Diaquatetrakis(1H-imidazole)copper(II) bis[tris-(1H-imidazole)(pyridine-2,4,6-tricarboxylato-$\kappa^3N,O^2:O^6$)cuprate(II)] dihydrate

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Key indicators

Single-crystal X-ray study
$T = 143$ K
Mean σ(C–C) = 0.002 Å
R factor = 0.025
wR factor = 0.070
Data-to-parameter ratio = 14.6

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

The asymmetric unit of the title complex, $[Cu(C_3H_4N_2)_4(H_2O)_2][Cu(C_8H_2NO_6)(C_3H_4N_2)_3]_2\cdot2H_2O$, contains half of a centrosymmetric diaquatetrakis(1H-imidazole)copper(II) cation and a complex anion comprising copper(II) coordinated by a pyridine-2,4,6-tricarboxylate anion and three imidazole ligands, together with a water molecule.

Comment

Coordination polymers containing bridging carboxylate ligands and secondary non-bridging ligands have been studied in our laboratory (Cheng *et al.*, 2001, 2002*a*,b, 2003, 2004). Recent efforts in our laboratory to synthesize coordination polymers with pyridine-2,4,6-tricarboxylic acid (PTC) and imidazole (im) with transition metals resulted in the synthesis of the title complex, $[Cu(im)_4(H_2O)_2][Cu(C_8H_2NO_6)(im)_3]_2\cdot2H_2O$, (I). Recent reports have described the first accounts of coordination polymers with PTC and zinc, copper, iron or cobalt (Gao *et al.*, 2005; Ghosh *et al.*, 2004).

(I)
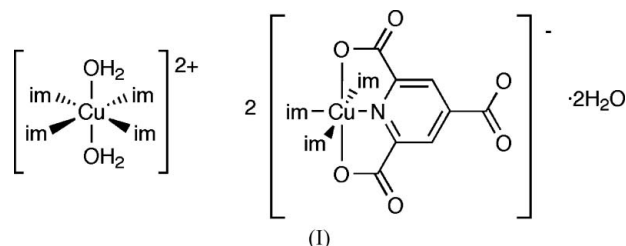
The title complex comprises a simple diaquatetrakis(1H-imidazole)copper(II) cation and two tris(1H-imidazole)-(pyridine-2,4,6-tricarboxylato)cuprate(II) anions, together with two water molecules. Atom Cu1 sits on a special position and therefore half of the cation is in the asymmetric unit, which also contains one anion and one water molecule. The carboxylic acid groups on the PTC ligands are fully deprotonated, making the PTC ligand anionic with a 3− charge. The PTC ligands are tridentate and coordinate to copper *via* the pyridyl N atom and the 2- and 6-carboxylate groups. The remainder of the coordination sites around atom Cu2 are occupied by three imidazole ligands, resulting in a distorted octahedral coordination.

Experimental

The title compound, (I), was synthesized by adding an aqueous solution of copper(II) sulfate (2.52 g, 10 mmol) to a slightly basic (pH > 8) solution of pyridine-2,4,6-tricarboxylic acid (1.41 g, 6.67 mmol), followed by the addition of imidazole (2.04 g, 30 mmol) with stirring. The reaction mixture was filtered and the filtrate was allowed to stand at room temperature. Deep-blue prism-shaped crystals were obtained

after one week (yield: 2.53 g, 47%). Analysis calculated for $C_{46}H_{52}Cu_3N_{22}O_{16}$: C 40.63, H 3.85, N 22.66%; found: C 40.73, H 3.74, N 22.80%. FT–IR (cm^{-1}): 3521 (m), 3136 (s), 1617 (s), 1594 (m), 1546 (s), 1506 (w), 1419 (m), 1357 (s), 1342 (s), 1262 (m), 1073 (s), 1029 (w), 718 (s), 657 (s), 619 (m).

Crystal data

[Cu(C$_3$H$_4$N$_2$)$_4$(H$_2$O)$_2$]-
[Cu(C$_8$H$_2$NO$_6$)(C$_3$H$_4$N$_2$)$_3$]$_2$·-
2H$_2$O
$M_r = 1359.72$
Triclinic, $P\bar{1}$
$a = 8.7101$ (6) Å
$b = 11.8947$ (8) Å
$c = 15.1194$ (10) Å
$\alpha = 109.920$ (1)°
$\beta = 102.599$ (1)°
$\gamma = 98.444$ (1)°

$V = 1394.87$ (16) Å^3
$Z = 1$
$D_x = 1.619$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5941
reflections
$\theta = 2.8–28.3°$
$\mu = 1.22$ mm^{-1}
$T = 143$ (2) K
Prism, blue
$0.56 \times 0.46 \times 0.32$ mm

Data collection

Bruker SMART CCD area-detector
diffractometer
ω scans
Absorption correction: multi-scan
(SADABS; Bruker, 2001)
$T_{min} = 0.531$, $T_{max} = 0.675$
13967 measured reflections

5985 independent reflections
5821 reflections with $I > 2\sigma(I)$
$R_{int} = 0.013$
$\theta_{max} = 27.0°$
$h = -10 \rightarrow 11$
$k = -15 \rightarrow 15$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.070$
$S = 1.05$
5985 reflections
410 parameters
H atoms treated by a mixture of
independent and constrained
refinement

$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 0.8171P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.004$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu2—N6	1.9935 (12)	Cu2—N5	2.0437 (12)
Cu2—N10	2.0152 (13)	Cu2—O7	2.3819 (11)
Cu2—N8	2.0214 (13)	Cu2—O2	2.5143 (11)
N6—Cu2—O7	93.31 (5)	N5—Cu2—O2	71.42 (4)
N5—Cu2—O7	76.23 (4)	O7—Cu2—O2	147.60 (3)
N6—Cu2—O2	119.06 (4)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O6^i	0.88	1.86	2.7152 (16)	164
N4—H4A···O2^{ii}	0.88	2.05	2.8986 (17)	161
N7—H7A···O5^{iii}	0.88	1.83	2.7009 (17)	168
N9—H9A···O8^{iv}	0.88	1.86	2.7297 (19)	167
N11—H11A···O6^v	0.88	1.96	2.8209 (17)	166
O1—H1D···O4^{iii}	0.84 (2)	1.93 (2)	2.7576 (17)	171 (2)
O1—H1E···O3^{vi}	0.82 (2)	2.11 (2)	2.8873 (17)	157 (2)
O8—H8D···O3	0.87 (2)	1.85 (2)	2.6750 (16)	157 (3)
O8—H8E···O2^{vi}	0.87 (2)	1.95 (2)	2.8146 (16)	172 (3)

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

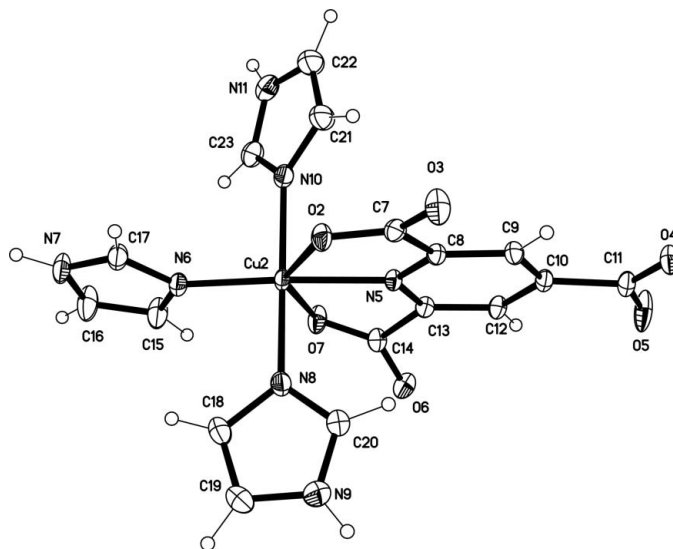**Figure 1**
View of the [Cu(C$_8$H$_2$NO$_6$)(im)$_3$]$^-$ anion in the title complex, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.
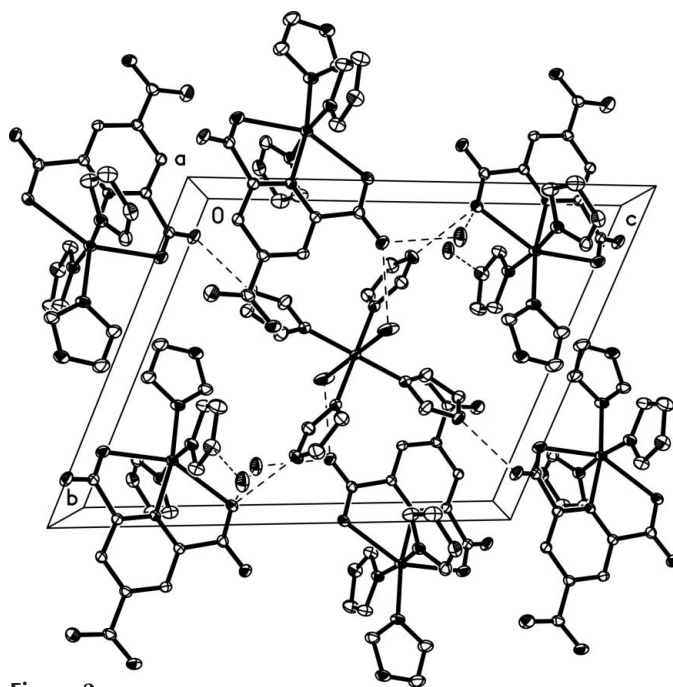

Figure 2
The packing of the title complex, viewed along the a axis. H atoms have been omitted for clarity. Dashed lines indicate hydrogen-bonding interactions. Displacement ellipsoids are drawn at the 50% probability level.

All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry, with C—H distances of 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$, but each group was allowed to rotate freely about its C—C bond. The position of the amine H atom was refined freely along with an isotropic displacement parameter. All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.95–1.00 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve

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