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Crystal Cchemical Peculiarities of 6-Aminoquinolinium bis(citrsto)borate Dihidrate Structure

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Abstract: **6-Aminoquinolinium bis(citrato)borate dihydrate $[(6\text{-}NH_2C_9H_6NH)(C_6H_6O_7)_2B]\cdot 2H_2O$ (I) has been synthesized for the first time. The single crystals have been obtained and the full X-ray diffraction analysis of the title compound has been carried out. The structural units of the compound I crystal are large complex bis(citrato)borate anions possessing a spiran structure, 6-aminoquinolinium cations and two molecules of crystallization water. In complex anion two citric acid molecules are bidentately coordinated to the boron atom via the O atoms of central carboxyl and α-hydroxyl groups. The complex anion has pseudosymmetry C_2. In 6-aminoquinoline molecule is protonated the nitrogen atom of the heterocyclic ring. The non-hydrogen atoms in 6-aminoquinolinium cation (except the nitrogen atom of the amino group) are coplanar within the limits of ± 0.039(3) Å. There are eight hydrogen bonds of the O─H…O, N─H…O type in the crystals. Crystal structure obtained for compound I have been compared with the corresponding data for investigated crystalline hydrates bis(citrato)borates of 7-, 8-hydroxy- and 8- and 4-aminoquinolinium cations. X-ray diffraction analysis data allow to elucidate the influence of the mono-substituted quinolinium cations on the complicated crystal structures of bis(citrato)borates crystal hydrates.**

C_{21} H_{25} $N_2O_{16}B$, triclinic: P-1 (No. 2), a = 9.346(2) Å, b = 11.326(3) Å, c = 12.646(3) Å, α = 97.46(2)º, β = 106.59(2)º, γ = 101.66(2)º, V = 1231.1(5) Å, Z = 2, ρ_{calc} = 1.544 g/cm^3, ρ_{exp} = 1.529 g/cm^3, R = 0.0449, R_w = 0.0795, T = 293 K.

Keywords: **boron coordination compounds, bis(citrato)borates, X-ray analysis, hydrogen bonds**

I. Introduction

In the Laboratory of boron chemistry of the Riga Technical University Institute of Inorganic chemistry the interaction of boric acid with hydroxyl and carboxyl groups-containing polyoxy compounds has been studied [1]. The structural investigations of the boron coordination compounds (BCC) have been started by the studies of crystal structures of complexes containing metal and ammonium cations. The structural investigations of BCC with organic cations were not performed because of the definite difficulties to crystallize these compounds. The interest in studies of the boron complex amine salts is caused by the series of advantageous properties of the compounds. The BCC amine salts are widely applied as antipyretics, metal corrosion inhibitors, antioxidants, etc. Some BCC with amines have been synthesized and studied using the physicochemical methods in the Laboratory of boron chemistry earlier [2]. In the course of a search for the experimental material for the X-ray analysis the purposeful synthesis of new compounds as well as the repeated synthesis of the compounds synthesed earlier have been carried out. Some BCC containing monosubstituted quinolinium cations have been synthesized in the form of single crystals and the X-ray diffraction studies of them have been performed. The crystal structures of 7-hydroxyquinolinium bis(citrato)borate semihydrate $2\{[(7\text{-}OH)C_9H_6NH)\ (C_6H_6O_7)_2B]\}\cdot H_2O$ [3] (II), 8-hydroxyquinolinium bis(citrato)borate dihydrate $[(8\text{-}OH)C_9H_6NH]\ [(C_6H_6O_7)_2B]\cdot 2H_2O$ [4] (III), 8-aminoquinolinium bis(citrato)borate terahydrate $[(8\text{-}NH_2)C_9H_6NH]\ [(C_6H_6O_7)_2B]\cdot 4H_2O$ [5] (IV) and 4-aminoquinolinium bis(citrato)borate monohydrate $[(4\text{-}NH_2)C_9H_6NH]\ [(C_6H_6O_7)_2B]\cdot H_2O$ [6] (V) have been investigated.

The synthesis of BCC with 6-aminoquinolinium cation along with their X-ray diffraction investigations and studies concerning the influence of the substituent in cation on the structure and properties of the compounds seem to be purposeful. The methodology of synthesis and results of X-ray diffraction analysis of crystals of 6-aminoquinolinium bis(citrato)borate dihydrate $[(6\text{-}NH_2C_9H_6NH][(C_6H_6O_7)_2B]\cdot 2H_2O$ (I) have been considered in the present work.

II. Experimental

A Synthesis of 6-aminoquinolinium bis(citrato)borate dihydrate (I)

Boric acid (0.05 mol; 3.1 g) and re-crystallized citric acid (0.1 mol; 21.03 g) were dissolved in 17 ml of water under heating. Then 0.05 mol (7.11 g) of twice re-crystallized (from isooctane) 6-aminoquinolinium were added and dissolved. The reaction mixture was slowly cooled and then kept at constant temperature. The formation of the title compound in the form of finely crystalline mass was started after some months. The formed compound was filtered, washed with cold distilled water, alcohol and ether. In the series of repeated synthesis single crystals of the compound I, large enough for X-ray diffraction studies were not obtained. For the X-ray analysis the most perfect crystals were sorted out from the crystalline mass.

Found for I, %: B 1.93; C 44.65; N 4.85; H 4.50.

Calculated for $C_{21}H_{25}N_2BO_{16}$, %:

B 1.89; C 44.09; N 4.90; O 4.73; H 4.41.

Specific weight of the crystalline specimen was 1.529 g/cm^3 and it was determined using the flotation method in the systems acid-water, chloroform-carbon tetrachloride.

B X-ray diffraction analysis

The single crystal experiment was performed on Xcalibur system from "Oxford Diffraction" with Saphire CCD detector. The structure was solved by direct method [7] and refined by matrix least squares method using SHELXL package [8]. Crystallographic characteristics and refinement parameters are reported in Table 1, the final coordinates and thermal parameters of the basic atoms of structure ─ in Tables 2, 3; selected geometric parameters of the bis(citrato)borate complex anion and organic cation ─ in Tables 4-6. The geometric characteristics of hydrogen bonds are given in Table 7.

TABLE 1

DATA COLLECTION AND HANDLING

Parameter	Value
Empirical formula	C_{21} H_{25} $N_2O_{16}B$
Crystal system	triclinic
Crystal colour	colorless
crystal size	0.20 x 0.25 x 0.10 mm
Radiation type	MoK_α
Wavelength	0.71073 Å
μ	0.134 cm^{-1}
Diffractometer	Xcalibur system from "Oxford Diffraction" with Saphire CCD detector
Scan mode	θ/2θ
$2\theta_{max}$	55.26°
$N(hkl)_{measured}$, $N(hkl)_{unique}$	7509, 4982
Criterion for I_{obs}, $N(hkl)_{gt}$	$I_{obs} > 2\ \sigma(I_{obs})$, 1746
$N(param)_{refined}$	405
Programs	SHELXS-86 [7], SHELXL-93 [8]
R-factor	$R = 0.0449$, $R_w = 0.0795$

III. RESULTS AND DISCUSSION

The crystal structure of the complex I is formed from the complex bis(citrato)borate anions $[(C_6H_6O_7)_2B]^-$ possessing the spiran-type structure, 6-aminoquinoline cations $[(6\text{-}NH_2C_9H_6NH)]^+$ and two crystallization water molecules [9]. Identification and numbering of atoms of the complex is shown in Fig. 1.

Two molecules of citric acid are coordinated bidentatically by the boron atom via the oxygen atoms of the central carboxylic group and α-hydroxyl group. The C_2 symmetry pseudo-axis crosses the center of the anion through the boron atom. The B─O bonds follow the regularity ─ the bonds B─O(hydr.) with average length of 1.451 ± 0.002 Å are shorter than the bonds B─O(carb., hydr.) (average length 1.500 ± 0.004 Å) because the bonds C(sp^3)─O with average length of 1.426 ± 0.003 Å coordinated to the boron atom are longer than the bonds C(sp^2)─O(H) (average length 1.312 ± 0.003 Å) (Table 4).

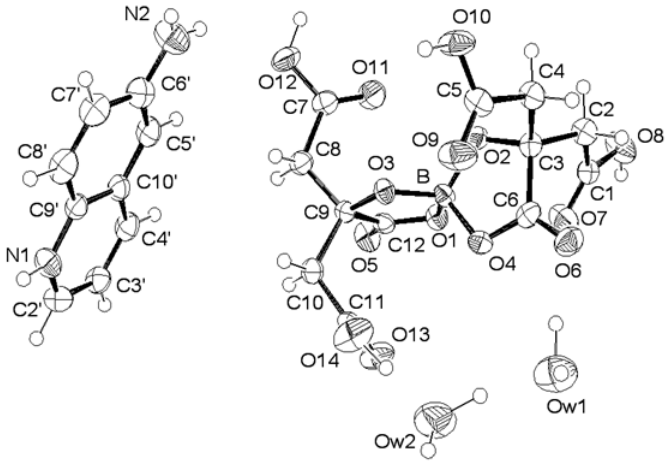

Fig. 1. The molecular structure of I with the nonhydrogen atom numbering scheme. H atoms are shown as small spheres

The average length of the corresponding bonds B─O amounts to 1.503(8) Å and 1.449(8) Å in the complex anions of 14 crystalline bis(citrato)borates [10]. The average length of four B─O bonds (1.471 Å) is close to the mean statistical value characteristic of the bonds B(sp^3)─O (1.468 Å [11]) and to the value of 1.475 Å (1.43 Å→1.55 Å) characteristic of the inorganic borates [12].

The bond angle O─B─O values in the boron-oxygen tetrahedron (Table 5) are in the range of 104.0(3)° to 115.6(3)° and they exceed the usual values characteristic of inorganic borates. The least are the intracyclic dihedral angles O(1)─B─O(3), O(2)─B─O(4) (average value 104.6° ± 0.6°). The bond angle O(1)─B─O(4) formed by atoms included in the carboxylic groups (109.9(3)°) is less than the angle O(2)BO(3) (115.6(3)°) between the oxygen atoms bound to the carbon atoms C(sp^3). The average values of the O─C and C─C bond length in citrate ligands of the complex anion lie outside of the corresponding values found for bonds in crystalline bis(citrato)borates with metal and ammonium cations studied earlier [10] as well as in 7-hydroxy- [3] (II), 8-hydroxy- [4] (III) and 8-amino- [5] (IV) and 4-aminoquinolinium bis(citrato)borates. In the terminal carboxyl groups the C─OH bonds (average length 1.321 ± 0.011 Å) are longer but the C=O bonds (average length 1.204 ± 0.009 Å) are shorter then the corresponding bonds in the citric acid molecule (average lengths 1.315 Å and 1.238 Å correspondingly).

On the contrary, the C─O(H) bonds (the average length 1.312±0.003 Å) are shortened, but the C=O bonds (the aver. length 1.222 ± 0.03 Å) are lengthened (1.331 Å and 1.210 Å in [13]) in the central carboxylic group coordinated to the boron atom. The lengths of the C(sp^3)─O(H) type bonds with the hydroxyl groups (the average length 1.426 ± 0.003 Å) are changed insignificantly. The bonds C(sp^3)─C(sp^2) with the terminal carboxylic groups (the average length 1.503 ± 0.009 Å) are shorter than the corresponding bonds with the central carboxylic group (the average length 1.530 ± 0.005 Å); the bond length values are close to the initial values of bond lengths in the molecule of citric acid (1.503 Å, 1.533 Å); the bonds C(sp^3)─C(sp^3) (the average length 1.535 ± 0.019 Å) are

somewhat shortened (1.540 Å in [13]). The dispersion of the individual bond length values amounts to ± 0.014 Å for C=O bonds and to ± 0.016 Å for C─OH bonds in the terminal carboxylic groups; to ± 0.025 Å and ± 0.015 Å for the corresponding bonds in central carboxylic groups, and to ± 0.021Å for the C(sp^3)─C(sp^3) bonds. The average values of the C─O and C─C bond lengths in the citrate ligands are close to their standard values: 1.214 Å for C*─C(sp^2)(OH)=O; 1.308 Å for C*─C(sp^2)(=O)─OH; 1.413 Å for C(sp^3)─OH with the alcohol groups; 1.502 Å for C(sp^3)─C(sp^2) in carboxylic acids; 1.530 Å for C(sp^3)─C(sp^3) (C* - the nearest atom C(sp^3) conjugated with the corresponding bond [11]).

TABLE 2

ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (IN Å^2, X10^3)

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	*U*eq
B	0.2075(5)	0.2802(4)	0.7604(3)	27(2)	24(3)	29(3)	7(2)	9(2)	10(2)	26(1)
O(1)	0.1245(2)	0.2363(2)	0.6361(2)	32(2)	23(2)	27(2)	1(1)	7(1)	5(1)	29(1)
O(2)	0.3169(2)	0.2089(2)	0.8005(2)	26(1)	25(1)	29(1)	5(1)	10(1)	7(1)	27(1)
O(3)	0.2734(2)	0.4106(2)	0.7718(2)	30(1)	20(1)	23(1)	1(1)	6(1)	5(1)	26(1)
O(4)	0.0956(2)	0.2584(2)	0.8243(2)	30(2)	30(2)	38(1)	7(1)	14(1)	13(1)	31(1)
O(5)	0.0936(3)	0.3166(2)	0.4804(2)	47(2)	36(2)	24(2)	1(1)	1(1)	10(1)	39(1)
O(6)	0.0695(3)	0.1547(2)	0.9603(2)	38(2)	50(2)	40(2)	12(1)	19(1)	9(1)	41(1)
O(7)	0.0236(3)	-0.0061(2)	0.6993(2)	44(2)	35(2)	53(2)	2(1)	-3(1)	11(1)	48(1)
O(8)	0.1347(3)	-0.1627(2)	0.7050(2)	53(2)	30(2)	50(2)	-1(2)	-3(2)	13(1)	49(1)
O(9)	0.3677(3)	0.3907(2)	1.0353(2)	41(2)	44(2)	71(2)	-12(2)	14(2)	17(2)	54(1)
O(10)	0.6107(3)	0.3759(3)	1.0806(2)	30(2)	35(2)	59(2)	-16(2)	-1(1)	5(1)	48(1)
O(11)	0.4610(3)	0.3262(2)	0.6289(2)	44(2)	30(2)	72(2)	-3(2)	26(2)	11(1)	48(1)
O(12)	0.6227(3)	0.5065(2)	0.6451(2)	27(2)	44(2)	79(2)	9(2)	21(2)	5(1)	50(1)
O(13)	-0.1257(3)	0.4216(2)	0.6387(2)	28(2)	44(2)	58(2)	-15(2)	10(2)	-1(1)	48(1)
O(14)	0.0058(3)	0.5447(3)	0.8047(2)	46(2)	64(2)	49(2)	-16(2)	20(2)	3(2)	56(1)
C(1)	0.1233(4)	-0.0519(3)	0.7448(3)	33(2)	23(2)	36(2)	5(2)	12(2)	7(2)	31(1)
C(2)	0.2508(4)	0.0083(3)	0.8536(3)	34(2)	27(2)	30(2)	-2(2)	6(2)	6(2)	32(1)
C(3)	0.2808(4)	0.1485(3)	0.8850(3)	28(2)	24(2)	23(2)	2(2)	6(2)	4(2)	26(1)
C(4)	0.4178(4)	0.1932(3)	0.9945(3)	35(2)	28(2)	30(2)	0(2)	6(2)	7(2)	33(1)
C(5)	0.4602(4)	0.3298(3)	1.0381(3)	35(3)	32(3)	28(2)	-1(2)	9(2)	12(2)	32(1)
C(6)	0.1371(4)	0.1875(3)	0.8952(3)	27(2)	24(2)	29(2)	-4(2)	8(2)	0(1)	29(1)
C(7)	0.4867(4)	0.4358(4)	0.6380(3)	29(3)	35(3)	32(2)	-1(2)	12(2)	8(2)	32(1)
C(8)	0.3721(4)	0.5104(3)	0.6391(3)	27(2)	30(2)	32(2)	5(2)	9(2)	6(2)	30(1)
C(9)	0.2308(4)	0.4481(3)	0.6659(3)	22(2)	19(2)	23(2)	0(2)	4(2)	5(2)	23(1)
C(10)	0.1299(4)	0.5397(3)	0.6663(3)	30(2)	23(2)	34(2)	2(2)	9(2)	6(2)	30(1)
C(11)	-0.0094(4)	0.4950(3)	0.7013(4)	38(3)	25(2)	42(3)	-1(2)	11(2)	16(2)	35(1)
C(12)	0.1422(4)	0.3271(3)	0.5823(3)	23(2)	25(2)	32(3)	-1(2)	8(2)	9(2)	27(1)
N(1)	0.3659(4)	1.0597(3)	0.6178(3)	49(3)	31(2)	47(3)	-1(2)	21(2)	15(2)	41(1)
N(2)	0.7932(5)	0.7970(5)	0.7821(4)	63(3)	63(3)	50(3)	17(3)	9(2)	28(3)	58(1)
C(2')	0.2508(4)	1.0191(4)	0.5214(3)	35(3)	47(3)	41(3)	7(2)	11(2)	14(2)	41(1)
C(3')	0.2375(4)	0.9081(3)	0.4551(3)	33(2)	34(3)	32(2)	1(2)	6(2)	4(2)	35(1)
C(4')	0.3426(4)	0.8408(3)	0.4907(3)	39(3)	31(2)	37(3)	-1(2)	13(2)	2(2)	37(1)
C(5')	0.5744(4)	0.8181(3)	0.6351(3)	41(3)	28(2)	34(3)	-3(2)	12(2)	5(2)	36(1)
C(6')	0.6883(5)	0.8620(4)	0.7369(3)	44(3)	45(3)	36(3)	11(2)	16(2)	12(2)	41(1)
C(7')	0.7000(5)	0.9808(4)	0.7981(3)	42(3)	48(3)	31(2)	3(2)	9(2)	3(2)	43(1)
C(8')	0.5969(4)	1.0469(4)	0.7597(3)	46(3)	36(3)	31(3)	-9(2)	10(2)	-1(2)	42(1)
C(9')	0.4758(4)	0.9988(3)	0.6587(3)	31(2)	26(2)	35(2)	1(2)	16(2)	5(2)	30(1)
C(10')	0.4647(4)	0.8833(3)	0.5940(3)	33(2)	24(2)	38(3)	3(2)	14(2)	5(2)	32(1)
O(1W)	-0.1757(4)	0.2520(3)	0.9900(3)	60(2)	67(2)	71(3)	-10(2)	25(2)	19(2)	67(1)
O(2W)	-0.2130(4)	0.4466(4)	0.8755(3)	84(3)	100(3)	89(3)	34(2)	59(2)	48(2)	79(1)

TABLE 3

HYDROGEN ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS (IN Å^2, x10^3)

Atom	*x*	*y*	*z*	U_{eq}
H(8)	-0.047(6)	0.197(5)	0.364(4)	114
H(10)	0.368(5)	0.540(4)	0.885(4)	97
H(12)	0.702(6)	0.464(5)	0.651(4)	120
H(14)	-0.079(7)	0.0504(5)	0.831(5)	145
H(4')	0.3326(4)	0.7602(3)	0.4427(3)	56
H(5')	0.5693(4)	0.7377(3)	0.5890(3)	54
H(7')	0.7860(5)	1.0159(4)	0.8706(3)	64
H(8')	0.6075(4)	1.1300(4)	0.8037(3)	62
H(1wA)	-0.159(9)	0.297(8)	1.056(8)	26
H(1wB)	-0.091(8)	0.229(6)	0.983(5)	16
H(2wA)	-0.190(7)	0.378(7)	0.922(5)	16
H(2wB)	-0.264(7)	0.489(6)	0.906(5)	16
H(2A)	0.3481(4)	-0.0119(3)	0.8483(3)	48
H(2B)	0.2250(4)	-0.0281(3)	0.9158(3)	48
H(4A)	0.3923(4)	0.1503(3)	1.0536(3)	49
H(4B)	0.5095(4)	0.1691(3)	0.9814(3)	49
H(8A)	0.3374(4)	0.5328(3)	0.5636(3)	46
H(8B)	0.4251(4)	0.5886(3)	0.6959(3)	46
H(10A)	0.1944(4)	0.6185(3)	0.7187(3)	45
H(10B)	0.0946(4)	0.5577(3)	0.5891(3)	45
H(N1)	0.363(4)	1.126(4)	0.656(3)	5
H(N2A)	0.781(6)	0.722(5)	0.748(4)	10
H(N2B)	0.854(5)	0.824(4)	0.859(4)	11
H(2')	0.1743(4)	1.0686(4)	0.4971(3)	61
H(3')	0.1522(4)	0.8768(3)	0.3818(3)	53

TABLE 4

SELECTED BOND LENGTHS (*D*) IN COMPLEX ANION IN CRYSTAL OF I

Bond	*d*, Å	Bond	*d*, Å
B–O(1)	1.504(4)	O(11)–C(7)	1.199(4)
B–O(2)	1.449(4)	O(12)–C(7)	1.329(4)
B–O(3)	1.452(4)	O(13)–C(11)	1.213(4)
B–O(4)	1.496(4)	O(14)–C(11)	1.310(4)
O(1)–C(12)	1.314(4)	C(1)–C(2)	1.506(5)
O(2)–C(3)	1.423(4)	C(2)–C(3)	1.534(4)
O(3)–C(9)	1.429(3)	C(3)–C(4)	1.535(4)
O(4)–C(6)	1.309(4)	C(3)–C(6)	1.529(5)
O(5)–C(12)	1.219(4)	C(4)–C(5)	1.504(5)
O(6)–C(6)	1.224(4)	C(7)–C(8)	1.494(5)
O(7)–C(1)	1.199(4)	C(8)–C(9)	1.516(4)
O(8)–C(1)	1.326(4)	C(9)–C(10)	1.537(4)
O(9)–C(5)	1.206(4)	C(9)–C(12)	1.531(4)
O(10)–C(5)	1.319(4)	C(10)–C(11)	1.506(5)

TABLE 5

SELECTED BOND ANGLES (*ω*) IN COMPLEX ANION OF CRYSTAL I

Angle	*ω*, deg	Angle	*ω*, deg
O(1)BO(2)	110.8(3)	O(2)BO(3)	115.6(3)
O(1)BO(3)	104.0(3)	O(2) BO(4)	105.1(3)
O(1)BO(4)	109.9(3)	O(3) BO(4)	111.5(3)
C(3)O(2)B	110.7(3)	O(4)C(6)C(3)	111.1(3)
C(6)O(4)B	109.6(3)	O(6)C(6)C(3)	123.9(3)
C(9)O(3)B	111.3(2)	O(11)C(7)O(12)	123.3(4)
C(12)O(1)B	110.6(3)	O(11)C(7)C(8)	125.5(4)
O(7)C(1)O(8)	123.8(4)	O(12)C(7)C(8)	111.2(4)
O(7)C(1)C(2)	124.6(3)	C(7)C(8)C(9)	115.3(3)
O(8)C(1)C(2)	111.6(3)	O(3)C(9)C(8)	111.1(3)
C(1)C(2)C(3)	115.1(3)	O(3)C(9)C(10)	111.1(3)
O(2)C(3)C(2)	112.7(3)	O(3)C(9)C(12)	103.4(3)
O(2)C(3)C(4)	108.9(3)	C(8)C(9)C(10)	107.6(3)
O(2)C(3)C(6)	103.5(3)	C(8)C(9)C(12)	111.9(3)
C(2)C(3)C(4)	107.4(3)	C(10)C(9)C(12)	111.8(3)
C(2)C(3)C(6)	103.5(3)	C(9)C(10)C(11)	114.1(3)
C(4)C(3)C(6)	112.5(3)	O(13)C(11)O(14)	123.4(4)
C(3)C(4)C(5)	114.0(3)	O(13)C(11)C(10)	122.9(4)
O(9)C(5)O(10)	123.6(3)	O(14)C(11)C(10)	113.7(3)
O(9)C(5)C(4)	124.2(4)	O(1)C(12)O(5)	124.7(3)
O(10)C(5)C(4)	112.2(3)	O(1)C(12)C(9)	110.4(3)
O(4)C(6)O(6)	125.0(3)	O(5)C(12)C(9)	124.9(3)

Two five-membered chelate rings have the mutual boron atom in the spiran complex anion. The boron-containing heterocycles C(9)O(3)BO(1)C(12) and C(3)O(2)BO(4)C(6) are planar in the limits of (± 0.030(1) Å) and (± 0.011(1) Å) correspondingly. The O(5) atom of the carbonyl group is declined from the first plane by 0.096(1) Å; its analog O(6) atom is coplanar (± 0.018(1) Å) with the adjacent plane. Dihedral angle value between of two planes of two heterocyclic rings amounts to 87.8(2)°.

The nitrogen atom N(1) of the heterocyclic ring in 6-aminoquinoline molecule is protonated in acidic media. The lengths of bonds with the nitrogen atom of the heterocyclic ring in the 6-aminoquinolinium cation as always differ: N(1)─C(2') 1.327(4) Å; N(1)─C(9') 1.370(5) Å. The average lengths of the corresponding bonds in the crystals of II-V amount to 1.324 ± 0.010 Å and 1.370 ± 0.004 Å (Table 6).

The length of the bond N(2)─C(6') with the amino group amounts to 1.384(5) Å (N(2)─C(8) 1.370(4) in IV) and it corresponds to the length of bonds of the C(*ar*)─NH_2, N(sp^3) type (1.394 Å [11]). The N(2)─C(4') bond length in 4-aminosubstituted cation (1.326 ± 0.03 Å in average) indicating that atom N(2) of the amino group must be sp^2 hybridized (C(*ar*)─NH_2, N(sp^2) is 1.355 Å [11]). Changes in the lengths of C─C bonds with substituted carbon atoms in the structures I, IV containing amino-substituted cations are longer than in the structures II, III containing hydroxy-substituted cations. The general regularity (the bonds alternating in pairs C(3')─C(4'); C(5')─C(6'); C(7')─C(8') with average length of

1.367(5) Å (I); 1.364(8) Å (II); 1.363(3) Å (III); 1.372(5) Å (IV); 1.378(4) Å (V) are shorter than the other C─C bonds is preserved in the monosubstituted quinolinium cations in structures I─V. The average length of all C─C bonds in 6-amonoquinolinium cation amounts to 1.385(5) Å that coincides with the mean statistical value 1.384 Å for the length of C(*ar*)─C(*ar*) bonds [11].

Ten non-hydrogen atoms of the cation lie in one plane in the limits of ± 0.039 Å; the nitrogen atom of the amino group N(2) is declined from the mutual plane of ten atoms by 0.110(1) Å.

The system of hydrogen bonds seems to be somewhat less developed in the crystals of complex I than in crystal hydrates of 4- (V) and 8- aminoquinoli-

nium (IV) bis(citrato)borates.

Eight independent hydrogen bonds (Table 7) are formed in which three hydroxyl groups from the four terminal carboxylic groups of anion and amino group of cation act as donors.

In structures (IV, V) the proton of nitrogen atom of the heterocyclic ring also participates in formation of hydrogen bonds.

TABLE 6

BOND LENGTHS AND THEIR ESTIMATED DEVIATIONS IN THE 6-AMINO- (I), 7-HYDROXY- (II), 8-HYDROXY- (III), 8-AMINO- (IV) AND 4-AMINOQUINOLINIUM (V) CATIONS IN FIVE BIS(CITRATO)BORATE HYDRATE STRUCTURES

Bond	(I)	(II)	(III)	(IV)	(V)	Mean
N(1)─C(2')	1.327	1.315	1.324	1.322	1.334	1.324
N(1)─C(9')	1.370	1.371	1.368	1.372	1.375	1.371
N(2)─C*	1.384	─	─	1.370	1.326	1.360
HO─C*	─	1.357	1.348	─	─	1.353
C(2')─C(3')	1.380	1.371	1.387	1.398	1.360	1.379
C(3')─C(4')	1.373	1.366	1.360	1.362	1.406	1.365
C(4')─C(10')	1.415	1.395	1.409	1.414	1.437	1.408
C(5')─C(10')	1.403	1.419	1.416	1.413	1.407	1.412
C(5')─C(6')	1.369	1.366	1.359	1.367	1.365	1.364
C(6')─C(7')	1.428	1.398	1.403	1.396	1.389	1.396
C(7')─C(8')	1.358	1.359	1.369	1.387	1.363	1.361
C(8')─C(9')	1.398	1.394	1.409	1.427	1.402	1.398
C(9')─C(10')	1.417	1.411	1.411	1.417	1.401	1.411

C* - substituted atom; bond lengths C─C* (in bold) are not used in mean bond length calculations

The spatial package of the crystals is lamellar. The structure layers are parallel to the plane (011). In the structural layers (Fig. 2) the complex anions are stacked so as the long axis of them is perpendicular to the plane of the layer.

The double chain of complex anions passes along the parameter *a* in the layer. In this anion chain four crystallization molecules are located among the four anions. The complex anions are connected in the chain directly by the hydrogen bond *1*, but the bonds *4–8* connect them via the molecules of crystallization water. 6-Aminoquinolinium cations are situated between the two complex anion chains in the layer. The amino groups of the each cation pair are directed to the opposite sides to the two no identical structural layers and form the hydrogen bonds *2*, *3* with anions of these layers as well as realize the connection of no identical layers in crystals.

The formation of lamellar structures is characteristic of the crystal structures of bis(citrato)borates with monosubstituted quinolinium cations (II-V). The chains (III, IV) or the interlayer of cations and complex anions (II) occur to be the initial elements in the layer. The interlayer contact can be realized on the level of van der Waals interactions (III) or strengthened by the action of separate hydrogen bonds (II, IV).

The three-dimensional package of the structural constituents is realized in the crystals (V). The crystals of III (100° C) and V (85° C) occur to be the thermally most stable ones; the stability of IV (45° C) is considerably below.

TABLE 7

GEOMETRY OF HYDROGEN BONDS IN THE STRUCTURE OF I

Nr.	A–H…B bond	Distances, Å		
		A–H	H...B	A…B
1.	O(12)–H(12)...O(13)^{i}	0.96	1.81	2.731 (3)
2.	N(2)–H(N2A)...O(12)	0.87	2.54	3.345 (3)
3.	N(2)–H(N2B)...O(6)^{ii}	0.95	2.15	3.069 (3)
4.	O(1w)–H(1wA)...O(10)iii	0.87	2.57	3.047 (3)
5.	O(1w)–H(1wA)...O(14)^{iv}	0.87	2.26	3.029 (3)
6.	O(1w)–H(1wB)...O(6)	0.91	1.93	2.830 (3)
7.	O(2w)–H(2wA)...O(1w)	1.05	1.77	2.816 (3)
8.	O(2w)–H(2wB)...O(9)^{iv}	0.87	2.01	2.868 (3)

Symmetry codes:(i)1+*x*, *y*, *z*; (ii)1-*x*, 1-*y*, 2-*z*; (iii)1-*x*, *y*, *z*; (iv)-*x*, 1-*y*, 2-*z*.

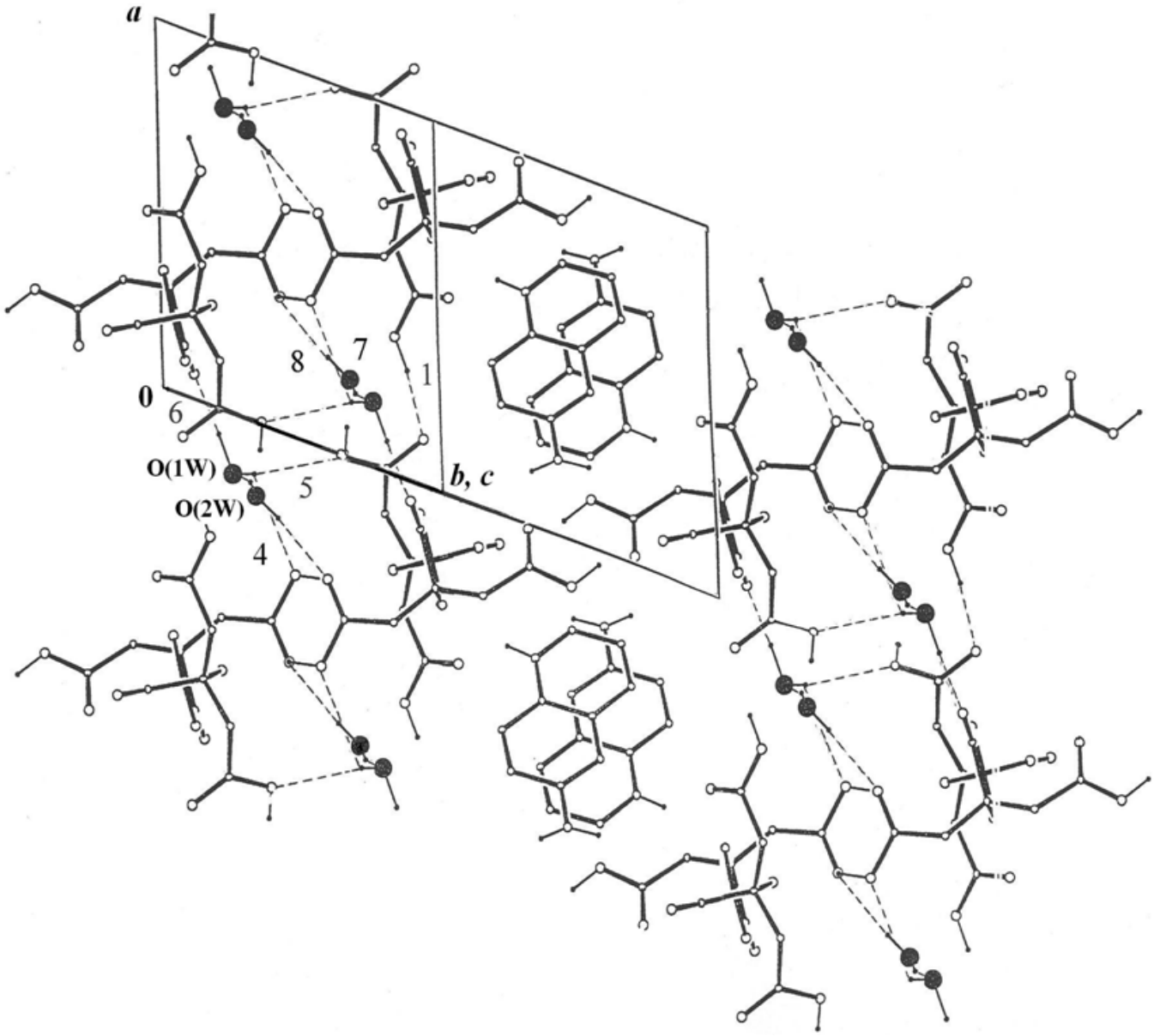

Fig. 2. Structural layer parallel to (011) plane. A solid line indicates unit cell; hydrogen bonds by dashed lines, numbering is according to Table 7

IV. CONCLUSIONS

In result of the performed X-ray diffraction studies of the complex I and structures II-V investigated earlier and containing monosubstituted quinolinium cations, the definite changes were established to occur in the geometry of cations, in the chemical composition of compounds (number of crystallization water molecules is from 1/2 to 4) and in the spatial package of crystal structures depending on the properties and position (4-, 6-, 7-, 8-) of the substituents (HO- and H_2N- groups) in monosubstituted quinolinium cations.

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Irēna Zviedre, Anatolijs Mišņovs. 6-Aminohinolīnija dicitrātoborāta dihidrāta sintēze un kristāliskā struktūra
Sintezēts 6-aminohinolīnija dicitrātoborāta dihidrāts $[(6\text{-}NH_2)C_9H_6NH][(C_6H_6O_7)_2B]\cdot 2H_2O$ (I), izaudzēti tā monokristāli un ar monokristālu rentgenstruktūranalīzes metodi noteikta savienojuma pilna kristāliskā struktūra. Kompleksa I kristālisko struktūru veido vienlādiņu spirānu uzbūves kompleksie dicitrātoborātanjoni, 6-aminohinolīnija katjoni un divas kristalizācijas ūdens molekulas.
Komplekso dicitrātoborātanjonu veido divas citronskābes molekulas, kas bidentāti koordinētas pie bora atoma ar centrālās karboksilgrupas un α-hidroksilgrupas skābekļa atomiem. Kompleksā anjona centrālais - bora atoms novietots uz pseidosimetrijas ass C_2. 6-Aminohinolīna molekulā protonēts heterocikliskais slāpekļa atoms. Aminohinolīnija katjona neūdeņraža atomi (izņemot aminogrupas slāpekļa atomu) ir planāri robežās ± 0.039(3) Å.
Kristālos veidotas astoņas O─H…O, N─H…O tipu ūdeņraža saites. Kristāliskā struktūra I izvērtēta salīdzinājumā ar iepriekš noteiktām 7-, 8-oksi- un 8-, 4-aminohinolīnija dicitrātoborātu hidrātu kristāliskajām struktūrām.
Rentgenogrāfisko pētījumu rezultātā noteikta aizvietotāju pozicijas un īpašību ietekme uz vienaizvietoto hinolīnija katjonu veidotajām dicitrātoborātu hidrātu kristāliskajām struktūrām un īpašībām.
C_{21} H_{25} $N_2O_{16}B$, triklīnā singonija: P-1 (No. 2), a = 9,346(2) Å; b = 11,326(3) Å; c = 12,646(3) Å; α = 97,46(2)º; β = 106,59(2)º; γ = 101,66(2)º; V = 1231,1(5) Å^3; Z = 2, $\rho_{teorēt}$ = 1,544 g/cm^3; ρ_{eksp} = 1,529 g/cm^3; R = 0,0449, R_w = 0,0795; T = 293 K.

Ирена Звиедре, Анатолий Мишнев. Синтез и кристаллическая структура дигидрата дицитратобората 6-аминохинолиния
Впервые синтезирован дигидрат дицитратобората 6-аминохинолиния состава $[(6\text{-}NH_2C_9H_6NH)(C_6H_6O_7)_2B]\cdot 2H_2O$ (I). Получены монокристаллы и проведен полный рентгеноструктурный анализ. Структурными единицами кристалла I являются крупные комплексные дицитратоборат-анионы спиранового строения, катионы 6-аминохинолиния и две молекулы кристаллизационной воды.
Дицитратоборат-анион образован путем бидентатной координации атомом бора двух молекул лимонной кислоты через атомы кислорода центральной карбоксильной и α-гидроксильной групп. Комплексный анион имеет псевдоось симметрии C_2, которая проходит через атом бора. В молекуле 6-аминохинолина протонирован атом азота гетероцикла. Неводородные атомы катиона (кроме атома азота аминогруппы) копланарны в пределах ± 0.039(3) Å.
В кристаллах образованы восемь независимых водородных связей типов O─H…O, N─H…O. Проводится сопоставление структуры I с кристаллическими структурами гидратов дицитратоборатов 7-, 8-окси- и 8-, 4-аминохинолиния.
В результате проведенных рентгеноструктурных исследований выявлено влияние положения и свойств заместителей в катионах однозамещенного хинолиния на кристаллические структуры и свойства гидратов дицитратоборатов.
C_{21} H_{25} $N_2O_{16}B$, триклинная сингония: P-1 (No. 2), a = 9,346(2) Å; b = 11,326(3) Å; c = 12,646(3) Å; α = 97,46(2)º; β = 106,59(2)º; γ = 101,66(2)º; V = 1231,1(5) Å^3; Z = 2, $\rho_{выч.}$ = 1,544 g/cm^3; $\rho_{эксп}$ = 1,529 g/cm^3; R = 0,0449, R_w = 0,0795; T = 293 K.