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CRYSTAL AND MOLECULAR STRUCTURE OF POTASSIUM β-D-GLUCOPYRANOSE 6-SULPHATE

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ABSTRACT

The crystal and molecular structure of potassium β-D-glucopyranose 6-sulphate has been determined by direct methods. The sugar ring has the expected $^4C_1$ conformation although the sulphate group causes flattening of the ring. The potassium ion has octahedral co-ordination involving oxygen atoms of five independent β-D-glucopyranose 6-sulphate molecules. The n.m.r. spectrum of the 6-sulphate in the solid state is consistent with the occurrence of two molecules in the unit cell related by a 2_1 symmetry axis.

INTRODUCTION

Carbohydrate sulphates, particularly sulphated polysaccharides, occur widely in Nature. In plants, sugar sulphates are components of many polysaccharides (carrageenan, fucoidan, porphyran) originating from both the cell wall and intercellular regions of marine algae[1]. In animals, they occur in the connective tissue polysaccharides of the extracellular matrix (chondroitins, keratin, and dermatan sulphates), in heparin and heparan, and in brain tissue as sulphated cerebrosides[2,3].

Attention has been focussed on the chemical and physical properties of carrageenan and keratan since the former is employed widely in the food industry as a gelling agent which forms thermoreversible gels[4], and the sulphate groups in the latter may be important as antigenic determinants[5]. It has been suggested that double-helical polysaccharide chains are involved in gel formation[6,7] and there is evidence that cations associated with sulphate groups play an essential role in the mechanism of gelation[8,9].

However, the exact function of the counter-ions is not well understood and it

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has been suggested that non-specific competition by cations for water may be more important in promoting the interactions amongst polysaccharide chains which lead to the formation of a gel network, rather than specific conformational transitions of the polysaccharide chains[10–12].

One approach to the determination of the stereochemical features that are important in polysaccharide interactions is to study model compounds of low molecular weight. For example, X-ray crystallographic studies can provide information on hydrogen bonding and cation co-ordination which may be useful for modelling the polymer chain, and high-resolution solid-state ^{13}C-n.m.r. spectroscopy may give complementary information on structure. Where the results from X-ray fibre diffraction of polysaccharides and computer modelling are uncertain, the interpretation of solid-state n.m.r. spectra alone may not be reliable. For example, the n.m.r. spectra of the crystalline components of native cellulose are variable and depend on the origin of the sample[13], and, although structural information is available from these spectra, their detailed interpretation is controversial[14,15]. In order to make sensible interpretations of solid-state n.m.r. spectra and the complex factors which determine chemical shifts in biopolymers, a body of data from well defined, related model compounds is required.

We now describe the crystal and molecular structure of the potassium salt of β-D-glucopyranose 6-sulphate, the first such study of a sulphated monosaccharide, although the crystal structure of the potassium salt of sucrose octasulphate heptahydrate has been described[16].

EXPERIMENTAL

X-Ray crystallography. — Crystals suitable for diffraction experiments were grown from commercial potassium β-D-glucopyranose 6-sulphate, using 1-butanol–ethanol–water (4:1:1), and had $[\alpha]_D^{20}$ +37° (water).

Oscillation and Weissenberg photographs indicated a monoclinic lattice with space group $P2_1$. A crystal (0.02 × 0.04 × 0.32 mm) was sealed in a Lindemann glass capillary and set on an Enraf–Nonius CAD-4F diffractometer. Accurate unit-cell parameters were determined by a least-squares fit of measurements of 44 reflections with $19° < \theta < 38°$. The crystal data are given in Table I.

The intensity data were collected in the ω–2θ scan mode, using Nickel-filtered CuK_α radiation up to $\theta = 60°$ for a total of 1798 reflections (h −6 to 6, k −8 to 0, l −14 to 14) of which 1525 were non-zero. The control reflection 3 0 1 was measured every hour of exposure time (60 measurements overall), with an average value of 912.5 counts and a standard deviation (of the distribution) of 43.7 (4.8%). Lorentz and polarisation corrections were applied, but no absorption correction was made. The data were merged using the *SHELX* program[17] to give 842 unique reflections, merging $R = 0.02$, of which 824 with $F_o > 2\sigma(F_o)$ were used for the structural analysis.

Structure determination and refinement. — The structure was solved by the

TABLE I

CRYSTAL DATA FOR POTASSIUM β-D-GLUCOPYRANOSE 6-SULPHATE

Molecular formula	$(C_6H_{11}O_9S)^- K^+$
Molecular weight	298.3
Crystal system	Monoclinic
Space group	$P2_1$
Cell dimensions	
a (Å)	5.780(1)
b	7.676(1)
c	12.731(2)
β (°)	100.26(1)
Cell volume (Å^3)	555.84
Z	2
$F(000)$ (e)	308.0
$\mu(CuK_\alpha)$ (cm^{-1})	6.37
D_c (kg.m^{-3})	1.782

use of the direct methods program *SHELX-84*[18]. The correct solution was identified by the negative quartet figure of merit. The E map computed for this phase set revealed all non-hydrogen atoms, and the initial residual calculated for these atomic positions was 0.216.

The structure was then refined isotropically (R = 0.076, unit weights) and anisotropically, minimising the function $\Sigma\omega(|Fo| - |F_c|)^2$ where $\omega = 1.3261/[\sigma^2(F_o) + 0.000240(F_o)^2]$, together with anisotropic refinement of the overall scale factor. Subsequent difference Fourier syntheses revealed all the hydrogen atoms. These were included in the later refinement with fixed U_{iso} values equal to the U_{eq} of the carrier atoms. The final R and R_ω values were 0.0297 and 0.0335, respectively. In the final cycle of SFLS refinement, the average shift/e.s.d. is 0.023. The final difference Fourier synthesis shows maximum and minimum electron densities of 0.24 and −0.22 eÅ^{-3}, respectively. The atomic scattering factors used were taken from the International Tables for X-Ray Crystallography[19].

The atomic positional and thermal parameters for all atoms are listed in Table II*.

N.m.r. spectroscopy. — The c.p.–m.a.s. ^{13}C-n.m.r. spectrum (Fig. 4) was obtained using the procedure and conditions described[15] with single contact pulses of 5-ms duration and a recovery time between acquisitions of 5 s. Chemical shifts are recorded relative to that of the signal for Me_4Si and based on those (38.6 and 29.5 p.p.m.) for the signals of adamantane.

*Anisotropic thermal vibration parameters of the heavy atoms and the observed and calculated structure factors have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, The Netherlands. Reference should be made to No. BBA/DD/396/*Carbohydr. Res.*, 180 (1988) 183–193.

TABLE II

ATOMIC POSITIONAL AND THERMAL PARAMETERS

Atom	x/a	y/b	z/c	U_{eq}[a]		x/a	y/b	z/c	U_{iso}
K	−0.9773(2)	0.4357(0)	−0.0253(1)	0.047	H-O-1	−0.155(10)	−0.404(9)	0.145(4)	0.051
S	−0.4589(2)	0.2497(3)	0.1245(1)	0.038	H-O-2	0.370(10)	−0.512(9)	0.286(5)	0.054
OS-1	−0.6897(6)	0.1919(6)	0.0837(3)	0.057	H-O-3	0.536(11)	−0.124(9)	0.516(5)	0.049
OS-2	−0.2889(6)	0.2188(6)	0.0573(3)	0.054	H-O-4	0.268(9)	0.134(9)	0.502(5)	0.049
OS-3	−0.4532(7)	0.4290(7)	0.1610(3)	0.056	H-C-1	−0.101(9)	−0.351(8)	0.316(4)	0.044
O-1	−0.0191(7)	−0.3974(6)	0.1656(3)	0.051	H-C-2	0.371(9)	−0.245(8)	0.267(4)	0.040
O-2	0.3515(8)	−0.4739(6)	0.3426(3)	0.055	H-C-3	0.194(9)	−0.252(9(	0.457(4)	0.038
O-3	0.5202(6)	−0.1830(6)	0.4689(3)	0.048	H-C-4	0.282(9)	0.039(8)	0.364(4)	0.036
O-4	0.1535(7)	0.0645(6)	0.4936(3)	0.048	H-C-5	−0.191(8)	−0.074(8)	0.373(4)	0.036
O-5	−0.0610(6)	−0.1305(5)	0.2346(3)	0.042	H-1-C-6	−0.031(9)	0.200(8)	0.247(5)	0.044
O-6	−0.3891(6)	0.1370(6)	0.2276(3)	0.050	H-2-C-6	−0.128(9)	0.242(9)	0.344(4)	0.044
C-1	0.0097(11)	−0.3047(8)	0.2608(5)	0.043					
C-2	0.2677(9)	−0.3021(8)	0.3160(3)	0.040					
C-3	0.2808(9)	−0.1969(8)	0.4168(4)	0.039					
C-4	0.1767(9)	−0.0170(7)	0.3955(4)	0.036					
C-5	−0.0645(9)	−0.0243(7)	0.3267(4)	0.037					
C-6	−0.1474(10)	0.1525(9)	0.2875(5)	0.044					

[a] $U_{eq} = 1/3\ \Sigma_i \Sigma_j\ U_{ij}\ a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

RESULTS AND DISCUSSION

The molecular configuration, conformation, and the atom-numbering scheme are shown in Fig. 1[20].

Molecular geometry. — The bond lengths and angles are listed in Table III and their values conform to those tabulated for other carbohydrates[21]. As usual in pyranosyl compounds, the C-1–O-1 (1.390 Å) bond is shorter than the C-1–O-5 bond (1.420 Å). This difference is ascribed to the anomeric effect, which also seems to influence the exocyclic C-5–C-6 (1.496 Å) and C-6–O-6 (1.472 Å) bonds since these are shorter and longer, respectively, than the accepted values for C–C (1.522 Å) and C–O (1.424 Å) bonds.

As shown in Table IV, the expected $^4C_1$ chair conformation is found for the pyranosyl residue with the C-1 and C-4 displaced out of the least-squares plane defined by C-2–C-3–C-5–O-5 by −0.730(6) and 0.604(5) Å. This finding suggests that the 6-sulphation flattens the chair conformation. Deviation from the ideal symmetry is also given in terms of the asymmetry parameter $\Delta C_s = 3.8°$[22].

The sulphate group is essentially tetrahedral with O–S–O angles ranging from 102.7(2) to 115.5(3)°. The pattern of the bond lengths and angles of the sulphate group allows S–OS-1 and S–OS-2 to be recognised as S=O bond types and S–OS-3 as an S–O$^-$ bond type. The sulphate group is in a staggered conformation with respect to the ester bond. The conformation along the C-5–C-6–O-6 sequence is *gauche–trans–trans*.

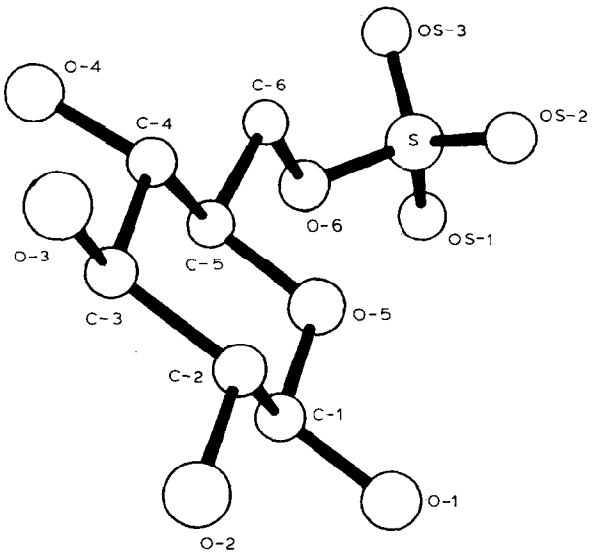

Fig. 1. Conformation and atom labelling of potassium β-D-glucopyranose 6-sulphate.

TABLE III

BOND LENGTHS (Å) AND ANGLES (DEGREES)

Bonds			
S–OS-1	1.414(4)	O-5–C-1	1.420(7)
S–OS-2	1.433(4)	O-5–C-5	1.431(7)
S–OS-3	1.451(5)	O-6–C-6	1.472(7)
S–O-6	1.563(4)	C-1–C-2	1.531(8)
O-1–C-1	1.390(7)	C-2–C-3	1.507(8)
O-2–C-2	1.425(7)	C-3–C-4	1.511(8)
O-3–C-3	1.428(7)	C-4–C-5	1.509(8)
O-4–C-4	1.424(7)	C-5–C-6	1.496(8)
Angles			
OS-1–S–OS-2	115.5(3)	O-2–C-2–C-3	109.3(5)
OS-1–S–OS-3	112.4(3)	C-1–C-2–C-3	107.2(5)
OS-1–S–O-6	102.7(2)	O-3–C-3–C-2	109.4(4)
OS-2–S–OS-3	111.7(3)	O-3–C-3–C-4	109.7(4)
OS-2–S–O-6	107.9(2)	C-2–C-3–C-4	112.3(5)
OS-3–S–O-6	105.6(2)	O-4–C-4–C-3	109.9(4)
C-1–O-5–C-5	112.9(4)	O-4–C-4–C-5	107.7(4)
S–O-6–C-6	118.0(4)	C-3–C-4–C-5	111.6(4)
O-1–C-1–O-5	107.0(5)	O-5–C-5–C-4	110.5(4)
O-1–C-1–C-2	111.3(5)	O-5–C-5–C-6	107.1(4)
O-5–C-1–C-2	108.2(5)	C-4–C-5–C-6	111.6(5)
O-2–C-2–C-1	111.0(5)	O-6–C-6–C-5	108.5(5)

Bonds and angles involving H

Type	*Number*	*Range*	*Mean*	σ_{av}
O–H	4	0.75–0.84	0.79	0.03
C–H	7	0.88–1.09	1.00	0.08
C–O–H	4	102–113	106	4
O–C–H	8	106–115	111	3
C–C–H	11	104–114	109	3
H–C–H	1	97(5)		

The potassium ion has an octahedral co-ordination which is shown in Fig. 2. Each potassium ion is co-ordinated to five independent β-D-glucopyranose 6-sulphate molecules (Table V).

Molecular packing. — The crystal packing involves alternating charged layers extending on the planes X = 0.0 and X = 0.5 (Fig. 3). The negatively charged layer is formed by lattice translation along the *b* axis of infinite chains of sulphated anions. The structure of this layer is stabilized by interactions of the SO_3^- moieties with the potassium cations and by a network of hydrogen bonds involving molecules belonging to the same layer and to symmetry-related layers (Table VI). The positively charged layer is formed by lattice translation along the *b* axis of the infinite chains of the co-ordination polyhedra of the potassium cation. The five anion

TABLE IV

TORSION ANGLES (DEGREES)

Endocyclic	
O-5–C-1–C-2–C-3	61.9(6)
C-1–C-2–C-3–C-4	−55.0(6)
C-2–C-3–C-4–C-5	49.9(6)
C-3–C-4–C-5–O-5	−49.6(6)
C-4–C-5–O-5–C-1	59.7(6)
C-5–O-5–C-1–C-2	−66.4(6)
Exocyclic	
O-1–C-1–C-2–O-2	−61.6(6)
O-2–C-2–C-3–O-3	62.4(6)
O-3–C-3–C-4–O-4	−68.8(5)
O-4–C-4–C-5–C-6	70.7(6)
C-5–O-5–C-1–O-1	173.6(4)
C-4–C-5–C-6–O-6	−176.1(4)
O-5–C-5–C-6–O-6	62.9(5)
C-5–C-6–O-6–S	−141.2(4)
Sulphate group	
C-6–O-6–S–OS-1	175.1(4)
C-6–O-6–S–OS-2	52.6(5)
C-6–O-6–S–OS-3	−66.9(4)

molecules surrounding the potassium cation form a nearly regular polyhedron and, through a screw-axis parallel to *b*, they generate infinitely extended chains of polyhedra sharing one edge.

Unfortunately, there have been few previous reports on the crystalline structures of carbohydrate sulphates with which to compare the present findings. A preliminary report on potassium sucrose octasulphate shows that seven of the eight potassium ions are surrounded by five to seven oxygen atoms from sulphate groups and water molecules[16], with the former contributing the most (4.7 oxygen atoms on

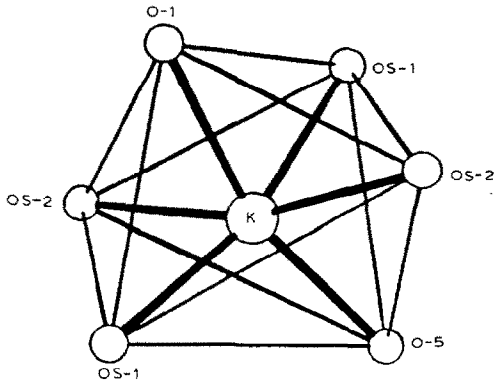

Fig. 2. Octahedral co-ordination of the potassium ion in potassium β-D-glucopyranose 6-sulphate.

TABLE V

GEOMETRY OF THE POTASSIUM CO-ORDINATION

Symmetry code

a	x	y	z	e	$-1+x$	$1+y$	z
b	$-2-x$	$1/2+y$	$-z$	f	$1-x$	$-1/2+y$	$1-z$
c	$-1+x$	y	z	g	x	$1+y$	z
d	$-1-x$	$1/2+y$	$-z$				

Bond length (Å)		*Angle (degrees)*	
K····OS-1[a]	2.715(4)	OS-1[a]····K····OS-2[c]	76.9(1)
K····OS-1[b]	2.760(4)	OS-1[a]····K····OS-2[d]	108.3(1)
K····OS-2[c]	2.793(4)	OS-1[b]····K····OS-2[c]	93.5(1)
K····OS-2[d]	2.735(4)	OS-1[b]····K····OS-2[d]	77.1(1)
K····O-1[e]	2.759(3)	O-1[e]····K····O-5[d]	163.3(1)
K····O-5[d]	2.796(4)		

average) and the average K····O distance being 2.832 Å (*cf.* average K····O distance of 2.759 Å in potassium D-glucose 6-sulphate); details of hydrogen-bonding patterns were not given.

The selenium atoms in streptomycin oxime selenate, which has been described in detail[23], like the sulphur atoms in the present study, are tetrahedral

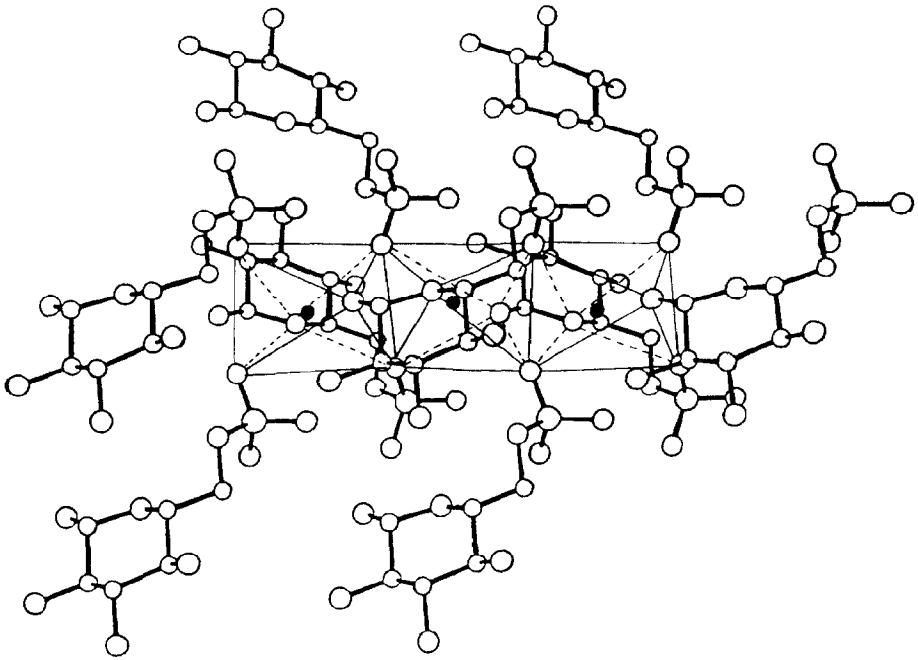

Fig. 3. Crystal packing of potassium β-D-glucopyranose 6-sulphate (*a b* plane). Potassium ions as black circles.

TABLE VI

GEOMETRY OF THE HYDROGEN-BONDING SYSTEM

A····*H–D*	*A*····*D* (Å)	*H–D* (Å)	*A*····*H* (Å)	<(*A*····*H–D*) (°)
OS-3····H–O-1^g	2.833(6)	0.78(6)	2.19(6)	140(6)
OS-3····H–O-2^e	2.847(6)	0.81(6)	2.09(6)	157(6)
O-2····H–O-3^f	2.873(6)	0.75(7)	2.13(7)	169(7)
O-3····H–O-4^f	2.687(5)	0.84(6)	1.86(6)	169(6)

but this is the only point of similarity. The selenate ions are considered to be doubly charged and the structure determined contains no metal ions. Another striking difference between potassium β-D-glucopyranose 6-sulphate and potassium sucrose octasulphate and the streptomycin derivative is the absence of water in the first compound. This, perhaps, is surprising in view of the accepted water-binding capacities of sulphated polysaccharides and it will be interesting to see if this is a general feature. In sodium hydrogen β-D-glucopyranose 6-phosphate, the conformation of the phosphate group is almost identical with that of the sulphate group in potassium D-glucopyranose 6-sulphate, and water of crystallisation is also absent[24]. At first sight, it is surprising that the one negatively charged oxygen atom in the sulphate group (OS-3) is not involved in co-ordination of the potassium ion, but, in the absence of knowledge concerning charge distributions, predictions of co-ordination geometry on the basis of simple electrostatic models may be misleading. OS-3 is the only oxygen atom of the sulphate group engaged as an acceptor of two hydrogen bonds (with HO-1 and HO-2). This involvement may result in a partial neutralisation of the negative charge as well as a distortion of the lone-pair electrons which would be expected to fit the potassium co-ordination shell. Accordingly, the negative charge needs to be spread over the OS-1 and OS-2 which participate in the potassium co-ordination, together with HO-1 and the ring oxygen (O-5). It follows that the observed participation of the sulphate group may be derived from its spatial accessibility rather than from a preferred chelation site due to its high negative charge.

There have been several studies of the interactions involving various alkali and alkaline-earth atoms and neutral and anionic carbohydrates[25] in solution and in the crystalline state, and it appears that cation–hydroxyl interactions are essential for the satisfactory formation of the complexes. This is true, even when the carbohydrates possess an anionic group such as a carboxylate ion[26–28]. In the present study, therefore, the fact that the charged OS-3 of the sulphate group is not involved in co-ordination of the potassium ion is not so surprising.

N.m.r. spectroscopy. — The ^{13}C-n.m.r. spectrum of solid potassium D-glucopyranose 6-sulphate shown in Fig. 4 is relatively simple: the assignments being 96.4 (C-1), 76.2 (C-2), 73.5 (C-3), 72.6 (C-4), 71.8 (C-5), and 70.4 p.p.m. (C-6). The absence of peak multiplicities implies that carbon atoms occupying the same ring position in each molecule within the unit cell are in a magnetically equivalent

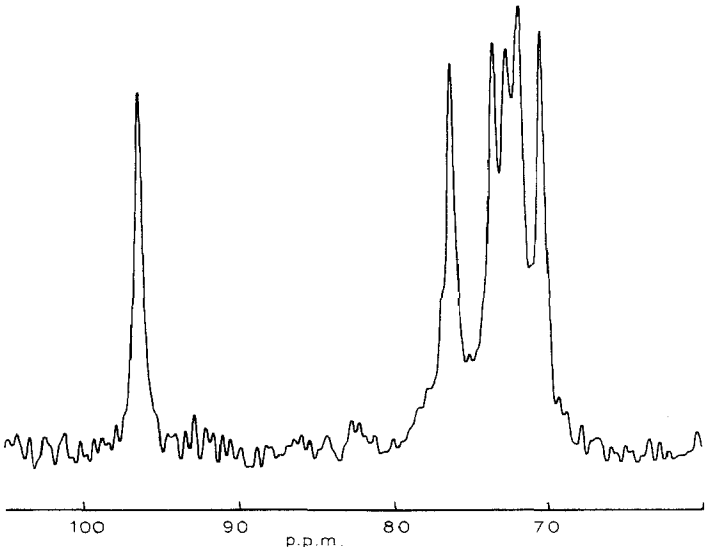

Fig. 4. Solid-state ^{13}C-n.m.r. spectrum of potassium β-D-glucopyranose 6-sulphate.

environment. Thus, the observed spectrum is consistent with the determined crystal structure which shows that the unit cell contains two molecules related by a 2_1 symmetry axis.

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