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1,3-Diamino-2-Hydroxypropane-*N*,*N*,*N'*,*N'*-Tetraacetic Acid: Crystal and Molecular Structures

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Abstract—The synthesis, IR spectroscopic study, and X-ray diffraction analysis (CIF file CCDC no. 1574078) are carried out for 1,3-diamino-2-hydroxypropane-*N*,*N*,*N'*,*N'*-tetraacetic acid (**I**). The structural units of a crystal of compound **I** are $(H_{4.5}HPdta)^{0.5-}$ anions, $(H_{5.5}HPdta)^{0.5+}$ cations, and molecules of water of crystallization joined by a branched network of hydrogen bonds: strong intermolecular O–H···O and intramolecular N–H···O bonds.

Keywords: synthesis, X-ray diffraction analysis, crystal and molecular structures, 1,3-diamino-2-hydroxypropane-*N*,*N*,*N'*,*N'*-tetraacetic acid

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INTRODUCTION

1,3-Diamino-2-hydroxypropane-*N*,*N*,*N'*,*N'*-tetraacetic acid (H_5HPdta) is among the most universal chelating ligands due to seven donor centers (two nitrogen atoms, four carboxyl groups, and one hydroxyl group) in its molecules and their fortune mutual arrangement. Its complexes with metals of various electronic blocks are being actively studied and find wide use in many areas of technology, chemistry, and medicine [1–3].

The ability of H_5HPdta to form binuclear complexes is of special interest [4–6]. This is favored by the presence of an additional hydroxyl group in its molecule compared to ethylenediaminetetraacetic and propylenediaminetetraacetic acids. Our attempts to obtain a homobinuclear germanium(IV) complex with H_5HPdta were unsuccessful in spite of the studies performed.

Earlier we pioneered to synthesize a series of heteronuclear germanium(IV) complexes with *s*-, *d*-, and *f*-metal ions and comprehensively characterized them using an array of modern physical and chemical methods [7–12]. These compounds were classified according to the following structural types: cation-cationic $(Cat)_3[Ge(OH)_2(HPdta)]$ (Cat = NH_4^+, Na^+, K^+) and $(Cat)[Ge(H_2O)(OH)(HPdta)]$ (Cat = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}); heterobinuclear with the bridging ligand $[(H_2O)(OH)Ge(\mu\text{-}HPdta)Cu(H_2O)]$; tetranuclear with the bridging ligand $[(OH)_2Ge(\mu\text{-}HPdta)_2\text{-}M_2(H_2O)_4]$ (M = Co^{2+}, Ni^{2+}, Zn^{2+}); and heterobinuclear with the bridging ligand and OH group $[(OH)Ge(\mu\text{-}OH)(\mu\text{-}HPdta)M(H_2O)_4]$ (M = La^{3+}, Cr^{3+}), $[(OH)Ge(\mu\text{-}OH)(\mu\text{-}HPdta)Ln(H_2O)_3(OH)]$ (Ln = Pr^{3+}, Nd^{3+}, Sm^{3+}), and $[(OH)Ge(\mu\text{-}OH)(\mu\text{-}HPdta)Ln(H_2O)_3]$ (Ln = Eu^{3+}, Lu^{3+}) [7].

However, experimental data for the structure of H_5HPdta have not been obtained to the present time because, most likely, of its poor crystallization. In this work, we grew the single crystals and conducted the X-ray diffraction analysis of 1,3-diamino-2-hydroxypropane-*N*,*N*,*N'*,*N'*-tetraacetic acid.

EXPERIMENTAL

Synthesis. Water (10 mL) was added to a weighed sample (1.288 g, 4 mmol) of H_5HPdta (99%, Aldrich, Switzerland, CAS 3148-72-9), and the mixture was heated to boiling. The suspension was refluxed for 2–3 min with continuous stirring. The obtained solution was cooled and acidified with 0.1 N HCl to pH 2 for better crystallization. A crystalline precipitate was formed in 2 h, and its composition was determined by

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† Deceased.

Table 1. Crystallographic data and experimental characteristics for compound **I**

Parameter	Value
Empirical formula	$C_{11}H_{21.15}N_2O_{10.57}$
FW	350.65
Temperature, K	150(2)
Wavelength, Å	0.71073
Crystal system	Triclinic
Space group	$P\overline{1}$
a, Å	11.3085(13)
b, Å	11.3207(13)
c, Å	13.2976(15)
α, deg	90.330(2)
β, deg	93.086(2)
γ, deg	114.672(2)
V, Å^3	1544.0(3)
Z	4
ρ_{calc}, g/cm^3; μ, mm^{-1}	1.508; 0.135
$F(000)$	743
Crystal sizes, mm	0.160 × 0.100 × 0.040
Ranges of θ angles, deg	2.433–26.414
Range of indices	$-14 \le h \le 14$, $-14 \le k \le 14$, $-16 \le l \le 16$
Total number of reflections	14257
Independent reflections (R_{int})	6330 (0.0441)
Filling by $\theta = 25.242°$, %	99.9
Absorption correction	Semiempirical by equivalents
Refinement method	Full-matrix least squares for F^2
Number of refined parameters	477
GOOF for F^2	1.028
R_1, wR_2 ($I > 2\sigma(I)$)	0.0581, 0.1332
R_1, wR_2 (all data)	0.1057, 0.1555
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	0.350, −0.511

X-ray diffraction analysis as $(H_{5.5}HPdta)(H_{4.5}HPdta) \cdot 3.15H_2O$ (**I**).

For $C_{11}H_{21.15}N_2O_{10.57}$

Anal. calcd., %	C, 37.69	H, 6.04	N, 7.91
Found, %	C, 38.02	H, 5.96	N, 8.21

Analyses to carbon, nitrogen, and hydrogen were carried out on a CE-440 C,N,H-analyzer. The IR absorption spectra (400–4000 cm^{-1}) of the sample in the form of pellets with KBr were recorded on a Frontier spectrophotometer (PerkinElmer).

X-ray diffraction analysis. A set of intensities of diffraction reflections for the crystal of compound **I** was obtained at the Center for Collective Use of the Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences [13]. Selected crystallographic data and experimental characteristics are presented in Table 1. An absorption correction was applied [14]. The structure was solved by a direct method. The oxygen atoms of one of the carboxyl groups are disordered over two positions (O(14), O(15) and O(14*A*), O(15*A*)) with equal occupancies. The O(4*w*) water molecule is located near the inversion center. The occupancy of its position ($q = 0.15$)

Table 2. Selected interatomic distances and bond angles in the structure of compound **I**

Bond	*d*, Å	Bond	*d*, Å
O(1)–C(2)	1.206(4)	O(12)–C(15)	1.223(5)
O(2)–C(2)	1.304(4)	O(13)–C(15)	1.276(4)
O(3)–C(4)	1.226(3)	O(14*A*)–C(20)	1.245(19)
O(4)–C(4)	1.283(3)	O(15*A*)–C(20)	1.357(11)
O(5)–C(9)	1.243(3)	O(14*B*)–C(20)	1.25(2)
O(6)–C(9)	1.251(3)	O(15*B*)–C(20)	1.300(12)
O(7)–C(11)	1.233(3)	O(16)–C(22)	1.228(3)
O(8)–C(11)	1.289(3)	O(17)–C(22)	1.269(3)
O(9)–C(6)	1.401(3)	O(18)–C(17)	1.431(4)
N(1)–C(1)	1.491(4)	O(18)–H(182)	0.97(7)
N(1)–C(5)	1.490(3)	N(3)–C(14)	1.496(5)
N(1)–C(3)	1.498(3)	N(3)–C(12)	1.497(4)
N(2)–C(8)	1.490(3)	N(3)–C(16)	1.505(4)
N(2)–C(7)	1.492(3)	N(4)–C(18)	1.496(4)
N(2)–C(10)	1.495(3)	N(4)–C(21)	1.500(4)
O(10)–C(13)	1.219(3)	N(4)–C(19)	1.504(3)
O(11)–C(13)	1.286(3)		
Angle	ω, deg	Angle	ω, deg
C(1)N(1)C(5)	113.5(2)	C(18)N(4)C(19)	113.8(2)
C(1)N(1)C(3)	113.0(2)	C(21)N(4)C(19)	114.0(3)
C(5)N(1)C(3)	111.0(2)	N(3)C(12)C(13)	110.4(3)
C(8)N(2)C(7)	114.5(2)	O(10)C(13)O(11)	126.3(3)
C(8)N(2)C(10)	111.1(2)	O(10)C(13)C(12)	121.6(3)
C(7)N(2)C(10)	111.7(2)	O(11)C(13)C(12)	112.0(3)
N(1)C(1)C(2)	109.0(3)	N(3)C(14)C(15)	109.9(3)
O(1)C(2)O(2)	124.0(4)	O(12)C(15)O(13)	126.5(3)
O(1)C(2)C(1)	120.5(3)	O(12)C(15)C(14)	120.0(3)
O(2)C(2)C(1)	115.5(4)	O(13)C(15)C(14)	113.4(4)
N(1)C(3)C(4)	109.6(2)	N(3)C(16)C(17)	110.7(3)
O(3)C(4)O(4)	126.7(3)	O(18)C(17)C(18)	109.9(3)
O(3)C(4)C(3)	119.6(2)	O(18)C(17)C(16)	109.7(3)
O(4)C(4)C(3)	113.7(3)	N(4)C(18)C(17)	111.2(2)
N(1)C(5)C(6)	110.9(2)	C(20)C(19)N(4)	108.9(2)
O(9)C(6)C(7)	111.2(2)	O(14*B*)C(20)O(15*B*)	125.9(11)
O(9)C(6)C(5)	107.8(2)	O(14*A*)C(20)O(15*A*)	129.8(9)
N(2)C(7)C(6)	112.4(2)	O(14*A*)C(20)C(19)	117.1(8)
N(2)C(8)C(9)	109.3(2)	O(14*B*)C(20)C(19)	124.0(9)
O(5)C(9)O(6)	127.5(3)	O(15*B*)C(20)C(19)	110.1(6)
O(5)C(9)C(8)	117.0(2)	O(15*A*)C(20)C(19)	113.0(6)
O(6)C(9)C(8)	115.4(2)	N(4)C(21)C(22)	108.4(2)
N(2)C(10)C(11)	110.3(2)	O(16)C(22)O(17)	127.0(3)
O(7)C(11)O(8)	126.8(3)	O(16)C(22)C(21)	118.5(3)
O(7)C(11)C(10)	120.3(3)	O(17)C(22)C(21)	114.5(3)
O(8)C(11)C(10)	112.9(2)	H(11*w*)O(1*w*)H(12*w*)	115
C(14)N(3)C(12)	113.4(3)	H(21*w*)O(2*w*)H(22*w*)	95
C(14)N(3)C(16)	112.8(2)	H(31*w*)O(3*w*)H(32*w*)	109
C(12)N(3)C(16)	112.4(2)	H(31*w*)O(3*w*)H(33*w*)	112
C(18)N(4)C(21)	110.9(2)	H(41*w*)O(4*w*)H(42*w*)	100

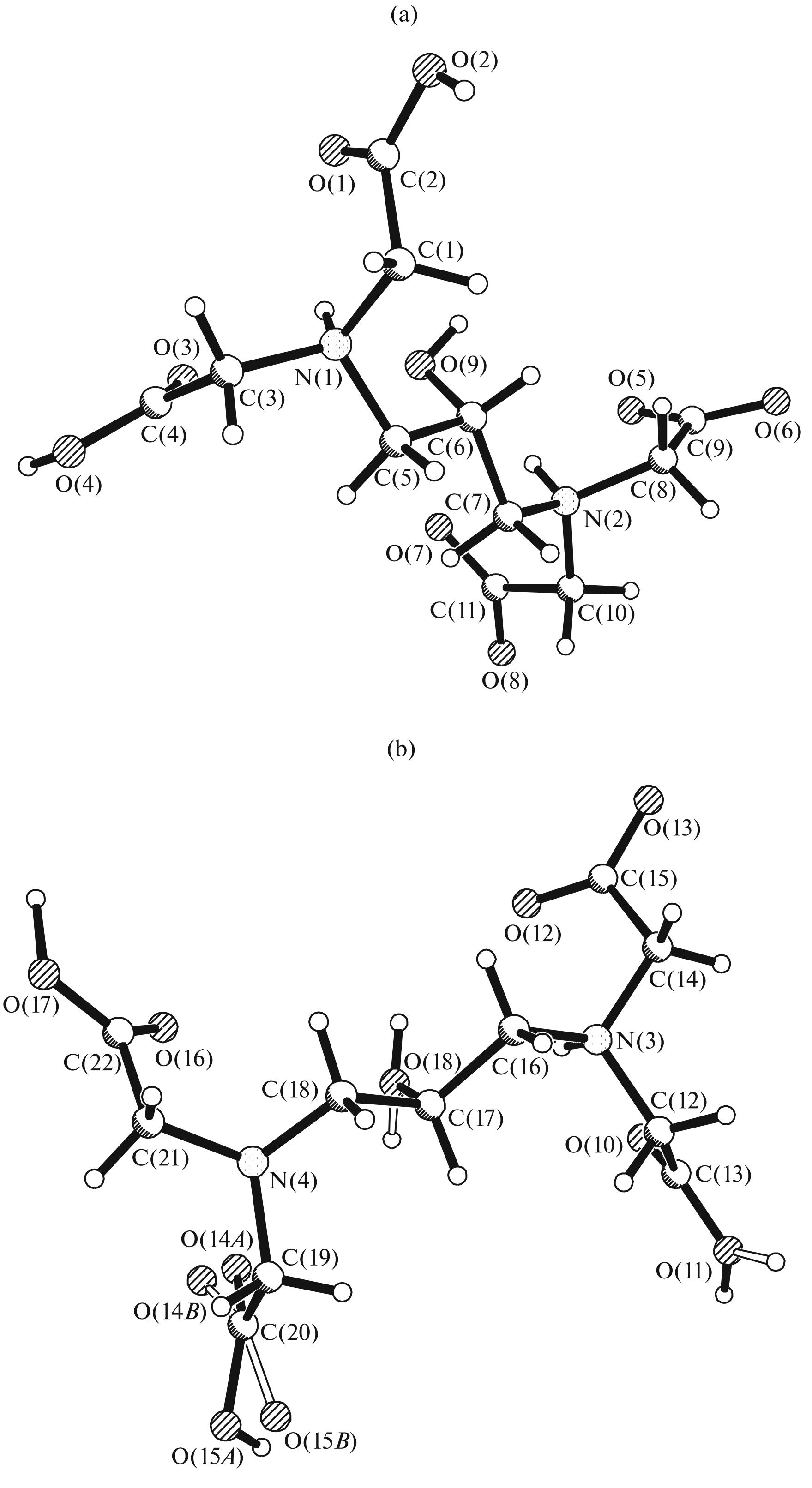

Fig. 1. Structures of the (a) $H_{4.5}HPdta^{0.5-}$ anion and (b) $H_{5.5}Hpdta^{0.5+}$ cation.

Table 3. Geometric parameters of hydrogen bonds in the structure of compound **I**

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
O(2)–H(2)···O(11)$^{\#2}$	0.85	1.91	2.761(4)	180
O(4)–H(4)···O(8)$^{\#3}$	1.11(4)	1.35(4)	2.450(3)	168(3)
O(9)–H(9)···O(6)$^{\#4}$	0.89(4)	1.73(4)	2.589(3)	162(3)
N(1)–H(1N)···O(1)	0.93(3)	2.07(3)	2.627(3)	117(3)
N(1)–H(1N)···O(9)	0.93(3)	2.22(3)	2.732(3)	114(2)
N(2)–H(2N)···O(7)	0.87(3)	2.16(3)	2.670(3)	117(3)
O(11)–H(111)···O(18)$^{\#2}$	1.02	1.58	2.595(3)	169
O(11)–H(112)···O(2)$^{\#2}$	1.19	1.57	2.761(4)	173
O(15*A*)–H(15)···O(15*A*)$^{\#5}$	0.96(8)	1.69(7)	2.58(2)	152(7)
O(17)–H(17)···O(13)$^{\#6}$	1.28(6)	1.23(6)	2.456(3)	156(6)
O(18)–H(181)···O(3*w*)	0.90	2.03	2.763(3)	138
O(18)–H(182)···O(11)$^{\#2}$	0.97	1.71	2.595(3)	150
N(3)–H(3N)···O(18)	0.79(3)	2.35(3)	2.886(5)	126(3)
N(4)–H(4N)···O(14*A*)	0.91(4)	2.03(4)	2.593(18)	119(3)
N(4)–H(4N)···O(14*B*)	0.91(4)	2.23(4)	2.727(18)	114(3)
N(4)–H(4N)···O(16)	0.91(4)	2.16(4)	2.638(3)	112(3)
N(4)–H(4N)···O(18)	0.91(4)	2.33(4)	2.831(4)	114(3)
O(1*w*)–H(11*w*)···O(3)$^{\#3}$	1.16	1.72	2.864(3)	171
O(1*w*)–H(12*w*)···O(3*w*)$^{\#7}$	1.18	1.81	2.953(4)	163
O(2*w*)–H(21*w*)···O(5)$^{\#8}$	1.00	1.78	2.768(3)	168
O(2*w*)–H(22*w*)···O(15*A*)	1.04	1.81	2.787(11)	154
O(2*w*)–H(22*w*)···O(15*B*)	1.04	2.02	3.056(12)	169
O(3*w*)–H(31*w*)···O(16)	1.04	1.87	2.782(4)	145
O(3*w*)–H(32*w*)···O(3*w*)$^{\#6}$	0.91	1.86	2.723(5)	157
O(3*w*)–H(33*w*)···O(18)	0.91	1.94	2.763(3)	150
O(4*w*)–H(41*w*)···O(1*w*)$^{\#9}$	0.84	2.52	3.30(2)	155
O(4*w*)–H(42*w*)···O(1*w*)$^{\#5}$	0.84	2.58	3.11(2)	122

* Symmetry transforms of equivalent atoms: $^{\#1}$ $-x, -y + 1, -z + 2$; $^{\#2}$ $-x + 1, -y + 2, -z + 1$; $^{\#3}$ $-x + 2, -y + 1, -z$; $^{\#4}$ $-x + 2, -y + 1, -z + 1$; $^{\#5}$ $-x + 1, -y + 1, -z + 1$; $^{\#6}$ $-x + 1, -y + 2$, $^{\#7}$ $x, y - 1$, $^{\#8}$ $x -1, y, z$; $^{\#9}$ $x - 1, y, z + 1$.

was determined at $U_{\text{iso}} = 0.08$ Å^2 and then fixed. All non-hydrogen atoms, except for O(4*w*), were refined by least squares in the approximation of anisotropic thermal vibrations. The coordinates of the O(4*w*) atom were refined at the fixed U_{iso}. The positions of the hydrogen atoms linked with the carbon atoms were calculated. The hydrogen atoms bound to the oxygen and nitrogen atoms were localized in the difference Fourier syntheses. The site occupancy of the acidic hydrogen atoms H(2), H(111), H(112), H(15), H(181), H(182), H(32*w*), and H(33*w*) is 0.5. The H(N) atoms and some H(O) atoms were refined in the isotropic approximation. The hydrogen atoms of the water molecule O(4*w*) were specified in the normalized positions (O–H 0.84 Å). The H(2), H(111), H(112), H(181), and H(182) atoms and the H(C) atoms were refined by the riding model with $U_{\text{H}} = 1.2U_{\text{equiv}}$ of the corresponding non-hydrogen atom. The calculations were performed using the SHELX-97 and SHELX-2014 program packages [15]. The interatomic distances and bond angles in the structure of compound **I** are given in Table 2.

The crystallographic data for the structure of compound **I** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1574078; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

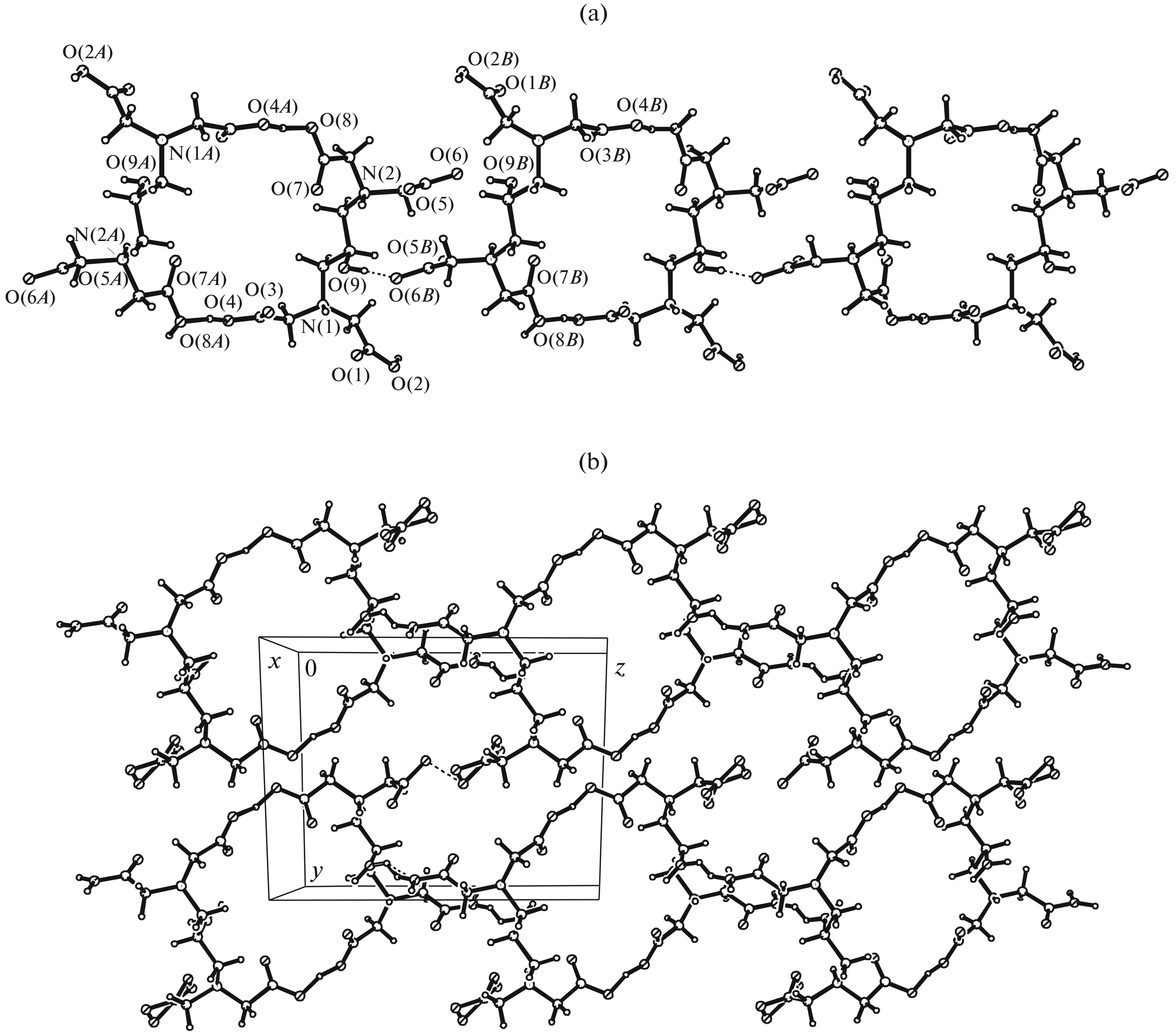

Fig. 2. (a) Anionic 1D chains and (b) cationic 2D layers.

RESULTS AND DISCUSSION

The obtained compound is the crystalline hydrate of 1,3-diamino-2-hydroxypropane-*N*,*N*,*N*′,*N*′-tetraacetic acid. The “building blocks” of crystals of compound **I** are $(H_{4.5}HPdta)^{0.5-}$ anions (Fig. 1a), $(H_{5.5}HPdta)^{0.5+}$ cations (Fig. 1b), and molecules of water of crystallization. The both nitrogen atoms are protonated in both the anion and cation.

All the eight oxygen atoms, four nitrogen atoms, and 20 hydrogen atoms (H(O), N(O) taking into account all disordered positions) are involved in hydrogen bonds: 18 intermolecular O–H···O (in some cases, very strong) and eight intramolecular N–H···O hydrogen bonds. The geometric parameters of hydrogen bonds are presented in Table 3. The anions and cations are separately joined by the networks of hydrogen bonds into 1D chains (Fig. 2a) and 2D layers (Fig. 2b), respectively.

The IR spectrum of the obtained acid was compared with the published data [1–7] taking into account the molecular and crystal structures. The observed main set of absorption bands in the spectrum (ν, cm^{-1}: 3441 ν(OH), 2994 ν(CH), 1716 ν(COOH), 1635 ν_{as}(COO), 1447, 1421 ν_s(COO), 1366 ν(HN–CH_2COO), 1227, 1140 ν(C–N)) corresponds to the crystallization of the acid in the zwitterionic form with the protonation of both nitrogen atoms and a complicated system of inter- and intramolecular hydrogen bonds involving water molecules.

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