Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

(Acetonitrile)[2,6-bis(pyrazol-1-yl)-pyridine](isonicotinamide)copper(II)–tetrafluoroborate–acetonitrile (1/2/2)

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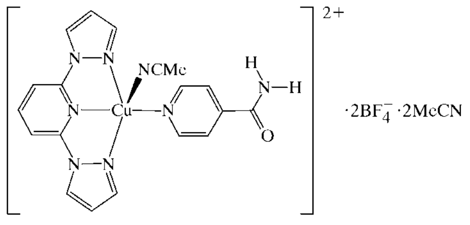
Received 19 September 2002
Accepted 2 October 2002
Online 22 October 2002

Molecules of the title compound, $[Cu(C_2H_3N)(C_{11}H_9N_5)(C_6H_6N_2O)](BF_4)_2 \cdot 2C_2H_3N$, comprise (acetonitrile)[2,6-bis(pyrazol-1-yl)pyridine](isonicotinamide)copper(II) cations, tetrafluoroborate anions and lattice acetonitrile molecules. The cations have distorted square-pyramidal geometries in which the N_3-donor, *viz.* 2,6-bis(pyrazol-1-yl)pyridine, and the N-donor, *viz.* the isonicotinamide ligand, occupy the four basal positions, with the coordinated acetonitrile N-donor atom occupying the apical position. Pairs of cations are linked by N—H···F hydrogen bonds through tetrafluoroborate anions, forming centrosymmetric dimers, which are further linked by C—H···O hydrogen bonds into two-dimensional undulating sheets, three of which interpenetrate to generate a two-dimensional network.

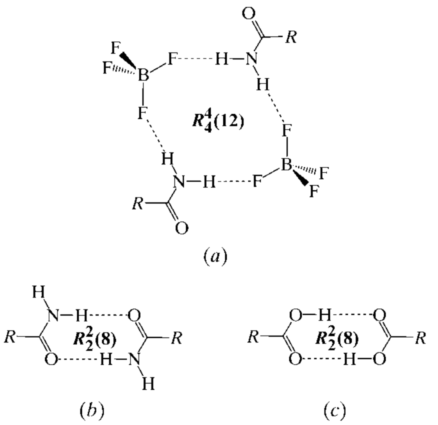
Comment

The title compound, (I), comprises an (acetonitrile)[2,6-bis(pyrazol-1-yl)pyridine](isonicotinamide)copper(II) cation (Fig. 1), two tetrafluoroborate anions and two lattice acetonitrile molecules. All four F atoms of both tetrafluoroborate anions are each disordered over two sites. The tridentate 2,6-bis(pyrazol-1-yl)pyridine ligand occupies three of the four basal positions of a distorted square-pyramidal CuN_5 coordination sphere. The isonicotinamide ligand occupies the fourth basal position and the coordinated acetonitrile molecule occupies the apical position. Of the three ligating N atoms of the tridentate ligand, the pyrazole N-donor atoms form much longer Cu—N bonds [2.024 (3) and 2.026 (3) Å] than the pyridine N-donor atom [1.946 (2) Å], which forms a Cu···N contact similar to the isonicotinamide N-donor atom [1.964 (2) Å]. Typical of square-pyramidal Cu^{II} centres, the apical acetonitrile-N atom is somewhat more distant [2.316 (3) Å]. The magnitude of the distortion of the Cu^{II} coordination sphere (Fig. 1) can be quantified by the geometric parameter τ [*i.e.* (171.42 − 156.94)/60] of 0.24 (τ = 0.0 for C_{4v} symmetry and τ = 1.0 for D_{3h} symmetry; Addison *et al.*, 1984). The conformation of the pyridine ring of the isonicotinamide ligand is such that it makes a dihedral angle of 47.8 (8)° with the pyridine ring of the tridentate ligand, which is effectively planar, with dihedral angles between the pyrazole and pyridine rings of 1.3 (2) and 6.3 (2)°.



(I)

The cations form centrosymmetrically related pairs (Fig. 2) linked through two tetrafluoroborate anions by an $R_4^4(12)$ hydrogen-bonding motif (Etter, 1990; Bernstein *et al.*, 1995).



Scheme 1

Pertinent structural parameters of the hydrogen-bonded contacts are collated in Table 2. The formation of this motif [Scheme 1(*a*)] was unexpected, the simpler $R_2^2(8)$ motif [see

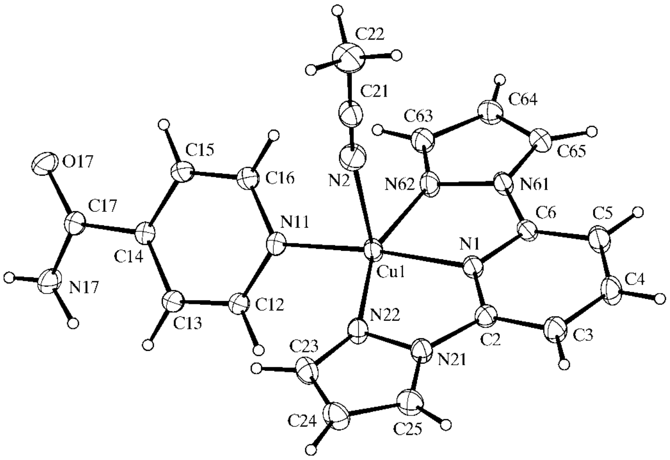


Figure 1
A view of the cation in (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

DOI: 10.1107/S0108270102018097

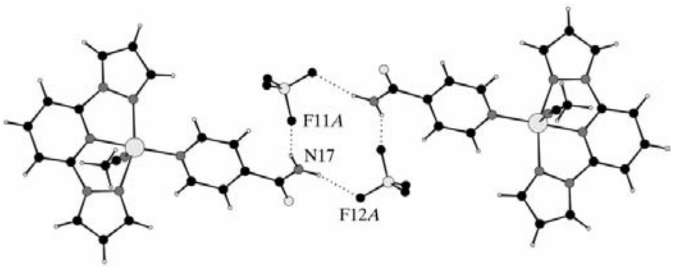


Figure 2

A view of the centrosymmetric hydrogen-bonded dinuclear construction generated by the N—H···F contacts of the hydrogen-bonded $R_4^4(12)$ motif. Only one set of F atoms (F11*A*, F12*A*, F13*A* and F14*A*) is shown for each tetrafluoroborate anion. (Key: Cu atoms are large pale-grey spheres, C are intermediate black spheres, N are intermediate dark-grey spheres, O are intermediate pale-grey spheres, B are small pale-grey spheres and F are intermediate black spheres.)

Scheme 1(*b*)] based on the amide functionalities being anticipated by analogy with the well known carboxylic acid-based $R_2^2(8)$ supramolecular synthon [Scheme 1(*c*)] (Desiraju, 1995, 2000). Presumably, despite the greater strength of the N—H···O═C hydrogen bond compared with the N—H···F—BF$_3$ hydrogen bond, the energy release associated with the formation of four of the latter is greater than that associated with the formation of two of the former. Two C—H···O hydrogen bonds, in the form of an $R_2^1(7)$ motif, link the dimers through the amide-O atom, generating an undulating sheet structure parallel to the (001) plane (Table 2 and Fig. 3). The periodicity of the undulation (24.5 Å) is such that the two-dimensional network comprises three interpenetrating sheets analogous to those observed in {[Co$_2$(μ-4,4′-azopyridine)$_3$(NO$_3$)$_4$]}$_n$ (Withersby *et al.*, 1999, 2000).

Experimental

The ligand 2,6-bis(pyrazol-1-yl)pyridine was synthesized by heating at reflux for 72 h the mixture formed by adding 2,6-dichloropyridine (4.12 g, 27.8 mmol) to a solution of sodium pyrazolate previously prepared in tetrahydrofuran (100 ml) by reaction of pyrazole (3.80 g, 55.8 mmol) with excess NaH (60% dispersion in mineral oil; 2.80 g, 70 mmol). After cooling, the mixture was poured into iced water and the resulting precipitate recovered by filtration (yield: 5.10 g, 23.7 mmol, 85%). For the preparation of the title compound, (I), isonicotinamide (0.040 g, 0.33 mmol) was added to a mixture of 2,6-bis(pyrazol-1-yl)pyridine (0.068 g, 0.32 mmol) and hydrated Cu(BF$_4$)$_2$·xH$_2$O (0.100 g, 0.32 mmol) in acetonitrile (25 ml). After stirring at ambient temperature for 24 h, the resulting green solution afforded a small crop of green plate-like crystals.

Crystal data

[Cu(C$_2$H$_3$N)(C$_{11}$H$_9$N$_5$)(C$_6$H$_6$N$_2$O)](BF$_4$)$_2$·2C$_2$H$_3$N
M_r = 693.68
Orthorhombic, *Pbca*
a = 8.1790 (16) Å
b = 22.747 (5) Å
c = 31.752 (6) Å
V = 5907 (2) Å^3
Z = 8
D_x = 1.560 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 955 reflections
θ = 2.5–25.5°
μ = 0.83 mm^{-1}
T = 193 (2) K
Plate, green
0.32 × 0.08 × 0.02 mm

Data collection

Stoe IPDS diffractometer
Area detector scans
Absorption correction: multi-scan (*IPDS*; Stoe & Cie, 1995)
$T_{\min}$ = 0.84, $T_{\max}$ = 0.95
19 461 measured reflections
6613 independent reflections
4385 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.052
$\theta_{\max}$ = 28.1°
$h = -9 \rightarrow 9$
$k = -30 \rightarrow 25$
$l = -42 \rightarrow 29$
Intensity decay: none

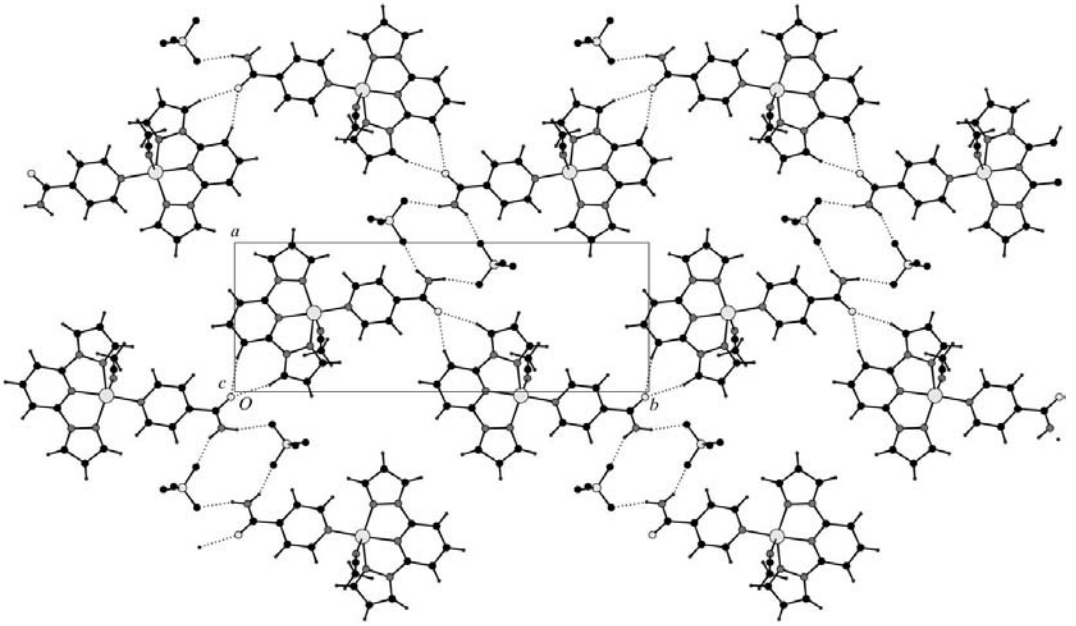


Figure 3

A projection of the structure of (I) on to the (001) plane, showing the two-dimensional sheet structure generated by the C—H···O contacts of the hydrogen-bonded $R_2^1(7)$ motif. The lattice acetonitrile molecules and tetrafluoroborate anions have been omitted for clarity. Only one set of F atoms (F11*A*, F12*A*, F13*A* and F14*A*) is shown for each tetrafluoroborate anion (atom types are as depicted in Fig. 2).

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.945 (3)	Cu1—N22	2.024 (3)
Cu1—N2	2.316 (3)	Cu1—N62	2.026 (3)
Cu1—N11	1.964 (3)		
N1—Cu1—N2	93.41 (12)	N2—Cu1—N22	93.70 (14)
N1—Cu1—N11	171.42 (13)	N2—Cu1—N62	93.29 (14)
N1—Cu1—N22	78.87 (12)	N11—Cu1—N22	101.55 (12)
N1—Cu1—N62	78.80 (11)	N11—Cu1—N62	99.67 (12)
N2—Cu1—N11	95.12 (12)	N22—Cu1—N62	156.94 (11)

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

D—H···A	D—H	H···A	D···A	D—H···A
N17—H17A···F11A^{i}	0.88	2.60	3.334 (6)	142
N17—H17B···F11A^{ii}	0.88	2.09	2.900 (6)	152
N17—H17B···F11B^{ii}	0.88	2.01	2.866 (7)	163
N17—H17A···F12A^{i}	0.88	2.12	2.971 (5)	163
N17—H17A···F12B^{i}	0.88	2.03	2.885 (7)	163
C5—H5···O17^{iii}	0.95	2.22	3.140 (5)	162
C65—H65···O17^{iii}	0.95	2.36	3.221 (4)	151

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.175$
$S = 1.01$
6613 reflections
401 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.115P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.88$ e Å^{-3}
$\Delta\rho_{\min} = -0.74$ e Å^{-3}

The tetrafluoroborate anions are affected by disorder; this was modelled by allowing alternative positions for each F atom, with extensive restraints applied to B—F distances and F—B—F angles. Around atom B1, the major and minor orientations refined to occupancies of 0.57 (2) and 0.43 (2), respectively, while the corresponding occupancies around atom B2 converged to 0.60 (1) and 0.40 (1). Aromatic and amide H atoms, after location from ΔF syntheses, were placed geometrically and refined with a riding model, for which the C—H and N—H distances were constrained to be 0.95 and 0.88 Å, respectively, and $U_{\rm iso}(\rm H) = 1.2U_{\rm eq}(\rm C, N)$. Methyl H atoms were located and treated similarly, with C—H distances constrained to be 0.98 Å and $U_{\rm iso}(\rm H) = 1.5U_{\rm eq}(\rm C)$

Data collection: *IPDS* (Stoe & Cie, 1995); cell refinement: *IPDS*; data reduction: *IPDS*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2002).

The authors thank the University of Nottingham for financial support (to MAW).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1141). Services for accessing these data are described at the back of the journal.

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