Figure 2.

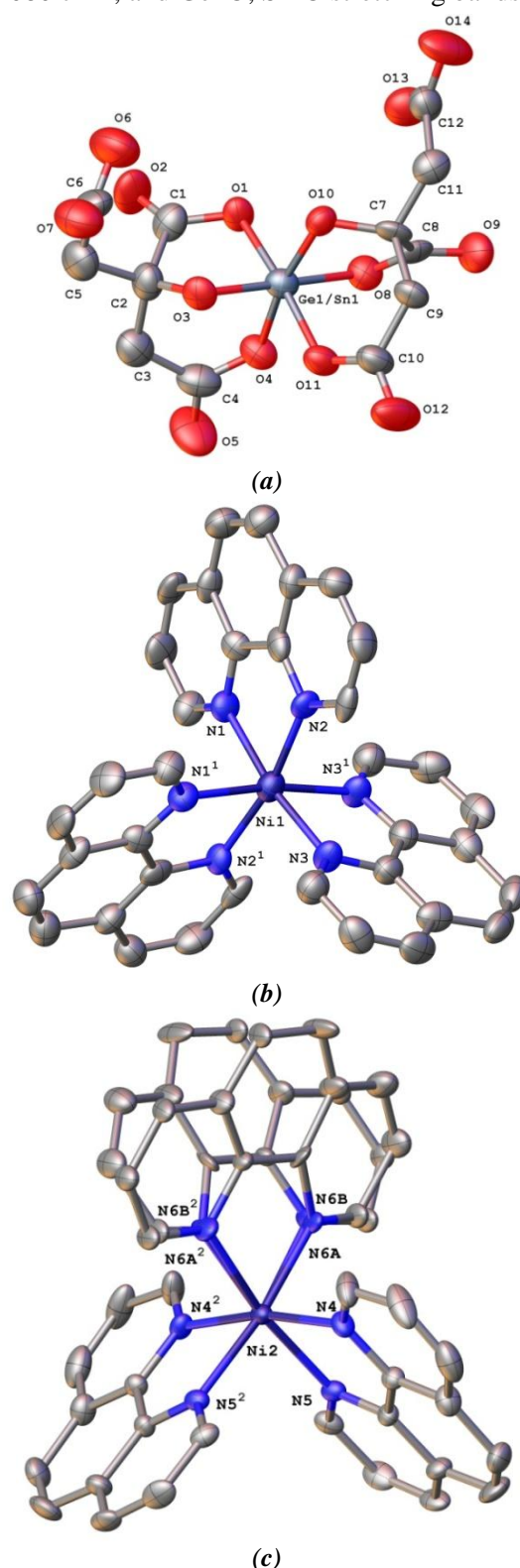
The thermal decomposition of **1** starts with an endotherm peak within the temperature range of 80-140°C, which is due to the elimination to the gas phase of two molecules of crystallized water. During further heating within the temperature range from 290 to 360°C, complex **1** eliminates one molecule of phenanthroline and two  $\text{CO}_2$  molecules from the malate ligands.

The first endothermic peak on the thermogravimetric curve of **2** is due to the elimination of three water molecules to the gas phase. The second endothermic peak corresponds to the loss of two  $\text{CO}_2$  molecules; complex **2** eliminates one molecule of phenanthroline (the third endothermic peak) within the temperature range 320-360°C.

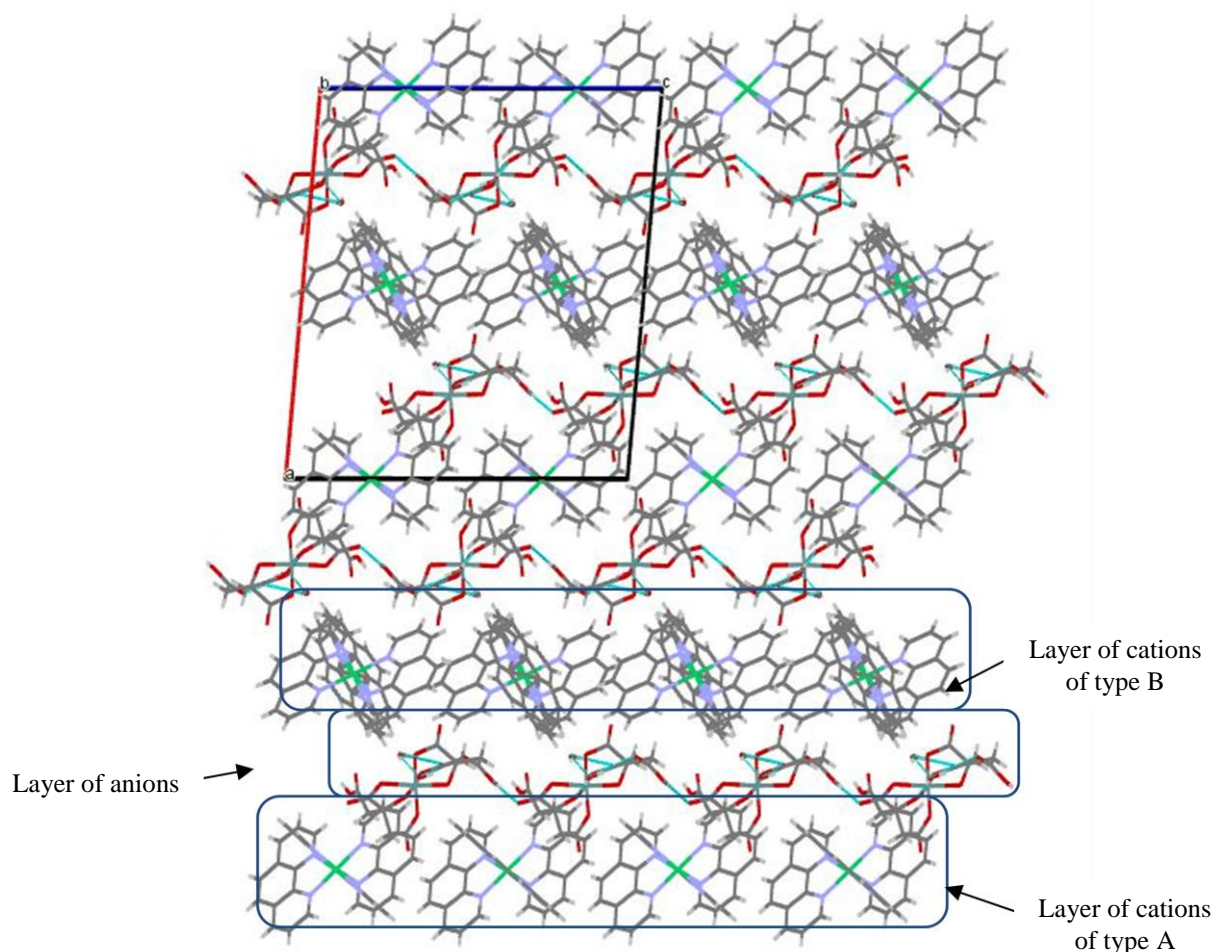
Finally, complexes **1** and **2** undergo oxidative thermal degradation and combustion of the organic part of their molecules. According to the calculated weight loss on the thermogravimetric curve of complexes, the extensive thermal decomposition (1000°C) of **1** gives nickel(II) metagermanate while in the case of **2**, nickel(II) stannate is formed.

The IR spectra of compounds **1** and **2** were found to exhibit similar sets of absorption bands, which were compared with the data obtained for other different-metal and different-ligand bis(citrato)germanates and bis(citrate)stannates [3,4,6,7]. The presence of a free carboxyl group  $-\text{COOH}$  in the molecules of the obtained

complexes is indicated by the  $\nu(\text{C}=\text{O})$  band at  $1720$   $\text{cm}^{-1}$  in their IR spectra [11]. In comparison with the IR spectrum of citric acid, the spectra of complexes **1** and **2** show characteristic  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  bands, alkoxide type  $\nu(\text{C}-\text{O})$  bands at  $1080$   $\text{cm}^{-1}$ , and Ge-O, Sn-O stretching bands.



**Figure 1.** Molecular structure of the  $[\text{Ge}/\text{Sn}(\text{HCit})_2]^{2-}$  anion (a) and  $[\text{Ni}(\text{phen})_3]^{2+}$  cations of type A (b) and B (c) in structure **1**, the one phen is disordered in two positions.



**Figure 2.** The crystal packing of  $[\text{Ni}(\text{phen})_3][\text{Ge}/\text{Sn}(\text{HCit})_2] \cdot n\text{H}_2\text{O}$ . View along the  $b$  crystallographic axis.

The absorption band at  $\sim 1340\text{ cm}^{-1}$  can be assigned to the  $\nu(\text{CN})$  heterocycle, the bands at  $\sim 1588, 1518\text{ cm}^{-1}$  - to the  $\nu(\text{C}-\text{C})$  phenanthroline ring vibrations. There are found deformation vibrations  $\delta(\text{C}-\text{H})$  of the aromatic rings: planar vibrations at  $1041\text{ cm}^{-1}$ ; non-planar vibrations at region  $987\text{--}905\text{ cm}^{-1}$  [12].

The  $[\text{Ni}(\text{phen})_3][\text{Ge}/\text{Sn}(\text{HCit})_2] \cdot n\text{H}_2\text{O}$  **1** and **2** were found to be complex salts that exist as hydrates in crystal phase. The bis(citrate)germanate  $[\text{Ge}(\text{HCit})_2]^{2-}$  in **1** and bis(citrate)stannate  $[\text{Sn}(\text{HCit})_2]^{2-}$  in **2** carries out the role of dianion while nickel  $[\text{Ni}(\text{phen})_3]^{2+}$  complexes are cations in both compounds. There are two parts of cations in the independent part of the unit cell in both structures. This is caused by the fact that Ni atoms are located in a special position on the 2-fold axis. Such a structure of compounds **1** and **2** is very similar to the previously described complexes [6].

The coordination polyhedrons of Ge/Sn atoms in **1** and **2** are distorted octahedrons, which are formed by two trident chelate  $\text{HCit}^{3-}$

ligands. As a result, three pairs of different types oxygen atoms coordinate Ge/Sn atoms: hydroxyl (the O3 and O10 atoms),  $\alpha$ -carboxylate (the O1 and O8),  $\beta$ -carboxylate (the O4 and O11 atoms) (Figure 1(a)). The Ge-O bond lengths in **1** are not equivalent to the ones obtained previously in related structures [3,6]. The lengths of Ge1-O3 and Ge1-O10 hydroxyl bonds are shorter than the carboxylate bonds (Table 1). In the germanium complex Ge1-O1 coordinative bonds with one ligand are different: the bond with the  $\alpha$ -carboxylate oxygen atom is slightly shorter than the bond with the  $\beta$ -carboxylate oxygen atom (Table 1). Similar coordinative bonds with another ligand are very close. It should be noted, that all coordinative bonds with carboxylate oxygen atoms are almost equal in the complex with the tin atom. The values of O—Ge/Sn—O bond angles in **1** and **2** varies within  $81.9(2)\text{--}98.5(2)^\circ$ .

The coordination of the Ge atom in **1** and the Sn atom in **2** by the organic ligands forms two five- and two six-membered metallocycles.

The Ge1-O4-C4-C3-C2-O3 and Ge1-O11-C10-C9-C8-O10 or Sn1-O4-C4-C3-C2-O3 and Sn1-O11-C10-C9-C8-O10 six-membered cycles adopt a half-chair conformation. Corresponding puckering parameters and atom deviations, and hydrogen bonds geometrical characteristics are given in Tables 2 and 3. Five-membered cycles in structures **1** and **2** adopt an envelope conformation. The O3 and O10 atoms in **1** and **2** deviate from the mean-square plane of the remaining atoms of the corresponding

cycles by 0.56 Å, -0.58 Å and 0.63 Å, -0.83 Å, respectively.

Ni atoms are coordinated by three molecules of phenanthroline in cations of the structures **1** and **2**. The location of Ni atoms in a special position causes the fact that only 1.5 phenanthroline molecules are symmetrically independent (Figure 1(b)). One of the 1,10-phenanthroline molecules is disordered over two positions with equal populations due to symmetrical position relatively the 2-fold axis in the cation B of structure **1** (Figure 1(c)).

Table 1

Selected bond lengths (Å) and bond angles (°) in structures **1** and **2**.

Structure 1			
Bond	Bond length, Å	Bond	Bond length, Å
Ge1—O1	1.909 (5)	Ni1—N2	2.075 (6)
Ge1—O3	1.808 (5)	Ni1—N3	2.072 (6)
Ge1—O4	1.940 (5)	Ni2—N4	2.108 (7)
Ge1—O8	1.925 (5)	Ni2—N5	2.084 (7)
Ge1—O10	1.824 (5)	Ni2—N6A	2.178 (11)
Ge1—O11	1.920 (6)	Ni2—N6B	2.03 (2)
Ni1—N1	2.111 (6)		
Bond angle	Bond angle value, deg	Bond angle	Bond angle value, deg
O1—Ge1—O4	88.6 (2)	N2—Ni1—N1	80.0 (2)
O1—Ge1—O8	89.8 (2)	N3—Ni1—N1 <sup>1</sup>	95.6 (2)
O3—Ge1—O1	86.7 (2)	N3—Ni1—N2 <sup>1</sup>	94.3 (2)
O3—Ge1—O4	92.6 (2)	N3—Ni1—N2	94.0 (2)
O3—Ge1—O10	98.5 (2)	N4 <sup>2</sup> —Ni2—N6A <sup>2</sup>	98.9 (5)
O3—Ge1—O11	92.3 (2)	N4 <sup>2</sup> —Ni2—N6A	89.2 (5)
O8—Ge1—O4	83.8 (2)	N4—Ni2—N6A	98.9 (5)
O10—Ge1—O1	94.7 (2)	N5 <sup>2</sup> —Ni2—N4	93.2 (3)
O10—Ge1—O8	85.3 (2)	N5—Ni2—N4	79.0 (3)
O10—Ge1—O11	91.6 (2)	N5 <sup>2</sup> —Ni2—N5	90.7 (4)
O11—Ge1—O4	85.3 (2)	N5—Ni2—N6A	93.8 (4)
O11—Ge1—O8	90.9 (2)	N6A—Ni2—N6A <sup>2</sup>	84.2 (8)
N1—Ni1—N1 <sup>1</sup>	90.5 (3)	N6B—Ni2—N4	90.8 (5)
N2—Ni1—N1 <sup>1</sup>	92.4 (2)		
Structure 2			
Bond	Bond length, Å	Bond	Bond length, Å
Sn1—O1	2.065 (4)	Ni1—N1	2.102 (5)
Sn1—O3	1.993 (4)	Ni1—N2	2.095 (5)
Sn1—O4	2.075 (4)	Ni1—N3	2.073 (3)
Sn1—O8	2.077 (3)	Ni2—N4	2.096 (5)
Sn1—O10	2.003 (4)	Ni2—N5	2.091 (4)
Sn1—O11	2.054 (4)	Ni2—N6	2.077 (4)
Bond angle	Bond angle value, deg	Bond angle	Bond angle value, deg
O1—Sn1—O4	87.23 (17)	N2—Ni1—N1 <sup>3</sup>	93.3 (2)
O1—Sn1—O8	92.87 (15)	N2—Ni1—N1	79.4 (2)
O3—Sn1—O1	81.97 (15)	N3—Ni1—N1 <sup>3</sup>	95.62 (19)
O3—Sn1—O4	89.46 (16)	N3—Ni1—N2	93.6 (2)
O3—Sn1—O11	95.07 (14)	N5 <sup>2</sup> —Ni2—N4	92.83 (17)
O4—Sn1—O8	87.30 (16)	N5—Ni2—N4	79.56 (17)
O10—Sn1—O1	97.40 (16)	N6—Ni2—N4	94.76 (17)
O10—Sn1—O8	81.02 (15)	N6—Ni2—N5	94.73 (17)
O10—Sn1—O11	88.45 (15)	N6—Ni2—N5 <sup>2</sup>	93.60 (17)
O11—Sn1—O4	87.40 (16)	N6—Ni2—N6 <sup>2</sup>	79.7 (2)
O11—Sn1—O8	89.78 (15)		

<sup>1</sup> -x+2, y, -z+3/2; <sup>2</sup> -x+1, y, -z+1/2; <sup>3</sup> -x, y, -z+1/2



Table 2

## The conformational characteristics of metalocycles in anions of structures 1 and 2.

Cyclic atoms	Mean plane accuracy, Å	Atom/Deviations from the mean plane, Å	Puckering parameters [13]		
			S	$\theta$ , °	$\psi$ , °
<i>Structure 1</i>					
Ge1–O4–C4–C3–C2–O3	0.02	C2 -0.3 O3 0.61	0.93	49.66	25.41
Ge1–O11–C10–C9–C8–O10	0.02	C8 -0.29 O10 0.61	0.97	32.65	26.21
<i>Structure 2</i>					
Sn1–O4–C4–C3–C2–O3	0.03	C2 -0.4 O3 0.63	0.96	52.18	26.91
Sn2–O11–C10–C9–C8–O10	0.02	C8 -0.31 O10 0.62	1.0	29.38	28.34

Table 3

## The hydrogen bonds geometrical characteristics for structures 1 and 2.

<i>D–H...A</i>	<i>H...A</i> , Å	<i>D...A</i> , Å	<i>D–H...A</i> , °
<i>Structure 1</i>			
O7—H7...O9 <sup>1</sup>	1.79	2.600 (9)	171
C41—H41...O13	2.30	3.227 (13)	171
O15—H15A...O6	2.08	2.903 (10)	164
O15—H15B...O10	1.99	2.823 (8)	166
O16—H16A...O5	2.01	2.860 (10)	178
O16—H16B...O15 <sup>2</sup>	2.02	2.815 (10)	155
<i>Structure 2</i>			
O13—H13...O17A	1.88	2.692 (10)	168
O13—H13...O17B	2.13	2.71 (3)	128
O15—H15A...O10	2.00	2.801 (7)	161
O16—H16A...O15	2.09	2.857 (9)	150
O17A—H17A...O5 <sup>3</sup>	2.01	2.808 (11)	156
O17B—H17C...O16	2.10	2.90 (2)	157

<sup>1</sup>  $x, -y+1, z+1/2$ ; <sup>2</sup>  $x, y-1, z$ ; <sup>3</sup>  $-y+2, z-1/2$ .

The Ni coordination polyhedron is octahedron in all cations of the structures 1 and 2. The Ni1-N bond lengths vary within the range of 2.073(6)-2.111(6) Å, and Ni2-N bonds have the lengths about of 2.077(4)-2.179(10) Å in structures 1 and 2. The former bond lengths are well within the expected values, as revealed by a search in the CSD [13] for structures containing [Ni(phen)<sub>3</sub>]<sup>2+</sup> cations (162 entries; range 2.04-2.19 Å). The N-Ni1-N bond angles vary within 80.0(2)-95.6(3)° in the cation of type A and within 79.0(3)-99.1(5)° in the cation of type B in structures 1 and 2 (Table 1).

In the crystal phase anions, cations, and water molecules of compounds 1 and 2 form alternate layers, which are parallel to the *bc* crystallographic plane (Figure 2). The layers can be divided into three types: 1) layers containing only anions; 2) layers containing cations of type A; 3) layers consisting of cations of type B. The anions within the layer are bound

by the O—H...O intermolecular hydrogen bonds (as shown in Table 3).

### Conclusions

Complexes of germanium(IV) and nickel(II) with citric acid and 1,10-phenanthroline were synthesized. The method of synthesis of tris(phenanthroline)nickel(II) bis(citrate)stannate using complex [Ni(H<sub>2</sub>O)<sub>6</sub>][Sn(HCit)<sub>2</sub>·4H<sub>2</sub>O] as a starting compound was proposed for the first time. It was established, that [Ge/Sn(HCit)<sub>2</sub>]<sup>2-</sup> anions with similar structure take part in the formation of obtained compounds. The coordination polyhedrons of the Ge/Sn are octahedral and are formed by three pairs of oxygen atoms of different types of two HCit<sup>3-</sup> ligands. The structure of these compounds is very similar to the structure of complexes [Co(phen)<sub>3</sub>][Ge(HCit)<sub>2</sub>·2H<sub>2</sub>O] and [Fe(phen)<sub>3</sub>][Ge(HCit)<sub>2</sub>·4H<sub>2</sub>O], that have been previously described by the authors. Changing of

metal from Co and Fe to Ni in the structure of cation does not influence the type and structure of formed bis(citrato)germanates.

## References

- Koenigsberger, L.C.; Koenigsberger, E.; May, P.M.; Heftler, G.T. Complexation of iron(III) and iron(II) by citrate. Implications for iron speciation in blood plasma. *Journal of Inorganic Biochemistry*, 2000, 78(3), pp. 175–184. DOI: [https://doi.org/10.1016/S0162-0134\(99\)00222-6](https://doi.org/10.1016/S0162-0134(99)00222-6)
- Kluska, M. Some aspects of the analysis of biologically active organogermanium substances. *Critical Reviews in Analytical Chemistry*, 2008, 38(2), pp. 84–92. DOI: <https://doi.org/10.1080/10408340701804459>
- Martsinko, E.E.; Minacheva, L.Kh.; Pesaroglo, A.G.; Seifullina, I.I.; Churakov, A.V.; Sergienko, V.S. Bis(citrato)germanates of bivalent 3d metals (Fe, Co, Ni, Cu, Zn): crystal and molecular structure of  $[\text{Fe}(\text{H}_2\text{O})_6][\text{Ge}(\text{HCit})_2] \cdot 4\text{H}_2\text{O}$ . *Russian Journal of Inorganic Chemistry*, 2011, 56(8), pp. 1243–1249. DOI: <https://doi.org/10.1134/S0036023611080171>
- Martsinko, E.E.; Minacheva, L.Kh.; Chebanenko, E.A.; Seifullina, I.I.; Sergienko, V.S.; Churakov, A.V. The Conditions of formation of heterometallic complexes in the  $\text{GeCl}_4$  ( $\text{SnCl}_4$ )–citric acid– $\text{M}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  systems. The crystal and molecular structures of  $[\text{M}(\text{H}_2\text{O})_6][\text{Ge}(\text{HCit})_2] \cdot 4\text{H}_2\text{O}$  (M= Mg, Mn, Co, Cu, Zn) and  $[\text{M}(\text{H}_2\text{O})_6][\text{Sn}(\text{HCit})_2] \cdot 4\text{H}_2\text{O}$  (M = Mg, Co, Ni). *Russian Journal of Inorganic Chemistry*, 2013, 58(5), pp. 515–522. DOI: <https://doi.org/10.1134/S003602361305015X>
- Seifullina, I.I.; Martsinko, E.E.; Afanasenko, E.V. Design and synthesis of new homo- and heterometal coordination compounds of germanium(IV) for preparation of low toxic drugs with a wide therapeutic action. *Odessa National University Herald. Chemistry*, 2015, 20(4(56)), pp. 6–17. DOI: [https://dx.doi.org/10.18524/2304-0947.2015.4\(56\).56690](https://dx.doi.org/10.18524/2304-0947.2015.4(56).56690)
- Seifullina, I.I.; Martsinko, E.E.; Chebanenko, E.A.; Pirozhok, O.V.; Dyakonenko, V.V.; Shishkina, S.V. Synthesis, thermal stability, and structure of bis(citrato)germanates:  $[\text{Co}(\text{Phen})_3][\text{Ge}(\text{HCit})_2] \cdot 2\text{H}_2\text{O}$ ,  $[\text{Fe}(\text{Phen})_3][\text{Ge}(\text{HCit})_2] \cdot 4\text{H}_2\text{O}$  ( $\text{H}_4\text{Cit}$ = citric acid, phen= 1,10-phenanthroline). *Russian Journal of Coordination Chemistry*, 2017, 43(8), pp. 505–511. DOI: <https://doi.org/10.1134/S1070328417080061>
- Seifullina, I.I.; Martsinko, E.E.; Chebanenko, E.A.; Pirozhok, O.V.; Dyakonenko, V.V.; Shishkina, S.V. Structure of bis(citrato)germanates with different types of cations:  $(\text{Hphen})_2[\text{Ge}(\text{HCit})_2 \cdot 3\text{H}_2\text{O}]$ ,  $[\text{CuCl}(\text{phen})_2]_2[\text{Ge}(\text{HCit})_2 \cdot 6\text{H}_2\text{O}]$ , where  $\text{H}_4\text{Cit}$  is citric acid, phen is 1,10-phenanthroline. *Journal of Structural Chemistry*, 2017, 58(3), pp. 532–538. DOI: <https://doi.org/10.1134/S0022476617030143>
- Shi, F.-N.; Cunha-Silva, L.; Hardie, M.J.; Trindade, T.; Paz, F.A.A.; Rocha, J. Heterodimetallic germanium(IV) complex structures with transition metals. *Inorganic Chemistry*, 2007, 46(16), pp. 6502–6515. DOI: [10.1021/ic700507j](https://doi.org/10.1021/ic700507j)
- Sheldrick, G.M. A short history of SHELX. *Acta Crystallographica Section A*, 2008, A64, pp. 112–122. DOI: <https://doi.org/10.1107/S0108767307043930>
- CCDC, The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, 44 1223 336408. E-mail: deposit@ccdc.cam.ac.uk <https://www.ccdc.cam.ac.uk/>
- Bellamy, L.J. *The Infra-Red Spectra of Complex Molecules*. London: Chapman and Hall, 1975, 433 p. DOI: [10.1007/978-94-011-6017-9](https://doi.org/10.1007/978-94-011-6017-9)
- Tarasevich, B.N. *Infrared Spectra Of Basic Class Of Organic Compounds. Reference Materials*. Moscow, 2012, 54 p. (in Russian). <https://www.twirpx.com/file/1302520/>
- Zefirov, N.S.; Palyulin, V.A.; Dashevskaya, E.E. Stereochemical studies. XXXIV. Quantitative description of ring puckering via torsional angles. The case of six-membered rings. *Journal of Physical Organic Chemistry*, 1990, 3(3), pp. 147–158. DOI: <https://doi.org/10.1002/poc.610030304>