Fluoride–Water Hydrogen Bonding: X-ray Structure of Tris(ethylenediamine)zinc(II) Fluoride Dihydrate

JOHN EMSLEY*, MUHAMMAD ARIF

Department of Chemistry, King's College, Strand, London WC2R 2LS (U.K.)

PAUL A. BATES and MICHAEL B. HURSTHOUSE

Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS (U.K.)

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Abstract

The X-ray crystal structure of the title compound shows it to be $[Zn(en)_3]^{2+}[F_2(H_2O)_2]^{2-}$. The dianion cluster has two fluoride ions strongly hydrogen bonded to two water molecules in a planar diamond shaped arrangement. The hydrogen bond lengths are 2.586 and 2.679 Å. Comparisons are made with fluoride–water hydrogen bonding in which either or both of these is also a ligand. The configuration of $[Zn(en)_3]^{2+}$ is given, and a previous determination for this cation is queried.

Introduction

In 1975 Harmon and Gennick analysed the infrared spectra of tetramethylammonium fluoride hydrates, and concluded that the monohydrate contained the complex anion cluster $[F_2(H_2O)_2]^{2-}$, held together by strong hydrogen bonds [1]. This entity was postulated as having two oxygens and two fluorides at the corners of a tetrahedron with protons lying at the centre of each face, i.e. forming three-centred hydrogen bonds [2, 3]. Theoretical calculations supported such a configuration for $[F_2(H_2O)_2]^{2-}$ [4, 5], but crystal structure investigation has yet to bring such a cluster to light.

We now report the structure of a ZnF_2 complex in which the counter anion is a water–fluoride cluster having the composition $[F_2(H_2O)_2]^{2-}$. However this does not have the predicted tetrahedral geometry.

Experimental

Synthesis and Tris(ethylenediamine)zinc(II) Fluoride Dihydrate

A suspension of powdered ZnF_2 (1.03 g, 10 mmol) in methanol (50 cm^3) was refluxed with ethylenediamine (2.0 g, 30 mmol). After 30 h a clear yellow solution was obtained. This was cooled and the volume reduced to about a third on a rotary evaporator; it was then allowed to stand. After a week white crystals of tris(ethylenediamine)zinc fluoride dihydrate were obtained, which were filtered and dried over silica gel. The compound is very hygroscopic, melting point (m.p.) 260 °C (decomp.). *Anal.* Found: C, 22.56; H, 8.66; N, 26.37. Calc. for $C_6H_{28}F_2N_6O_2Zn$: C, 22.52; H, 8.76; N, 26.28%.

The IR spectrum, run on a Perkin-Elmer 983G spectrometer, as a KBr disc, showed absorbances at 3245vs, br, 2944s, 2881s, 2180w, br, 2071w, 1635m, 1600m, br, 1582vs, 1455m, 1395vw, 1368w, 1328s, 1275s, 1144s, 1107w, 1075w, 1003vs, 977vs, 859w, 637s, br, 508s and 438m cm^{-1}.

The UV spectrum of a methanolic solution showed an absorbance at 260 nm, $e_{max} = 7.93$ dm^3 mol^{-1} cm^{-1}, and 215 nm, $e_{max} = 47.6$ dm^3 mol^{-1} cm^{-1}. The conductivity of a 16.39×10^{-3} mol dm^{-3} solution in methanol was 1345 μS cm^{-1}. The optical activity of a methanol solution, measured on a Perkin-Elmer A100, was zero.

X-ray Structure Determination

Crystal data

$C_6H_{28}F_2N_6O_2Zn$, $M = 254.32$, orthorhombic, space group *Pbcn* (No. 60), $a = 11.018(2)$, $b = 14.805(2)$, $c = 8.663(2)$ Å, $U = 1413.1(4)$ Å^3, $Z = 4$, $D_c = 1.195$ g cm^{-3}, $\lambda = 0.71069$ Å, $F(000) = 560$, μ(Mo Kα) = 1.0 cm^{-1}, crystal size $0.75 \times 0.63 \times 0.55$ mm.

Data Collection

Unit-cell dimensions were determined and intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation and an ω–2θ scan procedure [6]. A total of 1468 unique reflections were collected ($3 < 2\theta < 50°$). The segment of reciprocal space scanned was: (h) $0 \rightarrow 13$, (k) $0 \rightarrow 17$,

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*Author to whom correspondence should be addressed.

(l) 0 → 10. The reflection intensities were corrected for absorption using the azimuthal-scan method [7]; maximum transmission factor 1.00, minimum value 0.96.

Structure Solution and Refinement

The structure was solved by the application of routine heavy-atom methods (SHELX-86) [8], and refined by the full-matrix least-squares method (SHELX-76) [9]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms, including those of the lattice water molecules were refined isotropically. The final residuals R and R_w were 0.027 and 0.025 respectively for the 141 variables and 1020 data for which $F_o > 3\sigma(F_o)$. The function minimised was $\Sigma_w(|F_o| - |F_c|)^2$ with the weight, $w = 1/[\sigma^2(F_o) + 0.0005F_o^2]$. Atomic scattering factors and anomalous scattering parameters were taken from refs. 10 and 11 respectively. All computations were made on a DEC VAX-11/750 computer. Table 1 lists the atomic coordinates, Table 2 bond lengths and angles, and Table 3 the hydrogen bonds. A unit cell packing diagram is shown in Fig. 1, and the complex cation and anion in Fig. 2.

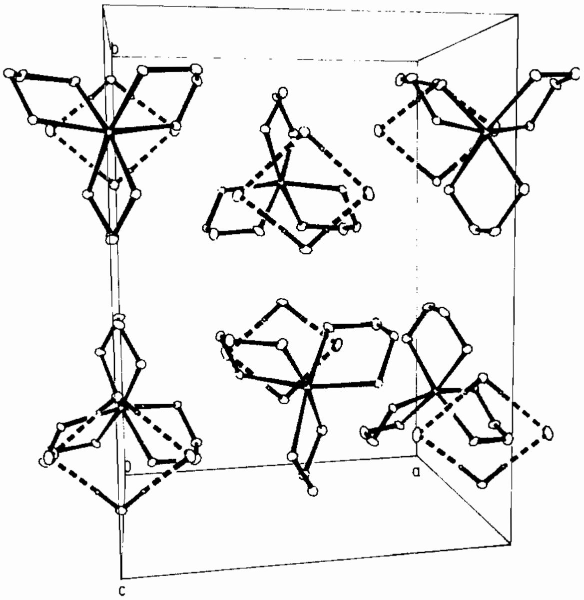

Fig. 1. Unit cell packing diagram for $[Zn(en)_3]^{2+}$ $[F_2(H_2O)_2]^{2-}$. For clarity only the hydrogen atoms of the water molecules are displayed.

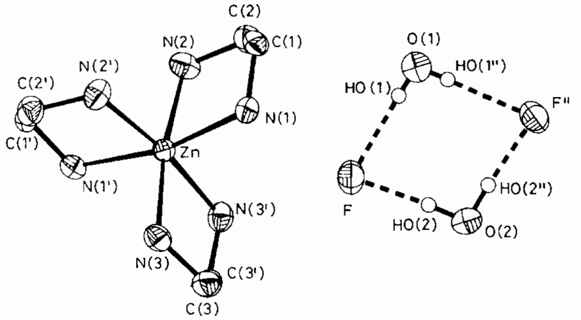

Fig. 2. The cation and anion subunits of $[Zn(en)_3]^{2+}$ $[F_2(H_2O)_2]^{2-}$. The cation is viewed along the pseudo three-fold axis of the octahedral coordination geometry, clearly showing its molecular conformation. The solvated dianion is planar diamond-shaped with the hydrogen atoms (located) on a direct line between the F and O atoms.

TABLE 1. Fractional atomic coordinates (×10^4) for $[Zn(en)_3]F_2 \cdot 2H_2O$

	x	y	z
Zn	0.0	2029.2(2)	2.500.0
F	3185(1)	3208(1)	2904(2)
O(1)	5000	2027(2)	2500
O(2)	5000	4290(2)	2500
N(1)	1723(2)	1856(2)	1307(3)
N(2)	866(2)	997(2)	3979(3)
N(3)	−623(2)	3165(2)	1094(3)
C(1)	2264(2)	1007(2)	1831(3)
C(2)	2154(2)	926(2)	3556(3)
C(3)	−15(3)	3989(2)	1632(3)

Discussion

In a recent paper we reported the solvated fluoride ion, $[F(H_2O)_4]^-$ in the crystal lattice of two complexes, $[Cu(cyclam)(H_2O)_2F_2 \cdot 4H_2O$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) and $[Cu(en)_2(H_2O)_2]F_2 \cdot 4H_2O$ (en = ethylenediamine) [12]. In both of these complexes we had expected the fluorides to be coordinated to the copper and then to form hydrogen bonds with lattice waters, as had been observed in other reported complexes [13–15].

In a similar complex the coordinated water molecules form hydrogen bonds to fluorides in the lattice, as in $[Cu(pn)_2(H_2O)_2]F_2$ (pn = 1,3-diaminopropane) [16]. Sometimes fluoride acts both as ligand and lattice counterion, as in, for example, $[Cu(bipyam)_2(H_2O)_2F]F \cdot 3H_2O$ (bipyam = 2,2′-bipyridylamine) and forms a variety of hydrogen bonds [17]. In one remarkable complex, $[Cu(Him)_4(H_2O)_2]F_2$ (Him = imidazole), fluoride acts only as a counterion but hydrogen bonds to ligand N–H groups as well as waters [18].

The interest in fluoride–water hydrogen bonding stems from the ability of fluoride to deactivate most enzymes, probably by attaching itself to the metal centre and deforming the structure around by acting as an acceptor for hydrogen bonds. In an earlier paper [13] we speculated that the strengths of hydrogen bonds to water molecules would depend upon the chemical status of the fluoride and/or the water

TABLE 2. Bond lengths (Å) and angles (°) for $[Zn(en)_3]F_2 \cdot 2H_2O$

Bond lengths			
N(1)–Zn	2.176(4)	N(2)–Zn	2.211(4)
N(3)–Zn	2.187(4)	C(1)–N(1)	1.465(4)
C(2)–N(2)	1.470(4)	C(3)–N(3)	1.467(4)
C(2)–C(1)	1.504(6)	C(3′)–C(3)	1.504(7)
HO(1)–O(1)	0.704(28)	HO(2)–O(2)	0.865(30)
HN(11)–N(1)	0.697(22)	HN(12)–N(1)	0.868(28)
HN(21)–N(2)	0.987(31)	HN(22)–N(2)	0.693(27)
HN(31)–N(3)	0.844(29)	HN(32)–N(3)	0.821(31)
H(11)–C(1)	1.080(26)	H(12)–C(1)	0.998(25)
H(21)–C(2)	1.004(27)	H(22)–C(2)	1.010(27)
H(31)–C(3)	0.985(26)	H(32)–C(3)	1.026(29)
Bond angles			
N(2)–Zn–N(1)	79.5(2)	N(3)–Zn–N(1)	95.7(2)
N(1′)–Zn–N(1)	166.5(1)	N(2′)–Zn–N(1)	91.1(2)
N(3′)–Zn–N(1)	94.7(2)	N(3)–Zn–N(2)	171.8(1)
N(2′)–Zn–N(2)	92.5(2)	N(3′)–Zn–N(2)	94.2(2)
N(3′)–Zn–N(3)	79.5(2)	C(1)–N(1)–Zn	108.0(2)
C(2)–N(2)–Zn	108.8(3)	C(3)–N(3)–Zn	108.6(3)
C(2)–C(1)–N(1)	110.1(3)	C(1)–C(2)–N(2)	108.6(3)
C(3′)–C(3)–N(3)	109.1(3)		
HN(11)–N(1)–Zn	104.4(19)		
HN(11)–N(1)–C(1)	106.4(20)	HN(12)–N(1)–Zn	116.1(19)
HN(12)–N(1)–C(1)	108.1(18)	HN(12)–N(1)–HN(11)	113.4(28)
HN(21)–N(2)–Zn	111.6(18)	HN(21)–N(2)–C(2)	105.1(18)
HN(22)–N(2)–Zn	107.7(27)	HN(22)–N(2)–C(2)	107.1(26)
HN(22)–N(2)–HN(21)	116.3(33)	HN(31)–N(3)–Zn	111.8(18)
HN(31)–N(3)–C(3)	106.1(19)	HN(32)–N(3)–Zn	115.3(22)
HN(32)–N(3)–C(3)	109.4(22)	HN(32)–N(3)–HN(31)	105.3(27)
H(11)–C(1)–N(1)	108.9(14)	H(11)–C(1)–C(2)	109.4(14)
H(12)–C(1)–N(1)	108.4(16)	H(12)–C(1)–C(2)	110.6(15)
H(12)–C(1)–H(11)	109.5(21)	H(21)–C(2)–N(2)	108.2(15)
H(21)–C(2)–C(1)	110.9(15)	H(22)–C(2)–N(2)	109.7(16)
H(22)–C(2)–C(1)	112.1(16)	H(22)–C(2)–H(21)	107.3(22)
H(31)–C(3)–N(3)	106.0(16)	H(32)–C(3)–N(3)	114.5(17)
H(31)–C(3)–C(3′)	110.0(16)	H(32)–C(3)–C(3′)	109.4(16)
H(32)–C(3)–H(31)	107.8(23)	HO(1)–O(1)–HO(1″)	101.4(54)
HO(2)–O(2)–HO(2″)	99.5(41)		

Key to symmetry operations relating designated atoms to reference atoms at (x, y, z): (′) $-x, y, 0.5 - z$; (″) $1.0 - x, y, 0.5 - z$.

TABLE 3. Hydrogen bonds of $[Zn(en)_3]F_2 \cdot 2H_2O$; bond lengths in Å (see Fig. 1)

F···O(1)	2.679	F···HN(11)	2.229
F···O(2)	2.586	F···HN(12a)	2.087
F···HO(1)	1.976	F···HN(31b)	2.141
F···HO(2)	1.722	O(2)···HN(21c)	2.058
		O(1)···HN(32d)	2.384

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

molecules giving rise to hydrogen bonds of relative strength: lattice $F^{-}\cdots$ligand $H_2O >$ ligand $F^{-}\cdots$ ligand $H_2O >$ lattice $F^{-}\cdots$lattice $H_2O >$ ligand $F^{-}\cdots$ lattice H_2O. We reasoned that complexing would reduce the ability of F^{-} to act as a hydrogen bond acceptor but increase the polarity of the O–H bond thereby making it a better hydrogen bond donor.

There is now enough data to examine this assumption more closely. Table 4 lists these hydrogen bond combinations with the averages of the shortest F··H–O bond distances in published structures. Although instances of lattice $F^{-}\cdots$ligand H_2O are rare, and the standard deviations mean there is considerable overlap in the ranges of values, the data in Table 4 refutes our earlier assumptions. The strongest bonds are formed when neither component is acting as a ligand, and when either is acting in this way, then the adverse effect on the fluoride ion to act as an

TABLE 4. Mean hydrogen bond lengths for fluoride–water hydrogen bonds

Hydrogen bond	Mean $R(F\cdot\cdot O)$ (Å)	n^a	Reference
lattice $F^- \cdots$ ligand H_2O	2.620 ± 0.069	4	b
ligand $F^- \cdots$ ligand H_2O	2.654 ± 0.053	6	b
lattice $F^- \cdots$ lattice H_2O	2.598 ± 0.050	10	c
ligand $F^- \cdots$ lattice H_2O	2.697 ± 0.082	10	d

[a] Number of bonds averaged, taking the shortest bond in each structure. [b] Taken from Table 4 of ref. 13. [c] Based on data from refs. 12, 17, 18, 22–27 and this paper. [d] Taken from Table 4 of ref. 14 and ref. 15.

acceptor is more pronounced than the adverse effect on water to act as a donor.

This being so, our attention in seeking the strongest fluoride–water hydrogen bond has been directed at compounds in which neither is acting as a ligand. In the present work we sought to achieve this by occupying all ligand sites around a metal with a chelating ligand. We reacted ZnF_2 with excess ethylenediamine (en) to form $[Zn(en)_3]^{2+}$, thereby ensuring that fluoride must act as a counterion in the lattice. What we did not expect was that under these conditions the fluoride would form a dianion cluster with water, $[F_2(H_2O)_2]^{2-}$. A preliminary communication reporting this unusual grouping has already been submitted [19].

Surprisingly the anion cluster $[F_2(H_2O)_2]^{2-}$ does not adopt the predicted geometry [1–3] which has the appeal of compactness and a high degree of symmetry. Instead it prefers to assume an alternative diamond shaped arrangement, see Fig. 2. Nor is there any evidence of the protons moving away from their parent oxygens towards centred hydrogen bonds; the low R factors indicate that we can be reasonably certain of their position, see Tables 2 and 3.

The hydrogen bonds within the cluster have $R(F\cdot\cdot O) = 2.586$ and 2.679 Å. The average hydrogen bond length, 2.63 Å, is almost the same as that of $[F(H_2O)_4]^-$, which has an average of 2.67 Å in the cyclam complex of copper and 2.64 Å in the en complex. These bonds are all substantially shorter than the sum of the van der Waals radii of oxygen and fluorine (2.90 Å), which is the hallmark of a strong hydrogen bond [20].

Figure 2 shows that the diamond-shaped cluster has the fluorides at the sharper points, as befits their charges. Yet the $R(F\cdot\cdot F)$ distance is still rather short at 4.06 Å, for ions of like charge. (In the lattice of ZnF_2, which adopts the rutile structure the interfluoride distance is 2.87 Å [21].)

As already mentioned, hydrogen bonding between lattice fluoride and lattice waters is relatively rare. One of the earliest examples was discovered in the caesium fluoride–water–thiourea (1/2/1) complex [22]. In this each fluoride is at the centre of an octahedral array of hydrogen bonds, two to water, with $R(F\cdot\cdot O) = 2.63$ Å, and four to the NH_2 groups of the thioureas, with $R(F\cdot\cdot N) = 2.92$ Å.

More relevant to the present work is the structure of tetraethylammonium fluoride–water (4/11) [23]. Each fluoride is tetrahedrally coordinated to four waters, and these tetrahedra share pairs of opposite edges to form infinite chains that are cross-linked by hydrogen bonding to other water molecules. In this complex network of FHO and OHO hydrogen bonds the shortest $R(F\cdot\cdot O)$ is 2.586 Å and the longest 2.851 Å [23]. The related tetramethylammonium fluoride water (1/4) has $[F(H_2O)_4]^-$ units with $R(F\cdot\cdot O) = 2.630$ Å, these units being interlinked by hydrogen bonding between their waters [24].

In the complex $[Cr(H_2O)_6]F_3\cdot 3H_2O$ there is a chair-shaped arrangement of $[F_3(H_2O)_3]^{3-}$ with $R(F\cdot\cdot O)$ 2.636 and 2.651 Å around the ring [25]. Each fluoride and water oxygen atom is at the centre of a tetrahedral array of hydrogen bonds, with the exocyclic hydrogen bonds being to ligand waters. These exocyclic bonds to F^- are about the same length as those of the ring, 2.611 and 2.633 Å.

The diamond arrangement reported by us occurs as a part of the structure of other lattices. In $Ag_7I_2F_5\cdot 2.5H_2O$ some fluorine atoms are engaged in a cluster at the heart of which is a diamond-shaped $[F_2(H_2O)_2]^{2-}$. Each fluorine however is at the centre of three hydrogen bonds to water molecules. The $R(F\cdot\cdot O)$ distances are 2.550, 2.566 and 2.588 Å [26]. However the unique feature of this crystal is a lattice fluoride which forms a single hydrogen bond to a lattice water and which has a bond length of only 2.516 Å. The $[F_2(H_2O)_2]^{2-}$ moiety occurs also in $Te(OH)_6\cdot 2CsF\cdot 2H_2O$ [27], with ring bonds of 2.62 and 2.73 Å, but again the F^- is at the centre of three bonds to waters.

The structure of $CuF_2\cdot 2H_2O$ has been the subject of three structure determinations, including a neutron diffraction study [28–30]. This too has the fragment $[F_2(H_2O)_2]$ except that both the fluorides and both the waters are ligands on four different copper atoms. The neutron data gave $R(F\cdot\cdot O) = 2.645$ and 2.715 Å, both slightly longer than their counterparts reported in this paper. The protons of the hydrogen bond were located and for the shorter of these two bonds the distances were $R(H\cdot\cdot F) = 1.687$ Å and $R(O-H) = 0.98$ Å. The hydrogen bond angle FHO was 165°.

The question posed by $[F_2(H_2O)_2]^{2-}$ is why has it not adopted the predicted tetrahedral geometry? The implication is that the formation of a three-centre hydrogen bond is energetically unfavourable compared to the two-centre hydrogen bond of Fig. 2. In the tetrahedron the two fluoride atoms would approach each other even more closely, and it seems unlikely that charge delocalisation by the protons would not be sufficient to compensate for this.

The $[F_2(H_2O)_2]^{2-}$ cluster also poses a further question: could it persist in solution, especially in concentrated solutions of fluorides? Generally deviations from ideal electrolyte behaviour in such solutions are attributed to ion-pairing between cation and anion, never to our knowledge between anions. Yet clearly in the structure reported here we have an example of such a stable dianion pair. This is perhaps the best testimony so far to the strength of the hydrogen bonding between fluoride and water.

The Configuration of $[Zn(en)_3]^{2+}$

A recent structure determination of the complex between $ZnCl_2$ and ethylenediamine also shows it to exist as the dihydrate, $[Zn(en)_3]Cl_2\cdot 2H_2O$ [31]. The hydrogen bonding in this lattice was not reported in detail except that the average $R(Cl\cdot\cdot O)$ was said to be 2.67 Å. This was commented upon for its shortness which was attributed to a 'disordered' chloride. Our own calculations on their data show the distances that were averaged to give 2.67 were 2.186 and 3.152 Å. Obviously the former is far too short as it is very much less than the sum of the van der Waals radii of chlorine and oxygen (3.25 Å). However, the latter is a typical hydrogen bond distance, and due to disorder is probably the only one to occur in the lattice.

In the above paper [31] the emphasis was on the bite angles of the chelate rings, which were 80.3 and 81.1°, and the stereochemistry of the $[Zn(en)_3]^{2+}$ cations, which was reported as a racemic mixture of $\Lambda\lambda\lambda\lambda$ and $\Delta\lambda\lambda\lambda$ conformations. Our investigations also question this assignment. In the complex reported here the bite angles are 79.5° for both N(1)–Zn–N(2) and N(3)–Zn–N(3′) and the cation is a racemic mixture of the conformers $\Lambda\delta\delta\delta$ and $\Delta\delta\delta\delta$, as we also found to be the case in the $[Zn(en)_3]Cl_2\cdot 2H_2O$ paper.

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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