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Bis(citrato)germanates of Bivalent 3*d* Metals (Fe, Co, Ni, Cu, Zn): Crystal and Molecular Structure of $[Fe(H_2O)_6][Ge(HCit)_2] \cdot 4H_2O$

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Abstract—In continuation of a systematic study of bis(citrate)germanates, we synthesized a number of heterometallic germanium(IV) and 3*d* metal complexes based in citric acid (H_4Cit) with the molecular formula $[M(H_2O)_6][Ge(HCit)_2] \cdot nH_2O$, where M = Fe, $n = 4$ (**I**); Co, $n = 2$ (**II**); Ni, $n = 2$ (**III**); Cu, $n = 1$ (**IV**); Zn, $n = 3$ (**V**). The complexes were characterized by elemental analysis, X-ray diffraction, thermogravimetry, and IR spectroscopy. The X-ray diffraction analysis of compound **I** was performed. Crystals are monoclinic, $a = 10.091(4)$ Å, $b = 11.126(4)$ Å, $c = 10.996(4)$ Å, $\beta = 100.966(6)°$, $V = 1212.1(8)$ Å^3, $Z = 4$, space group $P2_1/n$, $R1 = 0.0561$ for 2266 reflections with $I > 2\sigma(I)$. Compound **I** is composed of centrosymmetric octahedral complexes— $[Ge(HCit)_2]^{2-}$ anions and $[Fe(H_2O)_6]^{2+}$ cations—and crystallization water molecules. Structural units in compound **I** are combined by a hydrogen bond system.

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The hitherto studied heterometallic coordination compounds can be classified into two basic groups. The first group comprises heteronuclear complexes in which several metal atoms, both of the same and different types, are incorporated, and a ligand acts as a bridge. In this case, complexes are formed if the ligand is sufficiently extended to prevent steric hindrances for chelation of the groups at the different ends of its molecule. A heteronuclear complex of this type—barium bis(citrato)germanate—was studied by us earlier [1]. The second group comprises the complexes in which a polydentate ligand coordinates a metal atom of only one type, whereas a metal atom of another type with its own coordination sphere is incorporated into an independent counter-ion. These compounds are of interest from the viewpoint of both their structural features and practical application as efficient catalysts and precursors [2]. Mononuclear metal complexes containing a complex anion or cation are used as initial compounds for the synthesis of such cationic–anionic complexes.

The objective of the present work is to synthesize heterometallic complexes on the basis of bis(citrate)germanate and some 3*d*-metal cations (Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}), and to determine their properties, structure, and type.

EXPERIMENTAL

Synthesis of compounds I–V. At the first stage, GeO_2 (1.046 g, 0.01 mol) and citric acid monohydrate (4.2 g, 0.02 mol) were introduced into 400 mL of hot water. The mixture was heated up to 80–90°C under continuous stirring, until the reagents were completely dissolved. The resulting transparent solution (pH 1.5–2.0) was concentrated on a water bath to 100 mL (~2.0 h) and cooled.

At the second stage, a precisely weighed portion of $FeSO_4 \cdot 7H_2O$ (for **I**), $Co(CH_3COO)_2 \cdot 4H_2O$ (for **II**), $Ni(CH_3COO)_2 \cdot 4H_2O$ (for **III**), $Cu(CH_3COO)_2 \cdot H_2O$ (for **IV**), or $Zn(CH_3COO)_2 \cdot H_2O$ (for **V**) was added to a saturated solution of bis(citrato)germanic acid (20.0 mL, 0.002 mol) at the molar ratio Ge : Fe(Co, Ni, Cu, Zn) = 1 : 1 under continuous stirring until complete dissolution. The mixtures were stirred for 5.0 min without heating and filtered. The resulting solutions (pH = 4.0–5.0) were allowed to stand at room temperature for crystallization. Light yellow (**I**), pink (**II**), light green (**III**), blue (**IV**), or white (**V**) crystals precipitated from the corresponding solutions in 1–2 days were filtered off on a Schott glass filter, washed with cold water, and dried at room temperature (20°C). The crystals of $[Fe(H_2O)_6][Ge(HCit)_2] \cdot 4H_2O$ (**I**) suitable for X-ray diffraction analysis were obtained by adding an equal volume of acetonitrile to the corresponding solution. The yield of the products was 80–85%.

Elemental analysis. The content of germanium and other metals was determined by inductively coupled plasma atomic emission spectroscopy on a Perkin Elmer Optima 2000 DV spectrometer, and the analysis for carbon and hydrogen was performed with the use of a semiautomated C,N,H analyzer. The content of hydrates was calculated from thermogravimetric curves.

Table 1. Atomic coordinates ($\times 10^4$, $\times 10^3$ for H) and thermal parameters U_{eq}/U_{iso}(Å^2, $\times 10^3$) in the structure of compound **I***

Atom	*x*	*y*	*z*	U_{eq}/U_{iso}
Ge	5000	0	5000	13(1)
Fe	10000	0	5000	15(1)
O(1)	3739(2)	736(2)	5831(2)	16(1)
O(2)	3591(3)	2357(2)	6972(2)	21(1)
O(3)	6303(2)	721(2)	6133(2)	15(1)
O(4)	4918(2)	1399(2)	3921(2)	18(1)
O(5)	5444(3)	3215(2)	3385(2)	23(1)
O(6)	5435(3)	788(2)	8835(2)	22(1)
O(7)	7610(3)	1174(3)	9556(3)	25(1)
O(8)	8421(3)	973(3)	3832(3)	22(1)
O(9)	9096(3)	−1679(2)	4553(3)	21(1)
O(10)	9019(3)	205(2)	6551(3)	20(1)
O(11)	7356(3)	−237(3)	11408(3)	25(1)
O(12)	10675(3)	−3304(2)	3798(2)	26(1)
C(1)	4263(3)	1667(3)	6478(3)	16(1)
C(2)	5787(3)	1839(3)	6494(3)	13(1)
C(3)	5947(4)	2799(3)	5538(3)	18(1)
C(4)	5411(3)	2458(3)	4204(3)	18(1)
C(5)	6570(4)	2209(3)	7752(3)	16(1)
C(6)	6467(3)	1323(3)	8750(3)	15(1)
H(1)	746(4)	70(5)	1012(4)	33(14)
H(2)	788(5)	60(5)	358(5)	30(14)
H(3)	865(5)	156(5)	336(5)	43(14)
H(4)	841(6)	−174(5)	430(6)	53(19)
H(5)	956(6)	−241(5)	423(6)	68(18)
H(6)	834(6)	35(6)	651(6)	60(20)
H(7)	931(5)	65(5)	706(6)	44(16)
H(8)	665(5)	−57(4)	1146(4)	30(13)
H(9)	785(7)	−73(6)	1128(6)	70(20)
H(10)	1055	−394	401	31
H(11)	1040	−338	303	31

* Coordinates of the hydrogen atoms involved in hydrogen bonds are given.

Table 2. Selected bond lengths (*d*) and bond angles (ω) in the structure of compound **I**

Bond	*d*, Å
Ge–O(3)	1.817(2)
Ge–O(1)	1.889(2)
Ge–O(4)	1.949(2)
Fe–O(9)	2.096(3)
Fe–O(10)	2.140(3)
Fe–O(8)	2.141(3)
O(1)–C(1)	1.310(4)
O(2)–C(1)	1.218(4)
O(3)–C(2)	1.434(4)
O(4)–C(4)	1.294(4)
O(5)–C(4)	1.238(4)
O(6)–C(6)	1.218(4)
O(7)–C(6)	1.325(4)
C(1)–C(2)	1.547(5)
C(2)–C(5)	1.514(4)
C(2)–C(3)	1.528(4)
C(3)–C(4)	1.512(5)
C(5)–C(6)	1.494(5)
Angle	ω, deg
O(3)GeO(1)	86.78(10)
O(3)GeO(4)	90.35(10)
O(1)GeO(4)	89.64(10)
O(9)FeO(10)	92.03(11)
O(9)FeO(8)	93.96(12)
O(10)FeO(8)	91.15(11)
C(1)O(1)Ge	111.5(2)
C(2)O(3)Ge	108.61(19)
C(4)O(4)Ge	127.7(2)
C(6)O(7)H(1)	108(3)
FeO(8)H(2)	112(4)
FeO(8)H(3)	118(3)
H(2)O(8)H(3)	118(5)
FeO(9)H(4)	123(4)
FeO(9)H(5)	125(3)
H(4)O(9)H(5)	105(6)
FeO(10)H(6)	124(6)
FeO(10)H(7)	119(4)
H(6)O(10)H(7)	98(6)
H(8)O(11)H(9)	107(6)
H(10)O(12)H(11)	100
O(2)C(1)O(1)	122.6(3)
O(2)C(1)C(2)	123.6(3)
O(1)C(1)C(2)	113.7(3)
O(3)C(2)C(5)	109.6(3)
O(3)C(2)C(3)	108.9(3)
C(5)C(2)C(3)	109.5(3)
O(3)C(2)C(1)	107.6(3)
C(5)C(2)C(1)	112.9(3)
C(3)C(2)C(1)	108.3(3)
C(4)C(3)C(2)	115.3(3)
O(5)C(4)O(4)	120.5(3)
O(5)C(4)C(3)	118.8(3)
O(4)C(4)C(3)	120.8(3)
C(6)C(5)C(2)	113.2(3)
O(6)C(6)O(7)	122.4(3)
O(6)C(6)C(5)	124.0(3)
O(7)C(6)C(5)	113.6(3)

Thermogravimetric analysis (TGA) was conducted on a Q-1500D derivatograph in air within the temperature range of 20–1000°C at a heating rate of 10 K/min.

X-ray power diffraction analysis was performed on a DRON-0.5 diffractometer with a copper anticathode and a nickel filter.

IR-absorption spectra (400–4000 cm^{-1}) of compounds **I–V** were recorded on a Shimadzu FTIR-8400S spectrophotometer.

X-ray diffraction analysis. Crystals of compound **I** (FW = 686.80) are monoclinic, $a = 10.091(4)$ Å, $b =$

Table 3. Composition of compounds **I**–**V** by elemental analysis data

No.	Gross formula of a complex	Found, %				Calcd., %			
		Ge	M	C	H	Ge	M	C	H
I	$C_{12}H_{30}FeGeO_{24}$	10.50	8.10	20.89	4.35	10.57	8.16	20.97	4.37
II	$C_{12}H_{26}CoGeO_{22}$	10.98	8.95	22.01	3.89	11.11	9.03	22.03	3.98
III	$C_{12}H_{26}GeNiO_{22}$	10.96	8.97	22.02	3.90	11.11	9.03	22.03	3.98
IV	$C_{12}H_{24}CuGeO_{21}$	11.31	9.90	22.43	3.69	11.33	9.99	22.48	3.75
V	$C_{12}H_{28}GeO_{23}Zn$	10.65	9.51	21.20	4.09	10.71	9.59	21.25	4.13

11.126(4) Å, c = 10.996(4) Å, β = 100.966(6)°, V = 1212.1(8) Å^3, ρ_{calc} = 1.882 g/cm^3, $\mu(MoK_\alpha)$ = 1.948 mm^{-1}, $F(000)$ = 704, Z = 2, space group $P2_1/n$.

Experimental reflection intensities (11581 reflections, 3476 of them were independent, R(int) 0.0813) were collected at 153(2) K from a crystal 0.20 × 0.10 × 0.08 mm in size on an automated Bruker SMART APEX II diffractometer (MoK_α, λ = 0.71073 Å, graphite monochromator, ω scanning). Reflections were collected within the index range of $-14 \le h \le 14$, $-15 \le k \le 15$, $-15 \le l \le 15$ ($2.51° \le \theta \le 30.57°$, the θ completeness was 93.4%). The absorption correction was introduced on the basis of measurements of equivalent reflection intensities [3].

The structure was solved by direct methods (SHELXS-97, [4]) and refined by least-squares calculations on F^2 (SHELXL-97, [5]) in the full-matrix anisotropic approximation for all non-hydrogen atoms. The positions of all the 11 hydrogen atoms at oxygen atoms in five water molecules and the uncoordinated carboxyl group of the $HCit^{3-}$ ligand were determined experimentally from difference electron density syntheses and refined in the isotropic approximation, except the H(10) and H(11) atoms in one of the two crystallization water molecules. These hydrogen atoms, as well as the hydrogen atoms at the carbon atoms introduced in geometrically calculated positions, were refined as riding on their bonded atoms with the isotropic thermal parameters U_H being 1.2 times higher than the parameter U_j of the carbon (oxygen) atom bonded to a given hydrogen atom.

The final refinement parameters were $R1$ = 0.0561, $wR2$ = 0.1274, GOOF = 0.986 for 2266 reflections with $I > 2\sigma(I)$; $R1$ = 0.0914 and $wR2$ = 0.1460 for all independent reflections. The total number of refined parameters was 211, and $\Delta\rho_{max}$ and $\Delta\rho_{min}$ were 1.803 and −1.530 e A^{-3}, respectively.

The atomic coordinates and thermal parameters for structure **I** are listed in Table 1, and the interatomic distances and bond angles are given in Table 2.

The crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CCDC no. 768370).

RESULTS AND DISCUSSION

The elemental analysis of bis(citrato) complexes of germanium (IV) with 3*d* metals (**I**–**V**) has demonstrated that compounds with the composition M(Fe, Co, Ni, Cu, Zn) : Ge : ligand = 1 : 1 : 2 are formed in all the cases (Table 3). According to X-ray powder diffraction analysis data, compounds **I**–**V** are crystalline, and their X-ray diffraction patterns are characterized by an individual set of interplanar spacings, which rules out the presence of the impurity of the initial compounds.

When studying the thermal stability of the synthesized complexes, we have established that their thermolysis proceeds in similar ways and has a complicated staged character. At the first stage, the endotherm is observed within the range of 60–250°C. The wide temperature range, high process temperature, and corresponding weight loss recorded in TGA curves allow us to conclude that the complexes incorporate both crystallization and coordinated water molecules joined by hydrogen bonds (10, 8, 8, 7, and 9 H_2O molecules in **I**, **II**, **III**, **IV**, and **V**, respectively). According to weight loss calculations and X-ray powder diffraction analysis, the final thermodestruction products of all the five complexes at 1000°C represent mixtures of GeO_2 and FeO(**I**), CoO (**II**), NiO (**III**), CuO (**IV**), or ZnO (**V**).

The same character of thermolysis implies a similar structure of compounds **I**–**V**. In this case, their IR spectra should also be similar within the frequency range of the functional groups responsible for bonding with a complexing agent. Therefore, in the comparative analysis of their IR spectra, most attention was paid to establishing the similarity between them. The sets of characteristic absorption bands in the IR spectra of compounds **I**–**V** turned out to be almost the same (Table 4). Their IR spectra contain bands ν(C=O) = 1704–1710 cm^{-1}; ν(C–O) = 1249–1255 cm^{-1}; two $\nu_{as}(COO^-)$ bands (1672–1677 and 1597–1601 cm^{-1}) and two $\nu_s(COO^-)$ bands (1416–1421 and 1357–1361 cm^{-1}) in the higher- and lower-frequency ranges, three ν(Ge–O) bands; bending $\delta(H_2O)$, rocking $\rho(H_2O)$, and wagging w(H_2O) vibrations typical of hexaaqua complexes of 3*d* metals, and also alcoholate ν(C–O) at 1069–1073 cm^{-1} [6] (in the absence of the C–OH bending vibrations.

Table 4. Characteristic frequencies in the IR spectra of compounds **I–V**

Assignment, ν, cm^{-1}	Complex				
	I	**II**	**III**	**IV**	**V**
ν(OH) (H_2O)	3523	3524	3524	3528	3529
ν(OH) (COOH)	3264	3232	3239	3280	3270
ν(C=O) (free COOH)	1705	1706	1709	1704	1710
$\nu_{as}(COO^-)$	1677	1672	1675	1679	1676
	1601	1599	1598	1597	1600
$\nu_s(COO^-)$	1421	1420	1420	1416	1418
	1359	1360	1360	1361	1357
ν(C–O) (COOH)	1255	1255	1254	1249	1253
ν(C–O) (OH)	1072	1072	1072	1069	1073
δ(H_2O)	1641	1639	1639	1638	1636
ρ(H_2O) rocking	731	730	730	735	731
ω(H_2O) wagging	471	470	470	531	541
ν(Ge–O)	695	701	703	697	697
	665	670	670	668	669
	633	634	633	631	628

The found magnetic moments of the cobalt (**II**) and nickel (**III**) complexes (μ_{eff} = 5.0 and 3.0 μB, respectively) indicate the octahedral structure of their coordination polyhedra [7]. This is also confirmed by the analysis of their diffusion reflectance spectra, which contain two bands corresponding to the transitions $^4T_{1g}(F) \longrightarrow {}^4T_{2g}$ (6858 cm^{-1}) and $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ (19790 cm^{-1}) for Co(II) and three bands corresponding to the transitions $^3A_{2g} \longrightarrow {}^3T_{2g}$ (8510 cm^{-1}), $^3A_{2g} \longrightarrow {}^3T_{1g}$ (14025 cm^{-1}), and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ (24654 cm^{-1}) for Ni(II) [8].

For compound **I**, we grew a single crystal and performed its X-ray diffraction analysis. The structural units of the single-crystal of compound **I** are $[Ge(HCit)_2]^{2-}$ complex anions, $[Fe(H_2O)_6]^{2+}$ cations, and crystallization water molecules.

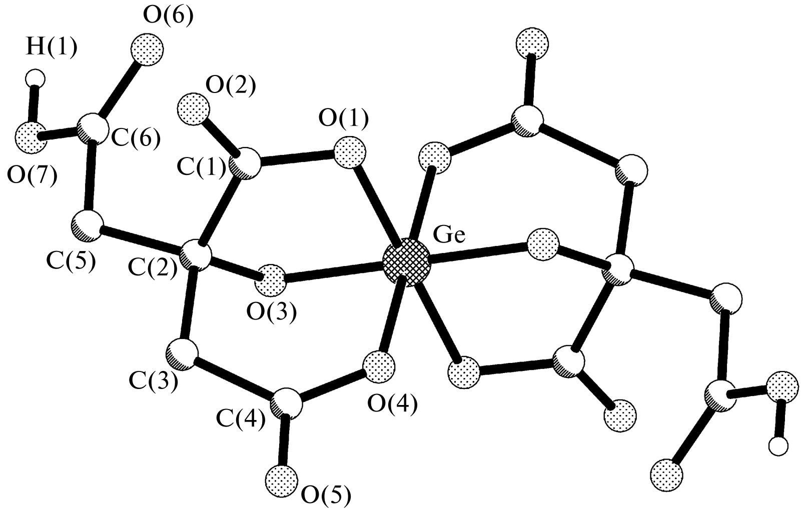

Fig. 1. Structure of the $\left[Ge(HCit)_2\right]^{2-}$ anion.

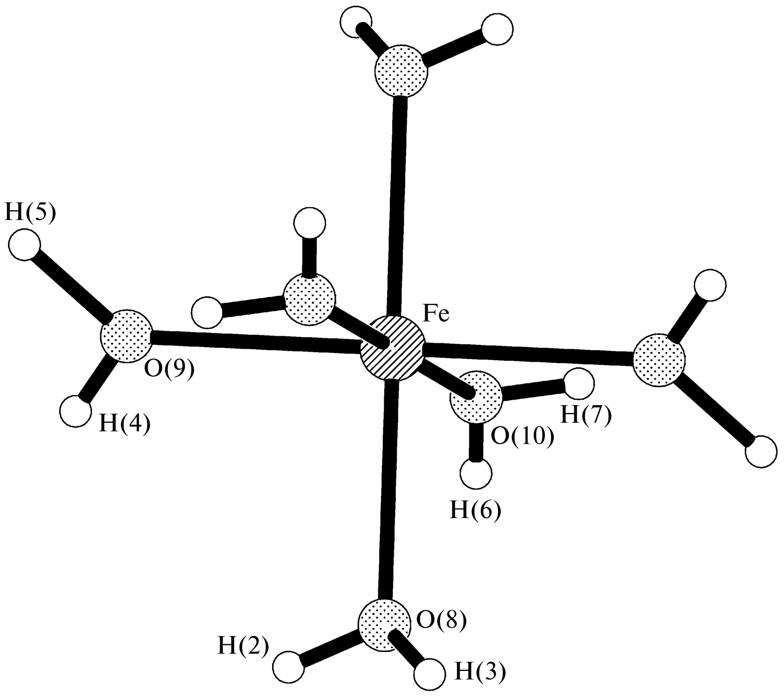

Fig. 2. Structure of the $\left[\mathrm{Fe}(\mathrm{H_2O})_6\right]^{2+}$ cation.

In the monomeric centrosymmetric complex anion (Fig. 1), the coordination polyhedron of Ge atom is a slightly distorted octahedron (meridional isomer) formed by three oxygen atom pairs of three types of two tridentate bis(chelating) $\mathrm{HCit^{3-}}$ ligands: hydroxyl (O(3)), α-carboxylate (O(1)), and β-carboxylate (O(4)). The second (protonated) β-carboxylate $\mathrm{CH_2CO_2H}$ arm is not coordinated to the Ge atom.

The coordination of the citrate ligand results in the formation of the fused five- and six-membered $\mathrm{GeO_2C_3}$ and $\mathrm{GeO_2C_2}$ chelate rings. The six-membered ring has a sofa conformation: the O(3) atom is

Table 5. Geometric parameters of the hydrogen bonds in the structure of compound **I**

D–H···A contact	Distance, Å			DHA angle, deg	Coordinates of the A atom
	D–H	H···A	D···A		
O(7)–H(1)···O(11)	0.85(5)	1.78(5)	2.623(4)	172(4)	x, y, z
O(8)–H(2)···O(1)	0.70(5)	2.38(5)	2.968(4)	142(5)	$-x + 1, -y, -z + 1$
O(8)–H(3)···O(2)	0.90(6)	1.93(6)	2.792(4)	160(5)	$x + 1/2, -y + 1/2, z - 1/2$
O(9)–H(4)···O(2)	0.70(6)	2.33(6)	3.001(4)	161(6)	$-x + 1, -y, -z + 1$
O(9)–H(4)···O(1)	0.70(6)	2.42(6)	3.000(4)	142(6)	$-x + 1, -y, -z + 1$
O(9)–H(5)···O(12)	1.04(6)	1.64(7)	2.646(4)	163(5)	x, y, z
O(10)–H(6)···O(3)	0.70(6)	2.06(6)	2.752(4)	172(8)	x, y, z
O(10)–H(7)···O(5)	0.76(6)	2.10(6)	2.850(4)	170(5)	$x + 1/2, -y + 1/2, z + 1/2$
O(11)–H(8)···O(6)	0.81(5)	2.08(5)	2.845(4)	156(4)	$-x + 1, -y, -z + 2$
O(11)–H(9)···O(5)	0.77(7)	2.06(7)	2.785(4)	157(7)	$-x + 3/2, y - 1/2, -z + 3/2$
O(12)–H(10)···O(6)	0.77	2.06	2.775(4)	155	$x + 1/2, -y - 1/2, z - 1/2$
O(12)–H(11)···O(4)	0.84	2.12	2.954(4)	170	$-x + 3/2, y - 1/2, -z + 1/2$

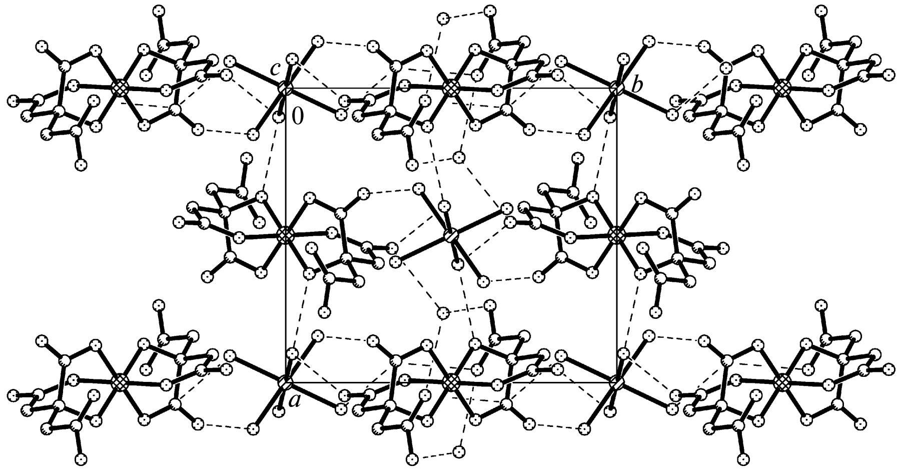

Fig. 3. Projection of the structure of compound **I** along the *c* axis.

0.829 Å out of the plane passing through the Ge, O(4), C(2), C(3), and C(4) atoms (plane 1, Δ_{av} = 0.069 Å)[1]. The five-membered chelating ring has an envelope conformation with the O(3) flap atom lying 0.547 Å out of the plane passing through the Ge, O(1), C(1), and C(2) atoms (plane 2, Δ_{av} = 0.023 Å). The 1/2 dihedral angle is 78.8°.

As usual, the Ge–O bonds have different lengths. The Ge–O(hydroxyl) bonds (1.817(2) Å) are much shorter than the Ge–O(carboxylate) bonds. The Ge–O(4) bond for the β-carboxylate arm (1.949(2) Å) is noticeably longer than the Ge–O(1) bond for the α-carboxylate arm (1.889(2) Å).

The C–O bonds in the crystal of compound **I** can be classified into four groups depending on the structural function of the citrate oxygen atom. The terminal C–O(carbonyl) bonds are the shortest (av. 1.225(4) ± 0.009 Å). The C–O(carboxyl) bonds in the coordinated and terminal (protonated) carboxylate aims have intermediate lengths (1.302(4) ± 0.0073 and 1.325(4) Å, respectively). The C–O bond with the coordinated (deprotonated) hydroxyl oxygen atom is the longest one (1.434(4) Å).

In the structure of compound **I**, the C–C(Cit) distance range is 1.494(5)–1.528(4) Å, and the octahedral OGeO angles (86.78(10)°–93.22(10)°) do not deviate appreciably from the ideal value of 90°.

For the $\mathrm{HCit^{3-}}$ ligand, the ordinary tridentate bis(chelate) monomer coordination similar to that in compound **I** has also be found in the structure of $\mathrm{(HNic)_2[Ge(HCit)_2] \cdot 3H_2O}$ ($\mathrm{HNic^+}$ is the protonated form of nicotinic acid) (**VI**) [9], $\mathrm{(HDphg)_2[Ge(HCit)_2] \cdot 1.08H_2O}$ ($\mathrm{HDphg^+}$ is the protonated diphenylguanidine molecule) (**VII**) [10], and $\mathrm{[Ge(HCit)Cl(Bipy)] \cdot 3.25CH_3CN}$ (Bipy is bipyridine) (**VIII**) [11]. The bond length and bond angle ratios in the $\mathrm{Ge(HCit)}_n$ moiety (*n* = 1, 2) of compounds **VI**–**VIII** are mainly the same as those in compound **I**.

It is worth noting the following structural feature of compound **I**. The above coordination mode of the $\mathrm{H_4Cit}$ molecule leads to the formation of two isomers of compound **I** with different positions of the protonated uncoordinated β arms of the citrate ligand relative to its deprotonated coordinated β arm. These arms are *trans* to ech other in compounds **I**, **VI**, and **VIII** (the C(3)C(2)C(5)C(6) torsion angle is 179.7°, av. 173.9°, and 168.3°, respectively) and are *gauche* to each other in compound **VII** (the C(3)C(2)C(5)C(6) torsion angle is 76.8°).

In the centrosymmetric $\mathrm{[Fe(H_2O)_6]^{2+}}$ cation (Fig. 2) of compound **I**, the coordination polyhedron of the iron ion is a slightly distorted octahedron formed by the oxygen atoms of six water molecules. The Fe–O bond lengths and OFeO angles are 2.096(3)–2.141(3) Å and 91.15(11)°–93.96(12)°, respectively.

In the crystal of compound **I**, the $\mathrm{Fe(H_2O)_6^{2+}}$ cations and $\mathrm{[Ge(HCit)_2]^{2-}}$ anions are joined with each other, both directly and through crystallization water molecules, by hydrogen bonds (Table 5, Fig. 3) into a three-dimensional framework. All the available eleven donor hydrogen atoms of five water molecules and the hydroxyl group of the uncoordinated protonated β-carboxylate $\mathrm{CH_2CO_2H}$ arm take part in the formation of hydrogen bonds. Three coordinated and three uncoordinated oxygen atoms of the $\mathrm{HCit^{3-}}$ ligand act as the acceptors of hydrogen bonds.

The comparison of the IR spectra of compounds **I**–**V** on the basis of the structural data for compound **I** allows us to answer a number of questions concerning the presence and location of the bands typical of different functional groups. In particular, the band at 1704–1710 $\mathrm{cm^{-1}}$ was assigned to the C=O stretching vibrations of the protonated uncoordinated carboxylate group. The presence of the three ν(Ge–O) bands

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[1] Δ_{av} is the average deviation of a nearly coplanar atoms from the corresponding plane.

responsible for the vibrations of bonds of different lengths with the deprotonated hydroxyl group (ν(Ge–O(3)) = 628–634 cm^{-1}) and two carboxylate oxygen atoms (ν(Ge–O(1)) = 665–670 cm^{-1} and ν(Ge–O(4)) = 695–703 cm^{-1}) has become clear (Table 4.).

On the basis of the obtained data indicating that the structures of compounds **I–V** are similar, we proposed the molecular formula $[M(H_2O)_6][Ge(HCit)_2] \cdot nH_2O$, where M = Fe, *n* = 4 (**I**); Co, *n* = 2 (**II**); Ni, *n* =2 (**III**); Cu, *n* = 1 (**IV**); Zn, *n* = 3 (**V**), for these complexes.

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