ELSEVIER

Carbohydrate Research 337 (2002) 787–801

CARBOHYDRATE RESEARCH

www.elsevier.com/locate/carres

Synthesis and X-ray structures of sulfate esters of fructose and its isopropylidene derivatives. Part 1: 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose 1-sulfate and 4,5-*O*-isopropylidene-β-D-fructopyranose 1-sulfate

Tomasz Popek, Tadeusz Lis*

Faculty of Chemistry, University of Wrocław, F. Joliot-Curie 14, PL-50-383 Wrocław, Poland

Received 8 August 2001; received in revised form 25 January 2002; accepted 6 February 2002

Abstract

2,3:4,5-Di-*O*-isopropylidene-β-D-fructopyranose 1-sulfate have been synthesized by treatment of 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose with pyridine–sulfur trioxide complex. Direct hydrolysis of the isopropylidene group at C-4, C-5 gave 2,3-*O*-isopropylidene-β-D-fructopyranose 1-sulfate. The crystal and molecular structures of ammonium (**1a**) and potassium (**1b**) salts of diisopropylidene derivative and ammonium (**2**) salt of monoisopropylidene derivative were determined by X-ray crystallography. Data for **1a** and **1b** were collected in 120 K and in 150 K for **2**. All salts crystallized in $P2_12_12_1$ space group. There are three independent anions in asymmetric unit in **1b**. Pyranose rings in the diisopropylidene derivative salts studied adopt $^2S_0$ twist boat conformation, whereas in the monoisopropylidene exists in a slightly distorted chair conformation ($^4C_1$). A staggered conformation is preferred by the sulfate group as indicated by values of C–O(ester)–S–O(terminal) torsion angles: − 173.2(4)° in **1a**, 175.1(6)° in anion **A** of **1b**, 170.8(6)° in anion **C** of **1b** and 177.9(2)° in **2**. However, strong interactions such as potassium–oxygen and H-bonds may affect the geometry: in anion **B** of **1b** the value of the torsion angle is 139.4(6)°. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Sugar sulfates; Fructopyranose; Molecular structure; Crystal structure; β-D-Fructopyranose, protected isopropylidene derivative; Hydrogen bonds

1. Introduction

The sulfate esters of carbohydrates occur widely in nature[1–5] and play an essential role in many biological processes. In animals they are components of connective tissues, glands, kidney, brain tissue etc. In plants, sulfate ester groups appear in many polysaccharides, originating both from cell walls and intercellular regions. Special attention has been given to the gelling properties of galactans widely used, both in food and pharmaceutical industries. Interactions between cations associated with sulfate groups and water molecules seem to be especially important for interactions of

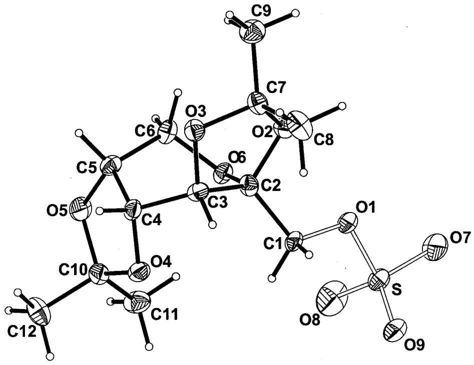

Fig. 1. Molecular structure and numbering scheme of the anion in the structure of ammonium 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose 1-sulfate (**1a**). The thermal ellipsoids are given with 50% probability.

---

* Corresponding author. Tel.: + 48-71-3282348; fax: + 48-71-3204338.

E-mail address: tlis@wchuwr.chem.uni.wroc.pl (T. Lis).

PII: S0008-6215(02)00046-0

Table 1
The puckering parameters for **1a**, **1b**, and **2**

Structure	Ring	Q (Å)	θ (°)	ϕ (°)	Conformation
1a	O-6–C-2–C-3–C-4–C-5–C-6	0.690(6)	94.5(5)	148.5(5)	$^{2}S_{0}$
	O-2–C-7–O-3–C-3–C-2	0.312(6)		71.1(10)	^{2}E
	O-4–C-10–O-5–C-5–C-4	0.248(6)		138.8(13)	$^{4}E \rightarrow {}^{4}T_{3}$
Anion **A** of **1b**	O-6–C-2–C-3–C-4–C-5–C-6	0.656(9)	95.4(8)	152.6(9)	$^{2}S_{0}$
	O-2–C-7–O-3–C-3–C-2	0.326(10)		71.0(17)	^{2}E
	O-4–C-10–O-5–C-5–C-4	0.284(10)		126.8(20)	$^{4}T_{3}$
Anion **B** of **1b**	O-6–C-2–C-3–C-4–C-5–C-6	0.598(9)	106.3(8)	145.9(9)	$^{2}S_{0}$
	O-2–C-7–O-3–C-3–C-2	0.264(9)		57.2(18)	$^{2}T_{1} \rightarrow {}^{2}E$
	O-4–C-10–O-5–C-5–C-4	0.335(9)		217.0(15)	^{1}E
Anion **C** of **1b**	O-6–C-2–C-3–C-4–C-5–C-6	0.681(11)	95.1(9)	148.2(9)	$^{2}S_{0}$
	O-2–C-7–O-3–C-3–C-2	0.320(10)		81.0(18)	$^{2}E \rightarrow {}^{2}T_{3}$
	O-4–C-10–O-5–C-5–C-4	0.261(11)		165.3(24)	$^{4}T_{0}$
2	O-6–C-2–C-3–C-4–C-5–C-6	0.531(3)	15.2(3)	269.2(9)	$^{4}C_{1}$
	O-2–C-7–O-3–C-3–C-2	0.348(3)		123.7(4)	$^{4}T_{3}$

polysaccharide chains. There is evidence that various sulfated polysaccharides inhibit human immunodefiancy virus replication.[6]

The X-ray crystallography studies of simple compounds—sulfated monosugars—may be the way to determine the stereochemical features that are important in view of understanding polysaccharide chain interactions. The structural data are also necessary for force-field calculations,[7] but unfortunately only few crystal molecular structures of sulfated sugars are known to date.[8]

We undertook to synthesize and investigate by X-ray methods 1-sulfate derivatives of D-fructose. The present paper describes the synthesis and results of structural investigations of di- and monoisopropylidene derivatives of D-fructose 1-sulfate, which are intermediates in the synthesis of β-D-fructose 1-sulfate.

2. Results

*Structure of ammonium 2,3:4,5-di-*O*-isopropylidene-β-*D*-fructopyranose 1-sulfate* (**1a**).—The crystal consists of sulfated sugar anions and ammonium cations. The molecular structure and atom-numbering scheme are presented in Fig. 1.

The pyranose ring adopts $^{2}S_{0}$ twist boat conformation. The five-membered ring formed by O-2, C-7, O-3, C-3, and C-2 atoms adopts an ^{2}E envelope conformation whereas the ring formed by O-4, C-10, O-5, C-5, and C-4 atoms adopts an intermediate conformation between ^{4}E and $^{4}T_{3}$. The puckering parameters[9,10] are summarized in Table 1.

Similarly as in other sulfate esters,[8] the sulfate group adopts an almost fully staggered conformation, i.e., the value of the C-1–O-1–S–O-7 torsion angle is −173.2(4)° and the O-6–C-2–C-1–O-1 and C-2–C-1–O-1–S torsion angles, describing the orientation of the sulfate group are 66.4(5) and −147.6(4)°, respectively. The lengths of the bonds formed by the ester O-1 atom are: 1.613(3) (S–O-1) and 1.432(6) Å (O-1–C-1). Two S–O^{T}† bonds are longer than the third one. Comparison of selected bond lengths, valence angles, and torsion angles for **1a**, **1b**, and **2** is presented in Table 2.

Ammonium cations are linked via O-1, O-2, O-7, and O-9 atoms of anions by hydrogen bonds. A two-dimensional hydrogen bond network, parallel to the *ab* plane is formed and consistently arranged hydrophilic and hydrophobic layers can be distinguished in the crystal (Fig. 2). Two O^{T}, O-1, and O-2 atoms are acceptors for hydrogen bonds, and the donors are solely N atoms of ammonium cations. The geometry of the hydrogen bond is summarized in Table 3.

*The structure of potassium 2,3:4,5-di-*O*-isopropylidene-β-*D*-fructopyranose 1-sulfate hemihydrate* (**1b**).—The crystal consists of sulfated sugar anions, potassium cations, and water molecules in 1:1:0.5 ratio. There are three anions, three cations, one water molecule with full occupancy factor (O-1W), and one statistically disordered water molecule with occupancy factor equal 0.5 (O-2W) in the asymmetric unit. Overlapped structures of three independent anions denoted as **A**, **B**, and **C**, with C-2, C-3, and O-6 atoms used to fit the anions, are presented in Fig. 3. The numbering scheme used is the same as in **1a**.

---

† O^{T} = terminal O atom of sulfate group.

Table 2
Comparison of selected bond lengths (Å), valence angles (°) and torsion angles (°) in **1a**, **1b**, and **2**

	1a	**1b**			**2**
		Anion **A**	Anion **B**	Anion **C**	
Bond lengths					
S–O-1	1.613(3)	1.603(6)	1.615(5)	1.600(6)	1.599(2)
S–O-7	1.451(4)	1.438(6)	1.430(6)	1.418(6)	1.422(2)
S–O-8	1.424(4)	1.460(6)	1.445(5)	1.446(6)	1.447(2)
S–O-9	1.465(4)	1.427(6)	1.443(6)	1.444(6)	1.450(2)
C-1–O-1	1.432(6)	1.423(9)	1.425(9)	1.437(10)	1.442(2)
C-1–C-2	1.491(6)	1.508(12)	1.511(10)	1.506(12)	1.512(2)
C-2–O-2	1.450(6)	1.437(10)	1.407(10)	1.438(10)	1.410(2)
C-2–O-6	1.414(5)	1.411(9)	1.394(9)	1.394(10)	1.415(2)
C-2–C-3	1.541(6)	1.552(11)	1.575(10)	1.530(10)	1.538(2)
C-3–O-3	1.408(6)	1.447(10)	1.433(9)	1.427(10)	1.429(2)
C-3–C-4	1.513(6)	1.492(11)	1.492(11)	1.499(13)	1.531(2)
C-4–O-4	1.414(5)	1.411(10)	1.398(9)	1.412(10)	1.423(2)
C-4–C-5	1.550(6)	1.544(11)	1.549(10)	1.553(12)	1.522(2)
C-5–O-5	1.422(6)	1.435(10)	1.442(9)	1.401(11)	1.418(2)
C-5–C-6	1.513(6)	1.492(11)	1.516(10)	1.554(12)	1.516(2)
C-6–O-6	1.440(5)	1.435(10)	1.430(9)	1.418(11)	1.432(2)
O-2–C-7	1.469(5)	1.421(10)	1.452(10)	1.415(10)	1.447(2)
O-3–C-7	1.428(5)	1.421(10)	1.416(10)	1.442(12)	1.425(2)
O-4–C-10	1.429(6)	1.446(10)	1.444(11)	1.447(11)	
O-5–C-10	1.426(6)	1.412(11)	1.416(10)	1.437(11)	
Valence angles					
C-1–O-1–S	115.1(3)	116.8(5)	116.7(5)	114.9(5)	116.6(2)
O-1–S–O-7	100.6(3)	101.2(4)	102.9(4)	103.0(4)	102.1(2)
O-1–S–O-8	107.9(3)	106.1(4)	105.4(3)	104.4(3)	106.1(2)
O-1–S–O-9	104.3(3)	106.8(4)	104.0(4)	107.0(4)	105.5(2)
O-7–S–O-8	115.1(4)	112.5(4)	115.4(4)	113.4(4)	115.8(2)
O-7–S–O-9	113.3(3)	114.3(4)	113.5(4)	113.2(4)	113.2(2)
O-8–S–O-9	113.9(3)	114.5(4)	113.9(4)	114.6(4)	112.6(2)
O-1–C-1–C-2	109.0(4)	109.0(7)	108.3(6)	109.1(6)	106.1(2)
C-1–C-2–C-3	114.9(4)	116.1(7)	110.3(6)	116.0(7)	114.7(2)
C-2–C-3–C-4	112.1(4)	113.4(7)	116.9(7)	111.6(7)	115.8(2)
C-3–C-4–C-5	112.8(4)	113.4(7)	115.5(6)	113.9(8)	108.7(2)
C-4–C-5–C-6	111.4(4)	112.6(7)	112.4(7)	110.5(8)	110.0(2)
C-5–C-6–O-6	111.3(4)	111.7(7)	109.6(6)	110.1(8)	110.1(2)
C-6–O-6–C-2	112.2(4)	113.3(6)	112.8(6)	113.0(7)	114.9(2)
O-6–C-2–C-3	114.5(4)	113.2(6)	113.1(7)	115.5(8)	113.2(3)
C-2–O-2–C-7	109.2(4)	110.6(6)	110.0(6)	109.4(7)	109.1(2)
O-2–C-7–O-3	103.9(4)	104.3(7)	104.5(7)	106.6(7)	105.2(2)
C-7–O-3–C-3	107.1(4)	106.7(7)	109.3(6)	104.4(7)	108.8(2)
O-3–C-3–C-2	105.1(4)	102.5(7)	102.9(6)	104.5(7)	101.4(2)
C-3–C-2–O-2	103.0(4)	103.2(6)	104.9(7)	103.3(6)	101.9(2)
C-4–O-4–C-10	109.4(4)	110.0(7)	106.7(6)	108.3(7)	
O-4–C-10–O5	106.5(4)	105.7(7)	104.1(7)	105.3(7)	
C-10–O-5–C-5	110.7(4)	110.0(7)	106.5(6)	110.5(7)	
O-5–C-5–C-4	103.5(4)	102.5(7)	103.4(6)	105.0(7)	114.7(2)
C-5–C-4–O-4	103.0(4)	102.7(7)	105.4(6)	103.1(7)	109.8(2)
Torsion angles					
C-1–O-1–S–O-7	−173.2(4)	175.1(6)	139.4(6)	170.8(6)	177.9(2)
C-1–O-1–S–O-8	65.8(5)	57.5(6)	18.1(7)	52.2(6)	56.3(2)
C-1–O-1–S–O-9	−55.6(4)	−65.0(6)	−102.0(6)	−69.6(6)	−63.5(2)
C-2–C-1–O-1–S	−147.6(4)	−177.9(5)	169.9(6)	153.4(6)	172.9(2)
O-1–C-1–C-2–O-6	66.4(5)	169.0(6)	59.6(8)	174.0(6)	57.2(2)

Table 2 (*Continued*)

	1a	**1b**			**2**
		Anion **A**	Anion **B**	Anion **C**	
C-6–O-6–C-2–C-1	165.5(4)	166.6(7)	164.6(6)	166.4(7)	83.1(2)
O-6–C-2–C-3–C-4	22.1(5)	16.8(11)	7.5(9)	21.1(11)	40.8(2)
C-2–C-3–C-4–C-5	−50.5(5)	−47.6(11)	−29.8(10)	−49.5(11)	−44.1(2)
C-3–C-4–C-5–C-6	20.7(5)	22.2(11)	3.1(9)	20.5(11)	54.2(2)
C-4–C-5–C-6–O-6	36.8(5)	32.9(10)	45.7(9)	36.4(10)	−63.0(2)
C-2–O-6–C-6–C-5	−69.0(5)	−67.8(9)	−73.0(8)	−69.0(9)	60.2(2)
C-6–O-6–C-2–C-3	36.7(5)	40.3(10)	43.9(8)	38.3(10)	−48.4(2)
C-7–O-3–C-3–C-2	−33.3(4)	−33.8(8)	−24.8(7)	−34.1(8)	−31.0(2)
C-3–O-3–C-7–O-2	33.7(4)	35.6(8)	30.3(7)	32.0(8)	13.9(2)
C-2–O-2–C-7–O-3	−20.8(5)	−22.6(9)	−23.5(7)	−16.5(9)	11.1(2)
C-7–O-2–C-2–C-3	1.2(5)	1.8(9)	8.3(7)	4.5(9)	−29.3(2)
O-2–C-2–C-3–O-3	19.2(5)	19.1(8)	9.7(7)	24.0(9)	36.2(2)
C-4–O-4–C-10–O-5	14.6(5)	10.8(9)	36.2(8)	25.0(9)	
C-5–O-5–C-10–O-4	2.9(5)	9.8(9)	−10.4(10)	−36.5(8)	
C-10–O-5–C-5–C-4	−17.4(5)	−24.4(9)	22.9(8)	−6.5(10)	
O-4–C-4–C-5–O-5	25.1(5)	29.5(8)	−0.7(8)	21.2(10)	55.2(3)
C-10–O-4–C-4–C-5	−24.6(5)	−25.0(8)	−21.3(8)	−28.2(9)	

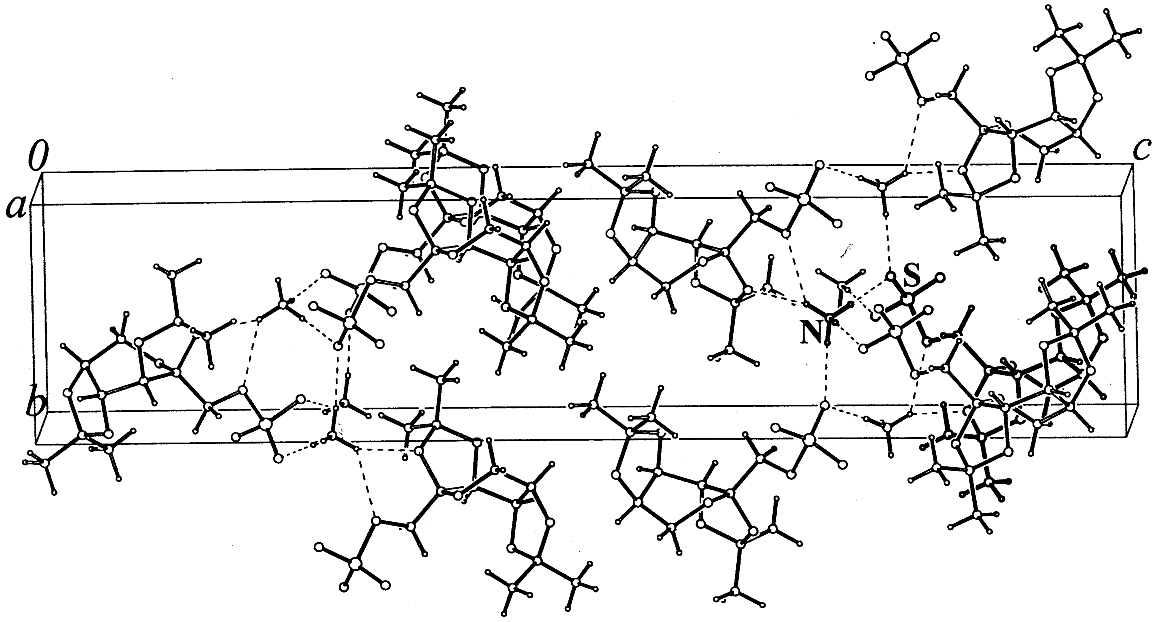

Fig. 2. The packing and hydrogen bonds in crystal of ammonium 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose 1-sulfate.

Table 3
Geometry of proposed hydrogen bonds in crystal of **1a**

Donor	H	Acceptor	H···O (Å)	N···O (Å)	N–H···O (°)
N	H-1N	O-1^{i}	2.37(3)	3.047(5)	134(3)
N	H-1N	O-2^{i}	2.22(3)	3.010(5)	150(4)
N	H-2N	O-7^{ii}	1.99(2)	2.812(6)	156(4)
N	H-3N	O-9	1.94(2)	2.803(6)	169(4)
N	H-4N	O-9^{iii}	2.00(2)	2.850(5)	162(4)

Symmetry codes: (i) $1-x$, $y-0.5$, $1.5-z$; (ii) $1+x$, y, z; (iii) $1-x$, $0.5+y$, $1.5-z$.

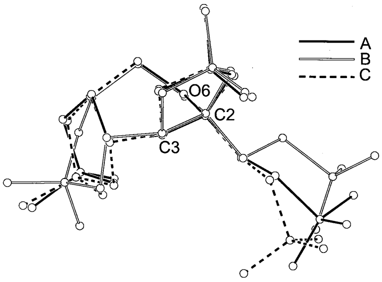

Fig. 3. Overlapped structures of three crystallographically independent anions in the crystal of potassium 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose 1-sulfate hemihydrate (**1b**). The H atoms and part of numbering were omitted for clarity. Numbering scheme used is the same as in **1a**.

Table 4
Shortest K···O and K···K distances (Å) in crystal of **1b**

K-1···O-7A	2.979(6)	K-3···O-2W	2.860(11)
K-1···O-8A	3.247(6)	K-3···O-7A^{ii}	2.865(6)
K-1···O-1B	2.931(6)	K-3···O-8A	2.764(6)
K-1···O-2B	3.117(5)	K-3···O-9A^{ii}	3.228(6)
K-1···O-7B^{i}	2.703(6)	K-3···O-1B^{iii}	2.896(6)
K-1···O-9B	3.102(6)	K-3···O-6B^{iii}	2.932(6)
K-1···O-8B^{iv}	2.814(6)	K-3···O-7B	3.322(6)
K-1···O-9B^{iv}	3.089(6)	K-3···O-7B^{iii}	3.184(6)
K-1···O-7C	3.035(6)	K-3···O-9B	2.900(6)
K-1···O-8C	2.737(6)	K-3···O-8B^{i}	2.733(6)
K-2···O-1W	2.692(3)	K-1···K-2	4.143(3)
K-2···O-7A^{ii}	2.710(6)	K-1···K-2^{iv}	4.110(3)
K-2···O-8A	2.712(6)	K-1···K-3	4.657(3)
K-2···O-9B	3.124(6)	K-1···K-3^{iv}	4.453(3)
K-2···O-7C^{ii}	2.784(6)	K-1···K-3^{i}	4.092(3)
K-2···O-8C	2.669(5)	K-2···K-3	4.007(3)
K-2···O-9C^{ii}	2.940(6)		

Symmetry codes: (i) $x-0.5$, $0.5-y$, $-z$; (ii) $1+x$, y, z; (iii) $0.5+x$, $0.5-y$, $-z$; (iv) $x-1$, y, z.

The pyranose rings of **A**, **B** and **C** anions adopt $^{2}S_{0}$ twist boat conformation, but conformation of **B** anion is slightly more distorted towards $^{2}H_{3}$ than those of **A** and **C** (Table 1). Isopropylidene rings at C-2, C-3 in all three anions adopt distorted envelope conformations ^{2}E, whereas the conformations of 4,5-isopropylidene rings vary from $^{4}T_{3}$ in **A** and $^{4}T_{0}$ in **C** to ^{1}E in **B**.

In addition to the above mentioned differences in pyranose ring conformations, the **B** anion differs from **A** and **C** by geometry and orientation of the sulfate group (Fig. 3). The most noticeable differences are values of O-1–C-1–C-2–O-6 and C-2–C-1–C-2–S torsion angles (Table 2). The value of O-1–C-1–C-2–O-6 is similar to that found in **1a**. Sulfate groups in **A** and **C** adopt staggered conformations, similar to **1a** and **2**, whereas the sulfate group **B** adopts a nearly eclipsed conformation.

The S–O-1 bonds of all three anions are equal within 3σ, but there are definite differences in S–O^{T} bonds—these ones range from 1.418(6) Å (S–O-7 in anion **C**) to 1.460(6) Å (S–O-9 in anion **A**) (Table 2).

The coordination numbers for K-1, K-2, and K-3 are 10, 7, and 10, respectively. The K···O distances range from 2.669(6) to 3.228(6) Å (Table 4). The K···K distances are relatively short and ranges from 4.007(3) to 4.657(3) Å (Table 4). The potassium ions and water molecules form one-dimensional, extending parallel to the *a*-axis, polymeric structure. The sulfate groups of anions points towards the above mentioned structure, while isopropylidene groups point away, so the overall shape, looking in direction *a*, resembles a honeycomb (Fig. 4).

No direct interactions between ‘pipes’ were observed. Despite both water molecules and O-9 atoms of **A** and **C** anions are involved in hydrogen bonds (Table 5), the K···O interactions are undoubtedly much more important for the stability of the crystal. These above explain why **1b** have a tendency to grow along the *a*-axis and to form very long, acicular crystals.

*Structure of ammonium 2,3-*O*-isopropylidene-β-*D*-fructopyranose 1-sulfate* (**2**).—The crystal consists of sulfated sugar anions, ammonium cations, and water molecules in 1:1:1 ratio. As it is shown in Fig. 5, the sugar ring adopts a distorted chair conformation [$\theta = 15.2(3)°$]. The five-membered ring adopts a twisted $^{4}T_{3}$ conformation (Table 1). The C-1 atom is located axially. The sulfate group adopts a staggered conformation with a value of C-1–O-1–S–O-7 torsion angle of 177.9(2)°. The values of O–S–O angles range from 102.1(2) to 115.8(2)° (Table 2).

The structure of the crystal is stabilized by extensive, three-dimensional hydrogen-bond networks (Fig. 6). All hydroxyl groups are engaged in two hydrogen bonds: both as a donor and as an acceptor. A water molecule is a donor of two hydrogen bonds (to O-2 and O-8 atoms) and an acceptor of another two hydrogen bonds: from the O–H group at C-4 atom and from NH_4^+. The NH_4^+ is engaged in six hydrogen bonds. The H-1N and H-4N are involved in bifurcated hydrogen bonds. Apart from the hydrogen bonds, weak interactions of C–H···O type are observed in the structure (Fig. 7). These interactions seem to be of special importance in view of structural stabilization along the *b*-axis. The geometry of proposed hydrogen bonds and short contacts is presented in Table 6.

Structural comparison.—There are no significant differences in values of O^{T}–S–O^{T} angles. O^{E}–S–O^{T} angles,[‡] in which O^{T} is trans located, are generally smaller than all other O–S–O angles. The above are in good agreement with those observed in structures of other sulfate esters.[8] The conformations of the sugar moieties of anions in **1a** and **1b** are similar and puckering parameters are very similar to these calculated for 2,3-*O*-isopropylidene-β-D-fructopyranose.[11] The most noticeable

---

[‡] O^{E} = ester O atom.

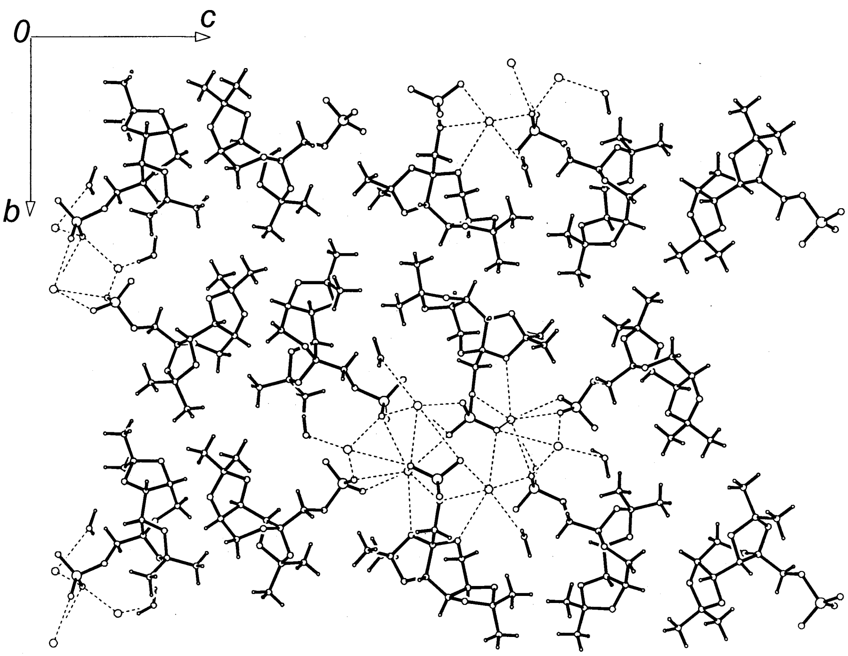

Fig. 4. Honeycomb-like structure in the crystal of potassium 2,3:4,5-di-O-isopropylidene-β-D-fructopyranose 1-sulfate hemihydrate. K···O interactions were marked as dashed lines.

Table 5
Geometry of proposed hydrogen bonds in **1b**

O	H	O	H···O (Å)	O···O (Å)	O–H···O (°)
O-1W	H-1W	O-9C	2.04(7)	2.829(8)	138(9)
O-1W	H-2W	O-2A	1.88(2)	2.829(8)	171(9)
O-2W	H-3W	O-5B^{iii}	2.43(17)	2.876(13)	108(12)
O-2W	H-4W	O-9A^{ii}	1.94(6)	2.871(11)	163(16)

Symmetry codes: (ii) $1+x$, y, z; (iii) $0.5+x$, $0.5-y$, $-z$.

difference is observed in the geometry of rings formed by isopropylidene groups at C-4, C-5. Two different orientations of sulfate groups are observed in anions of diisopropylidene derivatives. Fig. 8 shows a comparison of the geometries of all described anions of the diisopropylidene derivative. The structure of **1b** is the only one known to date, where the sulfate group does not adopt a staggered conformation.[8] The differences described above between the orientations of the sulfate group are undoubtedly the consequence of K···O interactions (Table 4). The O atoms of anion **A**, **B**, and **C** are involved in 7, 13, and 5 K···O contacts, respectively. These numerous and strong interactions force the sulfate group of **B** to assume an unfavorable eclipsed conformation (Fig. 9).

3. Experimental

Preparation of ammonium (**1a**) *and potassium* (**1b**) *salts of 2,3:4,6-di-*O*-isopropylidene-β-*D*-fructopyranose 1-sulfate.*—1 g of 2,3:4,5-Di-O-isopropylidene-β-D-fructopyranose,[12] 0.5 mL of pyridine, 1 g of finely powdered pyridine–sulfur trioxide complex,[13] and 50 mL of benzene were placed in a 75 mL round-bottomed flask, arranged so that the contents could be warmed and stirred under anhydrous conditions. The mixture was heated to 55 °C and stirred vigorously until the complex disappeared (~ 2 h). The mixture was cooled

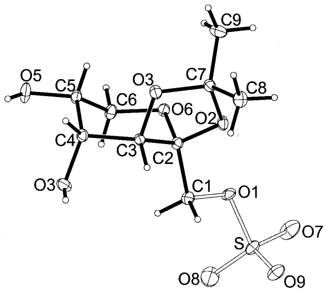

Fig. 5. Molecular structure and numbering scheme of the 2,3-O-isopropylidene-β-D-fructopyranose 1-sulfate anion in the crystal of **2**. The thermal ellipsoids are given with 50% probablility.

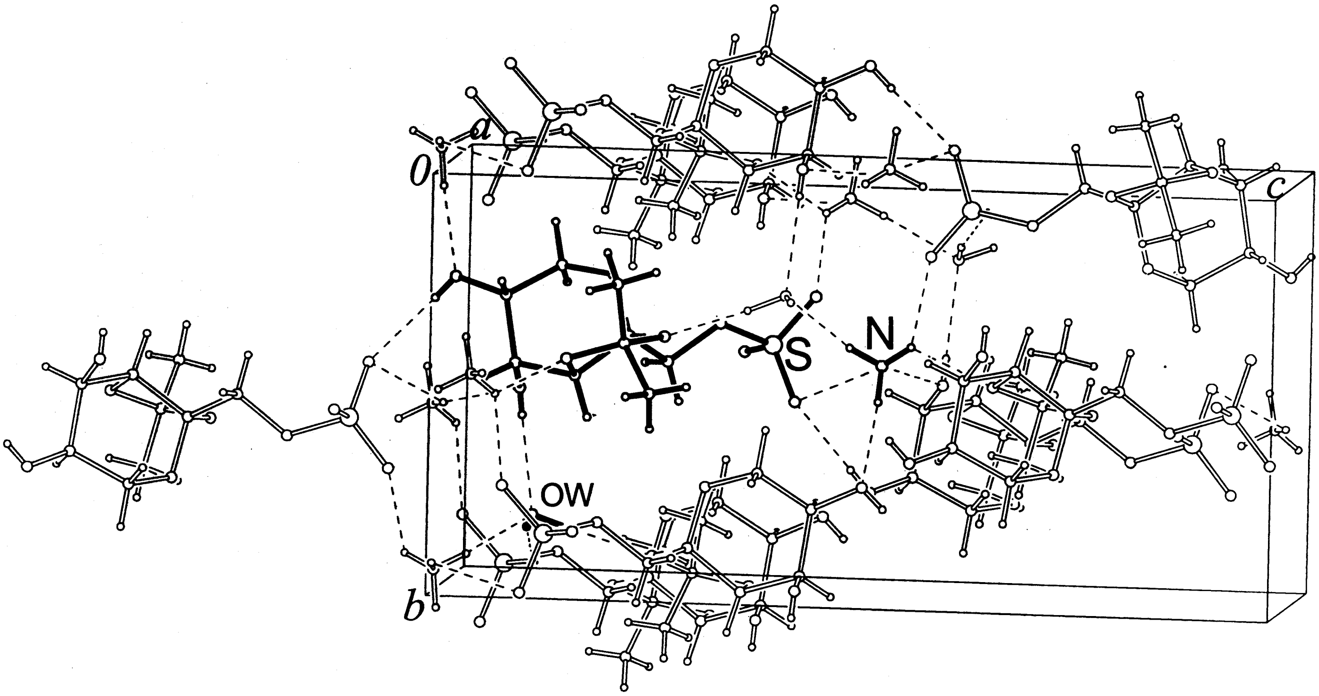

Fig. 6. Packing and hydrogen bonds in the crystal of ammonium 2,3-*O*-isopropylidene-β-D-fructopyranose 1-sulfate hydrate.

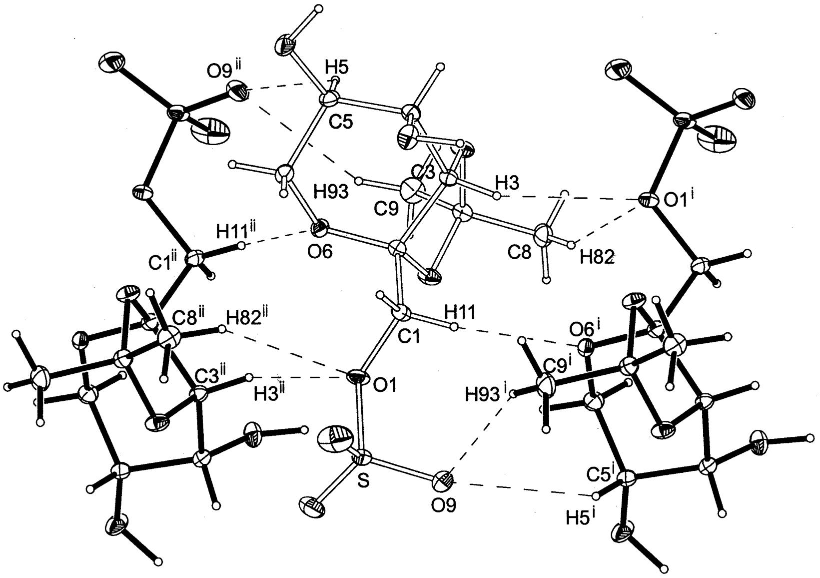

Fig. 7. The C–H···O interactions in the structure of ammonium 2,3-*O*-isopropylidene-β-D-fructopyranose 1-sulfate hydrate (symmetry codes: (i) $1-x$, $0.5+y$, $0.5-z$; (ii) $1-x$, $-0.5+y$, $0.5-z$).

and then the solvents removed in a stream of nitrogen. The yellowish residue was washed thoroughly several times with *n*-hexane (totaling ~ 120 mL), then dissolved in water and excess finely powdered $BaCO_3$ added. The suspension was vigorously stirred for a few hours and filtered with suction through a layer of Celite. The filtrate was evaporated in a stream of nitrogen. The barium salt of 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose 1-sulfate obtained was dissolved in the minimal quantity of water and passed through a column (3 × 40 cm) of Dowex-50X2 (H^+ form, 100 mesh, Acros-Chimica). The eluate was immediately neutralized with a small excess of NH_3(aq) and evaporated. The resulting viscous oil turned into crystals within few hours with a yield of crystalline ammonium salt (1.13 g, 82%). A test with $Ba(OH)_2$ showed that final product was free from inorganic sulfates.

Table 6
Geometry of proposed hydrogen bonds and C–H···O interactions in crystal **2**

D	H	A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
O-W	H-1W	O-2^{i}	0.93(3)	1.93(3)	2.860(2)	171(3)
O-W	H-2W	O-8^{vi}	0.79(3)	1.98(3)	2.762(3)	167(3)
O-4	H-40	O-W	0.61(4)	2.23(4)	2.836(2)	177(5)
O-5	H-50	O-9^{iii}	0.67(3)	2.09(3)	2.751(2)	166(4)
N	H-1N	O-3^{iv}	0.85(4)	2.26(3)	2.870(2)	129(3)
N	H-1N	O-7^{v}	0.85(4)	2.20(3)	2.888(3)	139(3)
N	H-2N	O-W^{ii}	0.82(5)	2.15(5)	2.912(3)	153(4)
N	H-3N	O-5^{i}	0.89(4)	2.05(4)	2.933(3)	174(3)
N	H-4N	O-4^{vii}	0.91(4)	2.38(4)	3.189(3)	149(3)
N	H-4N	O-9	0.91(4)	2.44(4)	2.955(3)	116(3)
C-1	H-11	O-6^{i}	0.93(3)	2.41(3)	3.278(3)	156(3)
C-3	H-3	O-1^{i}	0.96(3)	2.63(3)	3.497(3)	149(2)
C-5	H-5	O-9^{ii}	0.90(3)	2.75(3)	3.414(3)	131(2)
C-8	H-82	O-1^{i}	0.94(3)	2.59(3)	3.459(3)	153(3)
C-9	H-93	O-9^{ii}	0.86(3)	2.73(3)	3.536(3)	155(3)

Symmetry codes: (i) $1-x, 0.5+y, 0.5-z$; (ii) $1-x, y-0.5, 0.5-z$; (iii) $0.5-x, 1-y, z-0.5$; (iv) $1.5-x, 1-y, 0.5+z$; (v) $0.5+x, 0.5-y, 1-z$; (vi) $-x, 0.5+y, 0.5-z$; (vii) $0.5-x, 1-y, 0.5+z$.

The potassium salt was prepared in an analogous way, but instead of aqueous ammonia, a solution of $KHCO_3$ in water was used for neutralization of the acidic eluate. Slow evaporation of water gave long, very thin (they did not exceed of 0.005 mm thickness) needles. Crystals of sufficient quality were obtained by slow diffusion of EtOH to the dilute solution of the salt.

Preparation of ammonium 2,3-O-isopropylidene-β-D-fructopyranose 1-sulfate (**2**).—0.5 g of **1a** was dissolved in a minimal quantity of water and passed through a column of Dowex (as described above). The acidic eluate was made up to 200 mL of water. The solution was heated (50 °C) for 24 h, neutralized by minimal excess of NH_3(aq), and evaporated under nitrogen yielding a viscous syrup, that crystallized within the next few days as the monohydrate salt.

Summary of synthesis.—To ensure that all of the 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose was utilized in the sulfonation reaction, a significant excess of pyridine–SO_3 complex was used. Our attempts at crystallization of different sugars sulfate esters showed that purity and absence of the free sugar are crucial for crystal forming. The unconverted complex was decomposed to pyridinium salt and inorganic sulfate by reaction with water and the resulting inorganic sulfates were precipitated as the barium salt. As the sugar sulfates are oxygen-sensitive in alkaline conditions, a $BaCO_3$ suspension was used instead of the usual $Ba(OH)_2$ solution. The final product, recrystallized from water, was a polyhydrate of barium 2,3:4,5-di-*O*-

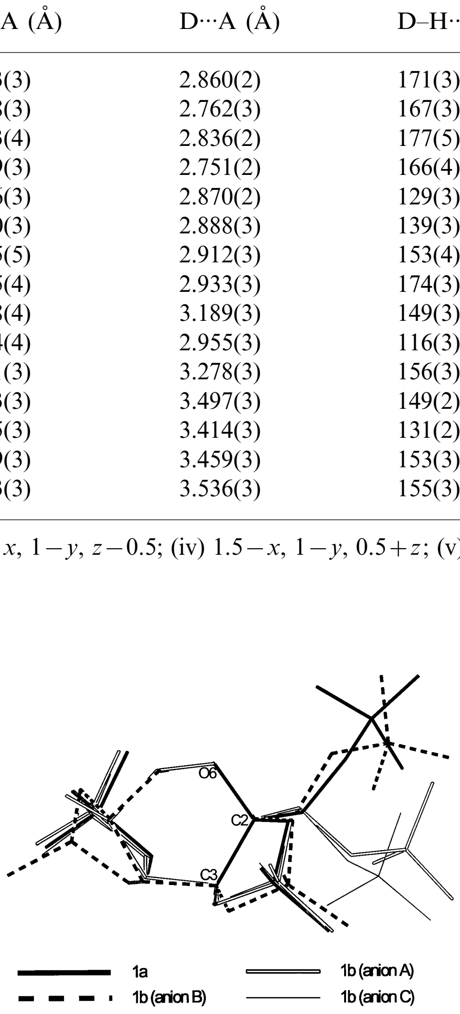

Fig. 8. Comparison of anions geometry in structures of **1a** and **1b**. C-2, C-3 and C-6 atoms were used to fit the moieties.

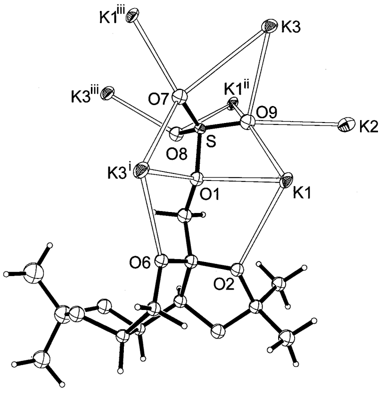

Fig. 9. The K···O interactions formed by oxygen atoms of anion **B** in the crystal of potassium 2,3:4,5-di-*O*-isopropylidene-β-D-fructopyranose 1-sulfate hemihydrate (symmetry codes: (i) $x-0.5, 0.5-y, -z$; (ii) $1+x, y, z$; (iii) $0.5+x, 0.5-y, -z$).

Table 7
Crystal data, particulars of analysis and data refinement for **1a**, **1b**, and **2**

	1a	**1b**	**2**
Empirical formula	$C_{12}H_{23}NO_9S$	$C_{12}H_{20}KO_{9.5}S$	$C_9H_{21}NO_{10}S$
Molecular weight	357.37	387.44	335.33
Dimensions of crystal (mm)	0.5 × 0.25 × 0.3	0.9 × 0.1 × 0.14	0.3 × 0.2 × 0.2
Temperature of measurements (K)	120(1)	120(1)	150(1)
Wavelength (Å)	0.71069	0.71073	0.71073
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	6.054(5)	6.057(3)	7.946(5)
b (Å)	7.725(5)	17.899(5)	9.368(5)
c (Å)	34.76(3)	46.37(2)	18.696(5)
V (Å^3)	1626(3)	5027(4)	1391.7(12)
Z	4	12	4
$D_{\text{calcd.}}$ (g/cm^3)	1.460	1.536	1.600
D_{measured} (g/cm^3) (flotation in room temperature)	1.44 ($C_6H_5CH_3$–CCl_4)	1.52 ($CHCl_3$–C_2H_5I)	1.54 ($CHCl_3$–C_2H_5I)
Linear absorption coefficient (mm^{-1})	0.245	0.487	0.285
$F(000)$	760	2436	712
θ Range (°)	2 → 30	2 → 25	2 → 30
h, k, l range	$-8 \leq h \leq 8$ $-10 \leq k \leq 10$ $-48 \leq l \leq 48$	$-7 \leq h \leq 7$ $0 \leq k \leq 21$ $0 \leq l \leq 55$	$-11 \leq h \leq 11$ $0 \leq k \leq 13$ $0 \leq l \leq 26$
Total data measured	3217	4954	3696
Unique data	2904	4843	3466
Data with $I > 2\sigma(I)$	2136	2926	2995
R_{int}	0.0272	0.0633	0.0246
R [$I > 2\sigma(I)$]	0.0593	0.0465	0.0295
$(\Delta\rho)_{\min}$ (e/Å^3)	−0.41	−0.41	−0.24
$(\Delta\rho)_{\max}$ (e/Å^3)	0.53	0.48	0.32

isopropylidene-β-D-fructopyranose 1-sulfate.[§] As the acidic form of the compound resulted from passing the barium salt through the column filled with H^+ form of the ion-exchanging resin, simple autocatalytic removal of the isopropylidene group was carried out and addition of strong acid was not necessary.

X-ray crystallography.—The approximate unit cell dimensions were determined by the preliminary oscillation and Weissenberg photographs. X-ray data were collected using Kuma-diffraction KM4 diffractometer (κ geometry, $\omega/2\theta$ scan, Mo K_α radiation, graphite monochromator) and Oxford cooling device. All structures were solved by direct methods.[14] The absolute configuration of all compounds was defined based on the known stereochemistry of D-fructose. Processing of crystal data and refinements for all crystals are given in Table 7.

Crystal of **1a**.—The crystal was readily available from synthesized material. Its lattice constants were determined based on 65 reflections. The intensities of three reference reflections were measured every 100 reflections—no significant changes in values were observed. The positions of N-bonded H atoms were found from difference-Fourier map. The remaining H-atoms were set into calculated positions. The lengths of all N–H bonds were fixed at 0.88 Å by means of DFIX instruction. All H-atoms were refined with U_{iso} greater (20%) than that of the parent atom. The full-matrix least-squares[15] was completed using anisotropic parameters for all non-hydrogen atoms. The final atomic parameters for **1a** are given in Tables 8 and 9.

Crystal of **1b**.—Crystals suitable for X-ray studies were obtained by slow diffusion of EtOH to the dilute solution of the compound. Cell parameters were determined on the basis of 57 reflections. Experimental data were corrected for absorption[16] ($T_{\min} = 0.718$, $T_{\max} = 0.954$). Due to relatively low reflection/parameter ratio,[¶] only potassium, sulfur, and O-1W and O-2W atoms were refined anisotropically.[15] Positions of C-bonded H-atoms were set into calculated positions. All other

---

[§] Conclusive proof was obtained in our laboratory by X-ray crystallography, however crystals were of too poor quality to determine number and positions of all water molecules in the asymmetric unit.

[¶] Despite many attempts, it was very difficult to grow both large and good quality crystal. This was, reciprocally with large unit cell dimensions, given the weak diffracting ability and problems with coinciding of the reflections.

H-atoms were located at Fourier differences. All H-atoms were included with temperature factors 20% greater than U_{eq} of the parent atom. Values of O–H bonds in water molecules were assumed as 0.96 Å by means of DFIX instruction. The final atomic parameters are given in Tables 10 and 11. The refinement process showed that occupancy factors for O-2W, H-3W, and H4-W atoms (one of two water molecules) are equal 0.5.

Crystal of **2**.—The crude product of synthesis was slowly recrystallized from water. Lattice constants were determined based on 50 reflections. Three reference reflections were measured every 100 data measured and no decay of reference reflections was observed. The

Table 8
Atomic coordinates and equivalent isotropic parameters for **1a**

	x	y	z	U_{eq}/U_{iso} (Å^2)
S	0.1933(2)	0.53325(14)	0.79290(3)	0.0201(3)
O-1	0.3263(6)	0.6934(4)	0.81158(9)	0.0229(7)
O-2	0.5229(5)	0.9549(4)	0.85016(9)	0.0198(7)
O-3	0.7619(5)	0.9555(4)	0.90092(9)	0.0200(7)
O-4	0.5369(6)	0.5465(4)	0.93274(9)	0.0226(7)
O-5	0.2913(8)	0.6853(4)	0.97213(10)	0.0291(8)
O-6	0.2798(5)	0.8018(4)	0.88805(9)	0.0184(6)
O-7	0.0801(8)	0.6201(5)	0.76157(12)	0.0396(11)
O-8	0.0530(8)	0.4628(7)	0.82182(13)	0.0470(11)
O-9	0.3664(7)	0.4144(5)	0.77990(11)	0.0306(9)
C-1	0.4783(9)	0.6477(6)	0.84148(13)	0.0218(9)
C-2	0.4887(7)	0.7919(6)	0.86997(13)	0.0182(8)
C-3	0.6859(8)	0.7837(5)	0.89793(13)	0.0189(8)
C-4	0.6186(8)	0.7195(6)	0.93735(13)	0.0183(8)
C-5	0.4167(7)	0.8177(6)	0.95392(14)	0.0187(9)
C-6	0.2856(7)	0.9057(6)	0.92244(12)	0.0179(8)
C-7	0.7266(7)	1.0358(6)	0.86443(13)	0.0194(8)
C-8	0.9124(7)	0.9984(7)	0.83666(16)	0.0275(11)
C-9	0.6845(10)	1.2256(6)	0.87002(15)	0.0279(10)
C-10	0.3574(8)	0.5187(6)	0.95872(14)	0.0226(10)
C-11	0.1695(9)	0.4321(6)	0.93720(16)	0.0278(10)
C-12	0.4418(9)	0.4152(7)	0.99286(16)	0.0307(12)
N	0.6709(7)	0.5479(5)	0.72685(11)	0.0211(7)
H-1	0.6266(9)	0.6270(6)	0.83041(13)	0.0261
H-11	0.4289(9)	0.5401(6)	0.85433(13)	0.0261
H-3	0.8046(8)	0.7081(5)	0.88709(13)	0.0227
H-4	0.7460(8)	0.7226(6)	0.95564(13)	0.0220
H-5	0.4663(7)	0.9049(6)	0.97336(14)	0.0225
H-6	0.1328(7)	0.9264(6)	0.93151(12)	0.0215
H-61	0.3531(7)	1.0193(6)	0.91652(12)	0.0215
H-800	0.8822(7)	1.0555(7)	0.81204(16)	0.0331
H-801	0.9240(7)	0.8732(7)	0.83264(16)	0.0331
H-802	1.0515(7)	1.0422(7)	0.84728(16)	0.0331
H-900	0.6603(10)	1.2805(6)	0.84495(15)	0.0335
H-901	0.8125(10)	1.2788(6)	0.88260(15)	0.0335
H-902	0.5533(10)	1.2414(6)	0.88614(15)	0.0335
H-110	0.2173(9)	0.3179(6)	0.92817(16)	0.0334
H-111	0.1272(9)	0.5036(6)	0.91510(16)	0.0334
H-112	0.0424(9)	0.4188(6)	0.95442(16)	0.0334
H-120	0.4881(9)	0.3001(7)	0.98419(16)	0.0368
H-121	0.3239(9)	0.4035(7)	1.01199(16)	0.0368
H-122	0.5680(9)	0.4753(7)	1.00443(16)	0.0368
H-1N	0.652(7)	0.490(5)	0.7053(6)	0.0253
H-2N	0.811(2)	0.545(5)	0.7333(11)	0.0253
H-3N	0.591(6)	0.500(5)	0.7452(8)	0.0253
H-4N	0.629(6)	0.656(2)	0.7234(11)	0.0253

Table 9
Anisotropic thermal parameters for **1a**

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S	0.0178(4)	0.0217(5)	0.0207(5)	−0.0044(4)	−0.0004(6)	−0.0027(5)
O-1	0.0303(16)	0.0196(14)	0.0187(17)	0.0047(11)	−0.0076(15)	−0.0026(13)
O-2	0.0197(14)	0.0181(13)	0.0214(18)	0.0011(12)	−0.0085(13)	−0.0004(13)
O-3	0.0199(14)	0.0213(14)	0.0188(16)	0.0001(12)	−0.0013(11)	−0.0037(12)
O-4	0.029(15)	0.0178(14)	0.0210(17)	−0.0024(12)	0.0057(14)	0.0002(13)
O-5	0.043(2)	0.0241(17)	0.0202(18)	0.0008(12)	0.0149(18)	−0.0058(16)
O-6	0.0177(14)	0.0210(14)	0.0166(16)	−0.0044(11)	−0.0030(13)	0.0041(11)
O-7	0.054(3)	0.0330(19)	0.032(3)	−0.0076(15)	−0.027(3)	0.0003(17)
O-8	0.048(3)	0.052(3)	0.041(3)	−0.005(2)	0.024(3)	−0.025(3)
O-9	0.043(3)	0.0244(17)	0.024(3)	−0.0073(13)	−0.0067(16)	0.0012(13)
C-1	0.031(3)	0.0192(19)	0.015(3)	−0.0050(15)	−0.010(2)	0.0043(16)
C-2	0.0160(18)	0.0215(19)	0.017(3)	0.0012(15)	−0.0008(16)	0.0034(15)
C-3	0.0198(18)	0.0159(17)	0.021(3)	−0.0030(14)	−0.001(2)	0.0010(16)
C-4	0.0199(18)	0.0207(19)	0.014(3)	−0.0028(15)	−0.0033(16)	0.0042(15)
C-5	0.0189(19)	0.018(2)	0.019(3)	−0.0031(15)	0.0035(17)	−0.0015(15)
C-6	0.0095(16)	0.0278(19)	0.016(3)	−0.0043(14)	0.0031(16)	0.0024(15)
C-7	0.0148(17)	0.0238(19)	0.019(3)	0.0032(16)	−0.0017(15)	0.0018(17)
C-8	0.0130(17)	0.038(3)	0.032(3)	0.0118(19)	0.0064(18)	−0.0003(16)
C-10	0.030(3)	0.019(2)	0.019(3)	0.0012(15)	−0.0014(17)	−0.0039(16)
C-11	0.027(3)	0.022(3)	0.035(3)	−0.0039(17)	−0.007(3)	−0.0017(18)
C-12	0.028(3)	0.036(3)	0.027(3)	0.0102(19)	−0.006(3)	0.0013(19)
N	0.0199(16)	0.0205(16)	0.023(2)	−0.0049(14)	−0.0012(16)	−0.0002(16)

Table 10
Atomic coordinates and equivalent isotropic parameters for **1b**

	x	y	z	U_{eq}/U_{iso} (Å^2)
K-1	0.1314(3)	0.18086(9)	0.05232(4)	0.0174(4)
K-2	0.6351(3)	0.24605(10)	0.10728(4)	0.0219(4)
K-3	0.6568(3)	0.36486(10)	0.03409(4)	0.0207(4)
O-1W	0.4093(9)	0.2801(4)	0.1555(2)	0.0309(16)
O-2W*	0.6890(16)	0.4902(6)	0.0721(3)	0.022(3)
H-1W	0.303(12)	0.261(6)	0.142(2)	0.037
H-2W	0.362(16)	0.330(2)	0.159(3)	0.037
H-3W	0.726(11)	0.538(4)	0.080(4)	0.027
H-4W	0.827(7)	0.464(5)	0.071(4)	0.027
Anion A				
S	0.1403(3)	0.37166(10)	0.07813(4)	0.0158(4)
O-1	0.1250(9)	0.4077(3)	0.10972(13)	0.0230(13)
O-2	0.2274(8)	0.4222(3)	0.16775(13)	0.0195(13)
O-3	−0.0257(9)	0.5067(4)	0.18125(13)	0.0214(12)
O-4	0.1876(8)	0.6377(4)	0.12965(13)	0.0231(13)
O-5	0.4029(9)	0.6927(4)	0.16392(14)	0.0304(15)
O-6	0.4585(8)	0.5205(3)	0.15539(13)	0.0190(12)
O-7	−0.0430(9)	0.3207(4)	0.07868(13)	0.0204(12)
O-8	0.3528(9)	0.3333(4)	0.07685(13)	0.0246(13)
O-9	0.1168(10)	0.4315(4)	0.05803(14)	0.0275(14)
C-1	0.2975(12)	0.4583(5)	0.11778(19)	0.0198(18)
C-2	0.2594(12)	0.4839(5)	0.14836(19)	0.0190(17)
C-3	0.0517(13)	0.5329(5)	0.1535(2)	0.0205(18)
C-4	0.1027(13)	0.6141(5)	0.1565(2)	0.024(2)
C-5	0.2955(12)	0.6302(5)	0.1773(2)	0.0229(19)
C-6	0.4440(12)	0.5644(5)	0.1812(2)	0.0210(18)

Table 10 (*Continued*)

	x	*y*	*z*	U_{eq}/U_{iso} (Å^2)
C-7	0.0232(13)	0.4292(5)	0.1826(3)	0.0208(18)
C-8	−0.1556(15)	0.3817(5)	0.1693(3)	0.032(3)
C-9	0.0637(15)	0.4069(6)	0.2138(3)	0.034(3)
C-10	0.3573(15)	0.6934(5)	0.1340(3)	0.0306(19)
C-11	0.2737(17)	0.7699(6)	0.1263(3)	0.043(3)
C-12	0.5571(14)	0.6699(6)	0.1166(3)	0.034(3)
H-1	0.2982(12)	0.5010(5)	0.10490(19)	0.0237
H-11	0.4396(12)	0.4335(5)	0.11633(19)	0.0237
H-3	−0.0593(13)	0.5244(5)	0.1385(2)	0.0246
H-4	−0.0292(13)	0.6426(5)	0.1618(2)	0.0287
H-5	0.2365(12)	0.6455(5)	0.1961(2)	0.0275
H-6	0.5903(12)	0.5817(5)	0.1865(2)	0.0252
H-61	0.3885(12)	0.5336(5)	0.1968(2)	0.0252
H-8	−0.2902(15)	0.3881(5)	0.1799(3)	0.0382
H-81	−0.1121(15)	0.3302(5)	0.1698(3)	0.0382
H-82	−0.1783(15)	0.3967(5)	0.1496(3)	0.0382
H-9	−0.0716(15)	0.4111(6)	0.2245(3)	0.0412
H-91	0.1726(15)	0.4394(6)	0.2221(3)	0.0412
H-92	0.1155(15)	0.3563(6)	0.2146(3)	0.0412
H-810	0.5211(14)	0.6709(6)	0.0964(3)	0.0404
H-811	0.6000(14)	0.6202(6)	0.1220(3)	0.0404
H-812	0.6769(14)	0.7037(6)	0.1203(3)	0.0404
H-910	0.2416(17)	0.7717(6)	0.1060(3)	0.0520
H-911	0.3843(17)	0.8065(6)	0.1308(3)	0.0520
H-912	0.1419(17)	0.7804(6)	0.1370(3)	0.0520
Anion ***B***				
S	0.6451(3)	0.17044(9)	0.01369(4)	0.0127(4)
O-1	0.4513(8)	0.1084(3)	0.01402(13)	0.0170(12)
O-2	0.1928(7)	0.0084(3)	0.04770(12)	0.0152(12)
O-3	0.2518(9)	−0.1155(3)	0.05439(12)	0.0193(12)
O-4	0.4961(8)	−0.1567(4)	−0.01322(13)	0.0207(13)
O-5	0.2004(8)	−0.1287(4)	−0.04074(13)	0.0204(13)
O-6	0.1850(7)	−0.0050(3)	−0.00154(12)	0.0156(12)
O-7	0.5788(8)	0.2192(4)	−0.00914(14)	0.0202(13)
O-8	0.8467(9)	0.1293(3)	0.00867(12)	0.0194(12)
O-9	0.6324(9)	0.2043(3)	0.04187(13)	0.0216(13)
C-1	0.5176(13)	0.0328(5)	0.01825(19)	0.0193(18)
C-2	0.3131(11)	−0.0138(5)	0.02321(18)	0.0163(18)
C-3	0.3781(12)	−0.0976(5)	0.02920(17)	0.0154(16)
C-4	0.3213(11)	−0.1532(5)	0.00642(17)	0.0143(16)
C-5	0.1143(11)	−0.1347(5)	−0.01185(17)	0.0151(15)
C-6	0.0142(11)	−0.0598(5)	−0.00392(19)	0.0156(17)
C-7	0.2047(11)	−0.0490(5)	0.06975(19)	0.0166(18)
C-8	0.3899(12)	−0.0287(5)	0.09066(18)	0.0191(18)
C-9	−0.0156(13)	−0.0551(5)	0.0834(2)	0.0227(19)
C-10	0.3997(13)	−0.1700(5)	−0.0412(3)	0.029(3)
C-11	0.3530(15)	−0.2502(5)	−0.0472(2)	0.0273(19)
C-12	0.5547(16)	−0.1342(6)	−0.0632(3)	0.039(3)
H-1	0.6151(13)	0.0292(5)	0.0348(2)	0.0232
H-11	0.5963(13)	0.0148(5)	0.0014(2)	0.0232
H-3	0.5360(12)	0.1008(5)	0.0337(2)	0.0185
H-4	0.3019(11)	−0.2024(5)	0.0154(2)	0.0172
H-5	0.0044(11)	−0.1747(5)	−0.0105(2)	0.0181
H-6	-0.0908(11)	−0.0447(5)	−0.0186(2)	0.0188
H-61	-0.0638(11)	−0.0639(5)	0.0143(2)	0.0188

Table 10 (*Continued*)

	x	y	z	U_{eq}/U_{iso} (Å^2)
H-8	0.3523(12)	0.0165(5)	0.1006(2)	0.0229
H-81	0.5246(12)	−0.0214(5)	0.0801(2)	0.0229
H-82	0.4092(12)	−0.0684(5)	0.1044(2)	0.0229
H-9	−0.0474(13)	−0.0100(5)	0.0938(2)	0.0272
H-91	−0.0168(13)	−0.0967(5)	0.0964(2)	0.0272
H-92	−0.1254(13)	−0.0626(5)	0.0687(2)	0.0272
H-810	0.4890(15)	−0.2777(5)	−0.0475(2)	0.0328
H-811	0.2810(15)	−0.2548(5)	−0.0655(2)	0.0328
H-812	0.2587(15)	−0.2698(5)	−0.0324(2)	0.0328
H-910	0.6909(16)	−0.1616(6)	−0.0638(3)	0.0467
H-911	0.5839(16)	−0.0835(6)	−0.0577(3)	0.0467
H-912	0.4870(16)	−0.1350(6)	−0.0819(3)	0.0467
*Anion **C***				
S	0.0775(3)	0.14369(11)	0.12317(5)	0.0166(5)
O-1	0.1320(9)	0.0713(3)	0.14209(12)	0.0200(12)
O-2	0.2692(9)	−0.0491(4)	0.17521(14)	0.0240(13)
O-3	0.0400(10)	−0.0311(4)	0.21390(15)	0.0286(15)
O-4	0.2523(10)	0.1555(4)	0.22240(14)	0.0294(14)
O-5	0.5098(11)	0.1134(4)	0.25478(15)	0.0325(16)
O-6	0.5147(9)	0.0299(4)	0.19807(14)	0.0239(14)
O-7	−0.0988(9)	0.1193(4)	0.10538(14)	0.0267(14)
O-8	0.2790(8)	0.1582(3)	0.10741(13)	0.0204(13)
O-9	0.0144(9)	0.2020(4)	0.14301(13)	0.0227(13)
C-1	0.3292(13)	0.0765(5)	0.15921(19)	0.0205(18)
C-2	0.3077(12)	0.0260(5)	0.1850(2)	0.0192(18)
C-3	0.1109(14)	0.0412(5)	0.2049(2)	0.025(2)
C-4	0.1783(14)	0.0842(5)	0.2311(3)	0.025(3)
C-5	0.3821(14)	0.0513(5)	0.2470(3)	0.028(3)
C-6	0.5167(14)	0.0001(6)	0.2264(2)	0.027(2)
C-7	0.0812(13)	−0.0785(5)	0.1893(3)	0.028(3)
C-8	−0.1144(14)	−0.0808(6)	0.1692(3)	0.033(3)
C-9	0.1320(18)	−0.1557(6)	0.2014(3)	0.045(3)
C-10	0.4189(14)	0.1805(6)	0.2426(3)	0.032(3)
C-11	0.3156(17)	0.2280(7)	0.2668(3)	0.046(3)
C-12	0.5951(18)	0.2197(7)	0.2251(3)	0.053(4)
H-1	0.3508(13)	0.1277(5)	0.1655(2)	0.0246
H-11	0.4562(13)	0.0618(5)	0.1478(2)	0.0246
H-3	−0.0071(14)	0.0671(5)	0.1944(2)	0.0305
H-4	0.0535(13)	0.0890(5)	0.2445(3)	0.0306
H-5	0.3359(14)	0.0235(5)	0.2642(3)	0.0342
H-6	0.6677(14)	−0.0037(6)	0.2332(2)	0.0329
H-61	0.4531(14)	−0.0496(6)	0.2263(2)	0.0329
H-8	0.0034(18)	−0.1751(6)	0.2109(3)	0.0538
H-81	0.2512(18)	−0.1521(6)	0.2150(3)	0.0538
H-82	0.1734(18)	−0.1885(6)	0.1860(3)	0.0538
H-9	−0.2400(14)	−0.1009(6)	0.1791(3)	0.0393
H-91	−0.0802(14)	−0.1118(6)	0.1529(3)	0.0393
H-92	−0.1475(14)	−0.0311(6)	0.1627(3)	0.0393
H-810	0.2548(17)	0.2729(7)	0.2587(3)	0.0549
H-811	0.4271(17)	0.2407(7)	0.2806(3)	0.0549
H-812	0.2006(17)	0.2000(7)	0.2761(3)	0.0549
H-910	0.5352(18)	0.2645(7)	0.2169(3)	0.0640
H-911	0.6445(18)	0.1871(7)	0.2099(3)	0.0640
H-912	0.7175(18)	0.2320(7)	0.2373(3)	0.0640

Occupancy factors of atoms marked with asterisk are equal 0.5.

Table 11
Anisotropic thermal parameters for **1b**

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K-1	0.0227(8)	0.0204(9)	0.0091(10)	0.0045(8)	0.0003(8)	0.0014(8)
K-2	0.0169(7)	0.0223(9)	0.0265(12)	0.0078(9)	−0.0001(9)	0.0015(8)
K-3	0.0253(8)	0.0197(9)	0.0170(11)	0.0051(8)	−0.0028(8)	−0.0024(8)
S-1	0.0189(8)	0.0171(10)	0.0115(11)	−0.0024(9)	−0.0004(9)	0.0008(9)
S-2	0.0157(8)	0.0089(9)	0.0133(11)	−0.0003(8)	0.0020(8)	−0.0004(8)
S-3	0.0222(9)	0.0168(10)	0.0107(12)	0.0013(10)	−0.0017(7)	0.002(8)
O-1W	0.027(4)	0.029(4)	0.037(5)	−0.013(4)	−0.005(3)	0.001(3)
O-2W*	0.022(6)	0.023(7)	0.021(8)	−0.008(6)	0.009(5)	0.006(5)

Occupancy factors of atoms marked with asterisk are equal 0.5.

Table 12
Atomic coordinates and equivalent isotropic parameters for **2**

	x	y	Z	U_{eq}/U_{iso} (Å^2)
S	0.25318(6)	0.39879(5)	0.39495(2)	0.01255(10)
O-1	0.36700(17)	0.35983(13)	0.32714(7)	0.0132(3)
O-2	0.64578(16)	0.41544(15)	0.24814(7)	0.0122(3)
O-3	0.68402(16)	0.47725(15)	0.13118(7)	0.0126(3)
O-4	0.23515(18)	0.51757(15)	0.09728(7)	0.0144(3)
O-5	0.29417(19)	0.26230(16)	0.01640(8)	0.0185(3)
O-6	0.46983(16)	0.25995(13)	0.19505(7)	0.0109(3)
O-7	0.2916(3)	0.28390(15)	0.44359(8)	0.0247(4)
O-8	0.08145(19)	0.4042(3)	0.36926(9)	0.0284(4)
O-9	0.31338(19)	0.53650(15)	0.41948(8)	0.0180(3)
C-1	0.3538(3)	0.45324(19)	0.26607(9)	0.0113(4)
C-2	0.4880(3)	0.4054(2)	0.21401(8)	0.0098(3)
C-3	0.5120(3)	0.50404(18)	0.14909(9)	0.0094(3)
C-4	0.4024(3)	0.47049(18)	0.08384(9)	0.0107(4)
C-5	0.4035(3)	0.30996(19)	0.07142(9)	0.0115(4)
C-6	0.3509(3)	0.23277(19)	0.13912(9)	0.0126(4)
C-7	0.7739(3)	0.44339(18)	0.19492(9)	0.0110(4)
C-8	0.8762(3)	0.5687(2)	0.22053(11)	0.0152(4)
C-9	0.8783(3)	0.3117(3)	0.18110(11)	0.0174(4)
O-W	0.2487(3)	0.81826(14)	0.11396(7)	0.0182(3)
N	0.6078(3)	0.4648(2)	0.50914(10)	0.0204(4)
H-11	0.369(4)	0.548(3)	0.2788(13)	0.009(6)
H-12	0.246(4)	0.448(3)	0.2444(13)	0.009(5)
H-3	0.503(3)	0.602(3)	0.1646(12)	0.002(5)
H-4	0.456(4)	0.513(3)	0.0440(15)	0.014(6)
H-5	0.511(4)	0.287(3)	0.0610(13)	0.009(6)
H-61	0.246(4)	0.264(3)	0.1505(12)	0.007(5)
H-62	0.348(4)	0.131(4)	0.1306(15)	0.022(7)
H-81	0.930(4)	0.554(3)	0.2616(15)	0.014(6)
H-82	0.802(4)	0.647(3)	0.2248(15)	0.019(7)
H-83	0.960(4)	0.584(4)	0.1888(15)	0.021(7)
H-91	0.930(4)	0.285(4)	0.2234(16)	0.028(8)
H-92	0.961(5)	0.336(4)	0.1440(18)	0.037(9)
H-93	0.823(4)	0.235(3)	0.1708(14)	0.014(6)
H-40	0.236(5)	0.582(4)	0.100(3)	0.041(11)
H-50	0.283(4)	0.314(4)	−0.008(2)	0.021(8)
H-1N	0.668(4)	0.424(4)	0.540(2)	0.025(7)
H-2N	0.615(6)	0.426(5)	0.470(3)	0.062(13)
H-3N	0.642(4)	0.554(4)	0.504(2)	0.029(8)
H-4N	0.495(5)	0.459(4)	0.517(2)	0.028(8)
H-1W	0.294(4)	0.852(3)	0.157(2)	0.025(8)
H-2W	0.152(4)	0.840(3)	0.112(2)	0.019(7)

Table 13
Anisotropic thermal parameters for **2**

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S	0.01523(18)	0.01377(17)	0.00864(16)	0.00087(14)	0.00318(17)	−0.00265(18)
O-1	0.0172(7)	0.0143(6)	0.0081(6)	0.0009(5)	0.0049(5)	0.0032(5)
O-2	0.0101(6)	0.0181(7)	0.0085(6)	0.0028(5)	−0.0011(5)	−0.0005(5)
O-3	0.0090(6)	0.0192(7)	0.0096(6)	0.0026(5)	0.0010(5)	−0.0002(5)
O-4	0.0122(7)	0.0121(6)	0.0190(7)	−0.0012(5)	−0.0021(6)	0.0028(6)
O-5	0.0316(9)	0.0122(6)	0.0118(6)	0.0008(6)	−0.0103(6)	−0.0019(6)
O-6	0.0144(7)	0.0085(6)	0.0099(6)	−0.0002(5)	−0.0019(5)	0.0014(5)
O-7	0.0414(10)	0.0178(7)	0.0149(7)	0.0040(6)	0.0081(6)	−0.0010(6)
O-8	0.0146(7)	0.0480(10)	0.0226(8)	−0.0034(8)	0.0030(6)	−0.0042(7)
O-9	0.0270(8)	0.0128(6)	0.0142(6)	−0.0030(5)	0.0033(6)	−0.0009(6)
C-1	0.0129(80	0.0120(8)	0.0091(8)	0.0023(6)	0.0018(6)	0.0002(7)
C-2	0.0111(8)	0.0096(7)	0.0088(7)	0.0007(6)	0.0002(6)	−0.0003(6)
C-3	0.0082(7)	0.0114(8)	0.0085(7)	0.0011(6)	−0.0003(6)	0.0005(6)
C-4	0.0123(8)	0.0106(8)	0.0092(8)	0.0014(6)	−0.0007(6)	0.0005(6)
C-5	0.0147(9)	0.0121(8)	0.0078(8)	−0.0003(6)	−0.0021(6)	0.0009(7)
C-6	0.0154(9)	0.0113(8)	0.0110(8)	−0.0011(6)	−0.0020(7)	−0.0018(7)
C-7	0.0095(9)	0.0127(8)	0.0107(7)	0.0012(6)	0.0001(6)	0.0006(6)
C-8	0.0151(9)	0.0143(9)	0.0162(9)	0.0002(7)	−0.0018(8)	−0.0039(7)
C-9	0.0153(9)	0.0159(9)	0.0211(10)	0.0004(8)	0.0024(8)	0.0055(8)
O-W	0.0185(7)	0.0207(7)	0.0155(6)	−0.0044(5)	−0.0037(7)	0.0035(7)
N	0.0240(10)	0.0194(9)	0.0178(9)	0.0035(8)	−0.0095(7)	−0.0005(7)

positions of all the H-atoms were found from the difference-Fourier map. The full-matrix least-squares[15] was completed using anisotropic parameters. Parameters of H-atoms were refined isotropically. The final parameters are given in Tables 12 and 13.

4. Supplementary material

Full crystallographic details, excluding structure features, have been deposited with the Cambridge Crystallographic data Centre. These data may be obtained, on request, from the CCDC, 12 union Road, Cambridge CB2 1EZ, UK (tel.: +44-1223-336508, fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk) quoting CCDC 163850 for **1a**, CCDC 163851 for **1b** and CCDC 163852 for **2**.

Acknowledgements

The financial support of this work by The Polish State Committee for Scientific Research under grant No. 3 T09A 015 12 is gratefully acknowledged.

References

1. Pole, A. R. *Biochem. J.* **1986**, *236*, 1–14.
2. Ruoslahti, E. *J. Biol. Chem.* **1989**, *264*, 13369–13372.
3. Freeman, C.; Hopwood, J. H. *Biochem. J.* **1992**, *282*, 605–614.
4. van Boeckel, A. A.; Petitou, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1671–1818.
5. Karlsson, K.-A.; Samuelsson, B. E.; Steen, G. O. *Eur. J. Biochem.* **1974**, *46*, 243–258.
6. De Clercq, E. In *Carbohydrates and Carbohydrate Polymers, Analysis, Biotechnology, Modification, Antiviral, Biomedical and Other Applications*; Yalpani, M., Ed. Anti-HIV Activity of Sulfated Polysaccharides; ATL Press: Mount Prospect, IL, USA, 1993; pp. 88–100.
7. Ferro, D. R.; Pumilia, P.; Ragazzi, M. *J. Comp. Chem.* **1997**, *18*, 351–367.
8. Allen, F. H.; Davies, J. E.; Gelloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187–204.
9. Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354–1358.
10. Altona, C.; Sundaralingam, M. *J. Am. Chem. Soc.* **1972**, *94*, 8205–8212.
11. Lis, T.; Weichsel, A. *Acta Crystallogr., Sect. C* **1987**, *43*, 1954–1956.
12. Pacsu, E.; Wilson, E. J., Jr.; Graf, L. *J. Am. Chem. Soc.* **1939**, *61*, 2675–2679.
13. Baumgarten, P. *Ber. Deutsch. Chem. Gesell.* **1926**, *59*, 1166–1171.
14. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
15. Sheldrick, G. M. *Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1993.
16. Sheldrick, G. M. *Program for the Refinement of Crystal Structures*; University of Göttingen: Germany, 1976.