

The Hydrogen Bonding of Ligand Fluoride: the X-ray Crystal Structure of Difluoro(2,2':6',2''-terpyridine)copper(II) Trihydrate

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Abstract

The X-ray crystal structure of the title compound shows it to be $[\text{Cu}(\text{terpy})\text{F}_2] \cdot 3\text{H}_2\text{O}$ (terpy = 2,2':6',2''-terpyridine) with a pentacoordinate copper in a square pyramidal configuration. The basal Cu–F bond is the shortest such bond so far reported (1.862–(4) Å). The hydrogen bonds between the apical fluoride and lattice waters are among the shortest known with $R(\text{F} \cdots \text{O})$ of 2.595 and 2.598 Å.

Introduction

The standard method for quenching enzyme activity is to add fluoride to the system. The mechanism by which the fluoride ion operates is probably by attachment as a ligand to the metal centre followed by strong hydrogen bonding to surrounding OH and NH groups. This was clearly seen in the case of cytochrome c peroxidase [1], where an X-ray study of the fluoride poisoned enzyme revealed significant structural distortions around the active site caused by fluoride hydrogen bonding.

It is difficult to assess the hydrogen bonding ability of a fluoride coordinated to a metal since few examples are known. However in those complexes that have been subjected to X-ray crystallography some hydrogen bonds have been observed. Fluoride complexes often have associated waters of crystallization to which such bonds form. The $R(\text{F} \cdots \text{O})$ hydrogen bond distances reported are usually longer than 2.70 Å but a few are shorter: $[\text{Cu}(\text{na})_2\text{F}_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (na = nicotinamide) 2.683 Å [2]; $[\text{Cu}(\text{bipy})\text{F}_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ 2.634–2.673 Å [3]; and in $[\text{Cu}(\text{phen})\text{F}_2(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ 2.670–2.691 Å [4]. The shortest recorded ligand fluoride–lattice water bond is 2.56 Å in $\text{Rb}[\text{VF}_4] \cdot 2\text{H}_2\text{O}$ [5] but here the complex is negatively charged which improves its ability to act as a hydrogen bond acceptor.

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In the copper fluoride complexes mentioned above, the ligand sphere is shared by one or more coordinated waters which are also capable of hydrogen bonding to lattice waters and invariably do so [2–4]. In choosing to investigate the complex between CuF_2 and terpy we hoped to exclude such ligand waters. This complex was first reported as green crystals by Levason *et al.* as $\text{Cu}(\text{terpy})\text{F}_2 \cdot 2\text{H}_2\text{O}$ [6] and later by Henke *et al.* as a very hygroscopic compound of presumed composition $[\text{Cu}(\text{terpy})\text{F}_2] \cdot n\text{H}_2\text{O}$ [7]. No other data were given although crystal structures of the corresponding $[\text{Cu}(\text{terpy})\text{Cl}_2]$ and $[\text{Cu}(\text{terpy})\text{Cl}_2] \cdot \text{H}_2\text{O}$ showed pentacoordinate copper, and a simultaneous report [8] on the latter compound also revealed that the long apical chloride of the square pyramid formed hydrogen bonds to two different lattice waters with $R(\text{Cl} \cdots \text{O})$ of 3.200 and 3.274 Å. The basal chloride was not involved in hydrogen bonding.

The complex of CuF_2 and terpy thus offered the possibility of forming a water-free complex and of strong hydrogen bonding between two different fluoride ligands and lattice waters.

Experimental

Synthesis of Difluoro(2,2':6',2''-terpyridine)copper(II) Trihydrate

CuF_2 (0.25 g, 2.5 mmol) was added to a solution of terpy (0.58 g, 2.5 mmol) in wet methanol (50 cm^3). The CuF_2 slowly dissolved and after 24 h a clear, dark green solution was obtained which was reduced to a third of its volume on a rotary evaporator and then left to stand. After two days large green crystals of the title compound were obtained which were dried over silica gel; melting point 265 °C (decomp.). *Anal.* Found: C, 46.66; H, 4.15; N, 10.70. Calc. for $\text{C}_{15}\text{H}_{17}\text{CuF}_2\text{N}_3\text{O}_3$: C, 46.29; H, 4.37; N, 10.80%. The original discoverers of this complex reported it to be the dihydrate [6] presumably due to vacuum drying of their crystals.

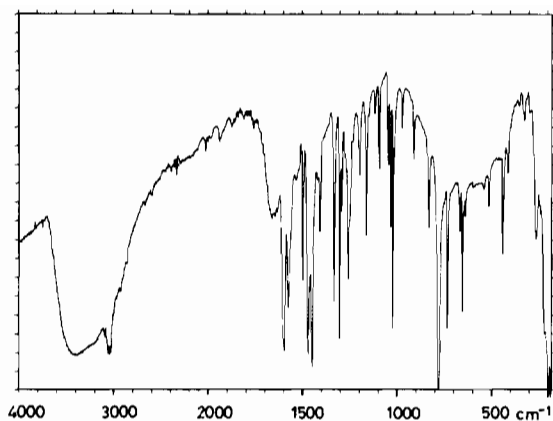


Fig. 1. IR spectrum of $[\text{Cu}(\text{terpy})\text{F}_2] \cdot 3\text{H}_2\text{O}$.

The IR spectrum of $[\text{Cu}(\text{terpy})\text{F}_2] \cdot 3\text{H}_2\text{O}$ recorded on a model 983 G Perkin-Elmer spectrometer, using a KBr disc, is shown in Fig. 1. This displays three broad regions characteristic of OH hydrogen bond absorptions centred at 3400, 1650 and 600 cm^{-1} . Superimposed on the lower of these are strong sharper signals at 779 $\nu(\text{Cu}-\text{N})$, 731 $\nu(\text{Cu}-\text{F})$, 665 $\nu(\text{Cu}-\text{N})$, 438 $\delta(\text{Cu}-\text{F})$ and 261 $\delta(\text{Cu}-\text{N})$ cm^{-1} . The assignments of the Cu-F modes are strongly supported by their counterparts at 730 and 475 in $[\text{Cu}(\text{dipy})\text{F}_2(\text{H}_2\text{O})]$ [3]. This complex has a band at 550 cm^{-1} attributed to $\nu(\text{Cu}-\text{OH}_2)$ which is absent from the terpy complex.

Crystal Data

$\text{C}_{15}\text{H}_{17}\text{CuF}_2\text{N}_3\text{O}_3$, $M_R = 388.860$, orthorhombic, space group $Pbcn$ (No. 60), $a = 13.189(6)$, $b = 14.666(4)$, $c = 16.225(6)$ Å, $V = 3138(2)$ Å³, $Z = 8$, $D_c = 1.646$ g cm^{-3} , $F(000) = 1592$, $\mu(\text{Mo K}\alpha) = 14.3$ cm^{-1} , crystal dimensions = 0.75 × 0.50 × 0.45 mm.

Data Collection

Unit cell parameters and intensity data were obtained by following previously detailed procedures [9] using a CAD4 diffractometer operating in the $\omega-2\theta$ scan mode, with graphite monochromated Mo K α radiation ($\lambda = 0.71069$ Å). A total of 2755 unique reflections were collected ($3 \leq 2\theta \leq 50^\circ$). The segment of reciprocal space scanned was: (h) $0 \rightarrow 15$; (k) $0 \rightarrow 17$; (l) $0 \rightarrow 19$. The reflection intensities were corrected for absorption using the azimuthal scan method [10]; maximum transmission scan factor 1.00, minimum value 0.86.

Structure Solution and Refinement

The structure was solved by the application of routine heavy-atom methods (SHELX86) [11] and refined by full-matrix least-squares (SHELX76) [12]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms of the terpy ligand

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) for $[\text{Cu}(\text{terpy})\text{F}_2] \cdot 3\text{H}_2\text{O}$

	x	y	z
Cu	1559.7(4)	765.2(4)	1910.7(3)
F(1)	1553(2)	272(2)	853(1)
F(2)	3117(2)	847(2)	2182(2)
O(1)	4359(3)	1425(2)	1053(2)
O(2)	3167(3)	597(2)	-142(2)
O(3)	3759(4)	660(4)	3684(2)
N(1)	1282(3)	-388(2)	2555(2)
N(2)	1196(3)	1289(3)	2965(2)
N(3)	1467(3)	2103(3)	1602(2)
C(1)	1309(4)	-1249(3)	2283(3)
C(2)	1202(4)	-1995(3)	2804(3)
C(3)	1051(4)	-1843(3)	3639(3)
C(4)	1011(4)	-961(3)	3928(3)
C(5)	1134(3)	-239(3)	3382(2)
C(6)	1111(3)	728(3)	3615(2)
C(7)	1027(4)	1087(3)	4409(3)
C(8)	1040(4)	2019(4)	4501(3)
C(9)	1126(4)	2597(3)	3820(3)
C(10)	1197(3)	2197(3)	3044(3)
C(11)	1289(3)	2667(3)	2245(3)
C(12)	1207(4)	3608(3)	2143(3)
C(13)	1308(4)	3959(3)	1354(3)
C(14)	1498(4)	3383(3)	700(3)
C(15)	1587(4)	2458(3)	848(3)

placed into calculated positions (C-H 0.96 Å; $U = 0.10$ Å²). Hydrogen atoms of the lattice water molecules were not included in the model. The final residual R and R_w were 0.039 and 0.041 respectively for the 217 variables and 1983 data for which $F_o > 6\sigma(F_o)$. The function minimized was $\sum_w (|F_o| - |F_c|)^2$ with the weight, w , being defined as $1/[\sigma^2(F_o) + 0.00009F_o^2]$.

Atomic scattering factors and anomalous scattering parameters were taken from refs. 13 and 14 respectively. All computations were made on a DEC VAX-11/750 computer. Table I lists the atomic coordinates, Table II the bond lengths and angles of $[\text{Cu}(\text{terpy})\text{F}_2] \cdot 3\text{H}_2\text{O}$ whose structure is shown in Fig. 2. A unit cell packing diagram is shown in Fig. 3 and the intermolecular hydrogen bonds listed in Table III.

Discussion

Contrary to expectations [7] a stable crystalline product was obtained by dissolving CuF_2 in wet methanol containing terpy, and allowing the solution slowly to evaporate. Chemical analysis showed it to be $\text{CuF}_2(\text{terpy}) \cdot 3\text{H}_2\text{O}$ and X-ray analysis proved it to be $[\text{Cu}(\text{terpy})\text{F}_2] \cdot 3\text{H}_2\text{O}$ with both fluorides as ligands in a square pyramidal complex, Fig. 2. The structure shows two unique features (i) the shortest

TABLE II. Bond Lengths (Å) and Angles (°) for [Cu(terpy)F₂] \cdot 3H₂O

Bond lengths			
F(1)–Cu	1.862(4)	F(2)–Cu	2.104(5)
N(1)–Cu	2.022(5)	N(2)–Cu	1.935(5)
N(3)–Cu	2.028(6)	C(1)–N(1)	1.339(7)
C(5)–N(1)	1.372(6)	C(6)–N(2)	1.343(6)
C(10)–N(2)	1.337(7)	C(11)–N(3)	1.352(6)
C(15)–N(3)	1.338(6)	C(2)–C(1)	1.389(7)
C(3)–C(2)	1.388(7)	C(4)–C(3)	1.376(7)
C(5)–C(4)	1.390(7)	C(6)–C(5)	1.469(7)
C(7)–C(6)	1.396(7)	C(8)–C(7)	1.374(8)
C(9)–C(8)	1.398(7)	C(10)–C(9)	1.392(7)
C(11)–C(10)	1.474(7)	C(12)–C(11)	1.394(7)
C(13)–C(12)	1.387(7)	C(14)–C(13)	1.379(8)
C(15)–C(14)	1.384(8)		
Bond angles			
F(2)–Cu–F(1)	102.7(2)	N(1)–Cu–F(1)	98.7(2)
N(1)–Cu–F(2)	96.7(2)	N(2)–Cu–F(1)	165.3(1)
N(2)–Cu–F(2)	92.0(2)	N(2)–Cu–N(1)	80.2(2)
N(3)–Cu–F(1)	98.5(2)	N(3)–Cu–F(2)	93.2(2)
N(3)–Cu–N(1)	157.8(1)	N(3)–Cu–N(2)	79.6(2)
C(1)–N(1)–Cu	127.8(4)	C(5)–N(1)–Cu	113.5(4)
C(5)–N(1)–C(1)	118.5(5)	C(6)–N(2)–Cu	118.2(4)
C(10)–N(2)–Cu	118.7(4)	C(10)–N(2)–C(6)	122.2(5)
C(11)–N(3)–Cu	114.3(4)	C(15)–N(3)–Cu	126.5(4)
C(15)–N(3)–C(11)	119.1(5)	C(2)–C(1)–N(1)	122.6(5)
C(3)–C(2)–C(1)	118.8(6)	C(4)–C(3)–C(2)	119.3(5)
C(5)–C(4)–C(3)	119.6(5)	C(4)–C(5)–N(1)	121.2(5)
C(6)–C(5)–N(1)	114.1(5)	C(6)–C(5)–C(4)	124.6(5)
C(5)–C(6)–N(2)	112.8(4)	C(7)–C(6)–N(2)	120.1(5)
C(7)–C(6)–C(5)	127.2(5)	C(8)–C(7)–C(6)	118.3(5)
C(9)–C(8)–C(7)	121.3(5)	C(10)–C(9)–C(8)	117.6(5)
C(9)–C(10)–N(2)	120.5(5)	C(11)–C(10)–N(2)	112.4(5)
C(11)–C(10)–C(9)	127.1(5)	C(10)–C(11)–N(3)	114.0(5)
C(12)–C(11)–N(3)	121.9(5)	C(12)–C(11)–C(10)	124.1(5)
C(13)–C(12)–C(11)	118.0(5)	C(14)–C(13)–C(12)	120.1(5)
C(15)–C(14)–C(13)	118.8(6)	C(14)–C(15)–N(3)	122.1(6)

reported Cu–F bond and (ii) the shortest F \cdots H–O hydrogen bonds between lattice water molecules and a fluoride ligand in a neutral complex.

Terpy as a ligand produces uncommon geometries by virtue of its stereochemistry [15] such as the distorted tetragonal pyramid of [Cu(terpy)Cl₂] [7, 8]. The same geometry is found for [Cu(terpy)F₂] in which the Cu–N bonds are fractionally shorter (0.01–0.02 Å) than in the chloro complex. The copper atom is 0.2 Å above the basal plane, whereas in the chloro complex it is 0.4 Å [8]. However it is the very short R(Cu–F) of 1.862(4) Å of the basal fluoride which is the notable feature. The apical fluoride has R(Cu–F) = 2.104(5) Å.

In a previous paper [4] we collated the Cu–F dimensions of all 17 complexes with this bond that are reported in the literature. These ranged from 2.07(1) to 2.467(2) Å for ‘apical’ bonds and from 1.884(4) to 1.934(3) Å for ‘equatorial’ bonds. And whereas the apical bond reported in this study is

not the shortest of its kind, as is the basal bond, this may be due to the two strong hydrogen bonds it forms. The effect of the hydrogen bonding causes a lengthening of the apical Cu–Cl bond from 2.469(2) Å in [Cu(terpy)Cl₂] to 2.554(2) Å in [Cu(terpy)Cl₂] \cdot H₂O [7, 8].

The two hydrogen bonds of the apex fluoride are 2.595 and 2.598 Å, shorter than that previously reported for a Cu–F \cdots H–O of a neutral complex of 2.634 Å [4]. The single hydrogen bond of the basal fluoride at 2.714 Å is still shorter than many. How strong are these short hydrogen bonds of 2.60 Å? One measure of the strength of a hydrogen bond is the degree of overlap (Δ) of the van der Waals radii of the heavy atoms involved [16]. In normal or weak A–H \cdots B hydrogen bonding $\Delta = 0$, *i.e.* the sum of the van der Waals radii of A and B is the same as the hydrogen bond length, R(A \cdots B). For an F \cdots H–O bond the sum of the van der Waals radii is 2.90 Å (F = 1.40, O = 1.50 Å [17]).

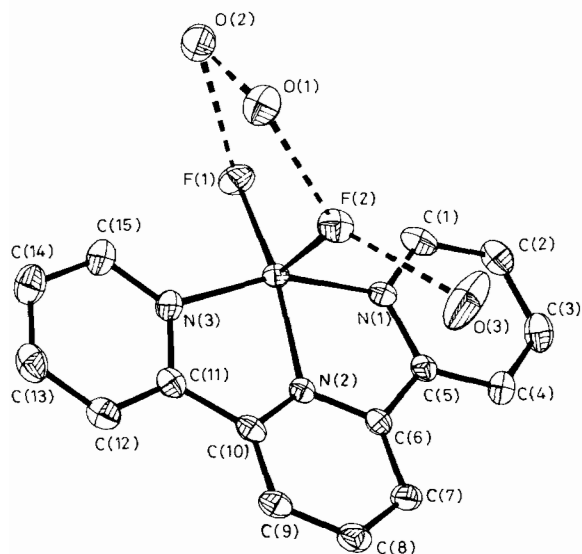


Fig. 2. Structure and atom labelling scheme for the asymmetric unit of $[\text{Cu}(\text{terpy})\text{F}_2] \cdot 3\text{H}_2\text{O}$. The potential hydrogen bonding within the unit is shown by the dashed lines.

TABLE III. Hydrogen Bonds (Å) of $[\text{Cu}(\text{terpy})\text{F}_2] \cdot 3\text{H}_2\text{O}^a$ (see Fig. 3)

F(1)···O(2)	2.714	O(1)···O(3a)	2.757
F(2)···O(1)	2.598	O(2b)···O(3c)	2.763
F(2)···O(3)	2.595		
O(1)···O(2)	2.776		

^aSymmetry operations: (a) $1.0 - x, y, 0.5 - z$. (b) $0.5 - x, 0.5 - y, 0.5 + z$. (c) $0.5 - x, 0.5 + y, z$.

The shortest hydrogen bond in $[\text{Cu}(\text{terpy})\text{F}_2] \cdot 3\text{H}_2\text{O}$ has $\Delta = 0.30$ Å. In the adduct $\text{KF} \cdot (\text{CH}_2\text{CO}_2\text{H})_2$ $R(\text{F} \cdots \text{O}) = 2.45$ Å so that $\Delta = 0.45$ Å and here the bond energy is computed to be 179 kJ mol^{-1} [18]. For a weak hydrogen bond ($\Delta = 0$) the energy is generally less than 30 kJ mol^{-1} [16], so that on a *pro rata* basis the current $\Delta = 0.30$ Å should correspond to a hydrogen bond energy of *ca.* 100 kJ mol^{-1} . With this sort of energy it is thus not surprising that a ligand fluoride can disrupt a network of weak hydrogen bonds in its immediate vicinity. This would explain why fluoride is so effective at poisoning enzymes compared to, say, other halides.

If strong $\text{F} \cdots \text{H}-\text{O}$ bonds are present in the crystal lattice they should betray themselves in the IR spectrum by lowering $\nu(\text{OH})$ of water below 2000 cm^{-1} [16]. Inspection of Fig. 1 does indeed show three broad hydrogen bonding modes. The one centred at 3400 cm^{-1} is due to inter-water hydrogen bonds. The one at 1650 cm^{-1} is therefore the stretching mode of the short $\text{F} \cdots \text{H}-\text{O}$ bonds. The band at 600 cm^{-1} is due to the hydrogen bonding bending vibrations.

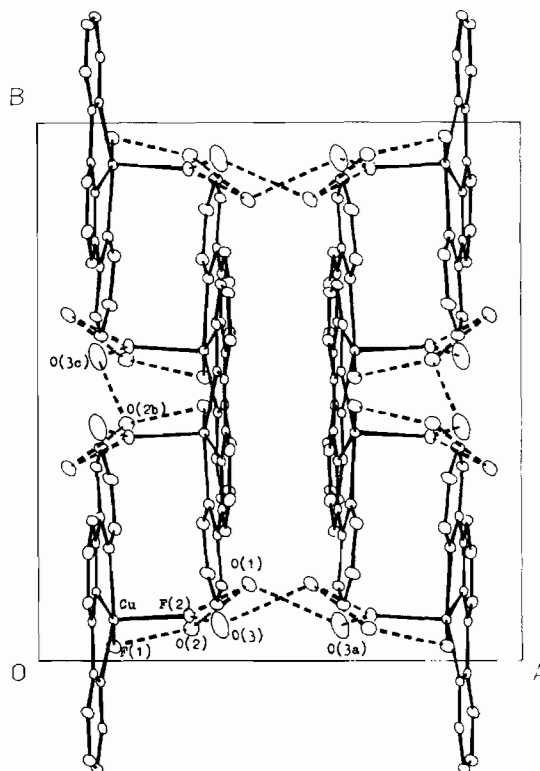


Fig. 3. A unit cell packing diagram viewed down the c axis of $[\text{Cu}(\text{terpy})\text{F}_2] \cdot 3\text{H}_2\text{O}$. Dashed lines show the potential hydrogen bonding network of the lattice water molecules.

Supplementary Material

Tables of thermal parameters, H-atom coordinates, bond lengths and angles are available from one of the authors (M.B.H.).

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