

A new decavanadate with a tricobalt(II) cation and 18-crown-6, tris{hexaaquacobalt(II)} decavanadate bis(18-crown-6) decahydrate

Uk Lee,^{a*} Yeon-Hwa Jung,^a
Hea-Chung Joo^a and Ki-Min
Park^b

^aDepartment of Chemistry, Pukyong National University, 599-1 Daeyeon-3dong Nam-ku, Pusan 608-737, South Korea, and ^bResearch Institute of Natural Sciences, Gyeongsang National University, Chinju 660-701, South Korea

Correspondence e-mail: uklee@mail.pknu.ac.kr

Key indicators

Single-crystal X-ray study

$T = 298\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$

H-atom completeness 93%

Disorder in solvent or counterion

R factor = 0.042

wR factor = 0.108

Data-to-parameter ratio = 17.5

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, $[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]_3[\text{V}_{10}\text{O}_{28}] \cdot (18\text{-Crown-6})_2 \cdot 10\text{H}_2\text{O}$, was obtained by mixing 18-crown-6 with $\text{K}_2[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]_2[\text{V}_{10}\text{O}_{28}] \cdot 4\text{H}_2\text{O}$. The centrosymmetric $[\text{V}_{10}\text{O}_{28}]^{6-}$ polyanion forms a three-dimensional network *via* $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds with water molecules. The $\text{V} \cdots \text{V}$ distances are in the range 3.068 (1)–3.266 (1) Å; the four types of $\text{V}-\text{O}$ bond lengths are in the ranges 1.599 (3)–1.611 (2) (*Ot*), 1.923 (2)–2.030 (2) (*Oc*), 1.668 (2)–2.110 (3) (*Ob*) and 2.062 (2)–2.365 (2) Å (*Oh*). The number of Co^{2+} cations in the structure could be controlled by the neutral, bulky 18-crown-6 ether. All of the six O atoms in the 18-crown-6 form hydrogen bonds with water molecules.

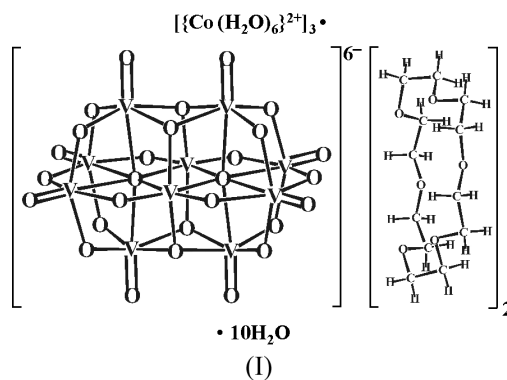
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Comment

Bulky adducts of crown-ethers are sometimes found in polyoxometalates *e.g.* (18-crown-6.K)₂.K[H₆CoMo₆O₂₄].12H₂O (Nagano & Lee, 1990), [Na(dibenzo-18-crown-6)(MeCN)]₃. [PMo₁₂O₄₀] (You *et al.*, 2001), (18-crown-6)[H₃PMo₁₂O₄₀].22H₂O (You, Wang, He *et al.*, 2000), H₃PW₁₂O₄₀(benzo-15-crown-5)₆.16H₂O (You, Wang, Zhang *et al.*, 2000), and [(H₃O)⁺(dibenzo-18-crown-6)]₂[HPMo₁₂O₄₀].(dibenzo-18-crown-6).(CH₃CN)₃.H₂O (You *et al.*, 2002).



Since the decavanadate anion, $[\text{V}_{10}\text{O}_{28}]^{6-}$, was reported by Evans (1966), the crystal structures of many of its salts have been characterized *e.g.* alkali metals (Durif *et al.*, 1980; Rigotti *et al.*, 1987), alkaline earth metals (Swallow *et al.*, 1966; Nieto *et al.*, 1993; Kamenar *et al.*, 1996; Strukan *et al.*, 1999), lanthanides (Saf'yanov & Belov, 1976; Saf'yanov *et al.*, 1978; Rivero *et al.*, 1984, 1985; Naruke *et al.*, 1999; Peng *et al.*, 2002), ammonium (Eglmeier *et al.*, 1993) and double salts (Avtamonova *et al.*, 1990; Crans *et al.*, 1994; Fratzky *et al.*, 2000). The double salts of transition elements and alkali metals or ammonium ions *e.g.* $\text{K}_2[\text{Zn}^{\text{II}}(\text{H}_2\text{O})_6]_2[\text{V}_{10}\text{O}_{28}] \cdot 4\text{H}_2\text{O}$ (Evans,

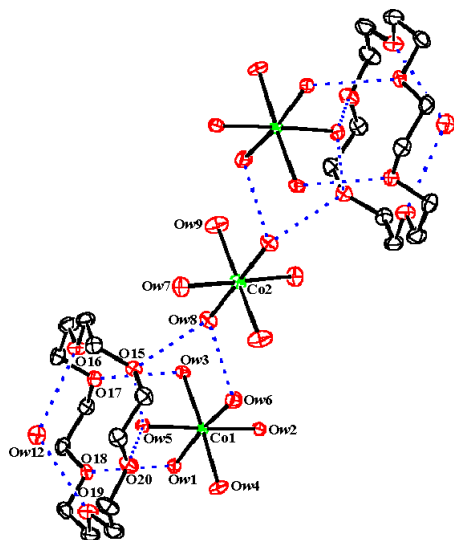


Figure 1
Hydrogen-bonding interactions between the 18-crown-6 and water molecules. Probable $O_{\text{water}} \cdots O$ hydrogen bonds are shown as broken blue lines. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

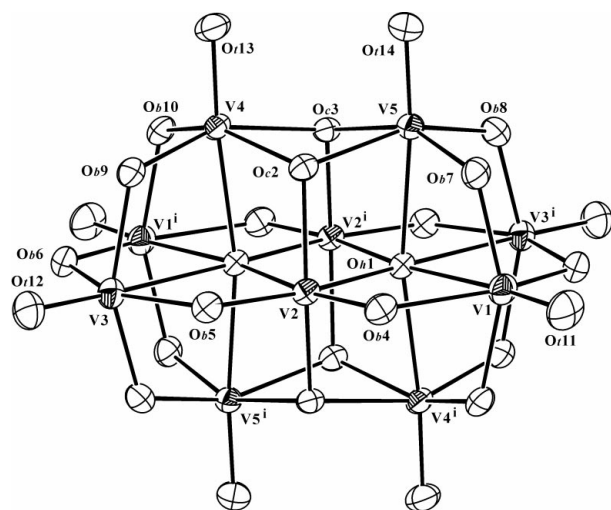


Figure 2
The polyanion structure in (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

1966), $[\text{Na}(\text{H}_2\text{O})_3]_2[\text{Ni}^{\text{II}}(\text{H}_2\text{O})_2]_2 \cdot [\text{V}_{10}\text{O}_{28}] \cdot 4\text{H}_2\text{O}$ (Higami *et al.*, 2002), $(\text{NH}_4)_4[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6][[\text{V}_{10}\text{O}_{28}] \cdot 4\text{H}_2\text{O}$ (Nowogrocki *et al.*, 1997), $\text{Na}_4[\text{Ni}^{\text{II}}(\text{H}_2\text{O})_6][[\text{V}_{10}\text{O}_{28}] \cdot 17\text{H}_2\text{O}$ (Sun *et al.*, 2002) and $\text{K}_2[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]_2[\text{V}_{10}\text{O}_{28}] \cdot 4\text{H}_2\text{O}$ (Lee *et al.*, 2003) have also been reported.

A structure of an $[\text{M}^{\text{II}}(\text{H}_2\text{O})_6]_3[\text{V}_{10}\text{O}_{28}]$ (where M is a transition element) salt has not yet been reported. We were able to prepare this type of salt by introducing 18-crown-6 into a decavanadate crystal system. The number of Co^{2+} cations in the decavanadate could be controlled by the neutral bulky 18-crown-6 ether. We report here the structure of $[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]_3[\text{V}_{10}\text{O}_{28}] \cdot (18\text{-crown-6})_2 \cdot 10\text{H}_2\text{O}$, (I), which was prepared by mixing 18-crown-6 with $\text{K}_2[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]_2 \cdot [\text{V}_{10}\text{O}_{28}] \cdot 4\text{H}_2\text{O}$ (Lee *et al.*, 2003). The role of the 18-crown-6 appears to be important in the crystal packing of (I).

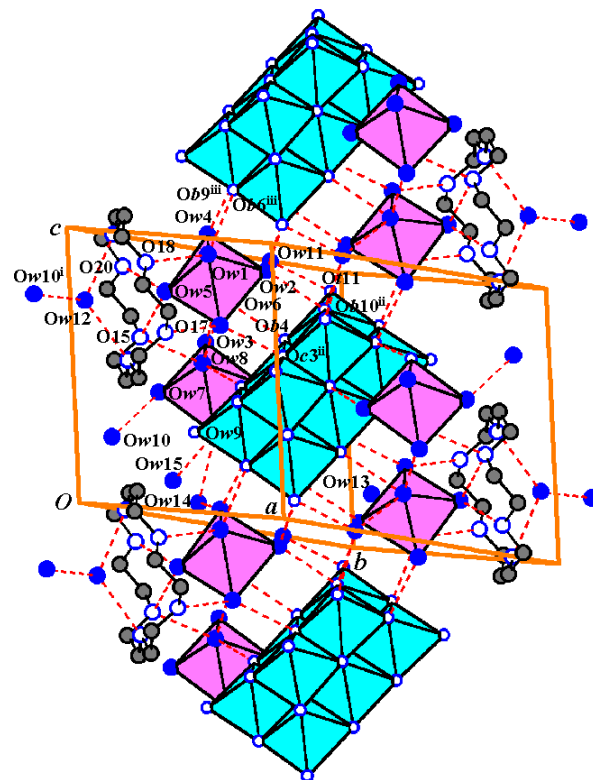


Figure 3
The crystal packing of (I) in the unit cell, shown as polyhedral model. The purple octahedron is $[\text{Co}(\text{H}_2\text{O})]^{2+}$. Probable $O_{\text{water}} \cdots O$ hydrogen bonds are shown as red broken lines. [Symmetry code: (i) $-x, -y, 1 - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $x, y, 1 + z$.]

Fig. 1 shows the hydrogen-bonding interactions of 18-crown-6 with the water molecules in (I). The $O_{\text{water}} - \text{H} \cdots O_{\text{crown ether}}$ hydrogen-bonding interactions with five water molecules involve all of the six O atoms in the 18-crown-6 ether. These distances are in the range 2.764 (4)–3.002 (4) Å. Because of the asymmetric hydrogen bonding, the six-membered O-atom ring in the 18-crown-6 does not form a planar hexagon. The dihedral angles formed by the $\text{O15} \cdots \text{O17} \cdots \text{O18} \cdots \text{O20}$ quadrilateral and $\text{O15} \cdots \text{O16} \cdots \text{O17}$ and $\text{O18} \cdots \text{O19} \cdots \text{O20}$ triangles are 60.2 (1) and 21.1 (2)°, respectively, and the ring is in a boat conformation.

The configuration of the $[\text{V}_{10}\text{O}_{28}]^{6-}$ in (I) is shown in Fig. 2. The centrosymmetric polyanion consists of five independent (VO_6) octahedra, sharing edges, and has approximate D_{2h} symmetry. The labeling of the O atoms in the polyanion is the same as the labeling in the previous structure (Lee *et al.*, 2003). The $\text{V} \cdots \text{V}$ distances are in the range 3.068 (1)–3.266 (1) Å; the four types of V–O bond lengths are in the ranges 1.599 (3)–1.611 (2) (Ot), 1.923 (2)–2.030 (2) (Oc), 1.668 (2)–2.110 (3) (Ob) and 2.062 (2)–2.365 (2) Å (Oh). The bond lengths and angles of the $[\text{V}_{10}\text{O}_{28}]^{6-}$ show a similar trend to those found in the literature. The framework of $[\text{V}_{10}\text{O}_{28}]^{6-}$ has been studied in detail previously (Evans, 1966; Nowogrocki *et al.*, 1997).

Fig. 3 shows the crystal packing in (I), with the hydrogen-bonding interactions. The $[\text{V}_{10}\text{O}_{28}]^{6-}$ polyanion is surrounded by $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ cations, water molecules and 18-crown-6

ethers, forming hydrogen bonds between them. Decavanadate-[Co(H₂O)₆]²⁺ layers are separated by layers formed by 18-crown-6 molecules. These layers are further linked to each other by O—H···O hydrogen bonds, as shown in Fig. 1. All of the O atoms in the polyanion except *Oh*1, *Ob*6, *Ob*8, *Or*12 and *Or*14 form strong O_{water}···O_{polyanion} hydrogen bonds with the coordinated water of [Co(II)(H₂O)₆]²⁺ and uncoordinated water molecules. In total, the formula unit contains 28 water molecules, of which 18 are coordinated to the three Co²⁺ ions, forming octahedra. The remaining water molecules fill the space in the unit cell, forming a network of hydrogen bonds. *Ow*14 and *Ow*15 were refined by reducing their site occupancies to 0.5, indicating one complete atom disordered over two sites within the structure. The distance *Ow*13···*Or*14ⁱⁱ [symmetry code: (ii) $-x, 1-y, 1-z$] is 3.080 (5) Å, but no suitable hydrogen bonds could be confirmed, because H atom positions for *Ow*13 could not be determined.

There are one and half crystallographically independent Co²⁺ ions in the asymmetric unit; Co2 lies on an inversion center in the space group $P\bar{1}$. The Co²⁺ ions are surrounded by six coordinated water molecules in the form of an irregular octahedron, with distances in the range 2.062 (3)–2.125 (3) Å. The probable O—H···O hydrogen-bond distances, less than 3.1 Å in (I), involving water are given in Table 2.

Experimental

Pale blue–brown crystals of the title compound were obtained by concentration of a solution of a stoichiometric mixture of 18-crown-6 and K₂[Co^{II}(H₂O)₆]₂[V₁₀O₂₈] (Lee *et al.*, 2003).

Crystal data

[Co(H ₂ O) ₆] ₃ [V ₁₀ O ₂₈] (C ₁₂ H ₂₄ O ₆) ₂ ·10H ₂ O	$Z = 1$
$M_r = 2167.26$	$D_x = 1.940 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 12.285$ (4) Å	Cell parameters from 26 reflections
$b = 13.924$ (3) Å	$\theta = 9.6$ – 10.5°
$c = 11.120$ (3) Å	$\mu = 1.97 \text{ mm}^{-1}$
$\alpha = 101.33$ (3) $^\circ$	$T = 298$ (2) K
$\beta = 92.63$ (2) $^\circ$	Plate, pale blue–brown
$\gamma = 84.26$ (2) $^\circ$	$0.38 \times 0.25 \times 0.13 \text{ mm}$
$V = 1855.1$ (9) Å ³	

Data collection

Stoe Stadi-4 diffractometer	$\theta_{\text{max}} = 27.5^\circ$
$\omega/2\theta$ scans	$h = -15 \rightarrow 15$
Absorption correction: numerical (X-SHAPE; Stoe & Cie, 1996)	$k = -18 \rightarrow 17$
$T_{\text{min}} = 0.608$, $T_{\text{max}} = 0.812$	$l = 0 \rightarrow 14$
8466 measured reflections	3 standard reflections
8466 independent reflections	frequency: 60 min
6530 reflections with $I > 2\sigma(I)$	intensity decay: 3.5%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 2.3315P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.108$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.54 \text{ e } \text{Å}^{-3}$
8466 reflections	$\Delta\rho_{\text{min}} = -0.48 \text{ e } \text{Å}^{-3}$
484 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (Å).

V1— <i>Oh</i> 1	2.292 (2)	V5— <i>Oc</i> 2	1.997 (2)
V1— <i>Ob</i> 4	2.110 (3)	V5— <i>Oc</i> 3	2.001 (2)
V1— <i>Ob</i> 6 ⁱ	1.803 (3)	V5— <i>Ob</i> 7	1.822 (2)
V1— <i>Ob</i> 7	1.868 (2)	V5— <i>Ob</i> 8	1.848 (3)
V1— <i>Ob</i> 10 ⁱ	1.904 (2)	V5— <i>Or</i> 14	1.604 (3)
V1— <i>Or</i> 11	1.609 (3)	O15—C1	1.425 (5)
V2— <i>Oh</i> 1 ⁱ	2.154 (2)	O16—C2	1.425 (5)
V2— <i>Oh</i> 1	2.062 (2)	O16—C3	1.437 (5)
V2— <i>Oc</i> 2	1.944 (2)	O17—C4	1.421 (5)
V2— <i>Oc</i> 3 ⁱ	1.923 (2)	O17—C5	1.429 (5)
V2— <i>Ob</i> 4	1.668 (2)	O18—C6	1.423 (5)
V2— <i>Ob</i> 5	1.723 (2)	O18—C7	1.422 (5)
V3— <i>Oh</i> 1 ⁱ	2.365 (2)	O19—C8	1.429 (6)
V3— <i>Ob</i> 5	2.002 (2)	O19—C9	1.420 (6)
V3— <i>Ob</i> 6	1.876 (3)	O20—C10	1.429 (5)
V3— <i>Ob</i> 8 ⁱ	1.823 (3)	O20—C11	1.437 (6)
V3— <i>Ob</i> 9	1.946 (2)	O15—C12	1.439 (5)
V3— <i>Or</i> 12	1.599 (3)	C1—C2	1.495 (6)
V4— <i>Oh</i> 1 ⁱ	2.246 (2)	C3—C4	1.497 (7)
V4— <i>Oc</i> 2	2.008 (2)	C5—C6	1.500 (6)
V4— <i>Oc</i> 3	2.030 (2)	C7—C8	1.491 (7)
V4— <i>Ob</i> 9	1.817 (2)	C9—C10	1.504 (8)
V4— <i>Ob</i> 10	1.833 (2)	C11—C12	1.501 (6)
V4— <i>Or</i> 13	1.611 (2)	<i>Ow</i> 13— <i>Or</i> 14 ⁱⁱ	3.080 (5)
V5— <i>Oh</i> 1	2.273 (2)		

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

Table 2

Hydrogen-bonding geometry (Å, $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
<i>Ow</i> 1—H21 <i>a</i> ··· <i>O</i> 18	0.84	1.94	2.764 (4)	165
<i>Ow</i> 1—H21 <i>b</i> ··· <i>Ob</i> 6 ⁱⁱⁱ	0.93	1.86	2.786 (4)	172
<i>Ow</i> 1—H21 <i>a</i> ··· <i>Ow</i> 5	0.84	2.83	2.912 (4)	87
<i>Ow</i> 2—H22 <i>b</i> ··· <i>Ob</i> 10 ⁱⁱⁱ	0.88	1.86	2.719 (4)	167
<i>Ow</i> 2—H22 <i>a</i> ··· <i>Ob</i> 10 ⁱ	0.94	1.88	2.817 (4)	179
<i>Ow</i> 3—H23 <i>a</i> ··· <i>Oc</i> 3 ⁱ	0.79	2.04	2.813 (4)	165
<i>Ow</i> 3—H23 <i>b</i> ··· <i>O</i> 17	0.85	2.06	2.853 (4)	157
<i>Ow</i> 4—H24 <i>b</i> ··· <i>Ob</i> 9 ⁱⁱⁱ	0.75	1.98	2.727 (4)	173
<i>Ow</i> 4—H24 <i>a</i> ··· <i>Ow</i> 14 ⁱⁱⁱ	0.90	1.93	2.747 (8)	150
<i>Ow</i> 5—H25 <i>a</i> ··· <i>O</i> 20	0.83	1.95	2.771 (4)	176
<i>Ow</i> 5—H25 <i>a</i> ··· <i>O</i> 15	0.83	2.73	3.002 (4)	101
<i>Ow</i> 6—H26 <i>b</i> ··· <i>Ow</i> 11	0.87	1.96	2.788 (5)	159
<i>Ow</i> 6—H26 <i>a</i> ··· <i>Ow</i> 8	0.79	2.17	2.868 (4)	148
<i>Ow</i> 6—H26 <i>a</i> ··· <i>Ob</i> 4	0.79	2.67	3.048 (4)	112
<i>Ow</i> 7—H27 <i>a</i> ··· <i>Oc</i> 2 ⁱⁱ	0.75	2.02	2.766 (4)	172
<i>Ow</i> 7—H27 <i>b</i> ··· <i>Ow</i> 10	0.94	2.00	2.785 (5)	140
<i>Ow</i> 7—H27 <i>b</i> ··· <i>Ow</i> 9	0.94	2.73	3.028 (4)	99
<i>Ow</i> 7—H27 <i>b</i> ··· <i>Ow</i> 9	0.94	2.73	3.028 (4)	99
<i>Ow</i> 8—H28 <i>a</i> ··· <i>Ob</i> 5	1.03	1.73	2.686 (4)	153
<i>Ow</i> 8—H28 <i>b</i> ··· <i>O</i> 15	0.88	1.94	2.807 (4)	168
<i>Ow</i> 9—H29 <i>a</i> ··· <i>Ow</i> 15	0.96	1.74	2.557 (9)	140
<i>Ow</i> 9—H29 <i>a</i> ··· <i>Ow</i> 14	0.96	2.48	2.917 (9)	108
<i>Ow</i> 9—H29 <i>b</i> ··· <i>Ob</i> 9	0.95	1.94	2.780 (4)	145
<i>Ow</i> 10—H30 <i>a</i> ··· <i>Ob</i> 7 ⁱⁱ	0.83	1.94	2.757 (4)	169
<i>Ow</i> 10—H30 <i>b</i> ··· <i>Ow</i> 12 ^{iv}	0.88	1.98	2.850 (5)	170
<i>Ow</i> 11—H31 <i>a</i> ··· <i>Ow</i> 15 ⁱⁱ	0.88	2.64	2.75 (1)	88
<i>Ow</i> 11—H31 <i>a</i> ··· <i>Ow</i> 14 ⁱⁱ	0.88	2.22	2.744 (9)	118
<i>Ow</i> 11—H31 <i>b</i> ··· <i>Or</i> 11	0.83	2.03	2.790 (5)	151
<i>Ow</i> 12—H32 <i>b</i> ··· <i>O</i> 19	0.81	2.11	2.895 (5)	163
<i>Ow</i> 12—H32 <i>a</i> ··· <i>O</i> 16	0.82	2.20	2.999 (5)	165

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

During the refinement process, sensible displacement parameters of *Ow*14 and *Ow*15 were obtained by reducing the occupancy of these atoms to 0.5 (O···O distance is 1.40 Å). The H atoms of the *Ow*13, *Ow*14 and *Ow*15 water molecules could not be located from electron-

density maps. These H atoms were not included in the calculations (although they are included in the empirical formula). All H atoms bonded to C atoms were included in the structure-factor calculation at idealized positions, and were allowed to ride on their parent atoms with relative isotropic displacement parameters $\{U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})\}$. The H atoms of the water atoms (except for those of Ow13, Ow14 and Ow15) were located in difference electron-density maps, refined using a riding model with the application of loose O–H bond-length restraints, and also refined isotropically $[U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})]$. This treatment gave O–H distances ranging from 0.75 to 1.03 Å. Anisotropic displacement parameters were used for all non-H atoms. The highest peak in the difference map is 1.09 Å from Ow14, and the deepest hole is 0.35 Å from H29a.

Data collection: *Stadi4* (Stoe & Cie, 1996); cell refinement: *Stadi4*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

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