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A macrocyclic binuclear copper(II) complex 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-dicarboxamide]bis[sulfatocopper(II)] hexahydrate, $[Cu_2(C_{18}H_{16}N_6O_2)_2(SO_4)_2]\cdot 6H_2O$, the pyrazine ligand coordinates in a tridentate–monodentate manner with the Cu atoms having N_3O_2 chromophores. A neutral centrosymmetric binuclear macrocyclic structure is formed, with the Cu atoms having almost perfect square-pyramidal geometry.

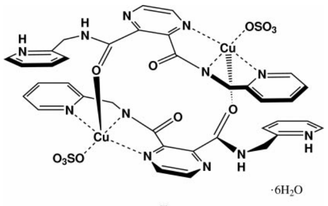
Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.005 Å
R factor = 0.029
wR factor = 0.060
Data-to-parameter ratio = 11.7

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

Comment

Structures of both copper(II) (Hausmann *et al.*, 2003; Cati *et al.*, 2004) and nickel(II) (Cati *et al.*, 2004) complexes of the ligand, *N,N′*-bis(pyridin-2-ylmethyl)pyrazine-2,3-dicarboxamide, (H_2L), including [2 × 2] grids, have been described recently. Cati *et al.* (2004) also described the synthesis of H_2L and the structure of its triclinic polymorph. The structure of the orthorhombic polymorph of H_2L has also been described recently (Cati & Stoeckli-Evans, 2004*a*). Hausmann *et al.* (2003) also reported the structure of a dimeric $Cu(BF_4)_2$ complex with the ligand in a zwitterion form 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*b*). The structure of a mononuclear cobalt(III) complex with the ligand in a zwitterion form, coordinating in a tridentate fashion, has also been reported (Cati & Stoeckli-Evans, 2004*c*). Binuclear copper(II) complexes with the ligand coordinating in the bis-tridentate coordination mode have also been observed (Cati *et al.*, 2004; Cati & Stoeckli-Evans, 2004*d*).



(I)

In the complex, (I), formed by the reaction of $CuSO_4$ with H_2L, it can be seen that the ligand coordinates in a tridentate-monodentate mode. This gives rise to the formation of a centrosymmetric neutral binuclear macrocyclic structure (Fig. 1). Selected geometric parameters are given in Table 1. The Cu atoms are coordinated by three N atoms and two O atoms; one O atom from the non-coordinated (pyridin-2-ylmethyl)amide moiety and the other from the sulfate anion. The Cu atoms have almost perfect square–pyramidal geometry, with a τ value (Addison *et al.*, 1984) of 0.05 (τ = 0 for SP, and = 1 for TBP). This is similar to the geometry observed in the $Cu(BF_4)_2$ and $Cu(NO_3)_2$ complexes

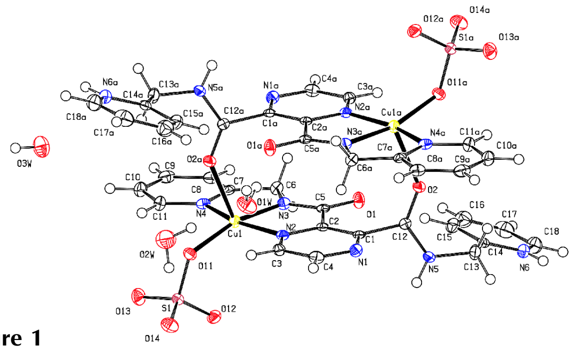


Figure 1

View of the complex, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (*a*) $1 - x, 1 - y, 1 - z$.]

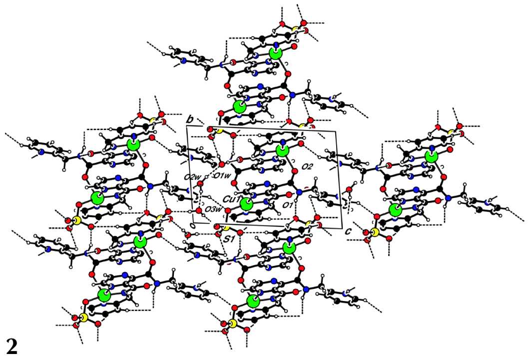


Figure 2

The molecular packing of the complex, viewed down the *a* axis. Hydrogen bonds are drawn as dashed lines.

mentioned above. The bond distances and angles are also comparable to those observed in these complexes.

The macrocyclic complex is formed with the ligand having an extended conformation, giving rise to a box-like structure (Fig. 1). This arrangement is similar to that observed in the $Cu(BF_4)_2$ or $Cu(NO_3)_2$ binuclear complexes. In the former the binuclear macrocycle is charged 4+, while in the latter it is charged 2+. This is in contrast to (I), which is neutral. The (pyridin-2-ylmethyl)amide moiety involving pyridine atom N4 is relatively planar, as shown by the dihedral angles about bonds C5—N3 and N3—C6 (Table 1). The pyridine ring involving atom N6, however, is twisted by almost 90° to the plane of the amide group, as shown by the dihedral angles involving bonds C13—N5 and N5—C12 (Table 1). The N4-pyridine ring and the N6-pyridine ring are inclined to the pyrazine ring by 0.9 (1) and 21.0 (1)°, respectively. The dihedral angle between the two pyridine rings is 20.2 (2)°. Within the macrocycle, the pyrazine rings are parallel to one another and separated by 3.61 (1) Å.

In contrast to the $Cu(BF_4)_2$ or $Cu(NO_3)_2$ complexes mentioned above, there is no intramolecular hydrogen bond involving the carbonyl O atom, O1, of the coordinated (pyridin-2-ylmethyl)amide moiety, and the NH H atom of the protonated N6-pyridine ring [(pyridinium-2-ylmethyl)amide moiety], where the carbonyl O atom, O2, coordinates to the symmetry related Cu atom. In (I), the protonated pyridine ring is twisted in the opposite direction and hydrogen bonds to a water molecule of crystallization ($O2W^{ii}$). The non-coordinated amide proton (N5—H) is hydrogen bonded to a sulfate O atom ($O12^{i}$) coordinated to a symmetry-related molecule; details are given in Table 2.

The complex crystallizes with six water molecules of crystallization. In the crystal structure, symmetry-related complex molecules are linked by an extensive hydrogen-bonding network involving the N—H protons, the sulfate O atoms and the water molecules, as shown in Fig. 2 and Table 2.

Experimental

The synthetic and analytical details concerning the ligand, H_2L, have been described elsewhere (Cati *et al.*, 2004). The title complex was synthesized by adding 39 mg of $CuSO_4.5H_2O$ (0.156 mmol) to a solution of H_2L (54 mg, 0.156 mmol) in 12 ml of EtOH and 2 ml of H_2O. The resulting green solution was refluxed for *ca* 4 h then filtered directly. The filtrate was left to cool and the solvent to slowly evaporate. After several days, blue–green block-like crystals appeared (yield 41 mg, 47%).

Crystal data

$[Cu_2(C_{18}H_{16}N_6O_2)_2(SO_4)_2]\cdot 6H_2O$
$M_r = 1124.03$
Triclinic, $P\overline{1}$
$a = 8.9507$ (8) Å
$b = 10.0094$ (9) Å
$c = 13.9732$ (12) Å
$\alpha = 90.953$ (10)°
$\beta = 100.442$ (10)°
$\gamma = 116.190$ (9)°
$V = 1098.10$ (17) Å^3
$Z = 1$
$D_x = 1.700$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5864 reflections
$\theta = 2.3$–25.9°
$\mu = 1.16$ mm^{-1}
$T = 153$ (2) K
Block, blue–green
0.20 × 0.20 × 0.08 mm

Data collection

Stoe Image Plate Diffraction System diffractometer
φ oscillation scans
Absorption correction: refined from ΔF (*DELABS* in *PLATON*; Spek, 2003)
$T_{min} = 0.718$, $T_{max} = 0.920$
8639 measured reflections
3966 independent reflections
2687 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 25.9°$
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -17 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.060$
$S = 0.99$
3966 reflections
340 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = [\exp\{2(\sin\theta/\lambda)^2\}]/[\sigma^2(F_o^2) + (0.0241P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Cu1—N3	1.912 (2)	Cu1—N2	2.045 (2)
Cu1—O11	1.9426 (18)	Cu1—O2^{iii}	2.3292 (19)
Cu1—N4	2.002 (2)		
N3—Cu1—O11	165.57 (9)	N3—Cu1—O2^{iii}	107.81 (9)
N3—Cu1—N4	81.69 (9)	O11—Cu1—O2^{iii}	86.39 (7)
O11—Cu1—N4	100.81 (8)	N4—Cu1—O2^{iii}	92.05 (8)
N3—Cu1—N2	81.08 (8)	N2—Cu1—O2^{iii}	94.45 (8)
O11—Cu1—N2	95.58 (8)	C12—O2—Cu1^{iii}	132.92 (15)
N4—Cu1—N2	162.72 (8)	S1—O11—Cu1	121.36 (10)
C6—N3—C5—C2	−177.0 (2)	C13—N5—C12—C1	−173.8 (2)
C5—N3—C6—C7	174.9 (2)	C12—N5—C13—C14	−93.1 (3)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5N···O12^{i}	0.88	2.05	2.864 (3)	153
N6—H6N···O2W^{ii}	0.88	1.77	2.644 (5)	173
O1W—H19···O1^{iii}	0.85 (5)	1.93 (5)	2.770 (4)	172 (5)
O1W—H20···O13^{iv}	0.82 (5)	2.00 (5)	2.821 (3)	176 (5)
O2W—H21···O1W	0.90 (5)	1.88 (5)	2.772 (4)	171 (4)
O2W—H22···O3W^{v}	0.88 (4)	1.87 (4)	2.715 (5)	160 (5)
O3W—H23···O13^{vi}	0.84 (4)	2.00 (4)	2.829 (3)	171 (4)
O3W—H24···O14^{vii}	0.82 (5)	2.00 (5)	2.817 (4)	172 (4)

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $x, y, 1+z$; (iii) $1-x, 1-y, 1-z$; (iv) $x, 1+y, z$; (v) $x-1, y, z$; (vi) $1-x, -y, -z$; (vii) $1+x, y, z$.

Both the N—H and C—H H atoms could be located in Fourier difference maps but were finally included in calculated positions and treated as riding atoms: N—H distances = 0.88 Å, C—H distances = 0.95–0.99 Å, and $U_{\rm iso}$(H) = 1.2 times $U_{\rm eq}$(parent N or C atom). The water H atoms were located in Fourier difference maps and refined isotropically; the distance O2W—H22 was restrained to be 0.86 (2) Å.

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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