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Ammonium and Potassium Citratogermanates(IV): Synthesis, Chemical Compositions, and Structures. The Crystal Structures of $(NH_4)[Ge(OH)(H_2Cit)_2] \cdot H_2O$ and $K_4[Ge(HCit)_2(H_2Cit)] \cdot 3H_2O$

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Abstract—Methods for the synthesis of ammonium citratogermanate $(NH_4)[Ge(OH)(H_2Cit)_2] \cdot H_2O$ (**I**) and potassium citratogermanate $(K_4[Ge(HCit)_2(H_2Cit)] \cdot 3H_2O$ (**II**), where H_4Cit is citric acid) in aqueous MeCN were developed. The individuality, chemical composition, and thermal stability of complexes **I** and **II** were proved by elemental analysis, thermogravimetry, and IR spectroscopy. According to X-ray diffraction data, the coordination numbers of the Ge atoms are 5 and 6 and their coordination polyhedra are a square pyramid and an octahedron in complexes **I** and **II**, respectively. In both complexes, the Ge atom coordinates the deprotonated OH group and the α-carboxyl group of the ligands H_nCit^{4-n} to form five-membered chelate rings. Hydrogen bonds in **I** as well as potassium cations in **II** serve to unite these complexes into frameworks.

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Earlier, we have synthesized the complex acid $[H_5O_2][Ge(H_2Cit)(H_{2.5}Cit)(OH)]_2 \cdot 2CH_3COOH \cdot 2H_2O$ by a reaction of $GeCl_4$ with citric acid in 85% CH_3COOH [1]. This provides direct evidence that complex citratogermanic acid exists not only in solution. As a next step in these investigations, we extended the range of citratogermanates studied by changing the solvent from proton-donating (acetic acid) to proton-withdrawing (acetonitrile) and employing other starting materials.

The goal of this study was to examine complexation between $GeCl_4$ and citric acid in acetonitrile and compare the chemical compositions and structures of the resulting complexes with those of the citratogermanates $[H_5O_2][Ge(H_2Cit)(H_{2.5}Cit)(OH)]_2 \cdot 2CH_3COOH \cdot 2H_2O$ [1] and $K_2[Ge(HCit)_2] \cdot 2H_2O$ [2] obtained earlier under other conditions.

EXPERIMENTAL

Synthesis of $(NH_4)[Ge(OH)(H_2Cit)_2] \cdot H_2O$ (I). Citric acid monohydrate (0.01 mol) was dissolved in 50% aqueous acetonitrile (40 mL). High-purity $GeCl_4$ (0.005 mol) was added and the mixture was heated at 40°C for 5 min. Then aqueous ammonia was added to pH 2–3. After 48 h, the reaction produced a crystalline precipitate of complex **I**. The yield was 50% (with respect to Ge). Single crystals of complex **I** suitable for X-ray diffraction were withdrawn from the reaction medium.

For $C_{12}H_{19}GeNO_{16}$ ($M = 505.6$)

anal. calcd., %:	C, 28.48;	H, 3.76;	Ge, 14.36;	N, 2.77.
Found, %:	C, 28.13;	H, 3.87;	Ge, 14.32;	N, 2.65.

Synthesis of $K_4[Ge(HCit)_2(H_2Cit)] \cdot 3H_2O$ (II). The complex $[H_5O_2][Ge(H_2Cit)(H_{2.5}Cit)(OH)]_2 \cdot 2CH_3COOH \cdot 2H_2O$ (**III**) (0.01 mol) was dissolved at 18–19°C in water (20 mL). Then $KHCO_3$ was gradually added in portions to pH 5. To reach equilibrium, the resulting solution was kept at room temperature for 24 h. Addition of an equal volume of acetonitrile initiated the formation of a white crystalline precipitate containing single crystals of complex **II** suitable for X-ray diffraction.

For $C_{18}H_{22}GeK_4O_{24}$ ($M = 851.36$)

anal. calcd., %:	C, 25.39;	H, 2.60;	Ge, 8.52;	K, 18.37.
Found, %:	C, 25.24;	H, 2.43;	Ge, 8.56;	K, 18.12.

Analyses for germanium and potassium were performed using inductively coupled plasma atomic emission spectroscopy with an Optima 2000 DV instrument (PerkinElmer); analyses for carbon,

Table 1. Selected crystallographic parameters and the data collection and refinement statistics for structures **I** and **II**

Parameter	Value	
	I	**II**
Temperature, K	293	296
Radiation; λ, Å	MoK_α; 0.71073	MoK_α; 0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a, Å	8.2494(11)	11.592(2)
b, Å	10.0269(15)	14.978(3)
c, Å	12.9473(16)	16.984(3)
α, deg	97.435(17)	90
β, deg	98.793(18)	94.548(4)
γ, deg	113.660(14)	90
V, Å^3	947.6(2)	2939.6(9)
Z	2	4
ρ_{calcd}, g/cm^3	1.773	1.924
μ, mm^{-1}	1.703	1.712
Crystal dimensions, mm	0.40 × 0.30 × 0.30	0.25 × 0.18 × 0.15
θ Scan range, deg	2.27–29.96	2.41–28.25
Ranges of h, k, and l indices	$-11 \le h \le 1$ $-13 \le k \le 14$ $-18 \le l \le 18$	$-15 \le h \le 15$ $-17 \le k \le 19$ $-20 \le l \le 22$
Number of measured reflections	6567	23512
Number of independent reflections	5508	7246
R_{int}	0.0441	0.0513
Number of reflections with $I > 2\sigma(I)$	4537	5050
Number of parameters refined	271	424
GOOF (F^2)	1.278	0.941
R_1, wR_2 ($I > 2\sigma(I)$)	0.0366, 0.1048	0.0429, 0.1072
R_1, wR_2 (for all reflections)	0.0565, 0.1478	0.0771, 0.1271
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$, e/Å^3	0.904, −1.060	0.850, −0.646

hydrogen, and nitrogen were carried out on a semiautomatic C,N,H-analyzer.

Thermogravimetric analysis (**TGA**) was performed on a Q-1500D derivatograph in air (temperature range 20–1000°C, heating rate 10°C/min).

X-ray powder diffraction from the final products of thermolysis of complexes **I** and **II** was studied using a DRON-0.5 diffractometer with a copper anticathode and a nickel filter.

The IR absorption spectra of the ligand and the complexes were recorded on a Frontier spectrophotometer (PerkinElmer) in the 400–4000 cm^{-1} range.

X-ray diffraction study. Experimental data were collected with Enraf-Nonius CAD4 (**I**) and Bruker SMART APEX II (**II**) diffractometers (Joint Use Center of the Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences). An absorption correction was applied semiempirically with the MULTISCAN (**I**) [3] and SADABS programs (**II**) [4]. Structures **I** and **II** were solved by combining direct methods and electron density maps. The H atoms of water molecules, the hydroxyl group, and ammonium are located in difference electron-density maps. The aliphatic H atoms were located geometrically. The structures were refined anisotropically by the full-matrix least-squares method with allowance for the H atoms. All calculations were performed with the SHELXS-97 and SHELXL-97 programs [5].

Selected crystallographic data are given in Table 1. Experimental data for complexes **I** and **II** have been deposited with the Cambridge Crystallographic Data Centre (nos. 920656 (**I**) and 920657 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Table 2. Thermolysis of complexes **I** and **II**

Complex	Processes and temperature ranges									
	$-n\text{H}_2\text{O}$			$-n\text{CO}_2 + x\text{H}_2\text{O}$			Thermal degradation and combustion		Final thermolysis product	
	$T_{\max}$*, (DTA), °C	Δ*m* (TG), %	Δ*m* (*C***), %	$T_{\max}$*, (DTA), °C	Δ*m* (TG), %	Δ*m* *C***, %	$T_{\max}$*, (DTA), °C	Δ*m* (TG), %	*m* (TG), %	*M* (*C***), %
I	70–120 (100↓)	3.60 $n = 1$	3.55	170–265 (200↓)	38.34 $n = 4$ $x = 1$	38.29	265–300 (280↑)	33.01	21.25	20.65 GeO_2
	120–170 (150↓)	3.80 $-\text{NH}_3$	3.75							
II	90–120 (100↓)	2.00 $n = 1$	2.10	170–245 (210↓)	10.12 $n = 2$ $x = 0$	10.34	370–500 (400↑) 500–700 (680↑) 700–980 (950↑)	43.65	34.00	34.37 K_4GeO_4
	120–170 (160↓)	4.10 $n = 2$	4.23	245–370 (350↓)	20.55 $n = 4$ $x = 0$	20.67				

Notes: * ↓ and ↑ denote endo- and exotermic effects, respectively.
** *C* is the calculated value.

RESULTS AND DISCUSSION

We found that a reaction of GeCl_4 with citric acid in acetonitrile upon the addition of aqueous ammonia yields a precipitate of ammonium bis(citrato)hydroxygermanate (**I**). The formation of this complex can be represented as follows:

$$\text{GeCl}_4 + 2\text{H}_4\text{Cit} + 5\text{NH}_3 + 2\text{H}_2\text{O} \xrightarrow[\text{of CH}_3\text{CN in water}]{\text{50\% aqueous solution}} (\text{NH}_4)[\text{Ge(OH)(H}_2\text{Cit)}_2] \cdot \text{H}_2\text{O} + 4\text{NH}_4\text{Cl}.$$

With acid **III** as the starting material, we obtained complex **II** in which the molar ratio of Ge : citric acid is 1 : 3. This ratio has not been noted earlier for citrate complexes of Ge(IV) [1, 2, 6–9] but can be explained under the assumption that complex **III** serves as a building block for two complexes. Complex **II** precipitates, while another complex remains dissolved because of double hydrolysis of a Ge species according to the equation:

$$[\text{H}_5\text{O}_2][\text{Ge(H}_2\text{Cit)(H}_{2.5}\text{Cit)(OH)}]_2 \cdot 2\text{CH}_3\text{COOH} \cdot 2\text{H}_2\text{O} + 5\text{KHCO}_3 \rightarrow \text{K}_4[\text{Ge(HCit)}_2(\text{H}_2\text{Cit})] \cdot 3\text{H}_2\text{O}\downarrow + \text{K[Ge(OH)}_2\text{HCit]} + 5\text{CO}_2 + 6\text{H}_2\text{O} + 2\text{CH}_3\text{COOH}.$$

This seems to be quite probable since it is the species Ge(OH)_2^{2+} that predominantly exists in aqueous solution at pH 5 [10].

Complexes **I** and **II** are white crystalline solids that are stable in air. The thermolysis of both complexes follows a complicated stepwise scheme (Table 2). The wide temperature range (90–170°C), the relatively high dehydration temperature, and the corresponding weight loss observed in the TGA curves suggest that complexes **I** and **II** contain hydrogen-bonded molecules of crystallization water and (for **I** only) the ammonium ion. The endothermic peak in a temperature range from 170 to 265°C is due to decarboxylation with elimination of four (**I**) or two CO_2 molecules (**II**). In addition, one water molecule is eliminated from complex **I** (that molecule is formed by an interaction of the carboxyl proton with the inner-sphere OH group bound to germanium [11]). On further heating, complex **II** eliminates other four CO_2 molecules from the citrate ligands. Finally, complexes **I** and **II** undergoes oxidative thermal degradation and combustion of the organic part of their molecules, with the corresponding one (for **I**) and three exothermic peaks (for **II**). According to the weight losses calculated from the TG curves, the final thermolysis products at 1000°C were GeO_2 (for **I**) and potassium orthogermanate (for **II**), which was confirmed by X-ray powder diffraction data.

The IR spectra of complexes **I** and **II** were analyzed by comparing them with spectroscopic data obtained for complex **III** [1]. The presence of water of crystallization in their structures, which was detected by thermogravimetric measurements, was confirmed by IR spectroscopy. Their IR spectra show absorption bands due to the ν(OH) stretching vibrations at 3450–3406 (**I**) and 3476–3335 cm^{-1} (**II**). Also, the IR spectra of the above three complexes contain the same set of characteristic bands due to main functional groups responsible for the coordination to germanium (**I, II**) and potassium (**II**): 1754 (**I**), 1733 (**II**, ν(C=O)), 1713 (**I**), 1688 (**II**, ν(C=O)), 1644 (**I**), 1663 (**II**, $\nu_{as}(\text{COO}^-)$); 1409, 1334 (**I**), 1444, 1350 cm^{-1} (**II**, $\nu_s(\text{COO}^-)$) (stretching vibrations of the free, coordinated, and carboxylate groups, respectively). The deprotonation of the alcoholic OH groups of the

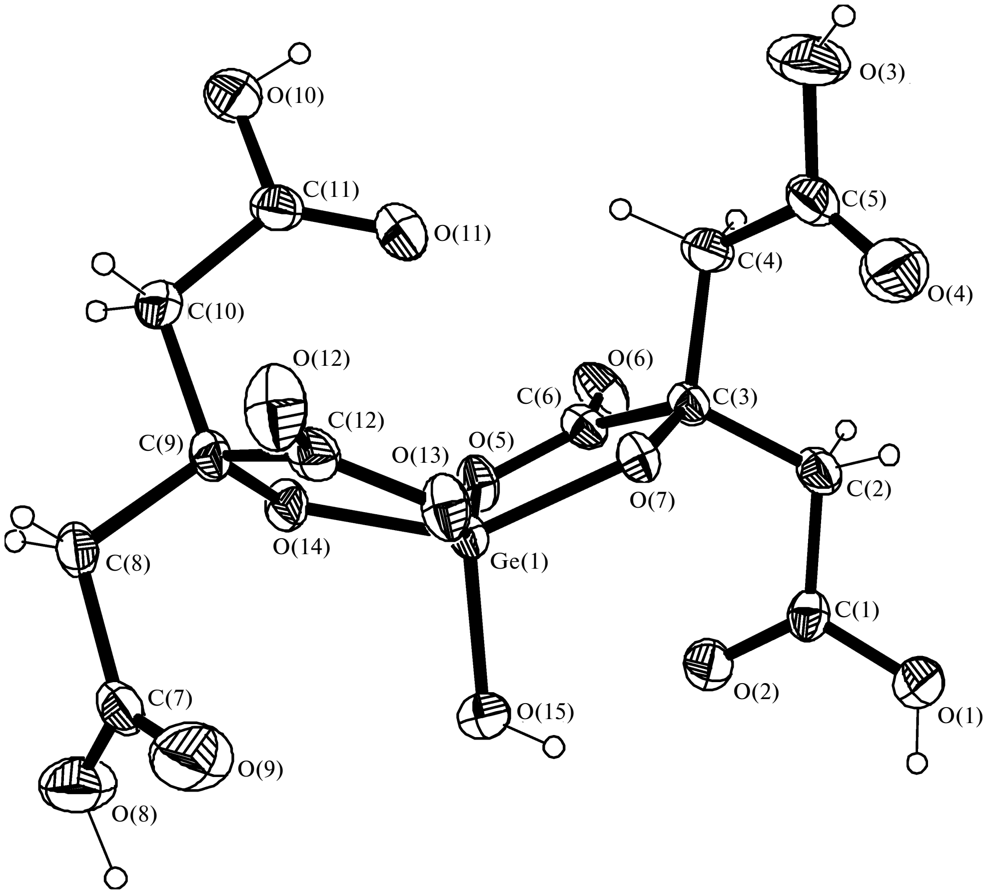

Fig. 1. Complex anion in structure **I**.

citrate ligands and their coordination to germanium are suggested by the absorption bands due to ν(C–O) at 1083 (**I**) and 1090 cm^{-1} (**II**). The ν(Ge–O) bands at 660, 636, and 607 cm^{-1} (**I**) and at 660 and 641 cm^{-1} (**II**) suggest chelate ring closure via formation of Ge–O bonds with different lengths. Therefore, one can conclude that complexes **I** and **II** retain the same monochelating bidentate way of coordination of citrate ligands as in structure **III**. In contrast to complexes **III** and **I**, the IR spectrum of complex **II** contains no absorption band at 820 cm^{-1} due to the δ(Ge–OH) bending vibrations.

Structure **I** is built from the complex anions $[Ge(OH)(H_2Cit)_2]^-$ (Fig. 1), the ammonium ions, and the molecules of crystallization water. The coordination polyhedron of the Ge atom is a square pyramid with an apical hydroxyl group. The coordinated O atoms of the carboxyl groups are *trans* to each other. All the "active" H atoms are involved in hydrogen bonding (Table 3). The system of hydrogen bonds serves to unite the structural units into a framework.

Structure **II** is made up of the complex anions $[Ge(HCit)_2(H_2Cit)]^{4-}$ (Fig. 2), the potassium cations, and potassium-coordinated water molecules. The Ge atom coordinates with one diprotonated and two monoprotonated citrate anions. The coordination polyhedron of the Ge atom is an octahedron. The complex molecules are united through the cations into a framework additionally stabilized by hydrogen bonds.

The formation of five-membered chelate rings (as in complexes **I** and **II**) is typical of metal citrates. Out of 333 complexes of *p*-, *d*-, and *f* metals with citric acid (CCDC, v. 5.33 [12]), 324 complexes show such chelate rings; in 124 complexes, the β-carboxyl branches are not coordinated.

In the organometallic complex $[Ge(Mft)(H_2Cit)_2] \cdot H_2O$ (Mft is N-methylmorpholinium) [13] with a germanium coordination number of 5 (as in **I**), the Ge atom has a trigonal-bipyramidal environment. The same germanium polyhedron (trigonal bipyramid) has been found in structure **III** [1]. The different structures of five-vertex polyhedra in complexes **I** and **III** are difficult to explain by different degrees of protonation. Most likely, this is due to the conformational flexibility of the anion, which can conform itself to the structural demands of its coordination partners.

The octahedral complex $[M(Cit)_3]$ (with no regard to the degree of protonation of the ligand), in which all three ligand molecules form five-membered chelate

Table 3. Geometrical parameters of the hydrogen bonds in structures **I** and **II**

Bond D–H···A	Distance, Å			Angle	Transformation matrix of the atom A
	D–H	H···A	D···A	DHA, deg	
			I		
O(1)–H(1)···O(2)	0.82	1.88	2.692(4)	173	$-x, -y, -z$
O(3)–H(2)···O(11)	0.87	2.11	2.890(5)	150	$-x, -y + 1, -z + 1$
O(8)–H(3)···O(16)	0.95	1.67	2.619(4)	176	
O(10)–H(4)···O(6)	0.78	1.88	2.643(4)	164	$-x + 1, -y + 1, -z + 1$
O(15)–H(5)···O(9)	0.83	1.93	2.753(4)	173	$-x, -y + 1, -z$
O(16)–H(6)···O(7)	0.76	2.12	2.868(4)	172	$-x, -y + 1, -z$
O(16)–H(7)···O(6)	0.83	2.08	2.828(4)	151	$-x + 1, -y + 1, -z$
N(1)–H(8)···O(14)	0.92	2.05	2.955(4)	171	$-x + 1, -y + 1, -z$
N(1)–H(9)···O(16)	0.86	2.06	2.895(5)	163	
N(1)–H(11)···O(15)	0.92	2.06	2.877(5)	147	
N(1)–H(10)···O(12)	0.90	2.03	2.907(5)	164	$-x, -y + 1, -z$
			II		
O(1)–H(1)···O(4)	1.00	1.48	2.481(4)	173	
O(8)–H(2)···O(16)	0.95	1.59	2.540(4)	173	$-x + 1, -y, -z + 1$
O(10)–H(3)···O(5)	0.93	1.93	2.803(3)	155	$x, -y + 1/2, z - 1/2$
O(17)–H(4)···O(3)	0.90	1.66	2.557(4)	172	$-x, y - 1/2, -z + 3/2$
O(22)–H(5)···O(2)	0.92	1.91	2.804(4)	164	$x + 1, y, z$
O(22)–H(6)···O(6)	0.96	2.05	2.958(4)	156	$x + 1, -y + 1/2, z - 1/2$
O(23)–H(7)···O(1)	0.95	1.91	2.850(4)	171	$-x, y - 1/2, -z + 1/2$
O(23)–H(8)···O(13)	0.95	1.89	2.806(4)	161	$x, -y + 1/2, z - 1/2$
O(24)–H(9)···O(12)	1.07	1.84	2.901(5)	169	$x, -y + 1/2, z - 1/2$
O(24)–H(10)···O(15)	1.04	2.15	3.146(5)	159	

rings, can exist as two isomers with the *mer*- and *fac*-arrangement of the O atoms of the coordinated central carboxylate branch. Structure **II** is a *fac* isomer. The Cambridge Crystallographic Data Centre contain data for 22 octahedral metal triscitrates with the *fac*-structure (as in **II**). Note that all these 22 complexes are Ti(IV) triscitrates, which makes it difficult to conclude about preference of one or the other isomer.

The Ge–O bond lengths (Table 4) for similar O atoms in complex **II** differ by more than 30σ (1.909 and 1.975 Å). Note that these values refer to the monoprotonated anions and that neither of these O atoms forms short hydrogen bonds, which provides additional evidence for lack of structural rigidity in Ge(IV) citrates. The uncoordinated β-carboxyl groups in complexes **I** and **II** exist in different conformations depending on hydrogen bonding. One monoprotonated citrate anion (C(1–5), Fig. 2) forms an intramolecular hydrogen bond, while the other two anions (mono- and diprotonated ones) are involved in intermolecular hydrogen bonds.

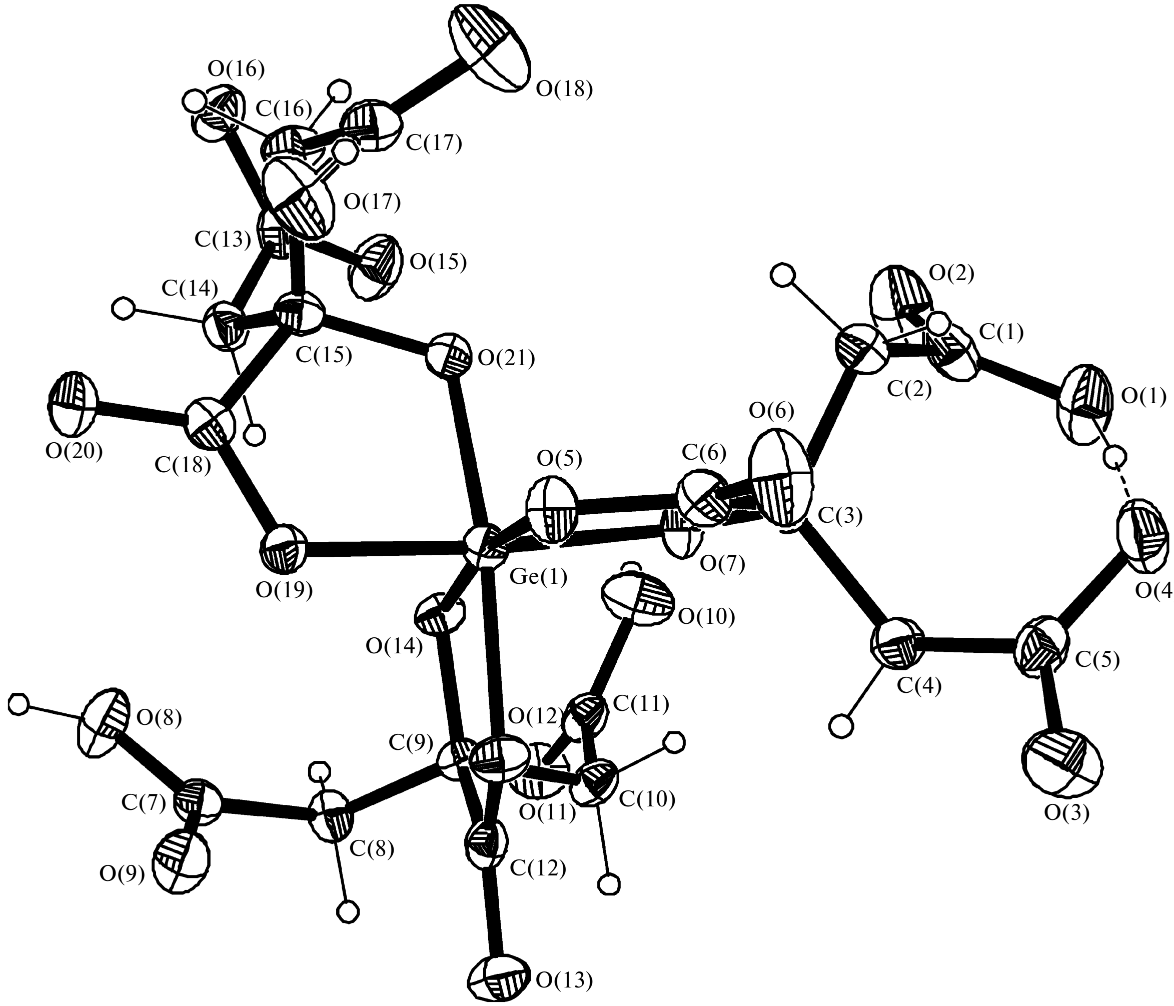

Fig. 2. Complex anion in structure **II**.

Table 4. Ge–O bond lengths in structures **I** and **II**

Bond	*d*, Å
I	
Ge(1)–O(15)	1.751(3)
Ge(1)–O(14)	1.800(2)
Ge(1)–O(7)	1.809(2)
Ge(1)–O(13)	1.887(2)
Ge(1)–O(5)	1.905(2)
II	
Ge(1)–O(21)	1.826(2)
Ge(1)–O(14)	1.828(2)
Ge(1)–O(7)	1.834(2)
Ge(1)–O(19)	1.909(2)
Ge(1)–O(12)	1.936(2)
Ge(1)–O(5)	1.975(2)

Based on the data obtained, one can conclude that the chemical compositions and structures of the complex anions in **I** and **III** substantially differ from those found in **II** and, even to a greater extent, from those for the *bis*(citrato)germanates synthesized earlier under different conditions [2, 6–9]. Therefore, the structural variety of the latter depends on the starting reagent (GeO_2, $GeCl_4$, or complex **III**), the solvent (acetonitrile, acetic acid, or water), pH of the medium, and the cations (*s*-, and *d* metals). Triscitrate complex **II** is a first representative of Ge(IV) complexes of this type.

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