

Aqua[bis(pyrimidin-2-yl- κ N)amine]- (carbonato- κ^2 O,O')copper(II) dihydrate

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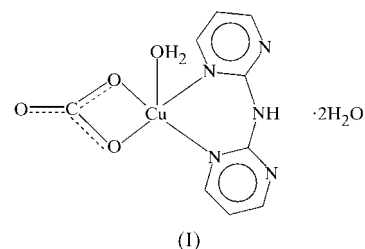
The title mononuclear complex, $[\text{Cu}(\text{CO}_3)(\text{C}_8\text{H}_7\text{N}_5)(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$, was obtained by fixation of CO_2 by a mixture of copper(II) tetrafluoroborate and the ligand bis(pyrimidin-2-yl)amine in ethanol/water. The Cu^{II} ion of the complex has a distorted square-pyramidal environment, with a basal plane formed by two N atoms of the ligand and two chelating O atoms of the carbonate group, while the apical position is occupied by the O atom of the coordinating water molecule. In the solid state, hydrogen-bonding interactions are dominant, the most unusual being the Watson–Crick-type coplanar ligand pairing through two $\text{N}—\text{H} \cdots \text{N}$ bonds. Lattice water molecules also participate in hydrogen bonding.

Comment

The title compound, (I), was obtained in the course of our ongoing research into ligands which can act as a trap for CO_2 by the insertion of atmospheric CO_2 into coordination compounds. Insertion reactions of CO_2 into metal–ligand bonds are not uncommon, and in the past few years many review papers have been published on the subject (Gibson, 1999; Walther *et al.*, 1999; Yin & Moss, 1999). Several dinuclear copper(II) compounds have been synthesized by means of fixation of CO_2 from air (Nishida *et al.*, 1999; Kitajima *et al.*, 1993; Kruger *et al.*, 1995; Youngme *et al.*, 2000). In order to build and control larger aggregates, we have started a research programme in which the ligands used also act as hydrogen-bond donors or acceptors.

The recently developed ligand bis(pyrimidin-2-yl)amine (abbreviated as dipm; Yao *et al.*, 2000) is a prototype, as it may form Watson–Crick-type hydrogen bonds, as already shown in the literature with the first-generation ligand 2-amino-pyrimidine (van Albada, Quiroz-Castro *et al.*, 2000; van

Albada, Smeets *et al.*, 2000). Continuing this work, we present here the crystal structure of the title complex, (I).



A structural analysis of (I) shows a neutral $[\text{Cu}(\text{dipm})(\text{CO}_3)(\text{H}_2\text{O})]$ unit and two non-coordinating water molecules. The Cu^{II} anion has a distorted square-pyramidal environment, with a basal plane formed by two N atoms of the dipm ligand and two O atoms of the carbonate group [basal $\text{Cu}—\text{N/O}$ distances vary from 1.9410 (16) to 1.9852 (17) Å]. The apical position is occupied by the O atom of the coordinating water molecule at a distance of 2.3004 (18) Å.

The distortion from square-pyramidal geometry can best be expressed with the parameter τ [for five-coordinate complexes, τ describes the relative amount of trigonality: $\tau = 0$

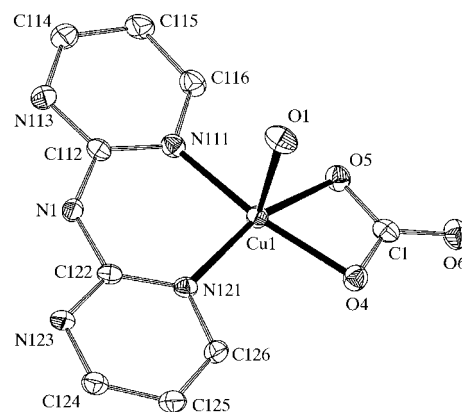


Figure 1

A view of the molecule of (I) with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The lattice water molecules have been omitted for clarity.

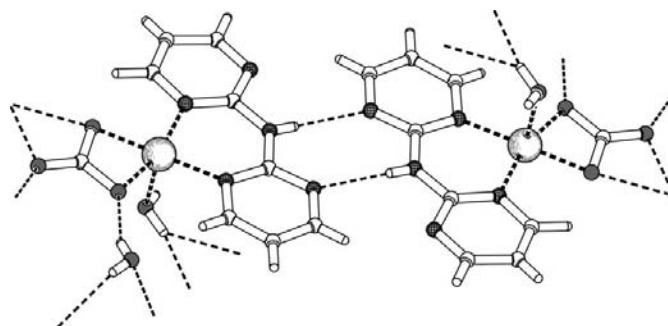


Figure 2

A plot showing a fragment of the hydrogen-bonded network in (I).

for a square pyramid and $\tau = 1$ for a trigonal bipyramid (Addison *et al.*, 1984)], and in the case of (I), $\tau = 0.045$, representing a very small distortion from a square pyramid and indicating a $d_{x^2-y^2}$ orbital ground state.

The aromatic ring–ring stacking interactions between neighbouring bipyrimidine rings, which help to stabilize the lattice structure, are characterized by a centroid–centroid distance of 3.59 (3) Å.

The Cu geometry in (I) is related to that in [Cu(dpyam)-(CO₃)(H₂O)]·2H₂O (dpyam is di-2-pyridylamine; Akhter *et al.*, 1991). In this latter structure, the distortion is slightly larger ($\tau = 0.097$).

Compound (I) has an additional hydrogen-bonding feature which generates dinuclear units; the amino N atom forms a Watson–Crick-type hydrogen bond with the neighbouring ring N atom [N1···N123 = 2.979 (3) Å] (Fig. 2). Additional hydrogen-bonding contacts occur between the O atom of the axial water molecule and the non-coordinating O atoms of a neighbouring carbonate anion and a lattice water molecule [O1···O5 = 3.018 (3) Å, O1···O6 = 2.841 (3) Å (a bifurcated hydrogen bond) and O1···O2 = 2.933 (3) Å]. The lattice water molecules form hydrogen bonds with neighbouring carbonate anions and uncoordinated water molecules, the O···O distances varying from 2.785 (3) to 2.960 (4) Å.

The IR spectrum of (I) clearly shows the out-of-plane mode of the CO₃ dianion, with a medium to strong band at 807 cm⁻¹, and this matches well with the bands observed in the literature (van Albada, Mutikainen *et al.*, 2000; Youngme *et al.*, 2000) for chelating carbonate ligands.

Experimental

The dipm ligand was synthesized according to the literature method of Yao *et al.* (2000). Metal salts and solvents were obtained commercially and were used without further purification. Copper(II) tetrafluoroborate (0.31 mg, 1.3 mmol) and dipm (0.22 mg, 1.3 mmol) were each dissolved in ethanol/water (1:1, 10 ml) and the solutions mixed carefully together. A few drops of 2 M sodium hydroxide solution were then added gradually, so that no precipitate was formed and the pH was approximately 5. The mixture was filtered to remove any solid particles and was then placed in a desiccator under a CO₂ atmosphere generated from solid CO₂ (van Albada, Mutikainen *et al.*, 2000). After a period of a few weeks to one month, long blue needles of (I) separated. The crystals were filtered off and washed with ethanol. Attempts to synthesize the compounds by the addition of sodium carbonate or potassium carbonate were unsuccessful. Satisfactory elemental analyses were obtained. A crystal was selected for X-ray measurements and was mounted on a glass fibre using the oil-drop method (Kottke & Stalke, 1993).

Crystal data

[Cu(CO₃)(C₈H₇N₅)(H₂O)]·2H₂O
M_r = 350.78
 Monoclinic, *P*2₁/*c*
a = 5.8520 (12) Å
b = 12.897 (3) Å
c = 16.801 (3) Å
 β = 90.87 (3)°
V = 1267.9 (4) Å³
Z = 4

D_x = 1.838 Mg m⁻³
 Cu *K*α radiation
 Cell parameters from 25 reflections
 θ = 12–27°
 μ = 2.83 mm⁻¹
T = 193 (2) K
 Column, blue
 0.40 × 0.25 × 0.25 mm

Table 1

Selected geometric parameters (Å, °).

Cu1–O1	2.3004 (18)	Cu1–N111	1.973 (2)
Cu1–O4	1.9852 (17)	Cu1–N121	1.971 (2)
Cu1–O5	1.9410 (16)		
O1–Cu1–O4	96.53 (7)	O4–Cu1–N111	164.43 (7)
O1–Cu1–O5	99.56 (7)	O4–Cu1–N121	100.25 (8)
O1–Cu1–N111	89.84 (8)	O5–Cu1–N111	97.79 (8)
O1–Cu1–N121	94.83 (7)	O5–Cu1–N121	161.79 (8)
O4–Cu1–O5	67.19 (7)	N111–Cu1–N121	93.33 (8)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–H1···N123 ⁱ	0.88	2.10	2.979 (3)	179
O1–H11···O5 ⁱⁱ	0.84 (3)	2.39 (3)	3.017 (3)	132 (2)
O1–H11···O6 ⁱⁱ	0.84 (3)	2.02 (3)	2.841 (3)	167 (3)
O1–H12···O2	0.83 (3)	2.14 (3)	2.933 (3)	160 (3)
O2–H21···O3	0.83 (3)	2.10 (3)	2.888 (3)	159 (4)
O2–H22···O4 ⁱⁱⁱ	0.83 (3)	2.10 (3)	2.886 (3)	156 (3)
O3–H31···O2 ^{iv}	0.83 (3)	2.14 (3)	2.960 (3)	171 (4)
O3–H32···O6 ^v	0.83 (3)	1.95 (4)	2.785 (4)	177 (4)

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

Data collection

Enraf–Nonius CAD-4
 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
*T*_{min} = 0.400, *T*_{max} = 0.493
 2955 measured reflections
 2144 independent reflections
 2079 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.041
 θ_{\max} = 65°
h = –6 → 6
k = –15 → 15
l = –19 → 19
 3 standard reflections
 every 200 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.036
wR (*F*²) = 0.103
S = 1.03
 2144 reflections
 208 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0754P)^2 + 1.1584P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.52 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.33 \text{ e } \text{Å}^{-3}$

Water H atoms were located in a difference map and refined using restraints for the O–H and H···H distances of 0.83 (1) and 1.34 (1) Å, respectively. Other H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms, at distances of 0.88 and 0.95 Å for N–H and C–H, respectively. For all H atoms, *U*_{iso}(H) = 1.2*U*_{eq}(carrier atom).

Data collection: *CAD-4 Software* (Nonius, 1998); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1995) and *PLATON* (Spek, 2001); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1478). Services for accessing these data are described at the back of the journal.

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