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Calcium disodium hexathiodiphosphate(IV) octahydrate

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Key indicators: single-crystal X-ray study; T = 223 K; mean σ(P–P) = 0.001 Å; R factor = 0.029; wR factor = 0.065; data-to-parameter ratio = 21.7.

Single crystals of the title compound, $CaNa_2(P_2S_6)\cdot 8H_2O$, were obtained by adding calcium hydroxide to an aqueous solution of $Na_4(P_2S_6)\cdot 6H_2O$. The structure is isotypic with that of its strontium analogue and consists of one Ca^{2+} cation, two Na^+ cations, one-half of a centrosymmetric $(P_2S_6)^{4-}$ anion with staggered confirmation and four water molecules in the asymmetric unit. The crystal structure can be described as being built up from layers of cations and anions extending parallel to (101). Within a layer, each CaO_8 polyhedron is connected *via* edge-sharing to two NaO_4S_2 octahedra and to one NaO_2S_4 octaedron. The NaO_4S_2 octahedra are, in turn, linked with two $(P_2S_6)^{4-}$ anions through common corners. Various O—H···S hydrogen-bonding interactions lead to cohesion of adjacent layers. The Ca^{2+} and one Na^+ cation are situated on a twofold rotation axis and the second Na^+ cation is situated on an inversion centre.

Related literature

For background to thiodiphosphates(IV), including their crystal structures, see: Jörgens *et al.* (2003); Klingen *et al.* (1973). For the synthesis of $Na_4(P_2S_6)\cdot 6H_2O$, see: Fincher *et al.* (1998). For the isotypic structure of $SrNa_2(P_2S_6)\cdot 8H_2O$, see: Ehrhardt & Gjikaj (2010).

Experimental

Crystal data

$CaNa_2(P_2S_6)\cdot 8H_2O$
M_r = 484.49
Monoclinic, $C2/c$
a = 14.702 (2) Å
b = 9.3081 (14) Å
c = 14.052 (2) Å
β = 115.383 (11)°
V = 1737.3 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.34 mm^{-1}
T = 223 K
0.29 × 0.24 × 0.23 mm

Data collection

Stoe IPDS 2 diffractometer
15223 measured reflections
2650 independent reflections
2369 reflections with $I > 2\sigma(I)$
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.065
S = 1.13
2650 reflections
122 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ca—O1	2.4244 (14)	Na2—O2	2.5282 (17)
Ca—O2	2.4614 (13)	Na2—S1^{i}	2.9242 (8)
Ca—O3	2.5123 (13)	Na2—S3	2.9673 (7)
Ca—O4	2.5249 (13)	P—S1	2.0156 (6)
Na1—O3	2.3523 (14)	P—S2	2.0241 (6)
Na1—O4	2.3713 (13)	P—S3	2.0282 (6)
Na1—S2^{i}	2.9768 (5)	P—P^{i}	2.2381 (8)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···S3^{ii}	0.78 (5)	2.58 (5)	3.2922 (17)	153 (4)
O1—H1B···S2^{iii}	0.79 (4)	2.62 (4)	3.2892 (16)	144 (4)
O2—H2A···S2^{ii}	0.79 (3)	2.54 (3)	3.3270 (15)	172 (3)
O2—H2B···S2^{i}	0.88 (3)	2.30 (3)	3.1877 (15)	179 (3)
O3—H3A···S1^{iv}	0.78 (3)	2.43 (3)	3.1908 (15)	168 (2)
O3—H3B···S1^{ii}	0.86 (3)	2.39 (3)	3.2174 (14)	161 (3)
O4—H4A···S3^{v}	0.85 (3)	2.41 (3)	3.2468 (14)	171 (3)
O4—H4B···S3	0.83 (3)	2.37 (3)	3.1957 (14)	171 (3)

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

Data collection: *X-AREA* (Stoe & Cie, 2008); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2004); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2364).

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supporting information

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Calcium disodium hexathiodiphosphate(IV) octahydrate

Claus Ehrhardt and Mimoza Gjikaj

S1. Comment

Alkaline earth hypothiodiphosphates were first reported by Klingen *et al.* (1973). The structure of the title compound is isotypic with that of the strontium analogue, $SrNa_2(P_2S_6).8H_2O$ (Ehrhardt & Gjikaj, 2010). The asymmetric unit of $CaNa_2(P_2S_6).8H_2O$ contains one Ca^{2+} cation, two Na^+ cations, one half of a $(P_2S_6)^{4-}$ anion in staggered conformation and four water molecules (Fig. 1).

Na(1) is octahedrally coordinated by four H_2O molecules and two sulfur atoms of two $(P_2S_6)^{4-}$ anions (Fig 2). Na(2) is also octahedrally coordinated by two H_2O molecules and four sulfur atoms of two $(P_2S_6)^{4-}$ anions (Fig. 3). The calcium cation is eightfold coordinated by water O atoms. The $[CaO_8]$ coordination polyhedron can be described as a bicapped trigonal prism. The crystal structure is built up from layers extending parallel to (101). These layers consists of edge-sharing CaO_8 and $Na(1)O_4S_2$ polyedra, CaO_8 and $Na(2)O_2S_4$ polyhadra, as well as corner-sharing $Na(1)O_4S_2$ and $(P_2S_6)^{4-}$ polyhedra.

The staggered $(P_2S_6)^{4-}$ anion is located on a centre of inversion, with a P—P distance of 2.2381 (8) Å. The P—P central bond links two PS_3 groups with P—S distances ranging from 2.0156 (6) to 2.0282 (6) Å. These values agree well with those reported previously for another hypothiodiphosphate structure (Jörgens *et al.*, 2003).

Neighbouring layers are held together by various O—H···S hydrogen bonding interactions. The donor—acceptor distances between O atoms of water molecules and S atoms of $(P_2S_6)^{4-}$ units range from 3.188 to 3.327 Å (Table 2).

S2. Experimental

$Na_4(P_2S_6).6H_2O$ has been prepared according to Fincher *et al.* (1998). The new ternary calcium disodium hexathiodiphosphate octahydrate was obtained by adding calcium hydroxide (2 mmol, 0.148 g) to a solution of $Na_4(P_2S_6).6H_2O$ (2 mmol, 0.910 g) in 40 ml distilled water at 333 K. Slow cooling to room temperature yielded colorless crystals of the title compound within some days.

S3. Refinement

Hydrogen atoms were found from the difference Fourier map and were refined independently from their respective oxygen atoms with individual isotropic displacement parameters.

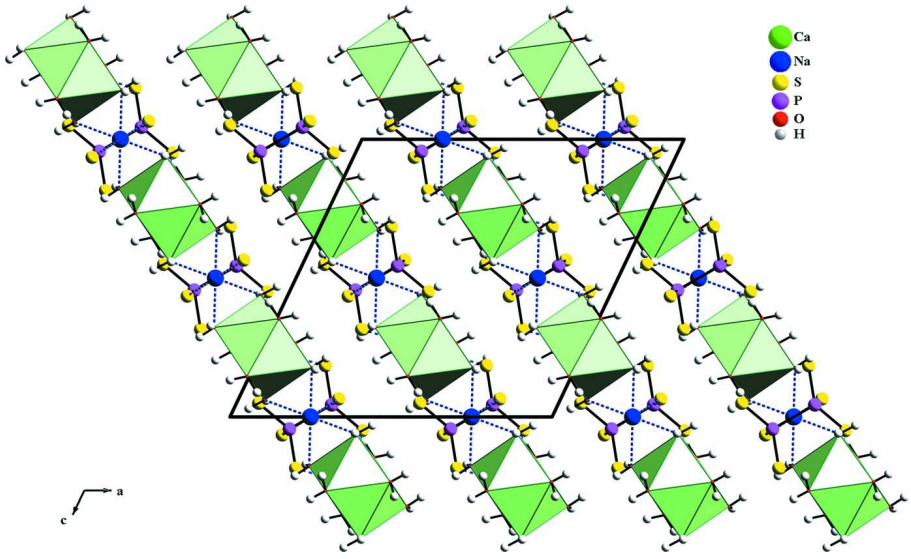

Figure 1

The crystal structure of $CaNa_2(P_2S_6).8H_2O$ in a projection along [010].

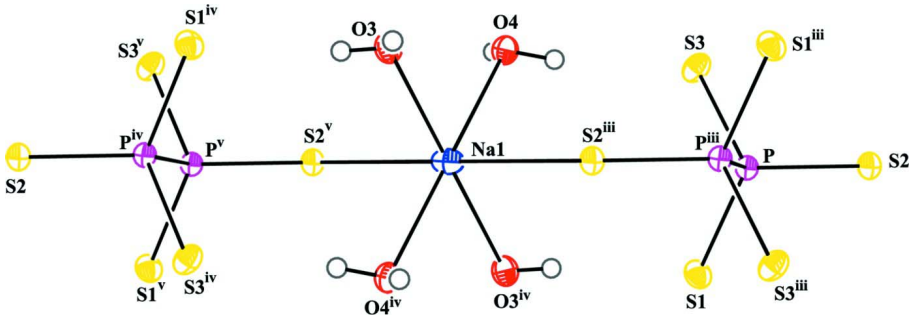

Figure 2

Coordination of Na1 with the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level. Symmetry codes as in Table 1. H atoms are represented as spheres of arbirtary radius.

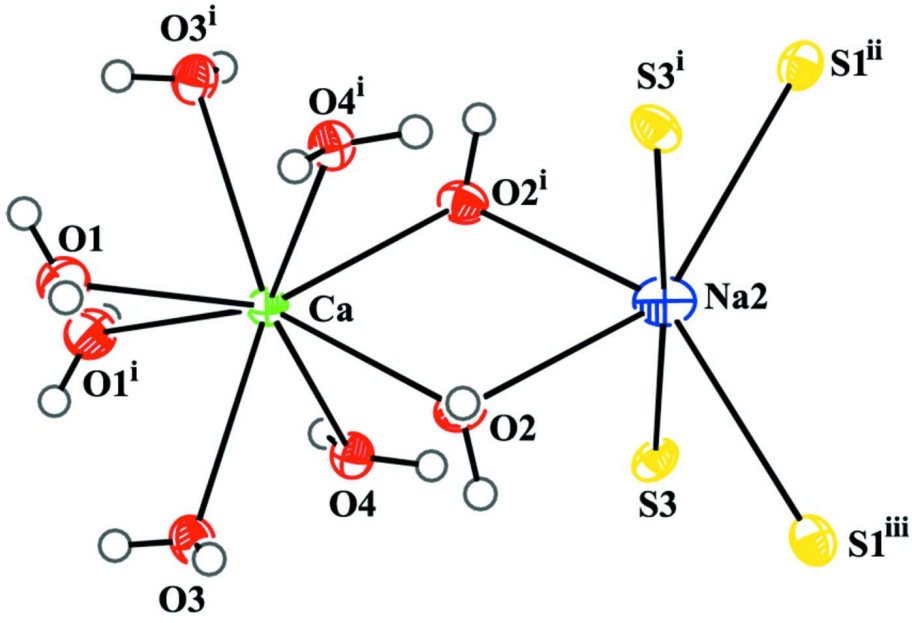

Figure 3

View of the edge-shared CaO_8 and $Na(2)O_2S_4$ polyhedra with the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level. Symmetry codes as in Table 1. H atoms are represented as spheres of arbirtary radius.

Calcium disodium hexathiodiphosphate(IV) octahydrate

Crystal data

$CaNa_2(P_2S_6)\cdot 8H_2O$
$M_r = 484.49$
Monoclinic, $C2/c$
Hall symbol: -C 2yc
$a = 14.702\ (2)$ Å
$b = 9.3081\ (14)$ Å
$c = 14.052\ (2)$ Å
$\beta = 115.383\ (11)°$
$V = 1737.3\ (4)$ Å^3
$Z = 4$

$F(000) = 992$
$D_x = 1.852$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 15599 reflections
$\theta = 1.0–30.5°$
$\mu = 1.34$ mm^{-1}
$T = 223$ K
Block, colorless
0.29 × 0.24 × 0.23 mm

Data collection

Stoe IPDS 2 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω–scans
15223 measured reflections
2650 independent reflections

2369 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 30.5°$, $\theta_{min} = 2.7°$
$h = -20\rightarrow20$
$k = -13\rightarrow13$
$l = -20\rightarrow17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.065$
$S = 1.13$
2650 reflections

122 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2 + 2.2311P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.68$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0046 (3)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ca	0.5000	0.24842 (5)	0.2500	0.01531 (10)
Na1	0.2500	0.2500	0.0000	0.0240 (2)
Na2	0.5000	0.67523 (13)	0.2500	0.0318 (2)
P	0.20227 (3)	0.76310 (4)	0.04363 (3)	0.01394 (9)
S1	0.06893 (3)	0.67248 (4)	−0.04913 (3)	0.02064 (10)
S2	0.18887 (3)	0.97575 (4)	0.06497 (3)	0.01807 (9)
S3	0.27954 (3)	0.66563 (4)	0.18473 (3)	0.02051 (10)
O1	0.59411 (11)	0.04315 (16)	0.23418 (13)	0.0268 (3)
O2	0.50720 (10)	0.45732 (14)	0.14604 (10)	0.0217 (2)
O3	0.41702 (10)	0.16862 (14)	0.06107 (10)	0.0216 (2)
O4	0.31872 (9)	0.32895 (14)	0.17753 (10)	0.0199 (2)
H1A	0.629 (4)	0.053 (5)	0.205 (4)	0.096 (15)*
H1B	0.627 (3)	0.002 (4)	0.287 (3)	0.068 (12)*
H2A	0.554 (3)	0.462 (3)	0.133 (3)	0.048 (9)*
H2B	0.453 (2)	0.477 (3)	0.088 (3)	0.045 (8)*
H3A	0.4123 (19)	0.085 (3)	0.059 (2)	0.029 (6)*
H3B	0.454 (2)	0.192 (3)	0.030 (2)	0.042 (8)*
H4A	0.288 (2)	0.294 (3)	0.212 (3)	0.049 (8)*
H4B	0.306 (2)	0.416 (3)	0.172 (2)	0.040 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca	0.0144 (2)	0.01655 (19)	0.01458 (19)	0.000	0.00584 (15)	0.000
Na1	0.0192 (5)	0.0302 (5)	0.0196 (5)	−0.0001 (4)	0.0053 (4)	−0.0011 (4)
Na2	0.0283 (6)	0.0396 (6)	0.0249 (5)	0.000	0.0089 (4)	0.000
P	0.01509 (18)	0.01411 (17)	0.01436 (17)	0.00019 (13)	0.00797 (14)	0.00016 (12)
S1	0.01688 (19)	0.02004 (18)	0.0257 (2)	−0.00401 (14)	0.00981 (15)	−0.00281 (14)
S2	0.01954 (19)	0.01504 (17)	0.01967 (18)	0.00092 (13)	0.00844 (14)	−0.00104 (13)
S3	0.0250 (2)	0.02236 (19)	0.01657 (17)	0.00676 (15)	0.01122 (15)	0.00515 (14)
O1	0.0201 (6)	0.0272 (6)	0.0298 (7)	0.0039 (5)	0.0075 (5)	−0.0023 (5)
O2	0.0197 (6)	0.0261 (6)	0.0187 (5)	−0.0009 (5)	0.0076 (5)	0.0038 (5)
O3	0.0241 (6)	0.0203 (6)	0.0227 (6)	0.0002 (5)	0.0124 (5)	−0.0026 (5)
O4	0.0210 (6)	0.0195 (5)	0.0214 (6)	0.0014 (4)	0.0112 (5)	−0.0002 (4)

Geometric parameters (Å, º)

Ca—O1	2.4244 (14)	Na2—S1^{iv}	2.9242 (8)
Ca—O1^{i}	2.4244 (15)	Na2—S3	2.9673 (7)

Ca—O2	2.4614 (13)	Na2—S3^{i}	2.9674 (7)
Ca—O2^{i}	2.4615 (13)	P—S1	2.0156 (6)
Ca—O3^{i}	2.5122 (13)	P—S2	2.0241 (6)
Ca—O3	2.5123 (13)	P—S3	2.0282 (6)
Ca—O4	2.5249 (13)	P—P^{iv}	2.2381 (8)
Ca—O4^{i}	2.5249 (13)	S1—Na2^{iv}	2.9242 (8)
Na1—O3	2.3523 (14)	S2—Na1^{vi}	2.9768 (5)
Na1—O3^{ii}	2.3523 (14)	O1—H1A	0.78 (5)
Na1—O4	2.3713 (13)	O1—H1B	0.79 (4)
Na1—O4^{ii}	2.3713 (13)	O2—H2A	0.79 (3)
Na1—S2^{iii}	2.9767 (5)	O2—H2B	0.88 (3)
Na1—S2^{iv}	2.9768 (5)	O3—H3A	0.78 (3)
Na2—O2	2.5282 (17)	O3—H3B	0.86 (3)
Na2—O2^{i}	2.5283 (17)	O4—H4A	0.85 (3)
Na2—S1^{v}	2.9242 (8)	O4—H4B	0.83 (3)

O1—Ca—O1^{i}	75.99 (8)	O4^{ii}—Na1—S2^{iii}	90.48 (3)
O1—Ca—O2	113.37 (5)	O3—Na1—S2^{iv}	89.02 (4)
O1^{i}—Ca—O2	148.04 (5)	O3^{ii}—Na1—S2^{iv}	90.98 (4)
O1—Ca—O2^{i}	148.04 (5)	O4—Na1—S2^{iv}	90.48 (3)
O1^{i}—Ca—O2^{i}	113.37 (5)	O4^{ii}—Na1—S2^{iv}	89.52 (3)
O2—Ca—O2^{i}	75.64 (6)	S2^{iii}—Na1—S2^{iv}	180.0
O1—Ca—O3^{i}	79.99 (5)	O2—Na2—O2^{i}	73.30 (7)
O1^{i}—Ca—O3^{i}	73.01 (5)	O2—Na2—S1^{v}	149.72 (4)
O2—Ca—O3^{i}	137.37 (4)	O2^{i}—Na2—S1^{v}	85.08 (3)
O2^{i}—Ca—O3^{i}	74.41 (4)	O2—Na2—S1^{iv}	85.08 (3)
O1—Ca—O3	73.01 (5)	O2^{i}—Na2—S1^{iv}	149.72 (4)
O1^{i}—Ca—O3	79.99 (5)	S1^{v}—Na2—S1^{iv}	122.01 (5)
O2—Ca—O3	74.42 (4)	O2—Na2—S3	96.20 (4)
O2^{i}—Ca—O3	137.37 (4)	O2^{i}—Na2—S3	81.01 (4)
O3^{i}—Ca—O3	145.61 (6)	S1^{v}—Na2—S3	101.16 (2)
O1—Ca—O4	137.92 (5)	S1^{iv}—Na2—S3	80.537 (18)
O1^{i}—Ca—O4	74.08 (5)	O2—Na2—S3^{i}	81.01 (4)
O2—Ca—O4	80.36 (5)	O2^{i}—Na2—S3^{i}	96.20 (4)
O2^{i}—Ca—O4	72.44 (4)	S1^{v}—Na2—S3^{i}	80.537 (17)
O3^{i}—Ca—O4	117.68 (4)	S1^{iv}—Na2—S3^{i}	101.16 (2)
O3—Ca—O4	73.21 (4)	S3—Na2—S3^{i}	176.55 (5)
O1—Ca—O4^{i}	74.08 (5)	S1—P—S2	112.06 (3)
O1^{i}—Ca—O4^{i}	137.92 (5)	S1—P—S3	115.28 (3)
O2—Ca—O4^{i}	72.44 (4)	S2—P—S3	109.99 (3)
O2^{i}—Ca—O4^{i}	80.36 (5)	S1—P—P^{iv}	105.34 (3)
O3^{i}—Ca—O4^{i}	73.21 (4)	S2—P—P^{iv}	108.14 (3)
O3—Ca—O4^{i}	117.68 (4)	S3—P—P^{iv}	105.48 (3)
O4—Ca—O4^{i}	145.46 (6)	P—S1—Na2^{iv}	105.07 (3)
O3—Na1—O3^{ii}	180.0	P—S2—Na1^{vi}	137.04 (2)
O3—Na1—O4	78.97 (4)	P—S3—Na2	111.63 (3)
O3^{ii}—Na1—O4	101.03 (4)	H1A—O1—H1B	105 (4)
O3—Na1—O4^{ii}	101.03 (4)	Ca—O2—Na2	105.53 (5)

O3^{ii}—Na1—O4^{ii}	78.97 (4)	H2A—O2—H2B	108 (3)
O4—Na1—O4^{ii}	179.999 (2)	Na1—O3—Ca	104.38 (5)
O3—Na1—S2^{iii}	90.98 (4)	Na1—O4—Ca	103.44 (5)
O3^{ii}—Na1—S2^{iii}	89.02 (4)	H4A—O4—H4B	106 (3)
O4—Na1—S2^{iii}	89.52 (3)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···S3^{vii}	0.78 (5)	2.58 (5)	3.2922 (17)	153 (4)
O1—H1*B*···S2^{viii}	0.79 (4)	2.62 (4)	3.2892 (16)	144 (4)
O2—H2*A*···S2^{vii}	0.79 (3)	2.54 (3)	3.3270 (15)	172 (3)
O2—H2*B*···S2^{iv}	0.88 (3)	2.30 (3)	3.1877 (15)	179 (3)
O3—H3*A*···S1^{ii}	0.78 (3)	2.43 (3)	3.1908 (15)	168 (2)
O3—H3*B*···S1^{vii}	0.86 (3)	2.39 (3)	3.2174 (14)	161 (3)
O4—H4*A*···S3^{ix}	0.85 (3)	2.41 (3)	3.2468 (14)	171 (3)
O4—H4*B*···S3	0.83 (3)	2.37 (3)	3.1957 (14)	171 (3)

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