metal-organic papers

Bis(pyrazine-2-carboxamide)bis(trifluoro-methanesulfonato)copper(II) monohydrate

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Key indicators

Single-crystal X-ray study
$T = 295$ K
Mean σ(C–C) = 0.003 Å
R factor = 0.037
wR factor = 0.105
Data-to-parameter ratio = 15.3

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

The copper(II) ion in $[Cu(C_5H_5N_3O)_2(CF_3SO_3)_2] \cdot H_2O$ lies on a center of symmetry and is coordinated by two pyrazine-carboxamide ligands in a square-planar geometry with Cu—O and Cu—N distances of 1.9445 (14) and 1.9680 (17) Å, respectively. The $Cu(C_5H_5N_3O)_2$ unit is approximately planar, with an average atomic deviation of 0.057 (4) Å from the least-squares plane. Each copper center is further coordinated, in the axial direction, by two symmetry-equivalent O atoms from trifluoromethanesulfonate anions with a Cu—O distance of 2.4871 (17) Å, giving the copper(II) ion a Jahn–Teller distorted-octahedral geometry.

Comment

The multifunctionality of the pyrazine-2-carboxamide (pyca) ligand offers interesting possibilities in crystal engineering, owing to its chelating properties, in addition to its potential as a linker molecule between metal centers. In this contribution, we present the crystal structure of bis(pyrazine-2-carboxamide)bis(trifluoromethanesulfonato)copper(II) monohydrate, (I). The copper(II) ion lies on a center of symmetry and is coordinated by two pyca ligands in a square-planar geometry (Fig. 1). The Cu^{2+} ion chelates the pyca ligand *via* N1 and O1 to form a five-membered ring. The N1—O1—Cu1—N1^i–O1^i moiety [symmetry code (i): $-x$, $-y$, $-z$] is strictly planar. The average atomic deviation from the least-squares plane defined by all the non-H atoms of the pyca ligand is 0.024 (4) Å. The ligand plane forms an angle of 5.83 (9)° with the five-membered ring plane, which results in a copper out-of-plane distance from the pyca ligand of 0.1422 (1) Å.

(I)
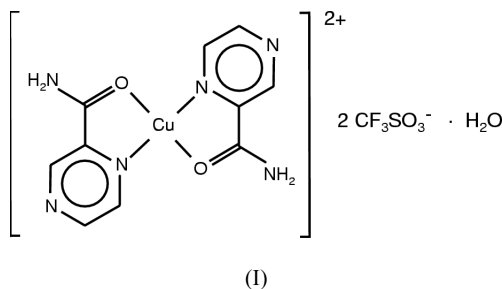
The changes of intermolecular geometry of the pyca molecule upon coordination to the Cu^{2+} cation are insignificant, with all distances within one standard deviation of the average value for the four crystalline polymorphs of pyca which have been structurally determined (Allen & Kennard, 1993). Each copper center is further coordinated, in the axial direction, by two symmetry-equivalent O atoms from trifluoromethanesulfonate anions. The geometry of the copper ion can thus be
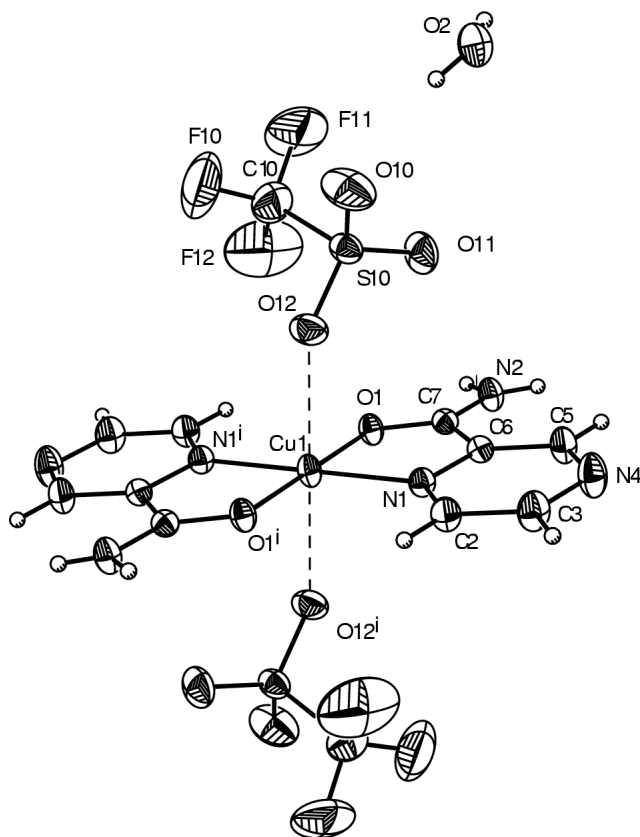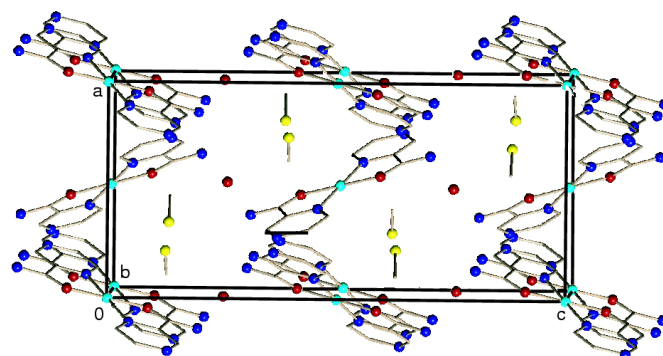
Figure 1
*ORTEP*II (Johnson, 1976) drawing of the molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level for all non-H atoms.

Figure 2
The packing in the unit cell, viewed along the *b* axis. H atoms, and O and F atoms of the trifluoromethanesulfonate anions are omitted for clarity.

Experimental

A mixture of $Cu(H_2O)_6(CF_3SO_3)_2$ (1 mmol) and pyrazine-3-carbox-amide (4 mmol) in water/ethanol (50:50) was stirred while boiling. The solution was allowed to evaporate slowly, affording X-ray quality crystals. The chosen crystals were coated with a hydrocarbon oil and mounted on a glass fibre.

Crystal data

$[Cu(C_5H_5N_3O)_2(CF_3SO_3)_2]\cdot H_2O$	Mo $K\alpha$ radiation
$M_r = 625.94$	Cell parameters from 1907
Orthorhombic, $Pbcn$	reflections
$a = 8.9014\,(7)$ Å	$\theta = 2.2–28.0°$
$b = 13.7809\,(11)$ Å	$\mu = 1.23$ mm^{-1}
$c = 18.8910\,(15)$ Å	$T = 295\,(2)$ K
$V = 2317.3\,(3)$ Å^3	Prism, blue
$Z = 4$	$0.30 \times 0.25 \times 0.18$ mm
$D_x = 1.794$ Mg m^{-3}	

Data collection

Bruker SMART CCD	2738 independent reflections
diffractometer	1907 reflections with $I>2\sigma(I)$
ω scans	$R_{int} = 0.035$
Absorption correction: multi-scan	$\theta_{max} = 28.0°$
(*SADABS*; Bruker, 1998)	$h = -11 \rightarrow 11$
$T_{min} = 0.710$, $T_{max} = 0.809$	$k = -18 \rightarrow 18$
13434 measured reflections	$l = -24 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0773P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.105$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.89$	$\Delta\rho_{max} = 0.53$ e Å^{-3}
2738 reflections	$\Delta\rho_{min} = -0.54$ e Å^{-3}
179 parameters	Extinction correction: *SHELXL*
H atoms treated by a mixture of	Extinction coefficient: 0.0034 (5)
independent and constrained	
refinement	

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.9445 (14)	O1—C7	1.253 (2)
Cu1—N1	1.9680 (17)	N2—C7	1.299 (3)
Cu1—O12	2.4871 (17)	C6—C7	1.496 (3)
O1^i—Cu1—N1	97.17 (6)	N1—Cu1—O12	84.10 (7)
O1—Cu1—N1	82.83 (6)	C7—O1—Cu1	114.37 (13)
O1—Cu1—O12^i	88.01 (6)	O1—C7—N2	122.17 (19)
N1—Cu1—O12^i	95.90 (7)	O1—C7—C6	117.09 (18)
O1—Cu1—O12	91.99 (6)		

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

considered as a Jahn–Teller distorted octahedron. The water molecule lies on a twofold axis and forms four hydrogen bonds by accepting two symmetry-equivalent protons from the amide groups and by donating two relatively weak, equivalent hydrogen bonds to trifluoromethanesulfonate O atoms. The hydrogen-bond pattern is completed by a relatively weak hydrogen bond between the amide group and the trifluoro-methanesulfonate atom O11. The packing in the unit cell, viewed along the *b* axis, is shown in Fig. 2.

In the closely related bis(pyca)copper(II) perchlorate (Sekisaki, 1973), the copper center is chelated by two symmetry-equivalent pyca ligands with Cu—O and Cu—N distances of 1.964 (4) and 1.999 (6) Å, respectively. In this case, however, the perchlorate anions are non-coordinating, and the axial positions of the copper ion are occupied by the ring N atom, corresponding to N4 of the title compound, of adjacent Cu(pyca)$_2$ complexes, resulting in a two-dimensional square-grid network. In acetylacetonato(pyca)copper(II) perchlorate monohydrate (Zhong *et al.*, 1990), which has a similar bidentate coordination mode to the title compound, the Cu—O and Cu—N distances are 2.008 (6) and 1.992 (3) Å, respectively. Interestingly, in this case the perchlorate anions occupy axial positions, with Cu—O distances of 2.543 (9) and 2.871 (4) Å, and each perchlorate anion bridges two adjacent copper centers to form extended chains.

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

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
N2—H1B···O11[i]	0.81 (3)	2.11 (3)	2.898 (3)	164 (3)
N2—H1A···O2[ii]	0.84 (3)	2.16 (3)	2.936 (3)	153 (2)
O2—H2B···O10	0.79 (3)	2.17 (3)	2.945 (3)	169 (3)

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $\frac{1}{2} + x, y - \frac{1}{2}, \frac{1}{2} - z$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART* and *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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