DALTON COMMUNICATION

Rectangular grid two-dimensional sheets of copper(II) bridged by both co-ordinated and hydrogen bonded 4,4′-bipyridine (4,4′-bipy) in $[Cu(\mu\text{-}4,4'\text{-bipy})(H_2O)_2(FBF_3)_2]\cdot 4,4'\text{-bipy}$

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The complex $[Cu(\mu\text{-}4,4'\text{-bipy})(H_2O)_2(FBF_3)_2]\cdot 4,4'\text{-bipy}$ (4,4′-bipy = 4,4′-bipyridine), in which copper atoms are linked by Cu–4,4′-bipy–Cu and Cu–$OH_2\cdots$4,4′-bipy$\cdots H_2O$–Cu assemblies, involving co-ordinated and hydrogen bonded 4,4′-bipy, respectively, to form two-dimensional rectangular grid sheets, has been isolated and structurally characterised.

Molecular framework structures formed by later transition metals (copper and zinc triads) bridged by N,N′-bidentate molecular rods vary with metal, anion and bridge.[1,2] Those based on 4,4′-bipyridine (4,4′-bipy) bridges range from stacked square grid cationic sheets $\{[Cd^{II}(\mu\text{-}4,4'\text{-bipy})_2(H_2O)_2][PF_6]_2\cdot 2(4,4'\text{-bipy})\cdot 4H_2O$[1]$\}$ through interpenetrating square grid cationic sheets $\{[Cd^{II}(\mu\text{-}4,4'\text{-bipy})_2(H_2O)(OH)][PF_6]$[1] and $[M^{II}(\mu\text{-}4,4'\text{-bipy})_2(H_2O)_2][SiF_6]$ (M = Cu, Zn or Cd)[3]$\}$ to interwoven cationic frameworks with T-shaped $\{[Ag^{I}(4,4'\text{-bipy})][NO_3]$[4]$\}$ or diamondoid architectures $\{[Cu^{I}(4,4'\text{-bipy})_2][PF_6]$[5] and $[Ag^{I}(4,4'\text{-bipy})_2][CF_3SO_3]$[6]$\}$. Neutral sheets, based on mutually perpendicular linear $[\{Cu(4,4'\text{-bipy})\}_n]$ and $[\{CuX_2\}_n]$ chains as in $[Cu(4,4'\text{-bipy})_2X_2]$ (X = Cl or Br) are also known.[7] We now report a novel arrangement, found in $[Cu^{II}(\mu\text{-}4,4'\text{-bipy})(H_2O)_2(FBF_3)_2]\cdot 4,4'\text{-bipy}$ **1**, based on stacked infinite rectangular grid sheets.

Addition of an aqueous solution (25 cm^3) of hydrated copper(II) tetrafluoroborate (0.309 g, 1.0 mmol) to a refluxing acetonitrile solution (25 cm^3) of 4,4′-bipy (0.312 g, 2.0 mmol) gave an immediate blue precipitate. After filtration, blue crystals, suitable for X-ray diffraction study, were grown by vapour diffusion of Et_2O into the mother-liquor. Elemental analysis, magnetochemistry and IR spectroscopy showed both products to have the formulation of **1**.†

The structure of complex **1** was determined by single-crystal X-ray diffraction.‡ Its unique feature is the differing role of the two 4,4′-bipy molecules. One bridges copper atoms directly [Cu$\cdots$Cu = 11.078(2) Å], while the other, through hydrogen-bonding interactions, bridges copper atoms *via* intermediate water molecules [Cu$\cdots$Cu = 14.951(2) Å]. A two-dimensional sheet structure, based on a rectangular arrangement of copper atoms, results (Fig. 1). The copper atom and the co-ordinated 4,4′-bipy molecule lie on a crystallographic two-fold axis. The copper atom has Jahn–Teller tetragonally elongated distorted octahedral geometry, provided equatorially by the 4,4′-bipy nitrogens [Cu–N(1) 1.983(9), Cu–N(2) 1.99(1) Å] and two symmetry related water oxygens [Cu–O(1) 1.966(5) Å] and axially by two symmetry related tetrafluoroborate fluorines [Cu–F(2) 2.383(5) Å]. The water molecule forms a strong hydrogen bond [O(1)–H(99)$\cdots$N(11)] to the non-co-ordinated 4,4′-bipy molecule [O$\cdots$N 2.688(9), O–H 0.95, H$\cdots$N 1.74 Å, O$\cdots$H$\cdots$N 172°]. The generation of a sheet structure containing both co-ordinated and hydrogen-bonded bridging N-donor ligands (Fig. 1) is novel although the use of 4,4′-bipy as a hydrogen-bonded spacer has been reported in the diamondoid structure of $[Mn(CO)_3(\mu_3\text{-}OH)]_4\cdot 2(4,4'\text{-bipy})\cdot 2MeCN$.[2] The structure of $[Cd(H_2O)_2(\mu\text{-}4,4'\text{-bipy})_2][PF_6]\cdot 2(4,4'\text{-bipy})\cdot 4H_2O$[1] also contains un-co-ordinated 4,4′-bipy molecules. They are not involved, however, in any bridging interaction. They simply occupy cavities in the three-dimensional

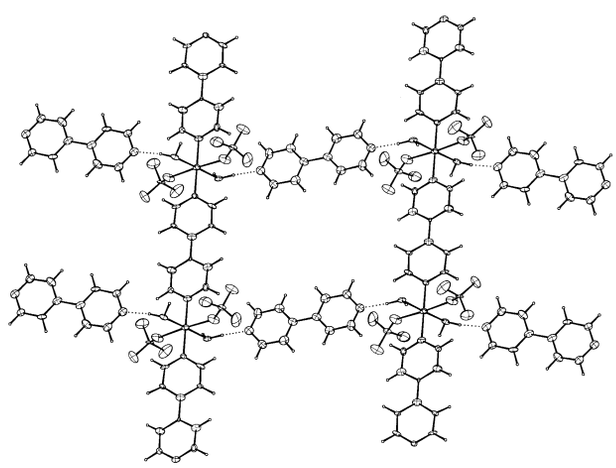

Fig. 1 Two-dimensional architecture[11] of the structure of $[Cu(\mu\text{-}4,4'\text{-bipy})(H_2O)_2(FBF_3)_2]\cdot 4,4'\text{-bipy}$, showing the Cu–4,4′-bipy–Cu (co-ordinated) and Cu–$OH_2\cdots$4,4′-bipy$\cdots H_2O$-Cu (hydrogen bonded) 4,4′-bipy bridges

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† Found (Calc.) for **1**: C, 41.50 (41.00); H, 3.35 (3.30); N, 10.05 (9.55%). IR (Nujol mull, KBr windows)/cm^{-1} (all bands due to 4,4′-bipy unless stated otherwise): 1610s, 1535w, 1493w, 1411s, 1222s, 1077s (br) (BF_4^-), 813s, 644w, 629w, 533w, 522w. $\mu_{eff} = 1.49\ \mu_B \approx 1.38 \times 10^{-23}$ J T^{-1}.

‡ Crystal data: $C_{20}H_{20}B_2CuF_8N_4O_2$, $M = 589.85$, monoclinic, space group $C2/c$ (no. 15), $a = 16.228(2)$, $b = 11.078(2)$, $c = 13.985(2)$ Å, $\beta = 114.43(1)°$, $U = 2287.9(6)$ Å^3, $Z = 4$, $F(000) = 1196$, $D_c = 1.710$, $D_m = 1.74$ g cm^{-3}, graphite-monochromated Mo-Kα radiation, $\lambda = 0.710\ 73$ Å, $\mu = 1.045$ mm^{-1}, blue column 0.24 × 0.16 × 0.14 mm. Stoe Stadi-4 four-circle diffractometer with Oxford Cryosystems open flow cryostat8 operated at 150.0(2) K, scan type ω–θ, $2\theta_{max} = 50.0°$, 1817 unique data. The structure was solved by direct methods (SIR 92[9]) and refined by full-matrix least squares (CRYSTALS[10]) on F^2 using all data. All hydrogen atoms were located by Fourier-difference syntheses. The non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of the 4,4′-bipy hydrogens, but not the water hydrogens, were refined with fixed U_{iso} (=0.05 Å^2). Refinement (unit weights) converged to $R = 0.1222$, $wR2 = 0.1975$ for all data and conventional $R = 0.0767$ for 1214 data with $I \geqslant 2\sigma(I)$; residual $\Delta\rho_{max} = 2.01$ e Å^{-3} [near Cu(1)], $\Delta\rho_{min} = -1.33$ e Å^{-3}; $(\Delta/\sigma)_{max} = 0.253$. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/417.

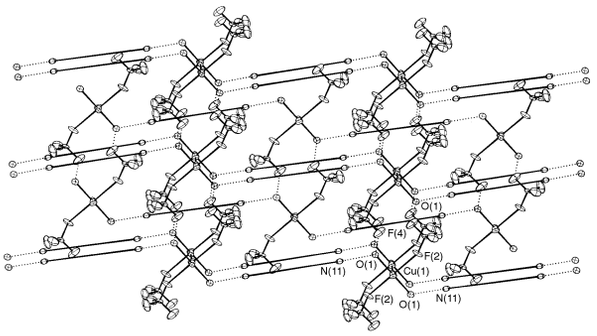

Fig. 2 Projection of the structure[11] of $[Cu(\mu\text{-}4,4'\text{-bipy})(H_2O)_2(FBF_3)_2]\cdot 4,4'$-bipy onto the *xz* plane, showing (*i*) the location of the BF_4^- anions in the cavities of the rectangular grid sheets, (*ii*) the stacking of the 4,4′-bipy molecules and (*iii*) the O(1)···F(4) as well as the O(1)···N(11) contacts. Carbon and hydrogen atoms are omitted for clarity; the 4,4′-bipy molecular rods are shown as single bold lines

framework built up of two-dimensional square grid sheets linked through four hydrogen-bonded water molecules.[1]

Since four juxtapositioned equatorial pyridine (py) molecules and two axially located BF_4^- anions are found in $[Cu(py)_4(FBF_3)_2]$ [Cu–N 2.012–2.044, Cu–F 2.400 and 2.464 Å],[12] the inclusion of the intermediate water molecules in the bridge cannot be due to steric requirements of the co-ordination site. It is attributed to the need to generate a cavity in the sheet structure sufficiently large (11.08 × 14.95 Å) to accommodate two anions from adjacent sheets (Fig. 2). The sheets are displaced such that the copper atoms are located close to the centres of the cavities of adjacent sheets thus enabling the BF_4^- anions to fit into these cavities. This arrangement is facilitated by the alternate parallel π–π stacking of the 4,4′-bipy molecules along the *c* axis (separation 3.50 Å; dihedral angle 4.94°). The two heterocyclic rings of the hydrogen-bonded 4,4′-bipy molecule are constrained to be parallel by symmetry; those of the co-ordinated 4,4′-bipy are slightly twisted with a dihedral angle of 9.29° (Fig. 2).

Although location of the weakly co-ordinating BF_4^- anion in the weakly binding axial co-ordination site is typical, the $Cu^{II}\cdots F$ contact is considerably shorter than any previously observed.[13,14] The tetrafluoroborate anion, which exhibits no disorder, is held in position by an intermolecular hydrogen bond [O(1)–H(98)···F(4)] to a water molecule in an adjacent sheet [O···F 2.865(8), O–H 1.01, H···F 1.93 Å; O–H···F 153°]. This is the only contact between parallel sheets (Fig. 2).

Although the longest B–F contact is that to the co-ordinated fluorine [F(2)], the standard deviations are such that geometrical differences [B–F 1.36(1)–1.39(1) Å; F–B–F 108.3(8)–110.9(7)°] are not significant and cannot be used to support an asymmetric structure for the BF_4^- ligand. Similarly, the IR spectrum (400–4000 cm^{-1}) of complex **1** measured in a Nujol mull between KBr windows, protected by polythene, is not consistent with the loss of tetrahedral symmetry; splitting of the triply degenerate ν(B–F) mode (T_2) of the free BF_4^- anion at 1080 cm^{-1},[15] resulting from reduced symmetry (C_{3v}, C_{2v} or C_s),[14] is not observed. The weakness of the Cu···F interaction is indicated, however, by differences between the IR spectrum of **1** measured in a pressed KBr pellet and in a Nujol mull; weakly bound BF_4^- is displaced by Br^- in pressed KBr pellets, giving spectra different from those in Nujol mulls.[13]

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