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Synthesis and Structure of Different-Metal Different-Ligand Germanium(IV) and Cobalt(II) or Copper(II) Complexes with 1-Hydroxyethylidenediphosphonic Acid and 1,10-Phenanthroline

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Abstract—Different-metal different-ligand complexes $[\{Co(Phen)_3\}_2\{Co(Phen)(H_2O)_4\}_2][\{Ge(\mu\text{-}OH)(\mu\text{-}Hedp)\}_6Cl_2]$ (**I**), $[\{Cu(Phen)_2(H_2O)\}_2(HPhen)_2][Ge(\mu\text{-}OH)(\mu\text{-}Hedp)]_6 \cdot 20H_2O$ (**II**) (H_4Hedp = 1-hydroxyethylidenediphosphonic acid, Phen = 1,10-phenanthroline) were synthesized and studied by X-ray diffraction. According to X-ray diffraction data (CIF files CCDC nos. 1573112 (**I**), 1573113 (**II**)), compounds **I** and **II** are cation–anion type complexes in which the anions are represented by $\{[Ge(\mu\text{-}OH)(\mu\text{-}Hedp)]_6\}^{6-}$ and, in the case of **I**, two additional Cl^- ions, while the cations are $[Co(Phen)_3]^{2+}$, $[Co(Phen)(H_2O)_4]^{2+}$ in **I** and $[Cu(Phen)_2(H_2O)]^{2+}$, $HPhen^+$ in **II**. In the crystals of compounds **I** and **II**, the cations, anions, and water molecules are combined by numerous intermolecular hydrogen bonds, giving rise to a 3D network.

Keywords: germanium 1-hydroxyethylidenediphosphonate, 1,10-phenanthroline, 3*d*-metal complexes, coordination compounds, molecular and crystal structure

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INTRODUCTION

1-Hydroxyethylidenediphosphonic acid (H4Hedp) refers to moderately toxic compounds, possessing no sensitizing or cumulative effects, which accounts for the use of this acid as a medication [1]. The coordination compounds of metals with H4Hedp were found to be highly efficient as agents for metastases pain relief (186Re) and bone cancer diagnosis (99mTc, 188Re) [2, 3].

Previously, we prepared a number of 1-hydroxyethylidenediphosphonate diphosphonate germanates with a structurally unique hexanuclear anion: $(HNic)_6[Ge(\mu\text{-}OH)(\mu\text{-}Hedp)]_6 \cdot 12H_2O$ (Nic = nicotinic acid) [4], $Mg_2[Ge_6(\mu\text{-}OH)_6(\mu\text{-}Hedp)_4(\mu\text{-}HHedp)_2] \cdot 40H_2O$ [4], $Ba_3[Ge(\mu\text{-}OH)(\mu\text{-}Hedp)]_6 \cdot 25H_2O$ [5], and $Zn_4[Ge_6(\mu\text{-}OH)_4(\mu\text{-}O)_2(\mu\text{-}Hedp)_6] \cdot 38H_2O$ [6]. Some of them were found to have cardiotropic, hepatoprotective, hypotensive, and cerebroprotective action [7, 8]. Subsequently, a group of English and French researchers synthesized organic-inorganic hybrid materials based on a supramolecular salt containing the same anion and a protonated 1,10-phenanthroline (Phen) molecule as the cation [9]. In the authors' opinion [9], these materials could find use in catalysis, medicine, and optics.

The purpose of this study was to develop a procedure for the synthesis of different-metal different-ligand complexes in the GeO_2–H_4Hedp–$CoCl_2$ ($CuCl_2$)–Phen systems and to establish their structures and dependence of structural features on the second metal.

EXPERIMENTAL

The complexes were prepared using commercial 1-hydroxyethylidenediphosphonic acid (H_4Hedp, ≥97%, Fluka) and GeO_2 (99.99%), Phen (99%), $CuCl_2 \cdot 2H_2O$ (99.99%), and $CoCl_2 \cdot 6H_2O$ (≥98%) (Sigma-Aldrich).

Elemental analysis was carried out on a semiautomated C,N,H-analyzer. The contents of germanium, copper, cobalt, and phosphorus were determined by inductively coupled plasma atomic emission spectroscopy on a Perkin Elmer Optima 2000 DV instrument and chlorine was quantified by mercurometric titration [10]. The IR absorption spectra (400–4000 cm^{-1}) of the complexes as KBr pellets were measured on a Frontier Perkin Elmer spectrophotometer.

Synthesis of complex I. Water (100 mL) was added to a mixture of dry GeO_2 (0.1046 g, 1 mmol) and H_4Hedp (0.206 g, 1 mmol) and the mixture was heated to boiling. The solution thus obtained was concentrated at 80°C for 4 h to 10 mL and cooled at room temperature (working solution). A solution containing $CoCl_2 \cdot 6H_2O$ (0.119 g, 0.5 mmol) and Phen (0.18 g, 1 mmol) in 10 mL of 95% ethanol was prepared separately, added to the working solution, and stirred. After 2 days, a light blue crystalline solid containing single crystals suitable for X-ray diffraction precipitated from the reaction mixture. The yield was 62%.

IR (ν, cm^{-1}): 3379 ν(OH), 3000 ν($C-H_{arom}$), 1625 δ(H_2O), 1583, 1518 ν($C-C_{arom}$), 1448, 1427 δ_{as}(CH_3), 1342 δ_s(CH_3), 1306 ν(C–N), 1176 ν(P=O), 1052, 976 ν(P–O), 850 δ(C–H), 814 δ(Ge–OH), 643 ν(Ge–O_{phosph}), 488 ν(Co–O), 402 ν(Co–N).

For $C_{108}H_{154}N_{16}O_{78}P_{12}Cl_2Co_4Ge_6$ (**I**)

Anal. calcd., %	C, 32.09	H, 3.81	N, 5.55
P, 9.21	Cl, 1.76	Co, 5.84	Ge, 10.79
Found, %	C, 31.92	H, 3.77	N, 5.48
P, 9.18	Cl, 1.70	Co, 5.90	Ge, 10.69

Synthesis of complex II was carried out similarly to the synthesis of **I** by adding 10 mL of an ethanol solution containing $CuCl_2 \cdot 2H_2O$ (0.085 g, 0.5 mmol) and Phen (0.18 g, 1 mmol) to the working solution. The yellow precipitate containing single crystals was formed in 24 h. The yield was 60%.

IR (ν, cm^{-1}): 3356 ν(OH), 3005 ν($C-H_{arom}$), 1629 δ(H_2O), 1585, 1520 ν($C-C_{arom}$), 1493, 1430 δ_{as}(CH_3), 1332 δ_s(CH_3), 1312 ν(C–N), 1178 ν(P=O), 1055, 979 ν(P–O), 853 δ(C–H), 814 δ(Ge–OH), 649 ν(Ge–O_{phosph}), 430 ν(Cu–O), 404 ν(Cu–N).

For $C_{84}H_{124}N_{12}O_{70}P_{12}Cu_2Ge_6$ (**II**)

Anal. calcd., %	C, 32.09	H, 3.81	N, 5.55	P, 9.21
Cl, 1.76	Co, 5.84			
Found, %	C, 39.97	H, 3.60	N, 5.00	P, 11.01
Cu, 3.77	Ge, 12.86			

X-ray diffraction. The unit cell parameters and reflection intensities for structures **I** and **II** were measured on an Xcalibur-3 diffractometer (MoK_α radiation, CCD detector, graphite monochromator, ω-scan mode). The structures were solved by the direct method using the SHELXTL program package [11, 12]. The hydrogen atom positions were found from the difference electron density map and refined by the riding model with $U_{iso} = nU_{equiv}$ of the non-hydrogen atom bonded to the given hydrogen atom ($n = 1.5$ for methyl and hydroxyl groups and for water molecules and $n = 1.2$ for other hydrogen atoms). The structures were refined on F^2 by full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms. The crystal data and X-ray experiment details are summarized in Table 1 and selected interatomic distances are in Table 2.

The atom coordinates and full tables of bond lengths and bond angles are deposited with the Cambridge Crystallographic Data Centre (nos. 1573112 (**I**), 1573113 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

According to elemental analysis data, the element ratios for compounds **I** and **II** are as follows: Ge : P : Co : N = 3 : 6 : 2 : 8 and Ge : P : Cu : N = 3 : 6 : 1 : 6. Hence, the molar ratios in these compounds are different: Ge : Hedp : Co : Phen = 3 : 3 : 2 : 4 and Ge : Hedp : Cu : Phen = 3 : 3 : 1 : 3.

The IR spectra of complexes **I** and **II** are similar. They show the P–O stretching bands at ~1055 and ~979 cm^{-1}, which implies the presence of only fully deprotonated PO_3^{2-} groups in their molecules [7]. The spectra also exhibit vibrational bands for germanium bonds with hydroxyl and phosphonic groups, δ(GeOH) and ν(Ge–O_{phosph}), and *d*-metal bonds with oxygen and nitrogen, ν(M–O) and ν(M–N) [7, 13]. The δ(HOH) bending modes at 1630 cm^{-1} indicate that both complexes contain coordinated water molecules. The set of bands in the region of characteristic frequencies for heterocyclic aromatic molecules confirms the presence of 1,10-phenanthroline [14].

According to X-ray diffraction data, compounds **I** and **II** are cation–anion type complexes in which the anions are represented by $\{[Ge(\mu\text{-}OH)(\mu\text{-}Hedp)]_6\}^{6-}$ and two additional Cl^- ions in the case of **I**, while the cations are $[Co(Phen)_3]^{2+}$ and $[Co(Phen)(H_2O)_4]^{2+}$ in **I** and $[Cu(Phen)_2(H_2O)]^{2+}$ and $HPhen^+$ in **II**. Both intricate complex compounds occur in the crystal in special positions relative to the center of symmetry.

In structures **I** and **II**, $\{[Ge(\mu\text{-}OH)(\mu\text{-}Hedp)]_6\}^{6-}$ (Fig. 1) is a centrosymmetric hexanuclear complex anion in which the Ge atoms are connected by two types of bridging ligands, namely, hydroxy and hydroxyethylidene diphosphonate ones. The coordi-

Table 1. Crystallographic data, X-ray experiment details for structures **I** and **II**

Parameter	Value	
	I	**II**
M	4038.26	3356.20
Temperature, K	294	
System	Triclinic	
Space group	$P\bar{1}$	
a, Å	13.8439(5)	14.2861(7)
b, Å	17.3943(7)	15.6396(8)
c, Å	18.6844(6)	16.5106(8)
α, deg	66.074(4)	79.393(4)
β, deg	82.626(3)	65.375(5)
γ, deg	82.173(3)	69.670(5)
V, Å^3	4061.1(3)	3141.2(3)
Z	1	1
ρ(calcd), g/cm^3	1.651	1.774
μ, mm^{-1}	1.743	2.009
Crystal size, mm	0.5 × 0.3 × 0.2	0.6 × 0.4 × 0.3
Number of reflections measured/unique	37199/15890	25816/12323
$R_{\rm int}$	0.074	0.080
Number of parameters	1067	850
S	1.042	1.011
R factor (reflections with $I > 2\sigma(I)$)	$R_1 = 0.078$, $wR_2 = 0.199$	$R_1 = 0.079$, $wR_2 = 0.200$
R factor (all reflections)	$R_1 = 0.115$, $wR_2 = 0.222$	$R_1 = 0.133$, $wR_2 = 0.232$
$\Delta\rho_{\rm max}/\Delta\rho_{\rm min}$, e Å^{-3}	2.83/–1.09	2.50/–0.58

nation polyhedron of the germanium atoms is a distorted octahedron formed by four oxygen atoms of four phosphonate groups of two $\rm Hedp^{4-}$ ligands and by two hydroxy anions. The Ge–O(Hedp) bond lengths are 1.863(4)–1.891(3) Å in **I** and 1.865(5)–1.902(5) Å in **II**; the Ge–O(OH) bond lengths are 1.824(4)–1.887(3) Å in **I** and 1.865(5)–1.902(5) Å in **II** (Table 2). The OGeO bond angles vary in the 86.98(3)°–95.57(3)° (**I**) and 86.4(2)°–94.3(3)° (**II**) ranges. Generally, the structure of the $\{[\rm Ge(\mu\text{-}OH)(\mu\text{-}Hedp)]_6\}^{6-}$ anion is similar to the structure of the germanium hydroxyethylidenediphosphonate complexes considered previously [4, 5].

The Co polyhedra in the $\rm [Co(Phen)_3]^{2+}$ and $\rm [Co(Phen)(H_2O)_4]^{2+}$ cations of structure **I** are octahedra. In $\rm [Co(Phen)_3]^{2+}$ (Fig. 2a), the metal atom is connected to six nitrogen atoms of phenanthroline molecules. The Co(1)–N bond lengths are 2.127(5)–2.153(4) Å and the NCo(1)N bond angles are 78.2(2)°–96.1(2)°. In the $\rm [Co(Phen)(H_2O)_4]^{2+}$ cation (Fig. 2b), the inner coordination sphere of Co(2) is formed by four aqua ligands and the bidentately coordinated phenanthroline molecule. The Co(2)–N bond lengths are 2.127(5)–2.137(5) Å and the Co(2)–O bond lengths are 2.068(4)–2.108(4) Å (Table 2); the

Table 2. Selected bond lengths (Å) in compounds **I** and **II**

Bond	d, Å	Bond	d, Å
I			
Ge(1)–O(1)	1.870(4)	Ge(3)–O(21)	1.864(4)
Ge(1)–O(3)	1.875(3)	Ge(3)–O(24)	1.881(3)
Ge(1)–O(6)	1.822(3)	Co(1)–N(1)	2.153(5)
Ge(2)–O(6)	1.824(3)	Co(1)–N(2)	2.124(5)
Ge(2)–O(7)	1.896(4)	Co(1)–N(3)	2.144(5)
Ge(2)–O(8)	1.896(4)	Co(1)–N(4)	2.124(5)
Ge(2)–O(9)	1.892(4)	Co(1)–N(5)	2.132(5)
Ge(2)–O(12)	1.904(4)	Co(1)–N(6)	2.127(5)
Ge(2)–O(14)	1.887(4)	Co(2)–O(26)	2.068(4)
Ge(3)–O(14)	1.860(4)	Co(2)–O(27)	2.128(4)
Ge(3)–O(15)	1.870(3)	Co(2)–O(28)	2.108(4)
Ge(3)–O(16)	1.871(4)	Co(2)–N(7)	2.127(5)
Ge(3)–O(17)	1.888(4)	Co(2)–N(8)	2.137(5)
II			
Ge(1)–O(6)	1.854(5)	Ge(3)–O(14)	1.874(5)
Ge(1)–O(24)	1.875(5)	Ge(3)–O(15)	1.882(5)
Ge(2)–O(14)	1.856(5)	Ge(3)–O(16)	1.886(5)
Ge(2)–O(12)	1.902(5)	Cu(1)–O(25)	2.028(7)
Ge(2)–O(9)	1.883(6)	Cu(1)–N(3)	1.985(7)
Ge(2)–O(6)	1.859(5)	O(4)–Cu(1)	2.770(6)
Ge(2)–O(8)	1.884(5)	Cu(1)–N(4)	2.056(7)
Ge(2)–O(7)	1.896(6)	Cu(1)–N(5)	2.231(8)
Ge(3)–O(17)	1.895(5)	Cu(1)–N(6)	1.987(7)
Ge(3)–O(21)	1.889(5)		

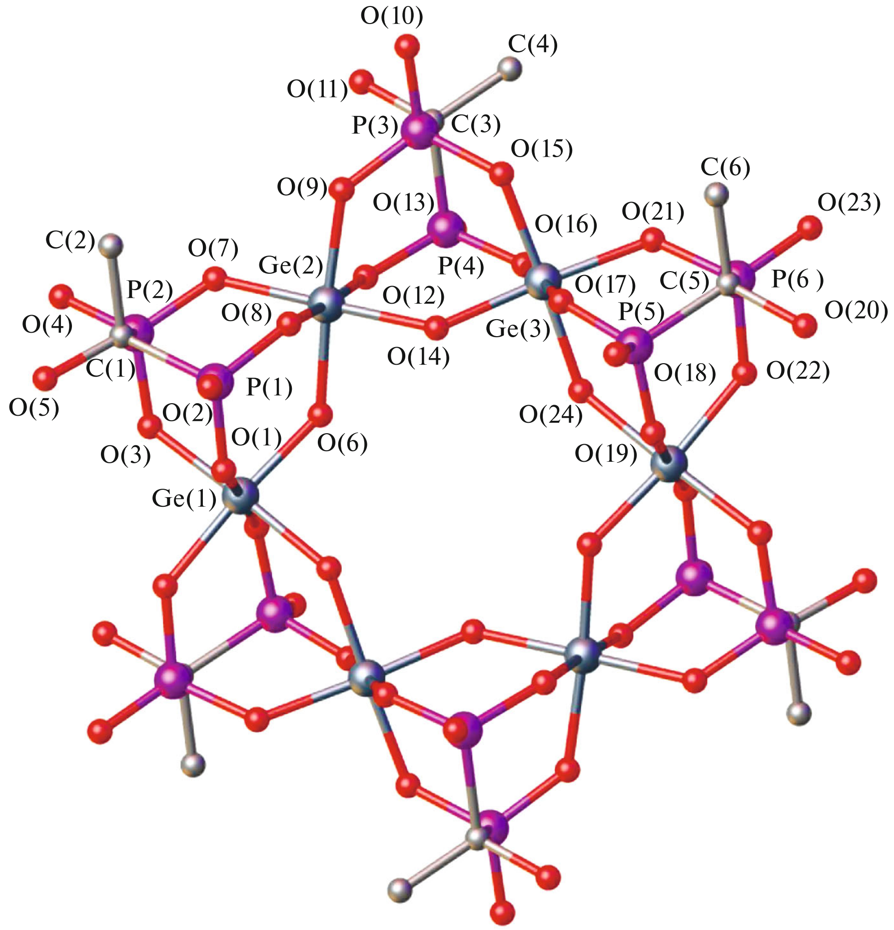

Fig. 1. Molecular structure of the $\{[Ge(\mu\text{-}OH)(\mu\text{-}Hedp)]_6\}^{6-}$ complex anion in **I** and **II**. The atom numbering is given for symmetrically independent part of the complex anion. The thermal vibration ellipsoids are shown at 50% probability level.

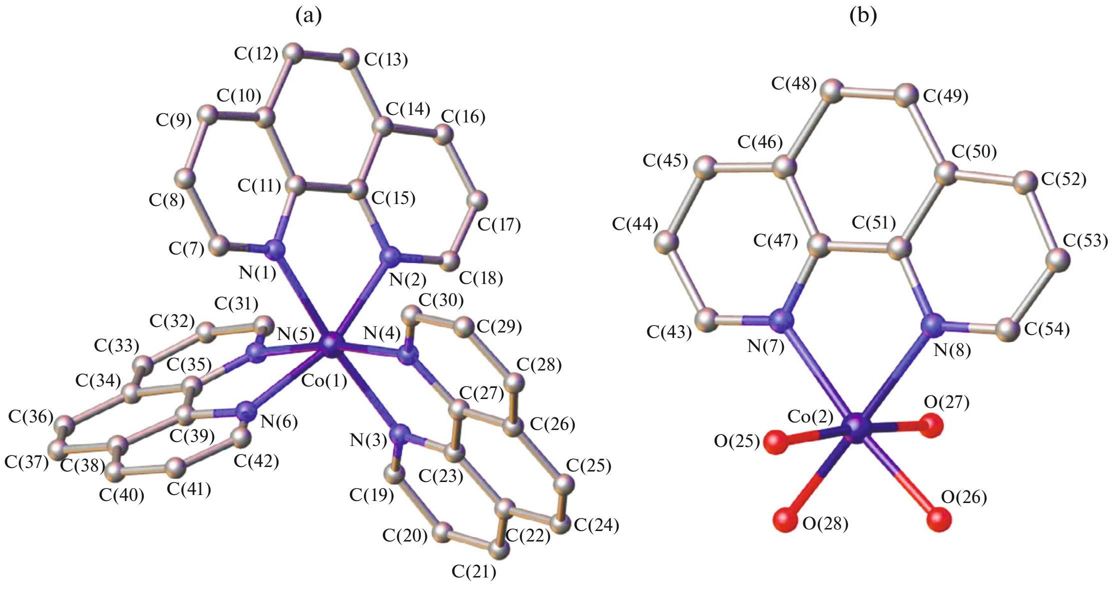

Fig. 2. Molecular structure of the (a) $[Co(Phen)_3]^{2+}$ and (b) $[Co(Phen)(H_2O)_4]^{2+}$ cations in **I**.

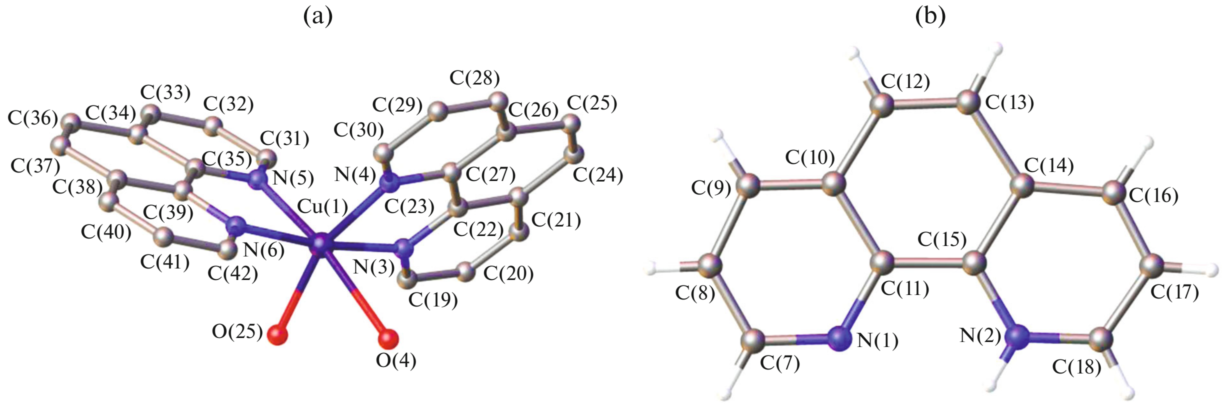

Fig. 3. Molecular structure of the (a) $[Cu(Phen)_2(H_2O)]^{2+}$ and (b) $HPhen^+$ cations in **II**.

NCo(2)N, OCo(2)N, and OCo(2)O bond angles are 78.3(2)°–97.02(2)°.

In the structure of **II**, the hexanuclear $\{[Ge(\mu\text{-}OH)(\mu\text{-}Hedp)]_6\}^{6-}$ anion is directly bonded to the Cu(1) atom via O(4). The Cu(1) coordination octahedron is completed by two phenanthroline molecules and one aqua ligand. The Cu–N lengths are 1.985(7)–2.231(7) Å and the Cu–O(H_2O) and Cu–O(Hedp) lengths are 2.028 and 2.770(6) Å, respectively. The NCuN, OCuO, and OCuN bond angles vary in the range of 79.1(3)°–98.1(3)° (Table 2). The non-coordinated phenanthroline is protonated at N(2) (Fig. 3b), as indicated by the hydrogen atom revealed in the difference Fourier maps. Thus, in the case of compound **II**, the charge of the $\{[Ge(\mu\text{-}OH)(\mu\text{-}Hedp)]_6\}^{6-}$ anion is counterbalanced by different-type $HPhen^+$ cations and the complex cation $[Cu(Phen)_2(H_2O)]^{2+}$.

In the crystals of compounds **I** and **II**, the cations, anions, and water molecules are connected by numerous intermolecular hydrogen bonds (Table 3), which give rise to a 3D network (Figs. 4a, 4b).

A distinction of the coordination compounds **I** and **II** from the previously studied germanium hydroxyethylidene diphosphonate complexes [4–7] is the formation of suprampolecular assemblies based on simple and complex cations and anions, which mutually counterbalance their charges. This is caused by both the replacement of Co^{2+} by Cu^{2+} and the incorporation of 1,10-phenanthroline, which is able to function simultaneously as a bidentate chelating ligand and an outer-sphere cation in the $HPhen^+$ monoprotonated form.

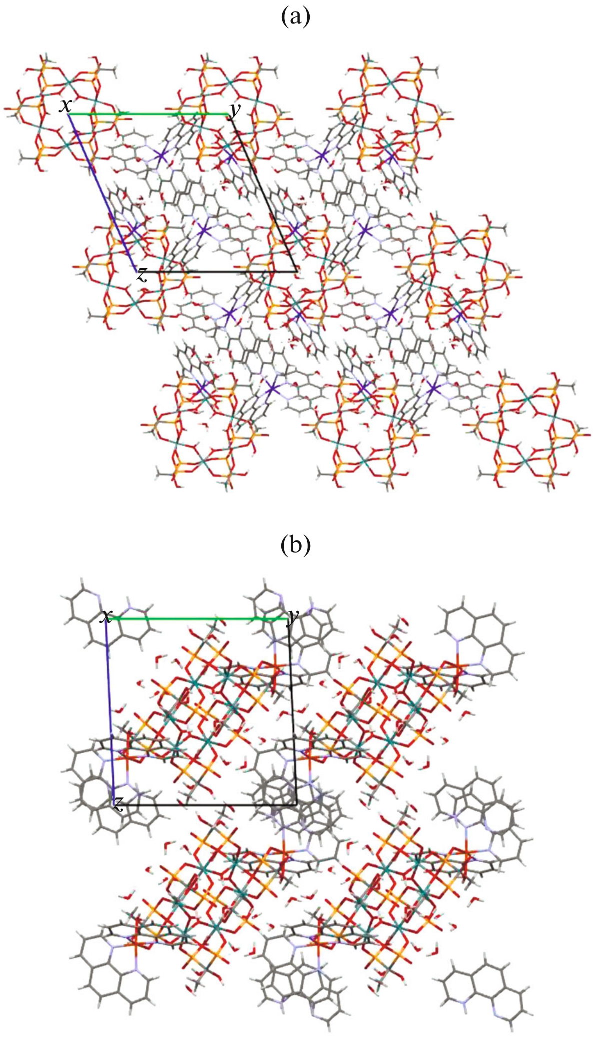

Fig. 4. Crystal structure of compounds (a) **I** and (b) **II** (view along the [100] crystallographic direction).

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

D–H···A	Distance, Å		D–H···A angle, deg
	H···A	D···A	
I			
O(5)–H(5)···O(36)	2.01	2.773(11)	154
O(6)–H(6)···C(l1)	1.91	2.690(4)	150
O(14)–H(14)···C(l1)^{1}	1.87	2.709(5)	163
O(24)–H(24*A*)···C(l1)	1.89	2.724(6)	162
O(25)–H(25*A*)···O(38)	1.89	2.751(6)	166
O(26)–H(26*A*)···O(19)^{2}	2.42	2.787(5)	107
O(26)–H(26*B*)···O(12)^{3}	2.15	2.788(6)	132
O(27)–H(27*A*)···O(34)^{3}	1.82	2.660(6)	164
O(28)–H(28*A*)···O(39)^{2}	1.85	2.728(5)	168
O(28)–H(28*B*)···O(13)^{3}	2.00	2.864(6)	164
O(29)–H(29*A*)···O(36)^{4}	1.90	2.739(15)	170
O(30)–H(30*A*)···C(l2)	1.90	2.744(7)	170
O(31)–H(31*B*)···O(10)	2.07	2.887(7)	161
O(32)–H(32*A*)···O(29)^{5}	1.98	2.701(9)	141
O(33)–H(33*A*)···O(4)	1.82	2.658(6)	170
O(33)–H(33*B*)···O(32)^{6}	1.86	2.695(7)	167
O(34)–H(34*A*)···O(33)	1.86	2.708(8)	175
O(36)–H(36*B*)···O(22)^{1}	2.09	2.932(10)	170
O(37)–H(37*A*)···O(17)	2.09	2.919(6)	165
O(37)–H(37*B*)···O(8)	1.99	2.834(6)	170
O(38)–H(38*A*)···O(37)	1.92	2.747(6)	165
O(38)–H(38*B*)···O(2)	1.85	2.684(6)	164
O(39)–H(39*A*)···O(38)	2.05	2.896(5)	171
O(39)–H(39*B*)···O(18)	2.03	2.844(6)	161
O(35)*A*–H(35*A*)···O(33)	1.86	2.676(12)	160
O(35)*A*–H(35*B*)···O(31)	1.91	2.754(13)	169
O(35)*B*–H(35*C*)···O(33)	1.94	2.724(19)	152
O(35)*B*–H(35*D*)···O(31)	1.67	2.362(19)	137
II			
O(20)–H(20)···O(30)^{7}	2.04	2.829(12)	162
O(14)–H(14)···O(35)^{8}	1.90	2.704(8)	166
O(11)–H(11)···O(13)^{9}	2.01	2.794(9)	159
O(6)–H(6)···O(35)	1.99	2.767(8)	158
O(24)–H(24)···O(35)^{8}	1.93	2.717(8)	162
O(5)–H(5)···N(1)	2.36	3.129(13)	156
O(25)–H(25*A*)···O(7)	2.21	3.023(9)	174
O(25)–H(25*B*)···O(33)	2.00	2.655(9)	137
O(31)–H(31*B*)···O(13)^{9}	1.92	2.748(10)	165
O(29)–H(29*A*)···O(18)^{10}	2.05	2.767(10)	142

Table 3. (Contd.)

D–H···A	Distance, Å		D–H···A angle, deg
	H···A	D···A	
O(29)–H(29*B*)···O(30)	2.01	2.672(12)	135
O(32)–H(32*A*)···O(31)	2.09	2.897(12)	166
O(32)–H(32*B*)···O(10)	1.94	2.724(9)	159
O(26)–H(26*A*)···O(12)	2.39	2.907(10)	120
O(26)–H(26*B*)···O(19)^{8}	2.18	2.895(9)	142
O(30)–H(30*B*)···O(23)^{9}	1.96	2.581(11)	132
O(35)–H(35*A*)···O(34)^{8}	2.04	2.761(9)	146
O(27)–H(27*A*)···O(28)	2.09	2.880(15)	153
O(34)–H(34*A*)···O(31)^{11}	2.00	2.780(12)	160
O(34)–H(34*B*)···O(2)	2.01	2.814(9)	165
O(33)–H(33*A*)···O(2)^{12}	2.11	2.782(8)	139
O(33)–H(33*B*)···O(32)	2.04	2.836(11)	163
O(28)–H(28*A*)···O(34)^{2}	1.98	2.802(11)	175
O(28)–H(28*B*)···O(18)^{2}	2.02	2.742(9)	147
N(2)–H(2)···O(4)	1.96	2.727(10)	147

Symmetry codes: $^{1}\,1 - x, 2 - y, -z$; $^{2}\,-x, 2 - y, -z$; $^{3}\,-1 + x, y, z$; $^{4}\,x, -1 + y, z$; $^{5}\,x, 1 + y, z$; $^{6}\,1 - x, 2 - y, 1 - z$; $^{7}\,-1 + x, y, 1 + z$; $^{8}\,1 - x, 1 - y, 1 - z$; $^{9}\,2 - x, 1 - y, 1 - z$; $^{10}\,1 + x, y, -1 + z$; $^{11}\,-1 + x, y, z$; $^{12}\,1 - x, 2 - y, 1 - z$.

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