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Complex Formation Products in the GeO_2–Tartaric Acid–$CuCl_2$–1,10-Phenanthroline System: Syntheses and Structures

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Abstract—The cation-anionic coordination compounds based on the copper(II) complexes with Phen and tartratogermanate anions, $[Cu(Phen)_3]_2[Ge_2(OH)(HTart)(\mu\text{-}Tart)_2] \cdot 11H_2O$ (**I**) and $[CuCl(Phen)_2]_4[\{Ge_2(OH)_2(\mu\text{-}Tart)_2\}Cl_2] \cdot 4H_2O$ (**II**), with different compositions and structures (CIF files CCDC nos. 1878102 (**I**) and 1878103 (**II**)) are isolated for the first time from the GeO_2–tartaric acid (H_4Tart)–$CuCl_2$–1,10-phenanthroline (Phen) system. The structures of compounds **I** and **II** contain the same bridging tartrate anions. A specific feature of compound **I** is the additional $HTart^{3-}$ anion, which does not perform the bridging function but is coordinated via the bis(chelate) mode, and the hydroxyl and carboxyl groups remain vacant. The dissociation of the carboxyl group results in the formation of the tartratogermanate anion with the charge –4.

Keywords: germanium dioxide, tartaric acid, 1,10-phenanthroline, copper(II), coordination compounds, molecular structure, X-ray diffraction analysis

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INTRODUCTION

The complex formation of biologically active germanium in the $GeO_2(GeCl_4)$–tartaric acid (H_4Tart)–*d* metal salt–H_2O system has previously been studied, but an attempt to isolate and structurally characterized the corresponding heterometallic coordination compounds failed [1]. The products with the molar ratio M : Ge : Tart = 2 : 2 : 3, where M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}, were obtained due to the replacement of an aqueous medium by a 50% solution of CH_3COOH [2]. As found by X-ray diffraction analysis (XRD), the structural units of the $[Cu_2(H_2O)_{10}Ge_2(\mu\text{-}Tart)_3]_n \cdot 3nH_2O$ complex are polymeric anions $\left[Ge_2(\mu\text{-}Tart)_3\right]_n^{4n-}$, $Cu(H_2O)_5$ moieties, and molecules of water of crystallization [3]. In continuation of these studies, it was decided to study the complex formation products in a more complicated system: GeO_2–tartaric acid–$CuCl_2$–Phen–H_2O/C_2H_5OH. This heteroaromatic amine was chosen as the second ligand due to its capability of structuring with the formation of complicated homo- and heterometallic heteroligand coordination compounds [4–9]. It should be mentioned that Phen, like the Cu(II) tartratogermanate complexes, is among biologically active compounds [10, 11] interesting as promising substances of lowly toxic drugs with a wide range of pharmacological effect [12].

The purpose of this study is to determine the conditions for the isolation of complex formation products depending on the concentrations of the initial reagents and their molar ratios, to establish their compositions and structures, and to compare them with the earlier characterized tartratogermanates of various metals.

EXPERIMENTAL

The initial reagents for the synthesis of the complexes were purchased from Sigma-Aldrich: GeO_2 (99.999%), D-tartaric acid $C_4H_6O_6$ (99%), $CuCl_2 \cdot 2H_2O$ (99.99%) (≥98%), and 1,10-phenanthroline (99%).

Elemental analyses were carried out on an Elemental Analyzer CE-440 semiautomated C,N,H analyzer. The contents of germanium and copper were determined by atomic emission spectroscopy with inductively coupled plasma on an Optima 2000 DV instrument (PerkinElmer), and the chlorine content was determined by the mercurometric method [13].

The IR absorption spectra (400–4000 cm^{-1}) of the complexes as KBr pellets were recorded on a Frontier spectrophotometer (PerkinElmer).

Synthesis of $[Cu(Phen)_3]_2[Ge_2(OH)(HTart)(\mu\text{-}Tart)_2] \cdot 11H_2O$ (I) was carried out at the molar ratios GeO_2 : H_4Tart = 2 : 3 and $CuCl_2$: Phen = 2 : 6. Weighed samples of GeO_2 (0.5 mmol) and tartaric acid (0.75 mmol) were dissolved in water (100 mL) on reflux, and the solution was evaporated at 50°C to a volume of 10 mL. A 95% ethanol solution (10 mL) containing Phen (0.75 mmol) and $CuCl_2$ (0.25 mmol) was added to the reaction mixture cooled to room temperature. A blue crystalline precipitate was formed in 24 h. The single crystals suitable for XRD were selected from the reaction mixture. The yield was 60%.

IR (ν, cm^{-1}): 3061 ν_s(C–H), 1667 $\nu_{as}(COO^-)$, 1585, 1518 $\nu(C–C_{arom})$, 1423 $\nu_s(COO^-)$, 1343 ν(C–N), 1278 δ(C–OH), 1082 ν(C–O), 852 δ(Ge–OH), 651 ν(Ge–O).

For $C_{84}H_{78}O_{30}N_{12}Cu_2Ge_2$ (**I**)

Anal. calcd., %	C, 50.20	H, 3.88	N, 8.37	Cu, 6.37	Ge, 7.23
Found, %	C, 50.25	H, 3.98	N, 8.32	Cu, 6.43	Ge, 7.34

Synthesis of $[CuCl(Phen)_2]_4[\{Ge_2(OH)_2(\mu\text{-}Tart)_2\}Cl_2] \cdot 4H_2O$ (II) was carried out according to the same procedure as that for compound **I** but at the molar ratios GeO_2 : H_4Tart = 2 : 2 and $CuCl_2$: Phen = 2 : 4. A blue-green crystalline precipitate was formed during 24 h and contained single crystals suitable for XRD. The yield was 70%.

IR (ν, cm^{-1}): 3064 ν_s(C–H), 1685 $\nu_{as}(COO^-)$, 1583, 1516 $\nu(C–C_{arom})$, 1427 $\nu_s(COO^-)$, 1342 ν(C–N), 1075 ν(C–O), 851 δ(Ge–OH), 662 ν(Ge–O).

For $C_{104}H_{78}O_{18}N_{16}Cl_6Cu_4Ge_2$ (**II**)

Anal. calcd., %	C, 50.89	H, 3.18	N, 9.14	Cl, 8.69	Cu, 10.44	Ge, 5.84
Found, %	C, 50.94	H, 3.21	N, 9.08	Cl, 8.63	Cu, 10.37	Ge, 5.92

The crystals of compound **I** (FW = 2007.84 g/mol) were monoclinic, space group $P2_1$, a = 15.084(1), b = 21.8032(9), c = 15.547(1) Å, β = 116.248(8)°, V = 4586.1(5) $Å^3$, Z = 2, T = 294.0 K, $\mu(MoK_\alpha)$ = 1.193 mm^{-1}, ρ_{calcd} = 1.454 g/cm^3. The number of measured reflections was 39488, and that of independent reflections was 17469 (R_{int} = 0.091). The final values were R_1 = 0.082 (for 9300 reflections with the intensity $I > 2\sigma(I)$), wR_2 = 0.219 (for all reflections), S = 0.955.

The crystals of compound **II** (FW = 2451.86 g/mol) were monoclinic, space group $C2$, a = 30.390(3), b = 14.225(2), c = 15.955(2) Å, β = 116.96(1)°, V = 6147(1) $Å^3$, Z = 2, T = 100 K, $\mu(MoK_\alpha)$ = 1.356 mm^{-1}, ρ_{calcd} = 1.325 g/cm^3. The number of measured reflections was 23695, and that of independent reflections was 9703 (R_{int} = 0.065). The final values were R_1 = 0.096 (for 8276 reflections with the intensity $I > 2\sigma(I)$), wR_2 = 0.254 (for all reflections), S = 1.040.

X-ray diffraction analyses of compounds **I** and **II** were carried out on an Xcalibur-3 diffractometer (MoK_α radiation, CCD detector, graphite monochromator, ω scan mode). The structures were solved by a direct method and refined for F^2 by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms (SHELXTL) [14, 15]. The positions of hydrogen atoms were revealed from the difference electron density synthesis and refined by the riding model with $U_{iso} = nU_{equiv}$ of the nonhydrogen atom linked with the H atom (n = 1.5 for the atoms of water molecules and n = 1.2 for other hydrogen atoms).

The coordinates of atoms and full tables of bond lengths and bond angles were deposited with the Cambridge Crystallographic Data Centre (CIF files 1878102 (**I**) and 1878103 (**II**); deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The data of IR spectroscopy for the complexes were interpreted in comparison with those for tartaric acid and previously synthesized tartarogermanates [2]. The IR spectra of complexes **I** and **II** have the common features: the absence of the band at 1738 cm^{-1} corresponding to the ν(C=O) stretching vibrations of tartaric acid and the appearance of broad intense bands at 1667 (**I**), 1685 cm^{-1} (**II**) and 1423 (**I**), 1427 cm^{-1} (**II**) caused by the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ vibrations, respectively, indicating that all carboxyl groups are deprotonated and bound. The following bands were detected (cm^{-1}): 651 (**I**), 662 (**II**) ν(Ge–O); 852 (**I**), 851 (**II**) δ (Ge–OH); 1082 (**I**), 1075 (**II**) ν(C–O) of the alcoholate type; 1585, 1518 (**I**), 1583, 1516 (**II**) of the skeletal vibrations of the ring C–C; 3061 (**I**), 3064 (**II**) $\nu_s(C–H_{arom})$; and 1343 (**I**), 1342 (**II**) ν(C–N) characteristic of Phen.

A specific feature of complex **I** is that its composition contains two different forms of the ligand: bridging $Tart^{4-}$ and nonbridging $HTart^{3-}$ bound to the germanium atom via the bidentate mode. This is consistent with the band at 1278 cm^{-1} present in the IR spectrum of complex **I** and caused by the δ(C–OH) vibrations of the hydroxyl group of $HTart^{3-}$ and the band of the ionized carboxylate group at 1519 cm^{-1}, whose charge compensates that of the complex cation.

The XRD data show that compounds **I** and **II** are complexes of the cation-anionic type in which the anions are $[Ge_2(OH)(HTart)(\mu\text{-}Tart)_2]^{4-}$ in complex **I** and $[\{Ge_2(OH)_2(\mu\text{-}Tart)_2\}Cl_2]^{4-}$ in complex **II**, whereas two $[Cu(Phen)_3]^{2+}$ in complex **I** and four $[CuCl(Phen)_2]^+$ in compound **II** play the role of cations. The anion in the structure of compound **II** exists in the partial position on the second-order symmetry axis. Complexes **I** and **II** exist in the crystal as 1 : 11 (**I**) or 1 : 4 (**II**) crystalline hydrates.

The $[Ge_2(OH)(HTart)(\mu\text{-}Tart)_2]^{4-}$ anion in the structure of compound **I** is the complex binuclear compound (Fig. 1a). The Ge(1) and Ge(2) atoms have different coordination modes. The coordination polyhedron of the Ge(1) atom is a distorted trigonal bipyramid, the equatorial plane of which contains the O(19), O(9), and O(3) atoms, and the O(1) and O(7) atoms occupy the axial positions. The Addison parameter [16] is $\tau_5 = 0.81$ (the bond angles in the coordination polyhedron are presented in Table 1). The τ parameter is determined as $\tau = (\alpha - \beta)/60$, $\alpha > \beta$ (α and β are the largest angles in the coordination polyhedron), whereas $\tau = 1$ for a trigonal bipyramid and $\tau = 0$ for a square pyramid. The Ge(1)–O bond lengths vary from 1.731(9) to 1.917(10) Å. The bond angles OGe(1)O in the axial direction range from 87.5(5)° to 92.2(6)°, and those in the equatorial direction vary in a range of 116.7(6)°–126.3(5)°. The coordination polyhedron of the Ge(2) atom is a distorted octahedron formed by six oxygen atoms of three molecules of tartaric acid. Two tartaric acid molecules with both deprotonated carboxyl and hydroxyl groups between the Ge(1) and Ge(2) atoms are bridging, and the third tartaric acid molecule is the terminal ligand with the deprotonated hydroxyl groups and one carboxyl group. The Ge(2)–O bond lengths in the structure of complex **I** range from 1.832(11) to 1.979(9) Å, and the OGe(2)O bond angles vary in a range of 83.5(5)°–93.7(4)°. This structure of the complex and the distribution of bond lengths and bond angles in the coordination polyhedron are well consistent with the structures of the anions, whose formation involves tartaric acid [2, 17].

Unlike the structure of complex **I**, the anion in compound **II** is a binuclear complex formed due to the bidentate coordination of the Ge atoms by two deprotonated molecules of tartaric acid. The anion exists in the partial position on the axis 2. The coordination polyhedron of the Ge(1) atom in complex **II** is a distorted trigonal bipyramid, whose equatorial plane contains the O(3), O(7), and O(6) atoms, and the axial positions are occupied by the O(1) and O(4) atoms (Fig. 1b). The Addison parameter is $\tau_5 = 0.9$, and the OGeO bond angles vary in ranges of 87.7(4)°–93.1(6)° and 118.6(5)°–120.9(5)° (Table 1). The Ge(1)–O bond lengths range from 1.771(5) to 1.929(11) Å, and the OGe(1)O bond angles vary in the ranges 87.5(5)°–92.2(6)° and 116.7(6)°–126.3(5)° (Table 1). This structure of complex **II** agrees with the structures of the anions described previously [2].

The symmetrically independent part of the unit cell of the structure of compound **I** contains two $[Cu(Phen)_3]^{2+}$ cations, *A* (Cu(1)) and *B* (Cu(2)), in which the copper atoms are bound to three Phen molecules (Fig. 2a). The coordination polyhedra of the copper cations in the structure of complex **I** are octahedral. The Cu–N bond lengths in cations *A* and *B* range from 1.959(9) to 2.001(11) Å, and the NCuN bond angles vary in the range 75.9(3)°–99.2(4)° (Table 1).

In the crystal structure of compound **II**, the coordination polyhedra of two symmetrically independent $[Cu(Phen)_2Cl]^+$ cations, *A* (Cu(1)) and *B* (Cu(2)), represent distorted trigonal bipyramids (Fig. 2b). The equatorial plane contains the N(2), N(4), and Cl(1) atoms in cation *A* and the N(5), N(7), and Cl(2) atoms in cation *B*. The axial positions are occupied by the N(1), N(3) and N(6), N(8) atoms in cations *A* and *B*, respectively. The Addison parameters are $\tau_5 = 0.6$ and 0.5 for cations *A* and *B*, respectively. The NCuN bond angles in the axial direction vary in the range 78.3(2)°–103.1(3)°, and the NCuCl bond angles range from 91.4(3)° to 93.1(2)°. The NCuN bond angles in the equatorial direction range from 105.2(4)° to 107.4(3)°, and the NCuCl bond angles range from 110.8(2)° to 141.6(3)° (Table 1). The Cu(1)–N bond lengths vary in the range 1.978(9)–2.087(3) Å, and the Cu–Cl bonds are 2.272(4) and 2.264(3) Å in cations *A* and *B*, respectively (Table 1).

In the crystal structures of compounds **I** and **II**, the anions, cations, and molecules of water of crystallization form alternating layers parallel to the crystallographic planes *ac* and *bc* for complexes **I** and **II**, respectively (Fig. 3). The layers formed can be grouped as follows: (1) containing the anions and water molecules and (2) containing the cations of the *A* and *B* types. The layers in the structure of compound **I** are joined by intermolecular hydrogen bonds O–H···O, whereas in the structure of compound **II** they are joined by weak hydrogen bonds C–H···O (Table 2).

The introduction of Phen into the reaction system was established to result in the formation of various cation-anionic complexes **I** and **II** with the starting ratios $GeO_2 : H_4Tart = 2 : 3$ and 2 : 2, respectively. This distinguishes them from the earlier synthesized coordination polymer of the constant composition $[Cu_2(H_2O)_{10}Ge_2(\mu\text{-}Tart)_3]_n \cdot 3nH_2O$, which was iso-

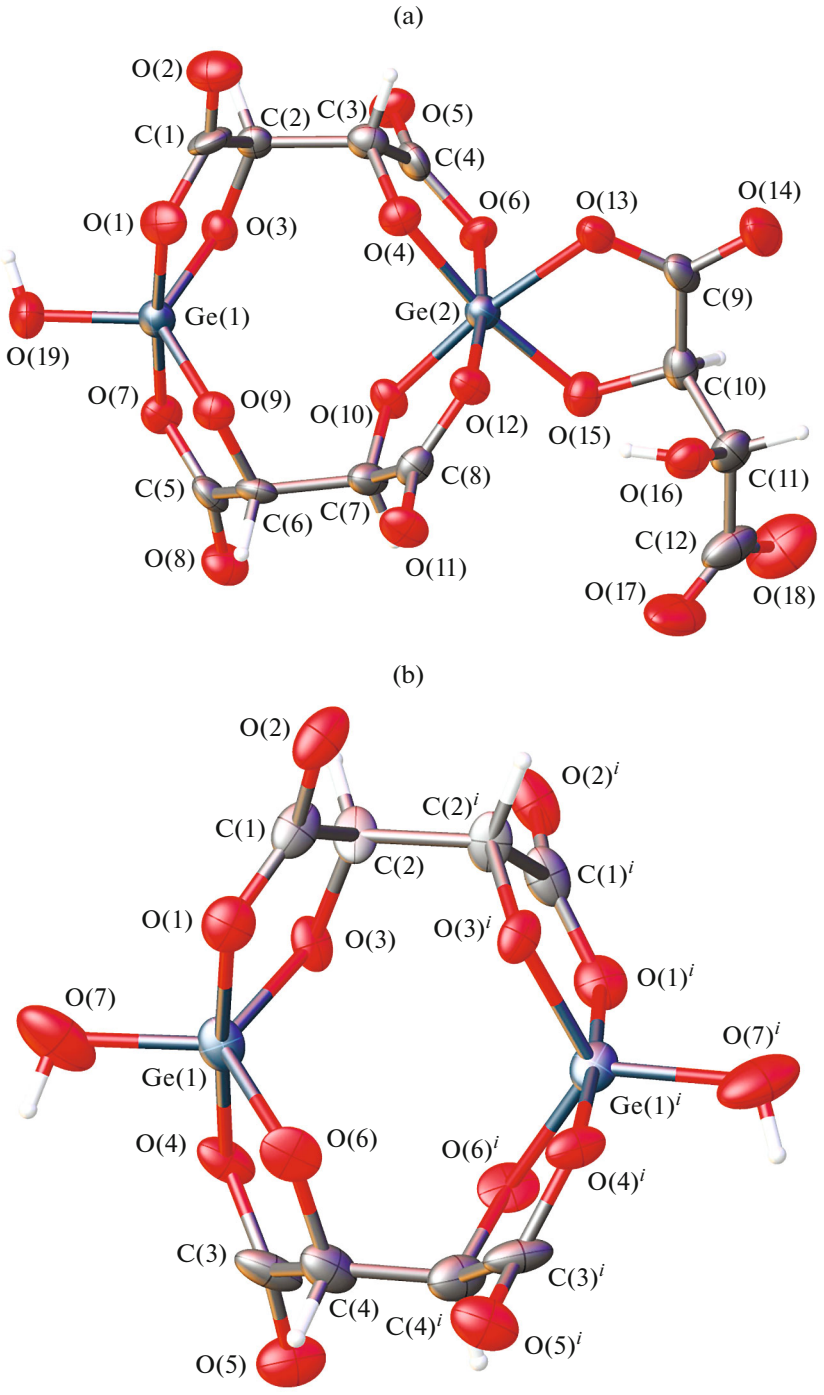

Fig. 1. Molecular structures of the anions in compounds (a) **I** and (b) **II**.

lated under the conditions of different reagent concentrations [3]. A specific feature of the structure of compound **I** is that the additional tartrate anion does not perform the bridging function but is coordinated via the (bis)chelate mode, and the hydroxyl and carboxyl groups remain vacant. The dissociation of the carboxyl group affords the tartratogermanate anion with the charge –4. The charge is compensated due to the electrostatic interaction with two $[Cu(Phen)_3]^{2+}$ cations. Complex **II** contains anions of two types: the dimer $[\{Ge_2(OH)_2(\mu\text{-Tart})_2\}]^{2-}$ similar to $K_4[Ge_2(OH)_2(\mu\text{-Tart})_2]_2 \cdot 9H_2O$ [18] and two chloride ions, whose total charge neutralizes four single-charge $[CuCl(Phen)_2]^+$

Table 1. Selected bond lengths (Å) and bond angles (deg) in compounds **I** and **II**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
		I			
Ge(2)–O(12)	1.939(9)	Ge(1)–O(9)	1.775(9)	Cu(1)–N(6)	2.142(8)
Ge(2)–O(15)	1.832(11)	Ge(1)–O(1)	1.917(10)	Cu(2)–N(8)	2.056(8)
Ge(2)–O(10)	1.829(8)	Ge(1)–O(19)	1.731(9)	Cu(2)–N(12)	2.121(7)
Ge(2)–O(6)	1.917(9)	Cu(1)–N(2)	2.070(6)	Cu(2)–N(9)	2.093(7)
Ge(2)–O(4)	1.836(10)	Cu(1)–N(5)	2.082(7)	Cu(2)–N(10)	2.067(7)
Ge(2)–O(13)	1.979(9)	Cu(1)–N(1)	2.151(8)	Cu(2)–N(7)	2.170(9)
Ge(1)–O(3)	1.765(9)	Cu(1)–N(4)	2.177(7)	Cu(2)–N(11)	2.232(8)
Ge(1)–O(7)	1.911(10)	Cu(1)–N(3)	2.168(8)		
		II			
Cu(1)–Cl(1)	2.272(4)	Cu(2)–Cl(2)	2.264(3)	Ge(1)–O(6)	1.783(7)
Cu(1)–N(2)	2.150(10)	Cu(2)–N(5)	2.080(9)	Ge(1)–O(3)	1.771(5)
Cu(1)–N(3)	2.012(11)	Cu(2)–N(6)	1.978(10)	Ge(1)–O(4)	1.872(6)
Cu(1)–N(4)	2.100(9)	Cu(2)–N(8)	1.982(5)	Ge(1)–O(7)	1.802(15)
Cu(1)–N(1)	1.978(9)	Cu(2)–N(7)	2.177(5)	Ge(1)–O(1)	1.929(11)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
		I			
O(12)Ge(2)O(13)	89.9(4)	O(3)Ge(1)O(1)	87.8(5)	N(3)Cu(1)N(4)	77.0(4)
O(15)Ge(2)O(12)	92.9(4)	O(7)Ge(1)O(1)	175.4(4)	N(6)Cu(1)N(1)	99.2(4)
O(15)Ge(2)O(6)	93.7(4)	O(9)Ge(1)O(7)	87.8(4)	N(6)Cu(1)N(3)	94.0(4)
O(15)Ge(2)O(4)	170.2(4)	O(9)Ge(1)O(1)	90.3(5)	N(8)Cu(2)N(12)	92.9(4)
O(15)Ge(2)O(13)	83.5(5)	O(19)Ge(1)O(3)	116.7(6)	N(8)Cu(2)N(9)	90.8(3)
O(10)Ge(2)O(12)	86.4(4)	O(19)Ge(1)O(7)	92.4(5)	N(8)Cu(2)N(10)	167.4(4)
O(10)Ge(2)O(15)	89.8(4)	O(19)Ge(1)O(9)	117.0(6)	N(8)Cu(2)N(7)	78.7(4)
O(10)Ge(2)O(6)	90.8(4)	O(19)Ge(1)O(1)	92.2(5)	N(8)Cu(2)N(11)	94.7(4)
O(10)Ge(2)O(4)	100.0(4)	N(2)Cu(1)N(1)	77.7(4)	N(12)Cu(2)N(7)	94.1(3)
O(10)Ge(2)O(13)	172.2(4)	N(2)Cu(1)N(4)	92.4(4)	N(12)Cu(2)N(11)	76.0(4)
O(6)Ge(2)O(12)	172.8(4)	N(2)Cu(1)N(3)	92.4(3)	N(9)Cu(2)N(7)	98.3(4)
O(6)Ge(2)O(13)	93.6(5)	N(2)Cu(1)N(6)	96.3(4)	N(9)Cu(2)N(11)	91.9(4)
O(4)Ge(2)O(12)	87.8(4)	N(5)Cu(1)N(1)	94.5(4)	N(10)Cu(2)N(12)	98.4(3)
O(4)Ge(2)O(6)	86.1(4)	N(5)Cu(1)N(4)	94.5(4)	N(10)Cu(2)N(9)	79.3(3)
O(4)Ge(2)O(13)	86.7(5)	N(5)Cu(1)N(3)	96.5(4)	N(10)Cu(2)N(7)	94.9(4)
O(3)Ge(1)O(7)	90.0(5)	N(5)Cu(1)N(6)	78.1(4)	N(10)Cu(2)N(11)	93.4(3)
O(3)Ge(1)O(9)	126.3(4)	N(1)Cu(1)N(4)	91.1(4)		
		II			
N(2)Cu(1)Cl(1)	114.0(3)	N(5)Cu(2)Cl(2)	141.6(3)	O(6)Ge(1)O(4)	88.1(2)
N(3)Cu(1)Cl(1)	93.0(3)	N(5)Cu(2)N(7)	107.4(3)	O(6)Ge(1)O(7)	118.6(5)
N(3)Cu(1)N(2)	102.0(4)	N(6)Cu(2)Cl(2)	92.9(3)	O(6)Ge(1)O(1)	90.1(4)
N(3)Cu(1)N(4)	80.7(4)	N(6)Cu(2)N(5)	81.8(4)	O(3)Ge(1)O(6)	120.9(3)
N(4)Cu(1)Cl(1)	140.8(3)	N(6)Cu(2)N(8)	172.8(3)	O(3)Ge(1)O(4)	90.2(2)
N(4)Cu(1)N(2)	105.2(4)	N(6)Cu(2)N(7)	103.2(2)	O(3)Ge(1)O(7)	120.5(5)
N(1)Cu(1)Cl(1)	91.4(3)	N(8)Cu(2)Cl(2)	93.1(2)	O(3)Ge(1)O(1)	87.7(4)
N(1)Cu(1)N(2)	81.1(4)	N(8)Cu(2)N(5)	91.1(3)	O(4)Ge(1)O(1)	176.0(4)
N(1)Cu(1)N(3)	173.0(4)	N(8)Cu(2)N(7)	78.3(2)	O(7)Ge(1)O(4)	90.8(5)
N(1)Cu(1)N(4)	92.5(4)	N(7)Cu(2)Cl(2)	110.8(2)	O(7)Ge(1)O(1)	93.1(6)

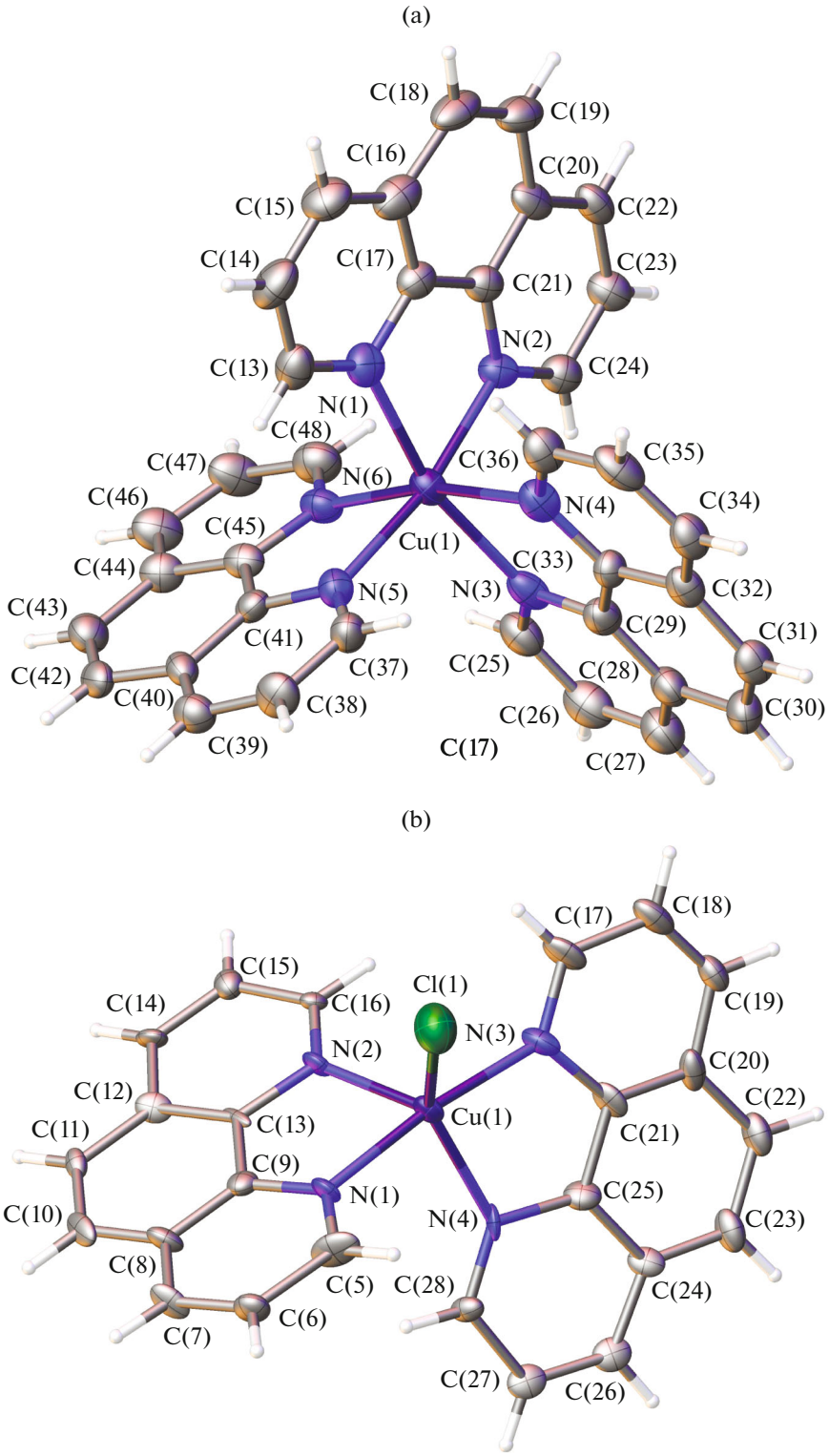

Fig. 2. Molecular structures of the cations (cations of the *A* type are present in compounds (a) **I** and (b) **II**).

Table 2. Geometric characteristics of hydrogen bonds in compounds **I** and **II**

D–H···A	Distance, Å		D–H···A, deg
	H···A	D···A	
	I		
O(16)–H(16)···O(12)	2.26	3.062(15)	165
O(19)–H(19*A*)···O(21)	1.93	2.72(3)	162
O(29)–H(29*A*)···O(30)	2.14	2.81(2)	136
O(29)–H(29*B*)···O(23)	1.97	2.82(3)	177
O(20)–H(20*A*)···O(5)[i]	1.97	2.801(16)	166
O(20)–H(20*B*)···O(11)	2.08	2.836(16)	148
O(30)–H(30*B*)···O(33)	2.04	2.79(2)	146
O(24)–H(24*B*)···O(33)	2.02	2.84(3)	164
O(22)–H(22*A*)···O(19)	1.97	2.798(16)	163
O(22)–H(22*B*)···O(23)[ii]	2.60	2.72(2)	90
O(32)–H(32*A*)···O(31)	2.10	2.93(3)	165
O(32)–H(32*B*)···O(2)[iii]	1.97	2.80(2)	161
O(23)–H(23*A*)···O(22)[iv]	2.16	2.72(2)	139
O(31)–H(31*A*)···O(11)[v]	2.20	2.99(2)	152
O(31)–H(31*B*)···O(17)[v]	1.97	2.82(3)	168
O(28)–H(28*A*)···O(18)[v]	2.15	3.00(3)	170
O(28)–H(28*B*)···O(24)[vi]	2.01	2.85(3)	165
O(25)–H(25*A*)···O(16)[vii]	2.19	3.01(3)	160
O(25)–H(25*B*)···O(20)[vii]	2.02	2.86(3)	165
O(21)–H(21*A*)···O(28)	2.39	3.12(5)	145
O(26)–H(26*A*)···O(27)	2.11	2.95(4)	164
O(26)–H(26*B*)···O(15)[v]	2.03	2.87(2)	163
O(27)–H(27*A*)···O(18)[v]	1.76	2.57(3)	157
O(27)–H(27*B*)···O(22)	2.01	2.87(3)	179
	II		
C(16)–H(16)···O(5)	2.16	3.089(14)	167
O(7)–H(7*A*)···O(9)[viii]	2.07	2.78(2)	141
O(8)–H(8*A*)···O(5)	2.11	2.923(17)	159

Symmetry codes: [i] $-x+3, y-1/2, -z+2$; [ii] $-x+2, y+1/2, -z+1$; [iii] $-x+2, y-1/2, -z+2$; [iv] $-x+2, y-1/2, -z+1$; [v] $x-1, y, z$; [vi] $-x+2, y+1/2, -z+2$; [vii] $x-1, y, z-1$; [viii] $x+1/2, y-1/2, z$.

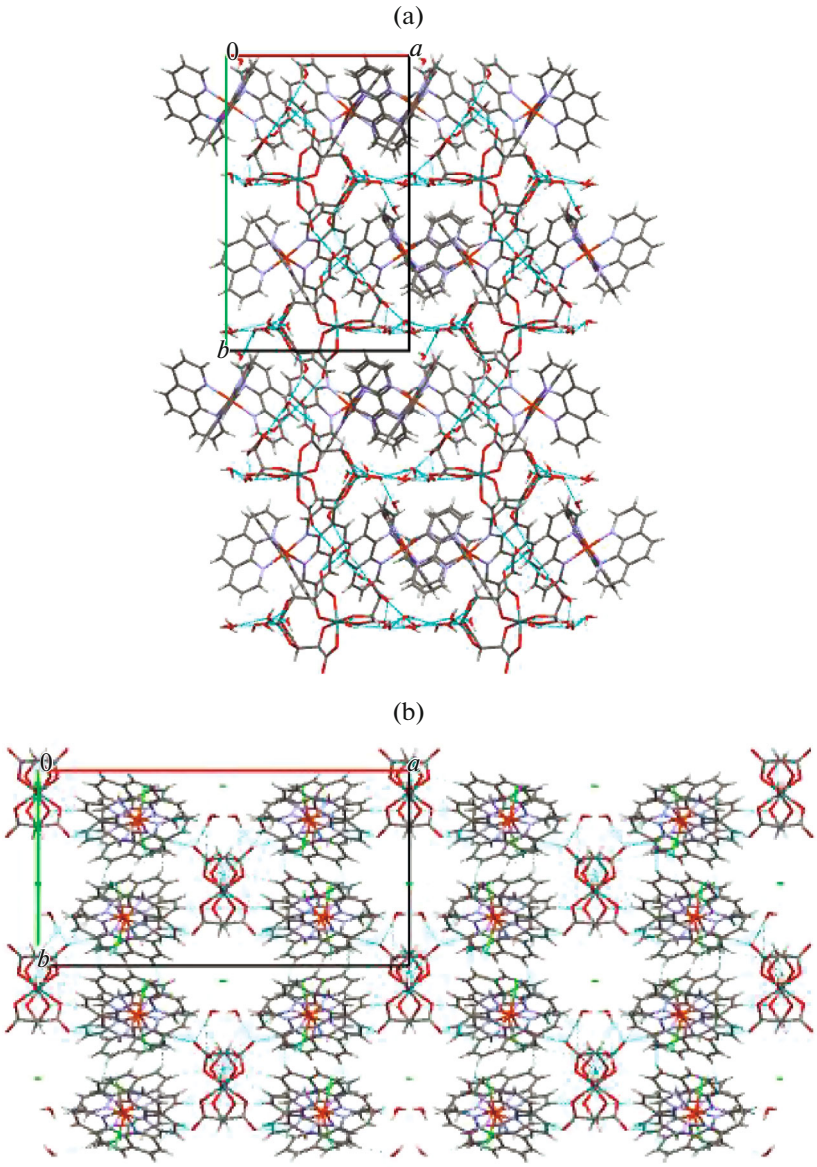

Fig. 3. Crystal structures of compounds (a) **I** and (b) **II**. The view along the crystallographic axis *c*.

cations. Thus, the Cu-containing complex cations with 1,10-phenanthroline different in composition are formed in compounds **I** and **II** depending on the complex anions.

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