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Synthesis, Thermal Stability, and Structure of Bis(citrato)germanates: $[Co(Phen)_3][Ge(HCit)_2] \cdot 2H_2O$, $[Fe(Phen)_3][Ge(HCit)_2] \cdot 4H_2O$ (H_4Cit = Citric Acid, Phen = 1,10-Phenanthroline)

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Abstract—Synthetic procedures were developed and the complexes $[Fe(Phen)_3][Ge(HCit)_2] \cdot 4H_2O$ (**I**) and $[Co(Phen)_3][Ge(HCit)_2] \cdot 2H_2O$ (**II**) (Phen is 1,10-phenanthroline, H_4Cit is citric acid) were obtained. The identity, composition, and thermal stability of the complexes were established by elemental analysis, thermogravimetry, and IR spectroscopy. According to X-ray diffraction data (CIF files CCDC nos. 1515837 (**I**) and 1515838 (**II**)), complexes **I** and **II** are different-metal cation–anion complexes with the same bis(citrato)germanate anion $Ge(HCit)_2]^{2-}$. The charge of the complex anions is counterbalanced by the octahedral complex cations, $[Fe(Phen)_3]^{2+}$ (**I**) or $[Co(Phen)_3]^{2+}$ (**II**).

Keywords: germanium dioxide, citric acid, 1,10-phenanthroline, iron(II), cobalt(II), coordination compounds, molecular structure, X-ray diffraction

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INTRODUCTION

The preparation and study of the structure and properties of the complexes of biogenic metals with citric acid is of interest for their potential use in medicine [1–6]. Quite a number of different-ligand citrate metal complexes have been synthesized to date [7–9].

Attention is attracted by the fact that 1,10-phenanthroline (Phen) and 2,2'-bipyridine (Bipy) have been often used in combination with citric acid in recent publications. In particular, mononuclear $[GeCl(Bipy)(HCit)] \cdot 2.5CH_3CN$ [10] and $[Ni(H_2Cit)(Phen)(H_2O)] \cdot 3H_2O$ [11], binuclear $[Zn_2(H_2Cit)_2(Bipy)_2] \cdot H_2O$, $[Zn_2(H_2Cit)_2(Phen)_2] \cdot 1.5H_2O$, $[Zn_2(HCit)(Bipy)Cl]$, and $[Zn_2(HCit)(Phen)Cl] \cdot H_2O$ [12], and heterometallic $[Ni(Phen)_3]_2V_2O_4(R\text{-}HCit)(OC_2H_5)][V_2O_4(S\text{-}HCit)(OC_2H_5)] \cdot 4H_2O$ [13] complexes were synthesized and structurally characterized. It can be seen by these examples that by varying pH of the medium, complexing atom, reactant molar ratio, and conditions of synthesis, it is possible to deliberately prepare coordination compounds differing in the composition, structure, and properties on the basis of these chelating ligands.

Therefore, we decided to continue our systematic research into biologically active different-metal bis(citrato)germanates(IV) with *d*-metal hexaaqua cations (Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) [14, 15] along this line, in particular, to attempt the preparation of bis(citrato)germanates, but with phenanthroline complexes rather than hexaaqua cations of *d*-metals. This introduces one more biologically active component into the complexes, which should necessarily affect their pharmacological action.

The purpose of this study was to develop procedures, synthesize, and comprehensively characterize new bis(citrato)germinates of "metals of life," iron(II) and cobalt(II).

EXPERIMENTAL

The complexes were prepared using GeO_2 (99.999%) (Aldrich), citric acid monohydrate (99%), 1,10-phenanthroline (99%) (Aldrich), $FeSO_4 \cdot 7H_2O$ (99%) (Merck), and $Co(CH_3COO)_2 \cdot 4H_2O$ (99%) (Merck).

Elemental analysis was performed on a semiautomated C,N,H-analyzer. Germanium, iron, and cobalt were quantified using inductive coupled plasma atomic emission spectroscopy on a Perkin Elmer Optima 2000 DV instrument.

The IR absorption spectra (400–4000 cm^{-1}) of the complexes as KBr pellets were measured on a Frontier Perkin Elmer spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a Q-1500D derivatograph (air, temperature range of 20–1000°C, heating rate of 10 K/min).

Synthesis $[Fe(Phen)_3][Ge(HCit)_2] \cdot 4H_2O$ (I). Weighed portions of germanium dioxide (0.5 mmol) and citric acid (1 mmol) were dissolved at reflux in 100 mL of water and evaporated at 50°C to a 20 mL volume. After cooling to room temperature, 20 mL of a 95% ethanol solution containing 1,10-phenanthroline (1.5 mmol) and iron(II) sulfate (0.5 mmol) were added at room temperature. After 3 days, a red-colored crystalline solid precipitated. Single crystals suitable for X-ray diffraction were taken from the reaction medium. Yield, 60%.

IR spectrum of **I** (ν, cm^{-1}): 3410 ν(OH), 1700 ν(C=O), 1627 ν_{as}(COO$^-$), 1582, 1521, 1425 ν(C–C$_{ar}$), 1400 ν_s(COO$^-$), 1353 ν(C–N), 1080 ν(C–O), 1148, 1222, 918, 848 δ(CH), 644 ν(Ge–O).

For $C_{48}H_{42}N_6O_{18}GeFe$ (**I**)

anal. calcd., %: C, 51.46; H, 3.75; N, 7.50; Fe, 4.99; Ge, 6.48.

Found, %: C, 51.65; H, 3.44; N, 7.85; Fe 5.20; Ge, 6.50.

Synthesis of $[Co(Phen)_3][Ge(HCit)_2] \cdot 2H_2O$ (II) was performed by a procedure similar to that used to prepare **I**, with a solution containing 1,10-phenanthroline (1.5 mmol) and cobalt(II) acetate in 20 mL of 95% ethanol being added at the final stage. Over a period of 24 h, a dark orange crystalline solid, containing single crystals suitable for X-ray diffraction, precipitated from the reaction medium. Yield, 70%.

IR spectrum of **II** (ν, cm^{-1}): 3411 ν(OH), 1700 ν(C=O), 1624 ν_{as}(COO$^-$), 1585, 1517, 1426 ν(C–C$_{ar}$), 1408 ν_s(COO$^-$), 1354 ν(C–N), 1082 ν(C–O), 1145, 1225, 913, 850 δ(CH), 642 ν(Ge–O).

For $C_{48}H_{38}N_6O_{16}GeCo$ (**II**)

anal. calcd., %: C, 53.02; H, 3.50; N, 7.73; Co, 5.42; Ge, 6.68.

Found, %: C, 53.25; H, 3.44; N, 7.95; Co, 5.30; Ge, 6.50.

X-ray diffraction. The crystals of **I** are monoclinic, space group $P2/c$, $a = 22.783(4)$, $b = 11.3532(9)$, $c = 18.337(4)$ Å, $\beta = 94.60(1)°$, $V = 4727.7(9)$ Å^3, $M = 1119.31$ g/mol, $Z = 4$, $T = 100.0$ K, $\mu(\text{Mo}K_\alpha) = 1.028$ mm^{-1}, ρ(calcd.) = 1.573 g/cm^3, 38106 reflections were measured, of which 8294 reflections were unique ($R_{\text{int}} = 0.123$). The final values: $R_1 = 0.098$ ($I > 2\sigma(I)$), $wR_2 = 0.237$ (for all reflections).

The crystals of **II** are monoclinic, space group $P2/c$, $a = 23.030(3)$, $b = 11.364(3)$, $c = 18.675(4)$ Å, $\beta = 94.735(6)°$, $V = 4879.1(6)$ Å^3, $Z = 4$, $M = 1086.36$ g/mol, $T = 294$ K, $\mu(\text{Mo}K_\alpha) = 1.033$ mm^{-1}, ρ(calcd.) = 1.479 g/cm^3, 41071 reflections were measured, of which 9507 reflections were unique ($R_{\text{int}} = 0.1340$). The final values: $R_1 = 0.095$ ($I > 2\sigma(I)$), $wR_2 = 0.258$ (for all reflections).

X-ray diffraction data for **I** and **II** were collected on a Xcalibur-3 diffractometer (MoK_α-radiation, CCD detector, graphite monochromator, ω-scan mode). The structures were solved by direct methods and refined on F^2 by the full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms (SHELXTL) [16]. The hydrogen atoms were located from difference Fourier maps and refined in the riding model with $U_{iso} = nU_{\text{equiv}}$ of the non-hydrogen atom bound to this H atom ($n = 1.5$ for hydroxyl groups and water molecules, $n = 1.2$ for other hydrogen atoms).

Atom coordinates and full tables of bond lengths and angles are deposited with the Cambridge Crystallographic Data Centre (nos. 1515837 (**I**), 1515838 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Complexes **I** and **II** are air-stable crystalline solids. Their thermal decomposition follows the same pattern, starting in the temperature range of 90–150°C (120°C↓) for **I** and 80–130°C (100°C↓) for **II** with an endotherm corresponding to removal of four ($\Delta m = 6.5\%$, **I**) or two ($\Delta m = 3.3\%$, **II**) water molecules. The fact that the complexes are crystal hydrates is also indicated by the ν(H_2O) stretching bands in their IR spectra at 3410 cm^{-1}.

The next endotherm in the 220–320°C range (280°C↓) for **I** and 240–360°C range (300°C↓) for **II** is matched by elimination to the gas phase of one 1,10-phenanthroline molecule and two CO_2 molecules formed upon decarboxylation of the free carboxyl groups of the citrate ligands (weight loss: 24% for **I** and 25% for **II**). The thermal decomposition of the complexes ends with the oxidative thermal destruction, which is accompanied by a broad exotherm in the temperature range of 450–630°C (570°C↓) for **I** and 460–650°C (550°C↑) for **II**. Considering the total weight loss (84.2% for **I** and 83.5% for **II**) and powder X-ray diffraction data, the final products at 1000°C are the metagermanates $FeGeO_3$ (for **I**) and $CoGeO_3$ (for **II**).

The IR spectra of compounds **I** and **II** were found to exhibit similar sets of absorption bands, which were assigned in line with the data obtained for bis(citrato)germanates with outer-sphere ligands and other metals [5, 6, 14, 15] and with published data for the carboxylate complexes for various metals [17, 18].

The presence of a free carboxyl group –COOH in the molecules of the obtained complexes is indicated by the ν(C=O) band at 1700 cm^{-1} in their IR spectra. In comparison with the IR spectrum of the citric acid, the spectra of complexes **I** and **II** exhibit characteristic ν_{as}(COO$^-$) and ν_s(COO$^-$) bands, alkoxide type ν(C–O) bands at 1080 cm^{-1} (in the absence of bending C–OH modes), and Ge–O stretching bands.

Aromatic molecules, to which 1,10-phenanthroline also belongs, tend to exhibit C–C stretching skeletal modes of the aromatic ring (1300–1600 cm^{-1}) and in-plane (1000–1500 cm^{-1}) and out-of-plane (700–1200 cm^{-1}) C–H bending modes. The bands in these frequency ranges in the IR spectra of the complexes confirm the presence of 1,10-phenanthroline in their molecules.

It follows from X-ray diffraction data that complexes **I** and **II** are different-metal cation–anion type compounds in which the role of the anion is played by bis(citrato)germanate [Ge(HCit)$_2$]$^{2-}$, while the cation is represented by the iron complex [Fe(Phen)$_3$]$^{2+}$ (in **I**) or cobalt complex [Co(Phen)$_3$]$^{2+}$ (in **II**). The cations in compounds **I** and **II** occur in special positions on 2 axis, i.e., the independent part of the unit cell comprises two halves of the cation. Complexes **I** and **II** exist in the crystal as hydrates with four (in **I**) or two (in **II**) water molecules.

The Ge polyhedron in the anions of **I** and **II** is a distorted octahedron formed by three pairs of oxygen atoms of three types of two tridentate HCit^{3-} chelating ligands: the hydroxyl (O(3) and O(10)), α-carboxylate (O(1) and O(8)), and β-carboxylate (O(4) and O(11)) atoms (Fig. 1). As noted previously [14, 18], the Ge–O bond lengths are non-equivalent (Table 1). The hydroxyl Ge(1)–O(3) (1.814(5) Å in **I** and 1.802(4) Å in **II**) and Ge(1)–O(10) (1.840(5) Å in **I** and 1.830(5) Å in **II**) bonds are much shorter than the carboxylate bonds. Unlike the structures reported previously [14, 15], in which the α-carboxylate Ge–O bond is markedly elongated compared with the β-carboxylate bond, no such trend is noted in **I** or **II**. The Ge(1)–O(1) bond with the α-carboxylate oxygen atom (1.911(5) Å in **I** and 1.907(5) Å in **II**) in one ligand is shorter than the Ge(1)–O(4) bond with the β-carboxylate oxygen atom of the same ligand (1.939(5) Å in **I** and 1.937(5) Å in **II**). The coordination of germanium by the second ligand gives rise to the opposite relationship of bond lengths: the Ge(1)–O(8) bond with the α-carboxylate atom (1.926(5) Å in **I** and 1.924(5) Å in **II**) is longer than the Ge(1)–O(11) bond with the β-carboxylate oxygen atom of the same ligand (1.906(3) Å in **I** and 1.889(5) Å in **II**). Presumably, this trend of coordination bond lengths is a consequence of repulsion between the ligands that have their neutral carboxyl groups in *cis*-positions (the C(6)C(2)C(9)C(12) pseudo-torsion angle is –67.9° in **I** and 67.2° in **II**).

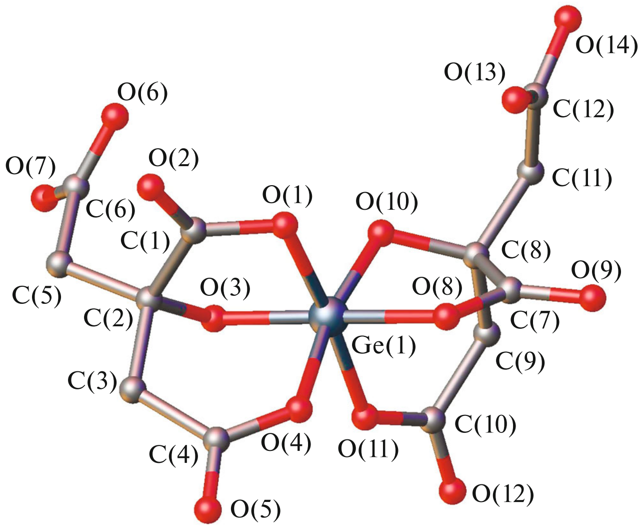

Fig. 1. Molecular structure of the [Ge(HCit)$_2$]$^{2-}$ anion in compounds **I** and **II**.

The coordination of the organic ligand to the Ge(IV) atom gives rise to five- and six-membered metal rings. The Ge(1)O(3)C(2)C(3)C(4)O(4) and Ge(1)O(10)C(8)C(9)C(10)O(11) rings are in the sofa conformation (the O(3) atom deviates by 0.8 ± 0.06 Å in **I** and **II** from the root-mean-square plane through the Ge(1), O(4), C(2), C(3), and C(4) atoms. The O(10) atom deviates by –0.8 Å in **I** and 0.8 Å in **II** from the root-mean-square plane through the Ge(1), O(11), C(8), C(9), and C(10) atoms to an accuracy of ±0.07 Å). The relevant folding parameters [19] are summarized in Table 2. The five-membered chelate rings are in the envelope conformation. The O(3) atom deviates by 0.6 Å in **I** and by –0.6 Å in **II** from the root-mean-square plane through the Ge(1), O(1), C(1), C(2) atoms (to an accuracy of ±0.02 Å), while the O(10) atom deviates by 0.5 Å in **I** and by –0.6 Å in **II** from the root-mean-square plane through the Ge(1), O(8), C(7), and C(8) atoms (to an accuracy of ±0.03 Å).

The cations [Fe(Phen)$_3$]$^{2+}$ in **I** and [Co(Phen)$_3$]$^{2+}$ in **II** are isomorphous (Fig. 2); both complexing ions are bound to three phenanthroline molecules. In the M(1)(Phen)$_3$ cation (below, cation A), the positions of the 1,10-phenanthroline molecules were determined unambiguously, while in the M(2)(Phen)$_3$ cation (below, cation B), the 1,10-phenanthroline molecule located on a 2 symmetry axis is disordered over two sites with equally probable occupancy.

The iron and cobalt coordination polyhedra for cations A and B in **I** and **II** are octahedra. In structure **I**, the Fe(1)–N bond lengths vary in the 1.962(6)–

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

Bond	*d*, Å	Bond	*d*, Å
I		**II**	
Ge(1)–O(8)	1.926(5)	Ge(1)–O(8)	1.924(5)
Ge(1)–O(3)	1.814(5)	Ge(1)–O(3)	1.802(4)
Ge(1)–O(1)	1.911(5)	Ge(1)–O(1)	1.907(5)
Ge(1)–O(10)	1.840(5)	Ge(1)–O(10)	1.830(5)
Ge(1)–O(11)	1.906(5)	Ge(1)–O(11)	1.889(5)
Ge(1)–O(4)	1.939(5)	Ge(1)–O(4)	1.937(5)
Fe(1)–N(2)	1.983(6)	Co(1)–N(2)	2.135(6)
Fe(1)–N(3)	1.974(6)	Co(1)–N(3)	2.118(6)
Fe(1)–N(1)	1.962(6)	Co(1)–N(1)	2.118(6)
Fe(2)–N(4)	1.978(6)	Co(2)–N(4)	2.134(7)
Fe(2)–N(5)	1.978(8)	Co(2)–N(5)	2.144(7)
Fe(2)–N(6*A*)	2.076(10)	Co(2)–N(6*A*)	2.213(8)
Fe(2)–N(6*B*)	1.924(9)	Co(2)–N(6*B*)	2.072(8)
Angle	ω, deg	Angle	ω, deg
I		**II**	
O(8)Ge(1)O(4)	83.4(2)	O(8)Ge(1)O(4)	83.2(2)
O(3)Ge(1)O(1)	86.9(2)	O(3)Ge(1)O(1)	86.5(2)
O(3)Ge(1)O(10)	99.0(2)	O(3)Ge(1)O(10)	98.9(2)
O(3)Ge(1)O(11)	91.9(2)	O(3)Ge(1)O(11)	91.5(2)
O(3)Ge(1)O(4)	92.5(2)	O(3)Ge(1)O(4)	92.6(2)
O(1)Ge(1)O(8)	89.6(2)	O(1)Ge(1)O(8)	90.3(2)
O(1)Ge(1)O(4)	88.8(2)	O(1)Ge(1)O(4)	88.4(2)
O(10)Ge(1)O(8)	85.4(2)	O(10)Ge(1)O(8)	85.5(2)
O(10)Ge(1)O(1)	94.9(2)	O(10)Ge(1)O(1)	94.4(2)
O(10)Ge(1)O(11)	91.5(2)	O(10)Ge(1)O(11)	91.8(2)
O(11)Ge(1)O(8)	91.2(2)	O(11)Ge(1)O(8)	91.3(2)
O(11)Ge(1)O(4)	85.0(2)	O(11)Ge(1)O(4)	85.8(2)
N(2)$^{1\#}$Fe(1)N(2)	88.6(3)	N(2)$^{1\#}$Co(1)N(2)	90.8(3)
N(3)$^{1\#}$Fe(1)N(2)	94.5(2)	N(3)$^{1\#}$Co(1)N(2)	95.4(2)
N(3)$^{1\#}$Fe(1)N(3)	82.7(3)	N(3)Co(1)N(3)$^{1\#}$	79.2(3)
N(1)Fe(1)N(2)	83.1(2)	N(3)Co(1)N(1)$^{1\#}$	94.2(2)
N(1)Fe(1)N(2)$^{1\#}$	91.9(2)	N(1)$^{1\#}$Co(1)N(2)	92.9(2)
N(4)Fe(2)N(4)$^{2\#}$	89.1(3)	N(1)Co(1)N(2)	79.1(2)
N(4)Fe(2)N(5)$^{2\#}$	92.4(3)	N(4)Co(2)N(4)$^{2\#}$	90.5(4)
N(4)Fe(2)N(5)	82.5(3)	N(4)$^{2\#}$Co(2)N(5)$^{2\#}$	77.8(3)
N(4)$^{2\#}$Fe(2)N(6*A*)	91.7(4)	N(4)Co(2)N(5)$^{2\#}$	94.2(3)
N(5)Fe(2)N(6*A*)$^{2\#}$	98.4(5)	N(4)$^{2\#}$Co(2)N(6*A*)$^{2\#}$	93.6(3)
N(5)Fe(2)N(6*A*)	86.8(5)	N(5)$^{2\#}$Co(2)N(6*A*)	85.2(2)

* Symmetry codes: $^{1\#}$ $1 - x, y, 1/2 - z$; $^{2\#}$ $-x, y, 1/2 - z$.

Table 2. Folding parameters in structures **I** and **II** for the rings: Ge(1)–O(3)–C(2)–C(3)–C(4)–O(4) (ring 1) and Ge(1)–O(10)–C(8)–C(9)–C(10)–O(11) (ring 2)

Structure	*S*		θ, deg		Ψ, deg	
	ring 1	ring 2	ring 1	ring 2	ring 1	ring 2
I	0.94	0.96	49.07	33.9	15.28	15.17
II	0.95	0.96	33.9	33.0	15.17	16.16

1.983(6) range and Fe(2)–N bond lengths are 1.924(9)–2.076(10) Å (Table 1). The NFe(1)N bond angles in cation A vary in the 82.7(3)°–92.8(3)° range and the NFe(2)N angles in cation B are 81.3(4)°–98.4(5)°. In structure **II**, the Co(1)–N bond lengths in cation A are 2.118(6)–2.135(6) Å and the Co(2)–N bond lengths in cation B are 2.072(8)–2.213(8) Å. The NCo(1)N bond angles in cation A are 79.1(2)°–95.4(2)° and the NCo(2)N angles in cation B are 77.8(3)°–97.4(3)°.

In the crystal structures of compounds **I** and **II**, the anions, cations, and water molecules form alternating layers parallel to the crystallographic *yz* plane (Fig. 3). The layers can be classified into three sorts: (1) layers

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

D–H···A	Distance, Å		D–H···A, deg
	H···A	D–A	
		I	
O(7)–H(7)···O(9)$^{1\#}$	1.77	2.582(7)	161
O(14)–H(14)···O(17)$^{2\#}$	2.03	2.691(10)	133
O(18)–H(18*A*)···O(15)$^{3\#}$	2.04	2.823(9)	147
O(18)–H(18*B*)···O(5)$^{1\#}$	1.99	2.836(8)	172
O(15)–H(15*A*)···O(10)	2.07	2.807(8)	141
O(15)–H(15*B*)···O(6)	2.14	2.872(10)	143
O(17)–H(17*A*)···O(5)$^{4\#}$	2.27	2.789(10)	125
O(17)–H(17*B*)···O(16)	2.85	2.649(13)	155
O(16)–H(16*A*)···O(7)	2.13	2.945(11)	159
O(16)–H(16*B*)···O(18)	2.08	2.883(10)	156
		II	
O(7)–H(7)···O(9)$^{5\#}$	1.77	2.585(9)	170
O(16)–H(16*A*)···O(5)$^{6\#}$	2.02	2.869(9)	171
O(16)–H(16*B*)···O(17)	2.05	2.871(11)	159
O(17)–H(17*B*)···O(10)	2.03	2.846(9)	159
C(33)–H(33)···O(13)	2.34	3.269(13)	173

* Symmetry codes: $^{1\#}$ *x*, –3 – *y*, –1/2 + *z*; $^{2\#}$ *x*, –2 – *y*, 1/2 + *z*; $^{3\#}$ *x*, –2 – *y*, –1/2 + *z*; $^{4\#}$ *x*, 1 + *y*, *z*; $^{5\#}$ *x*, 1 – *y*, 1/2 + *z*; $^{6\#}$ *x*, –1 + *y*, *z*.

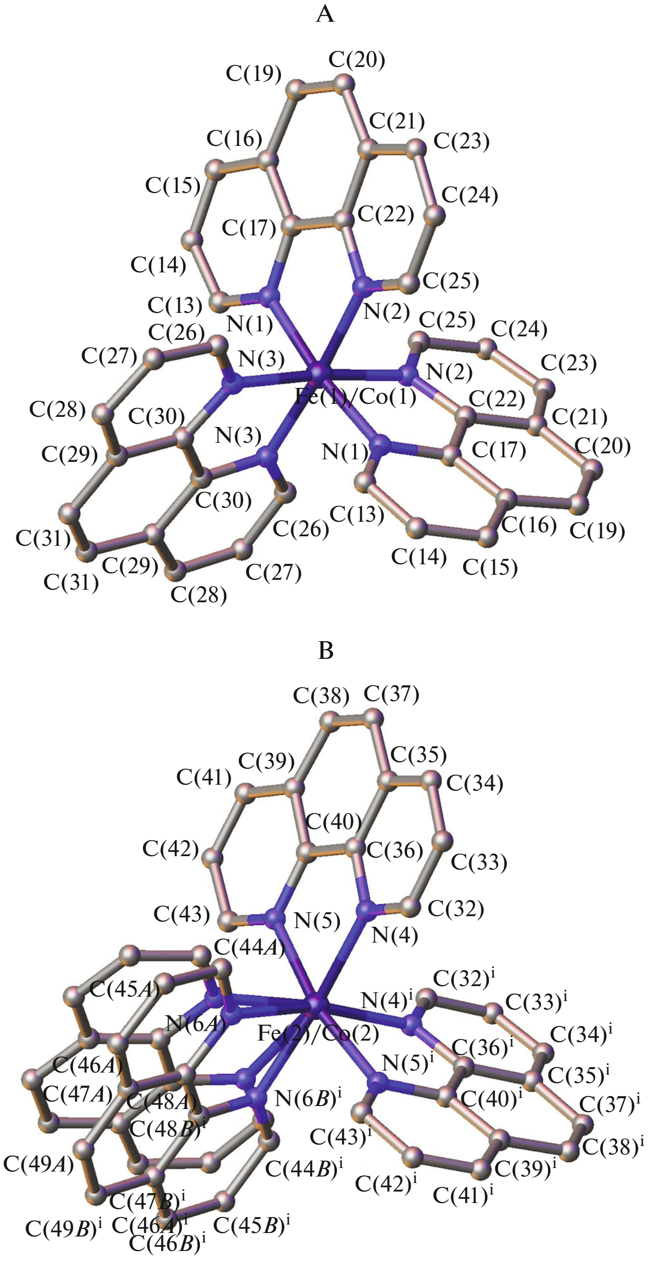

Fig. 2. Molecular structure of the $[Fe(Phen)_3]^{2+}$ cations in **I** and the $[Co(Phen)_3]^{2+}$ cations in **II** (cations A and B are shown).

containing anions; (2) layers containing cations A; and (3) layers composed of cations B. The anions in the layer are linked by intermolecular O—H···O hydrogen bonds (Table 3).

The obtained data indicate that bis(citrato)germanate anions are fairly stable in solution and are not destroyed on treatment with the phenanthroline complexes formed by typical complexing ions, Fe^{2+} and Co^{2+}. The structure of anions remains nearly the same as in the case of coordination compounds with the 3*d*-metal aqua cations [14, 15]. Thus, it was found that bis(citrato)germanate anions can act as building blocks, metallotectons, in hydrogen-bonded crystalline associates with chemically different cations.

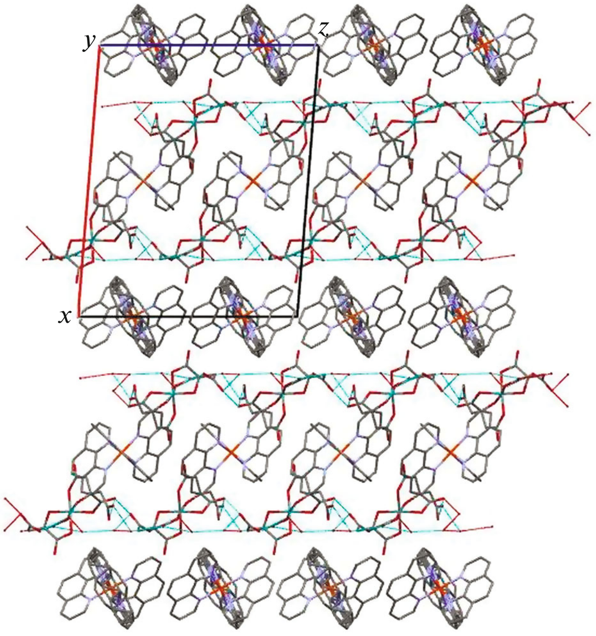

Fig. 3. Crystal structure of compounds **I** and **II (**projection along the *y* crystallographic axis).

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