trans-Diaquabis(6-hydroxypicolinato-$\kappa^2 N,O^2$)copper(II)

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In the title compound, [Cu(C$_6$H$_4$NO$_3$)$_2$(H$_2$O)$_2$], the Cu^{II} ion lies on an inversion centre and has an elongated octahedral environment, equatorially *trans*-coordinated by two *N,O*-bidentate picolinate ligands and axially coordinated by two water O atoms. The complex molecules form layers, which are linked by O—H···O hydrogen bonds between the aqua ligands and neighbouring carboxylate groups. An intramolecular hydrogen bond between the coordinated carboxylate O atom and the hydroxy H atom is also observed.

Comment

Copper complexes play an important role in catalysing enzymatic activity, and much interest has been shown in copper complexes of organic acids because of their special biocatalytic functions (Hong *et al.*, 2002). Recently, considerable attention has been paid to the complexes of hydroxypicolinates, which pose structural ambiguities since they display a number of possible bonding modes (Constantino *et al.*, 1994; Gatto *et al.*, 1998). It is well known that the incorporation of carboxylic acid groups into coordination compounds gives interesting supramolecular architectures (Puddephatt *et al.*, 2002). The 6-hydroxypicolinate ligand (HP) is a potential chelate with interesting possibilities, exhibiting either *N,O*-chelation [through the pyridine (py) N atom and the carboxylate group, forming a five-membered chelate ring] (Nogueira *et al.*, 2000) or *N,O,O*-chelation (through the pyridine N atom and the carboxylate group, and further through the deprotonated hydroxy group as a bridging ligand). The latter coordination mode was reported for [Mn$_2$(μ-O)(C$_6$H$_3$NO$_3$)$_2$(py)$_4$]·H$_2$O by Bian *et al.* (2004). Owing to the inherent coordination and hydrogen-bonding donor/acceptor functionalities, this dimanganese complex forms a three-dimensional structure. To the best of our knowledge, no crystal structures of metal complexes with the HP ligand, other than those with dimanganese (see above), have been reported to date, although there are several crystal structures of complexes with analogous ligands, *viz.* the 2-, 3-

and 4-hydroxy derivatives (Quintal *et al.*, 2000). We report here our efforts to establish the preferred coordination mode of HP to copper(II) in the structure of the title compound, (I).

(I)
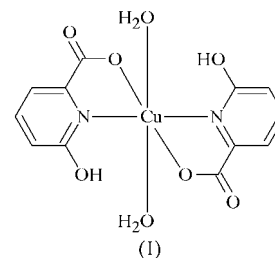
An *ORTEP-3* (Farrugia, 1997) view of (I) and a packing diagram are shown in Figs. 1 and 2, respectively, and selected bond lengths and angles are given in Table 1. Compound (I) displays a distorted octahedral coordination geometry, with the metal ion at a centre of inversion. The two bidentate ligands are necessarily *trans* to one another, and coordinate to the central metal ion through the pyridine N atoms and the carboxylate O atoms to form five-membered rings in the equatorial plane. Two aqua O atoms complete the octahedron at the axial positions.

The coordination bond length in the axial direction [Cu1—O4 = 2.491 (2) Å] is longer than the bond lengths in the equatorial plane [Cu1—O1 = 1.9364 (16) Å and Cu1—N1 = 1.9931 (18) Å]. A similar behaviour is found for both *trans*-bis-(5-*n*-butylpyridine-2-carboxylato-$\kappa^2 N,O$)bis(methanol-κO)-copper(II) [2.596 (3) and 1.952 (2) Å, respectively; Okabe *et al.*, 2002] and hydrated bis(pyridine-2-carboxylato)-copper(II) [2.752 (2) and 1.940 (2) Å, respectively; Faure *et al.*, 1973]. Long bonds in the axial direction, compared with those in the equatorial plane, are usually observed in copper complexes of octahedral coordination geometry and are usually explained by a Jahn–Teller effect. This agrees with the electron paramagnetic resonance (EPR) spectrum of the title compound, which resembles those of the analogously distorted octahedral Cu^{II} complexes (Hathaway & Billing, 1970).

As shown in Table 1, the Cu1—O1 distance is slightly shorter than the Cu1—N1 distance. This effect is usually observed for the metal complexes of analogous compounds, such as bis(μ-6-hydroxypicolinato)-μ-oxo-bis[dipyridineman-ganese(III)] monohydrate [Mn1—O2$_{eq}$ = 1.939 (2) Å and
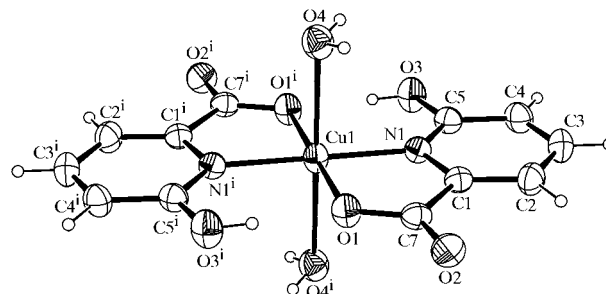
Figure 1
A view of compound (I), with displacement ellipsoids shown at the 40% probability level. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]
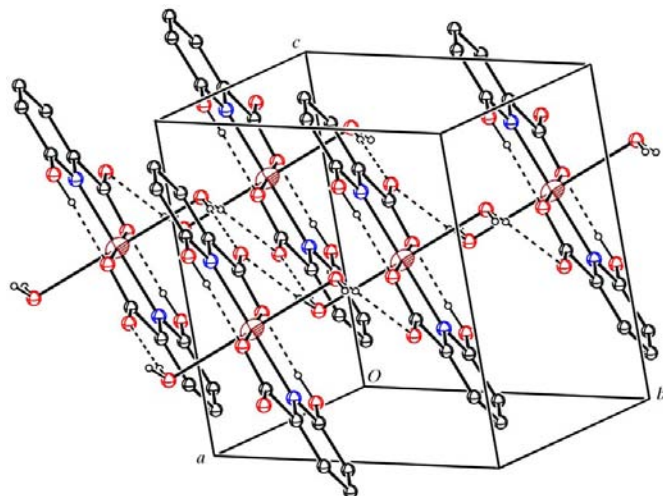
metal-organic compounds

Figure 2
A packing diagram for (I). Hydrogen bonds are indicated by dashed lines.

Mn1—N1 = 2.094 (2) Å; Bian *et al.*, 2004], (5-*n*-butylpyridine-2-carboxylato)copper(II) [Cu—O_{eq} = 1.952 (2) Å and Cu—N = 1.977 (2) Å; Okabe *et al.*, 2002] and *trans*-bis(isoquinoline-3-carboxylato-$\kappa^2 N,O$)bis(methanol-κO)copper(II) [Cu—O_{eq} = 1.963 (2) Å and Cu—N = 1.979 (2) Å; Okabe *et al.*, 2004]. In the title compound, the angles around the Cu atom are slightly distorted from an ideal octahedral configuration [O1—Cu1—N1 = 83.07 (7)°]. Similar bond angles are observed in some related metal complexes, such as *trans*-bis-(isoquinoline-3-carboxylato-$\kappa^2 N,O$)bis(methanol-κO)copper(II) [O—Cu—N = 83.77 (7)°; Okabe *et al.*, 2004] and *trans*-diaquabis(3-hydroxypicolinato)zinc(II) [O—Zn—N = 79.3 (1)°; Di Marco *et al.*, 2004].

The molecular packing of (I) is shown in Fig. 2. The intramolecular O3—H3A···O1[i] hydrogen bonds (Table 2) between the carbonyl and hydroxy groups of the bidentate ligands reinforce the planarity of the equatorial groupings. The water molecules coordinated to the Cu atom in the apical position participate in two hydrogen bonds, O4—H1A···O2[ii] and O4—H1B···O2[iii], which link the layers to form a three-dimensional structure (Fig. 2).

Experimental

HP was dissolved in aqueous ammonia and refluxed for 2 h. Upon complete dissolution of the solid, the solvent was evaporated under vacuum to dryness. The residue was redissolved in methanol, and copper(II) acetate in methanol in a 2:1 molar ratio was added with vigorous stirring at 333 K. After stirring at this temperature for 2 h, the mixture was filtered and the deep-blue filtrate was left to stand, allowing slow evaporation of the solvent at room temperature. Finally, blue crystals of (I) were obtained by repeated recrystallization from acetonitrile at room temperature. Analysis calculated for $C_{12}H_{12}CuN_2O_8$: C 38.36, H 3.22, N 7.46%; found: C 38.40, H 3.32, N 7.47%. IR (KBr pellet, cm^{-1}): 3420 (*b*), 3093 (*m*), 2792 (*sh*), 2597 (*sh*), 1666 (*s*), 1617 (*vs*), 1575 (*s*), 1394 (*s*), 1319 (*vs*), 1253 (*s*), 1149 (*m*), 1070 (*w*), 1018 (*m*), 827 (*s*), 746 (*s*), 554 (*m*), 431 (*m*). EPR (77.0 K): g1 = 2.26, g2 = 2.07 and g3 = 2.01.

Crystal data

[Cu($C_6H_4NO_3$)$_2$(H_2O)$_2$]	Mo $K\alpha$ radiation
M_r = 375.78	Cell parameters from 7424
Triclinic, $P\bar{1}$	reflections
a = 6.1036 (8) Å	θ = 2.4–27.2°
b = 7.2946 (11) Å	μ = 1.65 mm^{-1}
c = 8.5571 (13) Å	T = 296 K
α = 99.605 (12)°	Prism, blue
β = 92.776 (12)°	0.24 × 0.18 × 0.14 mm
γ = 113.758 (11)°	
V = 340.98 (9) $Å^3$	
Z = 1	
D_x = 1.830 Mg m^{-3}	

Data collection

Stoe IPDS-II diffractometer	1190 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.057
Absorption correction: by integration (*X-RED*; Stoe & Cie, 2002)	θ_{max} = 26.0°
	$h = -7 \rightarrow 7$
T_{min} = 0.726, T_{max} = 0.826	$k = -8 \rightarrow 8$
5001 measured reflections	$l = -10 \rightarrow 10$
1341 independent reflections	

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)]$ = 0.029	
$wR(F^2)$ = 0.071	
S = 0.99	$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2]$
1341 reflections	where $P = (F_o^2 + 2F_c^2)/3$
118 parameters	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max}$ = 0.38 e $Å^{-3}$
	$\Delta\rho_{min}$ = −0.35 e $Å^{-3}$

Table 1
Selected geometric parameters (Å, °).

C5—O3	1.328 (3)	N1—Cu1	1.9931 (18)
C7—O2	1.218 (3)	O1—Cu1	1.9364 (16)
C7—O1	1.290 (3)	O4—Cu1	2.491 (2)
O3—C5—N1	120.3 (2)	O1—Cu1—N1	83.09 (7)
O2—C7—O1	124.2 (2)	O1[i]—Cu1—O4	90.57 (8)
O2—C7—C1	121.0 (2)	O1—Cu1—O4	89.43 (8)
O1—C7—C1	114.81 (19)	N1—Cu1—O4	89.99 (7)
N1—C1—C7—O2	178.7 (2)	N1—C1—C7—O1	−1.0 (3)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3A···O1[i]	0.78 (3)	1.86 (3)	2.631 (2)	172 (3)
O4—H1A···O2[ii]	0.77 (4)	2.14 (4)	2.902 (3)	168 (4)
O4—H1B···O2[iii]	0.75 (4)	2.09 (4)	2.831 (3)	169 (4)

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

The three aromatic H atoms were refined using a riding model [with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C)]. The O-bound H atoms were refined freely.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1676). Services for accessing these data are described at the back of the journal.

References

Bian, G.-Q., Kuroda-Sowa, T., Konaka, H., Maekawa, M. & Munakata, M. (2004). *Acta Cryst.* C**60**, m338–m340.

Constantino, V. L., Oliverie, L. C., Santos, P. S. & Toma, H. (1994). *Transition Met. Chem.* **19**, 103–106.

Di Marco, V. B., Tapparo, A., Dolmella, A. & Bombi, G. G. (2004). *Inorg. Chim. Acta*, **357**, 135–142.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Faure, P. R., Loiseleur, H. & Thomas-David, G. (1973). *Acta Cryst.* B**29**, 1890–1893.

Gatto, S., Gerber, T. I. A., Bandoli, G., Perils, J. & Preez, J. G. H. (1998). *Inorg. Chim. Acta*, **269**, 235–240.

Hathaway, B. J. & Billing, D. E. (1970). *Coord. Chem. Rev.* **5**, 143–207.

Okabe, N., Muranishi, Y. & Odoko, M. (2004). *Acta Cryst.* C**60**, m345–m347.

Okabe, N., Muranishi, Y. & Wada, Y. (2002). *Acta Cryst.* C**58**, m511–m513.

Puddephatt, J., Qin, Z. & Jennings, M. C. (2002). *Inorg. Chem.* **41**, 5174–5185.

Quintal, S. M. O., Nogueria, H. I. S., Felix, V. & Drew, M. G. B. (2000). *New J. Chem.* **24**, 511–517.

Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.

Stoe & Cie (2002). *X-AREA* and *X-RED*. Stoe & Cie, Darmstadt, Germany.