metal-organic compounds

catena-Poly[[[triaquacopper(II)]-μ-2,2′-bipyridine-3,3′-dicarboxylato-$κ^3N,N′:O$] monohydrate]

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The title compound, $\{[Cu(C_{12}H_6N_2O_4)(H_2O)_3]·H_2O\}_n$, was synthesized under hydrothermal conditions. The Cu^{2+} ion is six-coordinated by three water O atoms, and two N atoms and one O atom of the 2,2′-bipyridine-3,3′-dicarboxylate bridging ligand in a sligthly distorted octahedral environment. The 2,2-bipyridine-3,3′-dicarboxylate bridges link the Cu^{2+} ions into chains along the b-axis direction. These chains are further linked by O—H···O hydrogen bonds involving the water solvent molecules, forming a three-dimensional framework.

Related literature

For potential applications of coordination polymers in drug delivery, shape-selective sorption/separation and catalysis, see: Chen & Tong (2007); Zeng et al. (2009). Their structures vary from one-dimensional to three-dimensional architectures, see: Du & Bu (2009); Qiu & Zhu (2009). For our recent research on the synthesis of coordination polymers, see: Pan et al. (2010a,b,c, 2011).
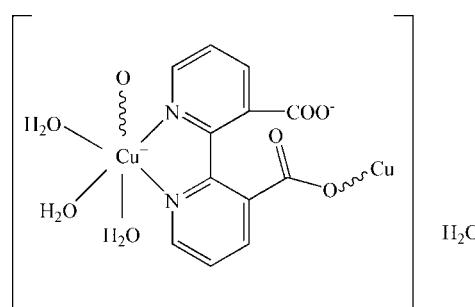
Experimental

Crystal data

$[Cu(C_{12}H_6N_2O_4)(H_2O)_3]·H_2O$	V = 1445.7 (10) Å³
M_r = 377.79	Z = 4
Monoclinic, $P2_1/n$	Mo $Kα$ radiation
a = 9.950 (4) Å	$μ$ = 1.56 mm⁻¹
b = 9.161 (4) Å	T = 296 K
c = 15.974 (7) Å	$0.30 × 0.18 × 0.15$ mm
$β$ = 96.848 (8)°	

Data collection

Bruker APEXII CCD area-detector diffractometer	10263 measured reflections
	3585 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)	2268 reflections with $I > 2σ(I)$
T_{min} = 0.722, T_{max} = 0.792	R_{int} = 0.062

Refinement

$R[F^2 > 2σ(F^2)]$ = 0.054	208 parameters
$wR(F^2)$ = 0.153	H-atom parameters constrained
S = 1.08	$Δρ_{max}$ = 1.02 e Å⁻³
3585 reflections	$Δρ_{min}$ = −1.13 e Å⁻³

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5A···O1W^i	0.85	1.84	2.669 (5)	167
O5—H5···O4^{ii}	0.85	1.86	2.689 (4)	167
O6—H6A···O3^{iii}	0.85	1.88	2.715 (5)	169
O6—H6···O1^i	0.85	2.43	3.282 (5)	180
O7—H7A···O4^i	0.85	1.80	2.642 (4)	170
O7—H7···O1^{ii}	0.85	1.95	2.711 (4)	149
O1W—H1WA···O1	0.85	2.11	2.850 (5)	146
O1W—H1W···O3	0.85	2.01	2.854 (6)	170

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; 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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supporting information

catena-Poly[[[triaquacopper(II)]-*μ*-2,2′-bipyridine-3,3′-dicarboxylato-*κ³N,N′:O*] monohydrate]

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S1. Comment

The design and synthesis of coordination polymers have attracted increasing attention in recent years because of their potential applications in drug delivery, shape-selective sorption/separation, and catalysis (Chen *et al.*, 2007 and Zeng *et al.*, 2009). Their structures vary from one-dimensional to three-dimensional architectures (Qiu *et al.*, 2009 and Du *et al.*, 2009). In our recent works, our research interest has been focused on the synthesis of coordination polymers (Pan *et al.*, 2010*a*,*b*,*c* and 2011). Here we present a Cu-containing coordination polymer with one-dimensional chain structure.

As shown in Fig. 1, the asymmetric part of crystal structure of the title compound consists of an Cu atoms, a 2,2′-bi-pyridine-3,3′-dicarboxylate (bpdc) unit, three coordinated water molecules and one solvate water molecules. The Cu center is six-coordinated by four O atoms and two N atoms. Three of the four O atoms are from three coordination water molecules and the last one is from the carboxylate of the bpdc unit, whereas both N atoms are from the bridging bpdc unit. By this way, the Cu centers and the bpdc units form a chain-like structure, and these chains are further linked by hrydrogen bonds involving the solvent water molecules to from a three-dimensional superamolecular framework (see Table 1).

S2. Experimental

In a typical synthesis, a mixture of $CuSO_4$ (0.032 g), bpdc (0.026 g), NaOH (0.008 g), 2,2′-bipyridine (0.016 g) and H_2O (10 ml), was placed into a 25 ml Teflon-lined reactor under autogenous pressure at 100 °C for 3 days.

S3. Refinement

All H atoms were positioned geometrically (C—H = 0.93 Å and O—H = 0.85 Å) and allowed to ride on their parent atoms with Uĩso~(H) = 1.2U_{eq}(parent atom).
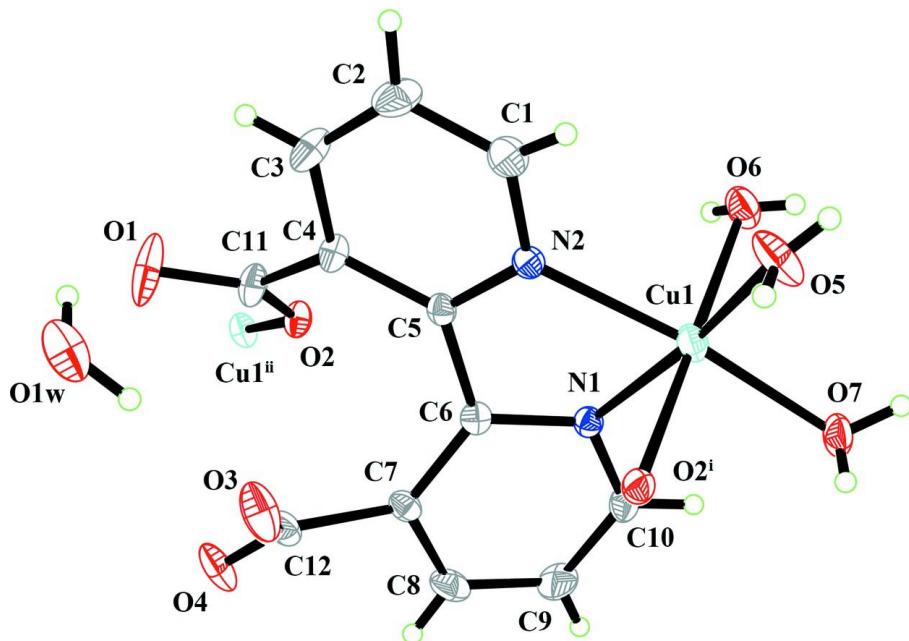
Figure 1

A view of the structure of complex. Ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) 1/2 - x, -1/2 + y, 1/2 - z; (ii) 1/2 - x, 1/2 - y, 1/2 - z.]

***catena*-Poly[[[triaquacopper(II)]-μ-2,2′-bipyridine-3,3′-dicarboxylato- $\kappa^3N,N′:O$] monohydrate]**

Crystal data
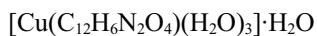
[Cu(C$_{12}$H$_6$N$_2$O$_4$)(H$_2$O)$_3$]·H$_2$O	$Z = 4$
$M_r = 377.79$	$F(000) = 772$
Monoclinic, $P2_1/n$	$D_x = 1.736$ Mg m^{-3}
Hall symbol: -P 2yn	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.950$ (4) Å	$\theta = 1.0$–28.4°
$b = 9.161$ (4) Å	$\mu = 1.56$ mm^{-1}
$c = 15.974$ (7) Å	$T = 296$ K
$\beta = 96.848$ (8)°	Rod-like, blue
$V = 1445.7$ (10) Å^3	0.3 × 0.18 × 0.15 mm

Data collection

Bruker APEXII CCD area-detector diffractometer	10263 measured reflections
	3585 independent reflections
Radiation source: fine-focus sealed tube	2268 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.062$
Detector resolution: 5.00 pixels mm^{-1}	$\theta_{max} = 28.4°$, $\theta_{min} = 2.3°$
phi and ω scans	$h = -10\rightarrow13$
Absorption correction: multi-scan	$k = -12\rightarrow12$
(*SADABS*; Bruker, 2005)	$l = -21\rightarrow21$
$T_{min} = 0.722$, $T_{max} = 0.792$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.054$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.153$	
$S = 1.08$	H-atom parameters constrained
3585 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 0.4177P]$ where $P = (F_o^2 + 2F_c^2)/3$
208 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 1.02$ e Å^{-3}
	$\Delta\rho_{min} = -1.13$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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	−0.03139 (5)	0.32126 (5)	0.24233 (3)	0.02945 (18)
O1	0.5391 (3)	0.5386 (4)	0.1205 (3)	0.0636 (12)
O2	0.4238 (3)	0.6377 (3)	0.21712 (17)	0.0274 (6)
O3	0.4864 (3)	0.2420 (4)	0.2535 (2)	0.0508 (9)
O4	0.6054 (3)	0.4033 (3)	0.3363 (2)	0.0453 (9)
O5	−0.1561 (3)	0.1917 (3)	0.1632 (2)	0.0487 (9)
H5A	−0.2390	0.2119	0.1489	0.058*
H5	−0.1267	0.1045	0.1642	0.058*
O6	−0.1426 (3)	0.5059 (3)	0.19990 (19)	0.0373 (7)
H6A	−0.1026	0.5863	0.2126	0.045*
H6	−0.2252	0.5142	0.1795	0.045*
O7	−0.1432 (3)	0.3074 (3)	0.3421 (2)	0.0375 (7)
H7A	−0.2269	0.3278	0.3398	0.045*
H7	−0.1294	0.2276	0.3689	0.045*
N1	0.1256 (3)	0.4331 (3)	0.31322 (19)	0.0232 (7)
N2	0.1029 (3)	0.3501 (3)	0.1547 (2)	0.0243 (7)
C1	0.0730 (4)	0.3334 (5)	0.0718 (3)	0.0346 (10)
H1	−0.0109	0.2945	0.0514	0.042*
C2	0.1597 (5)	0.3706 (6)	0.0152 (3)	0.0438 (12)
H2	0.1373	0.3541	−0.0422	0.053*
C3	0.2821 (5)	0.4335 (5)	0.0460 (3)	0.0399 (11)
H3	0.3430	0.4599	0.0088	0.048*
C4	0.3149 (4)	0.4575 (4)	0.1313 (2)	0.0264 (8)
C5	0.2231 (4)	0.4074 (4)	0.1854 (2)	0.0225 (8)
C6	0.2437 (4)	0.4159 (4)	0.2795 (2)	0.0230 (8)

C7	0.3662 (4)	0.4059 (4)	0.3308 (2)	0.0261 (9)
C8	0.3664 (4)	0.4325 (5)	0.4164 (3)	0.0370 (10)
H8	0.4477	0.4297	0.4517	0.044*
C9	0.2479 (5)	0.4629 (6)	0.4497 (3)	0.0420 (11)
H9	0.2483	0.4865	0.5063	0.050*
C10	0.1292 (4)	0.4572 (5)	0.3962 (3)	0.0336 (10)
H10	0.0479	0.4707	0.4186	0.040*
C11	0.4367 (4)	0.5507 (5)	0.1593 (3)	0.0335 (10)
C12	0.4963 (4)	0.3469 (4)	0.3029 (3)	0.0304 (9)
O1W	0.5895 (3)	0.2368 (4)	0.0943 (3)	0.0610 (11)
H1WA	0.5835	0.3265	0.0808	0.073*
H1W	0.5492	0.2392	0.1383	0.073*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0221 (3)	0.0281 (3)	0.0382 (3)	−0.0002 (2)	0.0039 (2)	0.0025 (2)
O1	0.054 (2)	0.065 (2)	0.082 (3)	−0.0323 (19)	0.051 (2)	−0.039 (2)
O2	0.0259 (14)	0.0270 (14)	0.0306 (15)	−0.0058 (12)	0.0086 (11)	−0.0046 (12)
O3	0.0329 (17)	0.044 (2)	0.076 (3)	0.0054 (15)	0.0063 (17)	−0.0190 (19)
O4	0.0202 (15)	0.0339 (17)	0.079 (3)	0.0038 (13)	−0.0036 (15)	−0.0010 (17)
O5	0.0301 (17)	0.0296 (17)	0.081 (3)	−0.0008 (13)	−0.0178 (16)	−0.0044 (16)
O6	0.0261 (15)	0.0325 (16)	0.0517 (19)	0.0042 (12)	−0.0018 (13)	0.0067 (14)
O7	0.0219 (14)	0.0347 (17)	0.058 (2)	0.0061 (12)	0.0150 (13)	0.0121 (14)
N1	0.0223 (16)	0.0232 (16)	0.0243 (17)	0.0012 (13)	0.0033 (13)	0.0001 (13)
N2	0.0232 (16)	0.0259 (17)	0.0237 (17)	−0.0036 (13)	0.0018 (13)	−0.0011 (13)
C1	0.034 (2)	0.038 (2)	0.031 (2)	−0.0079 (19)	0.0003 (18)	−0.0036 (19)
C2	0.057 (3)	0.049 (3)	0.026 (2)	−0.006 (2)	0.002 (2)	−0.006 (2)
C3	0.049 (3)	0.043 (3)	0.030 (2)	−0.008 (2)	0.016 (2)	−0.003 (2)
C4	0.027 (2)	0.026 (2)	0.028 (2)	−0.0050 (16)	0.0089 (16)	−0.0048 (16)
C5	0.0226 (18)	0.0193 (18)	0.026 (2)	0.0027 (15)	0.0040 (15)	−0.0014 (15)
C6	0.0201 (18)	0.0187 (18)	0.030 (2)	−0.0027 (15)	0.0026 (15)	−0.0003 (15)
C7	0.0236 (19)	0.0221 (19)	0.031 (2)	−0.0005 (15)	−0.0016 (16)	−0.0004 (16)
C8	0.033 (2)	0.040 (3)	0.034 (2)	−0.003 (2)	−0.0097 (19)	−0.001 (2)
C9	0.045 (3)	0.060 (3)	0.021 (2)	−0.007 (2)	0.0029 (19)	−0.003 (2)
C10	0.034 (2)	0.038 (2)	0.031 (2)	−0.0007 (19)	0.0101 (18)	−0.0053 (19)
C11	0.030 (2)	0.032 (2)	0.040 (3)	−0.0075 (18)	0.0146 (18)	−0.0015 (19)
C12	0.0213 (19)	0.025 (2)	0.044 (3)	0.0033 (16)	0.0005 (17)	0.0032 (18)
O1W	0.040 (2)	0.056 (2)	0.086 (3)	0.0137 (18)	0.0043 (19)	−0.014 (2)

Geometric parameters (Å, º)

Cu1—O5	2.043 (3)	N2—C5	1.344 (5)
Cu1—O7	2.053 (3)	C1—C2	1.365 (6)
Cu1—O2[i]	2.056 (3)	C1—H1	0.9300
Cu1—N2	2.064 (3)	C2—C3	1.383 (6)
Cu1—N1	2.085 (3)	C2—H2	0.9300
Cu1—O6	2.090 (3)	C3—C4	1.380 (6)

O1—C11	1.259 (5)	C3—H3	0.9300
O2—C11	1.239 (5)	C4—C5	1.408 (5)
O2—Cu1ⁱⁱ	2.056 (3)	C4—C11	1.506 (5)
O3—C12	1.241 (5)	C5—C6	1.495 (5)
O4—C12	1.261 (5)	C6—C7	1.388 (5)
O5—H5A	0.8500	C7—C8	1.389 (6)
O5—H5	0.8500	C7—C12	1.518 (5)
O6—H6A	0.8501	C8—C9	1.379 (6)
O6—H6	0.8509	C8—H8	0.9300
O7—H7A	0.8500	C9—C10	1.373 (6)
O7—H7	0.8499	C9—H9	0.9300
N1—C10	1.341 (5)	C10—H10	0.9300
N1—C6	1.359 (5)	O1W—H1WA	0.8500
N2—C1	1.332 (5)	O1W—H1W	0.8500
O5—Cu1—O7	95.69 (14)	C1—C2—C3	117.9 (4)
O5—Cu1—O2ⁱ	88.56 (12)	C1—C2—H2	121.1
O7—Cu1—O2ⁱ	90.86 (11)	C3—C2—H2	121.1
O5—Cu1—N2	92.82 (14)	C4—C3—C2	120.8 (4)
O7—Cu1—N2	171.37 (12)	C4—C3—H3	119.6
O2ⁱ—Cu1—N2	87.91 (12)	C2—C3—H3	119.6
O5—Cu1—N1	169.05 (13)	C3—C4—C5	117.4 (4)
O7—Cu1—N1	92.80 (12)	C3—C4—C11	118.1 (4)
O2ⁱ—Cu1—N1	84.41 (12)	C5—C4—C11	124.1 (3)
N2—Cu1—N1	78.58 (12)	N2—C5—C4	121.2 (3)
O5—Cu1—O6	90.61 (12)	N2—C5—C6	113.4 (3)
O7—Cu1—O6	89.24 (11)	C4—C5—C6	125.4 (3)
O2ⁱ—Cu1—O6	179.16 (12)	N1—C6—C7	121.0 (4)
N2—Cu1—O6	92.12 (12)	N1—C6—C5	112.5 (3)
N1—Cu1—O6	96.42 (12)	C7—C6—C5	126.5 (3)
C11—O2—Cu1ⁱⁱ	131.7 (3)	C6—C7—C8	117.8 (4)
Cu1—O5—H5A	122.6	C6—C7—C12	124.8 (4)
Cu1—O5—H5	110.6	C8—C7—C12	116.7 (4)
H5A—O5—H5	122.0	C9—C8—C7	121.0 (4)
Cu1—O6—H6A	114.2	C9—C8—H8	119.5
Cu1—O6—H6	130.3	C7—C8—H8	119.5
H6A—O6—H6	114.7	C10—C9—C8	117.7 (4)
Cu1—O7—H7A	124.9	C10—C9—H9	121.2
Cu1—O7—H7	111.9	C8—C9—H9	121.2
H7A—O7—H7	108.0	N1—C10—C9	122.8 (4)
C10—N1—C6	119.2 (3)	N1—C10—H10	118.6
C10—N1—Cu1	123.3 (3)	C9—C10—H10	118.6
C6—N1—Cu1	110.8 (2)	O2—C11—O1	125.8 (4)
C1—N2—C5	119.4 (3)	O2—C11—C4	115.8 (3)
C1—N2—Cu1	125.1 (3)	O1—C11—C4	118.3 (4)
C5—N2—Cu1	115.0 (2)	O3—C12—O4	125.9 (4)
N2—C1—C2	123.1 (4)	O3—C12—C7	117.1 (4)

| N2—C1—H1 | 118.4 | O4—C12—C7 | 116.8 (4) |
| C2—C1—H1 | 118.4 | H1WA—O1W—H1W | 99.2 |

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5*A*···O1*W*iii	0.85	1.84	2.669 (5)	167
O5—H5···O4i	0.85	1.86	2.689 (4)	167
O6—H6*A*···O3ii	0.85	1.88	2.715 (5)	169
O6—H6···O1iii	0.85	2.43	3.282 (5)	180
O7—H7*A*···O4iii	0.85	1.80	2.642 (4)	170
O7—H7···O1i	0.85	1.95	2.711 (4)	149
O1*W*—H1*WA*···O1	0.85	2.11	2.850 (5)	146
O1*W*—H1*W*···O3	0.85	2.01	2.854 (6)	170

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