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A neutral macrocyclic binuclear copper(II) complex of the deprotonated form of the ligand *N,N′*-bis(pyridin-2-ylmethyl)pyrazine-2,3-dicarboxamide

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In the complex, bis[μ-*N,N′*-bis(pyridin-2-ylmethyl)pyrazine-2,3-dicarboxamido(2-)]dicopper(II) octahydrate, $[Cu_2(C_{18}H_{16}N_6O_2)_2]\cdot 8H_2O$, the pyrazine ligand coordinates in a tridentate–bidentate manner as L^{2-}. A neutral centrosymmetric binuclear macrocyclic structure is formed, with the Cu atoms having extremely distorted square-pyramidal geometry.

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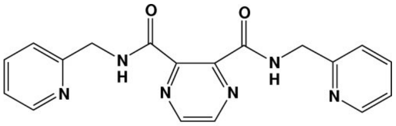
Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.006 Å
H-atom completeness 64%
Disorder in solvent or counterion
R factor = 0.045
wR factor = 0.114
Data-to-parameter ratio = 12.3

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

Comment

The ligand *N,N′*-bis(pyridin-2-ylmethyl)pyrazine-2,3-dicarboxamide (H_2L) has been shown to coordinate to various first-row transition metals in a number of coordination modes. The structure of two polymorphic forms of H_2L, triclinic (Cati *et al.*, 2004) and orthorhombic (Cati & Stoeckli-Evans, 2004*a*), have also been reported.

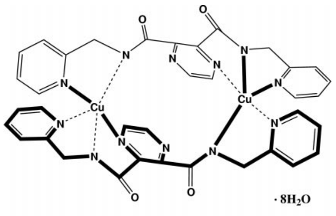


H_2L

Binuclear copper(II) complexes with the ligand coordinating in the bis-tridentate coordination mode (HL^-) have been observed (Cati *et al.*, 2004; Cati & Stoeckli-Evans (2004*b*). Structures of both copper(II) (Hausmann *et al.*, 2003; Cati *et al.*, 2004) and nickel(II) (Cati *et al.*, 2004) [2 × 2] grid complexes have been described with the ligand coordinating in a bis-tridentate manner as HL^-. Hausmann *et al.* (2003) also reported the structure of a dimeric $Cu(BF_4)_2$ complex with the ligand in a zwitterion form (H_2L) and coordinating in an unusual tridentate(N_3)–monodentate(O) fashion. A similar complex with $Cu(NO_3)_2$ has been observed by Cati & Stoeckli-Evans (2004*c*). The same coordination mode has been observed in the neutral dimeric complex $[Cu_2(H_2L)_2(SO_4)_2]\cdot 6H_2O$ (Cati & Stoeckli-Evans, 2004*d*). However here, in contrast to the $Cu(BF_4)_2$ or $Cu(NO_3)_2$ complexes, there is no intramolecular hydrogen bond involving the carbonyl O atom of the coordinated (pyridin-2-ylmethyl)amide moiety (O2) and the pyridinium N—H atom of the protonated (pyridinium-2-ylmethyl)amide moiety (N6H), where the carbonyl O atom coordinates to the symmetry-related Cu atom. The structure of a mononuclear cobalt(III) complex, with the ligand again in the zwitterion form and coordinating in a tridentate fashion, has also been reported (Cati & Stoeckli-Evans, 2004*e*).

In the title complex, (I) (Fig. 1), formed by the reaction of CuF_2 or $CuCO_3\cdot Cu(OH)_2$ with ligand H_2L, it can be seen that the ligand coordinates in a tridentate-bidentate mode as L^{2-}.

This gives rise to the formation of a neutral centrosymmetric binuclear macrocyclic structure. Selected geometric parameters are given in Table 1. The copper atoms are coordinated by five N atoms, and have extremely distorted square-pyramidal geometries with a τ value (Addison *et al.*, 1984) of 0.38 ($\tau = 0$ for SP and = 1 for TBP). This contrasts with the situation observed in the $Cu(BF_4)_2$, $Cu(NO_3)_2$ and $CuSO_4$ binuclear complexes mentioned above, where the τ values are *ca* 0.05. There is a considerable difference in the Cu1—N distances involving the amide N atoms. Bond distance Cu1—N3 [1.908 (3) Å], in the basal plane of the square pyramid, is much shorter than the apical distance Cu—N5 [2.100 (3) Å]. The other bond distances and angles are comparable to those observed in the binuclear copper(II) complexes.



(I)

The macrocyclic complex is formed with the ligand having an L-shape, giving rise to a box-like structure (Fig. 1). The (pyridin-2-ylmethyl)amide moieties are relatively planar as shown by the torsion angles about bonds N3—C5 and N5—C12 (Table 1). The pyridine ring involving atom N4 is inclined to the pyrazine ring by 21.4 (2)°, while the pyridine ring involving atom N6 is inclined to the pyrazine ring by 64.2 (2)°. The dihedral angle between the two pyridine rings is 81.3 (2)°. Within the macrocycle, the pyrazine rings are parallel and separated by 3.60 (1) Å.

The complex crystallizes with eight water molecules of crystallization, two of which are disordered over four sites (Fig. 2). The water H atoms could not be located; however, from the non-bonded O···O distances it is probable that symmetry-related complex molecules are linked by hydrogen bonds (further details are gven in the CIF).

Experimental

The synthetic and analytical details concerning the ligand, H_2L, have been described elsewhere (Cati *et al.*, 2004). The title complex could be synthesized by two methods. (i) By adding $CuF_2{\cdot}2H_2O$ (0.021 g, 0.156 mmol) to a solution of H_2L (54 mg, 0.156 mmol) in 25 ml of CH_3CN and 2 ml of H_2O. The resulting green suspension was refluxed for 5 h then filtered directly on celite through a chromatography tube. The filtrate was left to cool and the solvent to slowly evaporate. After several days, green block-like crystals appeared (yield 8 mg, 11%). (ii) By adding an excess of $CuCO_3{\cdot}Cu(OH)_2$ (344.9 mg, 1.56 mmol) to a solution of H_2L (54 mg, 0.156 mmol) in 15 ml of H_2O. The mixture was stirred for 1 h at room temperature. 20 ml of MeOH were added and the resulting green suspension heated to reflux for 4 h. The solution was then filtered and the filtrate allowed to cool and the solvent to slowly evaporate. After several days green rod-like crystals appeared (yield 60 mg, 85%).

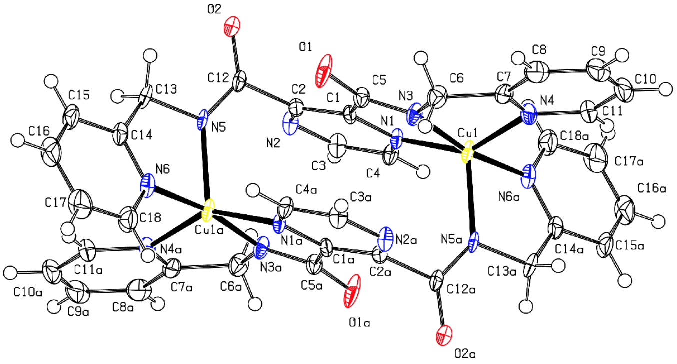


Figure 1
View of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The water molecules of crystallization have been omitted for clarity. [Symmetry code: (*a*) $-x$, $1 - y$, $1 - z$.]

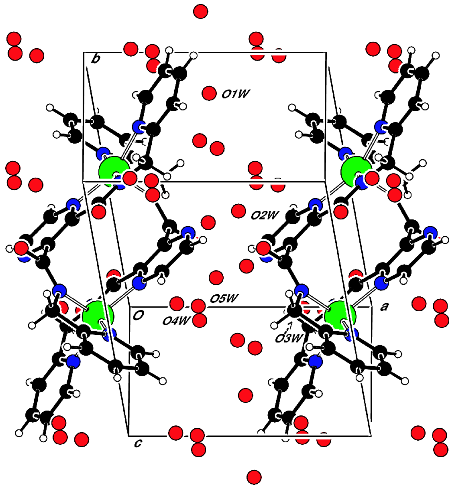


Figure 2
A view of the molecular packing of (I).

Crystal data

$[Cu_2(C_{18}H_{16}N_6O_2)_2]{\cdot}8H_2O$
$M_r = 963.91$
Triclinic, $P\overline{1}$
$a = 9.3201$ (10) Å
$b = 9.9743$ (12) Å
$c = 11.8877$ (13) Å
$\alpha = 114.331$ (13)°
$\beta = 90.178$ (13)°
$\gamma = 100.199$ (13)°
$V = 987.46$ (19) Å^3

$Z = 1$
$D_x = 1.621$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4800 reflections
$\theta = 1.9$–25.9°
$\mu = 1.16$ mm^{-1}
$T = 153$ (2) K
Block, green
0.35 × 0.30 × 0.30 mm

Data collection

Stoe IPDS diffractometer
φ oscillation scans
Absorption correction: none
7722 measured reflections
3577 independent reflections
2697 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.067$
$\theta_{\rm max} = 25.9°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.114$
$S = 0.97$
3577 reflections
290 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0633P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.64$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.76$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N3	1.908 (3)	Cu1—N5^{i}	2.100 (3)
Cu1—N6^{i}	1.997 (3)	O1—C5	1.240 (4)
Cu1—N1	2.062 (3)	O2—C12	1.260 (4)
Cu1—N4	2.081 (3)		
N3—Cu1—N6^{i}	169.89 (12)	N1—Cu1—N4	147.15 (11)
N3—Cu1—N1	80.17 (12)	N3—Cu1—N5^{i}	109.34 (12)
N6^{i}—Cu1—N1	99.60 (12)	N6^{i}—Cu1—N5^{i}	80.40 (11)
N3—Cu1—N4	80.73 (12)	N1—Cu1—N5^{i}	108.66 (11)
N6^{i}—Cu1—N4	94.67 (13)	N4—Cu1—N5^{i}	102.79 (12)
C6—N3—C5—C1	173.7 (3)	C13—N5—C12—C2	−174.4 (3)
C5—N3—C6—C7	−151.9 (3)	C12—N5—C13—C14	−151.6 (3)

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

The C—H H atoms were included in calculated positions and treated as riding atoms: C—H distances = 0.95–0.99 Å, and $U_{\rm iso}$(H) = 1.2 times $U_{\rm eq}$(parent C atom). It was not possible to locate the H atoms of the water molecules of crystallization. A total of three full water molecules of crystallization could be located per asymmetric unit. A further region of diffuse electron density was equated to a water molecule, but disordered over two sites; occupancy O4*W*/O5*W* = 0.59 (3)/0.41 (3). Atom O1 appeared to be disordered but attempts to correct for this by splitting the atom did not succeed.

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 2000); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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