

## Crystal structure of zwitterionic 2-[bis(2-methoxyphenyl)phosphaniumyl]-4-methylbenzenesulfonate monohydrate dichloromethane monosolvate

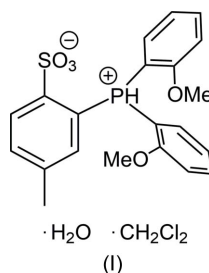
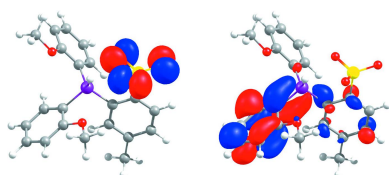
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e-mail: rfjordan@uchicago.eduEdited by V. V. Chernyshev, Moscow State  
University, Russia**Keywords:** crystal structure; sulfonic acid; zwitterion; hydrogen bonding**CCDC reference:** 1447138**Supporting information:** this article has  
supporting information at journals.iucr.org/e

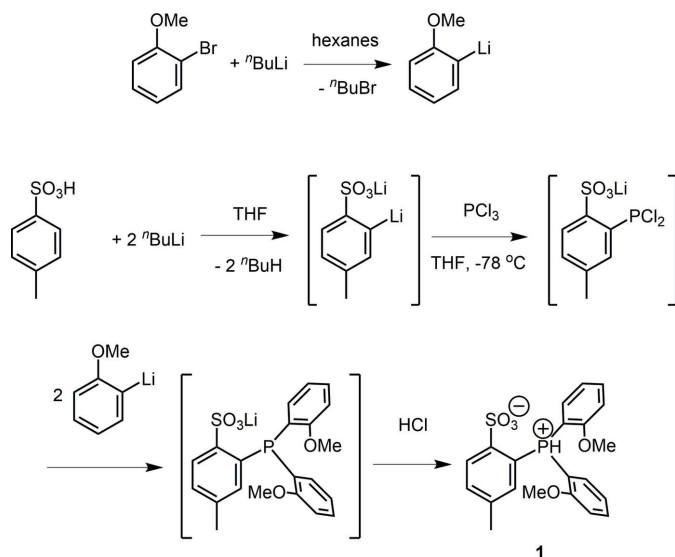
In the title compound,  $C_{21}H_{21}O_5PS \cdot H_2O \cdot CH_2Cl_2$ , the phosphonium–sulfonate zwitterion has the acidic H atom located on the P atom rather than the sulfonate group. The S–O bond lengths [1.4453 (15)–1.4521 (14) Å] are essentially equal. In the crystal, the water molecules bridge two zwitterions *via*  $O_{\text{water}} \cdots H \cdots O_{\text{sulfonate}}$  hydrogen bonds into a centrosymmetric dimer. The dimers are further linked by weak  $C_{\text{Aryl}}-H \cdots O_{\text{sulfonate}}$  hydrogen bonds into chains extending along [100]. The  $PH^+$  group is not involved in intermolecular interactions.

## 1. Chemical context

Phosphane ligands (Allen, 2014) are ubiquitous in coordination and organometallic chemistry and have been used to synthesize a wide variety of metal complexes and catalysts (Hartwig, 2010). Incorporation of additional potential donor groups within the phosphane structure provides added versatility to such ligands. For example, *ortho*-phosphanylbenzenesulfonate (PO) ligands, such as 2-[bis(2-methoxyphenyl)phosphanyl]benzenesulfonate, bind to  $Pd^{II}$  in a  $\kappa^2P,O$  mode to form (PO) $PdR$  species that are active for the polymerization of ethylene (Cai *et al.*, 2012; Contrella & Jordan, 2014; Zhou *et al.*, 2014), copolymerization of ethylene and polar monomers (Drent *et al.*, 2002a; Nakamura *et al.*, 2013), non-alternating copolymerization of ethylene and CO (Drent *et al.*, 2002b), and alternating copolymerization of CO with polar monomers (Nakamura *et al.*, 2011, 2012). Phosphanylarenesulfonate ligands derived from *para*-toluenesulfonic acid are useful because the extra methyl group provides a convenient NMR handle for characterizing complexes and monitoring reactions.

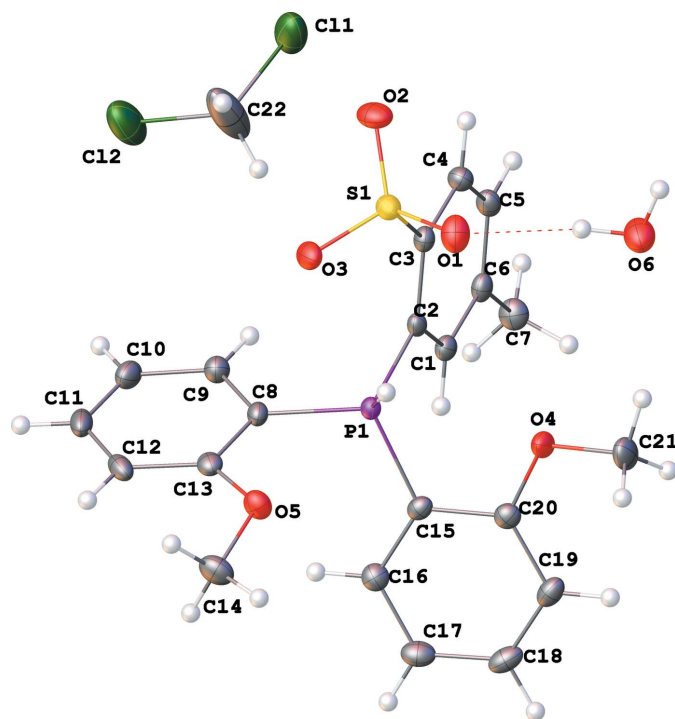


The zwitterion 2-[bis(2-methoxyphenyl)phosphaniumyl]-4-methylbenzenesulfonate (**1**, Scheme 1) was synthesized by sequential reaction of  $PCl_3$  with dilithiated *p*-toluenesulfonate and 1-lithio-2-methoxybenzene, followed by acidification of HCl (Scheme 2) (Vela *et al.*, 2007). Here we report the crystal structure of  $1 \cdot H_2O \cdot CH_2Cl_2$ , (I).



## 2. Structural commentary

Compound **1** crystallizes as the phosphonium–sulfonate zwitterion in which the acidic H atom is located on the P atom rather than the sulfonate group (Fig. 1). The S–O bond distances fall within the narrow range of 1.4453 (15) to 1.4521 (14) Å, and the P–C distances lie within the range of 1.7794 (18) to 1.7984 (18) Å. The P–H atom was located in a difference Fourier map and refined without additional



**Figure 1**  
The molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. The dashed line denotes a hydrogen bond.

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

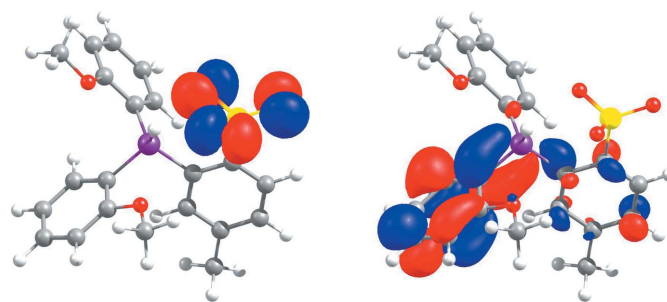
<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O6–H1O···O1	0.91 (3)	1.96 (3)	2.862 (2)	170 (3)
O6–H2O···O2 <sup>i</sup>	0.92 (3)	1.98 (3)	2.877 (2)	164 (3)
C19–H19···O3 <sup>ii</sup>	0.95	2.47	3.180 (2)	132

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

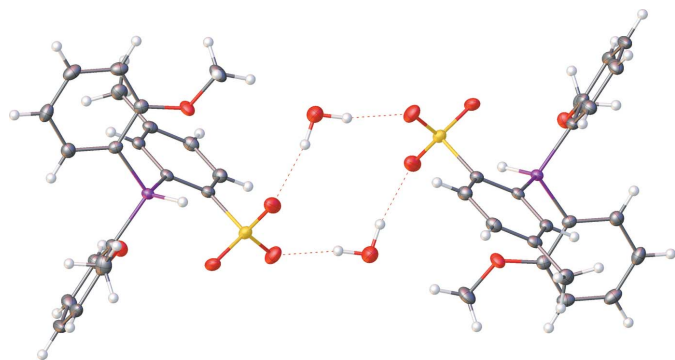
restraints. The P–H bond length is 1.22 (2) Å. Compound **1** adopts an *exo*<sub>3</sub> conformation, *i.e.* the *ortho* methoxy and sulfonate groups point toward the PH<sup>+</sup> group (Feng *et al.*, 2014). Tris(*ortho*-substituted aryl)phosphanes normally exhibit *exo*<sub>3</sub> conformations (Howell *et al.*, 1999) because the *ortho* substituents cause less steric congestion when they point toward the P lone pair (*exo*) rather than toward the other aryl rings (*endo*). Addition of an H<sup>+</sup> at phosphorous should not add significant steric congestion and therefore it is not surprising that **1** also adopts the *exo*<sub>3</sub> conformation. The O<sub>methoxy</sub>···P distances, 2.7691 (14) and 2.7940 (14) Å, are shorter than the sum of the O and P van der Waals radii (3.35 Å). The O3···H1(P1) distance is 2.44 (2) Å.

## 3. DFT calculations

The relative stability of the observed *exo*<sub>3</sub> conformation *versus* alternative *exo*<sub>2</sub> and *exo*<sub>1</sub> conformations was investigated by DFT calculations using the hybrid exchange–correlation functional PBE0 (Perdew *et al.*, 1996, 1997) and the 6-311G(d,p) basis set for all atoms. The optimized structure is the *exo*<sub>3</sub> conformer, in which the methoxy and sulfonate groups point toward the PH<sup>+</sup> group. Geometry optimizations were also carried out on two conformers in which the SO<sub>3</sub> group was kept *exo* but one (*exo*<sub>2</sub>) or two (*exo*<sub>1</sub>) methoxy groups were rotated away from the PH<sup>+</sup> group. The *exo*<sub>2</sub> and *exo*<sub>1</sub> conformers were calculated to be 1.2 and 2.5 kcal mol<sup>−1</sup> less stable than the *exo*<sub>3</sub> isomer, respectively. The HOMO of the *exo*<sub>3</sub> conformer is comprised of *p* orbitals of the sulfonate O atoms, while the LUMO is delocalized over the phenyl rings and P–C<sub>aromatic</sub> bonds (Fig. 2).



**Figure 2**  
HOMO (−0.2289 Hartrees, left) and LUMO (−0.0483 Hartrees, right) orbitals of **1**.



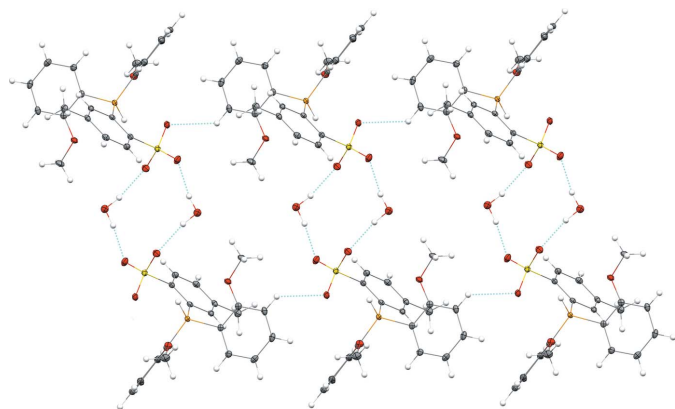
**Figure 3**  
Dimer formation through  $\text{O}_{\text{water}}-\text{H}\cdots\text{O}_{\text{sulfonate}}$  hydrogen bonds (dashed lines).

#### 4. Supramolecular features

Two O atoms of the  $\text{SO}_3^-$  group are hydrogen bonded with the co-crystallized water molecule, forming inversion dimers (Fig. 3). The  $\text{O}_{\text{water}}-\text{H}\cdots\text{O}_{\text{sulfonate}}$  contacts are 1.96 (3) and 1.98 (3) Å (Table 1). These dimers are further linked by  $\text{C}_{\text{Aryl}}-\text{H}\cdots\text{O}_{\text{sulfonate}}$  hydrogen bonds into infinite chains running along the [100] direction (Fig. 4). A similar  $\text{C}_{\text{Ar}}-\text{SO}_3^- \cdots \text{H}_2\text{O} \cdots \text{C}_{\text{Ar}}-\text{SO}_3^- \cdots \text{H}_2\text{O} \cdots$  hydrogen-bonding motif was observed in [Na(18-crown-6)(H<sub>2</sub>O)][2-((*o*-CF<sub>3</sub>-Ph)<sub>2</sub>P]-4-Me-benzenesulfonate] (Feng *et al.*, 2014).

#### 5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.36, last update May 2015; Groom & Allen, 2014) revealed structural reports for two analogues of **1** that contain 4-chloro-substituted methoxyphenyl (CSD refcode ODUNOS; Wucher *et al.*, 2013) or 2,6-dimethoxyphenyl substituents at phosphorous (CSD refcode: LEXLEG; Liu *et al.*, 2007). These compounds also crystallized as zwitterions in which the acidic proton is located on the P atom and feature



**Figure 4**  
A fragment of the crystal packing of the title compound with intermolecular hydrogen bonds shown as dashed light-blue lines. Color scheme: C grey, H white, O red, P orange, S yellow.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{21}\text{H}_{21}\text{O}_5\text{PS}\cdot\text{CH}_2\text{Cl}_2\cdot\text{H}_2\text{O}$
$M_r$	519.35
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	100
$a, b, c$ (Å)	9.6437 (6), 15.9441 (11), 15.9641 (11)
$\beta$ (°)	105.051 (2)
$V$ (Å <sup>3</sup> )	2370.4 (3)
$Z$	4
Radiation type	Mo $K\alpha$
$\mu$ (mm <sup>-1</sup> )	0.47
Crystal size (mm)	0.32 × 0.18 × 0.12
Data collection	
Diffractometer	Bruker D8 Venture PHOTON 100 CMOS
Absorption correction	Multi-scan (SADABS; Bruker, 2014)
$T_{\text{min}}, T_{\text{max}}$	0.693, 0.745
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	53574, 4888, 4349
$R_{\text{int}}$	0.030
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.627
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.038, 0.106, 1.05
No. of reflections	4888
No. of parameters	304
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.48, -0.66

Computer programs: APEX2 and SAINT (Bruker, 2014), SHELXT (Sheldrick, 2015a), SHELXL2014 (Sheldrick, 2015b), OLEX2 (Dolomanov *et al.*, 2009), Mercury (Macrae *et al.*, 2008) and publCIF (Westrip, 2010).

close  $\text{O}_{\text{methoxy}} \cdots \text{P}$  contacts (2.764 to 2.927 Å). The structure of the triethylammonium salt of 2-[bis(2-methoxyphenyl)phosphanyl]benzenesulfonate has also been reported (CSD refcode HAGKEH; Bettucci *et al.*, 2008). In this case, the acidic H atom is located at triethylamine rather than on the P atom and the  $\text{O}_{\text{methoxy}} \cdots \text{P}$  distances are 2.877 and 2.903 Å.

#### 6. Synthesis and crystallization

Compound **1** was synthesized by a modification of a previously reported procedure (Vela *et al.*, 2007) comprising sequential reaction of  $\text{PCl}_3$  with dilithiated *p*-toluenesulfonate and 1-lithio-2-methoxybenzene, followed by acidification of HCl, to afford **1** in 70–75% yield on a 3–4 g scale (Scheme 2). The product was purified by recrystallization ( $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ , volume ratio 1/3, layering at 273K). Crystals of  $\text{1}\cdot\text{H}_2\text{O}\cdot\text{CH}_2\text{Cl}_2$  (**I**) suitable for the X-ray diffraction analysis were obtained by layering  $\text{Et}_2\text{O}$  on a  $\text{CH}_2\text{Cl}_2$  solution of **1** at 277 K.

#### 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Carbon-bound H atoms were placed in calculated positions ( $\text{C}-\text{H} = 0.95\text{--}0.98$  Å) and were included in the refinement in the riding-model approximation,

with  $U_{\text{iso}}(\text{H})$  set to  $1.2\text{--}1.5U_{\text{eq}}(\text{C})$ . The P- and O-bound H atoms were located in a difference Fourier map and refined isotropically.

### Acknowledgements

This work was supported by the National Science Foundation (grants CHE-0911180 and CHE-1048528). Calculations were carried out with the GAMESS-US computational package provided by the University of Chicago Research Computing Center (Midway high-performance computing cluster).

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## supporting information

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## Crystal structure of zwitterionic 2-[bis(2-methoxyphenyl)phosphaniumyl]-4-methylbenzenesulfonate monohydrate dichloromethane monosolvate

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### Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINTE* (Bruker, 2014); data reduction: *SAINTE* (Bruker, 2014); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### 2-[Bis(2-methoxyphenyl)phosphaniumyl]-4-methylbenzenesulfonate monohydrate dichloromethane monosolvate

#### Crystal data

$C_{21}H_{21}O_5PS \cdot CH_2Cl_2 \cdot H_2O$

$M_r = 519.35$

Monoclinic,  $P2_1/n$

$a = 9.6437$  (6) Å

$b = 15.9441$  (11) Å

$c = 15.9641$  (11) Å

$\beta = 105.051$  (2)°

$V = 2370.4$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 1080$

$D_x = 1.455$  Mg m<sup>-3</sup>

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

Cell parameters from 9610 reflections

$\theta = 2.2$ – $26.4$ °

$\mu = 0.47$  mm<sup>-1</sup>

$T = 100$  K

Block, colorless

$0.32 \times 0.18 \times 0.12$  mm

#### Data collection

Bruker D8 Venture PHOTON 100 CMOS diffractometer

Radiation source: INCOATEC ImuS micro-focus source

Mirrors monochromator

Detector resolution: 10.4167 pixels mm<sup>-1</sup>

$\omega$  and  $\phi$  scans

Absorption correction: multi-scan (*SADABS*; Bruker, 2014)

$T_{\min} = 0.693$ ,  $T_{\max} = 0.745$

53574 measured reflections

4888 independent reflections

4349 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\max} = 26.5$ °,  $\theta_{\min} = 2.2$ °

$h = -12 \rightarrow 12$

$k = -19 \rightarrow 19$

$l = -20 \rightarrow 19$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.106$

$S = 1.05$

4888 reflections

304 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2 + 2.7024P]$

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

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

$$\Delta\rho_{\max} = 0.48 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.66 \text{ e } \text{\AA}^{-3}$$

### Special details

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

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
P1	0.63863 (5)	0.30456 (3)	0.33309 (3)	0.01288 (12)
H1P	0.592 (2)	0.2397 (14)	0.2950 (14)	0.018 (5)*
S1	0.43769 (5)	0.17697 (3)	0.41453 (3)	0.01702 (12)
O1	0.50338 (15)	0.10620 (9)	0.38266 (10)	0.0261 (3)
O2	0.34252 (15)	0.15453 (10)	0.46751 (10)	0.0269 (3)
O3	0.37411 (14)	0.23600 (9)	0.34604 (9)	0.0210 (3)
O4	0.86431 (15)	0.19197 (8)	0.35798 (9)	0.0210 (3)
O5	0.51406 (15)	0.34403 (9)	0.15930 (8)	0.0206 (3)
C1	0.77958 (19)	0.33171 (11)	0.50245 (12)	0.0155 (4)
H1	0.8372	0.3678	0.4781	0.019*
C2	0.66711 (19)	0.28789 (11)	0.44773 (11)	0.0139 (3)
C3	0.58188 (19)	0.23434 (11)	0.48294 (12)	0.0155 (4)
C4	0.6117 (2)	0.22566 (12)	0.57215 (12)	0.0188 (4)
H4	0.5552	0.1890	0.5966	0.023*
C5	0.7235 (2)	0.27025 (12)	0.62605 (12)	0.0187 (4)
H5	0.7417	0.2642	0.6871	0.022*
C6	0.8093 (2)	0.32358 (12)	0.59237 (12)	0.0170 (4)
C7	0.9324 (2)	0.37081 (13)	0.65044 (13)	0.0227 (4)
H7A	0.9220	0.3708	0.7099	0.034*
H7B	0.9323	0.4287	0.6299	0.034*
H7C	1.0231	0.3437	0.6493	0.034*
C8	0.51505 (19)	0.38810 (11)	0.29746 (12)	0.0159 (4)
C9	0.4711 (2)	0.44064 (12)	0.35526 (13)	0.0202 (4)
H9	0.5089	0.4336	0.4160	0.024*
C10	0.3720 (2)	0.50321 (13)	0.32356 (14)	0.0239 (4)
H10	0.3426	0.5402	0.3624	0.029*
C11	0.3158 (2)	0.51167 (13)	0.23483 (15)	0.0246 (4)
H11	0.2461	0.5540	0.2136	0.030*
C12	0.3583 (2)	0.46027 (12)	0.17634 (13)	0.0209 (4)
H12	0.3185	0.4670	0.1157	0.025*
C13	0.46023 (19)	0.39848 (12)	0.20784 (12)	0.0173 (4)
C14	0.4860 (2)	0.36077 (14)	0.06819 (13)	0.0261 (4)
H14A	0.3827	0.3561	0.0413	0.039*
H14B	0.5378	0.3201	0.0416	0.039*
H14C	0.5184	0.4176	0.0595	0.039*
C15	0.80656 (19)	0.32846 (12)	0.31142 (11)	0.0152 (4)



C16	0.8366 (2)	0.40458 (12)	0.27736 (12)	0.0192 (4)
H16	0.7672	0.4482	0.2665	0.023*
C17	0.9686 (2)	0.41647 (13)	0.25930 (13)	0.0224 (4)
H17	0.9894	0.4678	0.2349	0.027*
C18	1.0697 (2)	0.35248 (13)	0.27735 (13)	0.0226 (4)
H18	1.1612	0.3615	0.2670	0.027*
C19	1.0407 (2)	0.27600 (13)	0.30998 (13)	0.0208 (4)
H19	1.1106	0.2326	0.3208	0.025*
C20	0.9083 (2)	0.26368 (12)	0.32663 (12)	0.0173 (4)
C21	0.9467 (2)	0.11736 (13)	0.35617 (14)	0.0258 (4)
H21A	0.9509	0.1062	0.2965	0.039*
H21B	0.9012	0.0699	0.3775	0.039*
H21C	1.0442	0.1251	0.3932	0.039*
C22	0.2653 (5)	0.3457 (2)	0.5203 (2)	0.0676 (11)
H22A	0.2056	0.3047	0.4801	0.081*
H22B	0.3569	0.3518	0.5038	0.081*
C11	0.30192 (7)	0.30568 (5)	0.62409 (4)	0.04587 (19)
C12	0.17791 (9)	0.44136 (4)	0.50619 (5)	0.0517 (2)
O6	0.73753 (17)	-0.00322 (11)	0.45863 (11)	0.0308 (4)
H1O	0.656 (4)	0.027 (2)	0.436 (2)	0.049 (8)*
H2O	0.701 (3)	-0.053 (2)	0.4720 (19)	0.043 (8)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
P1	0.0121 (2)	0.0138 (2)	0.0124 (2)	0.00178 (16)	0.00263 (17)	0.00083 (16)
S1	0.0143 (2)	0.0180 (2)	0.0173 (2)	-0.00200 (17)	0.00148 (17)	0.00157 (17)
O1	0.0245 (7)	0.0214 (7)	0.0283 (8)	0.0011 (6)	-0.0007 (6)	-0.0049 (6)
O2	0.0227 (7)	0.0324 (8)	0.0255 (8)	-0.0092 (6)	0.0062 (6)	0.0041 (6)
O3	0.0141 (6)	0.0255 (7)	0.0207 (7)	-0.0009 (5)	-0.0003 (5)	0.0048 (6)
O4	0.0217 (7)	0.0174 (7)	0.0268 (7)	0.0068 (5)	0.0115 (6)	0.0045 (5)
O5	0.0244 (7)	0.0213 (7)	0.0148 (7)	0.0010 (6)	0.0027 (5)	0.0006 (5)
C1	0.0151 (8)	0.0143 (8)	0.0173 (9)	0.0025 (7)	0.0044 (7)	-0.0010 (7)
C2	0.0147 (8)	0.0138 (8)	0.0134 (8)	0.0043 (7)	0.0043 (7)	0.0012 (7)
C3	0.0137 (8)	0.0159 (9)	0.0162 (9)	0.0026 (7)	0.0025 (7)	0.0006 (7)
C4	0.0182 (9)	0.0209 (9)	0.0179 (9)	0.0014 (7)	0.0058 (7)	0.0035 (7)
C5	0.0213 (9)	0.0210 (9)	0.0139 (9)	0.0045 (7)	0.0047 (7)	0.0015 (7)
C6	0.0160 (9)	0.0168 (9)	0.0173 (9)	0.0047 (7)	0.0026 (7)	-0.0020 (7)
C7	0.0234 (10)	0.0239 (10)	0.0186 (9)	-0.0010 (8)	0.0017 (8)	-0.0030 (8)
C8	0.0123 (8)	0.0153 (9)	0.0198 (9)	0.0020 (7)	0.0038 (7)	0.0036 (7)
C9	0.0198 (9)	0.0202 (10)	0.0211 (9)	0.0029 (7)	0.0063 (8)	0.0025 (7)
C10	0.0229 (10)	0.0199 (10)	0.0323 (11)	0.0051 (8)	0.0131 (9)	0.0028 (8)
C11	0.0159 (9)	0.0206 (10)	0.0381 (12)	0.0039 (7)	0.0080 (8)	0.0117 (9)
C12	0.0162 (9)	0.0209 (9)	0.0229 (10)	-0.0024 (7)	0.0002 (7)	0.0093 (8)
C13	0.0133 (8)	0.0172 (9)	0.0211 (9)	-0.0029 (7)	0.0039 (7)	0.0027 (7)
C14	0.0339 (11)	0.0273 (11)	0.0166 (9)	-0.0028 (9)	0.0055 (8)	0.0023 (8)
C15	0.0136 (8)	0.0191 (9)	0.0131 (8)	-0.0004 (7)	0.0037 (7)	-0.0023 (7)
C16	0.0199 (9)	0.0189 (9)	0.0183 (9)	-0.0006 (7)	0.0040 (7)	-0.0011 (7)

C17	0.0247 (10)	0.0223 (10)	0.0213 (10)	-0.0082 (8)	0.0077 (8)	-0.0020 (8)
C18	0.0170 (9)	0.0303 (11)	0.0221 (10)	-0.0056 (8)	0.0083 (8)	-0.0079 (8)
C19	0.0158 (9)	0.0272 (10)	0.0196 (9)	0.0025 (8)	0.0049 (7)	-0.0045 (8)
C20	0.0183 (9)	0.0196 (9)	0.0140 (8)	-0.0001 (7)	0.0042 (7)	-0.0015 (7)
C21	0.0311 (11)	0.0198 (10)	0.0289 (11)	0.0109 (8)	0.0117 (9)	0.0024 (8)
C22	0.126 (3)	0.0495 (18)	0.0368 (15)	0.043 (2)	0.0374 (19)	0.0161 (13)
C11	0.0453 (4)	0.0621 (4)	0.0305 (3)	0.0225 (3)	0.0103 (3)	0.0118 (3)
C12	0.0798 (5)	0.0347 (3)	0.0452 (4)	0.0190 (3)	0.0245 (4)	0.0098 (3)
O6	0.0241 (8)	0.0272 (8)	0.0389 (9)	-0.0020 (7)	0.0040 (7)	0.0056 (7)

*Geometric parameters (Å, °)*

P1—C8	1.7794 (18)	C10—C11	1.386 (3)
P1—C15	1.7828 (18)	C10—H10	0.9500
P1—C2	1.7984 (18)	C11—C12	1.382 (3)
P1—H1P	1.22 (2)	C11—H11	0.9500
S1—O2	1.4453 (15)	C12—C13	1.390 (3)
S1—O1	1.4495 (15)	C12—H12	0.9500
S1—O3	1.4521 (14)	C14—H14A	0.9800
S1—C3	1.7816 (19)	C14—H14B	0.9800
O4—C20	1.359 (2)	C14—H14C	0.9800
O4—C21	1.435 (2)	C15—C16	1.391 (3)
O5—C13	1.354 (2)	C15—C20	1.402 (3)
O5—C14	1.434 (2)	C16—C17	1.389 (3)
C1—C2	1.391 (3)	C16—H16	0.9500
C1—C6	1.395 (3)	C17—C18	1.389 (3)
C1—H1	0.9500	C17—H17	0.9500
C2—C3	1.400 (3)	C18—C19	1.383 (3)
C3—C4	1.385 (3)	C18—H18	0.9500
C4—C5	1.388 (3)	C19—C20	1.384 (3)
C4—H4	0.9500	C19—H19	0.9500
C5—C6	1.388 (3)	C21—H21A	0.9800
C5—H5	0.9500	C21—H21B	0.9800
C6—C7	1.505 (3)	C21—H21C	0.9800
C7—H7A	0.9800	C22—C11	1.725 (3)
C7—H7B	0.9800	C22—C12	1.728 (3)
C7—H7C	0.9800	C22—H22A	0.9900
C8—C9	1.391 (3)	C22—H22B	0.9900
C8—C13	1.400 (3)	O6—H1O	0.91 (3)
C9—C10	1.384 (3)	O6—H2O	0.92 (3)
C9—H9	0.9500		
C8—P1—C15	110.16 (9)	C12—C11—C10	121.81 (18)
C8—P1—C2	110.40 (8)	C12—C11—H11	119.1
C15—P1—C2	108.82 (8)	C10—C11—H11	119.1
C8—P1—H1P	110.0 (10)	C11—C12—C13	118.80 (18)
C15—P1—H1P	108.8 (10)	C11—C12—H12	120.6
C2—P1—H1P	108.6 (10)	C13—C12—H12	120.6



O2—S1—O1	114.48 (9)	O5—C13—C12	125.99 (18)
O2—S1—O3	113.14 (9)	O5—C13—C8	114.20 (16)
O1—S1—O3	112.20 (9)	C12—C13—C8	119.81 (18)
O2—S1—C3	106.35 (9)	O5—C14—H14A	109.5
O1—S1—C3	105.80 (8)	O5—C14—H14B	109.5
O3—S1—C3	103.80 (8)	H14A—C14—H14B	109.5
C20—O4—C21	117.55 (15)	O5—C14—H14C	109.5
C13—O5—C14	117.51 (15)	H14A—C14—H14C	109.5
C2—C1—C6	121.17 (17)	H14B—C14—H14C	109.5
C2—C1—H1	119.4	C16—C15—C20	120.20 (17)
C6—C1—H1	119.4	C16—C15—P1	123.67 (14)
C1—C2—C3	119.83 (17)	C20—C15—P1	116.05 (14)
C1—C2—P1	116.93 (14)	C17—C16—C15	119.71 (18)
C3—C2—P1	123.24 (14)	C17—C16—H16	120.1
C4—C3—C2	119.16 (17)	C15—C16—H16	120.1
C4—C3—S1	119.96 (14)	C16—C17—C18	119.23 (19)
C2—C3—S1	120.87 (14)	C16—C17—H17	120.4
C3—C4—C5	120.43 (18)	C18—C17—H17	120.4
C3—C4—H4	119.8	C19—C18—C17	121.78 (18)
C5—C4—H4	119.8	C19—C18—H18	119.1
C6—C5—C4	121.25 (17)	C17—C18—H18	119.1
C6—C5—H5	119.4	C18—C19—C20	118.94 (18)
C4—C5—H5	119.4	C18—C19—H19	120.5
C5—C6—C1	118.16 (17)	C20—C19—H19	120.5
C5—C6—C7	121.47 (17)	O4—C20—C19	125.57 (18)
C1—C6—C7	120.37 (17)	O4—C20—C15	114.34 (16)
C6—C7—H7A	109.5	C19—C20—C15	120.09 (18)
C6—C7—H7B	109.5	O4—C21—H21A	109.5
H7A—C7—H7B	109.5	O4—C21—H21B	109.5
C6—C7—H7C	109.5	H21A—C21—H21B	109.5
H7A—C7—H7C	109.5	O4—C21—H21C	109.5
H7B—C7—H7C	109.5	H21A—C21—H21C	109.5
C9—C8—C13	120.48 (17)	H21B—C21—H21C	109.5
C9—C8—P1	122.19 (15)	C11—C22—C12	115.01 (17)
C13—C8—P1	117.32 (14)	C11—C22—H22A	108.5
C10—C9—C8	119.47 (19)	C12—C22—H22A	108.5
C10—C9—H9	120.3	C11—C22—H22B	108.5
C8—C9—H9	120.3	C12—C22—H22B	108.5
C9—C10—C11	119.59 (19)	H22A—C22—H22B	107.5
C9—C10—H10	120.2	H1O—O6—H2O	102 (3)
C11—C10—H10	120.2		
C6—C1—C2—C3	-0.2 (3)	C8—C9—C10—C11	1.2 (3)
C6—C1—C2—P1	179.37 (14)	C9—C10—C11—C12	-1.4 (3)
C8—P1—C2—C1	-91.04 (15)	C10—C11—C12—C13	0.0 (3)
C15—P1—C2—C1	29.98 (16)	C14—O5—C13—C12	12.9 (3)
C8—P1—C2—C3	88.50 (16)	C14—O5—C13—C8	-167.84 (16)
C15—P1—C2—C3	-150.48 (15)	C11—C12—C13—O5	-179.18 (17)

C1—C2—C3—C4	-0.3 (3)	C11—C12—C13—C8	1.6 (3)
P1—C2—C3—C4	-179.79 (14)	C9—C8—C13—O5	178.92 (16)
C1—C2—C3—S1	-179.67 (13)	P1—C8—C13—O5	-2.3 (2)
P1—C2—C3—S1	0.8 (2)	C9—C8—C13—C12	-1.7 (3)
O2—S1—C3—C4	21.46 (18)	P1—C8—C13—C12	177.04 (14)
O1—S1—C3—C4	-100.67 (16)	C8—P1—C15—C16	4.33 (19)
O3—S1—C3—C4	141.04 (15)	C2—P1—C15—C16	-116.84 (16)
O2—S1—C3—C2	-159.14 (15)	C8—P1—C15—C20	-172.54 (14)
O1—S1—C3—C2	78.73 (16)	C2—P1—C15—C20	66.29 (16)
O3—S1—C3—C2	-39.55 (17)	C20—C15—C16—C17	-0.7 (3)
C2—C3—C4—C5	0.8 (3)	P1—C15—C16—C17	-177.42 (15)
S1—C3—C4—C5	-179.82 (14)	C15—C16—C17—C18	-1.3 (3)
C3—C4—C5—C6	-0.8 (3)	C16—C17—C18—C19	2.3 (3)
C4—C5—C6—C1	0.4 (3)	C17—C18—C19—C20	-1.3 (3)
C4—C5—C6—C7	-178.82 (18)	C21—O4—C20—C19	-14.4 (3)
C2—C1—C6—C5	0.1 (3)	C21—O4—C20—C15	165.79 (17)
C2—C1—C6—C7	179.34 (17)	C18—C19—C20—O4	179.46 (18)
C15—P1—C8—C9	-109.47 (16)	C18—C19—C20—C15	-0.8 (3)
C2—P1—C8—C9	10.75 (19)	C16—C15—C20—O4	-178.46 (16)
C15—P1—C8—C13	71.78 (16)	P1—C15—C20—O4	-1.5 (2)
C2—P1—C8—C13	-168.00 (14)	C16—C15—C20—C19	1.7 (3)
C13—C8—C9—C10	0.3 (3)	P1—C15—C20—C19	178.73 (14)
P1—C8—C9—C10	-178.39 (15)		

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O6—H1O $\cdots$ O1	0.91 (3)	1.96 (3)	2.862 (2)	170 (3)
O6—H2O $\cdots$ O2 <sup>i</sup>	0.92 (3)	1.98 (3)	2.877 (2)	164 (3)
C19—H19 $\cdots$ O3 <sup>ii</sup>	0.95	2.47	3.180 (2)	132

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