X-Ray Structures of [Cu(cyclam)(H_2O)$_2$]F_2·4H_2O (cyclam = 1,4,8,11-tetra-azacyclotetradecane) and [Cu(en)$_2$(H_2O)$_2$]F_2·4H_2O (en = ethylenediamine) Reveal [F(H_2O)$_4$]$^-$ with Strong Hydrogen Bonds

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The much-discussed hydrated fluoride ion [F(H_2O)$_4$]$^-$ has turned up in two copper complexes whose structures show this ion to have four short hydrogen bonds with *r*(O · · · F) = 2.65 Å (av.).

The species [F(H_2O)$_4$]$^-$ has been speculated about many times and its dimensions and energy calculated.[1—6] In solution, [F(H_2O)$_4$]$^-$ has been discussed as the most likely form of the solvated fluoride ion.[7—11] However, it has never been directly observed in the lattices of metal fluoride hydrates.

We have been investigating the hydrogen bonding between F^- and water,[12—16] where either may be a ligand, a situation which is relevant to their role in fluoride deactivation of metal-containing enzymes. Several hydrated copper fluoride complexes have been analysed by *X*-ray diffraction and their structures revealed most to have ligand–fluoride to lattice-water hydrogen bonds.[12—15]

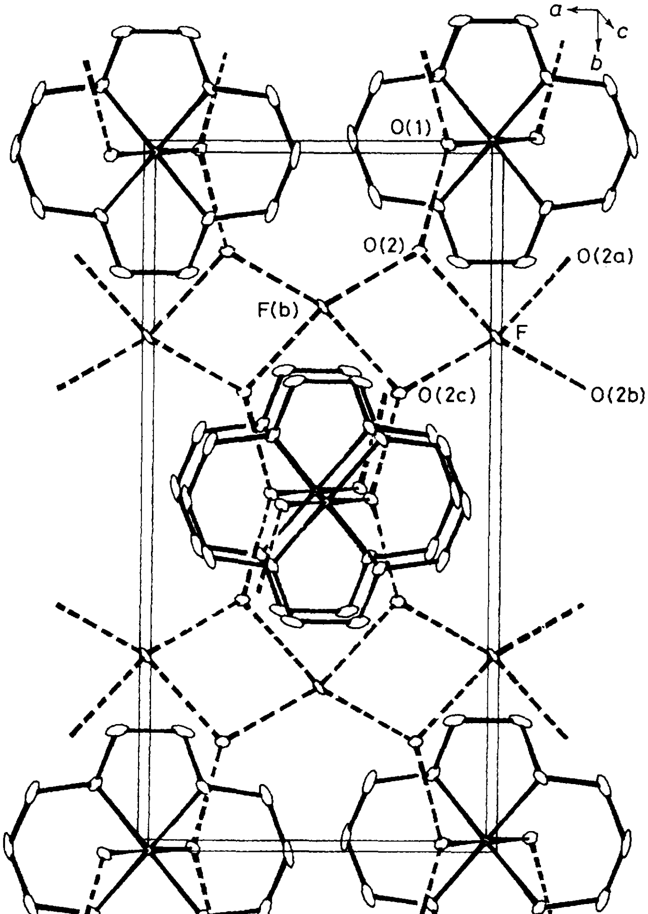

Figure 1. The structure of [Cu(cyclam)(H_2O)$_2$]F_2·4H_2O, (**1**). Selected bond lengths (Å) are: Cu–N 2.012(5), Cu–OH_2 2.484(6), hydrogen bonds: F · · · O(2), O(2a) 2.643 and F · · · O(2b), O(2c) 2.687. Symmetry operations relating designated atoms to reference atoms at (*x*, *y*, *z*): (a) −*x*, *y*, 1.0− *z*; (b) −0.5 −*x*, −0.5 −*y*, 1.0− *z*; (c) 0.5+ *x*, −0.5− *y*, *z*.

Much rarer are complexes in which the fluoride is in the lattice and forming hydrogen bonds to ligand-waters, but an example has recently come to light.[16] Occasionally the hydrated HF molecule has turned up in crystal structures, as in HF·H_2O and HF·2H_2O[17] but in effect these are respectively $H_3O^+F^-$, with *r*(O · · · F) = 2.464 Å, and $H_3O^+HF_2^-$, with *r*(F · · · O) = 2.453 Å. More recently in the lattice of a copper amidopyridine complex[18] the true hydrate HF·H_2O has been found with *r*(F · · · O) = 2.749 Å.

We now report two copper fluoride complexes which have unique fluoride environments. The first, [Cu(cyclam)(H_2O)$_2$]F_2·4H_2O (cyclam = 1,4,8,11-tetra-azacyclotetradecane) (**1**),† has discrete and interlinking units of [F(H_2O)$_4$]$^-$ in the lattice (Figure 1). The second, [Cu(en)$_2$(H_2O)$_2$]F_2·4H_2O (en = ethylenediamine) (**2**),† has the same [F(H_2O)$_4$]$^-$ grouping, except that in this crystal one of the solvating water molecules is attached as a ligand to copper (Figure 2). The anhydrous form of this complex, [Cu(en)$_2F_2$], has previously been reported.[19]

In both complexes the shortness of the four hydrogen bonds to the fluoride ion is the most unexpected feature. The average *r*(F · · · O) distance in the cyclam complex is 2.67 Å, and in the ethylenediamine complex it is 2.64 Å. These are 0.1 Å shorter either than predicted theoretically[2] or calculated from experimental data.[10] Other OHF hydrogen bonds not

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† *Crystal data* for (**1**): $C_{10}H_{36}CuF_2N_4O_6$, *M* = 409.96, monoclinic, space group *C*2/*m*, *a* = 8.179(2), *b* = 15.854(2), *c* = 7.123(3) Å, β = 101.98(3)°, *U* = 903.4(4) Å^3, *Z* = 2, D_c = 1.507 g cm^{-3}, *F*(000) = 438, λ = 0.71069 Å, µ(Mo-K_α) = 12.6 cm^{-1}, crystal dimensions 0.75 × 0.70 × 0.38 mm. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares using absorption corrected data. Measurements were made on a CAD-4 diffractometer using Mo-K_α radiation, graphite monochromator, $3 \leqslant 2\theta \leqslant 50°$, *h* ($-9 \rightarrow 9$) *k* ($0 \rightarrow 18$) *l* ($0 \rightarrow 8$), 901 reflections were observed, 822 of which were independent [$I \geqslant 1.5\sigma(I)$]. All non-hydrogen atoms were refined anisotropically, hydrogen atoms were not included; 58 parameters refined. The final residuals *R* and R_w were 0.052 and 0.059, respectively.

For (**2**): $C_4H_{28}CuF_2N_4O_6$, *M* = 329.83, monoclinic, space group *P*2$_1$/*a*, *a* = 8.977(1), *b* = 13.196(2), *c* = 6.785(2) Å, β = 110.22(2)°, *U* = 754.3(3) Å^3, *Z* = 2, D_c = 1.452 g cm^{-3}, *F*(000) = 350, λ = 0.71069 Å, (Mo-K_α) = 14.9 cm^{-1}, crystal dimensions 0.62 × 0.50 × 0.37 mm. Data collection, solution, and refinement as for (**1**) above; $3 \leqslant 2\theta \leqslant 50°$, *h*($0 \rightarrow 10$) *k*($0 \rightarrow 15$) *l*($-8 \rightarrow 8$), 1477 reflections were observed, 1135 of which were independent [$I \geqslant 3\sigma(I)$]. All non-hydrogen atoms were refined anisotropically, hydrogen atoms of the 1,2-diaminoethane ligands were placed in calculated positions (C–N, N–H 0.96 Å; *U* = 0.10 Å^3; 79 parameters refined. The final residuals *R* and R_w were 0.038 and 0.046, respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

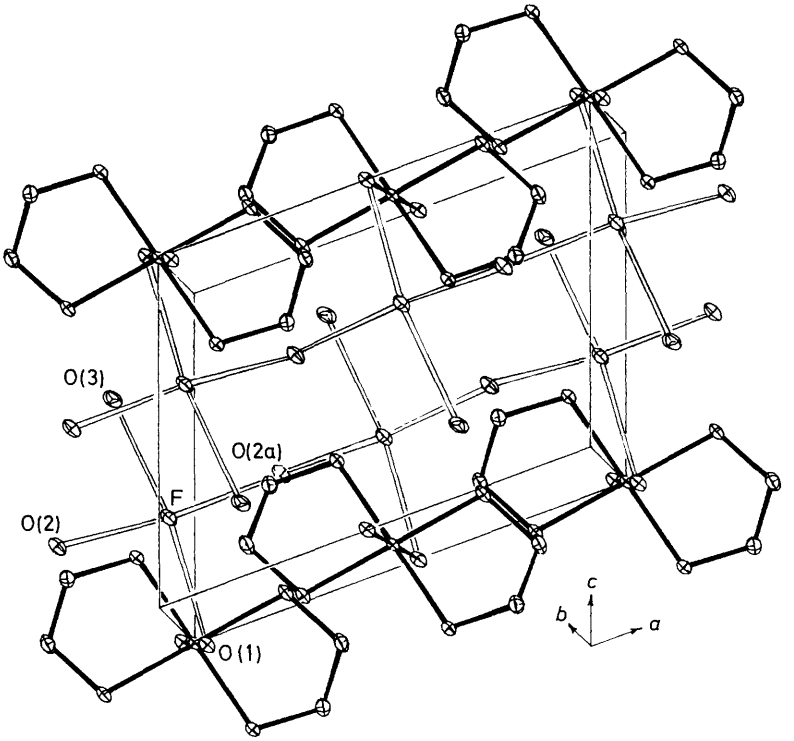

Figure 2. The structure of $[Cu(en)_2(H_2O)_2]F_2{\cdot}4H_2O$, (**2**). Selected bond lengths (Å) are: Cu–N 2.019(5), Cu–OH_2 2.571(6), hydrogen bonds: F · · · O(1) 2.617, F · · · O(2) 2.664, F · · · O(3) 2.606, and F · · · O(2a) 2.672. Symmetry operations relating designated atoms to reference atoms at (*x*,*y*,*z*): (a) 0.5+ *x*, −0.5− *y*, *z*.

involving water or H_3O^+ are shorter[17,20,21] but among those involving neutral water molecules those of $[F(H_2O)_4]^-$ are among the shortest known.[12—16]

Another noteworthy feature of $[F(H_2O)_4]^-$ is that in (**1**) there is a nearly tetrahedral co-ordination of oxygen atoms around the fluoride ion. However for (**2**), where one of the oxygens is acting as a ligand, there is considerable distortion from tetrahedral geometry. It seems that the fluoride is determining the tetrahedral arrangement against strong lattice forces. In view of the symmetry and strength of the $[F(H_2O)_4]^-$ unit, it is likely that this is the species present in fluoride solutions, where it will behave as a very weak nucleophile, as indeed it does.

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