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Crystal Structure of Trimethylammonium Bis(citrato)borate Monohydrate

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Abstract **– Trimethylammonium bis(citrato)borate monohydrate $(CH_3)_3NH[(C_6H_6O_7)_2B]\cdot H_2O$ (I) was synthesized for the first time. Its crystal structure was solved from single crystal X-ray diffraction data ($C_{15}H_{24}NO_{15}B$: a = 9.7795(3) Å, b = 10.7367(3) Å, c = 10.9245(4) Å, α = 84.883(1)°, β = 77.341(1)°, γ = 69.126(1)°, V = 1045.7(1) Å^3, Z = 2, space group P-1, 4888 reflections with R_{int} = 0.0230; $R1$ = 0.058, T = 173(2), ρ_{calc} = 1.490 g/cm^3, ρ_{exp} = 1.510 g/cm^3).**

The structural units of crystal I (the large bis(citrato)borate anion with a spirane structure, the trimethylammonium cation, and the crystal water molecule) form a layered packing with a system of six O─H...O, (O^I) and N─H...O, (O^I) type hydrogen bonds. In complex anion $[(C_6H_6O_7)_2B]^-$ 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. The XRD data were compared with crystal data for complexes of boron and citric acids and alkyl-substituted cations studied previously.

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

INTRODUCTION

During the course of study of interaction of boric and citric acids borodicitric acid and salts containing bis(citrato)borate anion have been synthesized [1]. In continuation of investigations new bis(citrato)borates have been prepared which contained metal cations, quinolinium cations and substituted ammonium cations [2]. Crystal structures of 28 bis(citrato)borates have been studied using the X-ray analysis method. 27 Borates contain univalent bis(citrato)borate anions $[(C_6H_6O_7)_2B]^-$ possessing the spiran-type structure. Borodicitric acid is five-valent and it can conform complex anions of rather higher valence depending on the conditions of synthesis. These anions can involve partially or totally deprotonated terminal carboxylic groups of ligands as with long-chain dialkylamines [1]. These salts are not X-ray examined due to their poor crystallizability. The tetraaquastrontium bis(citrato)borate trihydrate has been synthesized in the highly concentrated solution [3]. The synthesized compound contains bivalent bis(citrato)borate anion $[(C_6H_6O_7)B(C_6H_5O_7)]^{2-}$ formed from the two citric acid residues with different ionization degree.

The aim of this work is to study the crystal structure of trimethylammonium bis(citrato)borate monohydrate $(CH_3)_3NH[(C_6H_6O_7)_2B]\cdot H_2O$ I by XRD and to compare it with the previously found structures of methyl- $CH_3NH_3[(C_6H_6O_7)_2B]$ II [4, 5], dimethyl- $(CH_3)_2NH_2[(C_6H_6O_7)_2B]$ III [6, 7], diethyl- $(C_2H_5)_2NH_2[(C_6H_6O_7)_2B]$ IV [8, 9], triethylammonium $(C_2H_5)_3NH[(C_6H_6O_7)_2B]\cdot H_2O$ V [10, 11] and ammonium $NH_4[(C_6H_6O_7)_2B]\cdot 2H_2O$ VI [2] bis(citrato)borates.

EXPERIMENTAL

A. Synthesis

Synthesis of trimethylammonium bis(citrato)borate monohydrate I was carried out by reacting boric acid, citric acid, and trimethylamine in the ratio 1:2:1 in aqueous solution at pH 2-3. Boric acid (0.05 mol; 3.1 g) and recrystallized citric acid (0.1 mol; 21.03 g) were dissolved in 17 ml of distilled water under heating. Then 0.05 mol (7.11 g) of trimethylamine were added. The reaction mixture was slowly cooled and then kept at constant temperature. The colourless crystalline residue was filtered off, washed with cold distilled water, alcohol and ether. Single crystals were grown during repeated syntheses by evaporation of the reaction solution.

Found for I, %: B 2.25; C 38.45; N 3.05; H 5.30.
Calculated for $C_{15}H_{24}NBO_{15}$, %:
B 2.30; C 38.40; N 2.99; O 5.15; H 5.16.

Specific weight of the crystalline specimen was 1.510 g/cm^3 which was determined using the flotation method in the systems *acid-water*, *chloroform-carbon tetrachloride*.

B. X-Ray diffraction analysis

XRD data were collected from a perfect single crystal (Bruker-Nonius KappaCCD automated diffractometer). The structure was solved by direct methods with subsequent Fourier synthesis and refined by matrix least squares analysis using SHELXL package in the full-matrix anisotropic approximation for nonhydrogen atoms, taking into account the coordinates of the hydrogen atoms. Hydrogen atoms were placed both from differential synthesis and from idealized position and refined using riding model [12, 13]. Calculations were performed with software [14].

Crystallographic characteristics and the results of structure refinement are listed in Table I; the final coordinates and thermal parameters of the basic atoms of structure ─ in Table II; selected geometrical characteristics of the bis(citrato)borate complex anion and trimethylammonium cations ─ in Tables III and IV. The hydrogen bonds are characterized in Table V.

TABLE I

CRYSTALLOGRAPHIC PARAMETERS AND EXPERIMENTAL AND STRUCTURE REFINEMENT DETAILS FOR I

Parameter	Value
Molecular formula	$C_{15}H_{24}NO_{15}B$
Molecular mass	469.16
Temperature, K	173(2)
Crystal system	Triclinic
Space group	P-1
Unit cell parameters:	
a, Å	9.7795(3)
b, Å	10.7367(3)
c, Å	10.9245(4)
α, deg	84.883(1)
β, deg	77.341(1)
γ, deg	69.126(1)
V, $Å^3$,	1045.7(1)
Z	2
ρ_{calc}, g/cm^3	1.490
μ, mm-1	0.134
F(000)	492
Crystal dimensions, mm	0.21 x 0.26 x 0.35
Crystal color	Colourless
Scan mode	θ/2θ
$2\theta_{max}$, deg	54.98°
Radiation type	MoK_α
Wavelength	0.71073 Å
Reflection index range	$-12<h<12$, $-12<k<13$, $-12<l<14$
Reflections measured	7204
Independent reflections, [*R*=0.0230]	4888
Used reflections with $I>3\sigma(I)$	3968
Refinement method	Full-matrix least-squares calculation (on F^2)
Parameters refined	301
GOOF	1097
Data collection	KappaCCD
R for $[I>2\sigma(I_{obs})$	*R*1 = 0.058, *wR2* = 0.133
R for all reflections	*R*1 = 0.073, *wR2* = 0.192
Residual electron density (max /min), e/$Å^3$	1.48/-0.60

TABLE II

ATOMIC COORDINATES ($x10^4$, $x10^3$ FOR H) AND DISPLACEMENT PARAMETERS (IN $Å^2$, $x10^3$)

Atom	*x*	*y*	*z*	U_{11}
B	2025(3)	2653(2)	2194(2)	17(1)
O(1)	3403(2)	2622(1)	2509(1)	20(1)
O(2)	1781(2)	3674(1)	1161(1)	20(1)
O(3)	2050(2)	1365(1)	1827(1)	19(1)
O(4)	717(2)	3076(1)	3260(1)	19(1)
O(5)	3039(2)	4902(2)	6(2)	25(1)
O(6)	-1068(2)	2291(2)	4287(2)	26(1)
O(7)	3112(2)	5698(2)	4269(2)	37(1)
O(8)	1746(2)	5971(2)	2805(2)	48(1)
O(9)	4525(2)	1645(2)	-364(2)	33(1)
O(10)	6824(2)	539(2)	-7(2)	31(1)
O(11)	3583(2)	-1460 (2)	3987(2)	32(1)
O(12)	2171(2)	552(2)	4757(2)	36(1)
O(13)	-1427(2)	3246(2)	1393(2)	27(1)
O(14)	-362(2)	2000(2)	-308(2)	40(1)
C(1)	2913(3)	5448(2)	3171(2)	25(1)
C(2)	4303(2)	4483(2)	2415(2)	22(1)
C(3)	4050(2)	3451 (2)	1681(2)	17(1)
C(4)	5570(2)	2631(2)	925(2)	20(1)
C(5)	5544(2)	1563(2)	122(2)	21(1)
C(6)	2901(2)	4109(2)	853(2)	17(1)
C(7)	2416(2)	-360(2)	4056(2)	25(1)
C(8)	1374(2)	-318(2)	3210(2)	22(1)
C(9)	824(2)	1043(2)	2550(2)	17(1)
C(10)	-221(2)	941(2)	1718(2)	21(1)
C(11)	-649(3)	2095(2)	815(2)	23(1)
C(12)	38(2)	2194(2)	3479(2)	18(1)
C(1')	-2399(4)	8461(3)	2576(3)	44(2)
C(2')	-1523(4)	6495(3)	3983(3)	49(2)
C(3')	-1578(4)	6223(3)	1777(3)	50(2)
O(1w)	4807(2)	1306(2)	4418(2)	52(1)
N	-1375(2)	7062(2)	2650(2)	36(1)
H(N)	-24	699	248	39
H(2A)	471	507	189	27
H(2B)	497	403	297	27
H(4A)	604	320	32	23
H(4B)	630	219	148	23
H(7)	231	635	473	39
H(8A)	53	-51	371	26
H(8B)	190	-100	259	26
H(10)	676	-3	-54	33
H(10A)	-113	87	224	25
H(10B)	33	12	120	25
H(11)	414	-145	455	35
H(13)	-188	395	88	29
H(1'A)	-262(4)	907(3)	183(3)	46
H(1'B)	-219	901	311	46
H(1'C)	-350(4)	835(3)	288(3)	46
H(2'A)	-84	559	398	50
H(2'B)	-238(4)	635(4)	391(4)	50
H(2'C)	-131	702	453	50
H(3'A)	-81(4)	529(4)	186(3)	53
H(3'B)	-138	656	94	53
H(3'C)	-259	624	199	53
H1wA	435	182	384	57
H1wB	565	79	386	57

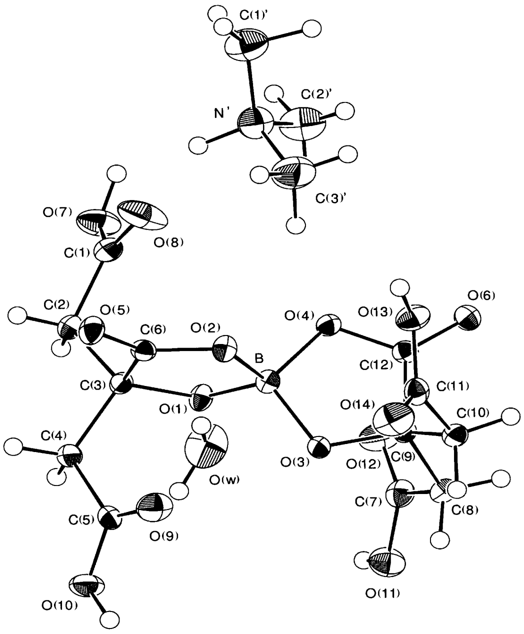

Fig.1. The molecular configuration and atom numbering scheme for the trimethylammonium bis(citrato)borate monohydrate $(CH_3)_3NH[(C_6H_6O_7)_2B] \cdot H_2O$. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

RESULTS AND DISCUSSION

The structural units of crystals I are the bis(citrato)borate anion $[(C_6H_6O_7)_2B]^-$ with a spirane structure, the trimethylammonium cation $[(CH_3)_3NH]^+$, and the crystal water molecule. The nonhydrogen atoms of compound I are identified and numbered in Fig. 1.

TABLE III

SELECTED BOND LENGTH IN DICITRATOBORATE ANION AND TRIMETHYLAMMONIUM CATION CRYSTAL OF I

Bond	*d*, Å	Bond	*d*, Å
B–O(1)	1.451(4)	O(11)–C(7)	1.312(4)
B–O(2)	1.498(4)	O(12)–C(7)	1.221(4)
B–O(3)	1.464(3)	O(13)–C(11)	1.328(3)
B–O(4)	1.492(3)	O(14)–C(11)	1.202(4)
O(1)–C(3)	1.421(3)	C(1)–C(2)	1.504(4)
O(2)–C(6)	1.306(3)	C(2)–C(3)	1.540(4)
O(3)–C(9)	1.419(3)	C(3)–C(4)	1.525(3)
O(4)–C(12)	1.316(3)	C(3)–C(6)	1.531(4)
O(5)–C(6)	1.220(3)	C(4)–C(5)	1.514(4)
O(6)–C(12)	1.215(3)	C(7)–C(8)	1.505(4)
O(7)–C(1)	1.321(4)	C(8)–C(9)	1.539(4)
O(8)–C(1)	1.218(4)	C(9)–C(10)	1.545(4)
O(9)–C(5)	1.202(4)	C(9)–C(12)	1.535(3)
O(10)–C(5)	1.329(4)	C(10)–C(11)	1.508(4)
N–C(1')	1.486(4)	N–C(2')	1.524(5)
N–C(3')	1.456(5)		

Table IV

SELECTED BOND ANGLES (*Ω*) AND TORSION ANGLES (*τ*) IN DICITRATOBORATE ANION CRYSTAL OF I

Angle	*ω*, deg	Angle	*ω*, deg
O(1)BO(2)	104.2(2)	O(2)BO(3)	112.2(2)
O(1)BO(3)	114.5(2)	O(2)BO(4)	108.9(2)
O(1)BO(4)	113.0(2)	O(3)BO(4)	104.2(2)
C(3)O(1)B	111.1(2)	O(2)C(6)C(3)	110.5(2)
C(6)O(2)B	110.5(2)	O(5)C(6)C(3)	124.4(2)
C(9)O(3)B	111.0(2)	O(11)C(7)O(12)	123.4(3)
C(12)O(4)B	110.8(2)	O(11)C(7)C(8)	114.4(3)
O(7)C(1)O(8)	123.5(3)	O(12)C(7)C(8)	122.2(3)
O(7)C(1)C(2)	112.3(3)	C(7)C(8)C(9)	112.5(2)
O(8)C(1)C(2)	124.1(3)	O(3)C(9)C(8)	111.1(3)
C(1)C(2)C(3)	112.1(2)	O(3)C(9)C(10)	111.4(2)
O(1)C(3)C(2)	110.9(2)	O(3)C(9)C(12)	103.8(2)
O(1)C(3)C(4)	110.9(2)	C(8)C(9)C(10)	106.9(2)
O(1)C(3)C(6)	103.5(3)	C(8)C(9)C(12)	112.5(2)
C(2)C(3)C(4)	107.1(2)	C(10)C(9)C(12)	111.7(2)
C(2)C(3)C(6)	112.1(2)	C(9)C(10)C(11)	114.5(2)
C(4)C(3)C(6)	112.4(2)	O(13)C(11)O(14)	122.6(3)
C(3)C(4)C(5)	114.8(2)	O(13)C(11)C(10)	112.7(2)
O(9)C(5)O(10)	124.4(3)	O(14)C(11)C(10)	124.6(3)
O(9)C(5)C(4)	124.8(3)	O(4)C(12)O(6)	124.9(2)
O(10)C(5)C(4)	110.7(2)	O(4)C(12)C(9)	110.2(2)
O(2)C(6)O(5)	125.0(3)	O(6)C(12)C(9)	125.0(2)

Angle	*τ*, deg
O(7)C(1)C(2)C(3)	140.5(3)
O(8)C(1)C(2)C(3)	41.3(2)
O(10)C(5)C(4)C(3)	-149.9(2)
O(9)C(5)C(4)C(3)	32.1(2)
O(11)C(7)C(8)C(9)	-137.5(3)
O(12)C(7)C(8)C(9)	43.6(2)
O(13)C(11)C(10)C(9)	-62.2(2)
O(14)C(11)C(10)C(9)	118.6(3)

The bis(citrato)borate anion with a BO_4 tetrahedron at the centre is formed by bidentate coordination of the B atom to two citric acid molecules via the O atoms of the central carboxyl and α-hydroxyl groups. It has a pseudoaxis of C_2 symmetry, which passes through the B atom and divides the O(1)─O(3) and O(2)─O(4) edges of the tetrahedron in two halves. The difference between the two functional groups is responsible for the nonequivalence of the B─O bonds and the distortion of the BO_4 tetrahedron. The B─O(hydr.) bonds (av. 1.458 ± 0.007 Å) are shorter than the bonds B─O(carb., hydr.) bonds (av. 1.495 ± 0.003 Å). The conjugated C(sp^3)─O bonds (av. 1.420 ± 0.001 Å) are longer than the C(sp^2)─O(H) bonds (av. 1.311 ± 0.005 Å) (Table III).

The average length of four B─O bonds, 1.476± 0.025 Å, differs slightly from the mean statistical length for B(sp^3)─O type bonds (1.468 Å [15]) and does not exceed 1.43─1.55 Å in the structures of inorganic borates [16].

The two OBO bond angles included in the five-membered boroheterocycles (av. 104.2 ± 0.0°) are smaller than the other four angles (av. 110.8° ± 2.2°) (Table IV).

The B atom is common for the two heterocycles. The O(5) and O(6) atoms are coplanar (0.013(1) Å and 0.006(1) Å) with the heterocyclic planes of the rings. The two chelate rings are planar (to an accuracy of 0.041(1) Å and 0.021(2) Å, respectively), the dihedral angle between them being 89.97(4)°. In complex anion, the O─C and C─C bonds in the citrato groups fall within the corresponding ranges found in the previously studied crystal structures of bis(citrato)borates [2] and are close to the corresponding values in the structures of I-VI.

In the terminal and central carboxyl groups of the anion, the average C─OH (C─O(H)) and C=O bond lengths are 1.323 ± 0.011 Å, 1.218 ± 0.016 Å, 1.311 ± 0.005 Å, and 1.218 ± 0.003 Å, respectively. The C(sp^3)─O(hydr.) bond length is 1.420 ± 0.001 Å. The C(sp^3)─C(sp^2) bonds with the terminal carboxyl groups (av. 1.508 ± 0.006 Å) are shorter than those with the central carboxyl group (av. 1.533 ± 0.002 Å); the C(sp^3)─C(sp^3) bonds are, on average 1.538 ± 0.013 Å (Table III).

The spatial rearrangement of the terminal carboxylic groups in relation to the planes of carbon chains is different. If as the starting point such a position of carboxylic groups is chosen, in which the carboxylic group lies in the plane corresponding to the carbon chain, the oxygen atom of the carboxyl group is situated approximately face to face with the centre of the nearest boron-containing ring. The direction of turning of the COOH group plane, that allows the carbonyl group oxygen atom to approach the double bound C=O to bind with boron-containing ring, can be considered as a positive direction. As follows from the values of torsion angles along the single C─C axes (Table IV), three carboxylic groups of the anion are turned just in this direction. Whereas the oxygen atom O(13) of the hydroxylic group occurs to be situated nearer to the plane of the boron-containing heterocyclic ring than the atom O(14) of the carbonyl group. The obtained results bear the evidence that the carboxylic groups in the bis(citrato)borate anion of the complex I crystals are highly mobile.

TABLE V
GEOMETRICAL PARAMETERS OF HYDROGEN BONDS FOR I

No.	A–H…B bond	Distances, Å		
		A–H	H...B	A…B
1.	O(7)–H(7)...O(6)i	0.93	1.79	2.701(3)
2.	O(3)ii O(10)–H(10) O(9)ii	0.91	1.96 2.50	2.740(2) 3.033(3)
3.	O(13)–H(13)...O(5)iii	0.94	1.73	2.656(3)
4.	O(11)–H(11)...O(1w)iv	0.91	1.74	2.643(3)
5.	O(1w)–H(1wA)...O(1)	0.89	1.87	2.753(3)
6.	O(8) N(1)–H(1) O(14)iii	1.06	1.95 2.56	2.891(3) 3.050(3)

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

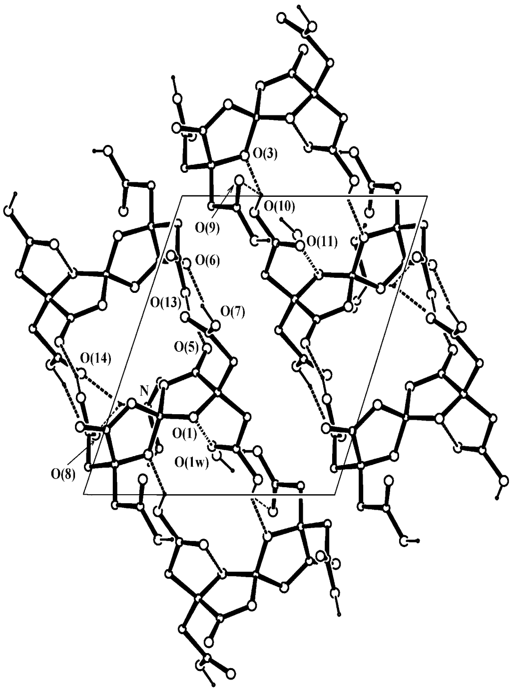

Fig.2. The packing of $(CH_3)_3NH[(C_6H_6O_7)_2B]\cdot H_2O$ in the unit cell, projected to the (001) plane.

The situation of the carboxylic groups is apparently determined mainly by the facility to form the intermolecular hydrogen bounds in the crystal.

According to the criteria of [17], crystal I has 6 independent hydrogen bonds of O─H...O,(O^I) and N─H...O, (O^I) types (Table V).

The formed hydrogen bounds connect nonidentical complex anions, the anions with cations and with water molecules. All hydroxylic groups of the four terminal carboxylic groups of the anions, water molecule and trimethylammonium cation appear to be the proton donors in the course of formation of hydrogen bounds. The oxygen atoms of the carbonyl groups in the central carboxylic groups and in the three terminal carboxylic groups as well as the oxygen atoms O(1) and O(3) from the α-hydroxylic groups of the organic ligands occur to be the proton acceptors. The oxygen atoms O(2) and O(4) from the central carboxylic groups of the citric acid residues traditionally do not participate in the formation of the hydrogen bond system in crystals of the compound I.

The spatial packing of the compound I crystals is lamellar. It is possible to distinguish the diagonal layers, parallel planes (001) (Fig. 2), in which the complex anions are oriented perpendicular to the layer plane. Cations and water molecule in the layer is situated alternate between the anions (Fig. 3). The stratified package of the crystals is one of the most prevalent package types in the crystal structures of bis(citrato)borates. The stratified crystal structure $NH_4[(C_6H_6O_7)_2B]\cdot 2H_2O$ [2] is similar to the lamellar structures of bis(citrato)borates containing large univalent cations of alkali metals potassium, rubidium and cesium.

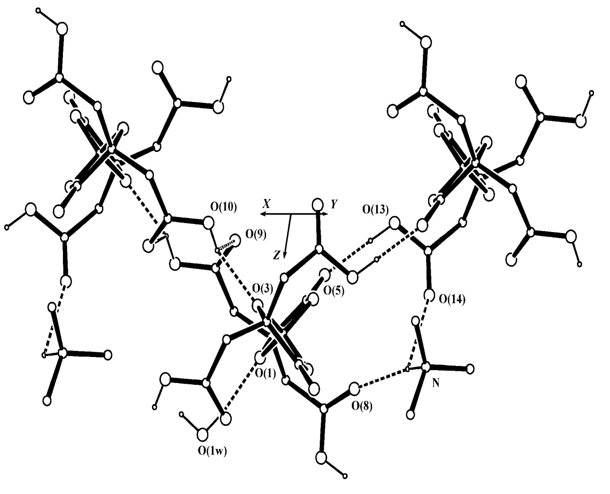

Fig.3. The fragment of packing the structure layer in the unit cel of I. Hydrogen-bonding associations are shown as broken lines (see Table V).

Substitution of one hydrogen atom in the ammonium cation by the methyl group in II [5] results in the lowering of the crystal symmetry from the rhombic VI [2] to the triclinic (in II [5]). In the substitution of the two hydrogen atoms by the methyl groups in III [7] the general motif of the lamellar packing is preserved. The further enlargement of the cation size in IV [9] disturbs the stability limit of the lamellar crystal package, and the formation of isolated ionic structures in the form of chain fragment consisting from cations and complex anions occurs in the structure. In structure V [11] further decrease of the ionic component of the Coulomb interaction between the large insignificantly changed ions takes place. The differently changed structural motifs are the layers of complex anions common with the water molecules as well as the cation layers. The interlamellar electrostatic interaction is supplemented by the influence of the hydrogen bounds.

The studies of thermal decomposition of compounds investigated by X-ray analysis have shown that for the series of complexes under study (I-VI) the regularity is observed - the thermal stabilities of the crystal hydrates of VI (100°C) [2], V (83°C) [10] and I (63°C) are lower than thermal stability of II (193°C) [4], III (185°C) [6] and IV (210°C) [8].

CONCLUSIONS

We report the crystal structure of a new compound from a series of salt of the bis(citrato)borate anions with alkylammonium cations. Complex I was synthesized for the first time; its single crystals were grown, and its crystal structure was studied by XRD. The XRD data were compared with crystal data for dicitratoborates with ammonium cations and alkylsubstituted ammonium cations studied previously.

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Irēna Zviedre, Sergejs Beļakovs. Trietilamonija dicitrātoborāta monohidrāta sintēze un kristāliskā struktūra

Sintezēts trimetilamonija dicitrātoborāta monohidrāts $CH_3NH[(C_6H_6O_7)_2B]\cdot H_2O$ (I), izaudzēti tā monokristāli, un ar monokristālu rentgenstruktūranalīzes metodi (automātiskais difraktometrs Bruker-Nonius KappaCCD) noteikta pilna kristāliskā struktūra. Kompleksa I kristālisko struktūru veido vienlādiņu spirānu uzbūves kompleksie dicitrātoborātanjoni, trimetilamonija katjoni un kristalizācijas ūdens molekula.

Komplekso dicitrātoborātanjonu veido divas citronskābes molekulas, kas bidentāti koordinētas pie bora atoma ar centrālās karboksilgrupas un α-hidroksīlgrupas skābekļa atomiem. Kompleksajā anjonā bora atoms novietots uz pseidosimetrijas ass C_2. Kristālos veidotas sešas O─H…O, (O^I), N─H…O, (O^I) tipu trīs- un četrcentru ūdeņraža saites. Kristālisko struktūru veido paralēli plāksnei (001) novietoti diagonālie slāņi, kuros kompleksie anjoni orientēti perpendikulāri struktūras slāņa plāksnei, bet trimetilamonija katjoni atrodas slāņa vidusdaļā. Kristāliskā struktūra I izvērtēta salīdzinājumā ar iepriekš noteiktām alkilamonija katjonus saturošām dicitrātoborātu struktūrām, kurās izvietojas pēc ķīmiskām īpašībām līdzīgi, bet pēc izmēriem dažādi katjoni, saglabājoties vienai un tai pašai anjonu daļai. Noteikts, ka ūdeņraža atomu aizvietošana amonija katjonā ar vienu, divām vai trim alkilgrupām saistās ar noteiktām savienojumu termiskās izturības, blīvuma, kristālisko struktūru telpiskā pakojuma un ūdeņraža saišu sistēmu izmaiņām.

$C_{15}H_{24}NO_{15}B$, triklīnā singonija: P-1 (No. 2), a = 9,7795(3) Å; b = 10,7367(3) Å; c = 10,9245(4) Å; α = 84,883(1)°; β = 77,341(1)°; γ = 69,126(1)°; V = 1045,7(1) Å^3; Z = 2, $\rho_{teorēt}$ = 1,490 g/cm^3; ρ_{eksp} = 1,510g/cm^3; R = 0,058, R_w = 0,0795; T = 173(2) K.

Ирена Звиедре, Сергей Беляков. Синтез и кристаллическая структура моногидрата дицитратобората триметиламмония

Синтезирован моногидрат дицитратобората триметиламмония $CH_3NH[(C_6H_6O_7)_2B]\cdot H_2O$ (I). В водном растворе выращены монокристаллы соединения и на автоматическом дифрактометре Bruker-Nonius KappaCCD проведен его полный рентгеноструктурный анализ. Структурными единицами кристалла I являются комплексные дицитратоборатанионы спиранового строения, катионы триметиламмония и молекула кристаллизационной воды.

Комплексный дицитратоборатанион 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 по центру аниона через атом бора. В кристаллах образованы шесть независимых водородных связей типов O─H…O, (O^I), N─H…O, (O^I). В кристаллах можно выделить диагональные слои, параллельные плоскости (001). Комплексные анионы в слое перпендикулярны плоскости слоя, катионы триметиламмония расположены между анионами в середине слоя. Проводится сопоставление структуры I с кристаллическими структурами дицитратоборатов с алкилзамещенными катионами аммония, исследованными ранее, в которых отличаются размеры катионов, в то время как анионная часть остается неизменной. Установлено, что замена атомов водорода в катионе аммония алкил-лигандами сопровождается закономерными изменениями термической устойчивости, плотности соединений, пространственной упаковки кристаллических структур и преобразованиями в системах водородных связей.

$C_{15}H_{24}NO_{15}B$, триклинная сингония: P-1 (No. 2), a = 9,7795(3) Å; b = 10,7367(3) Å; c = 10,9245(4) Å; α = 84,883(1)°; β = 77,341(1)°; γ = 69,126(2)°; V = 1045,7(1) Å^3; Z = 2, $\rho_{выч.}$ = 1,490 g/cm^3; $\rho_{эксп}$ = 1,510 g/cm^3; R = 0,058, R_w = 0,0795; T = 173(2) K.