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A two-dimensional network of $R_2^2(16)$ and $R_4^2(8)$ rings in *trans*-bis(4-aminopyridine-κN^1)bis(benzoato-$\kappa^2 O,O'$)copper(II) benzene 0.75-solvate

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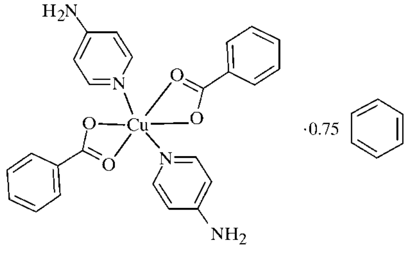
The structure of the title supramolecular complex, $[Cu(C_7H_5O_2)_2(C_5H_6N_2)_2]\cdot 0.75C_6H_6$, has been determined. The Cu^{2+} ion lies on an inversion centre and is coordinated by four O atoms of two opposing benzoate molecules and two pyridine N atoms of two opposing aminopyridine molecules. The partially occupied benzene site lies across a twofold rotation axis. The crystal structure is dominated by two-dimensional networks containing two different hydrogen-bonded rings [$R_2^2(16)$ and $R_4^2(8)$].

Comment

The self-assembly of coordination-based entities is based on the implementation of ligands containing specific molecular information stored in the arrangement of suitable binding sites and of metal ions reading out the structural information through the algorithm defined by their coordination geometry (Lehn, 2000). One approach for addressing this problem is to design molecular components built from binding subunits of different types. Of special interest are systems containing different binding units within their structure, so as to combine several distinct coordination (Funeriu *et al.*, 2001) or hydrogen-bonding (Etter, 1990) subprograms. Pyridine, carboxylate and amine as Cu^{2+} coordination groups are selected as competitive partners in coordination or hydrogen-bonding events. On the basis of the stability constants in water of the simple complexes, we expect a selective complexation of Cu^{II} ions by carboxylate ($\beta_1 = 2.46$; Ablov & Nazarova, 1961) and pyridine ($\beta_1 = 3.30$; Erlenmeyer *et al.*, 1968) moieties in competition with the very unstable amine complexes used as hydrogen-bonding motifs. In this paper, we describe the title complex, (I), a coordination architecture that is built up by self-assembly of 4-aminopyridine (L_1) and benzoic acid (L_2) molecules and Cu^{2+} ions as metal-coordination and hydrogen-bond templating centres.

The molecular structure of (I) is presented in Fig. 1. The Cu^{2+} ion lies on an inversion centre and is sixfold coordinated by two N atoms (N2 and N2*A*) of inversion-related L_1 ligands and four O atoms of inversion-related L_2 ligands (O9, O11, O9*A* and O11*A*), thus fulfilling the prediction based on the stability constants of the simple complexes. The Cu—O distances are short to the opposing O9 ions [1.962 (3) Å] and long to the opposing O11 atoms [2.706 (4) Å; just shorter than the sum of the van der Waals radii of Cu and O]. The Cambridge Structural Database (Version 5.25; Allen, 2002) gives for the shorter carboxylate Cu—O distance values of between 1.951 and 2.180 Å, and for the longer distance a range of 2.209–2.996 Å. Cu—N distances for L_1 ligands are in the range 1.980–2.006 Å (eight structures); this distance is slightly shorter in (I) [1.974 (5) Å]. Pertinent dimensions of the intramolecular structure are given in Table 1. The benzene site was found to be underoccupied (0.75), but the remaining atomic displacement parameters are still high, presumably as a result of some positional disorder. The straw representation in Fig. 2 shows that the Cu atom and its coordinating ligands are stacked in two-dimensional arrangements in the *ab* plane, with the L_1 ligands parallel to this plane and the L_2 ligands



(I)

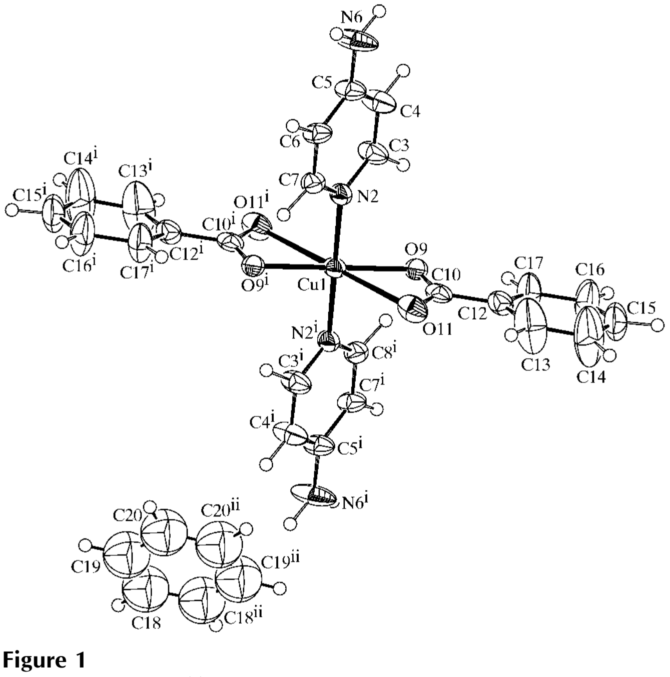


Figure 1
The structure of (I), showing displacement ellipsoids at the 30% probability level. [Symmetry codes: (i) $-x, -y, 1-z$; (ii) $1-x, y, \frac{1}{2}-z$.]

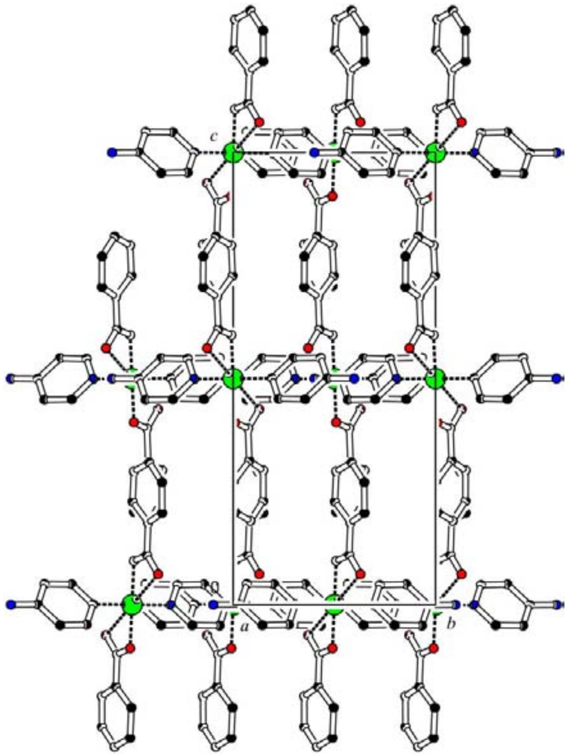


Figure 2
A straw representation of a projection of the crystal structure of (I) on to the *bc* plane. The benzene molecules in the cavities left by the ligand phenyl rings have been omitted for the sake of clarity.

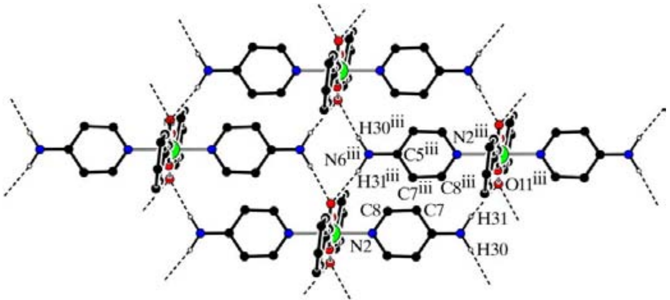


Figure 3
The $R_2^2(16)$ and $R_4^2(8)$ ring network in the *ab* plane. [Symmetry code: (iii) $-x, -1-y, 1-z$.]

perpendicular to it. There are no interactions (hydrogen bonds or π–π interactions) between the phenyl groups of L_2 ligands of adjacent stacks. It is interesting to note that bis(benzoato-*O*,*O′*)bis(nicotinamide-*N*)copper(II) [(II); Leban *et al.*, 1996] shows a similar two-dimensional arrangement, with pyridine moieties lying within and parallel to the stacks, while the carboxylate and phenyl groups are perpendicular to the stacking plane. The difference between this structure and (I), apart from the slightly different L_1 ligand, is the *trans* arrangement of the two carboxylate groups in (I); they are *cis* in (II). Another closely related compound, but this time with a *trans* arrangement of the carboxylate groups, *trans*-bis(benzoato-*O*,*O′*)bis(*N*,*N*-diethylnicotinamide-N^1)copper(II) (Hökelek *et al.*, 1996), does not show the typical two-dimensional structural arrangement of (I) and (II). Within each stack of the title compound, a two-dimensional network of $R_2^2(16)$ and $R_4^2(8)$ rings is present (Bernstein *et al.*, 1995); the two rings are connected *via* the two H atoms of the amine group of L_1 that are bonded to atoms O11 of the L_2 ligands (Fig. 3), the H30···O11 and H31···O11 hydrogen–acceptor distances being 2.04 and 2.01 Å, respectively. Details of the hydrogen-bonding geometry are given in Table 2. The C-atom displacement ellipsoids of the phenyl rings show a pronounced anisotropy in a direction perpendicular to the plane of the rings, probably due to the absence of any steric chemical constraints in that direction.

Experimental

A solution of 4-aminopyridine (10 mg, 1.06 mmol) (L_1) and benzoic acid (13 mg, 1.06 mmol) (L_2) in methanol (1 ml) was added to a solution of $CuTf_2$ (Tf is trifluoromethanesulfonate; 19.2 mg, 0.53 mmol) in methanol (1 ml) and the mixture was heated for 2 h at 333 K. Single crystals of the L_1–L_2–Cu complex were obtained by slow diffusion of suspended benzene into the resulting methanol solution at room temperature (yield 20.2 mg, 86.65%).

Crystal data

$[Cu(C_7H_5O_2)_2(C_5H_6N_2)_2]\cdot0.75C_6H_6$
$M_r = 552.59$
Monoclinic, $C2/c$
$a = 15.010$ (1) Å
$b = 9.0360$ (8) Å
$c = 20.450$ (2) Å
$\beta = 98.773$ (9)°
$V = 2741.2$ (4) Å^3
$Z = 4$
$D_x = 1.339$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2367 reflections
$\theta = 4.3$–$21.6°$
$\mu = 0.84$ mm^{-1}
$T = 173$ K
Prism, translucent pale blue
0.20 × 0.08 × 0.05 mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
ω scans
Absorption correction: Gaussian (Schwarzenbach & Flack, 1991)
$T_{min} = 0.910$, $T_{max} = 0.950$
50 463 measured reflections
4535 independent reflections
1725 reflections with $I > 2u(I)$
$R_{int} = 0.08$
$\theta_{max} = 32.3°$
$h = -22 \rightarrow 22$
$k = -13 \rightarrow 12$
$l = -29 \rightarrow 30$
4 frames standard reflections
frequency: 30 min
intensity decay: none

Table 1
Selected interatomic distances (Å).

Cu1—O9	1.962 (3)	Cu1—O11^i	2.706 (4)
Cu1—O11	2.706 (4)	Cu1—N2^i	1.974 (5)
Cu1—N2	1.974 (5)	O9—C10	1.271 (7)
Cu1—O9^i	1.962 (3)	O11—C10	1.245 (7)

Symmetry code: (i) $-x, -y, 1-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N6—H30···O11^{iv}	0.96	2.04	2.945 (7)	156
N6—H31···O11^{iii}	0.97	2.01	2.943 (6)	159
C3—H26···O9	1.06	2.51	3.040 (7)	110
C8—H29···O9^i	1.09	2.53	3.000 (7)	105

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.139$
$S = 0.95$
1725 reflections
161 parameters
H-atom parameters constrained

$p = P(6)\max(F_o^2,0) + [1 - P(6)]F_c^2$, $W = 1.0/[\sigma^2(F^*) + [P(1)p]^2 + P(2)p + P(4) + P(5)\sin\theta]$, where $P(1)$–$P(5)$ = 0.0859, 0.00, 0.00, 0.00 and 0.333, respectively
$(\Delta/\sigma)_{\max} = 0.006$
$\Delta\rho_{\max} = 0.51$ e Å^{-3}
$\Delta\rho_{\min} = -0.61$ e Å^{-3}

H atoms were placed geometrically and allowed to ride on their parent C and N atoms, with C—H distances of 1.00–1.09 Å and N—H distances of 0.96–0.97 Å. The partial benzene solvent molecule, which lies across a twofold rotation axis, was constrained to be a rigid planar hexagon, and the C atoms were assigned a common isotropic displacement parameter. This displacement parameter was refined for a number of values of the site occupancy, the lowest agreement factor being obtained for an occupancy of 0.75; the atomic displacement factor remains, however, rather high, possibly due to unresolved positional disorder. However, the quality of the diffraction data did not warrant a more detailed treatment of the partial solvent molecule.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1999); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2001); molecular graphics: *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1293). Services for accessing these data are described at the back of the journal.

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