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# Acetato(*N*-phenylpyridine-2-carboxamidato-$\kappa^2N,N$)(*N*-phenylpyridine-2-carboxamide-$\kappa^2N^1,O$)copper(II)

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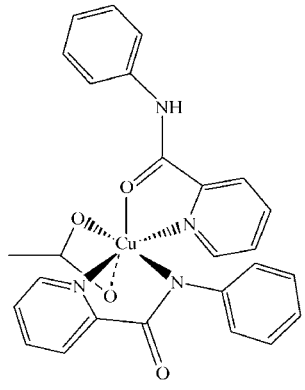
The title complex, $[Cu(C_{12}H_9N_2O)(C_2H_3O_2)(C_{12}H_{10}N_2O)]$, is a neutral $Cu^{II}$ complex with a primary $N_3O_2$ coordination sphere. The Cu centre coordinates to both a deprotonated and a neutral molecule of *N*-phenylpyridine-2-carboxamide and also to an acetate anion. The coordination around the metal centre is asymmetric, the deprotonated ligand providing two N donor atoms [Cu—N = 1.995 (2) and 2.013 (2) Å] and the neutral ligand providing one N and one O donor atom to the coordination environment [Cu—N = 2.042 (2) Å and Cu—O = 2.2557 (19) Å], the fifth donor being an O atom of the acetate ion [Cu—O = 1.9534 (19) Å]. The remaining O atom from the acetate ion can be considered as a weak donor atom [Cu—O = 2.789 (2) Å], conferring to the Cu complex an asymmetric octahedral geometry. The crystal structure is stabilized by intermolecular N—H···O, C—H···O and C—H···$\pi$ interactions.

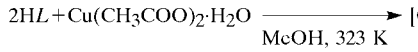
## Comment

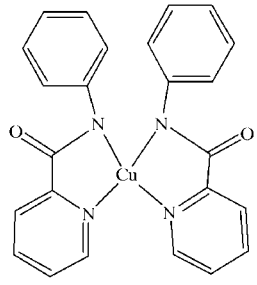
The title complex, (I), assumes a different geometry to previously reported cpmplexes in the literature with identical and similar ligands. In the $Cu^{II}$ complex with the same ligand (Ray *et al.*, 1994), the structure determination showed that the Cu complex is four-coordinate with a symmetric $N_4$ coordination environment, with the ligand assuming a *cis* conformation. A Cu complex with a similar ligand [*N*-(2-chloro-6-methylphenyl)pyridine-2-carboxamide] has also been reported (Patra *et al.*, 1999). In this case, the molecular structure determination showed that the Cu centre is five-coordinate in a distorted trigonal–bipyramidal geometry, having an $N_4O$ coordination environment, with the pyridine and the amide N atoms of each organic ligand occupying an axial and an equatorial position and the fifth coordination position being occupied by a water molecule.

The *N*-phenylpyridine-2-carboxamide ligand (*L*) was obtained by a condensation reaction between pyridine-2-carboxylic acid and phenylamide in a basic reductive reaction medium following a modification of the procedure described by Barnes *et al.* (1978) and a similar procedure described by Ray *et al.* (1994). The ligand, potentially bidentate, reacted with copper(II) acetate forming a five-coordinate complex, (I). The synthesis of the complex was performed in a fashion similar to that reported previously (Ray *et al.*, 1994) but using different reaction conditions. In the previous synthesis, the ligand (dissolved in ethanol) was allowed to react with an aqueous solution of $CuSO_4{\cdot}5H_2O$, while in the synthesis reported here, the ligand was dissolved in methanol and added to a methanol solution of $Cu(CH_3COO)_2{\cdot}H_2O$.

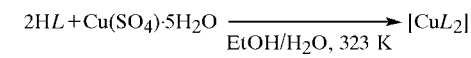



(I)




(Ray *et al.*, 1994)




A view of the structure of the title complex and the coordination environment around the Cu atom, together with the atomic numbering scheme, is shown in Fig. 1. The coordination environment around copper is of the $N_3O_2$-type and is asymmetric. One of the *N*-phenylpyridine-2-carboxamide molecules (ligand *A*) provides a pyridine N and an amide O donor atom. The second molecule (ligand *B*, labelled *X*4#, where *X* is the atom label and # is an integer) provides a pyridine and a deprotonated amide N donor atom. The remaining donor O atom, O3, is from the acetate anion. Atom O31 of the acetate residue can be considered to interact weakly with the $Cu^{II}$ ion [Cu1—O31 = 2.789 (2) Å]. In this

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case, the primary $N_3O_2$ five-coordination geometry gives place to an effective asymmetric octahedral elongated geometry (Kiani *et al.*, 2002; Burčák *et al.*, 2005). The primary Cu-atom geometry is a distorted square-based pyramid with a $\tau$ value of 0.10 [the structure index is defined as $\tau = (\beta - \alpha)/60$, where $\beta$ and $\alpha$ are the largest coordination angles; $\tau$ = 0 for square-pyramidal geometry and $\tau$ = 1 for trigonal–bipyramidal geometry (Addison *et al.*, 1984)]. Ligand *B* (providing two N donor atoms), an acetate O atom and the pyridine N atom of ligand *A* encompass the basal plane of the square pyramid [amide Cu1—N47 = 1.995 (2) Å, pyridine Cu1—N41 and Cu1—N1 = 2.013 (5) and 2.042 (2) Å, respectively, and acetate Cu1—O3 = 1.9534 (19) Å], from which the Cu atom is displaced by 0.1253 (11) Å towards an apical amide O donor atom [Cu1—O2 = 2.2557 (19) Å]. The apical Cu1—O2 bond length is 0.26 Å longer than the mean distance adopted by the basal atoms. The bond angles involving the coordinated metal centre and the donor atoms are given in Table 1. The largest distortions from square-pyramidal geometry are indicated by the N41—Cu1—N1 and O3—Cu1—N47 angles. These deviations can be attributed to steric effects imposed by the conformations assumed by the ligands.

The presence of the H atom on atom N27 in ligand *A* precludes this atom being coordinated to the Cu atom; instead, ligand *A* is rotated by approximately 180° and carbonyl atom O2 is the donor to the Cu atom, so that ligands *A* and *B* assume different conformations around the C2—C27 and C42—C47 bonds, the N1—C2—C27—N27 torsion angle in ligand *A* being 171.8 (2)°, and N41—C42—C47—N47, the corresponding torsion angle in ligand *B*, being 0.1 (3)°. In ligand *A*, the C27—N27—C21—C22 torsion angle is −174.7 (3)°, while the corresponding angle C47—N47—

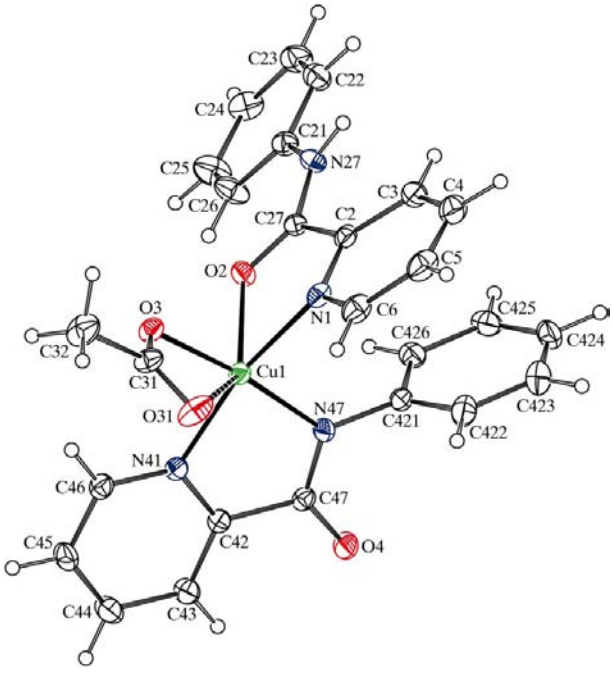


**Figure 1**
A view of (I), with our numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

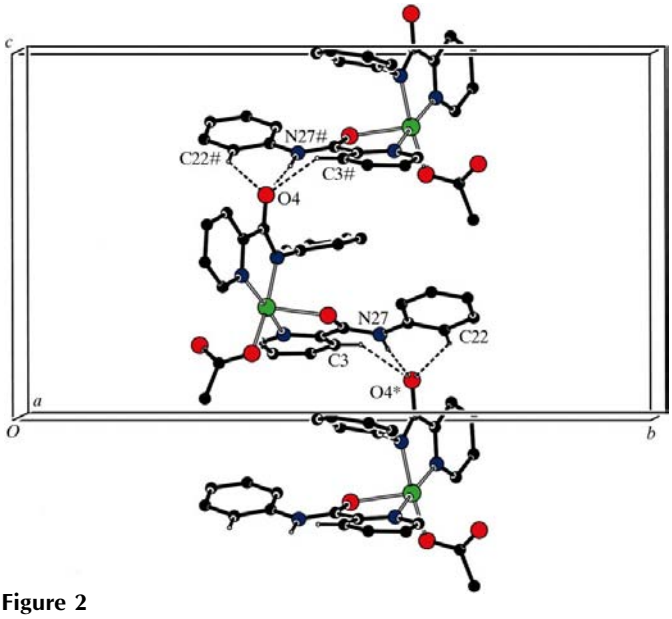


**Figure 2**
A view of the chain parallel to the *c* axis formed by the action of one N—H···O hydrogen bond augmented by two C—H···O hydrogen bonds, all involving atom O4 as the acceptor. Atoms labelled with an asterisk (*) or a hash (#) are at the symmetry positions $(1 - x, 1 - y, -\frac{1}{2} + z)$ and $(1 - x, 1 - y, \frac{1}{2} - z)$, respectively. H atoms not involved in the hydrogen bonding have been omitted for the sake of clarity.

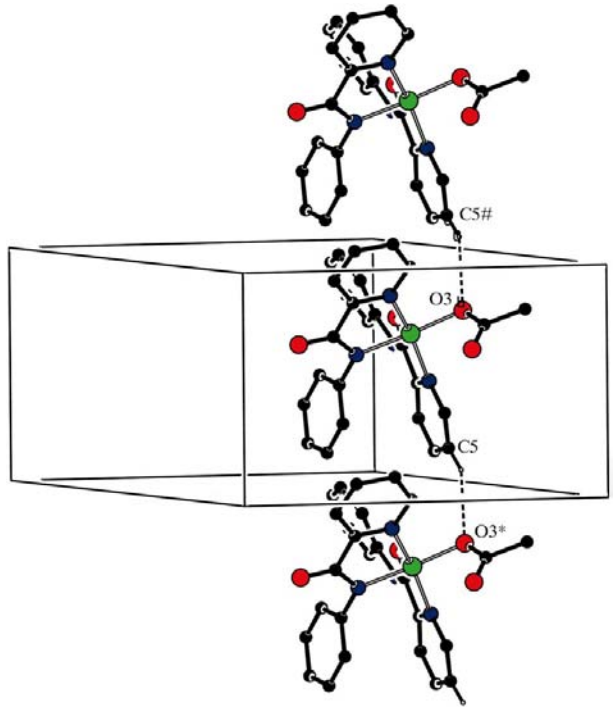


**Figure 3**
A view of the chain parallel to the *a* axis formed by a C—H···O hydrogen bond. Atoms labelled with an asterisk (*) or a hash (#) are at the symmetry positions $(-1 + x, y, z)$ and $(1 + x, y, z)$, respectively. H atoms not involved in the hydrogen bonding have been omitted for the sake of clarity.

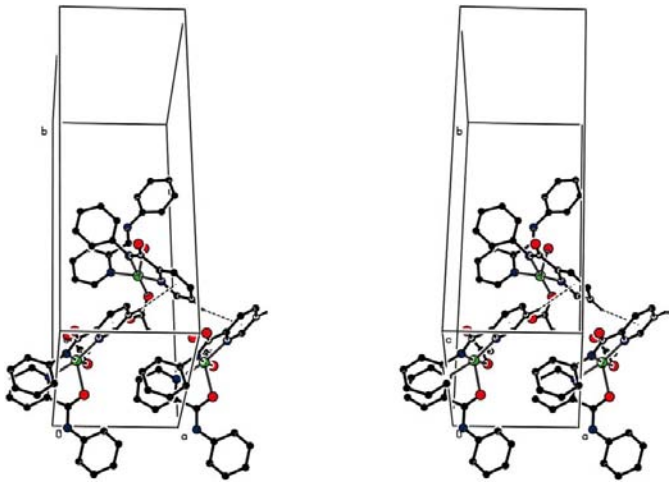

**Figure 4**
A stereoview of the chain formed by a C—H···$\pi$ interaction. H atoms not involved in the hydrogen bonding have been omitted for the sake of clarity.

C421—C422 in ligand *B* is −96.9 (3)°. The C27—N27 bond [1.346 (3) Å] is significantly longer than the C47—N47 bond [1.323 (3) Å] at the 3$\sigma$ level. Atom H27 is thus available for hydrogen bonding.

The supramolecular structure is defined by an N—H···O, three C—H···O and one C—H···$\pi$ hydrogen bond, which combine to form a three-dimensional network. Atom N27 acts as a hydrogen-bond donor, *via* H27, to O4$^{i}$ (all symmetry codes are given in Table 2). This is augmented by the C3—H3···O4$^{i}$ and C22—H22···O4$^{i}$ hydrogen bonds. These three hydrogen bonds link the molecules into a chain that runs parallel to the *c* axis (Table 2 and Fig. 2). Atom C5 acts as a hydrogen-bond donor, *via* H5, to O3$^{ii}$, thus linking the molecules into a chain that runs parallel to the *a* axis (Table 2 and Fig. 3). Finally, atom C45 is involved in a C—H···$\pi$ contact with the pyridine ring containing atom N41$^{iii}$ (Table 2 and Fig. 4).

## Experimental

*N*-Phenylpyridine-2-carboxamide was prepared following a modification of the procedure described by Barnes *et al.* (1978). A solution consisting of a mixture of pyridine-2-carboxylic acid (picolinic acid, 40 mmol), phenylamide (aniline, 40 mmol) and triphenyl phosphite (40 mmol) in 50 ml of pyridine was kept for 3 h in a boiling water bath. The resulting solution was cooled and maintained at room temperature for 48 h. The resulting white fibrous crystals were filtered off and washed with a small amount of a 1:1 mixture of acetone and diethyl ether (78% yield). Analysis found: C 72.9, H 5.10, N 14.01%; $C_{12}H_{10}N_2O$ requires: C 72.7, H 5.08, N 14.14%. For the synthesis of (I), a solution of copper(II) acetate monohydrate in methanol (2.5 mmol) was added to a solution of *N*-phenylpyridine-2-carboxamide (5.0 mmol) in methanol at 323 K. The resulting solution was left to cool for 24 h, allowing partial evaporation of the solvent. Single crystals were obtained by slow evaporation of the resulting solution at room temperature. These were collected and washed with a 1:1 mixture of acetone and diethyl ether, and dried under low pressure. Analysis found: C 60.23, H 4.45, N 10.78%; $C_{26}H_{22}CuN_4O_4$ requires: C 60.28, H 4.28, N 10.82%.

*Crystal data*

$[Cu(C_{12}H_9N_2O)(C_2H_3O_2)(C_{12}H_{10}N_2O)]$
$M_r$ = 518.02
Orthorhombic, $Pna2_1$
$a$ = 7.9604 (1) Å
$b$ = 23.057 (3) Å
$c$ = 13.227 (2) Å
$V$ = 2427.7 (5) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 0.94 mm$^{-1}$
$T$ = 120 (2) K
0.25 × 0.10 × 0.10 mm

*Data collection*

Stoe Stadi-4 diffractometer
Absorption correction: multi-scan (North *et al.*, 1968)
$T_{min}$ = 0.799, $T_{max}$ = 0.912
6079 measured reflections
5831 independent reflections
4590 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.022
10 standard reflections
frequency: 120 min
intensity decay: none

*Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.088
$S$ = 1.03
5831 reflections
317 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.21 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.26 e Å$^{-3}$
Absolute structure: Flack (1983), 2827 Friedel pairs
Flack parameter: 0.003 (11)

**Table 1**
Selected bond and torsion angles (°).

| | | | |
|---|---|---|---|
| O3—Cu1—N47 | 173.55 (9) | N41—Cu1—N1 | 167.38 (8) |
| O3—Cu1—N41 | 93.02 (9) | O3—Cu1—O2 | 95.35 (7) |
| N47—Cu1—N41 | 81.05 (9) | N47—Cu1—O2 | 89.43 (8) |
| O3—Cu1—N1 | 92.53 (9) | N41—Cu1—O2 | 114.30 (8) |
| N47—Cu1—N1 | 92.81 (9) | N1—Cu1—O2 | 76.41 (8) |
| | | | |
| N1—C2—C27—N27 | 171.8 (2) | N41—C42—C47—N47 | 0.1 (3) |
| C27—N27—C21—C22 | −174.7 (3) | C47—N47—C421—C422 | −96.9 (3) |

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

*Cg*5 is the centroid of the pyridine ring containing atom N41.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N27—H27···O4$^{i}$ | 0.89 | 1.92 | 2.805 (3) | 170 |
| C3—H3···O4$^{i}$ | 0.95 | 2.32 | 3.095 (4) | 138 |
| C5—H5···O3$^{ii}$ | 0.95 | 2.55 | 3.401 (4) | 150 |
| C22—H22···O4$^{i}$ | 0.95 | 2.52 | 3.279 (4) | 137 |
| C45—H45···*Cg*5$^{iii}$ | 0.95 | 2.78 | 3.582 (3) | 142 |

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

Compound (I) crystallized in the orthorhombic system; space groups $Pna2_1$ and *Pnma* were permitted from the systematic absences, and $Pna2_1$ was confirmed by the analysis. H atoms were treated as riding atoms, with C—H distances of 0.95 (aromatic) and 0.98 Å (methyl), an N—H distance of 0.89 Å, and $U_{iso}$(H) values of 1.5 (methyl) or 1.2 times $U_{eq}$(C,N). The correct orientation of the structure with respect to the polar-axis direction was established by means of the Flack (1983) parameter.

Data collection: *STADI4* (Stoe & Cie, 1996); cell refinement: *X-RED* (Stoe & Cie, 1996); data reduction: *X-RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* (McArdle, 2003) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3093). Services for accessing these data are described at the back of the journal.

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