

A novel (4,6)-connected double-layered Ba^{II} coordination polymer based on the flexible tricarboxylate ligand 2,2',2''-[1,3,5-triazine-2,4,6-triyltris(sulfanediyl)]triacetic acid

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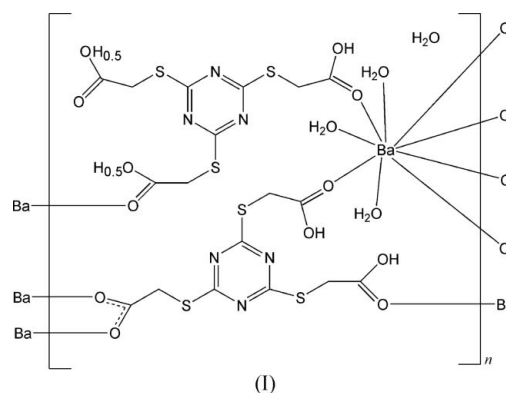
In the title compound, poly[[triqua{ μ_4 -2-[4,6-bis(carboxymethylsulfanyl)-1,3,5-triazin-2-ylsulfanyl]acetato}{ μ_2 -2-[4,6-bis(carboxymethylsulfanyl)-1,3,5-triazin-2-ylsulfanyl]acetato}barium(II)] monohydrate], $[\{\text{Ba}(\text{C}_9\text{H}_8\text{N}_3\text{O}_6\text{S}_3)_2(\text{H}_2\text{O})_3\} \cdot (\text{H}_2\text{O})_n]$, each Ba^{II} atom is nine-coordinated by six O atoms from carboxylate groups of four different 2-[4,6-bis(carboxymethylsulfanyl)-1,3,5-triazin-2-ylsulfanyl]acetate ligands and three O atoms from water molecules. The triazine ligand is partially deprotonated, as verified by intermolecular hydrogen-bonding parameters, and adopts μ_2 - η^1 : η^1 and μ_4 - η^1 : η^1 : η^2 coordination modes to connect the Ba^{II} centres, forming a novel double-layered structure. Topological analysis indicates that the whole structure is a novel (4,6)-connected net, considering the ligands and Ba^{II} centres as four- and six-connected nodes, respectively.

Comment

In recent years, metal-organic coordination polymers have attracted considerable attention, due to their fascinating molecular topologies and crystal-packing motifs, and their potential applications as smart optoelectronic, magnetic and porous materials (Moulton & Zaworotko, 2001; Kitagawa *et al.*, 2004; Ferey *et al.*, 2005; Murray *et al.*, 2009). Metal carboxylates are of particular interest (Rao *et al.*, 2004; Rowsell & Yaghi 2005; Ma *et al.*, 2007; Pan *et al.*, 2006; Rather & Zaworotko 2003). Generally, two kinds of these ligands have been used: rigid ones, such as benzenedicarboxylate and benzenetricarboxylate, and flexible ones, such as succinic and glutaric acids. The former exhibit limited conformations after coordination with the metal centre, and the final coordination supramolecular arrays are somewhat predictable. The latter, however, can adopt variable conformations according to the geometric requirements of different metal ions, and may

afford unpredictable and interesting architectures (Gomez-Lor *et al.*, 2005; Zang *et al.*, 2006; Dong *et al.*, 2007). To the best of our knowledge, only limited work has been carried out using polycarboxylate ligands with characteristics of both flexibility and rigidity (Jiang *et al.*, 2009; Harbuzaru *et al.*, 2008; Cen *et al.*, 2009). Likewise, in contrast with the well investigated transition and lanthanide metal systems, only a few alkaline earth coordination polymers have been studied. Until recently, the study of alkaline earth metal carboxylates has been an underdeveloped area (Murugavel *et al.*, 2001; Zhu *et al.*, 2005; Cote & Shimizu, 2003; Yang, *et al.*, 2006).

Our interest is the coordination chemistry of semi-rigid polycarboxylate ligands created by introducing $-\text{OCH}_2-$, $-\text{NCH}_2-$ or $-\text{NHCO}_2-$ groups between the aromatic ring and the carboxylate groups; examples are benzene-1,3,5-tri(carboxymethyl), N,N',N'' -1,3,5-triazine-2,4,6-triyltris(glycine) and N,N',N'' -1,3,5-benzenetricarboxamide. Systematic investigation of the traditional coordination chemistry of these ligands has been carried out (Wang *et al.*, 2006, 2007; Sun *et al.*, 2007). Compared with the corresponding rigid benzenedicarboxylate ligands, the additional $-\text{XCH}_2-$ ($X = \text{O}, \text{N}$) groups make the ligands more flexible, and the X atoms may also function as electron donors or acceptors of interesting hydrogen bonds. As a continuation of our work on alkaline earth coordination chemistry, we report here the structure of poly[[triqua{ μ_4 -2-[4,6-bis(carboxymethylsulfanyl)-1,3,5-triazin-2-ylsulfanyl]acetato}{ μ_2 -2-[4,6-bis(carboxymethylsulfanyl)-1,3,5-triazin-2-ylsulfanyl]acetato}barium(II)] monohydrate], (I), a novel (4,6)-connected double-layered Ba^{II} coordination polymer, formed through the reaction of 2,2',2''-[1,3,5-triazine-2,4,6-triyltris(sulfanediyl)]triacetic acid (H_3TTTA) with BaCl_2 in the presence of pyridine.



Single-crystal X-ray diffraction reveals that (I) is a two-dimensional coordination polymer. As shown in Fig. 1, the asymmetric unit is composed of one crystallographically independent Ba^{II} ion, two H_2TTTA^- anionic ligands, three coordinated water molecules and one solvent water molecule. Each Ba^{II} centre is nine-coordinated by six O atoms from different carboxylate groups of four discrete H_2TTTA^- anion ligands and three O atoms from water molecules. The whole geometry around the centre is distorted, forming neither a tricapped antiprism nor a monocapped square antiprism. The Ba–O bond distances range from 2.706 (2) to 2.951 (2) Å (Table 1), within the range of those observed for other barium

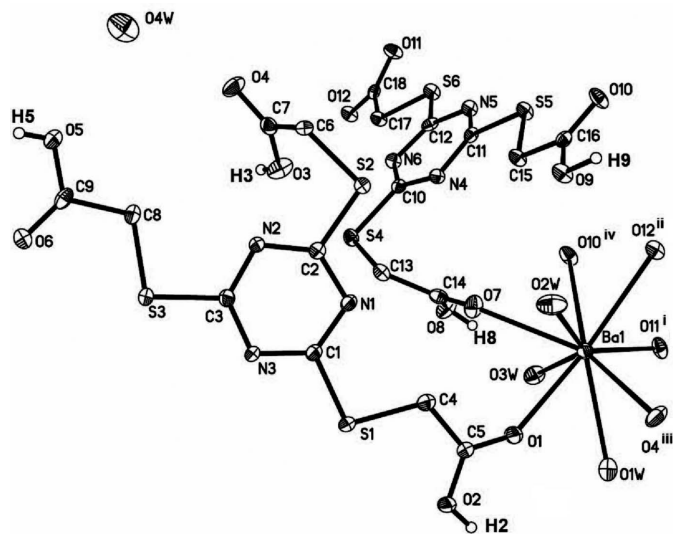


Figure 1
The local coordination environment for the Ba^{II} centres in (I). Only those H atoms on carboxylic acid groups are shown, for clarity. Displacement ellipsoids are drawn at the 30% probability level. Atoms H3, H8 and H9 are fully occupied, while H2 and H5 are half-occupied (see Table 1 and text). [Symmetry codes: (i) $-1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$; (ii) $-1 + x, y, -1 + z$; (iii) $-1 + x, y, z$; (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$.]

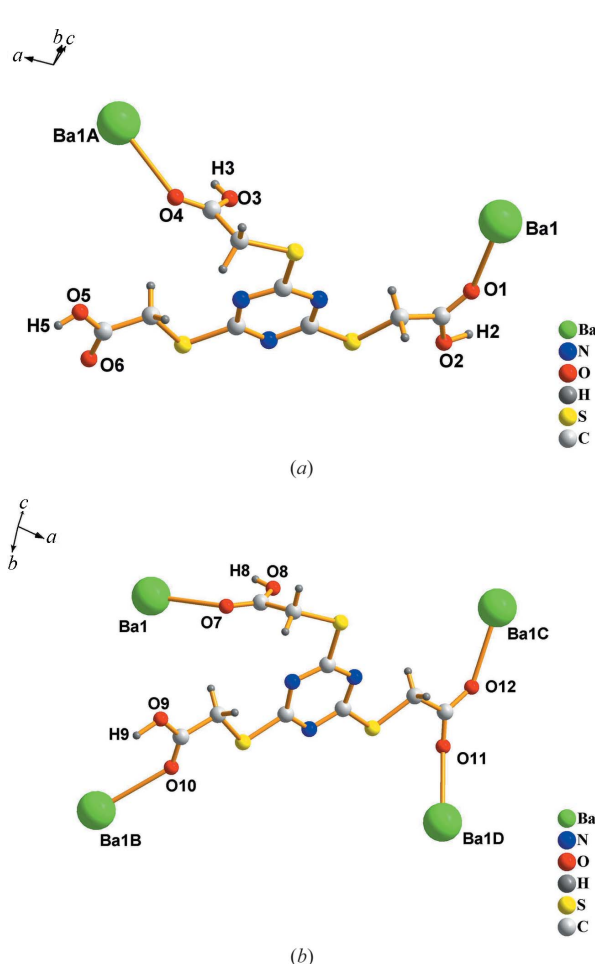


Figure 2
The coordination modes of the H₂TTTA⁻ ligand in complex (I), viz. (a) mode *a*, $\mu_2\text{-}\eta^1:\eta^1$, and (b) mode *b*, $\mu_4\text{-}\eta^1:\eta^1:\eta^2$. [Symmetry codes: (A) $1 + x, y, z$; (B) $x, \frac{1}{2} - y, -\frac{1}{2} + z$; (C) $1 + x, y, 1 + z$; (D) $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$.]

carboxylate complexes (Zhu *et al.*, 2005). The H atoms on atoms O2 and O5 are half-occupied because these hydroxy groups lie close to their symmetry-related counterparts across centres of inversion, which would result in impossibly short H...H distances if the H-atom sites were fully occupied. Thus, these H atoms are effectively disordered across the hydrogen bond between the adjacent carboxylate groups (Table 2). This arrangement is also consistent with the requirement for charge balance of the total structure. The incompletely deprotonated ligands adopt two different coordination geometries: $\mu_2\text{-}\eta^1:\eta^1$ (mode *a*) and $\mu_4\text{-}\eta^1:\eta^1:\eta^2$ (mode *b*) (Fig. 2). The three flexible arms of the ligand show significant deviation in their bending to the different sides of the central triazine ring. In mode *a*, the dihedral angles between the three carboxylic acid groups and the central triazine ring are 15.0 (4) (for the O1/O2 group), 70.5 (4) (O3/O4) and 8.4 (4)° (O5/O6), respectively. In mode *b*, the carboxylate group coordinated in a bidentate conformation (O11/O12) forms a dihedral angle of 18.7 (4)° with the triazine ring, while the two monodentate carboxylic groups make dihedral angles of 74.3 (4) (O7/O8) and 5.7 (5)° (O9/O10). Consequently, the tricarboxylate ligands act as both μ_2 - and μ_4 -bridges, connecting the alkaline earth metal centres.

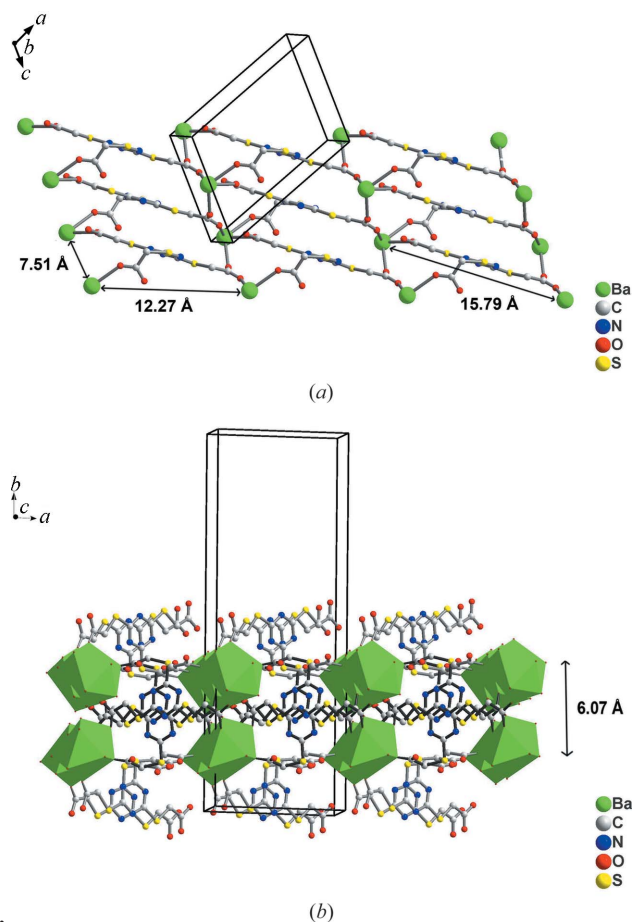
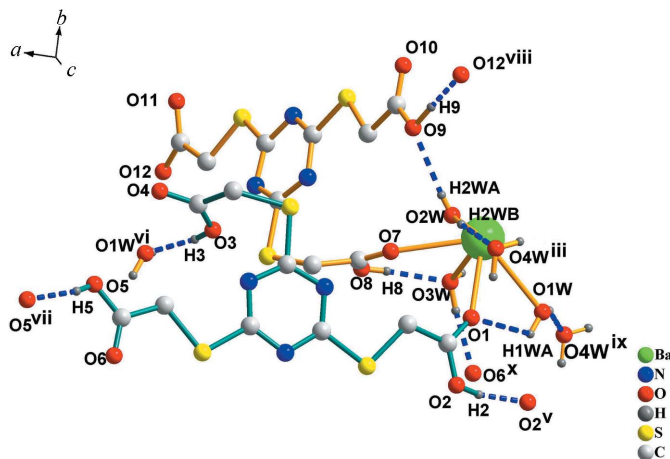
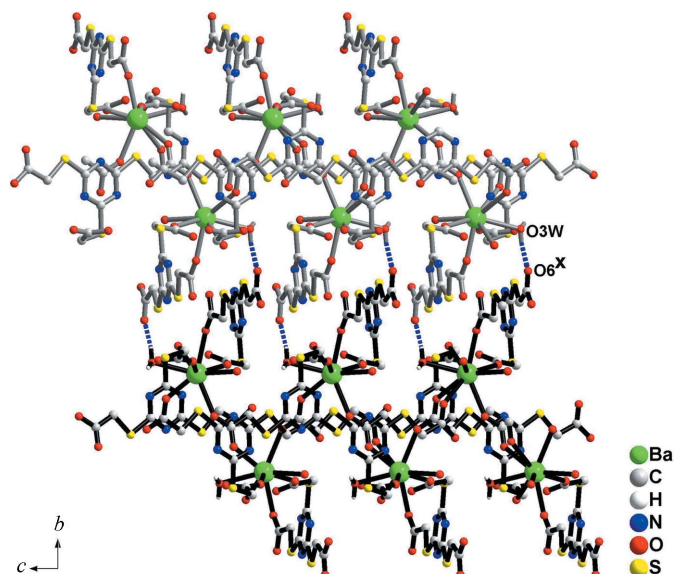


Figure 3
(a) A view of the two-dimensional layer constructed by the Ba^{II} centres and ligands in mode *b*. (b) A view of the two-dimensional double-layered structure of (I) in the *ac* plane. The polyhedral representation indicates the coordination environment of Ba^{II} centres. The bonds of the ligands in modes *a* and *b* are represented in grey and black, respectively.

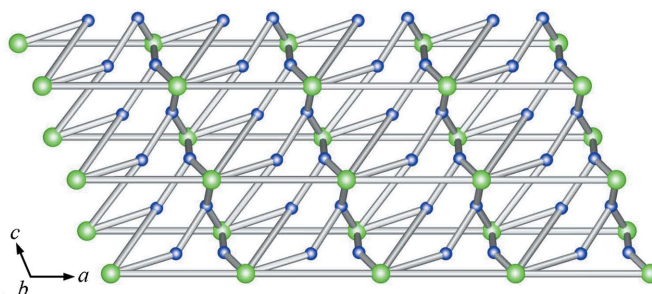

Figure 4

The hydrogen-bonding interactions in (I), shown as dashed lines; see Table 2 for full details. [Symmetry codes: (iii) $-1 + x, y, z$; (v) $-x, -y, 2 - z$; (vi) $1 + x, y, z$; (vii) $2 - x, -y, 1 - z$; (viii) $-1 + x, \frac{1}{2} - y, -\frac{3}{2} + z$; (ix) $-1 + x, y, 1 + z$; (x) $1 - x, -y, 2 - z$.]


Figure 5

A perspective view of the three-dimensional supramolecular structure of (I), showing the hydrogen-bonding interactions (dashed lines) between two adjacent layers. [Symmetry code: (x) $1 - x, -y, 2 - z$.]

The bidentate carboxylate groups in mode *b* bridge the Ba centres in a *syn-anti* conformation to form one-dimensional $\{\text{Ba}(\text{OCO})\}_n$ chains along the *c* axis. These chains are further connected by other monodentate carboxylate groups across the ligands, forming an infinite two-dimensional layer in the *ac* plane (Fig. 3*a*). The $\text{Ba} \cdots \text{Ba}$ distances, separated by the carboxylate group and across the ligand, are 7.51 (8) [Ba1 \cdots Ba1($x, \frac{1}{2} - y, -\frac{1}{2} + z$)], 12.27 (1) [Ba1 \cdots Ba1($1 + x, y, 1 + z$)] and 15.79 (5) Å [Ba1 \cdots Ba1($1 + x, \frac{1}{2} - y, \frac{3}{2} + z$)]. The H_2TTTA^- anion ligands in mode *a* are situated above and below the layer through the μ_2 -bridging carboxylate ligands. As a result, a novel double-layered structure in the *ac* plane is formed, with a mean thickness of *ca* 6.07 (8) Å along the *b* axis based on the metal centres (Fig. 3*b*). Due to the presence of the carboxylic acid groups, many hydrogen-bonding inter-


Figure 6

A topological representation of the (4,6)-connected structure of (I). Six- (the metal centres) and four-connected nodes (the tricarboxylates) are represented by the large and small balls, respectively.

actions are observed within the layer (Fig. 4 and Table 2). We note the less usual dimensions found for the interactions involving the half-occupied atoms H2 and H5 (entries 1 and 3 in Table 2). These double layers are held together further by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds between the coordinated aqua atom O3W and carboxylic acid atom O6 from a neighbouring ligand, resulting in a three-dimensional supramolecular structure (Fig. 5).

In order to identify further the connectivity between the ligands and the metal centres, a representation of one double layer is illustrated in Fig. 6. Topologically, the triazine ligands in modes *a* and *b* can be viewed as a linear linker and a planar four-connected node, respectively. The alkaline earth metal centre binds to two linear linkers and connects four four-connected nodes, which can then be considered as an irregular six-connected node. As a result, the whole topology of (I) is a novel binodal (4,6)-connected net with a Schläfli symbol of $(4^4 5^5 6^5 7)(4^4 5 6)$ (Wells, 1975). The long symbols for the two nodes are 4.4.4.4.5(2).5(3).5(3).5.5.6(3).6(2).6(3).6(2) and 4.4.4.4.5(4).6(2), respectively. To the best of our knowledge, topologies with (4,6)-connectivity are extremely rare (Li *et al.*, 2008; Lou *et al.*, 2009), and the net in this complex may represent the first example in alkaline earth coordination chemistry.

Experimental

$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.026 g, 0.1 mmol) and 2,2',2''-[1,3,5-triazine-2,4,6-triyl-tris(sulfanediyl)]triacetic acid (0.069 g, 0.2 mmol) were dissolved in a solution of water and pyridine (5 ml/0.10 ml) at room temperature, and colourless crystals of (I) were formed in 67% yield after several days. Elemental analysis calculated for $\text{C}_{18}\text{H}_{24}\text{BaN}_6\text{O}_{16}\text{S}_6$: C 23.75, H 2.66, N 9.23%; found: C 23.61, H 2.63, N 9.28%. FT-IR (KBr pellet, ν , cm^{-1}): 3425 (*br*), 1626 (*m*), 1480 (*s*), 1388 (*m*), 1268 (*m*), 1235 (*w*), 1119 (*w*), 1051 (*w*), 905 (*w*), 848 (*w*), 787 (*w*).

Crystal data

$[\text{Ba}(\text{C}_9\text{H}_8\text{N}_3\text{O}_6\text{S}_3)_2(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$	$V = 3134.3$ (7) Å ³
$M_r = 910.13$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 12.0121$ (15) Å	$\mu = 1.75$ mm ⁻¹
$b = 31.327$ (4) Å	$T = 298$ K
$c = 8.8522$ (11) Å	$0.27 \times 0.26 \times 0.25$ mm
$\beta = 109.794$ (2)°	

Table 1

Selected geometric parameters (Å, °).

Ba1—O1	2.706 (2)	Ba1—O4 ⁱⁱⁱ	2.875 (2)
Ba1—O2W	2.738 (4)	Ba1—O3W	2.893 (3)
Ba1—O7	2.784 (2)	Ba1—O1W	2.931 (3)
Ba1—O11 ⁱ	2.799 (3)	Ba1—O10 ^{iv}	2.951 (2)
Ba1—O12 ⁱⁱ	2.857 (2)		
O7—Ba1—O11 ⁱ	124.26 (7)	O4 ⁱⁱⁱ —Ba1—O3W	136.68 (8)
O1—Ba1—O12 ⁱⁱ	145.36 (8)	O2W—Ba1—O1W	129.50 (8)
O7—Ba1—O4 ⁱⁱⁱ	134.61 (7)	O4 ⁱⁱⁱ —Ba1—O10 ^{iv}	150.98 (7)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 ^v ··O2 ^v	0.82 (1)	1.69 (2)	2.491 (5)	165 (9)
O3—H3 ^v ··O1W ^{vi}	0.79 (4)	1.85 (4)	2.634 (4)	168 (5)
O5—H5 ^v ··O5 ^{vii}	0.75 (7)	1.73 (7)	2.467 (5)	166 (12)
O8—H8 ^v ··O3W	0.78 (4)	1.96 (4)	2.735 (4)	172 (4)
O9—H9 ^v ··O12 ^{viii}	0.83 (1)	1.68 (1)	2.511 (3)	174 (4)
O1W—H1WA··O1	0.80 (4)	2.54 (4)	2.949 (4)	113 (4)
O1W—H1WB··O4W ^{ix}	0.82 (4)	2.09 (4)	2.864 (5)	157 (4)
O2W—H2WA··O9	0.67 (4)	2.22 (4)	2.886 (4)	177 (6)
O2W—H2WB··O4W ⁱⁱⁱ	0.80 (4)	2.00 (4)	2.784 (5)	169 (5)
O3W—H3WA··O6 ^x	0.88 (4)	1.94 (4)	2.813 (4)	171 (4)
O4W—H4WA··O5	0.82 (1)	2.01 (1)	2.822 (4)	172 (6)

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

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.650, T_{\max} = 0.669$
15959 measured reflections
6052 independent reflections
4342 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.062$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.052$
 $S = 0.84$
6052 reflections
499 parameters
4 restraints
H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.58 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.56 \text{ e } \text{Å}^{-3}$

All H atoms were initially placed in positions derived from difference Fourier maps and then their positions were refined. For the balance of the total charge of the compound, half-occupancies were assigned to atoms H2 and H5; a high correlation (0.99) is noted for the x and z coordinates of H2. The H atoms on O4W, O2 and O9 were restrained, with $O-H = 0.82 (1) \text{ Å}$. All H atoms bound to O atoms were refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$, and all C-bound H atoms were refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2000); cell refinement: SMART; data reduction: SAINT (Bruker, 2000); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics:

SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3159). Services for accessing these data are described at the back of the journal.

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