metal-organic compounds

catena-Poly[[[aquacopper(II)]-*μ*-2-(hydroxyphosphonato)acetato] dihydrate]

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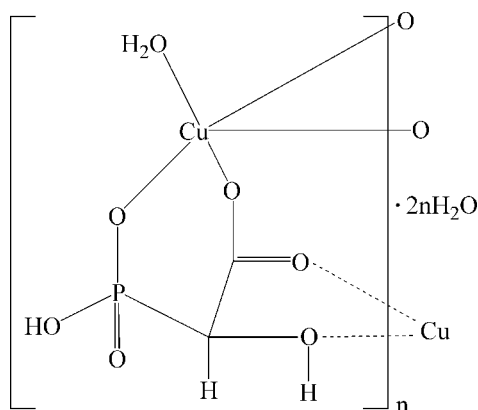Correspondence e-mail: szg188@163.com

The title compound, $[Cu\{HO_3PCH(OH)CO_2\}(H_2O)]\cdot 2H_2O$, was prepared by a hydrothermal reaction. The distorted square-pyramidal coordination geometry of copper(II) is built up of one phosphonate O atom, one hydroxy O atom, two carboxylate O atoms and one water molecule. In the crystal structure, a number of O—H⋯O hydrogen bonds involving the hydroxy groups, carboxylate O atoms, phosphonate O atoms, and uncoordinated and coordinated water molecules are found.

Related literature

For related literature, see: Alberti *et al.* (1992); Clearfield (1988, 1998); Li *et al.* (2007); Nonglaton *et al.* (2004); Riou *et al.* (2000); and Sharma & Clearfield (2000).

Experimental

Crystal data

$[Cu(C_2H_3O_6P)(H_2O)]\cdot 2H_2O$	$V = 1605.6\,(17)$ Å^3
$M_r = 271.60$	$Z = 8$
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 8.610\,(5)$ Å	$\mu = 2.95$ mm^{-1}
$b = 9.871\,(6)$ Å	$T = 273\,(2)$ K
$c = 18.892\,(12)$ Å	$0.10 \times 0.04 \times 0.03$ mm

Data collection

Bruker APEXII CCD diffractometer	8695 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	1659 independent reflections
	1187 reflections with $I > 2\sigma(I)$
$T_{min} = 0.757$, $T_{max} = 0.917$	$R_{int} = 0.072$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.084$	
$S = 1.04$	
1659 reflections	$\Delta\rho_{max} = 0.48$ e Å^{-3}
136 parameters	$\Delta\rho_{min} = -0.49$ e Å^{-3}
6 restraints	

Table 1
Selected geometric parameters (Å, °).

Cu1—O2	1.965 (3)	Cu1—O6^i	1.994 (3)
Cu1—O7	1.971 (3)	Cu1—O4^i	2.211 (3)
Cu1—O5	1.972 (3)		
O2—Cu1—O7	88.87 (13)	O5—Cu1—O6^i	87.97 (12)
O2—Cu1—O5	93.35 (12)	O2—Cu1—O4^i	98.97 (11)
O7—Cu1—O5	172.53 (12)	O7—Cu1—O4^i	97.25 (12)
O2—Cu1—O6^i	174.86 (11)	O5—Cu1—O4^i	89.46 (12)
O7—Cu1—O6^i	90.45 (13)	O6^i—Cu1—O4^i	76.07 (11)

Symmetry code: (i) $x + \frac{1}{2}, y, -z + \frac{1}{2}$.

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O3—H3A⋯O1^{ii}	0.82	1.84	2.651 (4)	171
O4—H4A⋯O6^{iii}	0.82	1.79	2.606 (4)	172
O7—H7A⋯O1W^{iv}	0.847 (10)	1.947 (12)	2.792 (5)	176 (5)
O2W—H2WA⋯O2^v	0.845 (10)	2.10 (3)	2.868 (5)	151 (5)
O1W—H1WA⋯O1^{ii}	0.846 (10)	1.965 (15)	2.797 (5)	167 (5)
O1W—H1WB⋯O2W^{vi}	0.843 (10)	2.08 (3)	2.844 (5)	151 (5)
O2W—H2WB⋯O2^{ii}	0.845 (10)	2.21 (3)	3.003 (5)	156 (5)
O7—H7B⋯O2W^{vii}	0.848 (10)	1.876 (13)	2.720 (5)	173 (5)

Symmetry codes: (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, z$; (iii) $-x + \frac{3}{2}, y - \frac{1}{2}, z$; (iv) $-x + \frac{5}{2}, y - \frac{1}{2}, z$; (v) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (vi) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (vii) $x + 1, y, z$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2059).

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supplementary materials

catena-Poly[[[aquacopper(II)]-*μ*-2-(hydroxyphosphonato)acetato] dihydrate]

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Comment

Metal phosphonates have been of increasing interest in the past decade due to their potential applications in the fields of catalysis (Sharma & Clearfield, 2000), ion exchange (Clearfield, 1988), proton conductivity (Alberti *et al.*, 1992), gas and liquid separations (Riou *et al.*, 2000), biology (Nonglaton *et al.*, 2004), and organic molecule sorption (Clearfield, 1998). Great efforts have been made to the syntheses of novel inorganic-organic hybrid materials based on metal phosphonates, which exhibt a variety of structures such as one-dimensional chains, two-dimensional layers, and three-dimensional networks. Recently, we also reported a novel one-dimensional Ni^{2+} coordination polymer containing 2-hydroxyphosphono-acetic acid (H_3L) (Li *et al.*, 2007). In this paper, we report the crystal structure of the copper(II) coordination polymer $Cu[(HO_3PCH(OH)CO_2)(H_2O)]_n.2n(H_2O)$, (I).

In the crystal structure of the title compound the Cu atom are in a distorted square-pyramidal coordination built up of five oxygen atoms from two symmetry related $O_3PCH(OH)CO_2$) anions and one coordinated water molecule. The values of the Cu—O bond lengths and O—Cu—O angles are in the range of 1.965 (3)–2.212 (3) Å and 76.07 (11) −174.87 (11) °, respectively (Table 1). The copper atoms are connected by the anions into chains, which elongate in the direction of the *c* axis. These chains are further be connected by O—H⋯O hydrogen bonding into layers, that are parallel to the a/b-plane. These layers are connected by the uncoordinated water molecules *via* hydrogen bonds into a three-dimensional hydrogen bonded network (Table 2 and Fig. 2).

Experimental

A mixture of 0.17 g (1.0 mmol) $CuCl_2·2H_2O$, 1.0 ml (4.0 mmol) 2-hydroxyphosphonoacetic acid (48.0 wt %) and 0.04 g (1.0 mmol) NH_4F (as a mineralizer) were dissolved in 8 ml of deionized water, and then ammonia was added with stirring to adjust the pH of the mixture to pH = 3.0. The mixture was transfered into a 23 ml Teflon-lined stainless steel autoclave, and then heated at 423 K for 72 h. After cooling to toom-temperature blue crystals of the title compound were obtained, which were washed with demineralized water and dried in air at room temperature.

Refinement

The C—H and hydroxyl H atoms were positioned with idealized geometry and refined isotropic (U_{iso}(H) = $1.2U_{eq}$(C)) $1.5U_{eq}$(O)) using a riding model with C—H = 0.98 and O—H = 0.82 Å. The water H atoms were located in difference map, refined isotropic with (U_{iso}(H) = $1.5U_{eq}$(O)) but their bond lengths were restraint to 0.84 Å.
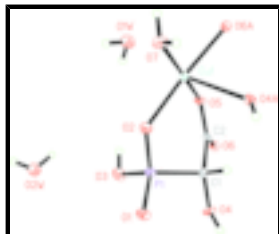
supplementary materials

Figures

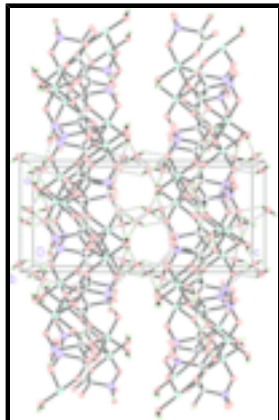Fig. 1. Crystal structure of (I) with labelling and displacement ellipsoids drawn at the the 30% probability level.

Fig. 2. Crystal structure of I with view along the *b* axis. Hydrogen bonding is shows as dashed lines.

catena-Poly[[[aquacopper(II)]-µ-2-(hydroxyphosphonato)acetato] dihydrate]

Crystal data

$[Cu(C_2H_3O_6P)(H_2O)]\cdot 2H_2O$	$D_x = 2.247$ Mg m^{-3}
$M_r = 271.60$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Orthorhombic, *Pbca*	Cell parameters from 1082 reflections
$a = 8.610\,(5)$ Å	$\theta = 3.2–23.6º$
$b = 9.871\,(6)$ Å	$\mu = 2.95$ mm^{-1}
$c = 18.892\,(12)$ Å	$T = 273\,(2)$ K
$V = 1605.6\,(17)$ Å^3	Plate, blue
$Z = 8$	$0.10 \times 0.04 \times 0.03$ mm
$F_{000} = 1096$	

Data collection

Bruker APEXII CCD diffractometer	1659 independent reflections
Radiation source: fine-focus sealed tube	1187 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.072$
$T = 273(2)$ K	$\theta_{max} = 26.5º$
ω scans	$\theta_{min} = 2.2º$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$h = -10 \rightarrow 9$

$T_{min} = 0.757$, $T_{max} = 0.917$

8695 measured reflections

$k = -12 \rightarrow 12$

$l = -23 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.035$	H atoms treated by a mixture of independent and constrained refinement
	$w = 1/[\sigma^2(F_o^2) + (0.0342P)^2 + 1.1295P]$
$wR(F^2) = 0.084$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.048$
1659 reflections	$\Delta\rho_{max} = 0.48$ e Å^{-3}
136 parameters	$\Delta\rho_{min} = -0.49$ e Å^{-3}
6 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cu1	1.12936 (5)	0.14810 (5)	0.35146 (3)	0.01657 (16)
P1	0.80368 (12)	0.01391 (10)	0.35635 (6)	0.0175 (3)
O1	0.7397 (3)	−0.1226 (3)	0.37296 (16)	0.0240 (7)
O2	0.9538 (3)	0.0507 (3)	0.39423 (15)	0.0225 (7)
O3	0.6732 (3)	0.1198 (3)	0.37279 (16)	0.0270 (7)
H3A	0.7100	0.1964	0.3717	0.040*
O4	0.7112 (3)	−0.0110 (3)	0.22203 (15)	0.0211 (7)
H4A	0.7111	−0.0932	0.2156	0.032*
O5	1.0010 (3)	0.2248 (3)	0.27486 (15)	0.0181 (6)
O6	0.8140 (3)	0.2309 (3)	0.19528 (15)	0.0171 (6)
O7	1.2579 (4)	0.0954 (3)	0.43328 (16)	0.0241 (7)
H7A	1.312 (5)	0.024 (3)	0.430 (3)	0.036*
H7B	1.317 (4)	0.162 (3)	0.442 (3)	0.036*
O1W	1.0708 (4)	0.3578 (3)	0.41515 (18)	0.0302 (8)

H1WA	0.979 (2)	0.377 (5)	0.402 (3)	0.045*
H2WA	0.416 (6)	0.356 (4)	0.5073 (19)	0.045*
O2W	0.4439 (5)	0.3037 (3)	0.47445 (19)	0.0387 (9)
H1WB	1.057 (7)	0.326 (5)	0.4561 (13)	0.058*
H2WB	0.487 (6)	0.355 (5)	0.444 (2)	0.058*
C1	0.8444 (4)	0.0260 (4)	0.2620 (2)	0.0162 (9)
H1B	0.9299	−0.0356	0.2503	0.019*
C2	0.8908 (4)	0.1696 (4)	0.2423 (2)	0.0150 (9)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0155 (3)	0.0165 (3)	0.0177 (3)	−0.0013 (2)	−0.0005 (2)	0.0011 (2)
P1	0.0165 (6)	0.0134 (5)	0.0225 (6)	−0.0016 (4)	0.0007 (5)	0.0013 (5)
O1	0.0249 (16)	0.0154 (17)	0.0317 (17)	−0.0033 (13)	0.0011 (13)	0.0046 (12)
O2	0.0215 (16)	0.0247 (16)	0.0214 (16)	−0.0051 (13)	−0.0022 (13)	0.0032 (13)
O3	0.0235 (17)	0.0180 (16)	0.039 (2)	0.0032 (12)	0.0077 (14)	0.0003 (14)
O4	0.0221 (16)	0.0119 (15)	0.0293 (17)	−0.0028 (12)	−0.0077 (13)	−0.0019 (13)
O5	0.0145 (14)	0.0144 (16)	0.0254 (17)	−0.0040 (11)	−0.0014 (13)	0.0013 (12)
O6	0.0181 (15)	0.0129 (15)	0.0203 (16)	0.0001 (12)	−0.0020 (13)	0.0029 (12)
O7	0.0250 (17)	0.0198 (17)	0.0275 (17)	0.0012 (13)	−0.0068 (14)	0.0010 (15)
O1W	0.0243 (17)	0.0299 (19)	0.036 (2)	0.0041 (15)	−0.0012 (16)	0.0010 (16)
O2W	0.051 (2)	0.034 (2)	0.031 (2)	−0.0119 (18)	0.0026 (18)	−0.0001 (15)
C1	0.018 (2)	0.012 (2)	0.018 (2)	0.0018 (16)	−0.0020 (17)	−0.0004 (16)
C2	0.014 (2)	0.015 (2)	0.017 (2)	0.0011 (17)	0.0023 (17)	0.0003 (17)

Geometric parameters (Å, °)

Cu1—O2	1.965 (3)	O4—H4A	0.8200
Cu1—O7	1.971 (3)	O5—C2	1.255 (4)
Cu1—O5	1.972 (3)	O6—C2	1.262 (5)
Cu1—O6^i	1.994 (3)	O6—Cu1^{ii}	1.994 (3)
Cu1—O4^i	2.211 (3)	O7—H7A	0.847 (10)
P1—O1	1.489 (3)	O7—H7B	0.848 (10)
P1—O2	1.522 (3)	O1W—H1WA	0.846 (10)
P1—O3	1.565 (3)	O1W—H1WB	0.843 (10)
P1—C1	1.820 (4)	O2W—H2WA	0.845 (10)
O3—H3A	0.8200	O2W—H2WB	0.845 (10)
O4—C1	1.421 (4)	C1—C2	1.519 (5)
O4—Cu1^{ii}	2.211 (3)	C1—H1B	0.9800
O2—Cu1—O7	88.87 (13)	C1—O4—H4A	109.5
O2—Cu1—O5	93.35 (12)	Cu1^{ii}—O4—H4A	127.6
O7—Cu1—O5	172.53 (12)	C2—O5—Cu1	128.1 (3)
O2—Cu1—O6^i	174.86 (11)	C2—O6—Cu1^{ii}	122.2 (2)
O7—Cu1—O6^i	90.45 (13)	Cu1—O7—H7A	118 (3)
O5—Cu1—O6^i	87.97 (12)	Cu1—O7—H7B	107 (3)
O2—Cu1—O4^i	98.97 (11)	H7A—O7—H7B	109 (4)

O7—Cu1—O4^i	97.25 (12)	H1WA—O1W—H1WB	102 (5)
O5—Cu1—O4^i	89.46 (12)	H2WA—O2W—H2WB	105 (5)
O6^i—Cu1—O4^i	76.07 (11)	O4—C1—C2	108.8 (3)
O1—P1—O2	115.56 (17)	O4—C1—P1	110.4 (3)
O1—P1—O3	107.27 (17)	C2—C1—P1	110.6 (3)
O2—P1—O3	110.90 (17)	O4—C1—H1B	109.0
O1—P1—C1	109.69 (17)	C2—C1—H1B	109.0
O2—P1—C1	106.32 (17)	P1—C1—H1B	109.0
O3—P1—C1	106.78 (17)	O5—C2—O6	122.2 (3)
P1—O2—Cu1	125.23 (18)	O5—C2—C1	118.9 (3)
P1—O3—H3A	109.5	O6—C2—C1	118.9 (3)
C1—O4—Cu1^{ii}	114.1 (2)		

Symmetry codes: (i) $x+1/2$, y, $−z+1/2$; (ii) $x−1/2$, y, $−z+1/2$.

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O3—H3A⋯O1^{iii}	0.82	1.84	2.651 (4)	171
O4—H4A⋯O6^{iv}	0.82	1.79	2.606 (4)	172
O7—H7A⋯O1W^v	0.847 (10)	1.947 (12)	2.792 (5)	176 (5)
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O1W—H1WA⋯O1^{iii}	0.846 (10)	1.965 (15)	2.797 (5)	167 (5)
O1W—H1WB⋯O2W^{vii}	0.843 (10)	2.08 (3)	2.844 (5)	151 (5)
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O7—H7B⋯O2W^{viii}	0.848 (10)	1.876 (13)	2.720 (5)	173 (5)

Symmetry codes: (iii) $−x+3/2$, $y+1/2$, z; (iv) $−x+3/2$, $y−1/2$, z; (v) $−x+5/2$, $y−1/2$, z; (vi) $x−1/2$, $−y+1/2$, $−z+1$; (vii) $x+1/2$, $−y+1/2$, $−z+1$; (viii) $x+1$, y, z.

Fig. 1

Fig. 2