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Di-μ-formato-1κ^2*O*:2κ^2*O*′-di-μ-pyridin-2-olato-1κ*O*:2κ*N*;1κ*N*:2κ*O*-bis[(2-pyridone-κ*O*)copper(II)] acetonitrile 1.02-solvate

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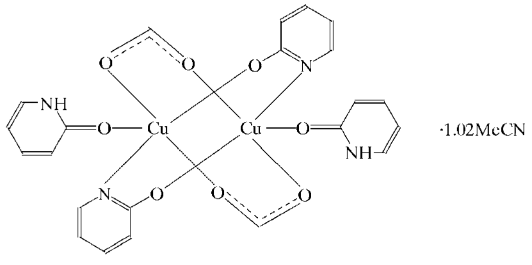
In the title compound, $[Cu_2(CHO_2)_2(C_5H_4NO)_2(C_5H_5NO)_2]\cdot 1.02CH_3CN$, the dimeric unit is centrosymmetric, with two bidentate pyridin-2-olate and two bidentate formate *syn–syn* bridges, and two apical 2-pyridone ligands coordinated through the O atoms. The N atom from the apical 2-pyridone ligand is a donor of a hydrogen bond to the O atom of the bridging pyridinolate ligand of the same complex. The coordination polyhedron of the Cu atom is a distorted square pyramid.

Comment

Copper(II) carboxylates are well known to form a variety of structures, even with ligands of the same homologous series. One of the objectives of our recent work was the development of new synthetic methods for the preparation of copper(II) formate with additional N- and O-donor ligands. We present here a new structure of copper(II) formate with 2-hydroxypyridine. It is interesting that among a large number of structures of dimeric copper(II) carboxylates there are only two structures containing this ligand, *viz.* tetrakis(μ-acetato)bis(2-pyridone)dicopper (Blake *et al.*, 1991; Sun *et al.*, 1994), which has four bidentate acetate bridges and two apical 2-pyridone ligands, and tetrakis(μ-2α-pyridinato-κ*N*,*O*)bis(dimethyl sulfoxide-κ*O*)dicopper (Yeh *et al.*, 1987), which has four *N*,*O*-bidentate pyridinate bridges and two apical dimethyl sulfoxide ligands. In contrast to these two structures, the title compound, (I), whose structure consists of di-μ-formato-di-μ-pyridin-2-olato-bis[(2-pyridone)copper(II)] dimers and acetonitrile solvent molecules (Fig. 1 and Table 1), contains 2-pyridone as a monodentate apical ligand and pyridin-2-olate as a bidentate bridging ligand. The dimeric unit is centrosymmetric, with two apical 2-pyridone ligands coordinated through atoms O2, and two *N*,*O*-bidentate pyridin-2-olate and two bidentate formate *syn–syn* bridges. This compound is the first example among dimeric copper(II) formates with four bridging ligands in which one or more formate bridges are replaced by some other kind of ligand, *i.e.* pyridinolate. Different kinds of bridges within dimers are also uncommon within the structures of copper(II) carboxylates.



(I)

In (I), the coordination polyhedron of the Cu atom is a slightly distorted square pyramid; τ is 0.023 (Addison *et al.*, 1984). The Cu atom is displaced by 0.188 (1) Å from the N2/O4/O11/O12 basal plane. The Cu···Cu separation within the dimer is 2.6468 (4) Å, which is comparable to separations in other dimeric copper(II) formates (Uekusa *et al.*, 1989; Yamanaka *et al.*, 1991; Cejudo *et al.*, 2002; Sapina *et al.*, 1994). Atom N1 from the apical 2-pyridone ligand is a donor of a hydrogen bond to atom O4 from the bridging pyridinolate ligand of the same complex; the N1···O4 distance is 2.768 (3) Å. Fig. 2 shows the packing of the title compound looking along the *c* axis. The apical pyridone ligand forms stacking interactions with two adjacent symmetry-related 2-pyridone ligands [at $(x, 1-y, -\frac{1}{2}+z)$ and $(x, 1-y, \frac{1}{2}+z)$]. The dihedral angles between π-stacked rings are in both cases 0.48°, and the distances between the ring centroids are 3.622 (2) Å. The stacking interactions run along the *c* axis and can be seen in projection along this direction in Fig. 2 as the overlapping of apical 2-pyridone rings. Fig. 2 also shows that the structure is layered, where layers of dimeric complex molecules are separated by layers of solvent acetonitrile molecules. All layers are parallel to the *ac* plane and stack along the [100] direction.

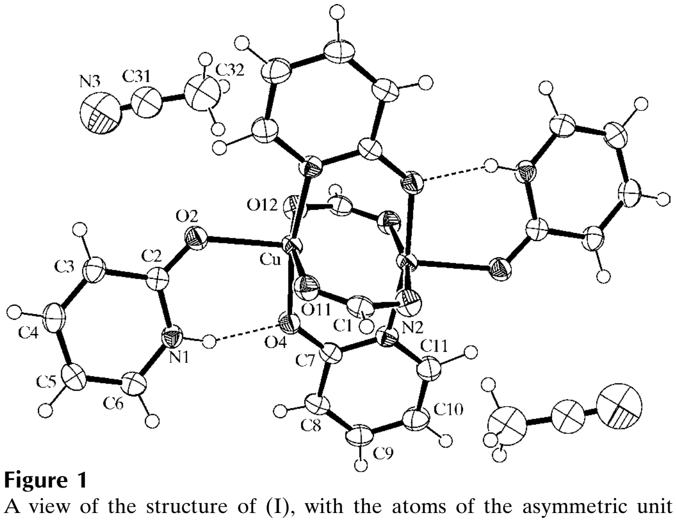


Figure 1
A view of the structure of (I), with the atoms of the asymmetric unit labeled. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate intramolecular hydrogen bonds.

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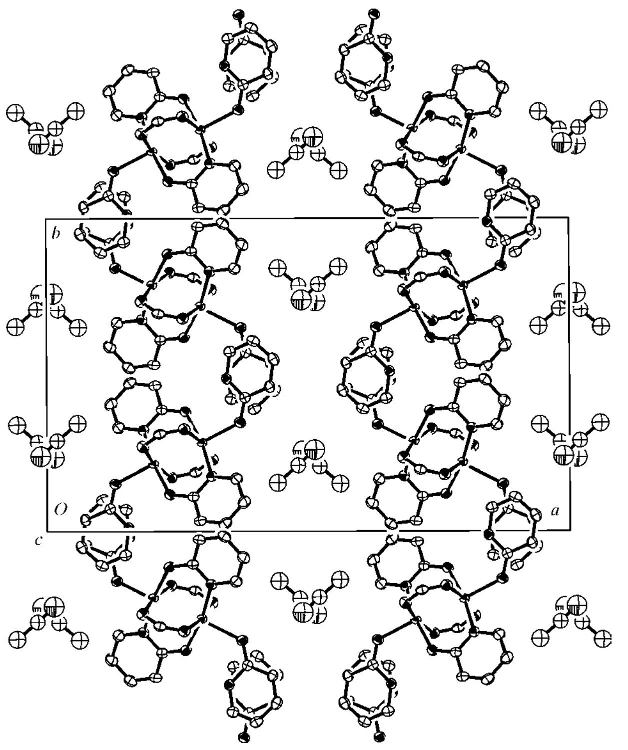

Figure 2
The packing of (I), viewed along the *c* axis. π–π stacking interactions are present between overlapping apical 2-pyridone rings. H atoms have been omitted.

On exposure of the crystals to air, the acetonitrile molecules can easily leave the structure, causing the destruction of the crystal. Despite the fact that the single crystal was protected with silicon grease and was transferred very quickly from the mother liquor into the stream of cold nitrogen, some acetonitrile molecules succeeded in escaping from the crystal. As a consequence, the sites of the acetonitrile molecules are only partially [0.51 (3)] occupied, resulting in there being 1.02 (3) solvent molecules per dimeric complex molecule. The disorder in that part of the structure is also exhibited in the deviation of the C31—C32 bond length [1.326 (17) Å] from the expected Csp^3—Csp length [1.470 (13) Å; Allen *et al.*, 1987]. The C31—N3 bond distance [1.12 (2) Å] is close to the reported Csp≡N bond distance [1.136 (10) Å; Allen *et al.*, 1987]. It seems that at the decay of the crystal structure, the dimeric complex does not decompose. This is supported by the results of elemental analysis, IR spectroscopy and gravimetric measurement, which will be published elsewhere. Unfortunately, attempts to prepare suitable crystals of such complexes with no or with other kinds of solvent (acetone, water, ethanol and chloroform) were unsuccessful.

Experimental

Single crystals of (I) were prepared by the reaction of $Cu_2(CHO_2)_4$(2-mpy)$_2$ (2-mpy is 2-methylpyridine) and 2-hydroxypyridine in acetonitrile. 2-Hydroxypyridine (0.38 g, 4 mmol) was dissolved in acetonitrile (27 ml). $Cu_2(CHO_2)_4$(2-mpy)$_2$ (0.31 g, 0.8 mmol) was added to the solution during mixing and heating. The undissolved solid residue was filtered off and the resulting solution was left to stand at 278 K for 24 h. Green crystals obtained from the solution were used for X-ray diffraction. The compound is very unstable in air.

Crystal data

$[Cu_2(CHO_2)_2(C_5H_4NO)_2$-
$(C_5H_5NO)_2]\cdot 1.02(3)CH_3CN$
M_r = 637.39
Monoclinic, $C2/c$
a = 26.1571 (8) Å
b = 15.3971 (5) Å
c = 7.1673 (2) Å
β = 101.078 (2)°
V = 2832.80 (15) Å^3
Z = 4

D_x = 1.495 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3136 reflections
θ = 2.6–27.5°
μ = 1.55 mm^{-1}
T = 150 K
Plate, green
0.20 × 0.10 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
ω scans with κ offsets
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{\min}$ = 0.73, $T_{\max}$ = 0.96
13938 measured reflections

3182 independent reflections
2605 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int}$ = 0.026
$\theta_{\max}$ = 27.5°
$h = -33 \rightarrow 33$
$k = -19 \rightarrow 19$
$l = -9 \rightarrow 9$

Refinement

Refinement on F
$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.044
S = 1.09
2986 reflections
186 parameters

Only H-atom displacement parameters refined
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 1.39 e Å^{-3}
$\Delta\rho_{\min}$ = −1.16 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—O2	2.146 (2)	O11—C1	1.256 (4)
Cu—O4	1.966 (2)	O12—C1$^{\rm i}$	1.251 (4)
Cu—O11	2.004 (2)	N1—C2	1.373 (4)
Cu—O12	1.988 (2)	N1—C6	1.360 (4)
Cu—N2	1.985 (3)	N2—C11	1.355 (4)
O2—C2	1.249 (4)	N2—C7$^{\rm i}$	1.359 (4)
O4—C7	1.290 (4)	N3—C31	1.12 (2)
O2—Cu—O4	94.92 (9)	C2—N1—C6	125.0 (3)
O2—Cu—O11	95.93 (9)	Cu—N2—C11	120.7 (2)
O2—Cu—O12	95.61 (9)	Cu—N2—C7$^{\rm i}$	119.0 (2)
O2—Cu—N2	95.18 (10)	C7$^{\rm i}$—N2—C11	120.3 (3)
O4—Cu—O11	89.55 (9)	O11—C1—O12$^{\rm i}$	127.4 (3)
O4—Cu—O12	89.76 (9)	N1—C2—C3	114.9 (3)
O4—Cu—N2	169.82 (10)	O2—C2—C3	124.1 (3)
O11—Cu—O12	168.46 (10)	O2—C2—N1	121.0 (3)
O11—Cu—N2	88.11 (10)	N1—C6—C5	120.0 (3)
O12—Cu—N2	90.56 (9)	N2$^{\rm i}$—C7—C8	119.3 (3)
Cu—O2—C2	129.0 (2)	O4—C7—C8	120.1 (3)
Cu—O4—C7	130.4 (2)	O4—C7—N2$^{\rm i}$	120.7 (3)
Cu—O11—C1	121.77 (19)	N2—C11—C10$^{\rm i}$	122.1 (3)
Cu—O12—C1$^{\rm i}$	122.2 (2)	N3—C31—C32	175.0 (13)

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

A Regina weighting scheme (Wang & Robertson, 1985) using the normal equation of the second order was applied for individual reflections so that $w = A(0,0) + A(1,0)V(F) + A(0,1)V(S) + A(2,0)V(F)^2 + A(0,2)V(S)^2 + A(1,1)V(F)V(S)$, where $V(F) = F_{\rm obs}/F_{\rm obs}(\max)$, $F_{\rm obs}(\max)$ = 274.38 and $V(S) = (\sin\theta/\lambda)/[(\sin\theta/\lambda)(\max)]$, $(\sin\theta/\lambda)(\max)$ = 0.6486; the parameters were $A(0,0)$ = 151.7662, $A(1,0)$ = 0.0099395, $A(0,1)$ = −587.9600, $A(2,0)$ = −0.0003962, $A(1,1)$ = 0.0243166 and $A(0,2)$ = 570.2360. All H atoms, with the exception of two bonded to the C atom of the acetonitrile solvent molecule, were located from difference Fourier maps; the remaining two positions were calculated. Owing to the disorder of the acetonitrile solvent molecules, their C and N atoms were refined isotropically, together with the occupancy parameter, which was constrained to be equal for all atoms of acetonitrile. The solvent H-atom parameters were not refined.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *Xtal3.6* (Hall *et al.*, 1999); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *Xtal3.6* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1269). Services for accessing these data are described at the back of the journal.

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