Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A dihydroxidotetracopper(II) framework supported by 4,4′-(adamantane-1,3-diyl)bis(1,2,4-triazole) and benzene-1,3,5-tricarboxylate bridges

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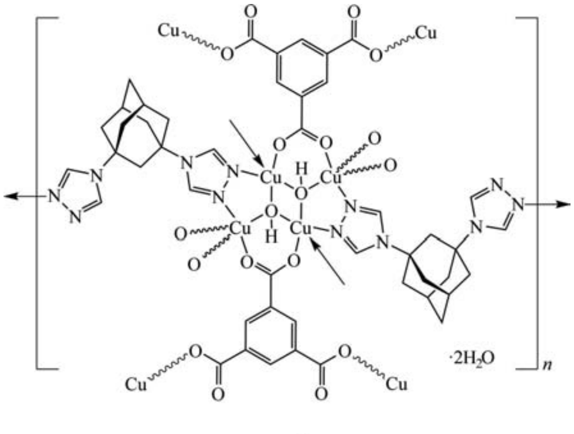
Received 27 May 2008
Accepted 30 May 2008
Online 7 June 2008

The new bifunctional ligand 4,4′-(adamantane-1,3-diyl)bis(1,2,4-triazole) (tr$_2$ad) and benzene-1,3,5-tricarboxylate sustain complementary coordination bridging for the three-dimensional framework of poly[[bis[μ_3-4,4′-(adamantane-1,3-diyl)bis(1,2,4-triazole)-$\kappa^3 N^1$:N^2:$N^{1'}$]bis(μ_4-benzene-1,3,5-tricarboxylato-$\kappa^4 O^1$:$O^{1'}$:O^3:O^5)di-μ_3-hydroxido-$\kappa^6 O$:O:O-tetracopper(II)] dihydrate], $\{[\mathrm{Cu}_4(\mathrm{C}_9\mathrm{H}_3\mathrm{O}_6)_2(\mathrm{OH})_2(\mathrm{C}_{14}\mathrm{H}_{18}\mathrm{N}_6)_2]\cdot 2\mathrm{H}_2\mathrm{O}\}_n$. The net node is a centrosymmetric (μ_3-OH)$_2$Cu$_4$ cluster [Cu—O = 1.9525 (14)–2.0770 (15) Å and Cu···Cu = 3.0536 (5) Å] involving two independent copper ions in tetragonal pyramidal CuO$_4$N and trigonal bipyramidal CuO$_3$N$_2$ environments. One carboxylate group of the anion is bridging and the other two are monodentate, leading to the connection of three hydroxide clusters and the generation of neutral coordination layers separated by 9.3583 (5) Å. The interlayer linkage is effected by μ_3-tr$_2$ad ligands, with one triazole group N^1:N^2-bridging and the second monodentate [Cu—N = 1.9893 (19), 2.010 (2) and 2.411 (2) Å]. In total, the hydroxide clusters are linked to six close neighbors within the carboxylate layer and to four neighbors *via* tr$_2$ad bridges. Hydrogen bonding of solvent water molecules to noncoordinated triazole N atoms and carboxylate groups provides two additional links for the net, which adopts a 12-connected topology corresponding to hexagonal closest packing. The study also introduces a new type of bis(triazole) ligand, which may find wider applications for supramolecular synthesis.

Comment

1,2,4-Triazole and its derivatives commonly adopt multiple N^1:N^2-coordination bridges that effectively transmit magnetic interactions between paramagnetic metal centers (van Koningsbruggen *et al.*, 1997), and these features are essential for the preparation of polynuclear complexes exhibiting diverse magnetic properties (Kahn *et al.*, 1992). For connecting many metal ions, the triazole bridges are especially applicable in combination with short inorganic (OH or Cl) or organic ($R\mathrm{CO}_2^-$ or $R\mathrm{PO}_3^{2-}$) links. They are complementary in their coordination preferences and may act synergetically in the generation of complicated polynuclear motifs, as was revealed by the structure of hydroxidotricopper(II) complexes with 4-amino-1,2,4-triazoles (Liu *et al.*, 2003). Further attractive possibilities for the extension of the polynuclear ensembles and their propagation into the lattice could be provided by the co-operation of triazole and polyfunctional anionic linkers, such as polycarboxylates (Zhai *et al.*, 2007), and also by employing organic modules bearing multiple triazole groups (Lysenko *et al.*, 2006). In this way, benzene-1,3,5-tricarboxylate and flexible 1,2-bis(1,2,4-triazol-4-yl)ethane were used for the preparation of highly connected topologies involving Ni$_3$ and Zn$_3$ units (Habib *et al.*, 2008). However, since the multivalency of the building block and inherently defined and proper binding geometry are equally important prerequisites from the design perspective, a suitable paradigm for new polytriazolyl ligands may be found with geometrically rigid molecular platforms (*cf.* adamantane functionalized at the bridgehead positions) rather than using flexible aliphatic spacers. In this context, we have examined systems combining the aforementioned components and report here the structure of a new coordination polymer, (I), that features assembly of a polynuclear copper(II)–hydroxide cluster and its propagation by combination of trifunctional benzene-1,3,5-tricarboxylate (btc) and bifunctional 4,4′-(adamantane-1,3-diyl)bis(1,2,4-triazole) (tr$_2$ad) bridges.



(I)

In (I), the three-dimensional framework architecture is organized by interconnection of copper(II) ions by three types of links, namely μ_3-hydroxide, μ_3-tr$_2$ad and μ_4-btc. The unique portion of the structure includes two Cu ions, one each of the hydroxide, bis(triazole) and carboxylate ligands, and a solvent water molecule. Two characteristic Cu$_3$(μ_3-OH) fragments share a Cu2···Cu2$^{\mathrm{iii}}$ edge [symmetry code: (iii) $-x + 1$, $-y + 1$, $-z + 1$], yielding a tetranuclear Cu$_4$(μ_3-OH)$_2$ hydroxide cluster situated across an inversion center (Fig. 1).

In the cluster, two pairs of $\mathrm{Cu1}\cdots\mathrm{Cu2}$ and $\mathrm{Cu1}\cdots\mathrm{Cu2}^{\mathrm{iii}}$ edges are bridged by bidentate carboxylate and triazole groups, respectively, and the coordination also involves four monodentate carboxylate O- and two triazole N-atom donors. This polynuclear ensemble formed by a set of hydroxide, carboxylate and azole bridges has several close precedents for molecular copper(II) species, such as pivalate complexes with 4-amino- and 4-*tert*-butyl-1,2,4-triazoles (Zhou *et al.*, 2005) and mixed-anion benzoate–pyrazolide compounds (Mezei *et al.*, 2004). Therefore, the present cluster may be regarded as a predictable feature of the system, and it demonstrates an attractive supramolecular synthon for crystal design. Within the central $\mathrm{Cu_2O_2}$ rhomb of the cluster, the $\mathrm{Cu2}\cdots\mathrm{Cu2}^{\mathrm{iii}}$ separation is relatively short [3.0536 (5) Å] and only slightly exceeds the shortest $\mathrm{Cu}\cdots\mathrm{Cu}$ distance found for $\mathrm{Cu_4(\mu_3\text{-}OH)_2}$ units [2.864 (1) Å; Knuuttila, 1982].

The μ_3-OH group sustains two short [Cu—O = 1.9525 (14) and 1.9715 (14) Å] and one slightly longer [$\mathrm{Cu2—O1}^{\mathrm{iii}}$ = 2.0770 (15) Å] coordination bond. Divergence of these parameters was much more appreciable for a molecular 4-*tert*-butyl-1,2,4-triazole analog [Cu—O = 1.927 (5)–2.302 (5) Å; Zhou *et al.*, 2005]; however, the relatively strong coordination interactions with the hydroxide group in the title compound facilitate elongation of one of the Cu—N bonds. Thus, the typically Jahn–Teller-distorted $\mathrm{CuO_4N}$ tetragonal pyramid around atom Cu1 involves four basal O-atom donors [from one hydroxide and three carboxylate groups; Cu—O = 1.9153 (17)–1.9993 (17) Å] and a distal triazole N atom at the apex [$\mathrm{Cu1—N2}^{\mathrm{iii}}$ = 2.411 (2) Å]. A second unique copper ion adopts a distorted trigonal bipyramidal $\mathrm{CuO_3N_2}$ coordination with a monodentate triazole N atom in the equatorial position [$\mathrm{Cu—N4}^{\mathrm{iv}}$ = 2.010 (2) Å; symmetry code: (iv) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; Fig. 1].

The carboxylate groups of the anion display three different coordination modes. The first (containing atom C15) is *O*:*O*′-bidentate bridging between two copper ions; the second carboxylate group (C16) acts as a single coordination donor and accepts a strong hydrogen bond from an adjacent hydroxide group [$\mathrm{Cu1—O4}^{\mathrm{ii}}$ = 1.9993 (17) Å and $\mathrm{O1—H1}W\cdots\mathrm{O5}^{\mathrm{ii}}$ = 2.652 (2) Å; symmetry code: (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; Table 2], while the remaining carboxylate group (C17) is coordinated in a monodentate fashion. The $\mathrm{tr_2ad}$ ligand, one triazole group of which is N^1:N^2-bidentate while the other is monodentate, connects two clusters, and the significant size of the adamantane spacer effects long-distance bridging [$\mathrm{Cu2}\cdots\mathrm{Cu2}^{\mathrm{vii}}$ = 11.6338 (5) Å; symmetry code: (vii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$].

Thus, the interconnection of the clusters is supported either by carboxylate or by $\mathrm{tr_2ad}$ bridges, and these generate two distinct topologies, which connect with one another through common net nodes. Firstly, interconnection of the $\mathrm{Cu_4(\mu_3\text{-}OH)_2}$ units by bis(triazole) bridges yields a corrugated (4,4)-net, which is parallel to the (101) plane, with a distance between the centroids of the linked clusters of 13.6029 (5) Å. Secondly, each cluster is bonded to six close neighbors by three-connecting carboxylate ligands, yielding a neutral coordination layer parallel to the ($\bar{1}$01) plane (Fig. 2). Its topology may be represented in the form of a regular hexagonal lattice with the hydroxide–copper clusters as six-connected nodes; furthermore, considering the ligands also as three-connected net points, a 3,6-coordinated ‘Kagome dual’ (kgd) isohedral lattice is found with two types of nodes. Such a layer is unprecedented for metal–tricarboxylate complexes, although it may be compared with a three-dimensional eight-connected framework involving closely related $[\mathrm{Fe_4(\mu_3\text{-}OH)_2}]^{10+}$ clusters (Choi *et al.*, 2007). These covalent layers are separated by 9.3583 (5) Å and are linked by neutral $\mathrm{tr_2ad}$ bridges (Fig. 3). Such a type of ‘pillared’ structure may favor the accommodation of guest molecules between the layers, in the same way as for clays or organic clay mimics (Biradha *et al.*, 1998).

The organic bridges support the connection of the $\mathrm{Cu_4(\mu_3\text{-}OH)_2}$ units to ten close neighbors, and this is one of the highest net node coordinations yet observed for metal–organic polymers. One example of a 12-connected coordination topology is known (Li *et al.*, 2005).

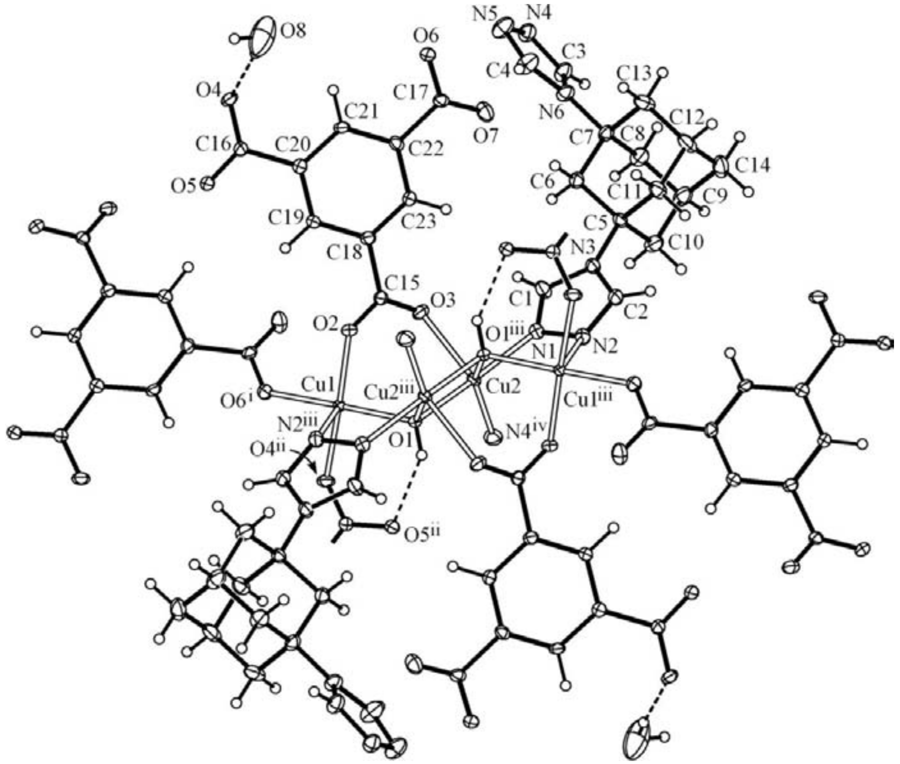


Figure 1
The structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$.]

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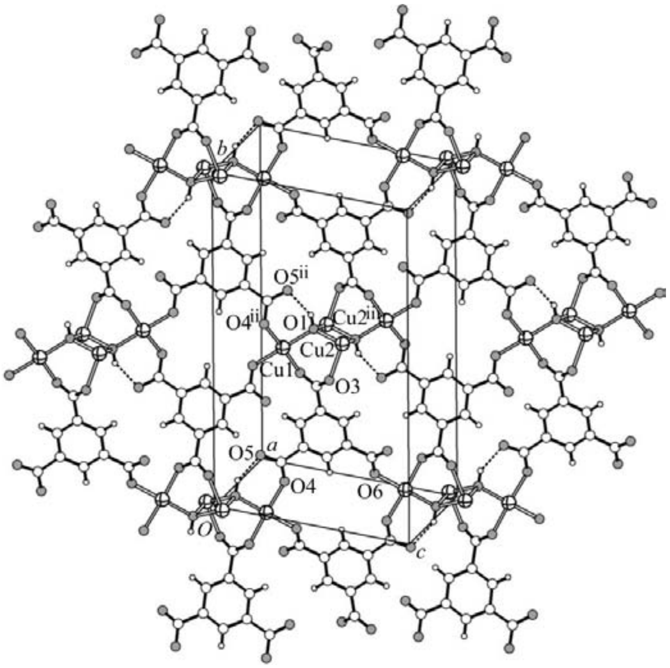

Figure 2
The carboxylate-bridged subtopology in the structure of (I), in the form of a planar 3,6-connected net supported by dihydroxidotetracopper(II) and benzene-1,3,5-tricarboxylate nodes. O atoms are shaded gray and dashed lines indicate hydrogen bonds. [Symmetry codes: (ii) $-x + \frac{1}{2}$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$; (iii) $-x + 1$, $-y + 1$, $-z + 1$.]

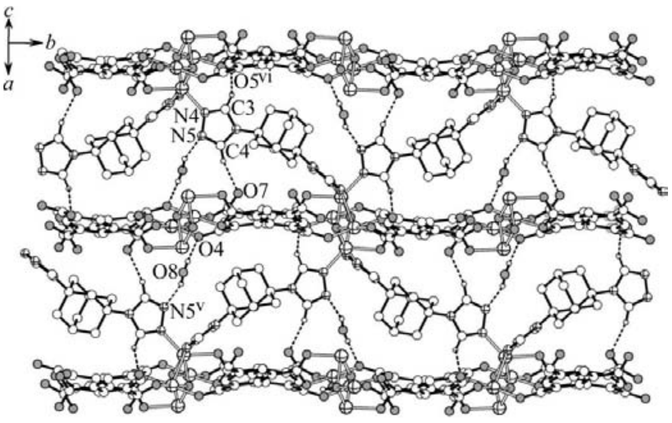

Figure 3
The interconnection of metal–carboxylate layers (which are orthogonal to the plane of the figure) by tr_2ad ligands in (I), showing a set of O—H···O, O—H···N and C—H···O bonds. Note that hydrogen-bonded water molecules (O8) provide additional links between the hydroxide–copper clusters. Dashed lines indicate hydrogen bonding, O atoms are shaded gray, N and Cu atoms are shown as crossed circles, and methylene H atoms have been omitted for clarity. [Symmetry codes: (v) $-x + 1$, $-y$, $-z + 1$; (vi) x, y, $z + 1$.]

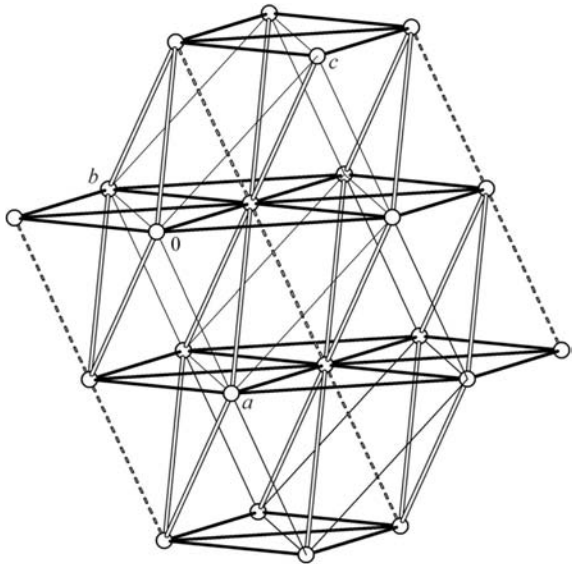

Figure 4
A schematic representation of the three-dimensional topology in (I), in the form of a 12-connected framework (hexagonal closest packing) that considers the hydroxide–copper clusters as the net nodes. Bold lines show links to carboxylate-bridged nodes, open lines are bis(triazole) bridges and dashed lines indicate hydrogen bonding with solvent water molecules.

Two more links for the network in (I) are provided by hydrogen bonding. Thus, the solvent water molecules are incorporated into the interlayer space and are involved in bonding with noncoordinated triazole N atoms and carboxylate O4 atoms [O8—H3*W*···O4 = 2.974 (3) Å and O8—H2*W*···$N5^{v}$ = 3.093 (4) Å; symmetry code: (v) $-x + 1$, $-y$, $-z + 1$]. This is accompanied by weak C—H···O bonding of the triazole ring [C···O = 3.078 (3) and 3.098 (3) Å; Table 2 and Fig. 3], which supports additional links between the clusters related by translation parallel to the *x* axis (symmetry code: $x - 1$, y, z). Therefore, the entire supramolecular architecture in (I) may be regarded as a 12-connected net corresponding to hexagonal closest packing (hcp) (Fig. 4).

In brief, the title compound reveals a potential for the construction of highly-connected coordination frameworks utilizing polynuclear secondary building blocks and complementary carboxylate and triazole bridges. The study also introduces a new type of bis(triazole) ligand, which may find wider applications for supramolecular synthesis.

Experimental

The tr_2ad ligand was prepared in 70% yield by reacting adamantane-1,3-diamine and dimethylformamide azine in boiling xylene in the presence of TsOH as catalyst; the product was crystallized from water as the trihydrate ($tr_2ad\cdot3H_2O$). For the synthesis of the title compound, $Cu(AcO)_2\cdot H_2O$ (6.0 mg, 0.03 mmol), benzene-1,3,5-tricarboxylic acid (6.3 mg, 0.03 mmol), $tr_2ad\cdot3H_2O$ (8.9 mg, 0.03 mmol) and water (7 ml) were added to a Teflon vessel and placed in a steel autoclave, heated at 453 K for 24 h and then cooled to room temperature over a period of 48 h, affording light-green plates of (I) (yield 85%, 8.1 mg).

Crystal data

$[Cu_4(C_9H_3O_6)_2(OH)_2$-
$(C_{14}H_{18}N_6)_2]\cdot 2H_2O$
$M_r = 1279.12$
Monoclinic, $P2_1/n$
$a = 10.1122$ (5) Å
$b = 18.9068$ (7) Å
$c = 13.3503$ (5) Å
$\beta = 112.241$ (2)°
$V = 2362.53$ (17) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.86$ mm^{-1}
$T = 213$ (2) K
0.22 × 0.18 × 0.11 mm

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Data collection

Stoe IPDS diffractometer
Absorption correction: numerical [*X-RED* (Stoe & Cie, 2001) and *X-SHAPE* (Stoe & Cie, 1999)]
$T_{min} = 0.684$, $T_{max} = 0.821$
18636 measured reflections
4592 independent reflections
3851 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.080$
$S = 0.99$
4592 reflections
352 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 1.18$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O6^{i}	1.9153 (17)	Cu2—O1	1.9525 (14)
Cu1—O2	1.9616 (16)	Cu2—N1	1.9893 (19)
Cu1—O1	1.9715 (14)	Cu2—N4^{iv}	2.010 (2)
Cu1—O4^{ii}	1.9993 (17)	Cu2—O1^{iii}	2.0770 (15)
Cu1—N2^{iii}	2.411 (2)	Cu2—O3	2.1652 (18)
O6^{i}—Cu1—O2	91.64 (7)	N1—Cu2—N4^{iv}	94.53 (8)
O6^{i}—Cu1—O1	179.15 (6)	O1—Cu2—O1^{iii}	81.51 (6)
O2—Cu1—O1	89.07 (5)	N1—Cu2—O1^{iii}	87.98 (7)
O6^{i}—Cu1—O4^{ii}	85.36 (7)	N4^{iv}—Cu2—O1^{iii}	144.16 (7)
O2—Cu1—O4^{ii}	175.99 (7)	O1—Cu2—O3	92.77 (5)
O1—Cu1—O4^{ii}	93.96 (5)	N1—Cu2—O3	87.83 (7)
O6^{i}—Cu1—N2^{iii}	94.68 (7)	N4^{iv}—Cu2—O3	121.73 (8)
O2—Cu1—N2^{iii}	94.82 (7)	O1^{iii}—Cu2—O3	94.07 (5)
O1—Cu1—N2^{iii}	84.78 (7)	Cu2—O1—Cu1	119.26 (6)
O4^{ii}—Cu1—N2^{iii}	88.08 (7)	Cu2—O1—Cu2^{iii}	98.49 (6)
O1—Cu2—N1	169.48 (7)	Cu1—O1—Cu2^{iii}	108.00 (6)
O1—Cu2—N4^{iv}	94.09 (6)		

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

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1*W*⋯O5^{ii}	0.85	1.90	2.652 (2)	147
O8—H2*W*⋯N5^{v}	0.85	2.29	3.093 (4)	158
O8—H3*W*⋯O4	0.85	2.13	2.974 (3)	173
C4—H4⋯O7	0.94	2.20	3.078 (3)	156
C3—H3⋯O5^{vi}	0.94	2.35	3.098 (3)	136

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

All H atoms were located from difference maps and then refined as riding, with O—H distances constrained to 0.85 Å, aromatic C—H distances constrained to 0.94 Å and adamantane C—H distances constrained to 0.98 Å, and with U_{iso}(H) equal to $1.2U_{eq}$(C) or $1.5U_{eq}$(O). The H atoms of the water molecule were also located and then fixed with O—H distances of 0.85 Å and a H—O—H angle of 108°. The *U* values of the water molecule are appreciably larger than those of the rest of the structure.

Data collection: *IPDS Software* (Stoe & Cie, 2000); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Version 1.70.01; Farrugia, 1999).

GAS acknowledges the support of a Leonard Euler fellowship from DAAD.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ3138). Services for accessing these data are described at the back of the journal.

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