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catena-Poly[[copper(II)-bis(μ-3-carboxypyridine-2-carboxylato)-$\kappa^3N,O^2:O^3;\kappa^3O^3:N,O^2$] methanol disolvate]

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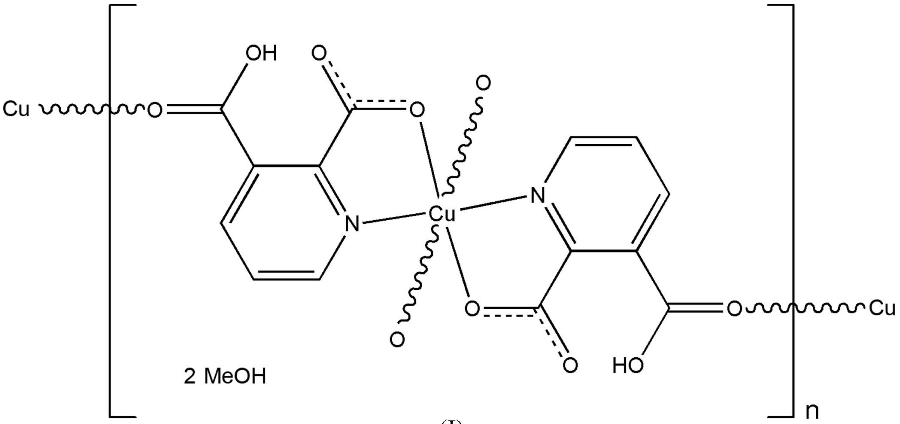
The title compound, $\{[Cu(C_7H_4O_4)_2]\cdot 2CH_3OH\}_n$, forms a square-planar complex through two *N*,*O*-chelating pyridine-2,3-dicarboxylate ligands. Axial interactions between Cu^{II} and O atoms of the CO_2H groups in the *meta*-positions of adjacent ligands form one-dimensional chains. Incorporation of methanol into the structure results in O—H···O hydrogen-bond interactions, which cross-link the chains into a three-dimensional network.

Key indicators
Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.004 Å
R factor = 0.034
wR factor = 0.081
Data-to-parameter ratio = 10.1

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

Comment

The study of ligands containing several different functional groups, such as pyridyine carboxylates, is of significant current interest. Whilst much work using pyridine-2,6-dicarboxylate has been carried out, copper complexes of pyridine-2,3-dicarboxylate are significantly less common. In addition to the structures of the non-hydrated (Suga & Okabe, 1996; Patrick *et al.*, 2003) and dihydrated (Xiang *et al.*, 2006) $[Cu(C_7H_4O_4)_2]$ complexes, both containing the mono-deprotonated pyridine-2,3-dicarboxylate ligand, there are very few other known structures: a series of clathrates containing a dipyridyl co-ligand (Maji *et al.*, 2005), a Cu/Na structure containing the doubly deprotonated ligand (Sileo *et al.*, 1999), a Cu^{II} coordination polymer of $(2,3\text{-}(CO_2)_2py)^{2-}$ charge-balanced by $[Mn(H_2O)_6]^{2+}$ (Patrick *et al.*, 2003), and a mononuclear Cu^I complex with phosphine co-ligands (Cariati *et al.*, 1983).



(I)

The title compound, (I), contains a one-dimensional chain structure similar to that seen in the non-solvated complex $[Cu(C_7H_4O_4)_2]$ (Suga & Okabe, 1996; Patrick *et al.*, 2003). The pyridine-2,3-dicarboxylate ligands are mono-deprotonated at the carboxylate in the *ortho*-position of the pyridine ring. The equatorial sites of the Cu^{II} atom are occupied by *N*,*O*-chelating ligands, forming five-membered chelate rings (Fig. 1).

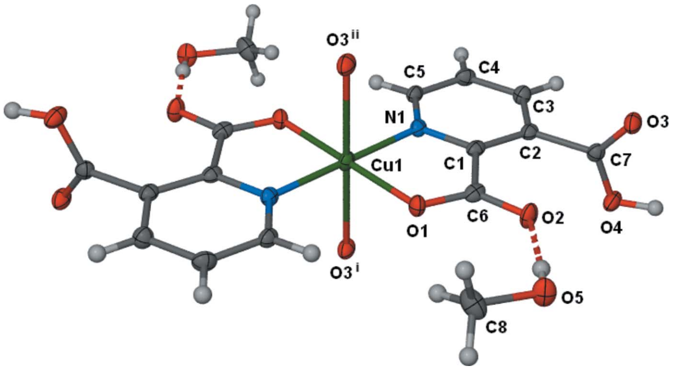


Figure 1
The molecular structure of (I), showing displacement ellipsoids drawn at the 50% probability level for non-H atoms. The dashed lines denote O—H···O hydrogen bonds. Unlabelled atoms are related to labelled atoms by the symmetry code ($-x$, $1 - y$, $-z$). [Symmetry codes: (i) $x - 1$, y, z, (ii) $1 - x$, $1 - y$, $-z$.]

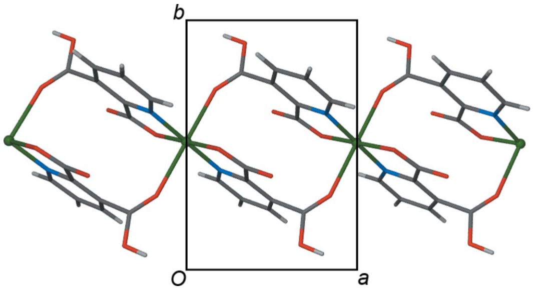


Figure 2
View of a single one-dimensional chain propagating parallel to the *a* axis.

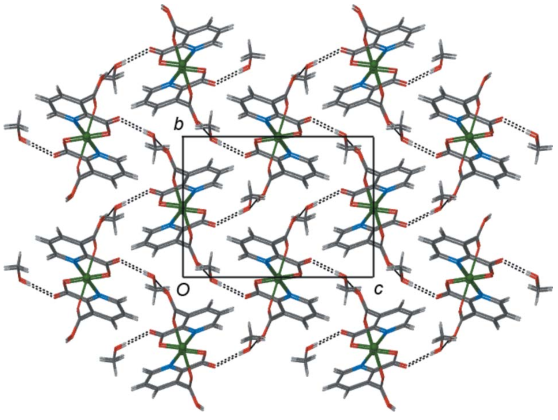


Figure 3
Projection of (I) along the *a* axis, showing the arrangement of the one-dimensional chains and the hydrogen-bonding interactions (dashed lines) involving the methanol solvent molecules lying between the chains.

The axial positions are occupied by O atoms from the carboxylic acid groups of ligands in adjacent complexes, forming one-dimensional chains that propagate parallel to the *a* axis (Fig. 2). Although these axial Cu—O interactions are clearly elongated on account of the Jahn–Teller distortion (Table 1), they are significantly shorter than those reported for the non-solvated complex [2.660 (3) or 2.616 (3)Å]. There is no significant difference between the equatorial bond lengths in the two structures.

Each one-dimensional chain is hydrogen bonded to four adjacent chains *via* the incorporated methanol molecules (Fig. 3 and Table 2). A carboxylic acid group from one chain donates a hydrogen bond to the O atom of the methanol, which in turn donates a hydrogen bond to a carboxylate group in an adjacent chain.

Experimental

The title compound was crystallized during an attempted preparation of a pseudohalide complex. $CuCl_2$ (0.014 g, 0.10 mmol), $K[C(CN)_2(CONH_2)]$ (0.025 g, 0.16 mmol) and pyridine-2,3-dicarboxylic acid (0.020 g, 0.12 mmol) were dissolved in methanol (20 ml). The solution was left to stand for 1 week during which time pale-blue crystals of (I) were obtained.

Crystal data

$[Cu(C_7H_4O_4)_2]\cdot 2CH_4O$
$M_r = 459.85$
Monoclinic, $P2_1/n$
$a = 6.6850\ (8)$ Å
$b = 9.7739\ (12)$ Å
$c = 13.2657\ (18)$ Å
$\beta = 93.136\ (7)^\circ$
$V = 865.46\ (19)$ Å^3
$Z = 2$
$D_x = 1.765$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.33$ mm^{-1}
$T = 123\ (1)$ K
Block, blue
0.26 × 0.14 × 0.10 mm

Data collection

Bruker X8 APEX-II CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
$T_{min} = 0.724$, $T_{max} = 0.879$
4342 measured reflections
1440 independent reflections
1274 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 25.0^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.081$
$S = 1.10$
1440 reflections
142 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.017$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9669 (18)	Cu1—O3^{i}	2.419 (2)
Cu1—N1	1.985 (2)	Cu1—O3^{ii}	2.419 (2)
O1—Cu1—N1	83.42 (8)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5*O*···O2	0.75 (4)	1.95 (4)	2.696 (3)	176 (4)
O4—H4*O*···O5^{iii}	0.92 (4)	1.67 (4)	2.578 (3)	174 (4)

Symmetry code: (iii) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

H atoms bound to C atoms were placed in calculated positions and refined as riding, with C—H = 0.95 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for aromatic H atoms or C—H = 0.98 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for the methyl group. The hydroxyl H atoms were located in a difference Fourier map and allowed to refine freely with an isotropic displacement parameter. The refined O—H bond distances are 0.92 (4) and 0.75 (4) Å for atoms H4*O* and H5*O*, respectively.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 1999); software used to prepare material for publication: *SHELXL97*.

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