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Crystal and molecular structure of [{Cu(pmdien)F(H_2O)}$_2$][BF_4]$_2$ (pmdien = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine): a novel dimeric cation with extremely short O–H · · · F interactions

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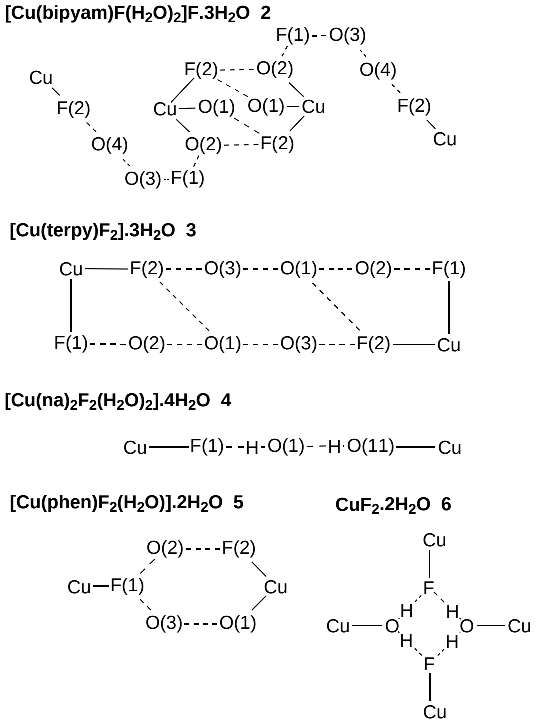
The crystal and molecular structure of [{Cu(pmdien)F(H_2O)}$_2$][BF_4]$_2$ **1** (pmdien = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine) has been determined. The cation exists in the solid state as a unique dimer, held together by O–H · · · F hydrogen-bonding interactions [O · · · F 2.567(2), O–H 0.83(3), F · · · H 1.74(3) Å, F · · · H–O 178.5(23)°]. The O · · · F separation is the shortest ligand fluoride–ligand water hydrogen-bonding interaction in any copper(II) complex. The copper atom is five-co-ordinate and has a square-based pyramidal geometry comprising equatorially located pmdien (mean Cu–N 2.052 Å), and fluoride [Cu–F 1.888(1) Å] and axially located water [Cu–O 2.211(1) Å].

The co-ordination chemistry of tridenate N-donor ligands with transition metals has been the subject of extensive research. A variety of such ligands is well documented; they can give either facial [*e.g.* tris(pyrazol-1-yl)hydroborates,[1] 1,4,7-triazacyclononane[2]] or meridional [*e.g.* diethylenetriamine (dien),[3] 2,6-bis(pyrazol-1-yl)pyridine (bppy)[4]] co-ordinations. In addition, there is considerable interest in the formation of multinuclear metal complexes, linked by a bridging N-donor ligand [*e.g.* 4,4′-bipyridine (4,4′-bipy),[5] *trans*-1,2-bis(pyridin-4-yl)ethene (bpe),[6] 3,6-bis(imidazol-1-yl)pyridazine (biimpydz)[7]].

We have been successful in combining tridentate N-donor chelating and bridging diimine ligands to generate complexes of the form [$(CuL)_2(\mu\text{-}L')]^{x+}[BF_4]_x$, where L = dien or bppy and L′ = 4,4′-bipy, bpe or biimpydz.[4,5c,7] The preparation of these complexes has formed part of our efforts to generate systems analogous to the active centre of the nitrite reductase enzyme isolated from *Achromobacter cycloclastes*, which contains T_1 and T_2 copper centres separated by a dipeptide bridge, with a Cu · · · Cu separation of 12.5 Å.[8]

Whilst attempting to extend these complexes to include [{Cu(pmdien)}$_2$(μ-diimine)][BF_4]$_4$ (pmdien = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine, diimine = 4,4′-bipy or bpe), we adventitiously obtained, instead of the desired diimine-bridged complex, the novel complex [{Cu(pmdien)F(H_2O)}$_2$][BF_4]$_2$ **1**, in which the dinuclear cation is held together by extremely short O–H · · · F hydrogen-bonding interactions. It is the crystal and molecular structure of this complex which we report here.

Although structural data have been reported for several aquated copper(II) fluoride complexes this is the first example of a discrete dinuclear system with direct ligand fluoride–ligand water hydrogen bonding. The F · · · O separation of 2.567(2) Å in **1** is shorter than any previously reported for ligand fluoride. It is however slightly longer than the shortest O–H · · · F interaction involving lattice fluoride, 2.517 Å in [Cu(bipyam)F(H_2O)$_2$]F·3H_2O **2** [bipyam = bis(pyridin-2-yl)amine].[9] Previously reported data for aquated copper fluoride systems show a variety of strong hydrogen-bonding interactions (Scheme 1), for which the ligand F · · · O distances are 2.632, 2.859 Å in **2**, 2.595–2.714 Å in [Cu(terpy)F_2]·2H_2O **3** (terpy = 2,2′:6′,2″-terpyridine),[10] 2.727 Å in [Cu(na)$_2F_2$(H_2O)$_2$]·4H_2O **4** (na = nicotinamide),[11] 2.595–2.691 Å in [Cu(phen)F_2(H_2O)]·2H_2O **5** (phen = 1,10-phenanthroline)[12] and 2.717 Å in CuF_2·2H_2O **6**.[13] Although all of these copper fluoride complexes show extensive hydrogen-bonding interactions between the fluoride ligand and lattice water molecules (Scheme 1), **1** is the only example in which such interactions are formed exclusively between ligand water and ligand fluoride, to give the novel hydrogen-bonded dimeric cation. Interestingly, this is only the second time the hydrogen atoms have been located in these complexes using X-ray diffraction techniques, the previous example being **4**. In **2**, **3** and **5** the hydrogens were not located; in **6** they were only located after neutron diffraction studies.



Scheme 1 Hydrogen-bonding interactions O–H · · · F in previously characterised aquated copper(II) fluoride complexes

Experimental

Complex **1** was characterised using elemental analyses, IR spectroscopy and FAB mass spectrometry. Carbon, hydrogen, and nitrogen analyses (microanalyses) were carried out by Mr. T. J. Spencer using a Perkin-Elmer 240B elemental analyser and FAB mass spectrometry by Mr. T. Hollingworth using a VG70E micromass spectrometer, in the University of Nottingham Chemistry Department. The IR spectra were

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measured using a Perkin-Elmer PE1600C spectrometer, as KBr pressed pellets.

The compounds $Cu(BF_4)_2 \cdot xH_2O$, pmdien, 4,4′-bipy and bpe (Aldrich) were used without further purification.

Synthesis of $[\{Cu(pmdien)F(H_2O)\}_2][BF_4]_2$

The compound $Cu(BF_4)_2 \cdot xH_2O$ (0.95 g, 3.2 mmol; $x = 3.4$ by analysis) was added to a solution of pmdien (0.66 cm^3, 0.55 g, 3.2 mmol) in ethanol (20 cm^3). To the resulting dark blue solution was added a boiling ethanolic solution of either 4,4′-bipy (0.25 g, 1.6 mmol) or bpe (0.29 g, 1.6 mmol). The solution was then boiled and reduced in volume to 20 cm^3, and toluene (20 cm^3) was added. The solution was cooled and left to stand for 48 h. A methanol–ethanol mixture (methcol) (20 cm^3) was added to the resulting oily blue residue, and the solution was placed in a sonic bath for 15 min and filtered. After addition of toluene (20 cm^3), the solution was allowed to stand overnight, resulting in the formation of dark blue crystals of complex **1** (0.296 g, 0.821 mmol, 26%) [Found (Calc. for $C_9H_{25}BCuF_5N_3O$): C, 30.45 (29.95); H, 7.20 (7.00); N, 11.70 (11.65)%]. IR: $\tilde{\nu}/cm^{-1}$ (all bands due to pmdien unless stated otherwise) 3557m, 3465m, 3024m (br), 2260 (br, $O-H\cdots F$), 1642 (br, H_2O), 1478s, 1289m, 1069 (br, BF_4^-), 969m, 942m, 917w, 811m, 781m, 474m and 450m. FAB mass spectrum: *m*/*z* 273, $[Cu(pmdien)(H_2O)F]^+$; 255, $[Cu(pmdien)F]^+$ and 236, $[Cu(pmdien)]^+$.

The experiment was repeated in the absence of a bridging diimine ligand, using identical quantities and conditions. A blue crystalline solid was again produced but was identified as $[Cu(pmdien)(H_2O)_2][BF_4]_2$ [Found (Calc. for $C_9H_{27}B_2CuF_8N_3O_2$): C, 24.40 (24.20); H, 6.35 (6.10); N, 9.65 (9.40)%]. IR: $\tilde{\nu}/cm^{-1}$ (all bands due to pmdien unless stated otherwise): 3451 (br), 2917s, 1470s, 1288m, 1039 (br, BF_4^-), 968m, 939m, 807m, 780m, 534m and 521m. FAB mass spectrum: *m*/*z* 236, $[Cu(pmdien)]^+$.

X-Ray crystallography

A suitable blue crystal was mounted in a sealed Lindeman tube. Preliminary oscillation and Weissenberg photographs indicated a triclinic cell. A second crystal was selected and mounted on a two-stage fibre, before being transferred to a Stöe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems open-flow cryostat and operated at 150(2) K.[14] Prior to data collection the cell constants were determined by least-squares refinement of 36 reflections, well positioned throughout reciprocal space. The data were corrected for Lorentz-polarisation effects. Absorption corrections were applied using ψ scans. Intensity-control reflections were monitored periodically throughout data collection, and no significant decrease in intensity was observed. 2769 Reflections were measured, of which 2709 were unique and 2606 had $I \geqslant 2\sigma(I)$.

Crystal data. $C_9H_{25}BCuF_5N_3O$, $M = 360.66$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.0269(15)$, $b = 10.0777(17)$, $c = 10.1093(16)$ Å, $\alpha = 103.306(15)$, $\beta = 94.231(15)$, $\gamma = 95.557(16)°$, $U = 788.17(16)$ Å^3, $Z = 2$, $F(000) = 374$, $D_c = 1.52$ g cm^{-3}, graphite monochromated Mo-Kα radiation, $\lambda = 0.710\ 73$ Å, $\mu = 1.436$ mm^{-1}, blue irregular block $0.25 \times 0.28 \times 0.35$ mm. Scan type ω-θ, $-9 \leqslant h \leqslant 9$, $-11 \leqslant k \leqslant 11$, $0 \leqslant l \leqslant 12$, $\theta_{min} = 2.56$, $\theta_{max} = 25.03°$.

The structure of complex **1** was solved by direct methods (SIR 92).[15] All hydrogen atoms were found by Fourier-difference synthesis (CRYSTALS).[16] Full-matrix least-squares refinement was carried out (CRYSTALS)[16] on F^2 using all data. The BF_4^- anion is disordered about two (50% occupancy) positions, related by a 36° rotation about the three-fold B(1)–F(11) axis. Non-hydrogen atoms, including the six 50% occupancy fluorines, were refined with anisotropic displacement parameters and hydrogen atoms with isotropic displacement parameters. The final cycle of refinement, for 308 parameters with a three-parameter Chebychev weighting scheme[17] (0.385, −0.201, 0.0597), gave $R = 0.0275$, $R' = 0.0205$, for all data, and 0.0259, 0.0201 for data with $I \geqslant 2\sigma(I)$; residual $\Delta\rho_{max} = 0.317$ e Å^{-3}, $\Delta\rho_{min} = -0.290$ e Å^{-3}; $(\Delta/\sigma)_{max} = 0.161$. Pertinent interatomic distances and angles are given in Table 1 and hydrogen-bond data in Table 2. The structure of **1** is shown in Fig. 1 (CAMERON).[18]

Table 1 Selected interatomic distances (Å) and angles (°) in $[\{Cu(pmdien)F(H_2O)\}_2][BF_4]_2$ **1**

Cu–N(1)	2.052(1)	Cu–N(4)	2.048(1)
Cu–N(7)	2.056(1)	Cu–F(1)	1.888(1)
Cu–O(1)	2.211(1)		
N(1)–Cu–N(4)	85.65(6)	N(4)–Cu–F(1)	170.21(5)
N(1)–Cu–N(7)	152.98(6)	N(4)–Cu–O(1)	96.61(5)
N(1)–Cu–F(1)	91.10(5)	N(7)–Cu–F(1)	92.68(5)
N(1)–Cu–O(1)	108.84(6)	N(7)–Cu–O(1)	97.65(6)
N(4)–Cu–N(7)	86.14(6)	F(1)–Cu–O(1)	93.18(5)
Cu–N(1)–C(11)	106.4(1)	Cu–N(4)–C(5)	106.3(1)
Cu–N(1)–C(12)	113.6(1)	Cu–N(7)–C(6)	106.2(1)
Cu–N(1)–C(2)	107.5(1)	Cu–N(7)–C(71)	107.0(1)
Cu–N(4)–C(3)	105.6(1)	Cu–N(7)–C(72)	114.1(1)
Cu–N(4)–C(41)	113.4(1)		

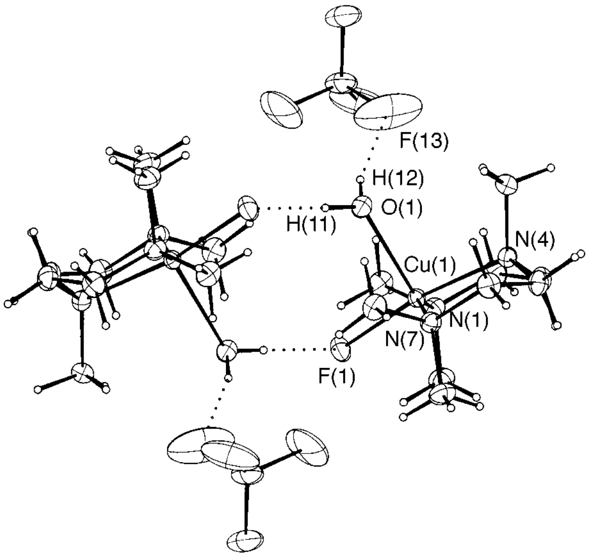

Fig. 1 Molecular structure of $[\{Cu(pmdien)F(H_2O)\}_2][BF_4]_2$, showing the intramolecular hydrogen-bonding interactions between ligand fluoride and ligand water molecules

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Discussion

The structure of complex **1** shows two unique features: (*i*) the presence of a discrete dimeric $[\{Cu(pmdien)F(H_2O)\}_2]^{2+}$ cation [$Cu\cdots Cu$ 5.251(1) Å], held together by ligand water–ligand fluoride hydrogen-bonding interactions and (*ii*) the shortest such $O-H\cdots F$ interaction yet reported in copper(II) complexes [$O\cdots F$ 2.567(2) Å].

The copper atom is five-co-ordinate and has a square-based pyramidal geometry. This is common to all other reported $[Cu(pmdien)]^{2+}$ complexes, the pmdien conformation sterically hindering the formation of octahedral, albeit Jahn–Teller distorted, geometries.[19] Of the other copper(II) fluoride complexes **2**–**6**, **2**, **3** and **5** are square-based pyramidal, while **4** and **6** are octahedral. The nitrogen atoms from the tridentate pmdien ligand (average Cu–N 2.052 Å) and the fluoride anion [Cu–F 1.888(1) Å] occupy the equatorial positions of the copper co-ordination sphere, and a water molecule [Cu–O 2.211(1) Å]

Table 2 Hydrogen-bonding interactions (distances/Å and angles/°) in $[\{Cu(pmdien)F(H_2O)\}_2][BF_4]_2$ **1**

Interaction X–H···X′	Symmetry of X′	X–H/Å	X···X′/Å	H···X′/Å	XHX′/°
O(1)–H(11)···F(1)	$(-x, -y, 1 - z)$	0.83(3)	2.567(2)	1.74(3)	178.5(23)
O(1)–H(12)···F(13)*	(x, y, z)	0.79(3)	2.872(9)	2.12(3)	161.8(23)
O(1)–H(12)···F(15)*	(x, y, z)	0.79(3)	2.901(4)	2.20(3)	149.7(23)

* For the BF_4^- anion three fluorine atoms are disordered about two positions, related by a 36° rotation about the three-fold B(1)–F(11) axis, each with 50% fractional occupancy.

occupies the apical position. The copper atom is 0.32 Å above the basal plane, in the direction of the water molecule. The Cu–F bond is among the shortest reported, the shortest being 1.862(4) Å in **3**. The BF_4^- anion is not co-ordinated but is involved in hydrogen-bonding interactions with the co-ordinated water molecule (Table 2).

The strength of the bridging O–H···F hydrogen bonding (Table 2) is presumably a driving force for the formation of the unique dimeric structure of complex **1**. The eight atoms involved in the hydrogen-bonding interaction are effectively planar, F(1) showing the greatest deviation (0.21 Å) from the best-fit least-squares plane. Estimates of the strength of similar hydrogen-bonding motifs by the degree of overlap of van der Waals radii of atoms $\{\Delta = [r_{vdW}(O) + r_{vdW}(F)] - r(O\cdots F) = 1.5 + 1.4 - 2.56 = 0.34\ Å\}$, has shown the energy of the bonding to be in the region of 100 kJ mol^{-1}.[10,20]

It is noteworthy that complexes **2**–**5** are all synthesized from the respective ligands and copper(II) fluoride. The source of fluoride in **1** must arise from the decomposition of the BF_4^- anion, a process that has been shown to be facile in alcohols containing strong bases with bulky substituents.[21] The fact that **1** was not produced when the reaction was repeated without the diimines gives further evidence for this conclusion. However, the ease with which this process occurs must question the role of BF_4^- as a non-co-ordinating anion, although this method is obviously a good synthetic route to species of this type.

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