



Synthesis and crystal structure of sodium (ethane-1,2-diyl)bis[(3-methoxypropyl)phosphinodithiolate] octahydrate

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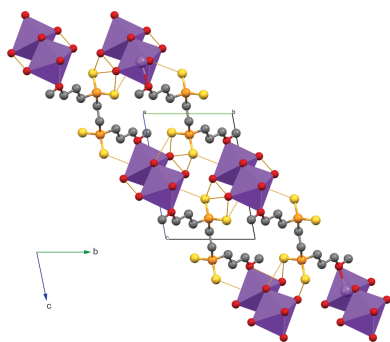
Keywords: dithiophosphate; phosphinodithiolate; crystal structure.**CCDC reference:** 2388007**Supporting information:** this article has supporting information at journals.iucr.org/e

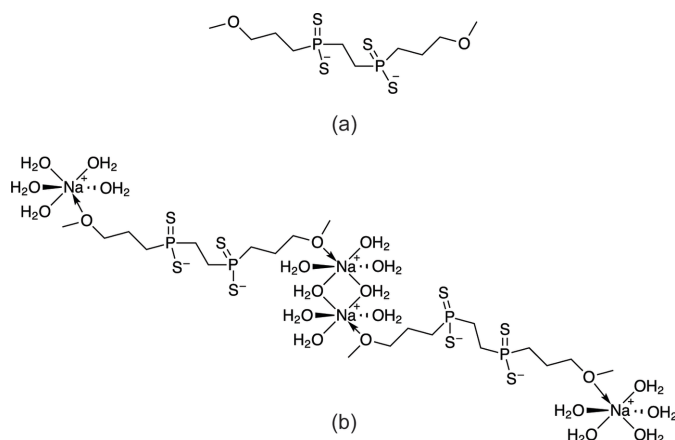
The title compound, *catena*-poly[[triaquasodium]-di- μ -aqua-[triaquasodium]- μ -(ethane-1,2-diyl)bis[(3-methoxypropyl)phosphinodithiolato]], $[\text{Na}_2(\text{C}_{10}\text{H}_{22}\text{O}_2\text{P}_2\text{S}_4)(\text{H}_2\text{O})_8]_n$, crystallizes in the triclinic space group $P1$. The dianionic $[\text{CH}_3\text{O}(\text{CH}_2)_3\text{P}(=\text{S})(\text{S}-)\text{CH}_2\text{CH}_2\text{P}(=\text{S})(\text{S}-)(\text{CH}_2)_3\text{OCH}_3]^{2-}$ ligand fragments are joined by a dicationic $[\text{Na}_2(\text{H}_2\text{O})_8]^{2+}$ cluster that includes the oxygen of the methoxypropyl unit of the ligand to form infinite chains.

1. Chemical context

Complexes of the type $\text{Fe}(\text{P}_2)_2\text{X}_2$ have been shown to react with dinitrogen at high pressure to form $[\text{Fe}(\text{P}_2)_2(\text{N}_2)\text{X}]^+$ (Miller *et al.*, 2002). This reaction can potentially be used to scrub dinitrogen-contaminated natural gas. Unfortunately, the phosphine ligands in these dinitrogen-scrubbing complexes slowly dissociate in aqueous solution leading to degradation of the complexes, preventing a practical pressure-swing process from being developed. One potential method to develop complexes that are more robust is to use a phosphine macrocycle in place of the two bidentate ligands. For background on phosphine macrocycles, see: Caminade & Majoral (1994); Swor & Tyler (2011). The ‘macrocycle effect’ predicts that the binding constant for a macrocyclic ligand is orders of magnitude higher than the binding constant for two bidentate ligands (Melson, 1979).

In addition to their usefulness in the N_2 -scrubbing scheme described above, macrocyclic phosphine compounds are sought after in general as ligands for transition-metal complexes because of their strong binding properties. However, the synthesis of phosphine macrocycles is a relatively underdeveloped area. One approach to macrocyclic phosphines is a template synthesis in which two secondary bidentate phosphines are coordinated to a common metal center and then covalently linked (Lambert & Desreux, 2000; Nell & Tyler, 2014). Previously, we showed that complexes of the $[\text{Cu}(\text{P}_2)_2]^+$ type (where P_2 is a bidentate secondary phosphine) can react under basic conditions with various dihalides to form macrocyclic tetraphosphine Cu complexes (Nell *et al.*, 2016). The title molecule is an unexpected side-product of the process of removing the Cu metal center using aqueous NaSH to react with the Cu metal (Costantino *et al.*, 2008). Interestingly in this case, the P_2 ligand was 1,2-bis(methoxypropyl)phosphinoethane (MeOPrPE), which has been oxidized to the dithiophosphinate species, a reaction commonly encountered between secondary phosphines and elemental sulfur.





2. Structural commentary

The title compound is a P,S,Na-complex in which there are two P(=S)(-S) groups consisting of two terminal sulfur atoms bonded to each phosphorus atom, providing a -2 charge. Two sodium cations and eight water molecules form $[\text{Na}_2(\text{H}_2\text{O})_8]^{2+}$ bridges between the anions. The oxygen of the methoxypropyl unit of the ligand is also bonded to the $[\text{Na}_2(\text{H}_2\text{O})_8]^{2+}$ cluster, completing a pseudo-octahedral coordination environment around each sodium cation and linking the cations and anions to form an infinite chain. The asymmetric unit (see Fig. 1) contains half of one dianionic bis(phosphinodithiolate) chain, one sodium cation, and four water molecules, one of which is disordered over two positions with 50:50 occupancy.

Interestingly the lengths of the two P-S bonds for the phosphorus atom P1 differ by 0.0206 (6) Å. While the structure can formally be described as having one phosphorus-sulfur single bond and one double bond, clearly these should be equivalent by resonance. Indeed, comparison to seven similar dialkylphosphinodithiolate structures (Pinkerton, 1990; Ebels *et al.*, 1997; Klevtsova *et al.*, 2003; Kokina *et al.*, 2008, 2010; Marc *et al.*, 2012; Guo *et al.*, 2022) shows that the average difference in phosphorus-sulfur bonds in these compounds is only 0.006 Å. A closer look at the hydrogen bonding in the structure shows that the asymmetry is likely

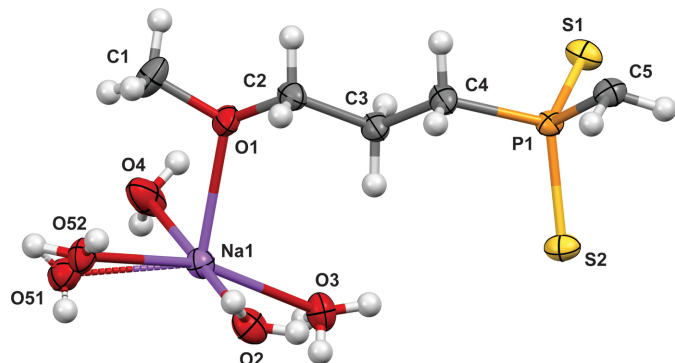


Figure 1
Displacement ellipsoid (50%) diagram and atom-numbering scheme for the asymmetric unit of the title compound.

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2C}\cdots\text{S1}^{\text{i}}$	0.78 (1)	2.52 (1)	3.2920 (13)	167 (2)
$\text{O52}-\text{H52}\cdots\text{S1}^{\text{i}}$	0.79 (2)	2.42 (2)	3.193 (3)	167 (4)
$\text{O3}-\text{H3AA}\cdots\text{S2}^{\text{ii}}$	0.79 (1)	2.50 (1)	3.2840 (13)	177 (2)
$\text{O4}-\text{H4C}\cdots\text{S2}^{\text{iii}}$	0.78 (1)	2.49 (2)	3.2535 (14)	169 (2)
$\text{O51}-\text{H51}\cdots\text{S2}^{\text{iv}}$	0.78 (1)	2.52 (1)	3.117 (2)	134 (2)
$\text{O52}-\text{H51}\cdots\text{S2}^{\text{iv}}$	0.83 (1)	2.52 (1)	3.314 (2)	162 (2)
$\text{O2}-\text{H2D}\cdots\text{O4}^{\text{v}}$	0.77 (1)	2.05 (1)	2.8069 (19)	170 (2)
$\text{O3}-\text{H3BB}\cdots\text{O3}^{\text{ii}}$	0.79 (2)	2.02 (2)	2.801 (2)	171 (4)
$\text{O3}-\text{H3C}\cdots\text{O52}^{\text{vi}}$	0.71 (4)	2.04 (4)	2.748 (3)	174 (5)
$\text{O4}-\text{H4D}\cdots\text{O51}^{\text{vii}}$	0.75 (1)	2.07 (2)	2.731 (3)	147 (3)
$\text{O51}-\text{H51A}\cdots\text{O3}^{\text{vi}}$	0.79 (2)	2.05 (2)	2.825 (3)	173 (5)

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

due to the fact that sulfur S1 has two hydrogen-bonding contacts (see Fig. 2, Table 1) compared to the three contacts for S2. A similar asymmetry in phosphorus-sulfur bond lengths is observed in the structure of sodium diethyldithiophosphinate dihydrate (Svensson & Albertsson, 1989), though the hydrogen-bonding network is quite symmetrical in that structure.

The sodium ion and water molecules form $[\text{Na}_2(\text{H}_2\text{O})_8]^{2+}$ dimers around an inversion center. The coordination sphere of the sodium ion is filled by two bridging water molecules (O2), three terminal water molecules (O3, O4, and O51/O52), and one ether oxygen of the ligand molecule (O1). As shown in Fig. 3, there is one intra-dimer hydrogen bond ($\text{O3}-\text{H3C}\cdots\text{O52}$). A similar contact, $\text{O51}-\text{H51A}\cdots\text{O3}$, is present in the second component of the disorder but is not shown in Fig. 3. The dimers are linked by additional hydrogen-bond contacts between atoms O2 and O4 of neighboring dimers ($\text{O2}-\text{H2D}\cdots\text{O4}$). An additional intradimer contact, $\text{O4}-\text{H4D}\cdots\text{O51}$, is present but not shown in Fig. 3.

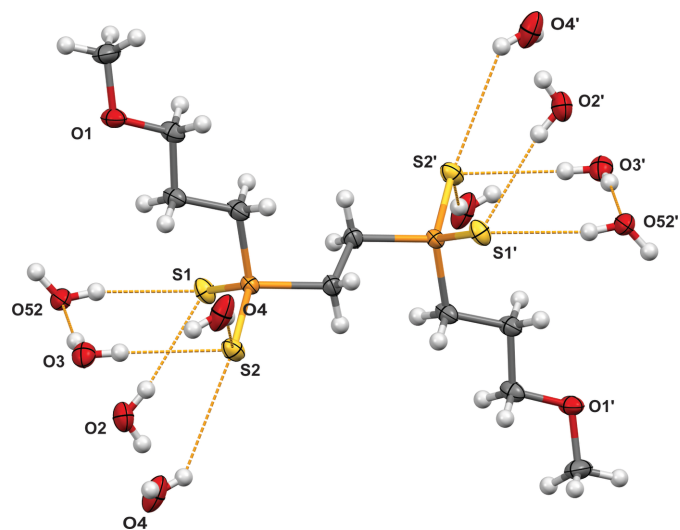


Figure 2
Displacement ellipsoid (50%) diagram showing O-H...S contacts in orange with selected atom labels. Only one position of the disordered water molecule is shown for clarity. See Table 1 for donor-acceptor distances and angles.

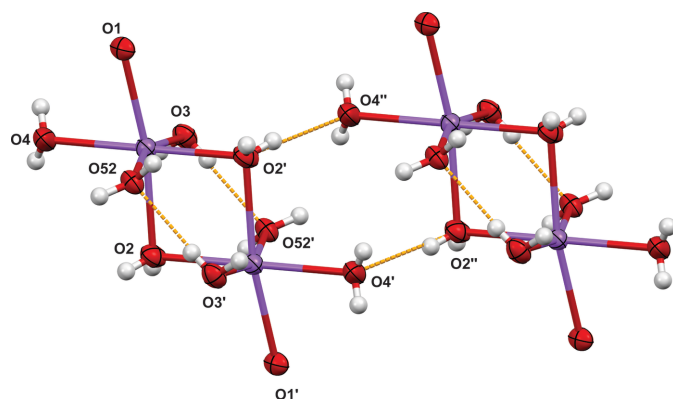


Figure 3
Displacement ellipsoid (50%) diagram showing O—H...O contacts in orange with selected atom labels. Only one position of the disordered water molecule is shown for clarity. See Table 1 for donor–acceptor distances and angles.

3. Supramolecular features

The sodium ion–water dimers can be visualized as edge-sharing octahedra (see Fig. 4) with two of the outer oxygen positions occupied by equivalent ether oxygen atoms from one end of the bis(phosphinodithiolate) ligand. The ligands then link successive sodium ion dimers, forming infinite zigzag chains running parallel to the (011) plane. The hydrogen-bonding interactions between the water molecules and the sulfur atoms (Table 1) create additional interactions linking the chains in all directions.

4. Database survey

A search of the CSD (version 2024.2.0; Groom *et al.*, 2016) demonstrates that there are relatively few structurally characterized dialkyldithiophosphinates and no existing examples of structures with dithiophosphate groups linked by an alkyl chain.

A number of structures contain diphenyldithiophosphinates as bidentate ligands coordinated to late transition metals such as platinum and palladium (Alison & Stephenson, 1971; Fackler *et al.*, 1982; Landtiser *et al.*, 1995). In some cases, the dialkyldithiophosphate ends up serving as a counter-ion instead of coordinating to the metal center (Kokina *et al.*, 2008). Diethyldithiophosphinates have also been used to form molybdenum(IV)sulfur clusters, $\text{Mo}_3\text{S}_4(\text{Et}_2\text{PS}_2)_4$ (Keck *et al.*, 1981).

The structure most closely related to the title compound is that of sodium diethyldithiophosphate dihydrate (CSD refcode SAGWUS; Svensson & Albertsson, 1989). Each sulfur atom is hydrogen bonded to two water molecules, forming an extended network in the *ab* plane, with successive layers separated by sodium cations. The sodium ions are found in a similar distorted octahedral environment, but with two of the six coordination sites occupied by sulfur instead of water. The octahedra are linked by edge sharing within the layer with every third octahedron missing.

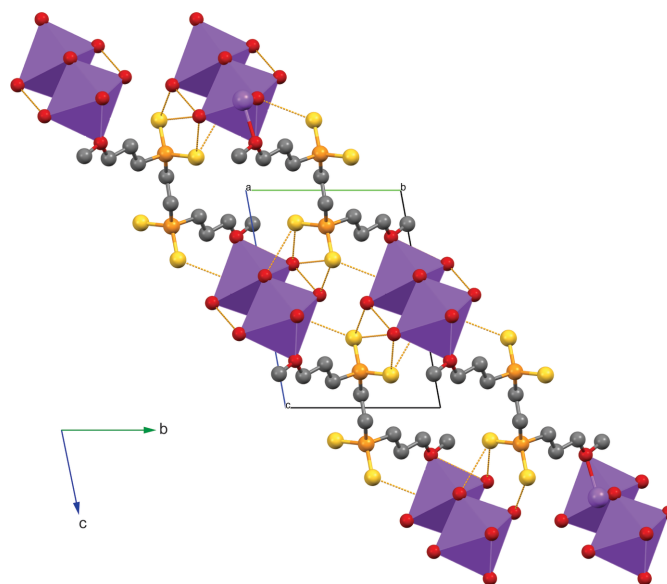


Figure 4
Polyhedral representation showing $[\text{Na}_2(\text{H}_2\text{O})_8]^{2+}$ dimers (purple) linked by bis(phosphinodithiolate) chains. The O—H...S contacts are shown in orange. Only one position of the disordered water molecule is shown and hydrogen atoms omitted for clarity.

5. Synthesis and crystallization

The title molecule was prepared serendipitously while attempting to remove the Cu^{I} template of a $[\text{Cu}(\text{P}_2)_2]^+$ complex. 1,2-Bis(methoxypropyl)phosphinoethane (MeOPrPE) (2 eq.) was reacted with $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (1 eq.) in acetonitrile to yield the corresponding $\text{Cu}(\text{MeOPrPE})_2\text{PF}_6$ complex. As a proof-of-concept, an attempt to remove the copper and yield the free phosphine back was performed. The copper complex was dissolved in 10 mL of THF and added to a solution of 10 eq. NaSH-hydrate in 30 mL of absolute EtOH. The mixture was refluxed for 24 h, forming Cu_2S as a black precipitate. The reaction mixture was cooled to RT, filtered through a celite plug, then the solvent was allowed to slowly evaporate at RT in air, yielding crystals of the title molecule.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms were located in the difference maps. Carbon-bonded hydrogen atoms were freely refined. For the water molecules the O—H distances were restrained (SADI) to have similar distances. The displacement parameters for the water hydrogen atoms were constrained to be $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The occupancy of the disordered water molecule (O51/O52) was fixed at 0.50 since free refinement gave an occupancy of 0.486 (8).

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Table 2

Experimental details.

Crystal data	
Chemical formula	[Na ₂ (C ₁₀ H ₂₂ O ₂ P ₂ S ₄)(H ₂ O) ₈]
<i>M_r</i>	277.28
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.7412 (8), 8.2961 (8), 11.8621 (17)
α , β , γ (°)	79.608 (2), 89.207 (2), 87.030 (1)
<i>V</i> (Å ³)	651.63 (14)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.56
Crystal size (mm)	0.19 × 0.12 × 0.06
Data collection	
Diffractometer	Bruker <i>SMART APEX</i> CCD area detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T_{min}</i> , <i>T_{max}</i>	0.838, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	7596, 3007, 2736
<i>R_{int}</i>	0.014
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.666
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.026, 0.068, 1.02
No. of reflections	3007
No. of parameters	210
No. of restraints	45
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.43, -0.20

Computer programs: *SMART* and *SAINT* (Bruker, 2003), *SHELXTL* (Sheldrick, 2008), *SHELXL2018/3* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2020), *OLEX2* (Dolomanov *et al.*, 2009) and *pubCIF* (Westrip, 2010).

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supporting information

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Synthesis and crystal structure of sodium (ethane-1,2-diyl)bis[(3-methoxypropyl)phosphinodithiolate] octahydrate

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Computing details

catena-Poly[[[triaquasodium]-di- μ -aqua-[triaquasodium]- μ -(ethane-1,2-diyl)bis[(3-methoxypropyl)phosphinodithiolato]]

Crystal data

$[\text{Na}_2(\text{C}_{10}\text{H}_{22}\text{O}_2\text{P}_2\text{S}_4)(\text{H}_2\text{O})_8]$

$M_r = 277.28$

Triclinic, $P\bar{1}$

$a = 6.7412$ (8) Å

$b = 8.2961$ (8) Å

$c = 11.8621$ (17) Å

$\alpha = 79.608$ (2)°

$\beta = 89.207$ (2)°

$\gamma = 87.030$ (1)°

$V = 651.63$ (14) Å³

$Z = 2$

$F(000) = 294$

$D_x = 1.413$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4713 reflections

$\theta = 2.5$ – 28.3 °

$\mu = 0.56$ mm⁻¹

$T = 173$ K

Block, colorless

$0.19 \times 0.12 \times 0.06$ mm

Data collection

Bruker SMART APEX CCD area detector
diffractometer

Radiation source: sealed tube

Graphite monochromator

phi and ω scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.838$, $T_{\max} = 1.000$

7596 measured reflections

3007 independent reflections

2736 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.014$

$\theta_{\max} = 28.3$ °, $\theta_{\min} = 2.5$ °

$h = -8 \rightarrow 8$

$k = -10 \rightarrow 10$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

$wR(F^2) = 0.068$

$S = 1.02$

3007 reflections

210 parameters

45 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2 + 0.2159P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.43$ e Å⁻³

$\Delta\rho_{\min} = -0.20$ e Å⁻³

Special details

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

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1	0.65743 (5)	0.71747 (4)	0.84910 (3)	0.02676 (10)	
S2	0.95943 (5)	0.52147 (4)	0.67995 (3)	0.02722 (10)	
P1	0.83354 (5)	0.52284 (4)	0.83414 (3)	0.01867 (9)	
C1	0.1587 (3)	−0.0034 (2)	0.84426 (17)	0.0374 (4)	
H1A	0.050 (3)	−0.019 (2)	0.7965 (17)	0.045 (5)*	
H1B	0.234 (3)	−0.108 (3)	0.8699 (17)	0.050 (6)*	
H1C	0.101 (3)	0.035 (3)	0.906 (2)	0.060 (7)*	
C2	0.4380 (2)	0.15096 (17)	0.85447 (12)	0.0257 (3)	
H2A	0.529 (3)	0.058 (2)	0.8688 (15)	0.032 (4)*	
H2B	0.381 (3)	0.164 (2)	0.9249 (16)	0.032 (4)*	
C3	0.5383 (2)	0.30505 (17)	0.79961 (12)	0.0254 (3)	
H3A	0.589 (3)	0.293 (2)	0.7283 (16)	0.034 (5)*	
H3B	0.443 (3)	0.396 (2)	0.7870 (15)	0.032 (4)*	
C4	0.7036 (2)	0.33531 (17)	0.87807 (12)	0.0258 (3)	
H4A	0.650 (3)	0.341 (2)	0.9483 (16)	0.035 (5)*	
H4B	0.801 (3)	0.250 (2)	0.8855 (16)	0.041 (5)*	
C5	1.0347 (2)	0.50194 (19)	0.93811 (11)	0.0243 (3)	
H5A	1.110 (3)	0.409 (2)	0.9306 (15)	0.035 (5)*	
H5B	1.112 (3)	0.591 (2)	0.9135 (15)	0.033 (5)*	
Na1	0.33236 (8)	0.08688 (6)	0.58806 (5)	0.02448 (13)	
O1	0.28216 (15)	0.11749 (12)	0.78382 (8)	0.0281 (2)	
O2	0.66857 (17)	−0.02101 (15)	0.60507 (10)	0.0331 (3)	
H2C	0.683 (3)	−0.089 (2)	0.6599 (14)	0.050*	
H2D	0.754 (3)	0.037 (2)	0.6050 (18)	0.050*	
O3	0.42969 (18)	0.35106 (14)	0.48142 (10)	0.0309 (2)	
H3AA	0.339 (3)	0.382 (2)	0.4406 (16)	0.046*	
H3BB	0.480 (6)	0.432 (3)	0.488 (4)	0.046*	0.5
H3C	0.501 (7)	0.313 (5)	0.448 (4)	0.046*	0.5
O4	−0.00709 (18)	0.18169 (19)	0.57874 (12)	0.0445 (3)	
H4C	−0.020 (4)	0.255 (2)	0.6113 (19)	0.067*	
H4D	−0.047 (4)	0.215 (3)	0.5202 (15)	0.067*	
O51	0.2410 (4)	−0.1906 (3)	0.6086 (2)	0.0316 (5)	0.5
H51	0.209 (3)	−0.259 (2)	0.6588 (15)	0.047*	
H51A	0.332 (5)	−0.242 (5)	0.589 (4)	0.047*	0.5
O52	0.3145 (4)	−0.2131 (3)	0.6610 (2)	0.0279 (5)	0.5
H52	0.391 (5)	−0.245 (5)	0.711 (3)	0.042*	0.5

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0338 (2)	0.02347 (17)	0.02226 (18)	0.00774 (14)	-0.00349 (14)	-0.00436 (13)
S2	0.03110 (19)	0.02942 (19)	0.01979 (17)	0.00183 (14)	0.00272 (13)	-0.00193 (13)
P1	0.02118 (17)	0.01825 (16)	0.01566 (16)	-0.00006 (12)	-0.00169 (12)	-0.00069 (12)
C1	0.0294 (8)	0.0350 (9)	0.0437 (10)	-0.0088 (7)	0.0076 (7)	0.0057 (7)
C2	0.0362 (8)	0.0205 (7)	0.0205 (7)	-0.0040 (6)	0.0011 (6)	-0.0036 (5)
C3	0.0343 (8)	0.0221 (7)	0.0195 (7)	-0.0055 (6)	-0.0003 (6)	-0.0017 (5)
C4	0.0368 (8)	0.0207 (7)	0.0194 (7)	-0.0054 (6)	-0.0027 (6)	-0.0007 (5)
C5	0.0223 (7)	0.0291 (7)	0.0199 (7)	0.0009 (6)	-0.0020 (5)	-0.0009 (5)
Na1	0.0237 (3)	0.0255 (3)	0.0249 (3)	-0.0031 (2)	-0.0013 (2)	-0.0055 (2)
O1	0.0341 (6)	0.0263 (5)	0.0237 (5)	-0.0114 (4)	0.0028 (4)	-0.0017 (4)
O2	0.0330 (6)	0.0364 (6)	0.0307 (6)	0.0025 (5)	-0.0107 (5)	-0.0089 (5)
O3	0.0313 (6)	0.0240 (5)	0.0379 (7)	-0.0031 (4)	-0.0060 (5)	-0.0061 (5)
O4	0.0266 (6)	0.0632 (9)	0.0524 (8)	0.0012 (6)	-0.0069 (5)	-0.0341 (7)
O51	0.0327 (13)	0.0287 (12)	0.0326 (13)	-0.0039 (10)	0.0035 (11)	-0.0027 (10)
O52	0.0267 (12)	0.0293 (12)	0.0274 (13)	-0.0076 (9)	-0.0047 (10)	-0.0017 (10)

Geometric parameters (\AA , $^\circ$)

S1—P1	1.9867 (5)	Na1—Na1 ⁱⁱ	3.4885 (11)
S2—P1	2.0073 (5)	Na1—O1	2.3986 (12)
P1—C4	1.8155 (14)	Na1—O2 ⁱⁱ	2.4494 (13)
P1—C5	1.8262 (14)	Na1—O2	2.3908 (13)
C1—H1A	0.96 (2)	Na1—O3	2.4413 (13)
C1—H1B	0.99 (2)	Na1—H3C	2.57 (4)
C1—H1C	0.93 (2)	Na1—O4	2.3783 (13)
C1—O1	1.4219 (18)	Na1—O51	2.383 (2)
C2—H2A	0.951 (18)	Na1—O52	2.491 (2)
C2—H2B	0.937 (18)	O2—H2C	0.783 (13)
C2—C3	1.5141 (19)	O2—H2D	0.768 (14)
C2—O1	1.4218 (18)	O3—H3AA	0.788 (14)
C3—H3A	0.929 (19)	O3—H3BB	0.786 (16)
C3—H3B	0.959 (18)	O3—H3C	0.71 (4)
C3—C4	1.521 (2)	O4—H4C	0.775 (14)
C4—H4A	0.911 (19)	O4—H4D	0.748 (14)
C4—H4B	0.93 (2)	O51—H51	0.782 (14)
C5—C5 ⁱ	1.530 (3)	O51—H51A	0.785 (16)
C5—H5A	0.918 (19)	O52—H51	0.826 (14)
C5—H5B	0.928 (18)	O52—H52	0.789 (16)
S1—P1—S2	116.51 (2)	O2—Na1—O3	92.52 (4)
C4—P1—S1	110.54 (6)	O2—Na1—H3C	80.5 (10)
C4—P1—S2	109.33 (5)	O2 ⁱⁱ —Na1—H3C	70.7 (10)
C4—P1—C5	102.98 (7)	O2—Na1—O52	74.03 (7)
C5—P1—S1	109.49 (5)	O2 ⁱⁱ —Na1—O52	86.90 (7)
C5—P1—S2	107.08 (5)	O3—Na1—Na1 ⁱⁱ	85.84 (4)

H1A—C1—H1B	110.3 (16)	O3—Na1—O2 ⁱⁱ	81.58 (4)
H1A—C1—H1C	105.4 (18)	O3—Na1—H3C	16.1 (10)
H1B—C1—H1C	110.3 (18)	O3—Na1—O52	162.66 (7)
O1—C1—H1A	109.7 (12)	O4—Na1—Na1 ⁱⁱ	136.49 (4)
O1—C1—H1B	111.5 (12)	O4—Na1—O1	80.67 (4)
O1—C1—H1C	109.5 (14)	O4—Na1—O2 ⁱⁱ	93.34 (5)
H2A—C2—H2B	107.4 (14)	O4—Na1—O2	176.86 (6)
C3—C2—H2A	111.9 (11)	O4—Na1—O3	90.54 (5)
C3—C2—H2B	110.5 (10)	O4—Na1—H3C	102.6 (10)
O1—C2—H2A	109.2 (10)	O4—Na1—O51	91.08 (8)
O1—C2—H2B	107.1 (11)	O4—Na1—O52	103.10 (7)
O1—C2—C3	110.62 (11)	O51—Na1—Na1 ⁱⁱ	75.92 (6)
C2—C3—H3A	109.8 (11)	O51—Na1—O1	97.55 (7)
C2—C3—H3B	109.9 (10)	O51—Na1—O2 ⁱⁱ	73.40 (7)
C2—C3—C4	108.62 (12)	O51—Na1—O2	86.43 (7)
H3A—C3—H3B	107.0 (14)	O51—Na1—O3	154.98 (8)
C4—C3—H3A	110.6 (11)	O52—Na1—H3C	146.6 (10)
C4—C3—H3B	110.9 (10)	C1—O1—Na1	112.06 (10)
P1—C4—H4A	106.5 (11)	C2—O1—C1	111.26 (12)
P1—C4—H4B	105.7 (12)	C2—O1—Na1	122.95 (9)
C3—C4—P1	116.31 (10)	Na1—O2—Na1 ⁱⁱ	92.22 (4)
C3—C4—H4A	108.2 (11)	Na1—O2—H2C	111.4 (16)
C3—C4—H4B	110.7 (12)	Na1 ⁱⁱ —O2—H2C	122.1 (16)
H4A—C4—H4B	109.2 (16)	Na1—O2—H2D	120.1 (16)
P1—C5—H5A	107.2 (11)	Na1 ⁱⁱ —O2—H2D	105.4 (16)
P1—C5—H5B	105.3 (11)	H2C—O2—H2D	106 (2)
C5 ⁱ —C5—P1	114.30 (13)	Na1—O3—H3AA	104.3 (15)
C5 ⁱ —C5—H5A	111.7 (11)	Na1—O3—H3BB	143 (3)
C5 ⁱ —C5—H5B	110.9 (11)	Na1—O3—H3C	92 (4)
H5A—C5—H5B	107.1 (15)	H3AA—O3—H3BB	104 (3)
Na1 ⁱⁱ —Na1—H3C	69.8 (10)	H3AA—O3—H3C	106 (4)
O1—Na1—Na1 ⁱⁱ	141.45 (4)	Na1—O4—H4C	108.4 (19)
O1—Na1—O2 ⁱⁱ	169.16 (4)	Na1—O4—H4D	116 (2)
O1—Na1—O3	107.34 (4)	H4C—O4—H4D	104 (3)
O1—Na1—H3C	119.4 (10)	Na1—O51—H51	136.6 (15)
O1—Na1—O52	85.69 (6)	Na1—O51—H51A	108 (3)
O2 ⁱⁱ —Na1—Na1 ⁱⁱ	43.22 (3)	H51—O51—H51A	95 (3)
O2—Na1—Na1 ⁱⁱ	44.56 (3)	Na1—O52—H51	120.9 (13)
O2—Na1—O1	97.76 (4)	Na1—O52—H52	112 (3)
O2—Na1—O2 ⁱⁱ	87.78 (4)	H51—O52—H52	120 (3)
S1—P1—C4—C3	69.75 (12)	C3—C2—O1—C1	-166.90 (13)
S1—P1—C5—C5 ⁱ	53.71 (16)	C3—C2—O1—Na1	56.02 (14)
S2—P1—C4—C3	-59.78 (13)	C4—P1—C5—C5 ⁱ	-63.91 (16)
S2—P1—C5—C5 ⁱ	-179.14 (13)	C5—P1—C4—C3	-173.38 (12)
C2—C3—C4—P1	-175.75 (10)	O1—C2—C3—C4	-179.89 (12)

Symmetry codes: (i) $-x+2, -y+1, -z+2$; (ii) $-x+1, -y, -z+1$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2—H2C \cdots S1 ⁱⁱⁱ	0.78 (1)	2.52 (1)	3.2920 (13)	167 (2)
O52—H52 \cdots S1 ⁱⁱⁱ	0.79 (2)	2.42 (2)	3.193 (3)	167 (4)
O3—H3AA \cdots S2 ^{iv}	0.79 (1)	2.50 (1)	3.2840 (13)	177 (2)
O4—H4C \cdots S2 ^v	0.78 (1)	2.49 (2)	3.2535 (14)	169 (2)
O51—H51 \cdots S2 ^{vi}	0.78 (1)	2.52 (1)	3.117 (2)	134 (2)
O52—H51 \cdots S2 ^{vi}	0.83 (1)	2.52 (1)	3.314 (2)	162 (2)
O2—H2D \cdots O4 ^{vii}	0.77 (1)	2.05 (1)	2.8069 (19)	170 (2)
O3—H3BB \cdots O3 ^{iv}	0.79 (2)	2.02 (2)	2.801 (2)	171 (4)
O3—H3C \cdots O52 ⁱⁱ	0.71 (4)	2.04 (4)	2.748 (3)	174 (5)
O4—H4D \cdots O51 ^{viii}	0.75 (1)	2.07 (2)	2.731 (3)	147 (3)
O51—H51A \cdots O3 ⁱⁱ	0.79 (2)	2.05 (2)	2.825 (3)	173 (5)

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