

SYNTHESIS AND STRUCTURAL CHARACTERISTICS OF BIS(CITRATE)GERMANATES(IV) (Hbipy)₂[Ge(HCit)₂]₂·2H₂O AND [CuCl(bipy)₂]₂[Ge(HCit)₂]₂·8H₂O

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Abstract. The crystalline compounds (Hbipy)₂[Ge(HCit)₂]₂·2H₂O (**1**) and [CuCl(bipy)₂]₂[Ge(HCit)₂]₂·8H₂O (**2**) (where H₄Cit is citric acid, bipy is 2,2'-bipyridine) were obtained for the first time and their structures were determined by the single-crystal X-ray diffraction method. Compounds were characterized by IR spectroscopy, thermogravimetric (TGA) and elemental analyses. Both compounds are formed with complex bis(citrate)germanate anion and protonated 2,2'-bipyridine or [Cu(bipy)₂Cl]⁺ as cations in compounds **1** and **2**, respectively.

Keywords: germanium(IV) compound, citric acid, 2,2'-bipyridine, copper(II) complex, structure.

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Introduction

Citric acid is the most interesting vital biological ligand for a range of metal ions in coordination chemistry. It is the direct participant of the Krebs cycle and is present in blood plasma [1]. This acid has many useful properties and applications in medicine, pharmaceutical and food industries.

In the past time, we have synthesized and studied a number of mixed-ligand and mixed-metal coordination compounds of germanium(IV) with citric acid [2–7]. The pharmacological activity of some of these compounds has been approved [8]. The complexes of germanium(IV) are interesting materials for modern technics [9,10]. We have obtained the Eu²⁺-doped Li₂CaGeO₄ material with luminescent properties by thermolysis of the complex precursor [Ca(H₂O)₆][Ge(HCit)₂] [10].

Addition of nitrogen-containing heterocyclic organic molecules such as 2,2'-bipyridine into composition of coordination compounds of germanium(IV) with citric acid can modify its properties. Similar compound with tris(oxalato-O,O')germanate anion (Hbipy)₂[Ge(C₂O₄)₃] has been isolated after a mild hydrothermal synthesis and its structure has been elucidated [11]. The chelate [GeCl(bipy)(HCit)]·2.5CH₃CN has also been synthesized by the reaction between the adduct [GeCl₄(bipy)] and citric acid in acetonitrile solution [12].

The objectives of the present work was to synthesize homo- and heterometallic complexes on the basis of bis(citrate)germanate and 2,2'-bipyridine, to determine their composition, thermal stability and structure.

Experimental

General

Chemicals were readily available from commercial sources and used as received without further purification: germanium(IV) oxide (GeO₂, 99.99%, Aldrich), citric acid monohydrate (H₄Cit·H₂O, ≥99%, Aldrich), 2,2'-bipyridine (bipy, ≥98%, Fluka), copper(II) chloride dihydrate (CuCl₂·2H₂O, ≥99%, Aldrich).

Instrumentation

Elemental analyses for germanium and copper were performed using inductively coupled plasma atomic emission spectroscopy with an Optima 2000 DV instrument (Perkin Elmer); chlorine was quantified by mercurimetry, analyses for C, H, and N were performed in Elemental Analyzer CE-440. Thermogravimetric analyses (TGA) were carried out using a Q-1500D with a heating rate of 10°C/min in air in the temperature range of 20–1000°C. The IR absorption spectra of the ligand and the complexes were collected from KBr pellets on a Frontier spectrophotometer (Perkin Elmer) in the 400–4000 cm⁻¹ range. The most important absorption bands in the IR spectra of complexes **1** and **2** were attributed in compliance with the literature data [13–16], including data for the germanium(IV) coordination compounds with citric acid [2–7] (*s.* - strong, *m.* - middle, *w.* - weak).

Crystal data for structures **1** and **2** were measured on an Xcalibur-3 diffractometer (graphite monochromated Mo-K_α radiation, CCD detector, φ and ω -scanning). The structures were solved by the direct method using SHELXTL package [17]. Full-matrix least-squares refinement against F^2 in anisotropic approximation was used for non-hydrogen atoms. Positions of hydrogen atoms were located from the electron density difference maps and refined by "riding" model with $U_{iso} = nU_{eq}$ of the carrier atom ($n = 1.5$ for hydroxyl groups and $n = 1.2$ for other hydrogen atoms). CCDC 1513407-1513408 contain the supplementary crystallographic data for **1** and **2**. 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 [18]. Full use of the CCDC package was also employed for searching in the CSD Database.

Synthesis

(Hbipy)₂[Ge(HCit)₂]·2H₂O (1). A mixture of 0.084 g GeO₂ (0.8 mmol), 0.336 g H₄Cit·H₂O (1.6 mmol) and 0.256 g bipy (1.6 mmol) was added to 100 mL of hot water. The resulting mixture was heated at stirring to completely dissolve the reagents and evaporated (80-90°C) in a water bath to a volume of 10 mL (~2 h). A white residue of complex **1** was precipitated in one day. The yield constituted 65% (with respect to Ge). Single crystals of **1** suitable for X-ray analysis were withdrawn from the reaction medium.

Calculated elemental composition (based on single-crystal data for C₃₂GeH₃₂N₄O₁₆, M=801.20; in %): C 47.93, Ge 9.06, N 6.99, H 3.99. Found for the as-synthesized bulk material (in %): C 47.89, Ge 9.00, N 6.54, H 3.65.

TGA data (weight losses inside parentheses): 150-220°C, endothermic peak 170°C (-5.0%); 220-260°C, endothermic peak 240°C (-20.0%); 260-320°C, endothermic peak 280°C (-45.0%); 480-620°C, exothermic peak 500°C (-17.0%).

Selected IR data for **1** (in cm⁻¹): ν(O-H) = 3471m; ν(C-H, bipy ring) = 3100w, 2930w; ν(C=O, uncoordinated carbonyl groups) = 1697s; ν_{as}(COO⁻) = 1643s; ν(C-C, skeletal vibration bipy ring) = 1582s, 1518m, 1478w; ν_s(COO⁻) = 1377s; ν(C-N, bipy) = 1340m; ν(C-O) = 1198s, 1079w; ν(C-H) = 1087w, 1036w, 995w, 949w, 900w; ν(Ge-O) = 698m, 668m.

Crystal data for **(Hbipy)₂[Ge(HCit)₂]·2H₂O (1)**. (M=801.20 g/mol): monoclinic, space group P2₁/c, *a* = 11.121(1) Å, *b* = 21.365(3) Å, *c* = 7.346(1) Å, β = 108.27(1), *V* = 1657.4(4) Å³, *Z* = 2, *T* = 294K, μ(MoKα) = 1.010 mm⁻¹, *D*_{calc} = 1.605 g/cm³, 10794 reflections measured (6.144° ≤ 2θ ≤ 50°), 2918 unique (*R*_{int} = 0.084, *R*_{sigma} = 0.079) which were used in all calculations. The final *R*₁ was 0.070 (*I* > 2σ(*I*)) and *wR*₂ was 0.178 (all data).

[CuCl(bipy)₂]₂[Ge(HCit)₂]·8H₂O (2). In the first step, 0.0523 g GeO₂ (0.5 mmol) and 0.21 g H₄Cit·H₂O (1 mmol) were added to the 50 mL of water. The mixture was heated up to 80°C and stirred until the reagents were completely dissolved, then concentrated on a water bath to 10 mL (~1 h) and cooled. In the second step, a mixture of 0.171 g CuCl₂·2H₂O (1 mmol) and 0.312 g bipy (2 mmol) in 10 mL of ethanol, previously heated for 10 min and cooled, was added to the obtained solution. The resulting solution was stirred for 5.0 min without heating and then filtered. A blue precipitate of complex **2**, which contained crystals suitable for X-ray crystallography, was formed in 2 days. The yield of the product was 75%.

Calculated elemental composition (based on single-crystal data for C₅₂Cl₂Cu₂GeH₅₈N₈O₂₂, M=1417.63; in %): C 44.02, Cl 5.01, Cu 9.03, Ge 5.12, N 7.90, H 4.09. Found for the as-synthesized bulk material (in %): C 43.22, Cl 4.49, Cu 9.00, Ge 5.02, N 7.85, H 4.00.

TGA data (weight losses inside parentheses): 80-180°C, endothermic peak 100°C (-10.0%); 270-330°C, endothermic peak 280°C (-44.0%); 330-370°C, exothermic peak 350°C (-6.0%); 530-670°C, exothermic peak 570°C (-14.0%); 670-820°C, exothermic peak 770°C (-7.7%).

Selected IR data for **2** (in cm⁻¹): ν(O-H) = 3442s; ν(C-H, aromatic) = 3118w, 2930w; ν(C=O, uncoordinated carbonyl groups) = 1680m; ν_{as}(COO⁻) = 1640s; ν(C-C, skeletal vibration bipy ring) = 1602s, 1500w, 1478w; ν_s(COO⁻) = 1393m; ν(C-N, bipy) = 1317m; ν(C-O) = 1176m, 1063w; ν(C-H) = 1085w, 1033w, 995w, 955w, 908w; ν(Ge-O) = 672m, 644m.

Crystal data for **[CuCl(bipy)₂]₂[Ge(HCit)₂]·8H₂O (2)** (M = 1417.63 g/mol): triclinic, space group P⁻, *a* = 8.7182(4) Å, *b* = 12.5675(5) Å, *c* = 13.9109(5) Å, α = 75.413(3), β = 81.155(3), γ = 88.650(3), *V* = 1457.3(1) Å³, *Z* = 1, *T* = 293K, μ(MoKα) = 1.414 mm⁻¹, *D*_{calc} = 1.615 g/cm³, 10339 reflections measured (5.84° ≤ 2θ ≤ 49.992°), 5101 unique (*R*_{int} = 0.056, *R*_{sigma} = 0.090) which were used in all calculations. The final *R*₁ was 0.055 (*I* > 2σ(*I*)) and *wR*₂ was 0.130 (all data).

Results and discussion

The newly-synthesized complexes represent stable in air crystalline compounds with the molar ratio Ge : citrate : bipy = 1:2:2 (**1**) and Ge : citrate : Cu : bipy = 1:2:2:4 (**2**).

During the study of thermal stability of the synthesized complexes, we have established that their thermolysis could be divided into distinct stages. At the first stage, the endotherm peak is observed within the range of 150-220°C (for **1**) and 80-180°C (for **2**). The wide temperature range and corresponding weight loss, which has been recorded in TGA, allow us to conclude that the complexes include molecules of crystallization water (2 and 8 H₂O molecules in **1** and **2**, respectively).

The presence of water of crystallization in their structures was confirmed by IR spectroscopy. Their IR spectra contain absorption bands due to the ν(O-H) stretching vibrations at 3471 (**1**) and 3442 cm⁻¹ (**2**).

The weight loss values derived from thermogravimetric curves of **1** show that at the second stage in the 220-260°C temperature range the endothermic peak occurs, which corresponds to the removal of one bipy molecule. In the temperature range of 260-320°C one more 2,2'-bipyridine molecule is removed simultaneously with the decarboxylation of the coordinated citrate ion in complex **1**. The main difference in the thermolysis of **2** is the contemporaneous release from 270 to 330°C of four molecules of 2,2'-bipyridine. Then, a number of exothermic effects is observed, that is connected to the oxidative thermal destruction of compounds **1** and **2**.

According to the weight loss calculations and to the data from the previous researches [2,3,5,6], the final thermo-destruction products of complexes at 1000°C are GeO₂ (for **1**) and Cu₂GeO₄ (for **2**).

IR spectra of **1** and **2** contain the absorption bands $\nu(\text{C}=\text{O})$, $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$, that indicate the presence of nonequivalent coordinated and free carboxyl groups in complexes. Due to the absorption bands of $\nu(\text{C}-\text{O})$ at 1079 (for **1**) and 1063 cm^{-1} (for **2**), it is suggested that alcoholic OH groups of the citrate ligands were deprotonated and coordinated to germanium atom. The stretching vibrations Ge-O are located at 698 and 668 cm^{-1} (for **1**) and at 672 and 644 cm^{-1} (for **2**).

X-ray diffraction study has shown that compounds **1** and **2** are of onium-type, where $[\text{Ge}(\text{HCit})_2]^{2-}$ is the complex anion. This anion is located in the particular position, where the Ge atom coordinates coincide with the symmetry center of coordinates. The cation is 2,2'-bipyridine molecule with one protonated nitrogen atom in compound **1** and $[\text{Cu}(\text{bipy})_2\text{Cl}]^+$ complex in compound **2**. Complexes **1** and **2** are hydrates with two (compound **1**) and eight (compound **2**) water molecules.

In the centrosymmetric anion of complexes **1** and **2** the coordination polyhedron of Ge atom is a distorted octahedron, which is formed from three pairs of three different types of O atoms in two tridentate bis(chelating) HCit^{3-} ligands: hydroxyl (atom O(3)), α -carboxylate (atom O(1)), β -carboxylate (atom O(4)) (Figure 1). Bond length Ge-O changes within a range 1.803(3) – 1.947(3) Å in **1** and 1.812(3) – 1.944(3) Å in **2**, bond angles O-Ge-O 87.51(15) – 92.15(15)° in **1** and 88.26(14) – 91.74(14)° in **2**. This differences are discussed in the previous works dedicated to bis(citrate)germanate complexes [2-7].

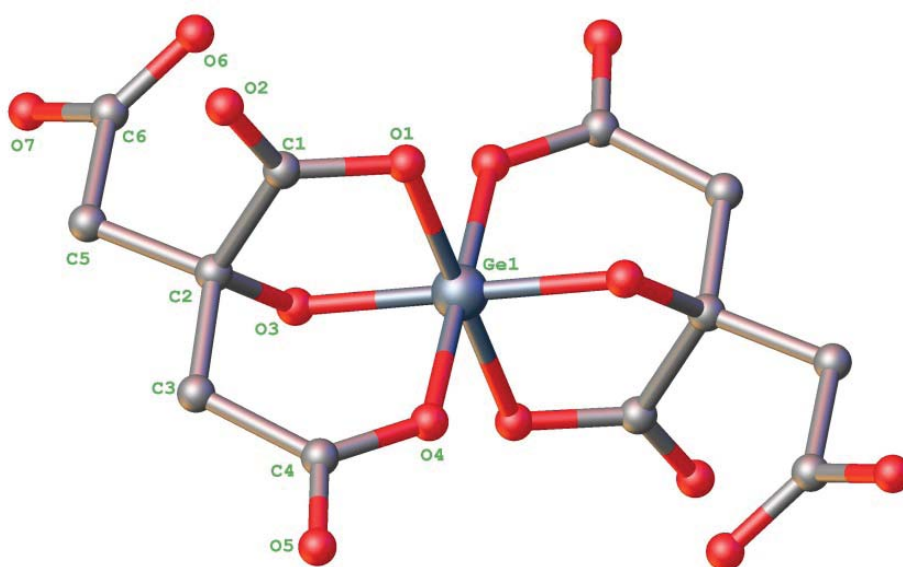


Figure 1. Molecular structure of $[\text{Ge}(\text{HCit})_2]^{2-}$ anion in **1** and **2** (the H atoms are omitted for clarity).

Owing to the developing of bis(citrate)germanate anion, five- and six-membered metallocycles are formed. The Ge-O(3)-C(2)-C(3)-C(4)-O(4) six-membered cycle adopts a sofa conformation in both compounds (the atom O(3) deviates from the mean plane of the remaining atoms of the cycle by -0.8 Å in **1** and **2**; the puckering parameters are listed in Table 1). The five-membered ring has an envelope conformation. The O(3) atom deviates from the mean squared plane of the remaining atoms by -0.5 Å in both compounds.

Table 1

Puckering parameters in the structures of 1 and 2 .			
Compound	<i>S</i>	Θ , (°)	Ψ , (°)
1	0.98	44.3	22.30
2	0.58	59.2	21.03

The localization of the positive charge on the 2,2'-bipyridine molecule (Figure 2) has been confirmed by the detection of the hydrogen atom at N(2) from the electron density difference maps and the N(2)-C(12) bond elongation up to 1.344(7) Å in comparison with its mean value of 1.339 Å [19].

The Cu atom coordination polyhedron in complex cation $[\text{CuCl}(\text{bipy})_2]^+$ of structure **2** is a distorted trigonal bipyramid (Figure 3). The N(1), N(3), Cl(1) atoms are located in the equatorial positions and in the N(2) and N(4) atoms coordinate the copper atom in axial positions. The Cu(1)-N bond lengths vary within 1.986(4) Å ÷ 2.096(3) Å, the Cu(1)-Cl bond length is 2.354(2) Å (Table 2). The valence angles have values within 111.5(2)° ÷ 127.7(2)° in the equatorial direction (ideal value is 120°) and within 79.7(2)° ÷ 98.4(3)° in the axial direction (ideal value is 90°).

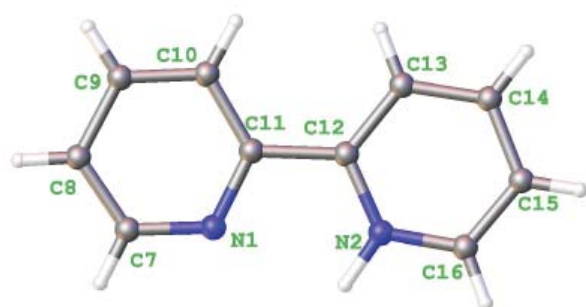


Figure 2. Molecular structure of protonated 2,2'-bipyridine fragment.

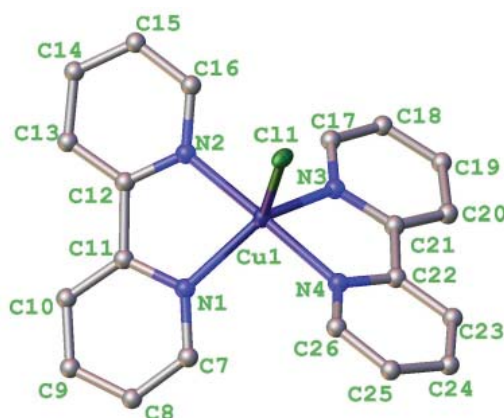


Figure 3. Molecular structure of $[\text{CuCl}(\text{bipy})_2]^+$ cation.

Table 2

Bond lengths (Å) and bond angles (°) in structures of 1 and 2 ($1-x, 1-y, -z$).

Bond lengths (Å) / bond angles (°)	1	2
Ge(1)-O(4)	1.947(3)	1.944(3)
Ge(1)-O(1)	1.897(3)	1.891(3)
Ge(1)-O(3)	1.803(3)	1.812(3)
Cu(1)-N(1)		2.087(4)
Cu(1)-N(2)		1.989(4)
Cu(1)-N(3)		2.096(4)
Cu(1)-N(4)		1.986(4)
Cu(1)-Cl(1)		2.354(3)
O(1)-Ge(1)-O(4) ¹	89.6(2)	89.9(1)
O(1)-Ge(1)-O(4)	90.4(2)	90.2(1)
O(3) ¹ -Ge(1)-O(1) ¹	87.9(1)	88.3(1)
O(3)-Ge(1)-O(1) ¹	92.2(1)	91.7(1)
O(3)-Ge(1)-O(1)	87.9(1)	88.3(1)
O(3) ¹ -Ge(1)-O(4)	89.7(2)	90.0(1)
O(3)-Ge(1)-O(4)	90.3(2)	90.1(1)
N(1)-Cu(1)-Cl(1)		127.7(1)
N(1)-Cu(1)-N(2)		79.9(2)
N(1)-Cu(1)-N(3)		120.8(2)
N(2)-Cu(1)-Cl(1)		91.5(1)
N(2)-Cu(1)-N(3)		99.8(2)
N(3)-Cu(1)-Cl(1)		111.5(1)
N(4)-Cu(1)-Cl(1)		90.8(1)
N(4)-Cu(1)-N(2)		177.7(2)
N(4)-Cu(1)-N(3)		79.7(2)

The cation, anion and water molecules in the crystal compound **1** are connected with the intermolecular hydrogen bonds (Table 3) and form a three-dimensional net (Figure 4). In the case of compound **2** the cations and anions are bonded by intermolecular hydrogen bonds through the bridging water molecules and form layers along the *ac* crystallographic plane (Figure 5).

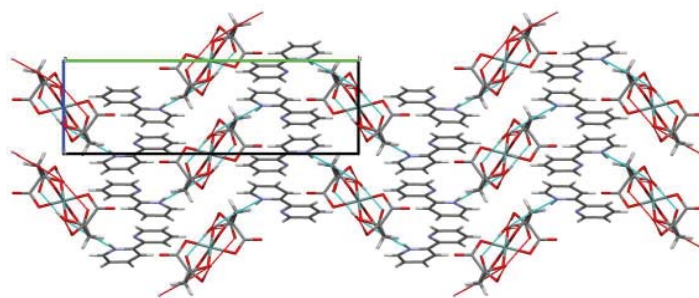


Figure 4. Crystallographic structure of 1 (projection along the crystallographic axis *a*).

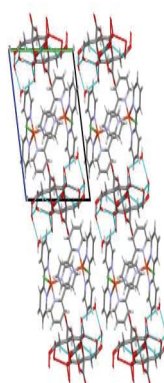


Figure 5. Crystallographic structure of 2 (projection along the crystallographic axis *a*).

Table 3

Geometric parameters of the hydrogen bonds in the structures 1 and 2.

<i>D-H...A</i>	<i>d(H...A)</i> , Å	<i>d(D...A)</i> , Å	<i>D-H...A</i> (°)
<i>Complex 1</i>			
N(2)-H(2)...O(5)	1.86	2.724(6)	144.0
C(15)-H(15)...O(1) ¹	2.37	3.250(7)	158.2
O(7)-H(7A)...O(8) ²	1.80	2.605(6)	168.2
O(8)-H(8A)...O(6) ³	2.07	2.915(6)	172.9
O(8)-H(8B)...O(5)	2.06	2.825(6)	149.6
<i>Complex 2</i>			
O(7)-H(7A)...O(9)	1.77	2.563(6)	163.1
O(10)-H(10B)...O(5)	1.92	2.756(5)	168.4
O(8)-H(8A)...O(6)	1.98	2.822(6)	171.2
O(8)-H(8B)...O(5) ⁴	2.09	2.913(6)	163.8
O(11)-H(11A)...O(10)	2.08	2.924(7)	167.2
O(11)-H(11B)...Cl(1)	2.66	3.308(5)	132.7

$$^1-1+x,+y,-1+z; ^21+x,+y,+z; ^31-x,1-y,2-z; ^4-x,1-y,-z$$

Conclusions

It is necessary to point out, that when organic cation (Hbipy)⁺ is displaced with the [CuCl(bipy)₂]⁺, the structure of complex anion almost remains, but in the case of **2** the distortion becomes a little higher. At the same time the crystal structure of complexes changes completely: three-dimensional net, in which cations, anions and water molecules are connected by the intermolecular hydrogen bonds is characteristic for **1** and alternating layer of anions and cations, connected with the bridging water molecules identifies complex **2**.

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