

Poly[[diaquabis(μ_2 -1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-carboxylato)copper(II)] dihydrate]

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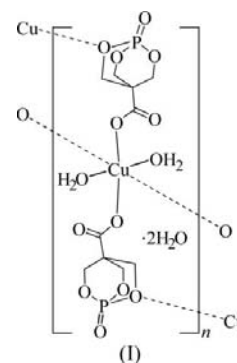
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The asymmetric unit of the title complex, $[\{\text{Cu}(\text{C}_5\text{H}_6\text{O}_6\text{P})_2(\text{H}_2\text{O})_2\} \cdot 2\text{H}_2\text{O}]_n$, consists of half a Cu atom, one complete 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-carboxylate anion ligand and two non-equivalent water molecules. The Cu atom lies on a crystallographic inversion centre and has an elongated axially distorted octahedral environment. A two-dimensional layer structure parallel to (100) is formed as a result of the connectivity brought about by each anion bonding to two different Cu atoms *via* a carboxylate O atom and a bridging O atom of a C—O—P group. The water molecules participate in extensive O—H...O hydrogen bonding. Neighbouring layers are linked together by intermolecular hydrogen-bonding interactions. The crystal structure is characterized by intra- and interlayer motifs of a hydrogen-bonded network. This study demonstrates the usefulness of carboxylates with caged phosphate esters in crystal engineering.

Comment

Compounds that contain caged phosphate esters can serve as host-guest systems and have been studied in the context of hydrogen-bond patterns. For example, in $\text{O}=\text{P}(\text{OCH}_2)_3\text{CCH}_2\text{OH}$ (Guo & Zang, 2007), the O atom of the $\text{P}=\text{O}$ group links with the H atom of the alcohol group to form hydrogen-bonded one-dimensional spiral molecular chains; in $\text{C}_{12}\text{H}_9\text{N}_2^+ \cdot \text{OP}(\text{OCH}_2)_3\text{CCOO}^- \cdot \text{OP}(\text{OCH}_2)_3\text{CCOOH} \cdot \text{H}_2\text{O}$ (Wang *et al.*, 2007), there is a hydrogen-bonding interaction of the O atom of the $\text{P}=\text{O}$ group of the neutral caged phosphate ester with a H atom of the monoprotonated 1,10-phenanthroline molecule. On the other hand, from a coordination standpoint, the use of a carboxylate that contains a caged phosphate ester, such as $\text{OP}(\text{OCH}_2)_3\text{CCOO}^-$, is of interest as a ligand in generating metal-organic coordination polymers of different dimensionalities, because it may act in monodentate, bidentate and combined modes of coordination *via* its carboxylate group and the $\text{P}=\text{O}$ group of the caged phosphate ester, and lead to a great variety of

structures. However, the literature data show that for metal-phosphate ester systems, especially for complexes involving Cu, only a few complexes have been reported to date (Taylor & Waugh, 1977; Shi *et al.*, 2001; Morise *et al.*, 2003). Complexes of Cu and carboxylate anions with caged phosphate ester complexes are rarely reported. When we use 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-carboxylate as ligand, interestingly, a novel six-coordinated Cu complex, (I), was obtained. Not only the carboxylate group but also, unexpectedly, the C—O—P group coordinates to the metal; in addition, a novel hydrogen-bond pattern is formed by a phosphoryl O atom of the caged phosphate ester and an H atom of a water molecule. We describe here the structure of the two-dimensional metal-caged phosphate ester framework, parallel to (100), with strong O—H...O intra- and interlayer hydrogen bonding, leading to a three-dimensional supramolecular network.



The asymmetric unit in (I) comprises half a Cu atom, one complete 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-carboxylate ligand and two non-equivalent water molecules, and is shown in Fig. 1 in a symmetry-expanded view, which displays the full coordination of the Cu atom. Selected geometric parameters are given in Table 1.

The Cu atom, lying on a crystallographic centre of symmetry, is octahedrally coordinated, with two O6 atoms and two water molecules in a planar arrangement and two O4 atoms forming the opposing apices of the octahedron. All of the *cis* O—Cu—O angles are close to 90° [range = $87.02(7)$ – $92.98(7)^\circ$] and, because of the site symmetry of Cu, all of the *trans* angles are exactly 180° . Thus, the coordination octa-

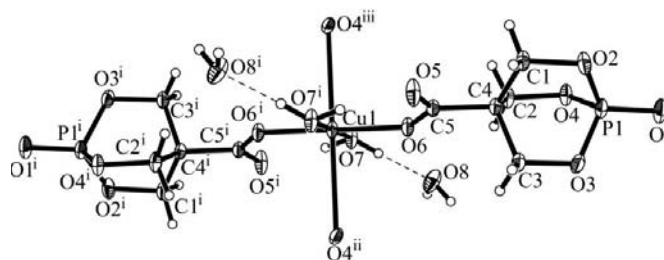


Figure 1

A view of the structure of (I), showing the atom-numbering scheme and the Cu coordination octahedra; displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$]

hedron of the Cu atoms can be visualized as having an elongated axial distortion.

The 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-carboxylate ligand contains both a carboxylate group and a bicyclic OP(OCH₂)₃C cage. The P1—O1 distance is the shortest of all four P—O bonds. These P—O distances are comparable to the values reported for another cage compound (Guo & Zang, 2007). The configuration around the P atom is distorted tetrahedral. As expected, atom O6 of the carboxylate group of the ligand coordinates to the Cu atom in a monodentate manner. The water and carboxylate Cu—O bonds (see Table 1) are shorter than those in both the six-coordinate diaquadimethanolbis(*N*-tosylvalinto- κ O)copper(II) complex (Battaglia *et al.*, 1987) and the five-coordinate polymeric *catena*-poly[tetraamminediaquabis(μ -2-pentane-1,5-dioato- κ O)dicopper(II) tetrahydrate] complex (Devereux *et al.*, 1999). This means that the coordinated interaction for the carboxylate O atom and water molecules with the metal is stronger. Interestingly, phosphoryl atom O1 of the caged phosphate ester does not coordinate to the Cu atom, but atom O4 of the P—O—C group in the bicyclic OP(OCH₂)₃C cage adopts an unexpected bridging bonding mode to another Cu atom. The Cu—O_{phosphate} distance [2.7045 (19) Å] is longer than that of the coordinated bonds involving an ether O atom bonding to a Cu atom in the poly[aquadi- μ -3-oxodiacetato-dicopper(II)] complex (Guo, 2008) and with a carboxylate group bridging to the metal in the *catena*-poly[[bis(1*H*-benzimidazole- κ N³)(salicylato- κ O)copper(II)]- μ -salicylato- κ^3 O,O':O''] complex (Li *et al.*, 2005). This coordinated bond is a weak interaction because its distance is comparable to the values reported for copper complexes involving carboxylate and other weak ligands, such as perchlorate (Burčák *et al.*, 2005) and nitrate anions (Choi *et al.*, 2006). To the best of our knowledge, the present structure is the first structurally characterized copper(II) complex having both a carboxylate group and a caged phosphate ester as ligands. In this complex, each Cu atom is bonded to four ligands, while each ligand connects two Cu atoms. These coordinations result in four Cu atoms being interconnected into a 24-membered ring and complete a

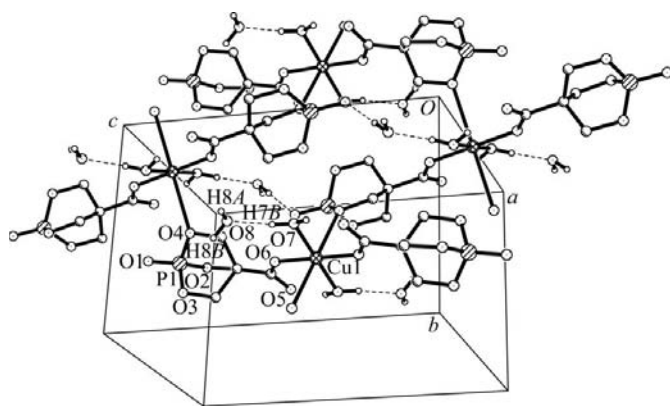


Figure 2
The packing in (I), showing the connectivity of a two-dimensional layer and the hydrogen-bonding interactions (as dashed lines) of the structure parallel to the *bc* plane, viewed down the *a* axis.

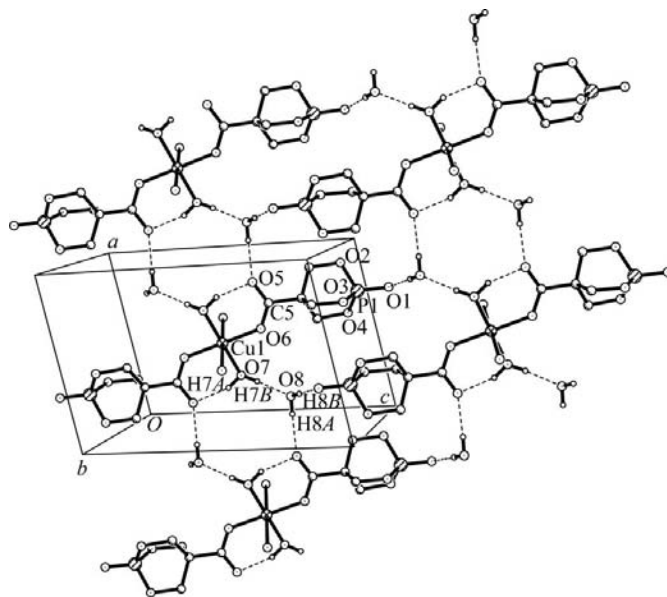


Figure 3
The packing, viewed down the *b* axis, showing the hydrogen-bonding interactions as dashed lines in the direction of the *ac* plane.

two-dimensional layer connectivity of the structure parallel to the *bc* plane (Fig. 2).

Connectivity is further enhanced by hydrogen-bonding interactions. The molecular interaction of the phosphoryl O1 atom and noncoordinated water molecule O8 creates a novel hydrogen-bond pattern. Within the *bc* plane along the crystallographic *c* direction (Fig. 2), O7—H7B···O8 and O8—H8B···O1^v hydrogen-bonding interactions (symmetry codes as in Table 2) are responsible for the formation of a 24-membered hydrogen-bonded $R_4^4(24)$ ring (Bernstein *et al.*, 1995), which links two ligands with two Cu atoms together. Atom H7A is involved in an intermolecular O7—H7A···O5ⁱ hydrogen bond and a six-membered hydrogen-bonded $R_1^1(6)$ ring *via* strong intermolecular hydrogen bonding (Brown, 1976).

In addition, noncoordinated O5 atom and atom H8A of water molecule O8 in the present structure engage in other distinct hydrogen-bonding interactions (see Table 2), which together are responsible for the conformation of the polymer. The structure consists of alternating layers in the [100] direction. Within the *ac* plane along the crystallographic *a* direction (Fig. 3), weak O8—H8A···O5^{iv} hydrogen-bonding interactions not only link two ligands from neighbouring layers together and build up a 20-membered hydrogen-bonded $R_4^4(20)$ ring, but also join two coordinated O7 water molecules from neighbouring layers together and form a 12-membered hydrogen-bonded $R_6^4(12)$ ring.

Experimental

An aqueous solution (20 ml) of anhydrous sodium carbonate (0.37 g, 3.5 mmol) and 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane-4-carboxylic acid (0.78 g, 4.0 mmol) was added dropwise to a solution of cupric nitrate (0.49 g, 2 mmol) in distilled water (20 ml) under stirring at room temperature for 20 min. After filtration, slow evaporation of

Table 1

Selected geometric parameters (Å, °).

Cu1—O7 ⁱ	1.9080 (17)	P1—O2	1.5602 (18)
Cu1—O6	1.9409 (16)	P1—O4	1.5640 (17)
Cu1—O4 ⁱⁱ	2.7045 (19)	C5—O5	1.230 (3)
P1—O1	1.4469 (17)	C5—O6	1.256 (3)
P1—O3	1.5521 (19)		
O7—Cu1—O6	87.02 (7)	O1—P1—O4	114.16 (10)
O6—Cu1—O4 ⁱⁱⁱ	91.81 (6)	O3—P1—O4	105.54 (11)
O7—Cu1—O4 ⁱⁱⁱ	89.19 (6)	O2—P1—O4	104.02 (10)
O1—P1—O3	112.57 (10)	O2—C1—C4	109.88 (18)
O1—P1—O2	114.60 (11)	O5—C5—O6	126.8 (2)
O3—P1—O2	104.97 (10)		

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

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O7—H7A \cdots O5 ⁱ	0.85	1.80	2.602 (2)	157
O7—H7B \cdots O8	0.85	1.77	2.616 (2)	173
O8—H8A \cdots O5 ^{iv}	0.85	1.98	2.799 (3)	162
O8—H8B \cdots O1 ^v	0.85	1.94	2.789 (3)	179

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (iv) $x-1, y, z$; (v) $-x+1, -y+1, -z+2$.

the filtrate over a period of two weeks at room temperature provided crystals of (I).

Crystal data

[Cu(C ₅ H ₆ O ₆ P) ₂ (H ₂ O) ₂] \cdot 2H ₂ O	$V = 915.8 (5) \text{ \AA}^3$
$M_r = 521.74$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 8.340 (3) \text{ \AA}$	$\mu = 1.45 \text{ mm}^{-1}$
$b = 8.863 (3) \text{ \AA}$	$T = 294 (2) \text{ K}$
$c = 12.565 (4) \text{ \AA}$	$0.20 \times 0.16 \times 0.12 \text{ mm}$
$\beta = 99.575 (5)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	4612 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1618 independent reflections
$T_{\min} = 0.756, T_{\max} = 0.842$	1462 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	134 parameters
$wR(F^2) = 0.074$	H-atom parameters constrained
$S = 1.10$	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
1618 reflections	$\Delta\rho_{\text{min}} = -0.36 \text{ e \AA}^{-3}$

All water H atoms were found in difference Fourier maps and were fixed during refinement [O—H = 0.85 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$]. The H atoms of CH₂ groups were treated as riding [C—H = 0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

Data collection: SMART (Bruker, 1997); cell refinement: SAINT (Bruker, 1997); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Version 6.12; Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; 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: SK3205). Services for accessing these data are described at the back of the journal.

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