

Diaquabis(1,3-diaminopropane)copper(II) Difluoride: X-ray Structure Reveals Short Hydrogen Bonds Between Ligand Waters and Lattice Fluorides

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Abstract

The X-ray crystal structure of $[\text{Cu}(\text{pn})_2(\text{H}_2\text{O})_2]\text{F}_2$, (pn = 1,3-diaminopropane) provides a rare example of short hydrogen bonds between ligand waters and lattice fluorides with $R(\text{F}\cdots\text{O}) = 2.644$ and 2.678 Å.

Introduction

In a previous publication on the crystal structure of $[\text{Cu}(\text{bipy})\text{F}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ we reported on the hydrogen bonding between the ligand fluoride of this five coordinate copper complex and the nearby lattice waters [1]. To date nine other complexes** have been reported with this type of hydrogen bonding, generally to metals other than copper [1, 2]. The reverse combination of ligand water hydrogen bonding to lattice fluoride is much less common.

The hydrogen bonding capability of ligand fluoride is of biological interest. The reported structure of a fluoride-poisoned enzyme, cytochrome *c* peroxidase [3] shows how a fluoride ligand attached to the metal centre distorts the surrounding framework by forming hydrogen bonds. Prior to taking its position as a ligand the fluoride ion is thought to displace an existing water ligand, to which it will be attracted by the formation of a hydrogen bond in its latter stages of approach. Formation of this bond can be imagined as the final step before the two switch position, so that the fluoride becomes the ligand and the water molecule escapes. It is of interest, therefore, to have some idea of the relative strengths of these two kind of hydrogen bonds, which can be judged by a comparison of their relative lengths.

We now report the structure of a copper complex in which the rarer ligand water–lattice fluoride hydrogen bonding is present.

Experimental

Synthesis of $[\text{Cu}(\text{pn})_2(\text{H}_2\text{O})_2]\text{F}_2$

Copper(II) fluoride (0.5 g, 5 mmol) was added to a solution of 1,3-diaminopropane (1.3 cm³ mmol) dissolved in wet methanol (50 cm³). The CuF_2 slowly dissolved on stirring and after 1 h a clear purple solution was obtained. This was filtered and reduced to a third of its original volume by pumping. To the viscous solution so obtained was added 1,3-dimethoxypropane (2 cm³) and the solution stirred at room temperature, then left to stand. After a few days large mauve crystals of $[\text{Cu}(\text{pn})_2(\text{H}_2\text{O})_2]\text{F}_2$ were formed which were filtered off and dried over silica gel. Melting point 255 °C (decomp). Anal. Found: C, 25.88; H, 8.66; N, 19.22. Calc. for $\text{C}_6\text{H}_{24}\text{CuF}_2\text{N}_4\text{O}_2$: C, 25.19; H, 8.40; N, 19.59%. The IR spectrum (4000–180 cm⁻¹) was recorded on a model 983G Perkin-Elmer IR spectrometer using a KBr disc. The significant peaks and likely assignments are 3418vs, br $[\nu(\text{H}_2\text{O})]$; 3238vs, 3219vs, 3138vs [all $\nu(\text{NH}_2)$]; 2938s, 2884s, $[\nu(\text{CH})]$; 1658m, 1584s, 1440m, 1401m, 1317w, 1291m, 1175s, 1122w, 1062m, 1026s, 913s, 884w, 690s $[\nu(\text{CuN})]$; 638s, br, 494s $[\nu(\text{CuN})]$ cm⁻¹. The spectral region 900–300 cm⁻¹ reveals a broad absorption band, characteristic of strong hydrogen bonding which we assign to F---H—O vibrational modes.

The conductivity of a 4.16×10^{-3} mol dm⁻³ solution of $[\text{Cu}(\text{pn})_2(\text{H}_2\text{O})_2]\text{F}_2$ in methanol was 422 $\mu\text{S cm}^{-1}$, showing it to be significantly ionized under these conditions.

Crystal Data

$\text{C}_6\text{H}_{24}\text{CuF}_2\text{N}_4\text{O}_2$, $M_r = 285.824$, orthorhombic, space group *Pccn* (no. 56), $a = 16.350(2)$, $b = 11.383(4)$, $c = 6.983(4)$ Å, $V = 1299.6(8)$ Å³, $Z = 4$, $D_c = 1.461$ g cm⁻³, $\lambda = 0.71069$ Å, $F(000) = 640$, $\mu(\text{Mo K}\alpha) = 17.0$ cm⁻¹, crystal size $0.86 \times 0.73 \times 0.43$ mm.

Data Collection

Unit-cell dimensions were determined and intensity data were collected at room temperature on an

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**Eight of these complexes, published before 1987, are listed in Table 4 of ref. 1.

Enraf-Nonius CAD 4 diffractometer using a graphite-monochromated Mo K α radiation and an ω - 2θ scan procedure [4]. A total of 1142 unique reflections was collected ($3^\circ < 2\theta < 50^\circ$). The segment of reciprocal space scanned was: (h) $0 \rightarrow 19$, (k) $0 \rightarrow 13$, (l) $0 \rightarrow 8$. The reflection intensities were corrected for absorption using the azimuthal scan method [5]; maximum transmission factor 1.00, minimum value 0.89.

Structure Solution and Refinement

The structure was solved by the application of routine heavy-atom methods (SHELX-86) [6], and refined by full matrix least-squares (SHELX-76) [7]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms of the 1,3-diaminopropane ligands were placed into calculated position (C-H and N-H 0.96 Å, $U = 0.10 \text{ \AA}^2$). Hydrogen atoms of the coordinated water molecules were not included in the model. The final residuals R and R_w were 0.055 and 0.049 respectively for the 70 variables and 988 data for which $F_o > 3\sigma(F_o)$. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weight, $w = 1/[\sigma^2(F_o) + 0.00001F_o^2]$. Interchanging the assignment of F and O resulted in higher residuals ($R = 0.060$, $R_w = 0.056$), therefore the initial assignment as given in Figs. 1 and 2 is correct.

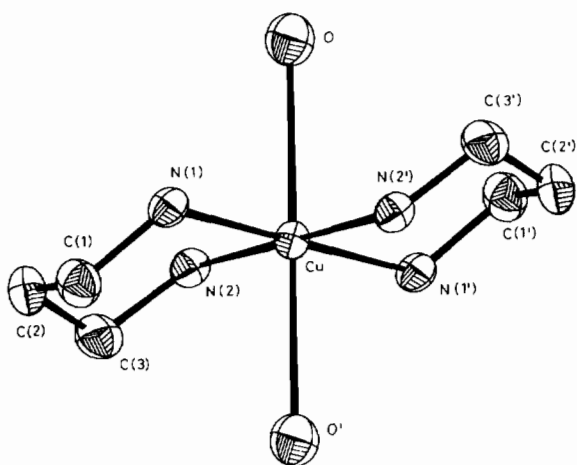


Fig. 1. Structure and atom labelling of $[\text{Cu}(\text{pn})_2(\text{H}_2\text{O})_2]\text{F}_2$.

Atomic scattering factors and anomalous scattering parameters were taken from refs. 8 and 9 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 $[\text{Cu}(\text{pn})_2(\text{H}_2\text{O})_2]\text{F}_2$ whose structure is shown in Fig. 1. Figure 2 shows unit cell packing diagram and displays the short F...O hydrogen bonds.

Discussion

The title compound was originally reported as an anhydrous complex $[\text{Cu}(\text{pn})_2\text{F}_2]$ [11]. It was

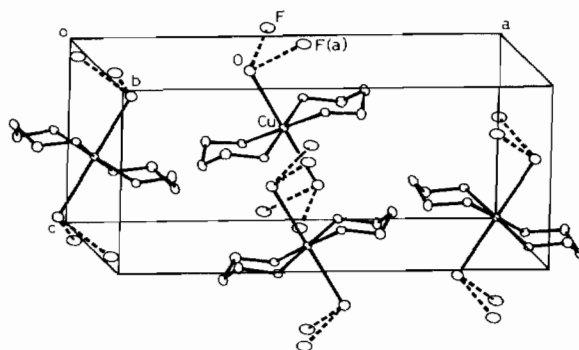


Fig. 2. Unit-cell packing diagram of $[\text{Cu}(\text{pn})_2(\text{H}_2\text{O})_2]\text{F}_2$ showing the potential F...O hydrogen bonding by dotted lines. Symmetry operator (a) $1 - x, -y, -z$.

TABLE I. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($\text{\AA}^2 \times 10^3$) for $[\text{C}_6\text{H}_{24}\text{CuN}_4\text{O}_2]^{2+}2\text{F}^-$

	x	y	z	$U(\text{eq})^a$
Cu	5000	0	5000	20.2(3)
F	4774(2)	-1611(2)	0	46(1)
O	4152(2)	224(3)	1808(5)	43(1)
N(1)	5823(2)	1132(3)	3846(5)	26(1)
N(2)	5607(2)	-1346(3)	3763(5)	25(1)
C(1)	6705(3)	837(4)	4066(7)	37(1)
C(2)	6913(3)	-324(4)	3091(7)	38(1)
C(3)	6508(3)	-1380(4)	3997(7)	36(1)

^a $U(\text{eq})$ according to Hamilton [10].

TABLE II. Bond Lengths (Å) and Bond Angles ($^\circ$) for $[\text{C}_6\text{H}_{24}\text{CuN}_4\text{O}_2]^{2+}2\text{F}^-$

Bond lengths (Å)			
O-Cu	2.637(6)	N(1)-Cu	2.030(5)
N(2)-Cu	2.020(5)	C(1)-N(1)	1.489(6)
C(3)-N(2)	1.482(6)	C(2)-C(1)	1.525(8)
C(3)-C(2)	1.511(8)		
Hydrogen bonds (Å)			
O-F	2.644	N(2)-F	2.975
O-F(a)	2.678	N(1)-F(a)	2.909
		N(1)-F(b)	2.863
		N(2)-F(c)	2.830
Bond angles ($^\circ$)			
N(1)-Cu-O	87.2(2)	N(2)-Cu-O	88.3(2)
N(2)-Cu-N(1)	89.2(2)	N(2')-Cu-N(1)	90.8(2)
C(1)-N(1)-Cu	117.2(3)	C(3)-N(2)-Cu	117.5(3)
C(2)-C(1)-N(1)	111.5(4)	C(3)-C(2)-C(1)	113.9(5)
C(2)-C(3)-N(2)	111.6(4)		

Key to symmetry operations relating designated atoms to reference atoms at (x, y, z): (') $1.0 - x, -y, 1.0 - z$; (a) $1.0 - x, -y, -z$; (b) $1.0 - x, 0.5 + y, 0.5 - z$; (c) $x, -0.5 - y, 0.5 + z$.

vacuum dried, which almost certainly accounts for the absence of water in the complex. However it is a 1:2 electrolyte in methanol.

The crystal structure of our compound shows it to be $[\text{Cu}(\text{pn})_2(\text{H}_2\text{O})_2]\text{F}_2$ of hexacoordinate copper(II), with two chelating pn ligands and two other ligands occupying more distant sites. These could be either water molecules or fluoride ions, and because the complex has a centre of symmetry must be equivalent. The conductivity of the complex in methanol solution clearly shows there to be ions present, although this in itself does not prove that in the crystalline phase the complex is ionic. However, that the other ligands are water, is supported by the $R(\text{Cu}-\text{O})$ bond lengths of 2.637(6) Å, which are much too long for Cu-F bonds, even allowing for the Jahn-Teller effect. Also the temperature factors for these apical atoms indicate them to be oxygens; assuming them to be fluorines leads to a worsening of the R factors.

The compound $[\text{Cu}(\text{pn})_2(\text{H}_2\text{O})_2]\text{F}_2$ is clearly a rare example of a complex with ligand waters, hydrogen bonded to lattice fluorides. Two other such copper complexes are known. In the first, $[\text{Cu}(\text{bipyam})(\text{H}_2\text{O})_2]\text{F}\cdot 3\text{H}_2\text{O}$, (bipyam = 2,2'-bipyridylamine) [12] there are two ligand water-lattice fluoride hydrogen bonds of length 2.517 and 2.621 Å, as well as a lattice water-lattice fluoride bond of 2.659 Å. In the second, more recent example, $[\text{Cu}(\text{Him})_4(\text{H}_2\text{O})_2]\text{F}_2$ (Him = imidazole) [13] the ligand water-lattice fluoride distances are 2.695 and 2.717 Å. In this complex $R(\text{Cu}-\text{O}) = 2.638(2)$ Å, the same as in $[\text{Cu}(\text{pn})_2(\text{H}_2\text{O})_2]\text{F}_2$. However there are significant differences between the crystal environments of the two complexes. Although the fluoride ions in the former are hydrogen bonded to ligand waters, they are also closely hydrogen bonded to the non-coordinating nitrogens of the ligands, producing a unique fluoride environment of four tetrahedrally arranged hydrogen bonds in which $R(\text{F}\cdots\text{N}) = 2.647$ and 2.661 Å, shorter than the hydrogen bonds to the water molecules.

Three examples of other metal complexes, with ligand water molecules hydrogen bonded to lattice fluorides, have been reported. These display the following $R(\text{F}\cdots\text{O})$ (Å) values: $[\text{W}(\text{PMe}_3)_4\text{H}_2(\text{H}_2\text{O})\text{F}]\text{F}$, 2.40 [14]; $[\text{NH}_4]_2[\text{Cr}(\text{H}_2\text{O})_6]\text{F}_5$, 2.53 and 2.57 [15]; and $[\text{Cr}(\text{H}_2\text{O})_6]\text{F}_3\cdot 3\text{H}_2\text{O}$, 2.61 [16]. In the first of these there are very short hydrogen bonds (2.59 Å) between the ligand fluoride and the ligand water on the same metal, as well as the longer bonds between the ligand water and the lattice fluoride.

In considering the relative strengths of hydrogen bonds formed between water and fluoride the participation of the water molecule as a ligand is expected to enhance its ability to act as a hydrogen bond donor, while the participation of F^- as a ligand is expected to weaken its ability to act as a hydrogen

bond acceptor. Thus we anticipate that, given the same metal centre, a $\text{Cu}-\text{OH}_2\cdots\text{F}^-$ bond would be significantly stronger than the corresponding $\text{Cu}-\text{F}\cdots\text{HOH}$ hydrogen bond, and that this should be reflected in the $R(\text{F}\cdots\text{O})$ distances.

Clearly the influence of the metal atom is important, witness the short ligand water-lattice fluoride hydrogen bonds of the tungsten and chromium complexes. Examples of ligand fluoride-lattice water hydrogen bonds involving these metals have not been reported so comparisons cannot be made of the two types of bond. The only examples of both types are to be found in copper complexes.

In the structure we report here the hydrogen bonds are marginally shorter than the reverse situation, exemplified by the hexacoordinate copper(II) complex $[\text{Cu}(\text{na})_2\text{F}_2(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$ (na = nicotinamide) [17]. In this complex the $R(\text{F}\cdots\text{O})$ distances were 2.683, 2.727 and 2.853 Å. However the difference is not such as to lead us to postulate a driving force favouring rearrangement between the two forms of hydrogen bond. Clearly attraction to and displacement of a water ligand by a fluoride will be aided by the intermediate formation of a strong hydrogen bond between the two, and having made the switch, the potential exists for even stronger hydrogen bonds to the surroundings. In this respect fluoride approach to an active site poses a serious threat to an enzyme's survival as a functioning unit, and explains the common practice of using fluoride salts to quench enzyme activity.

Supplementary Material

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

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