Aqua(2,2′-bipyridyl)difluorocopper(II) Dihydrate: *X*-Ray Structure reveals Short Hydrogen Bonds and Other Unusual Features *

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The *X*-ray crystal structure of $[Cu(bipy)F_2(H_2O)]\cdot 2H_2O$ shows it to contain five-co-ordinate copper in a square-pyramidal configuration. Each fluoride ligand is connected by short hydrogen bonds to two lattice waters with $R(F \cdots O) = 2.634$—2.673 Å. Moreover the Cu–F bonds at 1.884(4) and 1.889(4) Å are the shortest such bonds known.

Copper has an important role to play in several biological systems.[1] Some enzymes such as superoxide dismutases employ copper at the active site.[2] The well known deactivation of enzymes by the fluoride ion probably occurs by co-ordination at this site, and in the case of cytochrome c peroxidase an *X*-ray structure determination has shown this to be so for this iron-containing enzyme.[3] The co-ordinated fluoride proves to be an excellent hydrogen-bond acceptor for nearby groups. This results in local distortions that radically affect the molecular environment around the active site and which explain the deactivating effect of the fluoride.

To assess the ability of F^- bound to Cu to participate in hydrogen bonds, we have synthesized Cu–F complexes with heteronuclear nitrogen ligands as models for the biological environment. Inspection of the i.r. spectra of such complexes reveals whether strong hydrogen bonding is present.[4] In a previous paper[5] we reported one such complex, $[Cu(na)_2F_2(H_2O)_2]\cdot 4H_2O$ (na = nicotinamide), whose *X*-ray structure determination confirmed the presence of short hydrogen bonds between the ligand fluorides and lattice waters. We have also observed in the i.r. spectrum of a previously reported compound,[6] $Cu(bipy)F_2\cdot 2H_2O$ (bipy = 2,2′-bipyridine), the presence of absorption bands indicative of very short hydrogen bonding. The *X*-ray crystal structure of this substance is now reported.

Experimental

Synthesis of $[Cu(bipy)F_2(H_2O)]\cdot 2H_2O$.—Copper(II) fluoride (0.5 g, 5 mmol) was added to a solution of bipy (0.8 g, 5 mmol) dissolved in wet methanol (50 cm^3). The CuF_2 slowly dissolved on stirring and after 12 h a clear green solution was obtained. This was reduced, by pumping, to a third of its original volume and left to stand. Large turquoise-blue crystals of $[Cu(bipy)F_2(H_2O)]\cdot 2H_2O$ were formed which were filtered off and dried over silica gel (Found: C, 39.0; H, 4.35; N, 9.10. $C_{10}H_{14}CuF_2N_2O_3$ requires C, 38.5; H, 4.50; N, 9.00%). The original discoverers of this compound found it to be $Cu(bipy)F_2\cdot 2H_2O$ (probably due to vacuum drying), m.p. 260 °C (decomp.). The i.r. spectrum (4 000—180 cm^{-1}) was recorded on a model 983G Perkin-Elmer i.r. spectrometer using a KBr disc. The significant peaks and likely assignments are 3 384vs,br [$\nu(H_2O)$], 3 120s, 3 073s, 3 040s [all ν(CH)], 2 098m ($F \cdots H$–O), 1 676s, 1 598vs (bipy), 1 523vs,br [$\delta(H_2O)$], 1 444vs (bipy), 1 317s, 1 243s (bipy), 1 226s (bipy), 1 173m, 1 029s (bipy), and 1 014s cm^{-1}. The spectral region 900—300 cm^{-1} reveals a broad absorption band, characteristic of strong hydrogen bonding, superimposed upon which are peaks at 769vs (bipy), 730s [ν(CuF)], 659s (bipy), 636s (bipy), 593s,br [$\omega(H_2O)$], 550m [ν(CuO)], 473vs,br [δ(CuF), *etc.*], 414s (bipy), and 289m cm^{-1} [δ(CuN)]. The metal–ligand atom modes are assigned on the basis of those reported for $[Cu(na)_2F_2(H_2O)_2]\cdot 4H_2O$ with due allowance for the shorter Cu–F bonds in the present complex. These assignments are naturally tentative.

Crystallographic Studies.—Crystal data. $C_{10}H_{10}CuF_2N_2O\cdot 2H_2O$, $M = 311.775$, monoclinic, space group $P2_1/n$, $a = 10.697(2)$, $b = 16.968(2)$, $c = 6.918(1)$ Å, $\beta = 90.47(1)°$, $U = 1\,255.7(3)$ Å^3, $Z = 4$, $D_c = 1.649$ g cm^{-3}, $F(000) = 636$, $\mu(Cu\text{-}K_\alpha) = 27.1$ cm^{-1}, crystal size 0.60 × 0.45 × 0.30 mm.

Data collection. Unit-cell parameters and intensity data were obtained by following previously detailed procedures,[7] using a CAD4 diffractometer operating in the ω—2θ scan mode, with nickel-filtered Cu-K_α radiation ($\lambda = 1.5418$ Å). A total of 2 692 unique reflections were collected ($3 \leqslant 2\theta \leqslant 70°$). The segment of reciprocal space scanned was (*h*) −13 to 13, (*k*) 0 to 20, (*l*) 0 to 8. The reflection intensities were corrected for absorption, using the azimuthal-scan method;[8] maximum transmission factor 0.99, minimum 0.75.

Structure solution and refinement. The structure was solved by the application of routine heavy-atom methods (SHELX 86[9]), and refined by full-matrix least squares (SHELX 76[10]). All non-hydrogen atoms were refined anisotropically, and hydrogen atoms of the bipy ligand placed in calculated positions (C–H 0.96 Å, $U = 0.10$ Å^2). Hydrogen atoms of the lattice water molecules were not included in the model. The final residual *R* and *R′* were 0.041 and 0.045 respectively for the 164 variables and 2 130 data for which $F_o > 6\sigma(F_o)$. The function minimized was $\Sigma_w(|F_o| - |F_c|)^2$ with the weight, *w*, being defined as $1/[\sigma^2(F_o) + 0.000\,01F_o^2]$.

Atomic scattering factors and anomalous scattering parameters were taken from refs. 11 and 12 respectively. All computations were made on a DEC VAX-11/750 computer. Table 1 lists the atomic co-ordinates, Table 2 the bond lengths and angles of $[Cu(bipy)F_2(H_2O)]$ whose structure is shown in Figure 1. A unit-cell packing diagram is shown in Figure 2 and the intermolecular hydrogen bonds are listed in Table 3.

Discussion

The complex between CuF_2 and 2,2′-bipyridine was briefly reported by Levason and co-workers[6] in 1980 as $Cu(bipy)F_2\cdot H_2O$. We now record that its structure consists of $[Cu(bipy)F_2(H_2O)]$ units, with the following noteworthy features: the copper is five-co-ordinate with square-pyramidal geometry and a shorter than expected apical length; and the Cu–F bonds are shorter than other Cu–F bonds. In addition the crystal structure

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

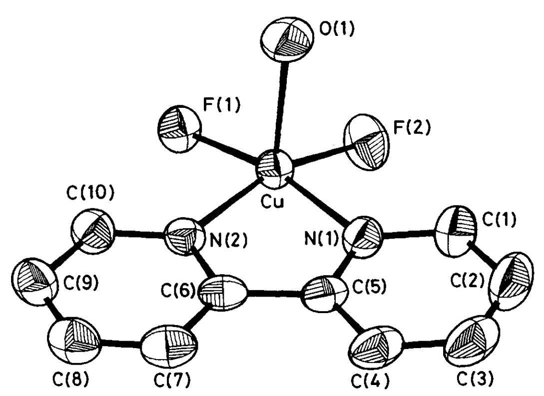

Figure 1. Structure and atom labelling of $[Cu(bipy)F_2(H_2O)]$

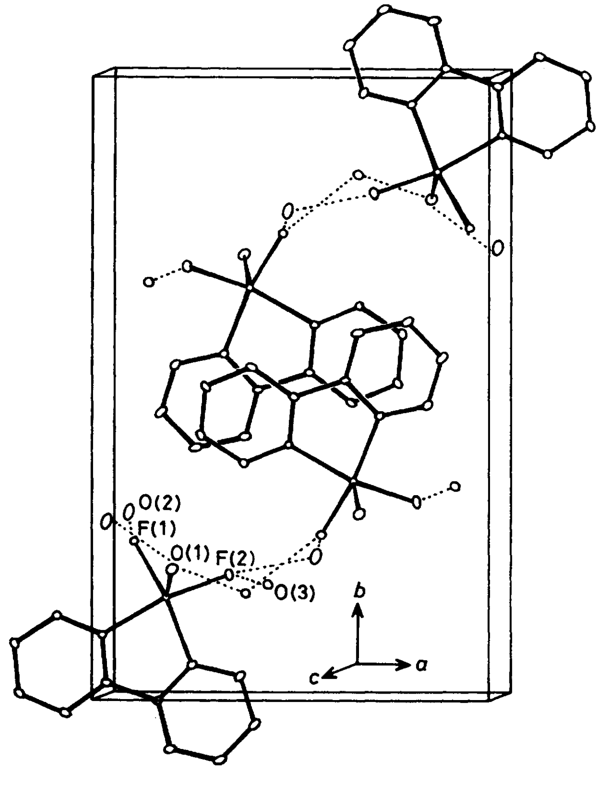

Figure 2. Unit-cell packing diagram of $[Cu(bipy)F_2(H_2O)]\cdot 2H_2O$ showing the potential hydrogen-bonding network within the lattice. All F···O and O···O distances less than 2.80 Å are shown by dotted lines

Table 1. Fractional atomic co-ordinates ($\times 10^4$) for $[Cu(bipy)_2F_2(H_2O)]\cdot 2H_2O$

Atom	*x*	*y*	*z*
Cu	1 398.8(4)	1 529.5(3)	1 644.1(7)
F(1)	529(2)	2 413(1)	677(3)
F(2)	2 932(2)	1 877(2)	611(4)
O(1)	1 715(3)	2 016(2)	4 577(4)
O(2)	186(3)	2 816(3)	−3 024(5)
O(3)	3 706(3)	1 666(2)	−3 002(4)
N(1)	2 091(3)	457(2)	2 279(5)
N(2)	−203(3)	938(2)	2 015(4)
C(1)	3 316(4)	279(3)	2 400(7)
C(2)	3 704(5)	−484(3)	2 836(8)
C(3)	2 839(5)	−1 059(3)	3 055(8)
C(4)	1 580(4)	−876(2)	2 922(6)
C(5)	1 239(4)	−113(2)	2 552(6)
C(6)	−67(4)	164(2)	2 425(5)
C(7)	−1 104(4)	−320(2)	2 650(6)
C(8)	−2 286(4)	−3(3)	2 475(6)
C(9)	−2 421(4)	787(3)	2 091(7)
C(10)	−1 354(3)	1 238(2)	1 864(6)

Table 2. Bond lengths (Å) and angles (°) for $[Cu(bipy)_2F_2(H_2O)]\cdot 2H_2O$

F(1)–Cu	1.884(4)	F(2)–Cu	1.889(4)
O(1)–Cu	2.214(5)	N(1)–Cu	2.011(5)
N(2)–Cu	2.004(5)	C(1)–N(1)	1.347(6)
C(5)–N(1)	1.344(6)	C(6)–N(2)	1.351(5)
C(10)–N(2)	1.336(5)	C(2)–C(1)	1.391(7)
C(3)–C(2)	1.355(8)	C(4)–C(3)	1.384(7)
C(5)–C(4)	1.368(6)	C(6)–C(5)	1.476(6)
C(7)–C(6)	1.390(6)	C(8)–C(7)	1.379(7)
C(9)–C(8)	1.373(7)	C(10)–C(9)	1.384(6)
F(2)–Cu–F(1)	92.6(2)	O(1)–Cu–F(1)	95.7(2)
O(1)–Cu–F(2)	96.0(2)	N(1)–Cu–F(1)	167.7(1)
N(1)–Cu–F(2)	92.6(2)	N(1)–Cu–O(1)	94.8(2)
N(2)–Cu–F(1)	91.4(2)	N(2)–Cu–F(2)	161.9(1)
N(2)–Cu–O(1)	101.2(2)	N(2)–Cu–N(1)	80.3(2)
C(1)–N(1)–Cu	125.0(4)	C(5)–N(1)–Cu	115.7(3)
C(5)–N(1)–C(1)	119.3(4)	C(6)–N(2)–Cu	115.0(3)
C(10)–N(2)–Cu	125.9(4)	C(10)–N(2)–C(6)	119.0(4)
C(2)–C(1)–N(1)	120.8(5)	C(3)–C(2)–C(1)	119.4(5)
C(4)–C(3)–C(2)	119.8(5)	C(5)–C(4)–C(3)	118.9(5)
C(4)–C(5)–N(1)	121.8(5)	C(6)–C(5)–N(1)	113.9(4)
C(6)–C(5)–C(4)	124.3(5)	C(5)–C(6)–N(2)	115.0(4)
C(7)–C(6)–N(2)	120.9(4)	C(7)–C(6)–C(5)	124.1(4)
C(8)–C(7)–C(6)	119.4(5)	C(9)–C(8)–C(7)	119.5(5)
C(10)–C(9)–C(8)	118.4(5)	C(9)–C(10)–N(2)	122.7(5)

Table 3. Hydrogen bonds (Å) involving lattice waters $H_2O(2)$ and $H_2O(3)$ of $[Cu(bipy)F_2(H_2O)]\cdot 2H_2O$

O(2)···F(2a)	2.634	O(2)···O(1c)	2.705
O(3)···F(2)	2.663	O(3)···O(1c)	2.764
O(3)···F(1b)	2.666		
O(2)···F(1)	2.673		

Symmetry operations: (a) $-0.5 + x$, $0.5 - y$, $-0.5 + z$; (b) $0.5 + x$, $0.5 - y$, $-0.5 + z$; (c) x, y, $-1.0 + z$

itself has a notable feature: very short hydrogen bonds between the ligand fluorides and lattice waters. It was the hope of finding such hydrogen bonds that attracted us to study this compound.

The Hydrogen Bonding.—Table 4 lists nine examples, including the current one, in which ligand fluoride is hydrogen bonded to lattice water. This type of interaction is postulated as one that would play an important part in fluoride-poisoned enzymes and it is significant that such hydrogen bonding would be strong.[4] Table 4 lists the shortest *R*(O··· F) distance in each case and it is worth noting that both Cu–F complexes have similar *R*(O··· F) as have both Al–F compounds. Whether the metal is really the determining factor in hydrogen-bond length will only be decided when more examples come to light.

The Copper Complex.—Among the several co-ordination arrangements around Cu^{II} the five-co-ordinate, square-planar (4 + 1) arrangement is known[13] and expected to have the apical atom somewhat further removed than normal, due to Jahn–Teller distortions. In $[Cu(bipy)F_2(H_2O)]$ with the water

Table 4. The hydrogen bonding (and Cu–F bonds) of crystals exhibiting ligand fluoride–lattice water hydrogen bonding

Complex	R(F···O)/Å	R(Cu–F)/Å	Ref.
$Sr[TiF_6]\cdot 2H_2O$	2.75, 2.77		*a*
$Rb[VF_4]\cdot 2H_2O$	2.56		*b*
$Rb_2[AlF_5]\cdot H_2O$	2.79		*c*
$[Cu(dpa)(H_2O)_2F]F\cdot 3H_2O$	*d*	1.934(3)	15
$NaCa[AlF_6]\cdot H_2O$	2.742, 2.788, 2.832, 2.862		*e*
$[Cu(na)_2F_2(H_2O)_2]\cdot 4H_2O$	2.683, 2.727, 2.853	1.911(3)	5
$[Co_3(tmtr)_4F_2(NCS)_4(H_2O)_2]\cdot 4H_2O$	2.753		*f*
$Ba[MnF_5]\cdot H_2O$	2.794		*g*
$[Cu(bipy)F_2(H_2O)]\cdot 2H_2O$	2.634, 2.663 2.666, 2.673	1.884(4) 1.889(4)	This work

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[d] No hydrogen bonding recorded between ligand F and lattice water, but lattice F^- bonds to both of the ligand and the lattice water with R(F···O) 2.517, 2.621, and 2.659 Å respectively.
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[g] W. Massa and V. Burk, *Z. Anorg. Allg. Chem.*, 1984, **516**, 119.

at the apex we find R(Cu–O) = 2.214(5) Å, rather short for such an arrangement. In the (4 + 1) complex [*N,N'*-propane-1,2-diylbis(salicylideneiminato)]copper(II) monohydrate, which has a similar (4 + 1) arrangement, the apical Cu–OH_2 bond is 2.53(1) Å.[14] However in a similar mononuclear five-cordinate complex to the one reported here, $[Cu(dpa)F(H_2O)_2]F\cdot 3H_2O$ (dpa = di-2-pyridylamine), there is also an apical water ligand with R(Cu–O) = 2.218(4) Å.[15]

Another interesting feature of the current compound is the shortness of the Cu–F bonds; at 1.884(4) and 1.889(4) Å they are the shortest known. Apart from the examples in Table 4, a few other Cu–F bonds are reported in the literature. In each case the shorter of the Cu–F bonds are 1.906(1) ($CuF_2\cdot 2H_2O$),[16] 1.93(3) (CuF_2),[17] 1.91(3) (Na_2CuF_4),[18] 1.92(4) (K_2CuF_4),[19] and 1.90(1) Å (Ba_2CuF_6).[20] A rare example of a fluoride bridging two copper atoms is found in $[Cu_2F_2(dmpz)_2(mpz)_4][BF_4]_2$ (dmpz = 3,5-dimethylpyrazole, mpz = 5-methylpyrazole) with R(Cu–F) = 1.904(2) and 2.258(2) Å.[21]

Copper(II) fluoride has recently been reported to be an excellent fluorinating agent for organic chlorides and bromides, resulting in 90% or better conversion.[22] The reactions are performed in refluxing acetonitrile in the presence of a six-fold excess of 2,2'-bipyridine, which is assumed to form $[Cu(bipy)_3]^{2+}$ $2F^-$.[23] This complex is soluble in MeCN and produces a solution of 'naked' fluoride ion. With only a 1 : 1 ratio of CuF_2 : bipy, the yields are much reduced. Clearly under these conditions the complex is $[Cu(bipy)F_2]$ which would explain the poorer nucleophilicity of the system.

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