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Preparation and X-ray analysis of potassium (2,3-dichlorophenyl)glucosinolate

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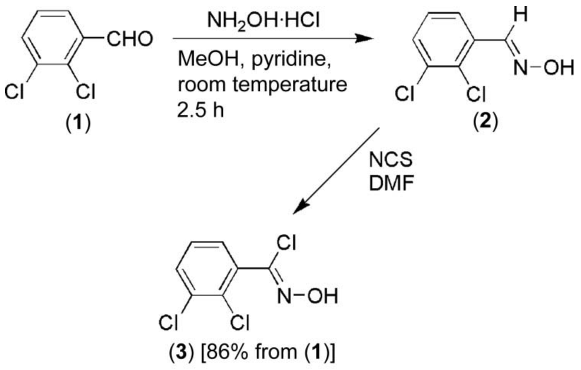
There has been much interest in obtaining crystals for crystallographic analysis of biologically active glucosinolates. Crystals of potassium (2,3-dichlorophenyl)glucosinolate were obtained as a dual solvate, containing one methanol and one ethanol molecule of crystallization, $K^+\cdot C_{13}H_{14}Cl_2NO_9S_2^-\cdot CH_3OH\cdot C_2H_5OH$. The three-dimensional polymeric network consists of chains containing the potassium ions coordinated and bridged by sugar O atoms, which run parallel to the *a* axis and are further crosslinked through the sugar molecules. The channels of this network are occupied by the dichlorophenyl substituents and the ethanol and methanol solvent molecules. The structure of the *S*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-2,3-dichlorophenylacetothiohydroxymate, $C_{21}H_{23}Cl_2NO_{10}S$, precursor has also been determined and the *β*-configuration and *Z* isomer of the thiohydroximate substituent is confirmed.

Keywords: crystal structure; 2,3-dichlorophenylglucosinolate; *β*-thioglucoside *N*-hydroxysulfates; biologically active compounds; natural products.

1. Introduction

Glucosinolates (GLs) are *β*-thioglucoside *N*-hydroxysulfates with a side chain (*R*) and a sulfur-linked *β*-D-glucopyranose moiety. These are natural compounds which are found in a large number of *Brassica* species such as cabbage, broccoli and canola (Clarke, 2010). The crystallization of GLs plays an important role in identifying their structure and has been studied previously (Fahey *et al.*, 2001). Kjaer *et al.* reported a list of GLs which had been crystallized as either potassium, sodium or rubidium salts, and another seven that had been characterized as crystalline acetates by 1959 (Kjaer *et al.*, 1956; Kjaer, 1961; Foo *et al.*, 2000). The data showed that these compounds were obtained as solids after crystallization; however, there was a lack of diagnostic structural information (X-ray analysis, NMR *etc*) to confirm the structures.



Scheme 1

Later, studies by Marsh & Waser (1970) and Thies (1988) reported the formation of crystalline sinigrin and glucotropaeolin salts. The potassium salt of sinigrin and the tetramethylamine salt of glucotropaeolin were crystallized in a suitable solvent and the HPLC (high-performance liquid chromatography), melting point, UV–vis and X-ray crystal structure analyses of sinigrin confirmed the high purity of the crystallized compounds. Unfortunately, since these studies there have not been any other published data on crystalline GLs. Thus, up to now, crystallization has been one of the most difficult issues in the study of GLs. This may be due to the very high polarity of GLs and the instability of GLs in the crystallizing solvent(s). The study of the crystallization of GLs in order to investigate the structure as well as the relationships between the structure and biological and medicinal properties of GLs, however, is a crucial issue. We report here success in the synthesis, crystallization and X-ray crystallographic analysis of potassium (2,3-dichlorophenyl)glucosinolate–ethanol–methanol (1/1/1), (**11**), and *S*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-2,3-dichlorophenylacetothiohydroxymate, (**9**).

2. Experimental

2.1. Synthesis and crystallization

2.1.1. *S*-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl)-2,3-dichlorophenylacetothiohydroxymate, (9). To stirred a solution of hydroxymoyl chloride, (**3**) [2.02 g, 9 mmol; see Scheme 1 and the *Supporting information* for the synthesis of (**3**)], in dry Et_2O–DCM (2:1 *v*/*v*, 45 ml; DCM is dichloromethane) was added a solution of 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl thiol, (**8**) [2.2 g, 6 mmol; see Scheme 2 and the *Supporting information* for the synthesis of (**8**)], in dry DCM (6 ml). The resulting mixture was treated with Et_3N (5 ml, 36 mmol) in Et_2O (12 ml). The reaction mixture was stirred for 2 h at room temperature under an N_2 atmosphere and then acidified with 1 *M* H_2SO_4 (42 ml). The mixture was left to stand for 10 min and then separated. The aqueous phase was extracted with DCM (3 × 30 ml). The combined organic layers

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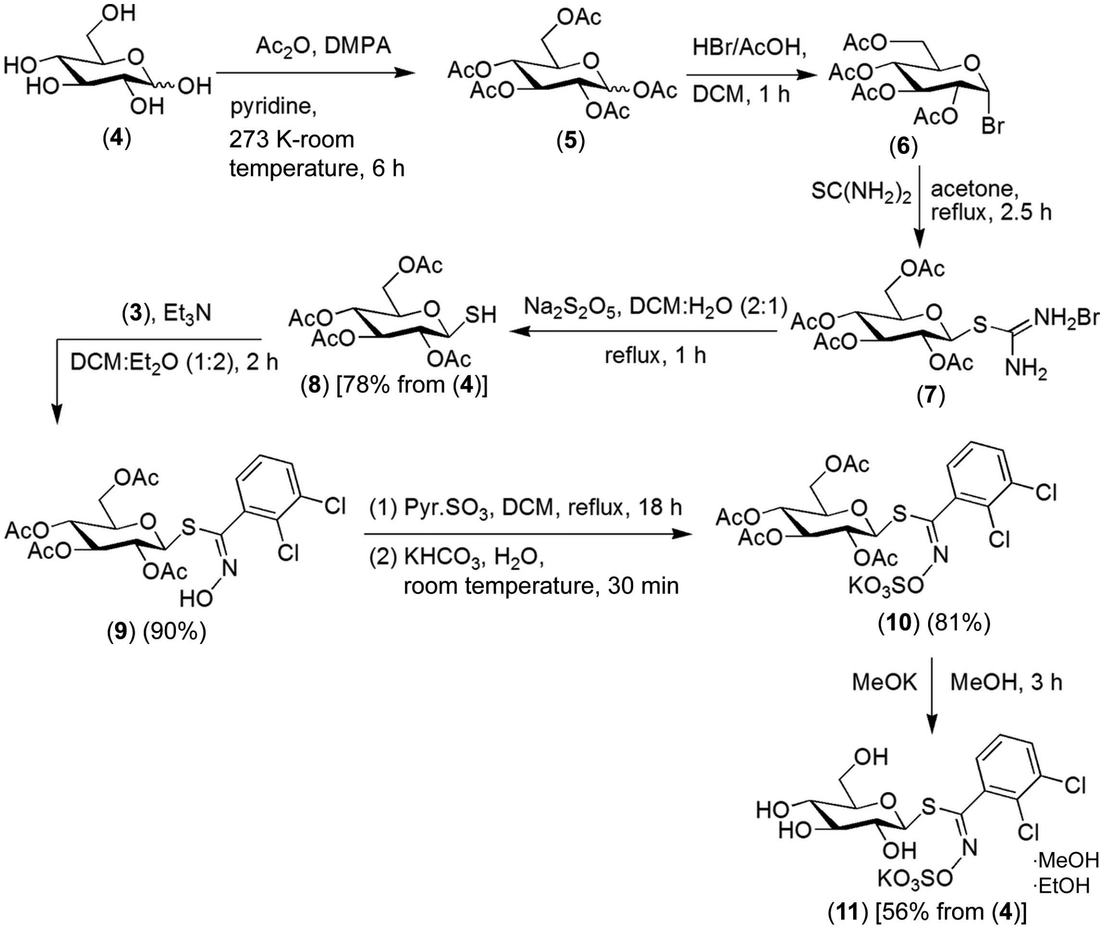

Scheme 2

were dried over $MgSO_4$, filtered and the filtrate was concentrated under reduced pressure. Thiohydroxymate (**9**) was purified by flash chromatography, eluting with 0–3% MeOH–DCM and then recrystallized from hexane–DCM. Thiohydroxymate (**9**) (50 mg) was completely dissolved in DCM. Hexane was then added until the solution became cloudy. The mixture was filtered and the filtrate was capped tightly and stored in room temperature up to two months to grown crystal.Pure (**9**) was obtained as white crystals (yield 3.55 g, 90%). R_F =0.36 in hexane–EtOAc (2:3 *v*/*v*) (m.p. 445–446 K). $[\alpha]$ = +22 (*c* 2.0, $CHCl_3$). λ_{max} (NaCl)/cm^{-1}: 3319 (OH), 1749 (C═O), 1602 (C═N), 1597, 1411, 1367, 1222, 1053. δ_H (300 MHz, $CDCl_3$, 300 K): δ 7.59–7.56 (*m*, 1H, H4′-Ph-H), 7.34–7.25 (*m*, 2H, H5′ and H6′-Ph-H), 5.02–4.97 (*m*, 3H, H2, H3 and H4), 4.14–4.03 (*m*, 2H, H1 and H6b), 3.89–3.84 (*m*, 1H, H6a), 2.86–2.84 (*m*, 1H, H5), 2.07, 2.03, 1.95, 1.93 (4 × *s*, 12H, CH_3COO). δ_C (75 MHz, $CDCl_3$, 300 K): 170.2, 169.9, 168.9, 168.8 (4 × $CH_3\mathit{C}OO$), 150.3 (C═N), 133.4 (C-3 of Ph), 132.5 (C-2 of Ph), 132.4 (C-4 of Ph), 131.7 (C-6 of Ph), 129.6 (C-1 of Ph), 126.7 (C-5 of Ph), 80.8 (C-1), 75.3 (C-5), 73.2 (C-3), 68.9 (C-2), 67.3 (C-4), 60.9 (C-6), 20.3, 20.2, 20.14, 20.08 (4 × $\mathit{C}H_3COO$). HRMS (ESI) *m*/*z* for $C_{21}H_{23}O_{10}Cl_2NNaS$ $[M + Na]^+$: calculated 574.0312, found 574.0283.

2.1.2. Potassium 2,3,4,6-tetra-*O*-acetyl-2,3-dichlorophenylglucosinolate, (10). To a stirred solution of thiohydroxymate (**9**) (800 mg, 1.45 mmol) in dry DCM (40 ml) was added pyridine sulfur trioxide complex (610 mg, 3.36 mmol). After stirring and refluxing under argon for 18 h, an additional portion of the complex (72.5 mg, 0.435 mmol) was added and stirring was continued for 2 h. After that, a solution of $KHCO_3$ (2.00 g, 17 mmol) in water (40 ml) was added and the mixture was stirred for 30 min and then concentrated under reduced pressure. The residue was dissolved in water and extracted first with chloroform (2 × 30 ml) and then with 80% $CHCl_3$–MeOH (3 × 30 ml). The organic layers were dried ($MgSO_4$), filtered and concentrated under reduce pressure. To remove excess pyridine, the mixture was co-distilled several times with toluene. Compound (**10**) was obtained by flash chromatography, eluting with 80–85% DCM–MeOH as a white solid (yield 780 mg, 81%). R_F = 0.31 in 15% MeOH–DCM [m.p. 415–417 K (decomposition)]. $[\alpha]$ = +15 (*c* 1.0, MeOH). λ_{max} (KBr drift)/cm^{-1}: 2942, 2884, 1754 (C═O), 1650, 1572, 1505, 1413, 1396, 1217, 1062. δ_H (300 MHz, CD_3OD, 300 K): 7.73–7.69 (*m*, 1H, H4′-Ph-H), 7.49–7.43 (*m*, 2H, H5′ and H6′-Ph-H), 5.12 (*t*, $J_{2,3}$ = $J_{3,4}$ = 9.3 Hz, 1H, H3), 4.97–4.91 (*m*, 2H, H2 and H4), 4.37 (*d*, $J_{1,2}$ = 10.2 Hz, 1H, H1), 4.11 (*dd*, $J_{5,6b}$ = 4.2, $J_{6a,6b}$ = 12.6 Hz, 1H, H6b), 3.90 (*dd*, $J_{5,6a}$ = 2.4, $J_{6a,6b}$ = 12.6 Hz, 1H, H6a), 3.06–3.01 (*m*, 1H, H5), 2.06, 2.02, 1.92, 1.92 (4 × *s*, 12H, CH_3COO). δ_C (75 MHz, CD_3OD, 300 K): 170.4, 169.7, 169.3, 169.1 (4 × $CH_3\mathit{C}OO$), 154.7 (C═N), 132.8 (C-3 of Ph), 131.8 (C-4 of Ph),

Table 1
Experimental details.

	(**9**)	(**11**)
Crystal data		
Chemical formula	$C_{21}H_{23}Cl_2NO_{10}S$	$K^+ \cdot C_{13}H_{14}Cl_2NO_9S_2^- \cdot CH_4O \cdot C_2H_6O$
M_r	552.36	580.48
Crystal system, space group	Monoclinic, $P2_1$	Orthorhombic, $P2_12_12_1$
Temperature (K)	130	115
a, b, c (Å)	7.1967 (2), 15.1383 (4), 11.9441 (3)	8.0043 (1), 15.5208 (4), 19.4586 (4)
α, β, γ (°)	90, 102.786 (3), 90	90, 90, 90
V (Å^3)	1268.99 (6)	2417.40 (9)
Z	2	4
Radiation type	Mo $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	0.39	6.09
Crystal size (mm)	0.37 × 0.32 × 0.14	0.65 × 0.07 × 0.04
Data collection		
Diffractometer	Oxford Diffraction SuperNova (Dual, Cu at zero, Atlas) diffractometer	Agilent SuperNova (Dual, Cu at zero, Atlas) diffractometer
Absorption correction	Gaussian (*CrysAlis PRO*; Oxford Diffraction, 2010)	Multi-scan (*CrysAlis PRO*; Agilent, 2012)
T_{min}, T_{max}	0.888, 0.949	0.716, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6348, 3790, 3535	17993, 5041, 4725
R_{int}	0.027	0.058
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.595	0.633
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.069, 1.05	0.054, 0.146, 1.03
No. of reflections	3790	5041
No. of parameters	324	327
No. of restraints	1	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.19	0.77, −0.84
Absolute structure	Flack (1983), 1466 Friedel pairs	Flack x determined using 1921 quotients (Parsons *et al.*, 2013)
Absolute structure parameter	−0.10 (5)	0.010 (12)

Computer programs: *CrysAlis PRO* (Oxford Diffraction, 2010), *CrysAlis PRO* (Agilent, 2012), *SHELXS2013* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012) and *WinGX* (Farrugia, 2012).

131.8 (C-1 of Ph), 131.7 (C-2 of Ph), 129.8 (C-6 of Ph), 127.2 (C-5 of Ph), 80.5 (C-1), 74.9 (C-5), 73.0 (C-3), 69.0 (C-2), 67.3 (C-4), 60.8 (C-6), 18.9, 18.8, 18.7 (2) (4 × CH$_3$COO). HRMS (ESI) m/z for $C_{21}H_{22}O_{13}Cl_2NS_2$ $[M - K]^-$: calculated 629.9915; found 629.9971.

2.1.3. Potassium (2,3-dichlorophenyl)glucosinolate–ethanol–methanol (1/1/1), (11). To a solution of *O*-acetylglucosinolate (**10**) (215 mg, 0.32 mmol) in anhydrous MeOH (20 ml) under an N_2 atmosphere was added dry MeOK (9 mg, 0.128 mmol) until a pH of 8–9 was reached. After stirring for 3 h at room temperature, the solution was made neutral by the addition of glacial acetic acid and then concentrated under reduced pressure. 2,3-Dichlorophenylglucosinolate (**11**) was purified by flash chromatography, eluting with EtOAc–MeOH–H_2O (16:4:1 *v*/*v*/*v*).

The vial-in-a-vial vapour diffusion method was used to grow the crystals of (**11**) as follows: 80 mg of the synthetic (**11**) was dissolved in H_2O (1–1.5 ml). MeOH was added until the solution became cloudy and the resulting solution was then filtered through Celite packed on tissue in a pipette to make sure that the solution was homogeneous. The resulting solution was poured into a small vial. Ethanol (6–10 ml) was placed in a scintillation vial and then the small vial with the sample solution was placed carefully inside the larger scintillation vial. The small vial was covered with plastic film and a few holes were made in the film with a needle. After that the large scintillation vial was capped tightly and stored at 273–278 K for up to two years to grow the crystals.

Pure (**11**) was obtained as white crystals (yield 145 mg, 99%). R_F = 0.14 in EtOAc–MeOH–H_2O (16:4:1 *v*/*v*/*v*) [m.p.

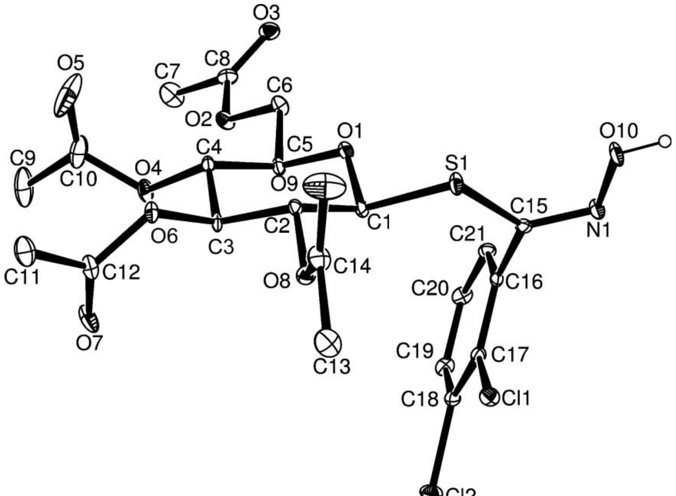

Figure 1
Displacement ellipsoid plot for (**9**), with ellipsoids drawn at the 20% probability level. All H atoms have been omitted, except for the hydroxy H atom.

390–392 K (decomposition)]. [α] = +60 (c 1.0, H_2O). λ_{max} (KBr drift)/cm^{-1}: 3354 (OH), 2882, 1566 (C=N), 1412, 1276, 1265, 1064. δ_H (300 MHz, D_2O, 300 K): 7.62–7.57 (m, 1H, H4′-Ph-H), 7.38–7.29 (m, 2H, H5′ and H6′-Ph-H), 4.01 (d, $J_{1,2}$ = 9.9 Hz, 1H, H1), 3.47–3.41 (m, 2H, H6a and H6b), 3.31–3.18 (m, 2H, H2 and H4), 3.10 (t, $J_{2,3} = J_{3,4}$ = 9.0 Hz, 1H, H3), 2.43–2.38 (m, 1H, H5). δ_C (75 MHz, D_2O, 300 K): 160.5 (C=N), 132.7 (C-3 of Ph), 132.4 (C-4 of Ph), 131.1 (C-1 of Ph), 130.3 (C-2 of Ph), 129.3 (C-6 of Ph), 127.7 (C-5 of Ph), 82.7 (C-1), 79.4 (C-5), 76.5 (C-3), 70.9 (C-2), 68.0 (C-4), 59.1 (C-6). HRMS (ESI) m/z for $C_{13}H_{14}O_9Cl_2NS_2$ [M − K]$^-$: calculated 461.9493; found 461.9470.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Crystals of (**9**) and (**11**) were mounted in low-temperature oil and flash cooled to 130 K using a low-temperature device. All H atoms bonded to C atoms and the methanol hydroxy H atom in (**11**) were placed in geometrically optimized positions and constrained to ride on their parent atoms, with U_{iso}(H) = 1.5U_{eq}(C,O) for methyl and hydroxy groups and 1.2U_{eq}(C) otherwise. The hydroxy H atoms of the nonsolvent molecules were refined isotropically, while the ethanol hydroxy H atom in (**11**) was constrained to ride on its parent atom in the position located in a difference Fourier map, with U_{iso}(H) refining freely.

3. Results and discussion

3.1. Synthesis of 2,3-dichlorophenylglucosinolate (11)

From our studies, the aldoxime pathway was the most convenient method to synthesize aromatic hydroxymoyl chlorides compared to the nitronate and nitrovinyl pathways (Vo, Trenerry, Rochfort, Wadeson *et al.*, 2013). Thus, 2,3-dichlorobenzohydroxymoyl chloride was synthesized by the aldoxime method from 2,3-dichlorobenzaldehyde, (**1**) (see Scheme 1 and the *Supporting information*) (Bialecki *et al.*, 2007).

Table 2
Hydrogen-bond geometry (Å, °) for (**11**).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
$O11—H11A\cdots O8$	0.84	2.05	2.861 (8)	163
$O10—H10\cdots O8$	0.94	1.80	2.738 (7)	174
$O3—H3A\cdots N1^{v}$	0.84 (6)	2.19 (7)	3.019 (6)	170 (5)
$O2—H2A\cdots O5^{vi}$	0.93 (8)	1.79 (8)	2.655 (5)	155 (7)
$O5—H5A\cdots O11^{vii}$	1.01 (10)	1.70 (10)	2.690 (7)	166 (9)
$O4—H4A\cdots O10^{viii}$	1.09 (10)	1.61 (10)	2.685 (8)	164 (9)

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

To increase the yield, in the first step, hydroxylamine hydrochloride was added in excess to the solution of reactants, dry MeOH and pyridine. After work-up, oxime (**2**) was obtained by recrystallization from hexane and ethyl acetate. In the chlorination step, the yield was affected by the amount of N-chlorosuccinimide (NCS) added (Liu *et al.*, 1980). This is because reaction of NCS with oximes in dimethylformamide (DMF) exhibits an induction period and the reaction can become strongly exothermic for most substrates if the reaction initiates after a considerable portion of the NCS has been added. It was found that it is desirable to initiate the reaction prior to addition of no more than one-fifth of the NCS required (Liu *et al.*, 1980). Therefore, to improve the yield, NCS (1.05 equivalents) was added one-fifth at a time (over a period of 30 min) into a cold stirred solution of oxime (**2**) and DMF. The reaction mixture was kept at 273 K for the duration of the reaction and the temperature was then allowed to increase to room temperature. After 4 h, the reaction was worked up, and the product was purified by flash column chromatography or recrystallization to provide chlorooxime (**3**) in excellent yield (86% yield over two steps).

2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl thiol, (**8**), was obtained in four steps from D-glucose (see Scheme 2 and the *Supporting information*) (Yu *et al.*, 2010; Floyd *et al.*, 2009). D-Glucose, (**4**), was peracetylated with acetic anhydride in pyridine in the presence of N,N-dimethylaminopyridine (DMAP) as catalyst to yield (**5**), which was able to undergo selective displacement of the acetate group at the anomeric position to yield, stereospecifically, 1α-bromo-2,3,4,6-tetra-O-acetyl-D-glucopyranose, (**6**). The α-bromide was then treated with thiourea to afford β-isothiouronium salt (**7**), followed by mild hydrolysis with sodium metabisulfite to yield, stereo-

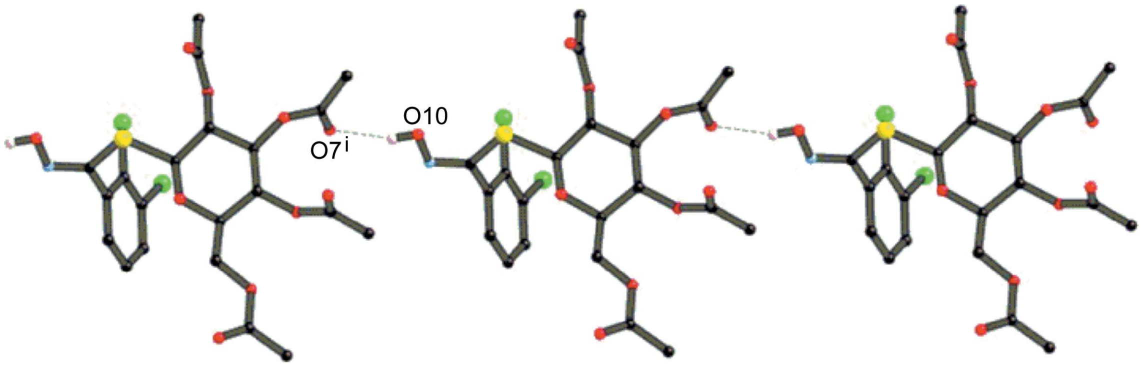

Figure 2
The hydrogen-bonded network of (**9**) extending along the c axis. [Symmetry code: (i) $x, y, z-1$.] (Atom colors: yellow = sulfur, red = oxygen, black = carbon, green = chlorine and white = nitrogen.)

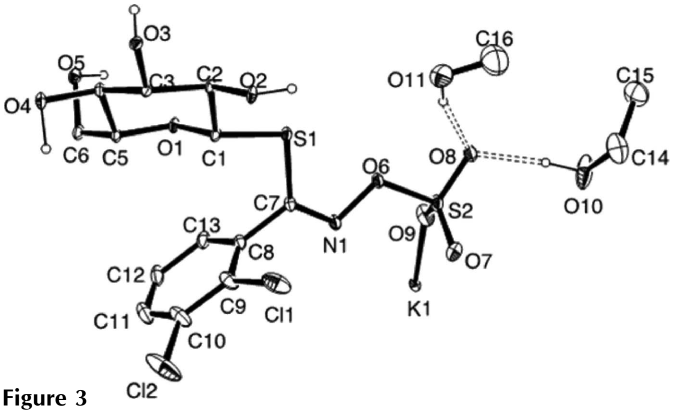

Figure 3
Displacement ellipsoid plot for glucosinolate (**11**)·EtOH·MeOH, with ellipsoids drawn at the 20% probability level. H atoms on C atoms have been omitted.

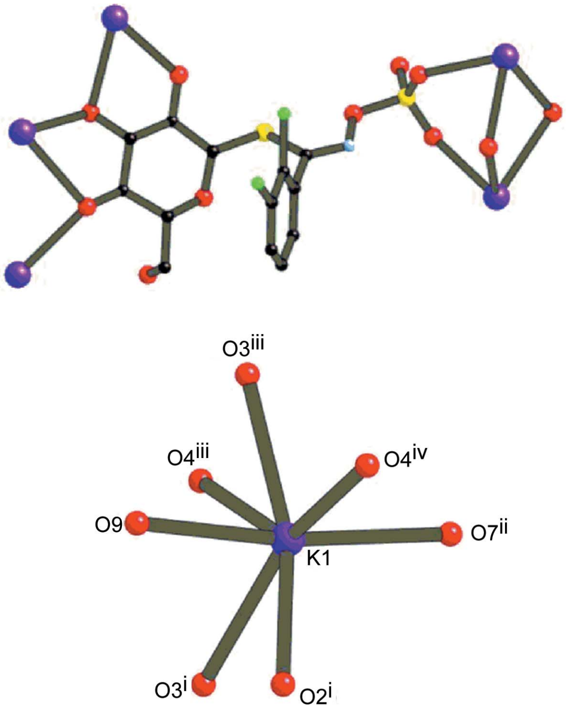

Figure 4
(Top) The sugar coordination mode to potassium ions and (bottom) the simplified coordination sphere about the potassium ion. The symmetry codes are as in Table 3. (Atom colors: purple = potassium, yellow = sulfur, red = oxygen, black = carbon, green = chlorine and white = nitrogen.)

specifically, 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl thiol, (**8**), in an excellent yield (78%) from glucose over four steps. The coupling of (**8**) with hydroxymoyl chloride (**3**) was conducted by a general method (see Scheme 2) (Benn, 1963, 1964; Streicher *et al.*, 1995). To guarantee that no thiol material was wasted, the coupling was carried out with an excess of hydroxymoyl chloride (**3**) to maximize the conversion of (**8**). The thiohydroximates were purified by flash chromatography eluting with DCM–MeOH in excellent yield (90%). The coupling was stereospecific in that only the *Z* isomers were formed (Viaud & Rollin, 1990). Single-crystal X-ray crystallographic analysis of *S*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-2,3-dichlorophenylacetothiohydroximate, (**9**), confirmed that the thiohydroxymate was obtained as a (*Z*)-thiohydroximate (Fig. 1).

The *O*-sulfation proved to be a tricky step, as evidenced by previous work (Zhang *et al.*, 1992; Morrison & Botting, 2007; Rossiter *et al.*, 2007; Vo, Trenerry, Rochfort & Hughes, 2013). From our studies (Vo, Trenerry, Rochfort, Wadeson *et al.*, 2013), to improve the yield, the sulfation was carried out in DCM at reflux temperature under an argon atmosphere rather than in pyridine at room temperature (Scheme 2). The sulfation product (**10**) can be lost due to the high polarity of the solvent which promotes hydrolysis. Therefore, in the work-up, the solvent mixture of 20% MeOH–chloroform should be used to extract organic phases instead of only chloroform in order to avoid losing the product in the aqueous phase. As a result, (**10**) was obtained in 81% yield. De-*O*-acetylation was carried out by treatment of potassium methoxide in MeOH (see Scheme 2) (Rollin & Tatibouët, 2011). 2,3-Dichlorophenylglucosinolate (**11**) was obtained in 56% overall yield (over seven steps from glucose) by flash column chromatography on silica gel eluting with EtOAc–MeOH–H_2O and then recrystallization following the vial-in-a-vial vapor diffusion method with H_2O–MeOH inside and EtOH outside at 273–278 K for a period of up to two years. The difficulties of the dual solvation of (**11**) with one molecule of methanol and one molecule of ethanol may be one of the main reasons for the slow crystal growth of (**11**).

3.2. Description of the structures

In (**9**) (Fig. 1), the C5—O1—C1—S1 torsion angle of 177.25 (17)° establishes the *β*-configuration of the thio-

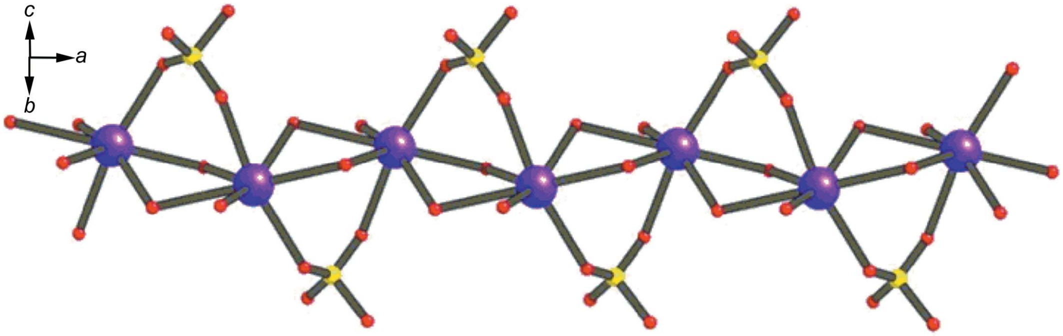

Figure 5
The chains of potassium ions linked by sulfonate and sugar O atoms extending along the *a* axis.

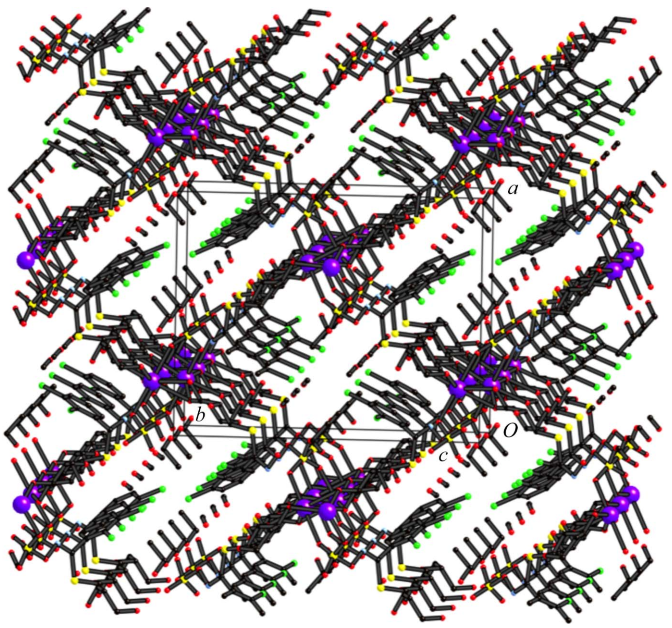

Figure 6
The three-dimensional polymeric network of (**11**), including the methanol and ethanol solvent molecules.

hydroximate substituent. The anomeric C—S bond length of 1.803 (3) Å compares with the value of 1.809 Å reported for another β-thiohydroximate derivative (Tocher & Truter, 1990), but is significantly shorter than that observed for a similar α-thiohydroximate, for which the C—S bond length was reported to be 1.838 Å (Durier *et al.*, 1992), which is consistent with a strong structural anomeric effect expected for this electronegative substituent (Kirby, 1983). The four C—OAc bond lengths in (**9**) range from 1.436 (3) to 1.444 (3) Å. The structure is stabilized by O—H$\cdots$O hydrogen bonds between the oxime hydroxy donor and acetate atom O7 as acceptor, with O10$\cdots$O7(x, y, $z - 1$) = 2.768 (3) Å and O10—H10$\cdots$O7(x, y, $z - 1$) = 159 (3)°, forming a chain extending along the c axis (Fig. 2).

Crystals of (**11**) were obtained as a dual solvate, containing one methanol and one ethanol molecule of crystallization. The methanol solvent molecule forms an intramolecular hydrogen-bonded bridge between the O2 hydroxy group and sulfonate atom O8 (Fig. 3), while the ethanol solvent molecule forms an intermolecular hydrogen-bonded bridge between atom O8 and the O4 hydroxy group (see Table 2 for a list of hydrogen-bonded contacts). The structure is stabilized by further hydrogen-bonding interactions which are also summarized in Table 2. The configuration at the anomeric centre is β, as defined by the C5—O1—C1—S1 torsion angle of 169.9 (2)°, while the anomeric C—S bond length is 1.805 (5) Å, which is comparable to the corresponding bond length in (**9**).

The potassium counter-ion is coordinated to seven O atoms with a geometry which can be described as a distorted pentagonal bipyramid, with atoms O3^{i}, O3^{iii}, O4^{iii}, O4^{iv} and O2^{i} (see Table 3 for symmetry codes) forming the pentagonal base and atoms O9 and O7^{ii} as the capping atoms. The simplified coordination sphere about the potassium ion and further coordination contacts are shown in Fig. 4. Each potassium ion bridges five sugar molecules and each sugar molecule coordinates to five potassium ions, resulting in an extensively crosslinked polymeric network (Table 3).

Table 3
Selected geometric parameters (Å, °) for (**11**).

K1—O2^{i}	2.645 (4)	K1—O4^{iv}	2.885 (4)
K1—O9	2.648 (5)	K1—O3^{i}	2.967 (4)
K1—O7^{ii}	2.713 (5)	K1—O4^{iii}	3.000 (4)
K1—O3^{iii}	2.751 (4)		
O2^{i}—K1—O9	83.25 (14)	O7^{ii}—K1—O3^{i}	111.09 (16)
O2^{i}—K1—O7^{ii}	100.10 (16)	O3^{iii}—K1—O3^{i}	127.98 (9)
O9—K1—O7^{ii}	168.68 (19)	O4^{iv}—K1—O3^{i}	149.51 (11)
O2^{i}—K1—O3^{iii}	152.88 (12)	O2^{i}—K1—O4^{iii}	130.97 (10)
O2^{i}—K1—O4^{iv}	90.35 (11)	O9—K1—O4^{iii}	82.14 (16)
O9—K1—O4^{iv}	93.23 (17)	O7^{ii}—K1—O4^{iii}	103.20 (15)
O7^{ii}—K1—O4^{iv}	76.01 (15)	O4^{iv}—K1—O4^{iii}	136.94 (9)
O2^{i}—K1—O3^{i}	59.46 (10)	O3^{i}—K1—O4^{iii}	71.98 (10)
O9—K1—O3^{i}	79.97 (14)		

Symmetry codes: (i) $-x+\frac{3}{2}, -y, z+\frac{1}{2}$; (ii) $x+\frac{1}{2}, -y-\frac{1}{2}, -z+1$; (iii) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+\frac{5}{2}, -y, z+\frac{1}{2}$.

The resulting three-dimensional polymeric network of (**11**) consists of chains containing the potassium ion and its coordinated O atoms, which extends down the a axis (Fig. 5). These chains are crosslinked in the bc direction by the sugar molecules to complete the three-dimensional polymeric network. The channels of this network are occupied by the dichlorophenyl substituents and the ethanol and methanol solvent molecules (Fig. 6).

4. Conclusion

In conclusion, 2,3-dichlorophenylglucosinolate (**11**) was successfully synthesized with a high overall yield (56%). The study has demonstrated success in growing crystals of a glucosinolate by the vial-in-a-vial vapour diffusion method. The X-ray data analysis of (**11**) also confirmed the absolute configuration of the glucosinolate structure.

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supplementary materials

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Preparation and X-ray analysis of potassium (2,3-dichlorophenyl)glucosinolate

Quan V. Vo, Craige Trenerry, Simone Rochfort, Jonathan White and Andrew B. Hughes

Computing details

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2010) for (9); *CrysAlis PRO* (Agilent, 2012) for (11). Cell refinement: *CrysAlis PRO* (Oxford Diffraction, 2010) for (9); *CrysAlis PRO* (Agilent, 2012) for (11). Data reduction: *CrysAlis PRO* (Oxford Diffraction, 2010) for (9); *CrysAlis PRO* (Agilent, 2012) for (11). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) for (9); *SHELXL2014* (Sheldrick, 2008) for (11). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) for (9); *SHELXL2014* (Sheldrick, 2008) for (11). For both compounds, molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

(9) *S*-(2,3,4,6-Tetra-*O*-acetyl-*α*-*D*-glucopyranosyl)-2,3-dichlorophenylacetothiohydroxymate

Crystal data

$C_{21}H_{23}Cl_2NO_{10}S$	$F(000) = 572$
$M_r = 552.36$	$D_x = 1.446$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å
$a = 7.1967$ (2) Å	Cell parameters from 3604 reflections
$b = 15.1383$ (4) Å	$\theta = 2.9$–$29.2°$
$c = 11.9441$ (3) Å	$\mu = 0.39$ mm^{-1}
$\beta = 102.786$ (3)°	$T = 130$ K
$V = 1268.99$ (6) Å^3	Block, colourless
$Z = 2$	0.37 × 0.32 × 0.14 mm

Data collection

Oxford Diffraction SuperNova (Dual, Cu at zero, Atlas) diffractometer	$T_{min} = 0.888$, $T_{max} = 0.949$
	6348 measured reflections
	3790 independent reflections
Radiation source: SuperNova (Mo) X-ray Source	3535 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.027$
Mirror monochromator	$\theta_{max} = 25.0°$, $\theta_{min} = 2.9°$
ω scans	$h = -8 \rightarrow 8$
Absorption correction: gaussian (*CrysAlis PRO*; Oxford Diffraction, 2010)	$k = -18 \rightarrow 18$
	$l = -14 \rightarrow 12$

Refinement

Refinement on F^2	1 restraint
Least-squares matrix: full	Primary atom site location: structure-invariant direct methods
$R[F^2 > 2\sigma(F^2)] = 0.031$	
$wR(F^2) = 0.069$	Secondary atom site location: difference Fourier map
$S = 1.05$	
3790 reflections	Hydrogen site location: inferred from neighbouring sites
324 parameters	

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2 + 0.0094P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Absolute structure: Flack (1983), **???? Friedel pairs**
Absolute structure parameter: −0.10 (5)

Special details

Experimental. Absorption correction: *CrysAlis PRO*, Oxford Diffraction Ltd., Version 1.171.34.40 (release 27–08-2010 CrysAlis171. NET) (compiled Aug 27 2010,11:50:40) Numerical absorption correction based on Gaussian integration over a multifaceted crystal model

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}
Cl1	0.44877 (9)	0.68631 (4)	0.52381 (6)	0.02509 (16)
S1	0.86715 (11)	0.55216 (4)	0.53502 (6)	0.02610 (17)
Cl2	0.42532 (10)	0.86903 (5)	0.64869 (7)	0.03281 (19)
O4	1.2021 (3)	0.61837 (13)	1.02012 (16)	0.0279 (5)
O8	0.6894 (2)	0.50165 (12)	0.74050 (16)	0.0227 (4)
O10	0.8321 (3)	0.56559 (14)	0.30744 (18)	0.0310 (5)
O1	1.1267 (3)	0.61058 (12)	0.70838 (15)	0.0224 (4)
O6	0.9346 (3)	0.47062 (11)	0.95260 (15)	0.0209 (4)
O3	1.7414 (3)	0.73702 (13)	0.86375 (17)	0.0328 (5)
O2	1.4752 (3)	0.71646 (12)	0.92931 (16)	0.0268 (5)
C21	0.9575 (4)	0.79530 (17)	0.5331 (2)	0.0206 (6)
H21	1.0686	0.7812	0.5094	0.025*
C4	1.1623 (4)	0.57708 (17)	0.9091 (2)	0.0203 (6)
H4	1.2477	0.5267	0.9087	0.024*
C12	0.8580 (4)	0.4836 (2)	1.0445 (2)	0.0262 (7)
O7	0.8170 (3)	0.55539 (16)	1.07422 (17)	0.0392 (5)
C5	1.1923 (4)	0.64628 (18)	0.8220 (2)	0.0209 (6)
H5	1.1214	0.7002	0.8307	0.025*
C18	0.6291 (4)	0.83854 (18)	0.6046 (2)	0.0206 (6)
C17	0.6391 (3)	0.75882 (17)	0.5485 (2)	0.0175 (6)
N1	0.8075 (3)	0.65176 (15)	0.34747 (19)	0.0234 (5)
O9	0.7200 (3)	0.36415 (16)	0.6768 (2)	0.0567 (7)
O5	1.3731 (6)	0.5010 (2)	1.0986 (3)	0.0947 (12)
C15	0.8233 (4)	0.65118 (17)	0.4559 (2)	0.0177 (6)
C20	0.9447 (4)	0.87462 (18)	0.5890 (2)	0.0247 (6)
H20	1.0472	0.9136	0.6024	0.030*
C6	1.3981 (4)	0.6682 (2)	0.8261 (2)	0.0282 (7)
H6A	1.4701	0.6143	0.8245	0.034*
H6B	1.4073	0.7035	0.7597	0.034*

C13	0.4108 (4)	0.4173 (2)	0.6887 (3)	0.0378 (8)
H13A	0.3661	0.3588	0.6660	0.057*
H13B	0.3499	0.4589	0.6316	0.057*
H13C	0.3810	0.4315	0.7610	0.057*
C1	0.9291 (4)	0.59086 (17)	0.6813 (2)	0.0198 (6)
H1	0.8545	0.6434	0.6906	0.024*
C9	1.3331 (6)	0.6248 (3)	1.2173 (3)	0.0652 (13)
H9A	1.4120	0.5925	1.2791	0.098*
H9B	1.2107	0.6350	1.2344	0.098*
H9C	1.3922	0.6804	1.2081	0.098*
C19	0.7815 (4)	0.89604 (18)	0.6248 (3)	0.0253 (6)
H19	0.7739	0.9492	0.6626	0.030*
C3	0.9558 (4)	0.54639 (18)	0.8831 (2)	0.0181 (5)
H3	0.8739	0.5944	0.8987	0.022*
C16	0.8047 (4)	0.73684 (17)	0.5125 (2)	0.0177 (6)
C7	1.7243 (5)	0.7944 (2)	1.0484 (3)	0.0496 (10)
H7A	1.6750	0.8536	1.0427	0.074*
H7B	1.8610	0.7962	1.0656	0.074*
H7C	1.6819	0.7636	1.1084	0.074*
C2	0.8905 (4)	0.51668 (17)	0.7593 (2)	0.0180 (6)
H2	0.9567	0.4625	0.7456	0.022*
C8	1.6544 (4)	0.74775 (18)	0.9377 (3)	0.0271 (7)
C14	0.6218 (4)	0.4212 (2)	0.7001 (3)	0.0318 (7)
C11	0.8368 (5)	0.3977 (2)	1.1018 (3)	0.0380 (8)
H11A	0.7584	0.4060	1.1564	0.057*
H11B	0.9600	0.3767	1.1407	0.057*
H11C	0.7783	0.3553	1.0452	0.057*
C10	1.3091 (5)	0.5728 (3)	1.1091 (3)	0.0476 (9)
H10	0.830 (5)	0.576 (2)	0.243 (3)	0.037 (10)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0204 (3)	0.0276 (4)	0.0278 (4)	−0.0048 (3)	0.0064 (3)	−0.0040 (3)
S1	0.0453 (4)	0.0192 (3)	0.0128 (3)	0.0041 (3)	0.0043 (3)	−0.0009 (3)
Cl2	0.0266 (4)	0.0364 (4)	0.0374 (4)	0.0075 (3)	0.0114 (3)	−0.0086 (4)
O4	0.0309 (12)	0.0367 (12)	0.0147 (10)	−0.0086 (10)	0.0020 (9)	−0.0029 (9)
O8	0.0230 (10)	0.0231 (10)	0.0209 (10)	0.0002 (8)	0.0028 (8)	−0.0028 (9)
O10	0.0527 (14)	0.0281 (12)	0.0145 (10)	0.0040 (10)	0.0121 (10)	−0.0014 (10)
O1	0.0288 (11)	0.0240 (10)	0.0155 (10)	−0.0007 (8)	0.0076 (9)	−0.0006 (8)
O6	0.0305 (10)	0.0179 (9)	0.0143 (10)	−0.0010 (8)	0.0051 (8)	0.0028 (8)
O3	0.0266 (11)	0.0334 (11)	0.0408 (13)	0.0014 (10)	0.0125 (10)	0.0032 (11)
O2	0.0268 (11)	0.0287 (11)	0.0263 (11)	−0.0068 (8)	0.0090 (9)	−0.0062 (9)
C21	0.0172 (13)	0.0221 (15)	0.0229 (15)	0.0005 (11)	0.0049 (12)	0.0036 (13)
C4	0.0260 (14)	0.0219 (15)	0.0139 (13)	0.0033 (11)	0.0066 (12)	0.0019 (12)
C12	0.0331 (16)	0.0309 (17)	0.0145 (14)	−0.0093 (13)	0.0048 (12)	−0.0008 (14)
O7	0.0681 (15)	0.0317 (12)	0.0251 (11)	−0.0016 (12)	0.0262 (11)	−0.0014 (11)
C5	0.0277 (15)	0.0197 (14)	0.0167 (14)	−0.0003 (12)	0.0079 (12)	−0.0019 (12)
C18	0.0199 (13)	0.0230 (14)	0.0181 (14)	0.0054 (11)	0.0024 (11)	0.0011 (12)
C17	0.0181 (13)	0.0198 (14)	0.0135 (13)	−0.0003 (11)	0.0011 (11)	0.0006 (12)

N1	0.0348 (14)	0.0202 (12)	0.0168 (12)	0.0014 (10)	0.0088 (11)	−0.0021 (10)
O9	0.0492 (15)	0.0298 (13)	0.093 (2)	−0.0068 (12)	0.0189 (15)	−0.0278 (15)
O5	0.137 (3)	0.057 (2)	0.057 (2)	0.016 (2)	−0.049 (2)	0.0103 (17)
C15	0.0163 (13)	0.0210 (14)	0.0166 (14)	0.0018 (11)	0.0055 (11)	0.0013 (12)
C20	0.0210 (14)	0.0194 (14)	0.0314 (16)	−0.0062 (12)	0.0010 (12)	−0.0023 (14)
C6	0.0306 (16)	0.0299 (16)	0.0263 (16)	−0.0046 (13)	0.0109 (14)	−0.0063 (14)
C13	0.0377 (18)	0.0399 (19)	0.0351 (19)	−0.0107 (16)	0.0065 (15)	−0.0075 (17)
C1	0.0273 (15)	0.0186 (14)	0.0134 (13)	0.0040 (11)	0.0046 (12)	−0.0020 (12)
C9	0.077 (3)	0.091 (3)	0.0199 (17)	−0.044 (3)	−0.0070 (18)	−0.002 (2)
C19	0.0289 (15)	0.0186 (14)	0.0253 (15)	0.0028 (12)	−0.0003 (13)	−0.0014 (13)
C3	0.0290 (14)	0.0142 (13)	0.0114 (12)	0.0002 (12)	0.0052 (11)	0.0031 (12)
C16	0.0228 (14)	0.0181 (14)	0.0114 (12)	0.0041 (12)	0.0021 (11)	0.0056 (12)
C7	0.044 (2)	0.056 (2)	0.050 (2)	−0.0164 (18)	0.0121 (18)	−0.016 (2)
C2	0.0216 (13)	0.0183 (14)	0.0146 (14)	0.0034 (11)	0.0051 (11)	0.0000 (12)
C8	0.0260 (15)	0.0177 (15)	0.0383 (17)	0.0006 (13)	0.0085 (14)	−0.0003 (14)
C14	0.0421 (18)	0.0273 (17)	0.0255 (17)	−0.0045 (15)	0.0063 (15)	−0.0090 (14)
C11	0.050 (2)	0.0381 (19)	0.0269 (17)	−0.0120 (15)	0.0119 (16)	0.0056 (15)
C10	0.052 (2)	0.058 (3)	0.0242 (18)	−0.0164 (19)	−0.0109 (16)	0.0083 (18)

Geometric parameters (Å, º)

Cl1—C17	1.729 (3)	N1—C15	1.275 (3)
S1—C15	1.763 (3)	O9—C14	1.188 (4)
S1—C1	1.803 (3)	O5—C10	1.199 (5)
Cl2—C18	1.727 (2)	C15—C16	1.482 (4)
O4—C10	1.355 (4)	C20—C19	1.375 (4)
O4—C4	1.436 (3)	C20—H20	0.9300
O8—C14	1.359 (3)	C6—H6A	0.9700
O8—C2	1.432 (3)	C6—H6B	0.9700
O10—N1	1.414 (3)	C13—C14	1.495 (4)
O10—H10	0.78 (3)	C13—H13A	0.9600
O1—C1	1.419 (3)	C13—H13B	0.9600
O1—C5	1.439 (3)	C13—H13C	0.9600
O6—C12	1.347 (3)	C1—C2	1.523 (4)
O6—C3	1.444 (3)	C1—H1	0.9800
O3—C8	1.201 (3)	C9—C10	1.490 (5)
O2—C8	1.357 (3)	C9—H9A	0.9600
O2—C6	1.434 (3)	C9—H9B	0.9600
C21—C20	1.387 (4)	C9—H9C	0.9600
C21—C16	1.390 (4)	C19—H19	0.9300
C21—H21	0.9300	C3—C2	1.517 (3)
C4—C3	1.522 (4)	C3—H3	0.9800
C4—C5	1.526 (4)	C7—C8	1.486 (4)
C4—H4	0.9800	C7—H7A	0.9600
C12—O7	1.200 (4)	C7—H7B	0.9600
C12—C11	1.493 (4)	C7—H7C	0.9600
C5—C6	1.508 (4)	C2—H2	0.9800
C5—H5	0.9800	C11—H11A	0.9600
C18—C19	1.379 (4)	C11—H11B	0.9600
C18—C17	1.390 (4)	C11—H11C	0.9600

C17—C16	1.394 (3)

C15—S1—C1	102.69 (12)	O1—C1—S1	108.04 (16)
C10—O4—C4	117.7 (2)	C2—C1—S1	108.29 (18)
C14—O8—C2	117.9 (2)	O1—C1—H1	110.5
N1—O10—H10	99 (2)	C2—C1—H1	110.5
C1—O1—C5	113.37 (18)	S1—C1—H1	110.5
C12—O6—C3	117.8 (2)	C10—C9—H9A	109.5
C8—O2—C6	114.9 (2)	C10—C9—H9B	109.5
C20—C21—C16	120.1 (2)	H9A—C9—H9B	109.5
C20—C21—H21	119.9	C10—C9—H9C	109.5
C16—C21—H21	119.9	H9A—C9—H9C	109.5
O4—C4—C3	107.93 (19)	H9B—C9—H9C	109.5
O4—C4—C5	107.6 (2)	C20—C19—C18	119.9 (3)
C3—C4—C5	110.5 (2)	C20—C19—H19	120.1
O4—C4—H4	110.3	C18—C19—H19	120.1
C3—C4—H4	110.3	O6—C3—C2	106.0 (2)
C5—C4—H4	110.3	O6—C3—C4	110.4 (2)
O7—C12—O6	123.1 (3)	C2—C3—C4	111.58 (19)
O7—C12—C11	126.6 (2)	O6—C3—H3	109.6
O6—C12—C11	110.4 (3)	C2—C3—H3	109.6
O1—C5—C6	103.19 (19)	C4—C3—H3	109.6
O1—C5—C4	108.6 (2)	C21—C16—C17	119.3 (2)
C6—C5—C4	114.5 (2)	C21—C16—C15	119.4 (2)
O1—C5—H5	110.1	C17—C16—C15	121.3 (2)
C6—C5—H5	110.1	C8—C7—H7A	109.5
C4—C5—H5	110.1	C8—C7—H7B	109.5
C19—C18—C17	120.5 (2)	H7A—C7—H7B	109.5
C19—C18—Cl2	118.3 (2)	C8—C7—H7C	109.5
C17—C18—Cl2	121.1 (2)	H7A—C7—H7C	109.5
C18—C17—C16	119.7 (2)	H7B—C7—H7C	109.5
C18—C17—Cl1	120.66 (18)	O8—C2—C3	106.53 (18)
C16—C17—Cl1	119.7 (2)	O8—C2—C1	109.6 (2)
C15—N1—O10	110.3 (2)	C3—C2—C1	108.6 (2)
N1—C15—C16	117.4 (2)	O8—C2—H2	110.7
N1—C15—S1	121.0 (2)	C3—C2—H2	110.7
C16—C15—S1	121.57 (18)	C1—C2—H2	110.7
C19—C20—C21	120.4 (2)	O3—C8—O2	122.7 (3)
C19—C20—H20	119.8	O3—C8—C7	126.2 (3)
C21—C20—H20	119.8	O2—C8—C7	111.1 (2)
O2—C6—C5	109.3 (2)	O9—C14—O8	123.4 (3)
O2—C6—H6A	109.8	O9—C14—C13	126.4 (3)
C5—C6—H6A	109.8	O8—C14—C13	110.2 (3)
O2—C6—H6B	109.8	C12—C11—H11A	109.5
C5—C6—H6B	109.8	C12—C11—H11B	109.5
H6A—C6—H6B	108.3	H11A—C11—H11B	109.5
C14—C13—H13A	109.5	C12—C11—H11C	109.5
C14—C13—H13B	109.5	H11A—C11—H11C	109.5
H13A—C13—H13B	109.5	H11B—C11—H11C	109.5

C14—C13—H13C	109.5	O5—C10—O4	123.0 (3)
H13A—C13—H13C	109.5	O5—C10—C9	126.6 (4)
H13B—C13—H13C	109.5	O4—C10—C9	110.4 (3)
O1—C1—C2	109.0 (2)		

C10—O4—C4—C3	105.2 (3)	O4—C4—C3—O6	−72.6 (2)
C10—O4—C4—C5	−135.6 (3)	C5—C4—C3—O6	170.10 (19)
C3—O6—C12—O7	−4.2 (4)	O4—C4—C3—C2	169.9 (2)
C3—O6—C12—C11	176.7 (3)	C5—C4—C3—C2	52.5 (3)
C1—O1—C5—C6	−175.6 (2)	C20—C21—C16—C17	0.0 (4)
C1—O1—C5—C4	62.5 (3)	C20—C21—C16—C15	−178.1 (2)
O4—C4—C5—O1	−171.7 (2)	C18—C17—C16—C21	−0.1 (4)
C3—C4—C5—O1	−54.1 (3)	Cl1—C17—C16—C21	−179.7 (2)
O4—C4—C5—C6	73.6 (3)	C18—C17—C16—C15	177.9 (2)
C3—C4—C5—C6	−168.9 (2)	Cl1—C17—C16—C15	−1.7 (3)
C19—C18—C17—C16	0.0 (4)	N1—C15—C16—C21	−78.0 (3)
Cl2—C18—C17—C16	179.0 (2)	S1—C15—C16—C21	101.6 (2)
C19—C18—C17—Cl1	179.6 (2)	N1—C15—C16—C17	104.0 (3)
Cl2—C18—C17—Cl1	−1.4 (3)	S1—C15—C16—C17	−76.5 (3)
O10—N1—C15—C16	178.9 (2)	C14—O8—C2—C3	−125.1 (2)
O10—N1—C15—S1	−0.7 (3)	C14—O8—C2—C1	117.6 (2)
C1—S1—C15—N1	167.6 (2)	O6—C3—C2—O8	67.9 (2)
C1—S1—C15—C16	−11.9 (2)	C4—C3—C2—O8	−171.9 (2)
C16—C21—C20—C19	0.2 (4)	O6—C3—C2—C1	−174.09 (19)
C8—O2—C6—C5	−173.7 (2)	C4—C3—C2—C1	−53.9 (3)
O1—C5—C6—O2	171.7 (2)	O1—C1—C2—O8	174.60 (18)
C4—C5—C6—O2	−70.4 (3)	S1—C1—C2—O8	−68.1 (2)
C5—O1—C1—C2	−65.3 (2)	O1—C1—C2—C3	58.6 (3)
C5—O1—C1—S1	177.25 (17)	S1—C1—C2—C3	175.90 (17)
C15—S1—C1—O1	−85.48 (18)	C6—O2—C8—O3	0.9 (4)
C15—S1—C1—C2	156.63 (17)	C6—O2—C8—C7	−178.4 (3)
C21—C20—C19—C18	−0.3 (4)	C2—O8—C14—O9	−2.2 (4)
C17—C18—C19—C20	0.2 (4)	C2—O8—C14—C13	178.7 (2)
Cl2—C18—C19—C20	−178.8 (2)	C4—O4—C10—O5	1.1 (5)
C12—O6—C3—C2	−136.3 (2)	C4—O4—C10—C9	−179.1 (2)
C12—O6—C3—C4	102.8 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O10—H10···O7^{i}	0.78 (3)	2.03 (3)	2.768 (3)	159 (3)

Symmetry code: (i) *x*, *y*, *z*−1.

(11) Potassium 2,3-dichlorophenylglucosinolate–ethanol–methanol (1/1/1)

Crystal data

$K^{+}\cdot C_{13}H_{14}Cl_{2}NO_{9}S_{2}^{-}\cdot CH_{4}O\cdot C_{2}H_{6}O$

M_r = 580.48

Orthorhombic, $P2_12_12_1$

a = 8.0043 (1) Å

b = 15.5208 (4) Å

c = 19.4586 (4) Å

V = 2417.40 (9) Å^3

Z = 4

$F(000) = 1200$
$D_x = 1.595$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å
Cell parameters from 8197 reflections
$\theta = 2.9$–$77.4°$
$\mu = 6.09$ mm^{-1}
$T = 115$ K
Needle, colourless
0.65 × 0.07 × 0.04 mm

Data collection

Agilent SuperNova (Dual, Cu at zero, Atlas) diffractometer
Radiation source: SuperNova (Cu) X-ray Source
Mirror monochromator
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2012)
$T_{\min} = 0.716$, $T_{\max} = 1.000$
17993 measured reflections
5041 independent reflections
4725 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.058$
$\theta_{\max} = 77.6°$, $\theta_{\min} = 3.6°$
$h = -9 \rightarrow 8$
$k = -19 \rightarrow 13$
$l = -24 \rightarrow 22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.146$
$S = 1.03$
5041 reflections
327 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0865P)^2 + 3.0655P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.77$ e Å^{-3}
$\Delta\rho_{\min} = -0.84$ e Å^{-3}
Absolute structure: Flack x determined using 1921 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: 0.010 (12)

Special details

Experimental. Absorption correction: *CrysAlis PRO*, Agilent Technologies, Version 1.171.36.20 (release 27–06-2012 CrysAlis171. NET) (compiled Jul 11 2012,15:38:31) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

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.

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
K1	0.81320 (13)	−0.24630 (7)	0.54647 (5)	0.0245 (2)	
S1	0.89551 (15)	0.07667 (8)	0.29475 (6)	0.0219 (3)	
S2	0.59342 (18)	−0.06282 (10)	0.43921 (8)	0.0350 (3)	
Cl1	0.7777 (3)	−0.10597 (15)	0.17322 (11)	0.0665 (6)	
Cl2	1.0311 (6)	−0.2152 (2)	0.08482 (12)	0.1080 (14)	
O3	1.0458 (4)	0.2622 (2)	0.08230 (18)	0.0203 (7)	
O5	1.5311 (4)	0.1603 (3)	0.2366 (2)	0.0267 (8)	
O2	0.8047 (4)	0.1761 (2)	0.16045 (18)	0.0223 (7)	
O6	0.7190 (5)	−0.0153 (3)	0.3848 (2)	0.0291 (8)	
O1	1.1917 (4)	0.0953 (2)	0.23779 (18)	0.0215 (7)	
O4	1.3631 (4)	0.1715 (3)	0.07274 (19)	0.0264 (8)	

N1	0.8248 (6)	−0.0757 (3)	0.3505 (2)	0.0275 (9)	
O7	0.4930 (7)	−0.1219 (4)	0.3995 (3)	0.0570 (15)	
O8	0.5063 (6)	0.0133 (3)	0.4636 (3)	0.0414 (11)	
C1	1.0208 (6)	0.0930 (3)	0.2187 (3)	0.0212 (10)	
H1	1.0023	0.0438	0.1864	0.025*	
C3	1.0813 (6)	0.1843 (3)	0.1183 (3)	0.0184 (9)	
H3	1.0497	0.1355	0.0873	0.022*	
O9	0.6961 (7)	−0.1038 (4)	0.4892 (3)	0.0527 (14)	
C7	0.9104 (6)	−0.0353 (4)	0.3054 (3)	0.0240 (10)	
O11	0.4829 (10)	0.1584 (4)	0.3734 (3)	0.0644 (17)	
H11A	0.5067	0.1130	0.3948	0.097*	
C16	0.334 (2)	0.1827 (10)	0.3897 (8)	0.112 (5)	
H16A	0.3314	0.1995	0.4382	0.168*	
H16B	0.2555	0.1351	0.3820	0.168*	
H16C	0.3015	0.2320	0.3611	0.168*	
C8	1.0288 (7)	−0.0883 (4)	0.2635 (3)	0.0294 (12)	
C9	0.9775 (10)	−0.1233 (4)	0.2015 (3)	0.0427 (16)	
C6	1.4737 (6)	0.0837 (3)	0.2030 (3)	0.0267 (11)	
H6A	1.4803	0.0347	0.2354	0.032*	
H6B	1.5476	0.0709	0.1635	0.032*	
O10	0.1919 (8)	−0.0183 (6)	0.5129 (5)	0.099 (3)	
H10	0.2991	−0.0035	0.4973	0.08 (3)*	
C4	1.2672 (6)	0.1744 (3)	0.1345 (2)	0.0208 (10)	
H4	1.3039	0.2255	0.1620	0.025*	
C2	0.9727 (6)	0.1770 (3)	0.1828 (2)	0.0176 (9)	
H2	0.9928	0.2272	0.2140	0.021*	
C5	1.2961 (6)	0.0930 (3)	0.1778 (3)	0.0222 (10)	
H5	1.2663	0.0413	0.1497	0.027*	
C13	1.1917 (8)	−0.1008 (4)	0.2867 (4)	0.0406 (15)	
H13	1.2278	−0.0766	0.3290	0.049*	
C10	1.0905 (14)	−0.1718 (5)	0.1626 (4)	0.060 (2)	
C12	1.3005 (9)	−0.1497 (5)	0.2465 (5)	0.054 (2)	
H12	1.4118	−0.1584	0.2620	0.064*	
C11	1.2519 (12)	−0.1850 (5)	0.1859 (4)	0.061 (3)	
H11	1.3280	−0.2186	0.1597	0.073*	
C14′	0.0611 (12)	0.0318 (9)	0.4869 (5)	0.075 (3)	0.52 (5)
H14A	−0.0084	−0.0075	0.4588	0.090*	0.52 (5)
H14B	0.1128	0.0731	0.4544	0.090*	0.52 (5)
C15′	−0.050 (5)	0.080 (3)	0.5272 (15)	0.099 (11)	0.52 (5)
H15A	−0.1305	0.1092	0.4973	0.148*	0.52 (5)
H15B	−0.1102	0.0410	0.5584	0.148*	0.52 (5)
H15C	0.0121	0.1224	0.5540	0.148*	0.52 (5)
C14	0.0611 (12)	0.0318 (9)	0.4869 (5)	0.075 (3)	0.48 (5)
H14C	−0.0440	−0.0017	0.4849	0.090*	0.48 (5)
H14D	0.0878	0.0534	0.4403	0.090*	0.48 (5)
C15	0.048 (5)	0.1024 (18)	0.5358 (12)	0.077 (11)	0.48 (5)
H15D	−0.0421	0.1414	0.5215	0.115*	0.48 (5)
H15E	0.0228	0.0794	0.5815	0.115*	0.48 (5)
H15F	0.1536	0.1341	0.5373	0.115*	0.48 (5)

H3A	1.083 (7)	0.304 (4)	0.106 (3)	0.012 (13)*
H2A	0.729 (10)	0.178 (5)	0.197 (4)	0.05 (2)*
H5A	1.515 (13)	0.150 (6)	0.287 (5)	0.07 (3)*
H4A	1.326 (13)	0.107 (7)	0.055 (5)	0.07 (3)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K1	0.0226 (5)	0.0307 (5)	0.0202 (5)	0.0033 (4)	0.0022 (4)	−0.0027 (4)
S1	0.0186 (5)	0.0239 (6)	0.0231 (5)	0.0026 (4)	0.0055 (4)	0.0060 (5)
S2	0.0316 (7)	0.0313 (7)	0.0422 (8)	0.0042 (6)	0.0169 (6)	0.0100 (6)
Cl1	0.0847 (15)	0.0602 (12)	0.0545 (10)	0.0270 (11)	−0.0256 (10)	−0.0196 (9)
Cl2	0.190 (4)	0.0905 (19)	0.0438 (11)	0.066 (2)	0.0056 (16)	−0.0192 (12)
O3	0.0199 (15)	0.0196 (17)	0.0214 (16)	−0.0008 (14)	0.0015 (13)	0.0034 (14)
O5	0.0158 (16)	0.033 (2)	0.031 (2)	0.0000 (15)	−0.0004 (14)	0.0055 (16)
O2	0.0103 (15)	0.0333 (19)	0.0233 (17)	−0.0015 (14)	0.0010 (13)	0.0065 (14)
O6	0.0277 (19)	0.0267 (19)	0.0330 (19)	0.0064 (15)	0.0146 (16)	0.0071 (16)
O1	0.0117 (15)	0.0277 (18)	0.0252 (16)	0.0000 (13)	0.0019 (13)	0.0066 (14)
O4	0.0203 (17)	0.034 (2)	0.0246 (18)	0.0009 (14)	0.0096 (14)	0.0028 (15)
N1	0.028 (2)	0.027 (2)	0.028 (2)	0.0066 (19)	0.0098 (18)	0.0057 (18)
O7	0.039 (3)	0.054 (3)	0.078 (4)	−0.017 (2)	0.017 (3)	−0.012 (3)
O8	0.037 (2)	0.035 (2)	0.052 (3)	0.0096 (19)	0.023 (2)	0.008 (2)
C1	0.010 (2)	0.023 (2)	0.030 (2)	−0.0001 (18)	0.0017 (17)	0.0057 (19)
C3	0.016 (2)	0.018 (2)	0.022 (2)	−0.0015 (17)	0.0024 (17)	0.0045 (19)
O9	0.060 (3)	0.056 (3)	0.042 (2)	0.022 (3)	0.015 (2)	0.024 (2)
C7	0.019 (2)	0.030 (3)	0.023 (2)	0.004 (2)	0.0032 (18)	0.003 (2)
O11	0.087 (5)	0.060 (4)	0.046 (3)	−0.003 (3)	0.015 (3)	0.019 (3)
C16	0.112 (11)	0.107 (11)	0.116 (11)	0.022 (9)	0.023 (10)	0.024 (9)
C8	0.031 (3)	0.024 (3)	0.033 (3)	0.007 (2)	0.013 (2)	0.012 (2)
C9	0.062 (4)	0.033 (3)	0.032 (3)	0.018 (3)	0.010 (3)	0.007 (3)
C6	0.015 (2)	0.027 (3)	0.038 (3)	0.001 (2)	0.005 (2)	0.006 (2)
O10	0.042 (3)	0.119 (6)	0.137 (7)	0.020 (4)	0.028 (4)	0.094 (6)
C4	0.016 (2)	0.025 (2)	0.021 (2)	0.0005 (18)	0.0052 (17)	0.0029 (18)
C2	0.0104 (19)	0.021 (2)	0.021 (2)	−0.0021 (17)	0.0000 (16)	0.0031 (17)
C5	0.013 (2)	0.024 (2)	0.030 (2)	0.0026 (18)	0.0063 (18)	0.0041 (19)
C13	0.032 (3)	0.030 (3)	0.060 (4)	0.007 (3)	0.019 (3)	0.018 (3)
C10	0.101 (7)	0.041 (4)	0.038 (4)	0.028 (4)	0.028 (4)	0.006 (3)
C12	0.041 (4)	0.040 (4)	0.079 (6)	0.017 (3)	0.034 (4)	0.022 (4)
C11	0.082 (6)	0.041 (4)	0.059 (5)	0.027 (4)	0.045 (5)	0.017 (4)
C14′	0.057 (5)	0.113 (9)	0.055 (5)	0.025 (5)	−0.005 (4)	0.017 (6)
C15′	0.062 (17)	0.12 (2)	0.11 (2)	0.020 (15)	−0.023 (14)	−0.054 (18)
C14	0.057 (5)	0.113 (9)	0.055 (5)	0.025 (5)	−0.005 (4)	0.017 (6)
C15	0.09 (2)	0.091 (17)	0.051 (11)	0.002 (15)	0.012 (12)	−0.013 (11)

Geometric parameters (Å, º)

K1—O2^{i}	2.645 (4)	C1—H1	1.0000
K1—O9	2.648 (5)	C3—C4	1.529 (6)
K1—O7^{ii}	2.713 (5)	C3—C2	1.531 (6)
K1—O3^{iii}	2.751 (4)	C3—K1^{vi}	3.487 (5)

K1—O4^{iv}	2.885 (4)	C3—H3	1.0000
K1—O3^{i}	2.967 (4)	C7—C8	1.496 (7)
K1—O4^{iii}	3.000 (4)	O11—C16	1.291 (16)
K1—C3^{iii}	3.487 (5)	O11—H11A	0.8400
K1—S2^{ii}	3.7264 (18)	C16—H16A	0.9800
K1—K1^{v}	4.3933 (8)	C16—H16B	0.9800
K1—K1^{ii}	4.3933 (8)	C16—H16C	0.9800
S1—C7	1.754 (6)	C8—C9	1.385 (10)
S1—C1	1.805 (5)	C8—C13	1.393 (9)
S2—O9	1.423 (5)	C9—C10	1.400 (10)
S2—O7	1.443 (6)	C6—C5	1.511 (7)
S2—O8	1.452 (5)	C6—H6A	0.9900
S2—O6	1.636 (4)	C6—H6B	0.9900
S2—K1^{v}	3.7263 (18)	O10—C14′	1.399 (11)
Cl1—C9	1.713 (8)	O10—H10	0.9383
Cl2—C10	1.723 (10)	C4—C5	1.536 (7)
O3—C3	1.427 (6)	C4—H4	1.0000
O3—K1^{vi}	2.751 (4)	C2—H2	1.0000
O3—K1^{vii}	2.967 (4)	C5—H5	1.0000
O3—H3A	0.84 (6)	C13—C12	1.394 (9)
O5—C6	1.432 (7)	C13—H13	0.9500
O5—H5A	1.01 (10)	C10—C11	1.384 (14)
O2—C2	1.414 (5)	C12—C11	1.358 (13)
O2—K1^{vii}	2.645 (4)	C12—H12	0.9500
O2—H2A	0.93 (8)	C11—H11	0.9500
O6—N1	1.429 (6)	C14′—C15′	1.40 (3)
O1—C1	1.418 (6)	C14′—H14A	0.9900
O1—C5	1.436 (6)	C14′—H14B	0.9900
O4—C4	1.427 (6)	C15′—H15A	0.9800
O4—K1^{viii}	2.884 (4)	C15′—H15B	0.9800
O4—K1^{vi}	3.000 (4)	C15′—H15C	0.9800
O4—H4A	1.09 (10)	C15—H15D	0.9800
N1—C7	1.278 (7)	C15—H15E	0.9800
O7—K1^{v}	2.713 (5)	C15—H15F	0.9800
C1—C2	1.529 (7)		

O2^{i}—K1—O9	83.25 (14)	O1—C1—C2	109.9 (4)
O2^{i}—K1—O7^{ii}	100.10 (16)	O1—C1—S1	108.9 (3)
O9—K1—O7^{ii}	168.68 (19)	C2—C1—S1	110.7 (3)
O2^{i}—K1—O3^{iii}	152.88 (12)	O1—C1—H1	109.1
O9—K1—O3^{iii}	73.85 (13)	C2—C1—H1	109.1
O7^{ii}—K1—O3^{iii}	99.86 (16)	S1—C1—H1	109.1
O2^{i}—K1—O4^{iv}	90.35 (11)	O3—C3—C4	112.4 (4)
O9—K1—O4^{iv}	93.23 (17)	O3—C3—C2	110.6 (4)
O7^{ii}—K1—O4^{iv}	76.01 (15)	C4—C3—C2	112.1 (4)
O3^{iii}—K1—O4^{iv}	76.91 (11)	O3—C3—K1^{vi}	48.3 (2)
O2^{i}—K1—O3^{i}	59.46 (10)	C4—C3—K1^{vi}	89.2 (3)
O9—K1—O3^{i}	79.97 (14)	C2—C3—K1^{vi}	156.1 (3)
O7^{ii}—K1—O3^{i}	111.09 (16)	O3—C3—H3	107.2

O3^{iii}—K1—O3^{i}	127.98 (9)	C4—C3—H3	107.2
O4^{iv}—K1—O3^{i}	149.51 (11)	C2—C3—H3	107.2
O2^{i}—K1—O4^{iii}	130.97 (10)	K1^{vi}—C3—H3	75.0
O9—K1—O4^{iii}	82.14 (16)	S2—O9—K1	149.9 (4)
O7^{ii}—K1—O4^{iii}	103.20 (15)	N1—C7—C8	116.3 (5)
O3^{iii}—K1—O4^{iii}	60.61 (10)	N1—C7—S1	122.0 (4)
O4^{iv}—K1—O4^{iii}	136.94 (9)	C8—C7—S1	121.6 (4)
O3^{i}—K1—O4^{iii}	71.98 (10)	C16—O11—H11A	109.5
O2^{i}—K1—C3^{iii}	170.01 (12)	O11—C16—H16A	109.5
O9—K1—C3^{iii}	87.52 (14)	O11—C16—H16B	109.5
O7^{ii}—K1—C3^{iii}	89.69 (16)	H16A—C16—H16B	109.5
O3^{iii}—K1—C3^{iii}	22.77 (11)	O11—C16—H16C	109.5
O4^{iv}—K1—C3^{iii}	94.00 (11)	H16A—C16—H16C	109.5
O3^{i}—K1—C3^{iii}	115.14 (10)	H16B—C16—H16C	109.5
O4^{iii}—K1—C3^{iii}	43.23 (10)	C9—C8—C13	120.3 (6)
O2^{i}—K1—S2^{ii}	118.66 (9)	C9—C8—C7	120.1 (5)
O9—K1—S2^{ii}	155.30 (12)	C13—C8—C7	119.5 (6)
O7^{ii}—K1—S2^{ii}	18.59 (13)	C8—C9—C10	119.4 (8)
O3^{iii}—K1—S2^{ii}	81.92 (8)	C8—C9—Cl1	119.7 (5)
O4^{iv}—K1—S2^{ii}	76.46 (8)	C10—C9—Cl1	120.9 (7)
O3^{i}—K1—S2^{ii}	119.94 (8)	O5—C6—C5	111.8 (4)
O4^{iii}—K1—S2^{ii}	90.17 (8)	O5—C6—H6A	109.3
C3^{iii}—K1—S2^{ii}	71.17 (8)	C5—C6—H6A	109.3
O2^{i}—K1—K1^{v}	91.78 (8)	O5—C6—H6B	109.3
O9—K1—K1^{v}	61.72 (14)	C5—C6—H6B	109.3
O7^{ii}—K1—K1^{v}	128.52 (13)	H6A—C6—H6B	107.9
O3^{iii}—K1—K1^{v}	90.01 (8)	C14′—O10—H10	115.5
O4^{iv}—K1—K1^{v}	154.39 (10)	O4—C4—C3	110.6 (4)
O3^{i}—K1—K1^{v}	38.03 (7)	O4—C4—C5	110.8 (4)
O4^{iii}—K1—K1^{v}	40.71 (7)	C3—C4—C5	110.0 (4)
C3^{iii}—K1—K1^{v}	80.44 (8)	O4—C4—H4	108.4
S2^{ii}—K1—K1^{v}	123.94 (5)	C3—C4—H4	108.4
O2^{i}—K1—K1^{ii}	132.91 (8)	C5—C4—H4	108.4
O9—K1—K1^{ii}	99.84 (12)	O2—C2—C1	111.8 (4)
O7^{ii}—K1—K1^{ii}	69.91 (14)	O2—C2—C3	106.8 (4)
O3^{iii}—K1—K1^{ii}	41.64 (8)	C1—C2—C3	107.1 (4)
O4^{iv}—K1—K1^{ii}	42.71 (8)	O2—C2—H2	110.4
O3^{i}—K1—K1^{ii}	167.62 (8)	C1—C2—H2	110.4
O4^{iii}—K1—K1^{ii}	95.69 (7)	C3—C2—H2	110.4
C3^{iii}—K1—K1^{ii}	52.61 (8)	O1—C5—C6	106.7 (4)
S2^{ii}—K1—K1^{ii}	57.43 (3)	O1—C5—C4	109.7 (4)
K1^{v}—K1—K1^{ii}	131.28 (5)	C6—C5—C4	113.4 (4)
C7—S1—C1	101.4 (2)	O1—C5—H5	109.0
O9—S2—O7	113.8 (4)	C6—C5—H5	109.0
O9—S2—O8	114.7 (3)	C4—C5—H5	109.0
O7—S2—O8	115.1 (3)	C8—C13—C12	118.6 (8)
O9—S2—O6	106.8 (3)	C8—C13—H13	120.7
O7—S2—O6	106.4 (3)	C12—C13—H13	120.7
O8—S2—O6	98.0 (2)	C11—C10—C9	120.3 (8)

O9—S2—K1^{v}	86.6 (3)	C11—C10—Cl2	119.2 (6)
O7—S2—K1^{v}	36.8 (2)	C9—C10—Cl2	120.5 (8)
O8—S2—K1^{v}	109.5 (2)	C11—C12—C13	121.8 (8)
O6—S2—K1^{v}	140.95 (17)	C11—C12—H12	119.1
C3—O3—K1^{vi}	109.0 (3)	C13—C12—H12	119.1
C3—O3—K1^{vii}	103.8 (3)	C12—C11—C10	119.5 (7)
K1^{vi}—O3—K1^{vii}	100.33 (11)	C12—C11—H11	120.2
C3—O3—H3A	108 (4)	C10—C11—H11	120.2
K1^{vi}—O3—H3A	113 (4)	O10—C14′—C15′	124.6 (14)
K1^{vii}—O3—H3A	122 (4)	O10—C14′—H14A	106.2
C6—O5—H5A	106 (6)	C15′—C14′—H14A	106.2
C2—O2—K1^{vii}	126.4 (3)	O10—C14′—H14B	106.2
C2—O2—H2A	113 (5)	C15′—C14′—H14B	106.2
K1^{vii}—O2—H2A	113 (5)	H14A—C14′—H14B	106.4
N1—O6—S2	111.8 (3)	C14′—C15′—H15A	109.5
C1—O1—C5	110.4 (4)	C14′—C15′—H15B	109.5
C4—O4—K1^{viii}	128.3 (3)	H15A—C15′—H15B	109.5
C4—O4—K1^{vi}	112.7 (3)	C14′—C15′—H15C	109.5
K1^{viii}—O4—K1^{vi}	96.58 (11)	H15A—C15′—H15C	109.5
C4—O4—H4A	98 (5)	H15B—C15′—H15C	109.5
K1^{viii}—O4—H4A	124 (6)	H15D—C15—H15E	109.5
K1^{vi}—O4—H4A	91 (5)	H15D—C15—H15F	109.5
C7—N1—O6	108.5 (4)	H15E—C15—H15F	109.5
S2—O7—K1^{v}	124.6 (4)		

O9—S2—O6—N1	61.6 (4)	O3—C3—C4—O4	−61.4 (6)
O7—S2—O6—N1	−60.3 (4)	C2—C3—C4—O4	173.3 (4)
O8—S2—O6—N1	−179.5 (4)	K1^{vi}—C3—C4—O4	−17.9 (4)
K1^{v}—S2—O6—N1	−44.4 (5)	O3—C3—C4—C5	175.9 (4)
S2—O6—N1—C7	175.3 (4)	C2—C3—C4—C5	50.6 (6)
O9—S2—O7—K1^{v}	45.9 (4)	K1^{vi}—C3—C4—C5	−140.7 (3)
O8—S2—O7—K1^{v}	−89.4 (4)	K1^{vii}—O2—C2—C1	−143.9 (3)
O6—S2—O7—K1^{v}	163.2 (3)	K1^{vii}—O2—C2—C3	−27.1 (5)
C5—O1—C1—C2	−68.6 (5)	O1—C1—C2—O2	177.7 (4)
C5—O1—C1—S1	169.9 (3)	S1—C1—C2—O2	−61.9 (5)
C7—S1—C1—O1	−81.6 (4)	O1—C1—C2—C3	61.1 (5)
C7—S1—C1—C2	157.4 (4)	S1—C1—C2—C3	−178.5 (3)
K1^{vi}—O3—C3—C4	67.1 (4)	O3—C3—C2—O2	61.1 (5)
K1^{vii}—O3—C3—C4	173.4 (3)	C4—C3—C2—O2	−172.7 (4)
K1^{vi}—O3—C3—C2	−166.8 (3)	K1^{vi}—C3—C2—O2	36.1 (9)
K1^{vii}—O3—C3—C2	−60.5 (4)	O3—C3—C2—C1	−179.1 (4)
K1^{vii}—O3—C3—K1^{vi}	106.2 (2)	C4—C3—C2—C1	−52.8 (5)
O7—S2—O9—K1	4.9 (7)	K1^{vi}—C3—C2—C1	156.0 (6)
O8—S2—O9—K1	140.4 (5)	C1—O1—C5—C6	−172.6 (4)
O6—S2—O9—K1	−112.2 (6)	C1—O1—C5—C4	64.1 (5)
K1^{v}—S2—O9—K1	30.4 (6)	O5—C6—C5—O1	−69.5 (5)
O6—N1—C7—C8	−179.6 (5)	O5—C6—C5—C4	51.4 (6)
O6—N1—C7—S1	2.4 (6)	O4—C4—C5—O1	−176.9 (4)
C1—S1—C7—N1	−173.0 (5)	C3—C4—C5—O1	−54.3 (5)

C1—S1—C7—C8	9.1 (5)	O4—C4—C5—C6	63.9 (6)
N1—C7—C8—C9	91.8 (7)	C3—C4—C5—C6	−173.4 (4)
S1—C7—C8—C9	−90.2 (6)	C9—C8—C13—C12	−0.5 (9)
N1—C7—C8—C13	−89.4 (7)	C7—C8—C13—C12	−179.3 (5)
S1—C7—C8—C13	88.6 (6)	C8—C9—C10—C11	0.3 (11)
C13—C8—C9—C10	0.4 (9)	Cl1—C9—C10—C11	179.7 (6)
C7—C8—C9—C10	179.2 (6)	C8—C9—C10—Cl2	−179.3 (5)
C13—C8—C9—Cl1	−179.1 (5)	Cl1—C9—C10—Cl2	0.1 (9)
C7—C8—C9—Cl1	−0.3 (8)	C8—C13—C12—C11	0.0 (10)
K1^{viii}—O4—C4—C3	142.0 (3)	C13—C12—C11—C10	0.7 (11)
K1^{vi}—O4—C4—C3	22.8 (5)	C9—C10—C11—C12	−0.8 (12)
K1^{viii}—O4—C4—C5	−95.7 (4)	Cl2—C10—C11—C12	178.8 (6)
K1^{vi}—O4—C4—C5	145.1 (3)		

Symmetry codes: (i) −*x*+3/2, −*y*, *z*+1/2; (ii) *x*+1/2, −*y*−1/2, −*z*+1; (iii) −*x*+2, *y*−1/2, −*z*+1/2; (iv) −*x*+5/2, −*y*, *z*+1/2; (v) *x*−1/2, −*y*−1/2, −*z*+1; (vi) −*x*+2, *y*+1/2, −*z*+1/2; (vii) −*x*+3/2, −*y*, *z*−1/2; (viii) −*x*+5/2, −*y*, *z*−1/2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O11—H11*A*···S2	0.84	2.95	3.770 (6)	167
O11—H11*A*···O6	0.84	2.63	3.300 (8)	138
O11—H11*A*···O8	0.84	2.05	2.861 (8)	163
C16—H16*C*···Cl1^{ix}	0.98	2.68	3.613 (15)	160
C6—H6*B*···O2^{x}	0.99	2.63	3.124 (6)	111
O10—H10···S2	0.94	2.77	3.586 (7)	146
O10—H10···O8	0.94	1.80	2.738 (7)	174
C11—H11···O11^{iii}	0.95	2.52	3.428 (10)	160
C14′—H14*A*···O6^{xi}	0.99	2.62	3.461 (11)	143
C15′—H15*B*···Cl1^{xii}	0.98	2.79	3.40 (3)	121
C14—H14*C*···O9^{xi}	0.99	2.62	3.601 (14)	173
C15—H15*F*···Cl2^{i}	0.98	2.97	3.92 (4)	163
O3—H3*A*···N1^{vi}	0.84 (6)	2.19 (7)	3.019 (6)	170 (5)
O2—H2*A*···O5^{xi}	0.93 (8)	1.79 (8)	2.655 (5)	155 (7)
O5—H5*A*···O11^{x}	1.01 (10)	1.70 (10)	2.690 (7)	166 (9)
O4—H4*A*···O10^{vii}	1.09 (10)	1.61 (10)	2.685 (8)	164 (9)

Symmetry codes: (i) −*x*+3/2, −*y*, *z*+1/2; (iii) −*x*+2, *y*−1/2, −*z*+1/2; (vi) −*x*+2, *y*+1/2, −*z*+1/2; (vii) −*x*+3/2, −*y*, *z*−1/2; (ix) −*x*+1, *y*+1/2, −*z*+1/2; (x) *x*+1, *y*, *z*; (xi) *x*−1, *y*, *z*; (xii) −*x*+1/2, −*y*, *z*+1/2.