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(Acetato-κ^2O,O')(di-2-pyridylamine-κN)-(trifluoroacetato-κO)copper(II)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.037
wR factor = 0.125
Data-to-parameter ratio = 11.6

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

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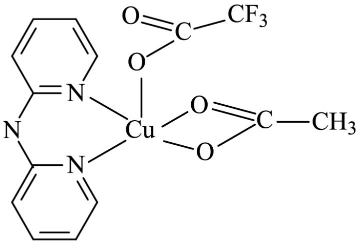
The title complex, $[Cu(C_2F_3O_2)(C_2H_3O_2)(C_{10}H_9N_3)]$, has been prepared. The Cu^{II} cation has a slightly distorted square-pyramidal environment, with a basal plane formed by two N atoms of the di-2-pyridylamine ligand and two O atoms of the acetate group. The apical position is occupied by an O atom of the trifluoroacetate group. Two molecules related by a crystallographic center of symmetry are linked into a dimer by hydrogen bonds and further hydrogen bonds link the dimers into sheets.

Comment

Di-2-pyridylamine (dpa) has been used widely as a ligand in transition metal complexes. In its complexes with copper(II), the structures of mononuclear and polynuclear compounds have been reported. In most mononuclear complexes, the Cu^{II} atom is surrounded by two chelating dpa ligands and some anions (Johnson & Jacobson, 1973; Jacobson & Jensen, 1986; Akhter *et al.*, 1991; Hill *et al.*, 1997; Youngme *et al.*, 1998, 1999); bridged dinuclear species are also reported in a few compounds, such as oxamidate (oa)-bridged $[Cu_2(dpa)_2(oa)(NO_3)_2]_6$ and dihydroxo-bridged $[Cu_2(dpa)_2(OH)_2(BF_4)_2]$ and $[Cu(dpa)_2(OH)_2(H_2O)]Cl_2\cdot2H_2O$ (Wu *et al.*, 1992). In recent years, increasing attention has been paid to the dpa ligand because it is used as a basic material for metal chain complexes.



(I)

In the framework of our current work concerning the synthesis and characterization of mononuclear and polynuclear compounds of transition metals by using multidentate nitrogen donor groups as ligands (Sheu *et al.*, 1996; Shieh *et al.*, 1997; Lai *et al.*, 1999; Peng *et al.*, 2000; Li *et al.*, 2003), copper(II) complexes with the dpa ligand have been particularly examined, and the structure of the title compound, (I), is reported here.

The title complex is five-coordinate and crystallizes in the triclinic space group $P\overline{1}$. The geometry is very similar to that of (acetato-κ^2O,O')chloro(2,2′-dipyridylamine)copper (Ugozzoli *et al.*, 1997). The basal plane of the square-pyramidal environment around the copper(II) cation consists of N1, N3, O1 and O2; the mean deviation from the plane of the four atoms is

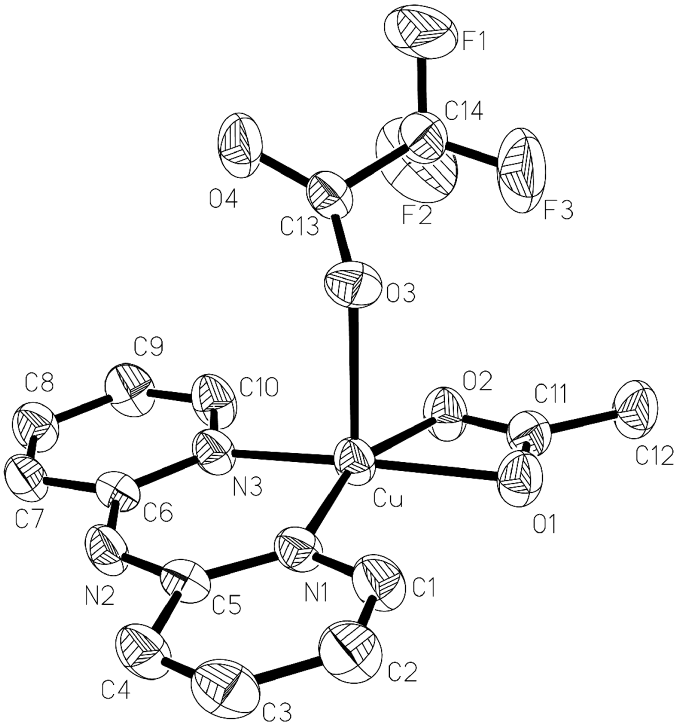


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 35% probability level. H atoms have been omitted.

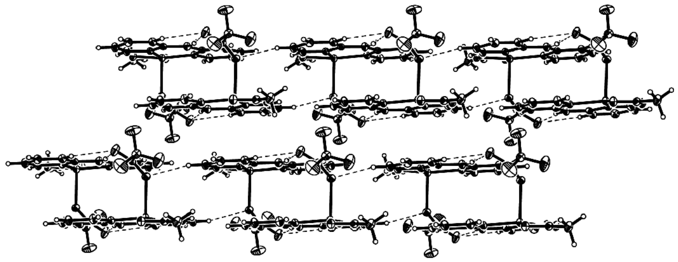


Figure 2
A packing diagram for (I). Hydrogen bonds are shown as dashed lines.

0.0125 (2) Å and the maximum deviation is only 0.0143 (3) Å for atoms O1 and O2. The structure of the complex is very similar to the structure described by Ugozzoli *et al.* (1997). The Cu^{II} center is displaced out of the basal plane by 0.1796 (13) Å in the direction of atom O3 of the trifluoroacetate group, which occupies the apical position of the pyramidal geometry, with a Cu—O3 distance of 2.264 (2) Å. This means that the Cu atom together with the surrounding N1, N3, O1 and O2 atoms are almost coplanar, the O3—Cu—O1 and O3—Cu—O2 angles of 92.39 (10) and 91.31 (9)°, respectively, being very close to a right angle. The other, uncoordinated, O atom (O4) of the trifluoroacetic group is far from the Cu^{II} center, at a distance of 4.060 (3) Å. It plays an important role in forming molecular pairs through hydrogen bonding. The bite angle of the dpa ligand, N1—Cu—N3, is 94.57 (10)° and is similar to that in other dpa complexes (Muñoz *et al.*, 1993), where the angle lies in the range 86–96°. The two rings of the dpa ligand are essentially coplanar, with a dihedral angle of only 0.97 (17)°. The molecules are associated together in pairs related by a crystallographic center of symmetry and are held together *via* stacking interactions between the rings of dpa and through the hydrogen bonds $N2—H2B\cdots O4^{i}$ [$D\cdots A$ = 2.785 (3) Å and $D—H\cdots A$ = 170°; symmetry code: (i) $-x$, $1-y$, $1-z$] and $C4—H4A\cdots O4^{i}$ [$D\cdots A$ = 3.204 (10) Å and $D—H\cdots A$ = 136°], as shown in Fig. 2. The pairs are linked into layers by the $C2—H2A\cdots O3^{ii}$ hydrogen bond [$D\cdots A$ = 3.315 (10) Å and $D—H\cdots A$ = 168°; symmetry code: (ii) $1-x$, $-y$, $1-z$], but there are no classic hydrogen-bond contacts between the layers, in which van der Waals interactions are dominant and contribute to the crystal stability. Selected bond lengths and angles are listed in Table 1.

The structure analysis indicated that the title complex is a representative example for the pyramidal structure of Cu^{II} complexes with dpa as a ligand. The distortion from square-pyramidal geometry can best be expressed by the value of the parameter τ. For five-coordinated complexes, this describes the relative amount of trigonality: $\tau = 0$ for a square pyramid and $\tau = 1$ for a trigonal bipyramid (Addison *et al.*, 1984). In the case of (I), $\tau = \{[N3—Cu—O1] - [N1—Cu—O2]\}/60 = 0.026$, which is relatively close to that of an ideal square-pyramidal structure ($\tau = 0$).

Experimental

$Cu(CF_3CO_2)_2$ and dpa (1:1 molar ratio) were placed together in a flask. Methanol was used as solvent and anhydrous acetic acid (in a 1:1 molar ratio with dpa) was added slowly. The mixture was stirred for 2 h at room temperature under a nitrogen atmosphere, kept overnight and then filtered. Black crystals of (I) were obtained by recrystallization from a mixture of methanol and ether.

Crystal data

$[Cu(C_2F_3O_2)(C_2H_3O_2)(C_{10}H_9N_3)]$
$M_r = 406.81$
Triclinic, $P\bar{1}$
$a = 8.2533$ (11) Å
$b = 8.7907$ (15) Å
$c = 11.3643$ (14) Å
$\alpha = 87.199$ (15)°
$\beta = 84.592$ (14)°
$\gamma = 73.620$ (11)°
$V = 787.3$ (2) Å^3

$Z = 2$
$D_x = 1.716$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 30 reflections
$\theta = 2.0$–25.0°
$\mu = 1.45$ mm^{-1}
$T = 293$ (2) K
Block, black
0.56 × 0.50 × 0.34 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.456$, $T_{max} = 0.612$
2985 measured reflections
2775 independent reflections
2332 reflections with $I > 2\sigma(I)$

$R_{int} = 0.012$
$\theta_{max} = 25.0°$
$h = -9 \rightarrow 0$
$k = -10 \rightarrow 10$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.125$
$S = 1.03$
2775 reflections
239 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.014 (3)

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Table 1
Selected geometric parameters (Å, °).

Cu—N1	1.945 (2)	Cu—O1	2.005 (2)
Cu—N3	1.953 (3)	Cu—O3	2.262 (2)
Cu—O2	1.993 (2)		
N1—Cu—N3	94.58 (11)	N1—Cu—O3	99.66 (9)
N3—Cu—O2	99.61 (10)	N3—Cu—O3	96.25 (10)
N1—Cu—O1	98.99 (10)	O2—Cu—O3	91.21 (10)
O2—Cu—O1	64.90 (9)	O1—Cu—O3	92.31 (10)

H atoms were positioned geometrically, with N—H = 0.86 Å and C—H = 0.93 Å, and refined in the riding-model approximation, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.

Akhter, P., Fitzsimmons, P. & Hathaway, B. J. (1991). *Acta Cryst.* C**47**, 308–310.

Bruker (2000). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.

Enraf–Nonius (1989). *CAD*-4 *Software*. Enraf–Nonius, Delft, The Netherlands.

Hill, S. J., Hubberstey, P. & Li, W. S. (1997). *Polyhedron*, **16**, 2447–2450.

Jacobson, R. A. & Jensen, W. P. (1986). *Inorg. Chim. Acta*, **114**, L9–10.

Johnson, J. E. & Jacobson, R. A. (1973). *J. Chem. Soc. Dalton Trans.* pp. 580–584.

Lai, S. Y., Lin, T. W., Chen, Y. H., Wang, C. C., Lee, G. H., Yang, M. H., Leung, M. K. & Peng, S. M. (1999). *J. Am. Chem. Soc.* **121**, 250–254.

Li, H., Lee, G. H. & Peng, S. M. (2003). *Inorg. Chem. Commun.* **6**, 1–4.

Muñoz, M. C., Lazaro, J. M., Faus, J. & Julve, M. (1993). *Acta Cryst.* C**49**, 1756–1761.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Peng, S. M., Wang, C. C., Jang, Y. L., Chen, Y. H., Li, F. Y., Mou, C. Y. & Leung, M. K. (2000). *J. Magn. Magn. Mater.* **209**, 80–83.

Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.

Sheu, J. T., Liu, C. C., Chao, I., Wang, C. C. & Peng, S. M. (1996). *Chem. Commun.* pp. 315–316.

Shieh, S. J., Chou, C. C., Lee, G. H., Wang, C. C. & Peng, S. M. (1997). *Angew. Chem. Int. Ed. Engl.* **36**, 56–59.

Ugozzoli, F., Lanfredi, A. M. M., Marsich, N. & Camus, A. (1997). *Inorg. Chim. Acta*, **256**, 1–7.

Wu, L. P., Keniry, M. E. & Hathaway, B. J. (1992). *Acta Cryst.* C**48**, 35–37.

Youngme, S., Chandavong, K., Pakawatchai, C., Zhou, Z. Y. & Fun, H.-K. (1998). *Acta Cryst.* C**54**, 1221–1223.

Youngme, S., Chinnakali, K., Chankraproma, S. & Fun, H.-K. (1999). *Acta Cryst.* C**55**, 899–901.

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