Title	The first crystal structure of an alkaline metal salt of thioglucose : potassium 1-thio-β-D-glucoside monohydrate
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metal-organic compounds

The first crystal structure of an alkaline metal salt of thioglucose: potassium 1-thio-β-D-glucoside monohydrate

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In the crystal structure of the title hydrated salt, poly[(μ_2-aqua)(μ_4-1-sulfido-β-D-glucoside)potassium], [K(C$_6$H$_{11}$O$_5$S)-(H$_2$O)]$_n$ or K$^+$·C$_6$H$_{11}$O$_5$S$^-$·H$_2$O, each thioglucoside anion coordinates to four K$^+$ cations through three of its four hydroxy groups, forming a three-dimensional polymeric structure. The negatively charged thiolate group in each anion does not form an efficient coordination bond with a K$^+$ cation, but forms intermolecular hydrogen bonds with four hydroxy groups, which appears to sustain the polymeric structure. The Cremer–Pople parameters for the thioglucoside ligand ($Q = 0.575$, $\theta = 8.233°$ and $\varphi = 353.773°$) indicate a slight distortion of the pyranose ring.

Comment

In recent years, thiosugars, especially thiol-containing monosaccharides, have attracted considerable attention; this is because of their unique chemical reactivity due to the presence of the thiol group, as well as the physicochemical and biochemical properties that are inherent in sugars (Witczak & Culhane, 2005). Among this class of compounds, 1-thio-β-D-glucose (H$_5$tg) is one of the simplest thiol-containing hexoses and is commonly used as a raw material for artificial organic thioglycosides. In the field of coordination chemistry, H$_5$tg has been used as a chiral ligand toward thiophilic metal centres, giving metal complexes with a deprotonated thiolate donor (Okamoto *et al.*, 1994; Leipnitz *et al.*, 2001). Owing to the presence of a sugar backbone in their structures, metal complexes derived from H$_5$tg often show hydrophilicity and biocompatibility. Hence, H$_5$tg and/or its metal complexes have been applied not only as antirheumatoid drugs (Shaw, 1999), but also as coating reagents for gold nanoparticles (Watanabe *et al.*, 2010).

While the applications of H$_5$tg have developed rapidly, crystallographic information is not extensive. The first structural investigation was made by Waser & Watson (1963) who elucidated the molecular structure of a H$_5$tg residue in Sinigrin

[potassium (*E*)-1-{[(2*S*,3*R*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]sulfanyl}but-3-enylideneamino sulfate], which is a kind of thioglycoside extracted from cruciferous plants. After this investigation, a number of S-substituted derivatives of H$_5$tg were prepared and structurally characterized (Marsh & Waser, 1970; Jaki *et al.*, 2002; Kuhn *et al.*, 2004). Nevertheless, the structural determination of H$_5$tg itself has not yet been reported and, furthermore, only two transition metal complexes derived from H$_5$tg, namely [Co(H$_3$tg-κ^2S,O)-(en)$_2$]NO$_3$ (en is ethylenediamine) [Cambridge Structural Database (CSD) refcode ZIGGOL; Okamoto *et al.*, 1994] and [ReO(tren)(H$_4$tg-κS)] [tren is tris(2-aminoethyl)amine; CSD refcode AMONUL; Leipnitz *et al.*, 2001], have been structurally characterized to date. In these complexes, H$_5$tg is partially deprotonated and strongly bound to the metal centre through its thiolate donor group.

(I)
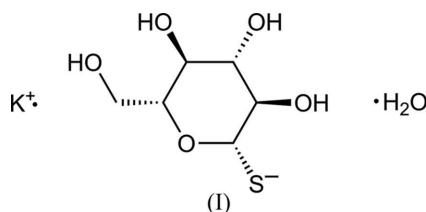
In the course of our study on the preparation of metal complexes derived from H$_5$tg, we found that the hydrolysis of 2,3,4,6-*O*-acetyl-1-thio-β-D-glucose with KOH gave a monohydrate form of potassium 1-thio-β-D-glucose, *viz.* KH$_4$tg·H$_2$O, (I), which was easily crystallized from water by diffusing acetone. Herein we report the molecular and supramolecular structure of (I). This is the first structural determination of an alkaline metal salt of thioglucose.

Salt (I) consists of one K$^+$ cation, one H$_4$tg$^-$ anion and one water molecule, all in general positions in the asymmetric unit (Fig. 1). The absolute configuration of five asymmetric C atoms (C1, C2, C3, C4 and C5) in the H$_4$tg$^-$ anion were determined to be *S*, *R*, *S*, *S* and *R*, respectively, based on the Flack (1983) parameter. For the H$_4$tg$^-$ anion, a thiol group is
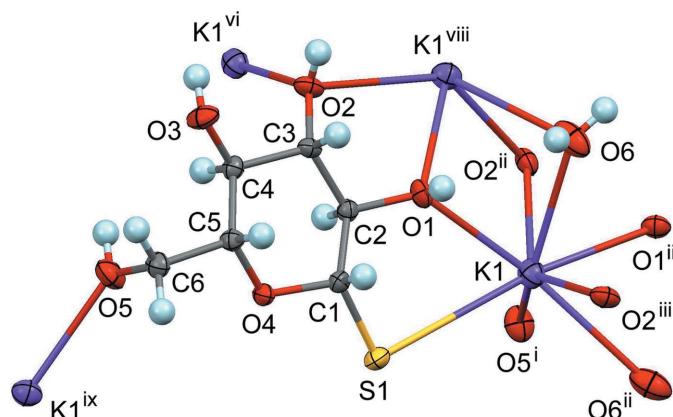
Figure 1
A perspective view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 70% probability level. [Symmetry codes: (i) $-x + \frac{3}{2}, -y, z + \frac{1}{2}$; (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iii) $x - 1$, y, z; (vi) $x + 1, y, z$; (viii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ix) $-x + \frac{3}{2}, -y, z - \frac{1}{2}$.]
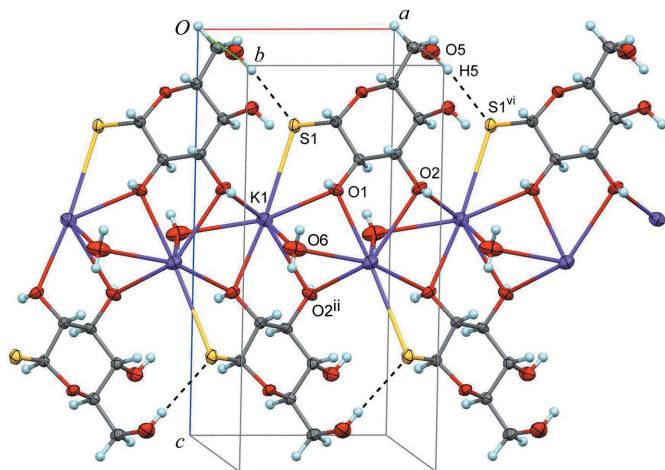
Figure 2
A view of the one-dimensional chain structure along the crystallographic a axis in (I). Dashed lines indicate O—H···S hydrogen bonds. [Symmetry codes: (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (vi) $x + 1, y, z$.]

deprotonated while four hydroxy groups remain protonated. This is consistent with the higher acidity of a thiol group compared with a hydroxy group. As shown in Fig. 1, a thiolate S atom and three of four hydroxy O atoms in each H_4tg^- anion, together with a water O atom, bind to symmetry-related K^+ ions. On the other hand, the K^+ ion is eight-coordinate, being bound by one thiolate S atom (S1), four bridging hydroxy O atoms (O1, O1^{ii}, O2^{ii} and O2^{iii}, with the bridges being to adjacent K^+ cations) and one monodentate hydroxy O atom (O5^i) from four H_4tg^- anions, as well as two bridging water O atoms (O6 and O6^{ii}) (symmetry codes as in Fig. 1). It is noteworthy that the K—S distance [K1—S1 = 3.5273 (6) Å; Table 1] is longer than the distances found in general potassium thiolates (3.055–3.216 Å; Chadwick *et al.*, 1997). This

implies that the thiolate group in the H_4tg^- anion does not have a high coordination ability to a K^+ ion. The other bond lengths and angles, including K—O bonds [2.7669 (14)– 3.099 (2) Å], are in the ranges normally observed for related compounds.

In (I), each K^+ cation is triply bridged to each of two neighbouring K^+ cations by O atoms (O1, O2, O6 and their symmetry-related counterparts) to give a one-dimensional chain structure along the crystallographic a axis (Fig. 2). This chain structure is supported by K—S bonding interactions and intermolecular O—H···S hydrogen bonds [O5···S1^{vi}; symmetry code: (vi) $x + 1, y, z$]. Moreover, each one-dimensional chain connects with four neighbouring chains through a linkage involving the K1—O5^i bond (symmetry code as in Fig. 1), completing a three-dimensional network structure in the crystal packing (Fig. 3). There exist four different O— H···O hydrogen bonds (Table 2) which also support the three-dimensional structure in (I).

As described above, the thiolate group of the H_4tg^- anion does not form an efficient coordination bond with a K^+ cation but forms intermolecular hydrogen bonds with four hydroxy groups in (I). This result obviously shows that the thiolate group in the H_4tg^- anion acts as a good hydrogen-bonding acceptor even when an alkaline metal ion exists in its vicinity. Note that the thiolate group in $[Co(H_3tg-\kappa^2S,O)(en)_2]NO_3$ forms only one intermolecular N—H···S hydrogen bond (N···S = 3.29 Å) and $[ReO(tren)(H_4tg-\kappa S)]$ does not form any hydrogen bonds involving the S atom, which is understood by the formation of a strong coordination bond with the transition metal centre.

In order to estimate the distortion of the pyranose ring, the Cremer–Pople theory (Cremer & Pople, 1975) is useful. The parameters of (I), $[Co(H_3tg-\kappa^2S,O)(en)_2]NO_3$ and $[ReO(tren)-(H_4tg-\kappa S)]$ are as follows: $Q = 0.575$, $\theta = 8.233°$ and $\varphi =$
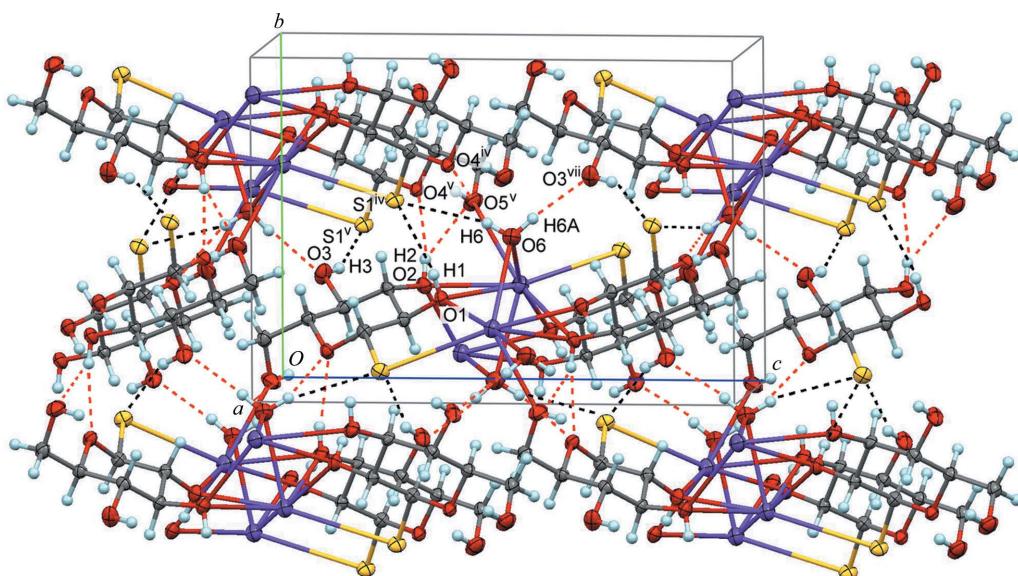
Figure 3
A view of the three-dimensional framework structure in (I). Darker and lighter (black and red in the electronic version of the paper) dashed lines indicate O—H···S and O—H···O hydrogen bonds, respectively. [Symmetry codes: (iv) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$; (vi) $x + 1, y, z$; (vii) $-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$.]

353.773° for (I); $Q = 0.577$, $\theta = 14.303°$ and $\varphi = 52.810°$ for [Co(H_3tg-$\kappa^2 S,O$)(en)$_2$]NO$_3$; $Q = 0.555$, $\theta = 3.112°$ and $\varphi = 313.544°$ for [ReO(tren)(H_4tg-κS)]. The θ value increases for the pyranose ring, which measures the deviation from an ideal chair conformation ($\theta = 0$ or $180°$), in the sequence [ReO-(tren)(H_4tg-κS)] < (I) < [Co(H_3tg-$\kappa^2 S,O$)(en)$_2$]NO$_3$. This trend in the ring distortion is explained by the fact that the thioglucoside ligand coordinates to a metal centre in a chelating mode in (I) and [Co(H_3tg-$\kappa^2 S,O$)(en)$_2$]NO$_3$, while the ligand coordinates to a metal centre in a monodentate mode in [ReO(tren)(H_4tg-κS)]. In addition, the ligand coordinates to a K$^+$ centre much more weakly than to a Co^{3+} centre, which is responsible for the less distorted pyranose ring in (I) compared with that in [Co(H_3tg-$\kappa^2 S,O$)(en)$_2$]NO$_3$.

In summary, this study provides a significant insight into the molecular and supramolecular structures of an alkaline metal salt of 1-thio-β-D-glucose for the first time. The crystal structure of (I) is composed of one-dimensional chains sustained by K—O coordination bonds, which are further assembled into a three-dimensional structure by forming K—O coordination bonds and O—H···O hydrogen bonds. Unlike the known transition metal complexes derived from H$_5$tg, the thiolate group in H$_4$tg$^-$ does not form an efficient coordination bond with K$^+$ in (I) but forms multiple O—H···S hydrogen bonds. This observation demonstrates that the thiolate group in H$_4$tg$^-$ acts as a good hydrogen-bond acceptor, which should contribute to the design and development of new thioglucose-based supramolecular systems.

Experimental

A sample of 2,3,4,6-O-acetyl-1-thio-β-D-glucose (4.99 g, 0.144 mol) was added to a solution containing KOH (2.23 g, 0.391 mol) in methanol (200 ml). After stirring for 9 h under an N$_2$ atmosphere, the resulting white powder was collected by filtration, washed with ethanol and acetone, and dried *in vacuo* (yield 2.47 g, 70%). Analysis calculated for C$_6$H$_{13}$KO$_6$S: C 28.56, H 5.19%; found: C 28.53, H 4.95%. ^{1}H NMR [400 MHz, D$_2$O, p.p.m. from sodium 3-(trimethyl-silyl)propane-1-sulfonate (DSS)]: δ 4.52 (1H, t, $J = 9.0$ Hz), 3.84 (1H, dd, $J = 12.5$, 1.5 Hz), 3.67–3.64 (1H, m), 3.42–3.37 (3H, m), 3.03–2.99 (1H, m). Single crystals of (I) suitable for X-ray analysis were obtained by diffusion of acetone to its aqueous solution.

Crystal data

[K(C$_6$H$_{11}$O$_5$S)(H$_2$O)]	$V = 970.88$ (7) Å^3
$M_r = 252.32$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 6.8625$ (3) Å	$\mu = 0.76$ mm^{-1}
$b = 10.0319$ (4) Å	$T = 200$ K
$c = 14.1026$ (6) Å	$0.30 \times 0.15 \times 0.15$ mm

Table 1
Selected bond lengths (Å).

K1—O5^i	2.7669 (14)	K1—O6	2.8774 (16)
K1—O1^{ii}	2.7699 (14)	K1—O2^{ii}	3.0795 (15)
K1—O1	2.7890 (14)	K1—O6^{ii}	3.099 (2)
K1—O2^{iii}	2.8387 (14)	K1—S1	3.5273 (6)

Symmetry codes: (i) $-x+\frac{3}{2}, -y, z+\frac{1}{2}$; (ii) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (iii) $x-1, y, z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···S1^{iv}	0.80 (2)	2.49 (2)	3.2659 (14)	164 (2)
O2—H2···O4^v	0.80 (2)	2.27 (2)	3.0505 (18)	167 (3)
O2—H2···O5^v	0.80 (2)	2.55 (2)	3.026 (2)	119 (2)
O3—H3···S1^v	0.83 (2)	2.41 (2)	3.1839 (15)	156 (2)
O5—H5···S1^{vi}	0.85 (2)	2.61 (2)	3.3971 (16)	154 (2)
O6—H6···O4^{iv}	0.82 (2)	2.55 (2)	3.163 (2)	134 (3)
O6—H6···S1^{iv}	0.82 (2)	2.79 (2)	3.5839 (16)	164 (3)
O6—H6A···O3^{vii}	0.82 (2)	2.08 (2)	2.892 (2)	175 (3)

Symmetry codes: (iv) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (v) $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$; (vi) $x+1, y, z$; (vii) $-x+\frac{3}{2}, -y+1, z+\frac{1}{2}$.

Data collection

Rigaku R-AXIS RAPID diffractometer	9524 measured reflections
Absorption correction: multi-scan (*ABSCOR*; Rigaku, 1995)	2209 independent reflections
	2171 reflections with $I > 2\sigma(I)$
$T_{min} = 0.803$, $T_{max} = 0.894$	$R_{int} = 0.079$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.078$	
$S = 1.10$	
2209 reflections	$\Delta\rho_{max} = 0.60$ e Å^{-3}
145 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
6 restraints	Absolute structure: Flack (1983), 913 Friedel pairs
	Flack parameter: -0.01 (4)

H atoms bound to C atoms were placed at calculated positions [C—H = 0.99 (CH$_2$) and 1.00 Å (CH)] and refined as riding, with U_{iso}(H) = 1.2U_{eq}(C). All H atoms bound to O atoms were located in a difference Fourier map and were refined with distance restraints and constrained displacement parameters [O—H = 0.84 (2) Å and U_{iso}(H) = 1.2U_{eq}(O)].

Data collection: *RAPID-AUTO* (Rigaku, 2000); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Yadokari-XG 2009* (Kabuto *et al.*, 2009); software used to prepare material for publication: *Yadokari-XG 2009*.

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supplementary materials

The first crystal structure of an alkaline metal salt of thioglucose: potassium 1-thio-*β*-D-glucoside monohydrate

Nobuto Yoshinari, Naoki Kitani and Takumi Konno

Poly[(μ_2-aqua)(μ_4-1-sulfido-*β*-D-glucoside)potassium]

Crystal data

$K^+ \cdot C_6H_{11}O_5S^- \cdot H_2O$	$F(000) = 528$
$M_r = 252.32$	$D_x = 1.726$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 9342 reflections
$a = 6.8625$ (3) Å	$\theta = 3.3–27.5°$
$b = 10.0319$ (4) Å	$\mu = 0.76$ mm^{-1}
$c = 14.1026$ (6) Å	$T = 200$ K
$V = 970.88$ (7) Å^3	Block, colourless
$Z = 4$	$0.30 \times 0.15 \times 0.15$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer	9524 measured reflections
Radiation source: rotating-anode X-ray tube	2209 independent reflections
Detector resolution: 10.000 pixels mm^{-1}	2171 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.079$
Absorption correction: multi-scan (*ABSCOR*; Rigaku, 1995)	$\theta_{max} = 27.5°, \theta_{min} = 3.3°$
$T_{min} = 0.803, T_{max} = 0.894$	$h = -8 \rightarrow 8$
	$k = -12 \rightarrow 12$
	$l = -18 \rightarrow 17$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.038$	
$wR(F^2) = 0.078$	$w = 1/[\sigma^2(F_o^2) + (0.0268P)^2 + 0.2347P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	
2209 reflections	$(\Delta/\sigma)_{max} < 0.001$
145 parameters	$\Delta\rho_{max} = 0.60$ e Å^{-3}
6 restraints	$\Delta\rho_{min} = -0.30$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 913 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: -0.01 (4)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
K1	0.31561 (6)	0.16793 (4)	0.45442 (3)	0.01885 (13)
S1	0.48800 (7)	0.05321 (4)	0.23337 (3)	0.01553 (13)
O1	0.6474 (2)	0.27794 (13)	0.37124 (9)	0.0157 (3)
H1	0.593 (3)	0.3434 (19)	0.3516 (18)	0.019*
O2	1.0557 (2)	0.34495 (14)	0.36133 (9)	0.0164 (3)
H2	1.077 (4)	0.4226 (17)	0.3659 (18)	0.020*
O3	1.1838 (2)	0.38611 (14)	0.16017 (10)	0.0196 (3)
H3	1.268 (3)	0.409 (2)	0.1990 (17)	0.023*
O4	0.80599 (19)	0.13386 (11)	0.14342 (9)	0.0130 (3)
O5	1.1684 (2)	0.07274 (13)	0.04992 (10)	0.0220 (3)
H5	1.251 (4)	0.097 (2)	0.0918 (16)	0.026*
O6	0.4025 (3)	0.44051 (14)	0.50182 (11)	0.0285 (4)
H6	0.415 (4)	0.481 (3)	0.4519 (15)	0.034*
H6A	0.377 (4)	0.493 (2)	0.5441 (17)	0.034*
C1	0.6660 (3)	0.18275 (17)	0.21185 (12)	0.0117 (3)
H1A	0.5982	0.2622	0.1846	0.014*
C2	0.7766 (3)	0.22580 (17)	0.30113 (13)	0.0116 (4)
H2A	0.8406	0.1448	0.3284	0.014*
C3	0.9375 (3)	0.32768 (17)	0.27842 (12)	0.0116 (4)
H3A	0.8759	0.4149	0.2616	0.014*
C4	1.0637 (3)	0.28117 (18)	0.19605 (13)	0.0121 (4)
H4	1.1473	0.2051	0.2170	0.015*
C5	0.9372 (3)	0.23761 (16)	0.11335 (13)	0.0122 (4)
H5A	0.8579	0.3158	0.0922	0.015*
C6	1.0506 (3)	0.18609 (18)	0.02932 (13)	0.0152 (4)
H6B	0.9579	0.1624	−0.0217	0.018*
H6C	1.1353	0.2584	0.0052	0.018*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.0211 (2)	0.0184 (2)	0.0171 (2)	−0.00043 (16)	0.00256 (16)	0.00053 (15)
S1	0.0118 (2)	0.0161 (2)	0.0188 (2)	−0.00296 (17)	−0.00001 (18)	−0.00087 (16)
O1	0.0179 (8)	0.0166 (6)	0.0125 (6)	0.0018 (5)	0.0037 (6)	−0.0004 (5)
O2	0.0194 (8)	0.0155 (6)	0.0144 (6)	−0.0014 (5)	−0.0051 (5)	−0.0025 (5)
O3	0.0193 (8)	0.0237 (7)	0.0156 (7)	−0.0105 (6)	0.0001 (6)	0.0021 (5)
O4	0.0135 (7)	0.0134 (6)	0.0120 (6)	−0.0027 (5)	0.0026 (5)	−0.0017 (4)

O5	0.0263 (8)	0.0176 (7)	0.0220 (7)	0.0064 (6)	−0.0021 (6)	−0.0056 (5)
O6	0.0476 (11)	0.0181 (7)	0.0197 (8)	0.0009 (7)	0.0056 (7)	0.0001 (6)
C1	0.0103 (9)	0.0125 (8)	0.0123 (8)	0.0003 (7)	−0.0002 (6)	−0.0007 (6)
C2	0.0109 (9)	0.0131 (8)	0.0107 (8)	0.0006 (7)	0.0005 (7)	−0.0001 (6)
C3	0.0127 (9)	0.0110 (7)	0.0112 (8)	−0.0010 (7)	−0.0022 (6)	−0.0015 (6)
C4	0.0117 (10)	0.0123 (8)	0.0123 (8)	0.0003 (6)	0.0008 (7)	0.0013 (6)
C5	0.0129 (10)	0.0117 (8)	0.0120 (8)	−0.0012 (6)	−0.0002 (7)	0.0006 (6)
C6	0.0164 (10)	0.0163 (9)	0.0128 (8)	−0.0016 (7)	0.0029 (7)	0.0000 (6)

Geometric parameters (Å, º)

K1—O5^i	2.7669 (14)	O4—C1	1.447 (2)
K1—O1^{ii}	2.7699 (14)	O5—C6	1.425 (2)
K1—O1	2.7890 (14)	O5—K1^{vi}	2.7669 (14)
K1—O2^{iii}	2.8387 (14)	O5—H5	0.852 (17)
K1—O6	2.8774 (16)	O6—K1^{iv}	3.099 (2)
K1—O2^{ii}	3.0795 (15)	O6—H6	0.815 (18)
K1—O6^{ii}	3.099 (2)	O6—H6A	0.816 (17)
K1—S1	3.5273 (6)	C1—C2	1.532 (2)
K1—H1	2.97 (2)	C1—H1A	1.0000
S1—C1	1.8092 (18)	C2—C3	1.538 (3)
O1—C2	1.427 (2)	C2—H2A	1.0000
O1—K1^{iv}	2.7699 (14)	C3—C4	1.522 (3)
O1—H1	0.803 (17)	C3—H3A	1.0000
O2—C3	1.434 (2)	C4—C5	1.518 (3)
O2—K1^v	2.8388 (14)	C4—H4	1.0000
O2—K1^{iv}	3.0795 (15)	C5—C6	1.509 (3)
O2—H2	0.795 (16)	C5—H5A	1.0000
O3—C4	1.430 (2)	C6—H6B	0.9900
O3—H3	0.830 (17)	C6—H6C	0.9900
O4—C5	1.440 (2)		
O5^i—K1—O1^{ii}	75.85 (4)	K1^{iv}—O2—H2	94.2 (19)
O5^i—K1—O1	121.18 (5)	C4—O3—H3	111.8 (19)
O1^{ii}—K1—O1	129.49 (4)	C5—O4—C1	111.49 (12)
O5^i—K1—O2^{iii}	142.74 (5)	C6—O5—K1^{vi}	128.28 (11)
O1^{ii}—K1—O2^{iii}	91.49 (4)	C6—O5—H5	107.0 (18)
O1—K1—O2^{iii}	94.07 (4)	K1^{vi}—O5—H5	123.9 (18)
O5^i—K1—O6	135.07 (5)	K1—O6—K1^{iv}	84.39 (4)
O1^{ii}—K1—O6	72.17 (4)	K1—O6—H6	107 (2)
O1—K1—O6	63.42 (5)	K1^{iv}—O6—H6	104 (2)
O2^{iii}—K1—O6	69.09 (5)	K1—O6—H6A	138 (2)
O5^i—K1—O2^{ii}	62.06 (4)	K1^{iv}—O6—H6A	106 (2)
O1^{ii}—K1—O2^{ii}	58.81 (4)	H6—O6—H6A	110 (3)
O1—K1—O2^{ii}	86.25 (4)	O4—C1—C2	108.34 (14)
O2^{iii}—K1—O2^{ii}	138.82 (2)	O4—C1—S1	108.46 (11)
O6—K1—O2^{ii}	74.52 (4)	C2—C1—S1	113.52 (12)
O5^i—K1—O6^{ii}	68.46 (5)	O4—C1—H1A	108.8
O1^{ii}—K1—O6^{ii}	60.71 (4)	C2—C1—H1A	108.8
O1—K1—O6^{ii}	165.85 (4)	S1—C1—H1A	108.8

O2ⁱⁱⁱ—K1—O6ⁱⁱ	74.74 (4)	O1—C2—C1	111.40 (15)
O6—K1—O6ⁱⁱ	118.48 (5)	O1—C2—C3	110.28 (14)
O2ⁱⁱ—K1—O6ⁱⁱ	107.86 (4)	C1—C2—C3	111.82 (14)
O5ⁱ—K1—S1	97.60 (3)	O1—C2—H2A	107.7
O1ⁱⁱ—K1—S1	171.19 (3)	C1—C2—H2A	107.7
O1—K1—S1	58.91 (3)	C3—C2—H2A	107.7
O2ⁱⁱⁱ—K1—S1	90.35 (3)	O2—C3—C4	109.74 (14)
O6—K1—S1	116.48 (4)	O2—C3—C2	108.46 (14)
O2ⁱⁱ—K1—S1	123.54 (3)	C4—C3—C2	111.31 (14)
O6ⁱⁱ—K1—S1	111.61 (3)	O2—C3—H3A	109.1
O5ⁱ—K1—H1	136.8 (4)	C4—C3—H3A	109.1
O1ⁱⁱ—K1—H1	125.7 (5)	C2—C3—H3A	109.1
O1—K1—H1	15.6 (4)	O3—C4—C5	105.65 (15)
O2ⁱⁱⁱ—K1—H1	78.9 (4)	O3—C4—C3	111.86 (14)
O6—K1—H1	54.4 (5)	C5—C4—C3	110.45 (15)
O2ⁱⁱ—K1—H1	95.4 (4)	O3—C4—H4	109.6
O6ⁱⁱ—K1—H1	153.1 (4)	C5—C4—H4	109.6
S1—K1—H1	63.1 (5)	C3—C4—H4	109.6
C1—S1—K1	98.07 (6)	O4—C5—C6	107.83 (14)
C2—O1—K1ⁱᵛ	115.34 (11)	O4—C5—C4	109.83 (15)
C2—O1—K1	130.80 (11)	C6—C5—C4	114.00 (16)
K1ⁱᵛ—O1—K1	92.55 (4)	O4—C5—H5A	108.3
C2—O1—H1	110.3 (19)	C6—C5—H5A	108.3
K1ⁱᵛ—O1—H1	109.8 (18)	C4—C5—H5A	108.3
K1—O1—H1	95.2 (18)	O5—C6—C5	113.95 (15)
C3—O2—K1ᵛ	131.08 (10)	O5—C6—H6B	108.8
C3—O2—K1ⁱᵛ	112.36 (10)	C5—C6—H6B	108.8
K1ᵛ—O2—K1ⁱᵛ	85.39 (4)	O5—C6—H6C	108.8
C3—O2—H2	106.8 (18)	C5—C6—H6C	108.8
K1ᵛ—O2—H2	117.2 (19)	H6B—C6—H6C	107.7
O5ⁱ—K1—S1—C1	−132.51 (7)	K1—S1—C1—O4	159.21 (10)
O1—K1—S1—C1	−10.54 (7)	K1—S1—C1—C2	38.74 (13)
O2ⁱⁱⁱ—K1—S1—C1	84.00 (7)	K1ⁱᵛ—O1—C2—C1	172.83 (10)
O6—K1—S1—C1	17.31 (7)	K1—O1—C2—C1	54.55 (19)
O2ⁱⁱ—K1—S1—C1	−71.11 (7)	K1ⁱᵛ—O1—C2—C3	−62.39 (15)
O6ⁱⁱ—K1—S1—C1	157.70 (7)	K1—O1—C2—C3	179.33 (10)
O5ⁱ—K1—O1—C2	57.77 (15)	O4—C1—C2—O1	178.78 (13)
O1ⁱⁱ—K1—O1—C2	155.14 (13)	S1—C1—C2—O1	−60.69 (18)
O2ⁱⁱⁱ—K1—O1—C2	−109.56 (14)	O4—C1—C2—C3	54.87 (18)
O6—K1—O1—C2	−173.73 (15)	S1—C1—C2—C3	175.40 (12)
O2ⁱⁱ—K1—O1—C2	111.72 (14)	K1ᵛ—O2—C3—C4	−53.89 (19)
O6ⁱⁱ—K1—O1—C2	−72.4 (2)	K1ⁱᵛ—O2—C3—C4	−157.98 (10)
S1—K1—O1—C2	−21.61 (13)	K1ᵛ—O2—C3—C2	67.90 (18)
O5ⁱ—K1—O1—K1ⁱᵛ	−69.41 (5)	K1ⁱᵛ—O2—C3—C2	−36.18 (15)
O1ⁱⁱ—K1—O1—K1ⁱᵛ	27.96 (6)	O1—C2—C3—O2	65.60 (18)
O2ⁱⁱⁱ—K1—O1—K1ⁱᵛ	123.26 (4)	C1—C2—C3—O2	−169.86 (15)
O6—K1—O1—K1ⁱᵛ	59.09 (5)	O1—C2—C3—C4	−173.58 (15)
O2ⁱⁱ—K1—O1—K1ⁱᵛ	−15.46 (4)	C1—C2—C3—C4	−49.0 (2)

O6^{ii}—K1—O1—K1^{iv}	160.44 (15)	O2—C3—C4—O3	−73.20 (18)
S1—K1—O1—K1^{iv}	−148.79 (5)	C2—C3—C4—O3	166.72 (15)
K1^{ii}—K1—O1—K1^{iv}	87.04 (5)	O2—C3—C4—C5	169.42 (13)
O5^{i}—K1—O6—K1^{iv}	58.21 (8)	C2—C3—C4—C5	49.34 (19)
O1^{ii}—K1—O6—K1^{iv}	104.88 (5)	C1—O4—C5—C6	−169.13 (14)
O1—K1—O6—K1^{iv}	−50.34 (4)	C1—O4—C5—C4	66.10 (17)
O2^{iii}—K1—O6—K1^{iv}	−156.37 (5)	O3—C4—C5—O4	−178.36 (13)
O2^{ii}—K1—O6—K1^{iv}	43.26 (3)	C3—C4—C5—O4	−57.22 (18)
O6^{ii}—K1—O6—K1^{iv}	145.49 (5)	O3—C4—C5—C6	60.52 (19)
S1—K1—O6—K1^{iv}	−76.91 (4)	C3—C4—C5—C6	−178.34 (14)
K1^{ii}—K1—O6—K1^{iv}	150.97 (4)	K1^{vi}—O5—C6—C5	128.85 (14)
C5—O4—C1—C2	−64.04 (17)	O4—C5—C6—O5	−62.2 (2)
C5—O4—C1—S1	172.33 (12)	C4—C5—C6—O5	60.1 (2)

Symmetry codes: (i) −x+3/2, −y, z+1/2; (ii) x−1/2, −y+1/2, −z+1; (iii) x−1, y, z; (iv) x+1/2, −y+1/2, −z+1; (v) x+1, y, z; (vi) −x+3/2, −y, z−1/2.

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯S1^{vii}	0.80 (2)	2.49 (2)	3.2659 (14)	164 (2)
O2—H2⋯O4^{viii}	0.80 (2)	2.27 (2)	3.0505 (18)	167 (3)
O2—H2⋯O5^{viii}	0.80 (2)	2.55 (2)	3.026 (2)	119 (2)
O3—H3⋯S1^{viii}	0.83 (2)	2.41 (2)	3.1839 (15)	156 (2)
O5—H5⋯S1^{v}	0.85 (2)	2.61 (2)	3.3971 (16)	154 (2)
O6—H6⋯O4^{vii}	0.82 (2)	2.55 (2)	3.163 (2)	134 (3)
O6—H6⋯S1^{vii}	0.82 (2)	2.79 (2)	3.5839 (16)	164 (3)
O6—H6A⋯O3^{ix}	0.82 (2)	2.08 (2)	2.892 (2)	175 (3)

Symmetry codes: (v) x+1, y, z; (vii) −x+1, y+1/2, −z+1/2; (viii) −x+2, y+1/2, −z+1/2; (ix) −x+3/2, −y+1, z+1/2.