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Crystal structures of $[Cu(phen)(H_2O)_3(MF_6)]\cdot H_2O$ (M = Ti, Zr, Hf) and $[Cu(phen)(H_2O)_2F]_2[HfF_6]\cdot H_2O$

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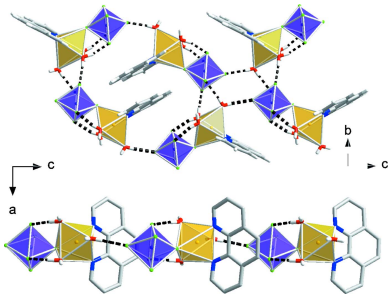
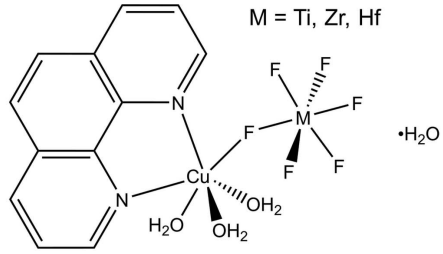
The crystal structures of three bridged bimetallic molecular compounds, namely, triaqua-2κ^3O-μ-fluorido-pentafluorido-1κ^5F-(1,10-phenanthroline-2κ^2N,N')-copper(II)titanium(IV) monohydrate, $[Cu(TiF_6)(phen)(H_2O)_3]\cdot H_2O$ (phen is 1,10-phenanthroline, $C_{12}H_8N_2$), (I), triaqua-2κ^3O-μ-fluorido-pentafluorido-1κ^5F-(1,10-phenanthroline-2κ^2N,N')copper(II)zirconium(IV) monohydrate, $[Cu(ZrF_6)(phen)(H_2O)_3]\cdot H_2O$, (II), and triaqua-2$\kappa^3O$-$\mu$-fluorido-pentafluorido-1κ^5F-(1,10-phenanthroline-2κ^2N,N')copper(II)hafnium(IV) monohydrate, $[Cu(HfF_6)(phen)(H_2O)_3]\cdot H_2O$, (III), and one molecular salt, bis[diaqua-fluorido(1,10-phenanthroline-κ^2N,N')copper(II)] hexafluoridohafnate(IV) dihydrate, $[CuF(phen)(H_2O)_2]_2[HfF_6]\cdot 2H_2O$, (IV), are reported. The bridged bimetallic compounds adopt Λ-shaped configurations, with the octahedrally coordinated copper(II) center linked to the fluorinated early transition metal *via* a fluoride linkage. The extended structures of these Λ-shaped compounds are organized through both intra- and intermolecular hydrogen bonds and intermolecular π–π stacking. The salt compound $[Cu(phen)(H_2O)_2F]_2[HfF_6]\cdot H_2O$ displays an isolated square-pyramidal $Cu(phen)(H_2O)_2F^+$ complex linked to other cationic complexes and isolated HfF_6^{2-} anions through intermolecular hydrogen-bonding interactions.

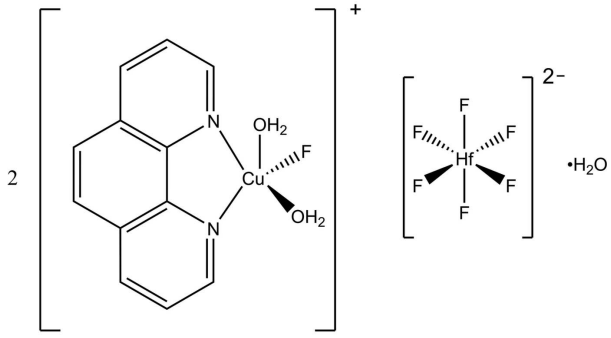
1. Chemical context

Lambda (Λ)-shaped molecules have been demonstrated as efficient building blocks in the synthesis of non-centrosymmetric (NCS) materials *via* arrangement into head-to-tail and accordion (head-to-head, tail-to-tail) structures (Yamamoto *et al.*, 1992; Tao *et al.*, 1994, 1995; Ostroverkhov *et al.*, 2001; Chang *et al.*, 2009). Although this concept was first applied to organic Λ-shaped molecules in crystalline materials and polymers, recently NCS compounds based on inorganic bimetallic Λ-shapes have been reported, namely $K_{10}(Mo_2O_4F_7)_3X$ (X = Cl, $([Br_3][Br])_{1/2}$, $([I_3][I])_{1/2}$), $K_{10}(Nb_2O_2F_9)_3X$ (X = Br, $([Br_3][Br])_{1/2}$, $([I_3][I])_{1/2}$), and $[Cu(H_2O)_5(VOF_4(H_2O))]\cdot H_2O$ (Donakowski *et al.*, 2012; Holland *et al.*, 2014). Here, we report the structures of three centrosymmetric compounds based on inorganic bimetallic Λ-shapes with the formula $[Cu(phen)(H_2O)_3(MF_6)]\cdot H_2O$ (M = Ti, Zr, Hf; phen = 1,10-phenanthroline). Although these compounds crystallize with inversion symmetry, the novel molecular building units are potential targets of future studies aimed to perturb their packing arrangement to form NCS structures. The salt compound $[Cu(phen)(H_2O)_2F]_2[HfF_6]\cdot H_2O$ provides a point of comparison as an unbridged analogue of $[Cu(phen)(H_2O)_3(HfF_6)]\cdot H_2O$.





Compounds (I), (II), & (III)



Compound (IV)

2. Structural commentary

Compound (I) has the formula $[Cu(phen)(H_2O)_3(TiF_6)]\cdot H_2O$ and crystallizes in the orthorhombic space group *Pbca* (Fig. 1). The structure of compound (I) features Cu1 in a tetragonally distorted octahedral environment with elongated axial Cu1—F1 [2.3643 (12) Å] and Cu1—O1 [2.2794 (17) Å] bonds owing to the Jahn–Teller effect of copper(II). The Cu1 center is linked to the TiF_6^{2-} anion through the bridging F1 ligand. The octahedral coordination environment of Ti1 is slightly distorted, with Ti1—F bond lengths ranging from 1.8395 (13) to 1.9035 (13) Å. The Λ-shape, indicated by the Cu1—F1—Ti1 bond angle of 134.93 (6)°, is enforced by the two intramolecular O2—H2*B*···F5 and O3—H3*B*···F6 hydrogen bonds (Table 1).

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···F2^{i}	0.70 (4)	2.08 (4)	2.775 (2)	175 (4)
O1—H1*B*···F4^{ii}	0.77 (4)	1.96 (4)	2.726 (2)	174 (3)
O2—H2*A*···O4	0.83 (3)	1.83 (3)	2.654 (2)	175 (3)
O2—H2*B*···F5	0.83 (4)	1.85 (4)	2.666 (2)	167 (3)
O3—H3*A*···F3^{i}	0.84 (4)	1.85 (4)	2.683 (2)	171 (4)
O3—H3*B*···F6	0.90 (4)	1.81 (4)	2.683 (2)	163 (3)
O4—H4*A*···F3^{iii}	0.75 (4)	2.00 (4)	2.718 (2)	163 (4)
O4—H4*B*···F2^{i}	0.77 (3)	1.96 (3)	2.691 (2)	156 (3)

Symmetry codes: (i) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, z$.

Compound (II) has the formula $[Cu(phen)(H_2O)_3(ZrF_6)]\cdot H_2O$ and crystallizes in the monoclinic space group $P2_1/n$ (Fig. 2). The structure of compound (II) features Cu1 in a tetragonally distorted octahedral environment with elongated axial Cu1—F1 [2.5184 (6) Å] and Cu—O1 [2.2758 (7) Å] bonds owing to the Jahn–Teller effect of copper(II). The Cu1 center is linked to the ZrF_6^{2-} anion through the bridging F1 ligand. The octahedral coordination environment of Zr1 is slightly distorted, with Zr1—F bond lengths ranging from 1.9910 (6) to 2.0430 (6) Å. The Λ-shape, indicated by the Cu1—F1—Zr1 bond angle of 132.59 (3)°, is enforced by an intramolecular O2—H2*B*···F6 hydrogen bond (Table 2). The single intramolecular hydrogen bond in compound (II) tilts the ZrF_6^{2-} group significantly relative to

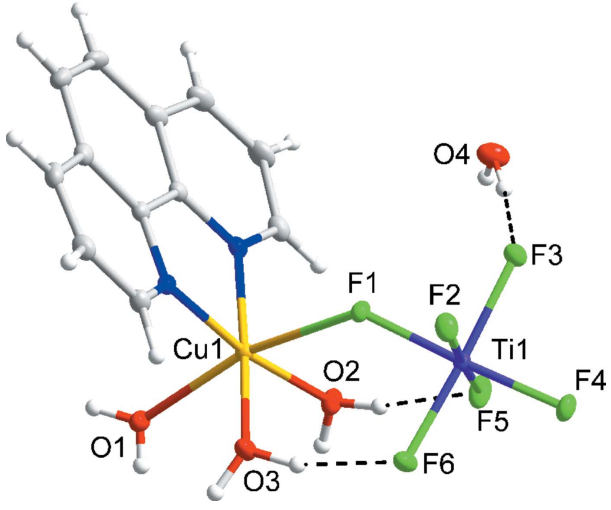


Figure 1
Molecular structure of compound (I), $[Cu(phen)(H_2O)_3(TiF_6)]\cdot H_2O$. Ellipsoids of non-H atoms are drawn at 50% probability. H atoms are drawn with an atomic radius of 0.135 Å.

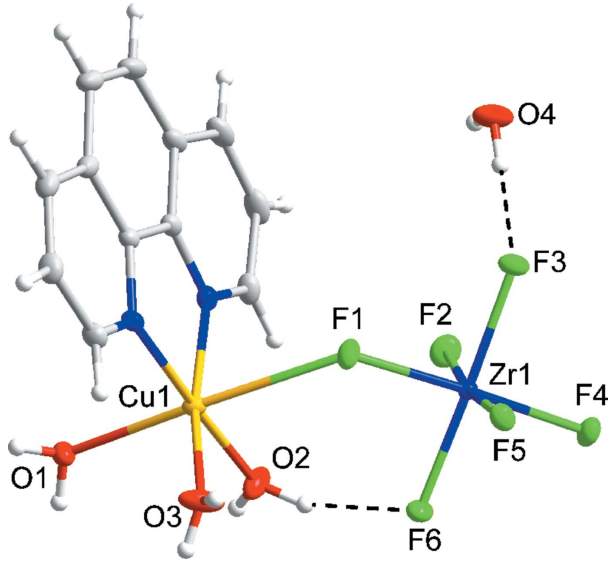


Figure 2
Molecular structure of compound (II), $[Cu(phen)(H_2O)_3(ZrF_6)]\cdot H_2O$. Ellipsoids of non-H atoms are drawn at 50% probability. H atoms are drawn with an atomic radius of 0.135 Å.

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···F5^{i}	0.794 (18)	1.944 (18)	2.7338 (9)	173.5 (18)
O1—H1B···F4^{ii}	0.78 (2)	1.93 (2)	2.7147 (10)	179 (2)
O2—H2A···F3^{i}	0.79 (2)	1.85 (2)	2.6324 (10)	171 (2)
O2—H2B···F6	0.82 (2)	1.87 (2)	2.6491 (10)	159.2 (19)
O3—H3A···F2^{iii}	0.79 (2)	1.85 (2)	2.6327 (10)	177.5 (19)
O3—H3B···O4^{iv}	0.79 (2)	1.87 (2)	2.6481 (12)	170 (2)
O4—H4A···F3	0.799 (19)	2.002 (19)	2.7691 (10)	160.9 (18)
O4—H4B···F5^{v}	0.78 (2)	2.02 (2)	2.7449 (11)	155 (2)

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $x-1, y, z$; (v) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.

Table 3
Hydrogen-bond geometry (Å, °) for (III).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···F5^{i}	0.80 (3)	1.94 (3)	2.7359 (13)	172 (3)
O1—H1B···F4^{ii}	0.77 (3)	1.95 (3)	2.7135 (13)	176 (3)
O2—H2A···F6	0.86 (3)	1.85 (3)	2.6456 (14)	154 (3)
O2—H2B···F3^{i}	0.77 (3)	1.87 (3)	2.6362 (14)	171 (3)
O3—H3A···O4^{iii}	0.81 (3)	1.85 (3)	2.6529 (17)	173 (3)
O3—H3B···F2^{iv}	0.77 (3)	1.86 (3)	2.6330 (15)	176 (3)
O4—H4A···F5^{v}	0.81 (3)	2.00 (3)	2.7429 (15)	154 (3)
O4—H4B···F3	0.81 (3)	2.01 (3)	2.7702 (14)	156 (3)

Symmetry codes: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x+1, y, z$; (iv) $x+\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$; (v) $x-\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$.

the TiF_6^{2-} group in compound (I), which is depicted in Fig. 5 and reflected in the F1—Cu1—N1 bond angle of 77.75 (3)° angle in compound (II) compared to 89.45 (6)° in compound (I).

Compound (III) has the formula $[Cu(phen)(H_2O)_3(HfF_6)]\cdot H_2O$ and crystallizes in the monoclinic space group $P2_1/n$ (Fig. 3). Compound (III) is isostructural to compound (II).

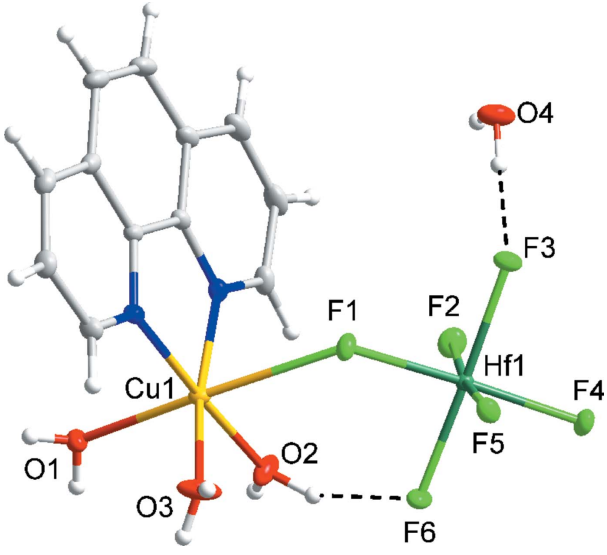


Figure 3
Molecular structure of compound (III), $[Cu(phen)(H_2O)_3(HfF_6)]\cdot H_2O$. Ellipsoids of non-H atoms are drawn at 50% probability. H atoms are drawn with an atomic radius of 0.135 Å.

Table 4
Hydrogen-bond geometry (Å, °) for (IV).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···F4	0.81 (3)	1.78 (3)	2.5926 (14)	176 (3)
O1—H1B···F1^{i}	0.74 (3)	1.85 (3)	2.5861 (13)	172 (3)
O2—H2A···O3	0.74 (3)	1.95 (3)	2.6906 (15)	176 (3)
O2—H2B···F1^{ii}	0.80 (3)	1.83 (3)	2.6255 (13)	175 (2)
O3—H3A···F2	0.78 (3)	1.94 (3)	2.7270 (17)	176 (3)
O3—H3B···F3^{iii}	0.75 (3)	1.96 (3)	2.7020 (15)	173 (3)

Symmetry codes: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+1, -y+2, -z+2$.

Compound (IV) has the formula $[Cu(phen)(H_2O)_2F]_2[HfF_6]\cdot H_2O$ and crystallizes in the monoclinic space group $P2_1/n$ (Fig. 4). The structure of compound (IV) features isolated square pyramidal $Cu(phen)(H_2O)_2F^{+}$ cations and octahedral HfF_6^{2-} anions. The free HfF_6^{2-} octahedron occupies an inversion center with three distinct bond lengths ranging between 1.9863 (10) and 1.9957 (9) Å.

3. Supramolecular features

The Λ-shaped building units in compounds (I)–(III) are arranged in head-to-tail chains via intermolecular hydrogen

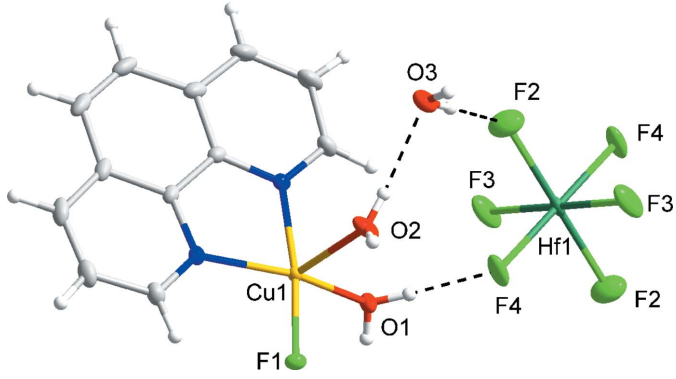


Figure 4
Molecular structure of compound (IV), $[Cu(phen)(H_2O)_2F]_2[HfF_6]\cdot H_2O$. Ellipsoids of non-H atoms are drawn at 50% probability. H atoms are drawn with an atomic radius of 0.135 Å.

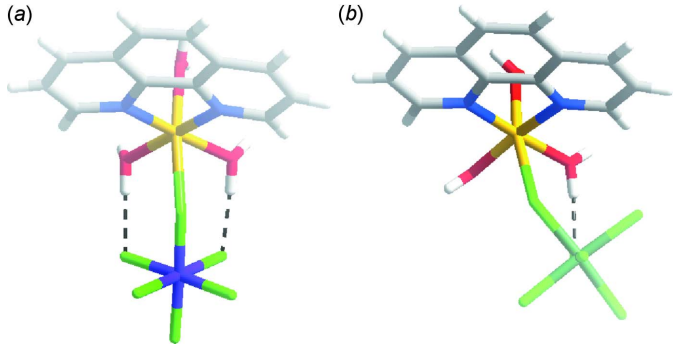


Figure 5
Comparison of the molecular structures of (*a*) compound (I) and (*b*) compound (III).

Table 5
π–π stacking interactions in compounds (I)–(IV).

Compound number	type	$d_{phenyl-pyridine}$	$d_{pyridine-pyridine}$	$d_{phenyl-phenyl}$	interplanar angle
(I)	face-to-face	3.699	4.162	3.583	0
(I)	displaced	6.042	4.128	8.111	8.68
(II)/(III)	parallel displaced	4.469	3.407	6.324	0
(II)/(III)	parallel displaced	3.510	4.472	4.035	0
(IV)	face-to-face	3.664	3.48	4.07	0
(IV)	parallel displaced	3.508	3.881	4.604	0

bonding with multiple hydrogen-bonding interactions and π–π stacking contacts to adjacent chains.

Each $[Cu(phen)(H_2O)_3(TiF_6)]$ complex in compound (I) participates in hydrogen bonding with four other $[Cu(phen)(H_2O)_3(TiF_6)]$ complexes and three free water molecules (Fig. 6, Table 1). The complexes pack with both face-to-face and displaced π–π stacking interactions (Table 5).

The $[Cu(phen)(H_2O)_3(MF_6)]$ (M = Zr, Hf) units in compound (II) and compound (III) are involved in five hydrogen-bonding contacts to adjacent $[Cu(phen)(H_2O)_3(MF_6)]$ complexes and three contacts to hydrating water molecules (Fig. 7, Table 2, and Table 3). The $[Cu(phen)(H_2O)_3(MF_6)]$ complexes participate in parallel displaced π–π stacking interactions (Table 5).

In compound (IV), each fluoride ligand forms two hydrogen bonds with the water ligands of adjacent $Cu(phen)(H_2O)_2F^+$ complexes (Fig. 8). The equatorial water ligands form O1—H1A···F1 hydrogen bonds with adjacent $Cu(phen)(H_2O)_2F^+$ complexes and O1—H1B···F4 hydrogen bonds with HfF_6^{2-} groups (Table 4). The apical water molecule forms an O2—H2B···F1 hydrogen bond to an adjacent $Cu(phen)(H_2O)_2F^+$ complex and a O2—H2A···O3 hydrogen bond with a free water molecule (Table 4). Each MF_6^{2-} group forms hydrogen bonds with four free water molecules and two $Cu(phen)(H_2O)_2F^+$ complexes. The $Cu(phen)(H_2O)_2F^+$ complexes pack with both face-to-face and parallel displaced π–π stacking interactions (Table 5).

4. Database survey

Aside from compounds (I), (II), and (III), the compound $[Cu(H_2O)_5(VO(H_2O)F_4)]\cdot H_2O$ (Donakowski *et al.*, 2012) is the only example of a molecular inorganic Λ-shape known to the authors. $[Cu(H_2O)_5(VOF_4(H_2O))]\cdot H_2O$ contains a molecular Λ-shaped $[Cu(H_2O)_5(VOF_4(H_2O))]$ molecule that is bridged *via* the Cu1—O8—V1 linkage with a bond angle of 142.88°. The Λ-shape of this complex is supported by a single intramolecular hydrogen bond as well as two hydrogen-

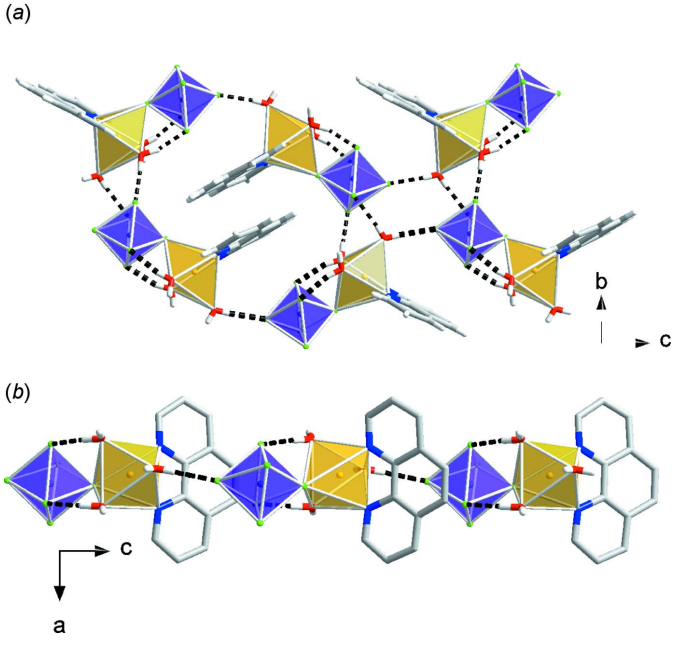


Figure 6
Packing diagrams of compound (I), $[Cu(phen)(H_2O)_3(TiF_6)]\cdot H_2O$. Yellow polyhedra represent $Cu(phen)(H_2O)_3^{2+}$ cations and purple polyhedra represent TiF_6^{2-} anions.

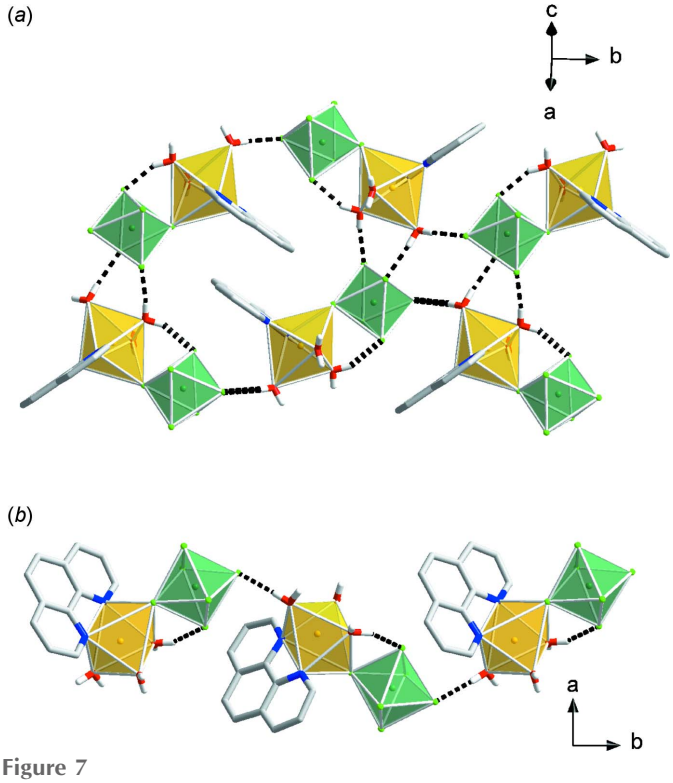


Figure 7
Packing diagrams of compound (II), $[Cu(phen)(H_2O)_3(ZrF_6)]\cdot H_2O$, and compound (III), $[Cu(phen)(H_2O)_3(HfF_6)]\cdot H_2O$. Yellow polyhedra represent $Cu(phen)(H_2O)_3^{2+}$ cations and green polyhedra represent ZrF_6^{2-} or HfF_6^{2-} anions.

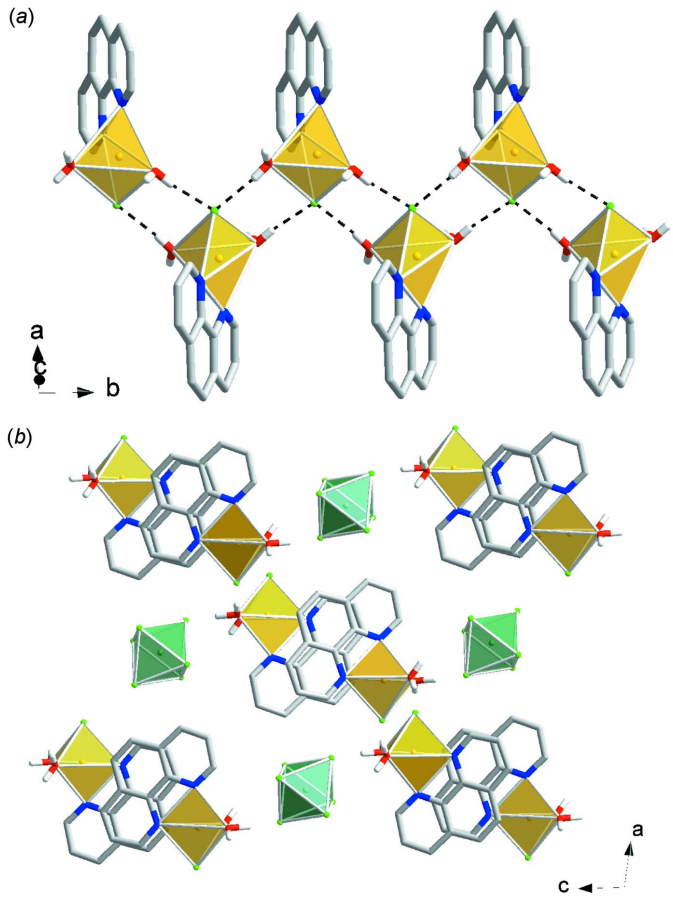


Figure 8
Packing diagrams of compound (IV), $[Cu(phen)(H_2O)_2F]_2[HfF_6]\cdot H_2O$. Yellow polyhedra represent $Cu(phen)(H_2O)_2F^+$ cations and green polyhedra represent HfF_6^{2-} anions.

bonding interactions with a free water molecule that serves as an intermolecular 'bridging molecule'. In contrast, the hydrating water molecules in compounds (I), (II), and (III) bridge between adjacent complexes rather than the same complex. The smallest O8—Cu—O bond angle in $[Cu(H_2O)_5(VOF_4(H_2O))]\cdot H_2O$ is 88.42°, meaning that the complex has a small tilt similar to compound (I).

The Λ-shapes in $[Cu(H_2O)_5(VO(H_2O)F_4)]\cdot H_2O$ are arranged in a polar NCS lattice containing head-to-head/tail-to-tail chains in which the polar moments of the Λ-shaped complexes are partially aligned perpendicular to the chain direction, with head-to-tail orientations between chains. In contrast, the Λ-shapes found in compounds (I), (II), and (III) are arranged in non-polar head-to-tail chains in which the polar moments of the Λ-shaped complexes are arranged in an antiparallel fashion within the chain, with a head-to-tail arrangement between chains.

5. Synthesis and crystallization

The compounds reported here were synthesized by the hydrothermal pouch method (Harrison *et al.*, 1993). In each reaction, reagents were heat-sealed in Teflon pouches. Groups of six pouches were then placed into a 125 mL Parr autoclave with 40 mL of distilled water as backfill. The autoclave was heated at a rate of 5 K min^{-1} to 423 K and held at 423 K for 24 h. The autoclaves were allowed to cool to room temperature at a rate of 6 K h^{-1}. Solid products were recovered by vacuum filtration. Compound (I) was synthesized in a pouch containing 1.69 mmol of CuO, 1.69 mmol of TiO_2, 2.56 mmol of 1,10-phenanthroline, 1.0 mL (27.6 mmol) of HF(*aq*) (48%), and 0.1 mL (5.5 mmol) of deionized H_2O. Compound (II) was synthesized in a pouch containing 1.69 mmol of CuO, 1.69 mmol of ZrO_2, 2.56 mmol of phen, 1.0 mL (27.6 mmol) of HF(*aq*) (48%), and 0.1 mL (5.5 mmol) of deionized H_2O. Compound (III) was synthesized in a pouch containing 1.69 mmol of CuO, 1.69 mmol of HfO_2, 2.56 mmol of phen, 1.0 mL (27.6 mmol) of HF(*aq*) (48%), and 0.1 mL (5.5 mmol) of deionized H_2O. Compound (IV) was synthesized in a pouch containing 1.69 mmol of CuO, 1.69 mmol of HfO_2, 2.56 mmol of phen, 0.4 mL (11.03 mmol) of HF(*aq*) (48%), and 0.7 mL (38.85 mmol) of deionized H_2O.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 6. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen-atom positions were assigned from difference map peaks with the exception of C—H hydrogen atoms of 1,10-phenanthroline, which were constrained to ride at distances of 0.95 Å from the associated C atoms with $U_{iso}(H) = 1.2U_{eq}(C)$ within *OLEX2* (Dolomanov *et al.*, 2009).

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Table 6
Experimental details.

	(I)	(II)	(III)	(IV)
Crystal data				
Chemical formula	$[CuTiF_6(C_{12}H_8N_2)(H_2O)_3]\cdot H_2O$	$[CuZrF_6(C_{12}H_8N_2)(H_2O)_3]\cdot H_2O$	$[CuHfF_6(C_{12}H_8N_2)(H_2O)_3]\cdot H_2O$	$[CuF(C_{12}H_8N_2)(H_2O)_2]_2[HfF_6]\cdot 2H_2O$
M_r	477.71	521.03	608.30	926.07
Crystal system, space group	Orthorhombic, *Pbca*	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	100	100	101	100
a, *b*, *c* (Å)	13.3603 (3), 14.1385 (3), 17.7895 (4)	9.9486 (4), 17.3006 (7), 10.0022 (4)	9.9411 (3), 17.2733 (4), 9.9972 (2)	13.6451 (2), 7.1161 (1), 15.7457 (3)
α, β, γ (°)	90, 90, 90	90, 95.1335 (18), 90	90, 95.116 (1), 90	90, 99.691 (1), 90
V (Å^3)	3360.34 (13)	1714.64 (12)	1709.84 (7)	1507.09 (4)
Z	8	4	4	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.83	1.93	7.39	4.93
Crystal size (mm)	0.09 × 0.07 × 0.05	0.24 × 0.12 × 0.11	0.17 × 0.12 × 0.05	0.16 × 0.16 × 0.10
Data collection				
Diffractometer	Bruker Kappa APEX CCD area detector	Bruker Kappa APEX CCD area detector	Bruker Kappa APEX CCD area detector	Bruker Kappa APEX CCD area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)	Multi-scan (*SADABS*; Bruker, 2016)	Multi-scan (*SADABS*; Bruker, 2016)	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.668, 0.746	0.683, 0.747	0.480, 0.747	0.489, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	36860, 4534, 3928	87607, 7546, 7052	43322, 8248, 7980	123138, 5034, 4982
R_{int}	0.043	0.031	0.026	0.033
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.686	0.807	0.835	0.737
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.030, 0.071, 1.10	0.018, 0.047, 1.04	0.015, 0.036, 1.13	0.014, 0.035, 1.15
No. of reflections	4534	7546	8248	5034
No. of parameters	267	267	267	230
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.46, −0.45	0.57, −0.67	1.03, −0.98	0.67, −0.70

Computer programs: *APEX2* and *SAINT* (Bruker, 2017), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), and *OLEX2* (Dolomanov *et al.*, 2009).

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supporting information

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Crystal structures of [Cu(phen)$(H_2O)_3(MF_6)]\cdot H_2O$ (M = Ti, Zr, Hf) and [Cu(phen)$(H_2O)_2F]_2[HfF_6]\cdot H_2O$

Matthew L. Nisbet and Kenneth R. Poeppelmeier

Computing details

For all structures, data collection: *APEX2*(Bruker, 2017); cell refinement: *SAINT* (Bruker, 2017); data reduction: *SAINT* (Bruker, 2017); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Triaqua-2κ^3O-μ-fluorido-pentafluorido-1κ^5F-(1,10-phenanthroline-2κ^2N,N')copper(II)titanium(IV) monohydrate (I)

Crystal data

$[CuTiF_6(C_{12}H_8N_2)(H_2O)_3]\cdot H_2O$
M_r = 477.71
Orthorhombic, *Pbca*
a = 13.3603 (3) Å
b = 14.1385 (3) Å
c = 17.7895 (4) Å
V = 3360.34 (13) Å^3
Z = 8
F(000) = 1912
D_x = 1.889 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9952 reflections
θ = 2.8–29.1°
μ = 1.83 mm^{-1}
T = 100 K
Block, blue
0.09 × 0.07 × 0.05 mm

Data collection

Bruker Kappa APEX CCD area detector diffractometer
Radiation source: sealed tube
Triumph monochromator
Detector resolution: 8 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
T_{min} = 0.668, T_{max} = 0.746
36860 measured reflections
4534 independent reflections
3928 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 29.2°, θ_{min} = 2.3°
h = −18→18
k = −19→19
l = −23→24

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.071
S = 1.10
4534 reflections
267 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0163P)^2 + 6.5495P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.56746 (2)	0.74025 (2)	0.36021 (2)	0.01008 (7)
Ti1	0.53873 (3)	0.60258 (3)	0.17156 (2)	0.00930 (8)
F1	0.53330 (10)	0.61607 (9)	0.27499 (7)	0.0133 (2)
F2	0.41521 (9)	0.54030 (9)	0.17056 (7)	0.0160 (3)
F3	0.59857 (10)	0.48206 (9)	0.18751 (7)	0.0146 (3)
F4	0.54844 (10)	0.58432 (9)	0.06857 (7)	0.0170 (3)
F5	0.66406 (10)	0.65896 (10)	0.17257 (8)	0.0194 (3)
F6	0.47531 (11)	0.71718 (9)	0.16027 (7)	0.0180 (3)
O1	0.58746 (13)	0.88113 (12)	0.42069 (10)	0.0153 (3)
H1A	0.586 (3)	0.923 (3)	0.400 (2)	0.036 (11)*
H1B	0.578 (2)	0.894 (2)	0.462 (2)	0.033 (9)*
O2	0.68191 (13)	0.76878 (12)	0.29363 (9)	0.0163 (3)
H2A	0.702 (2)	0.824 (2)	0.2876 (17)	0.025 (8)*
H2B	0.679 (3)	0.742 (2)	0.252 (2)	0.042 (10)*
O3	0.46639 (13)	0.80398 (12)	0.29423 (9)	0.0160 (3)
H3A	0.451 (3)	0.861 (3)	0.297 (2)	0.042 (10)*
H3B	0.468 (3)	0.787 (2)	0.246 (2)	0.040 (10)*
N1	0.46103 (13)	0.69042 (12)	0.42847 (10)	0.0105 (3)
N2	0.65702 (13)	0.66919 (12)	0.43147 (10)	0.0109 (3)
C1	0.36234 (16)	0.69370 (15)	0.42054 (12)	0.0129 (4)
H1	0.334951	0.722036	0.376706	0.015*
C2	0.29739 (16)	0.65669 (15)	0.47477 (13)	0.0149 (4)
H2	0.227049	0.659406	0.467260	0.018*
C3	0.33568 (17)	0.61635 (15)	0.53897 (13)	0.0150 (4)
H3	0.292095	0.593534	0.577071	0.018*
C4	0.44001 (17)	0.60926 (15)	0.54763 (12)	0.0136 (4)
C5	0.49937 (16)	0.64734 (14)	0.48989 (12)	0.0105 (4)
C6	0.48834 (18)	0.56371 (16)	0.60994 (13)	0.0166 (4)
H6	0.449007	0.539269	0.649962	0.020*
C7	0.58924 (18)	0.55511 (15)	0.61248 (12)	0.0166 (4)
H7	0.619530	0.524951	0.654432	0.020*
C8	0.65119 (17)	0.59062 (15)	0.55310 (12)	0.0146 (4)
C9	0.60562 (16)	0.63669 (14)	0.49233 (12)	0.0109 (4)
C10	0.75608 (18)	0.57771 (16)	0.54860 (13)	0.0176 (4)
H10	0.791122	0.547634	0.588454	0.021*
C11	0.80665 (17)	0.60883 (16)	0.48648 (14)	0.0179 (4)
H11	0.876860	0.599295	0.482704	0.022*

C12	0.75501 (16)	0.65480 (15)	0.42832 (13)	0.0145 (4)
H12	0.791179	0.676164	0.385595	0.017*
O4	0.74837 (14)	0.94525 (12)	0.28380 (11)	0.0194 (3)
H4A	0.782 (3)	0.961 (2)	0.253 (2)	0.036 (10)*
H4B	0.708 (2)	0.984 (2)	0.2893 (17)	0.026 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01007 (12)	0.01075 (12)	0.00941 (12)	0.00031 (9)	0.00038 (9)	0.00084 (9)
Ti1	0.00972 (17)	0.00994 (16)	0.00822 (16)	−0.00046 (13)	0.00042 (13)	−0.00037 (13)
F1	0.0171 (6)	0.0134 (6)	0.0092 (6)	−0.0008 (5)	0.0015 (5)	−0.0002 (4)
F2	0.0106 (6)	0.0187 (6)	0.0188 (7)	−0.0023 (5)	0.0008 (5)	−0.0042 (5)
F3	0.0143 (6)	0.0134 (6)	0.0161 (6)	0.0024 (5)	−0.0012 (5)	−0.0010 (5)
F4	0.0198 (7)	0.0222 (7)	0.0088 (6)	0.0007 (5)	0.0013 (5)	−0.0017 (5)
F5	0.0159 (6)	0.0246 (7)	0.0176 (7)	−0.0090 (5)	0.0053 (5)	−0.0060 (5)
F6	0.0273 (7)	0.0125 (6)	0.0143 (6)	0.0049 (5)	−0.0031 (5)	0.0002 (5)
O1	0.0225 (9)	0.0130 (8)	0.0103 (8)	0.0006 (6)	0.0004 (6)	−0.0001 (6)
O2	0.0184 (8)	0.0168 (8)	0.0137 (8)	−0.0046 (6)	0.0044 (6)	−0.0022 (6)
O3	0.0212 (8)	0.0135 (8)	0.0132 (8)	0.0053 (6)	−0.0026 (6)	−0.0013 (6)
N1	0.0105 (8)	0.0103 (8)	0.0105 (8)	−0.0002 (6)	0.0007 (6)	−0.0008 (6)
N2	0.0097 (8)	0.0105 (8)	0.0126 (8)	0.0014 (6)	−0.0002 (6)	−0.0018 (6)
C1	0.0115 (10)	0.0145 (9)	0.0127 (10)	0.0011 (8)	−0.0016 (8)	−0.0021 (8)
C2	0.0106 (10)	0.0143 (10)	0.0198 (11)	−0.0003 (8)	0.0008 (8)	−0.0024 (8)
C3	0.0159 (10)	0.0143 (10)	0.0149 (10)	−0.0025 (8)	0.0051 (8)	−0.0035 (8)
C4	0.0169 (10)	0.0112 (9)	0.0126 (10)	−0.0005 (8)	0.0010 (8)	−0.0026 (7)
C5	0.0116 (9)	0.0095 (9)	0.0103 (9)	0.0001 (7)	−0.0004 (7)	−0.0018 (7)
C6	0.0244 (12)	0.0137 (10)	0.0116 (10)	−0.0007 (8)	0.0020 (9)	0.0006 (8)
C7	0.0250 (12)	0.0131 (10)	0.0116 (10)	0.0015 (8)	−0.0053 (9)	0.0015 (8)
C8	0.0179 (11)	0.0120 (9)	0.0138 (10)	0.0020 (8)	−0.0054 (8)	−0.0023 (8)
C9	0.0126 (10)	0.0088 (9)	0.0111 (9)	0.0010 (7)	−0.0007 (8)	−0.0018 (7)
C10	0.0178 (11)	0.0153 (10)	0.0196 (11)	0.0037 (8)	−0.0091 (9)	−0.0029 (8)
C11	0.0119 (10)	0.0175 (10)	0.0245 (12)	0.0042 (8)	−0.0043 (9)	−0.0032 (9)
C12	0.0121 (10)	0.0133 (9)	0.0180 (10)	−0.0001 (8)	−0.0003 (8)	−0.0046 (8)
O4	0.0165 (8)	0.0163 (8)	0.0255 (9)	0.0008 (7)	0.0078 (7)	0.0021 (7)

Geometric parameters (Å, º)

Cu1—F1	2.3643 (12)	C1—H1	0.9500
Cu1—O1	2.2794 (17)	C1—C2	1.399 (3)
Cu1—O2	1.9758 (16)	C2—H2	0.9500
Cu1—O3	2.0032 (16)	C2—C3	1.375 (3)
Cu1—N1	1.9981 (18)	C3—H3	0.9500
Cu1—N2	2.0120 (18)	C3—C4	1.406 (3)
Ti1—F1	1.8511 (13)	C4—C5	1.405 (3)
Ti1—F2	1.8706 (13)	C4—C6	1.435 (3)
Ti1—F3	1.9035 (13)	C5—C9	1.428 (3)
Ti1—F4	1.8548 (13)	C6—H6	0.9500

Ti1—F5	1.8545 (13)	C6—C7	1.354 (3)
Ti1—F6	1.8395 (13)	C7—H7	0.9500
O1—H1A	0.70 (4)	C7—C8	1.433 (3)
O1—H1B	0.77 (4)	C8—C9	1.401 (3)
O2—H2A	0.83 (3)	C8—C10	1.416 (3)
O2—H2B	0.83 (4)	C10—H10	0.9500
O3—H3A	0.84 (4)	C10—C11	1.368 (3)
O3—H3B	0.90 (4)	C11—H11	0.9500
N1—C1	1.327 (3)	C11—C12	1.403 (3)
N1—C5	1.352 (3)	C12—H12	0.9500
N2—C9	1.362 (3)	O4—H4A	0.75 (4)
N2—C12	1.326 (3)	O4—H4B	0.77 (3)

O1—Cu1—F1	166.96 (6)	C5—N1—Cu1	112.35 (14)
O2—Cu1—F1	85.21 (6)	C9—N2—Cu1	111.68 (14)
O2—Cu1—O1	90.79 (7)	C12—N2—Cu1	129.58 (15)
O2—Cu1—O3	94.51 (7)	C12—N2—C9	118.66 (19)
O2—Cu1—N1	170.75 (7)	N1—C1—H1	119.0
O2—Cu1—N2	91.11 (7)	N1—C1—C2	122.0 (2)
O3—Cu1—F1	80.11 (6)	C2—C1—H1	119.0
O3—Cu1—O1	87.85 (7)	C1—C2—H2	120.1
O3—Cu1—N2	174.07 (7)	C3—C2—C1	119.8 (2)
N1—Cu1—F1	89.45 (6)	C3—C2—H2	120.1
N1—Cu1—O1	96.01 (7)	C2—C3—H3	120.4
N1—Cu1—O3	92.01 (7)	C2—C3—C4	119.3 (2)
N1—Cu1—N2	82.20 (7)	C4—C3—H3	120.4
N2—Cu1—F1	98.51 (6)	C3—C4—C6	124.2 (2)
N2—Cu1—O1	93.97 (7)	C5—C4—C3	116.9 (2)
F1—Ti1—F2	91.34 (6)	C5—C4—C6	118.8 (2)
F1—Ti1—F3	87.74 (6)	N1—C5—C4	123.3 (2)
F1—Ti1—F4	177.26 (6)	N1—C5—C9	116.67 (19)
F1—Ti1—F5	88.94 (6)	C4—C5—C9	119.90 (19)
F2—Ti1—F3	87.17 (6)	C4—C6—H6	119.5
F4—Ti1—F2	89.24 (6)	C7—C6—C4	120.9 (2)
F4—Ti1—F3	89.61 (6)	C7—C6—H6	119.5
F5—Ti1—F2	177.38 (6)	C6—C7—H7	119.4
F5—Ti1—F3	90.24 (6)	C6—C7—C8	121.3 (2)
F5—Ti1—F4	90.36 (6)	C8—C7—H7	119.4
F6—Ti1—F1	89.99 (6)	C9—C8—C7	118.7 (2)
F6—Ti1—F2	90.41 (6)	C9—C8—C10	116.5 (2)
F6—Ti1—F3	176.64 (6)	C10—C8—C7	124.6 (2)
F6—Ti1—F4	92.69 (6)	N2—C9—C5	116.19 (18)
F6—Ti1—F5	92.20 (7)	N2—C9—C8	123.4 (2)
Ti1—F1—Cu1	134.93 (6)	C8—C9—C5	120.3 (2)
Cu1—O1—H1A	119 (3)	C8—C10—H10	120.2
Cu1—O1—H1B	130 (2)	C11—C10—C8	119.5 (2)
H1A—O1—H1B	107 (4)	C11—C10—H10	120.2
Cu1—O2—H2A	122 (2)	C10—C11—H11	119.9

Cu1—O2—H2B	113 (2)	C10—C11—C12	120.1 (2)
H2A—O2—H2B	109 (3)	C12—C11—H11	119.9
Cu1—O3—H3A	125 (2)	N2—C12—C11	121.7 (2)
Cu1—O3—H3B	115 (2)	N2—C12—H12	119.2
H3A—O3—H3B	109 (3)	C11—C12—H12	119.2
C1—N1—Cu1	129.07 (15)	H4A—O4—H4B	107 (3)
C1—N1—C5	118.57 (19)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···F2^{i}	0.70 (4)	2.08 (4)	2.775 (2)	175 (4)
O1—H1*B*···F4^{ii}	0.77 (4)	1.96 (4)	2.726 (2)	174 (3)
O2—H2*A*···O4	0.83 (3)	1.83 (3)	2.654 (2)	175 (3)
O2—H2*B*···F5	0.83 (4)	1.85 (4)	2.666 (2)	167 (3)
O3—H3*A*···F3^{i}	0.84 (4)	1.85 (4)	2.683 (2)	171 (4)
O3—H3*B*···F6	0.90 (4)	1.81 (4)	2.683 (2)	163 (3)
O4—H4*A*···F3^{iii}	0.75 (4)	2.00 (4)	2.718 (2)	163 (4)
O4—H4*B*···F2^{i}	0.77 (3)	1.96 (3)	2.691 (2)	156 (3)

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) *x*, −*y*+3/2, *z*+1/2; (iii) −*x*+3/2, *y*+1/2, *z*.

Triaqua-2κ^3*O*-μ-fluorido-pentafluorido-1κ^5*F*-(1,10-phenanthroline-2κ^2*N*,*N*′)copper(II)zirconium(IV) monohydrate (II)

Crystal data

$[CuZrF_6(C_{12}H_8N_2)(H_2O)_3]\cdot H_2O$	*F*(000) = 1028
M_r = 521.03	D_x = 2.018 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo *Kα* radiation, λ = 0.71073 Å
a = 9.9486 (4) Å	Cell parameters from 9425 reflections
b = 17.3006 (7) Å	θ = 3.0–34.9°
c = 10.0022 (4) Å	μ = 1.93 mm^{-1}
β = 95.1335 (18)°	*T* = 100 K
V = 1714.64 (12) Å^3	Cuboid, blue
Z = 4	0.24 × 0.12 × 0.11 mm

Data collection

Bruker Kappa APEX CCD area detector diffractometer	87607 measured reflections
	7546 independent reflections
Radiation source: sealed tube	7052 reflections with $I > 2\sigma(I)$
Triumph monochromator	R_{int} = 0.031
Detector resolution: 8 pixels mm^{-1}	θ_{max} = 35.0°, θ_{min} = 2.4°
ω and φ scans	*h* = −15→16
Absorption correction: multi-scan (SADABS; Bruker, 2016)	*k* = −27→27
	l = −16→16
T_{min} = 0.683, T_{max} = 0.747	

Refinement

Refinement on F^2	*S* = 1.04
Least-squares matrix: full	7546 reflections
$R[F^2 > 2\sigma(F^2)]$ = 0.018	267 parameters
$wR(F^2)$ = 0.047	0 restraints

Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0222P)^2 + 0.6601P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Zr1	0.47531 (2)	0.17833 (2)	0.18511 (2)	0.00928 (2)
Cu1	0.23490 (2)	0.36879 (2)	0.23859 (2)	0.01147 (3)
F1	0.40575 (7)	0.28382 (3)	0.13913 (6)	0.01738 (11)
F2	0.55807 (7)	0.20897 (4)	0.36687 (6)	0.02055 (12)
F3	0.65583 (6)	0.20677 (4)	0.11564 (6)	0.01671 (11)
F4	0.53575 (7)	0.06931 (3)	0.22042 (7)	0.01918 (11)
F5	0.41618 (6)	0.14484 (4)	−0.00414 (6)	0.01543 (10)
F6	0.29772 (6)	0.15382 (4)	0.25277 (6)	0.01807 (11)
O1	0.09615 (8)	0.43805 (4)	0.36235 (8)	0.01672 (13)
H1A	0.0425 (17)	0.4171 (10)	0.4041 (17)	0.028 (4)*
H1B	0.0583 (19)	0.4762 (12)	0.3397 (19)	0.039 (5)*
O2	0.22635 (9)	0.28333 (4)	0.36875 (8)	0.02195 (15)
H2A	0.198 (2)	0.2842 (11)	0.440 (2)	0.043 (5)*
H2B	0.2341 (19)	0.2387 (11)	0.3444 (19)	0.039 (5)*
O3	0.08658 (9)	0.32098 (6)	0.12593 (9)	0.02716 (19)
H3A	0.0786 (18)	0.3133 (10)	0.048 (2)	0.034 (5)*
H3B	0.019 (2)	0.3082 (11)	0.155 (2)	0.040 (5)*
N1	0.40931 (8)	0.40912 (4)	0.32659 (8)	0.01241 (12)
N2	0.25539 (8)	0.45780 (4)	0.11410 (7)	0.01176 (12)
C1	0.48666 (10)	0.38078 (6)	0.42972 (10)	0.01668 (16)
H1	0.456184	0.336879	0.475402	0.020*
C2	0.61195 (11)	0.41331 (6)	0.47385 (10)	0.02059 (19)
H2	0.665231	0.391295	0.547766	0.025*
C3	0.65728 (10)	0.47718 (7)	0.40963 (11)	0.02061 (19)
H3	0.742169	0.499549	0.438437	0.025*
C4	0.57629 (9)	0.50917 (6)	0.30041 (10)	0.01582 (16)
C5	0.45370 (9)	0.47190 (5)	0.26198 (9)	0.01215 (14)
C6	0.61134 (10)	0.57674 (6)	0.22755 (11)	0.02057 (18)
H6	0.693485	0.602912	0.253555	0.025*
C7	0.52933 (11)	0.60382 (6)	0.12238 (11)	0.01943 (18)
H7	0.554529	0.648907	0.076505	0.023*
C8	0.40516 (10)	0.56548 (5)	0.07928 (9)	0.01432 (15)
C9	0.36882 (9)	0.49938 (5)	0.14917 (9)	0.01139 (13)
C10	0.31652 (11)	0.58914 (6)	−0.03080 (10)	0.01766 (17)

H10	0.336075	0.633809	−0.080793	0.021*
C11	0.20132 (11)	0.54697 (6)	−0.06530 (10)	0.01771 (16)
H11	0.140492	0.562526	−0.139020	0.021*
C12	0.17425 (9)	0.48094 (6)	0.00892 (9)	0.01485 (15)
H12	0.095257	0.451756	−0.016796	0.018*
O4	0.86608 (9)	0.29013 (6)	0.24604 (9)	0.02461 (17)
H4A	0.8042 (19)	0.2617 (10)	0.2257 (18)	0.031 (4)*
H4B	0.864 (2)	0.2988 (12)	0.322 (2)	0.042 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zr1	0.01037 (4)	0.00955 (4)	0.00795 (4)	−0.00034 (2)	0.00102 (3)	−0.00012 (2)
Cu1	0.01226 (5)	0.01299 (5)	0.00913 (5)	−0.00278 (3)	0.00070 (4)	0.00011 (3)
F1	0.0245 (3)	0.0125 (2)	0.0153 (2)	0.0038 (2)	0.0034 (2)	0.00169 (19)
F2	0.0276 (3)	0.0226 (3)	0.0105 (2)	−0.0005 (2)	−0.0032 (2)	−0.0021 (2)
F3	0.0134 (2)	0.0231 (3)	0.0138 (2)	−0.0050 (2)	0.0024 (2)	−0.0008 (2)
F4	0.0211 (3)	0.0117 (2)	0.0239 (3)	0.0020 (2)	−0.0028 (2)	0.0013 (2)
F5	0.0146 (2)	0.0202 (3)	0.0111 (2)	0.0012 (2)	−0.00087 (19)	−0.00385 (19)
F6	0.0169 (3)	0.0176 (3)	0.0209 (3)	−0.0025 (2)	0.0084 (2)	−0.0003 (2)
O1	0.0169 (3)	0.0148 (3)	0.0194 (3)	0.0016 (2)	0.0069 (3)	0.0026 (2)
O2	0.0385 (5)	0.0138 (3)	0.0155 (3)	0.0005 (3)	0.0134 (3)	0.0004 (2)
O3	0.0223 (4)	0.0459 (5)	0.0138 (3)	−0.0194 (4)	0.0047 (3)	−0.0101 (3)
N1	0.0129 (3)	0.0130 (3)	0.0111 (3)	0.0020 (2)	−0.0005 (2)	−0.0016 (2)
N2	0.0099 (3)	0.0147 (3)	0.0107 (3)	−0.0003 (2)	0.0012 (2)	0.0001 (2)
C1	0.0184 (4)	0.0180 (4)	0.0130 (4)	0.0059 (3)	−0.0024 (3)	−0.0022 (3)
C2	0.0165 (4)	0.0273 (5)	0.0167 (4)	0.0079 (4)	−0.0055 (3)	−0.0057 (4)
C3	0.0118 (4)	0.0282 (5)	0.0209 (4)	0.0019 (3)	−0.0030 (3)	−0.0099 (4)
C4	0.0110 (4)	0.0187 (4)	0.0177 (4)	−0.0007 (3)	0.0011 (3)	−0.0068 (3)
C5	0.0104 (3)	0.0136 (3)	0.0124 (3)	0.0002 (3)	0.0006 (3)	−0.0034 (3)
C6	0.0149 (4)	0.0201 (4)	0.0273 (5)	−0.0064 (3)	0.0053 (4)	−0.0079 (4)
C7	0.0193 (4)	0.0153 (4)	0.0248 (5)	−0.0050 (3)	0.0083 (4)	−0.0034 (3)
C8	0.0161 (4)	0.0118 (3)	0.0157 (4)	−0.0007 (3)	0.0054 (3)	−0.0014 (3)
C9	0.0103 (3)	0.0125 (3)	0.0116 (3)	0.0002 (2)	0.0023 (3)	−0.0013 (3)
C10	0.0238 (5)	0.0140 (4)	0.0159 (4)	0.0026 (3)	0.0058 (3)	0.0021 (3)
C11	0.0208 (4)	0.0189 (4)	0.0133 (4)	0.0051 (3)	0.0007 (3)	0.0030 (3)
C12	0.0129 (4)	0.0188 (4)	0.0125 (3)	0.0017 (3)	−0.0005 (3)	0.0011 (3)
O4	0.0210 (4)	0.0353 (4)	0.0176 (3)	−0.0141 (3)	0.0026 (3)	−0.0055 (3)

Geometric parameters (Å, º)

Zr1—F1	1.9910 (6)	C1—H1	0.9500
Zr1—F2	1.9991 (6)	C1—C2	1.4023 (15)
Zr1—F3	2.0430 (6)	C2—H2	0.9500
Zr1—F4	2.0014 (6)	C2—C3	1.3744 (17)
Zr1—F5	2.0163 (6)	C3—H3	0.9500
Zr1—F6	1.9933 (6)	C3—C4	1.4111 (15)
Cu1—F1	2.5184 (6)	C4—C5	1.4025 (13)

Cu1—O1	2.2758 (7)	C4—C6	1.4369 (15)
Cu1—O2	1.9768 (8)	C5—C9	1.4288 (13)
Cu1—O3	1.9580 (8)	C6—H6	0.9500
Cu1—N1	1.9997 (8)	C6—C7	1.3558 (17)
Cu1—N2	2.0021 (8)	C7—H7	0.9500
O1—H1A	0.794 (18)	C7—C8	1.4341 (14)
O1—H1B	0.78 (2)	C8—C9	1.4044 (12)
O2—H2A	0.79 (2)	C8—C10	1.4085 (14)
O2—H2B	0.82 (2)	C10—H10	0.9500
O3—H3A	0.79 (2)	C10—C11	1.3762 (15)
O3—H3B	0.79 (2)	C11—H11	0.9500
N1—C1	1.3245 (12)	C11—C12	1.4015 (13)
N1—C5	1.3577 (12)	C12—H12	0.9500
N2—C9	1.3577 (11)	O4—H4A	0.799 (19)
N2—C12	1.3292 (12)	O4—H4B	0.78 (2)

F1—Zr1—F2	94.21 (3)	C5—N1—Cu1	112.08 (6)
F1—Zr1—F3	89.92 (3)	C9—N2—Cu1	112.05 (6)
F1—Zr1—F4	175.79 (3)	C12—N2—Cu1	129.46 (6)
F1—Zr1—F5	88.87 (3)	C12—N2—C9	118.47 (8)
F1—Zr1—F6	88.46 (3)	N1—C1—H1	118.8
F2—Zr1—F3	86.70 (3)	N1—C1—C2	122.32 (10)
F2—Zr1—F4	89.81 (3)	C2—C1—H1	118.8
F2—Zr1—F5	172.66 (3)	C1—C2—H2	120.2
F4—Zr1—F3	91.58 (3)	C3—C2—C1	119.67 (9)
F4—Zr1—F5	87.29 (3)	C3—C2—H2	120.2
F5—Zr1—F3	86.64 (2)	C2—C3—H3	120.4
F6—Zr1—F2	93.04 (3)	C2—C3—C4	119.25 (9)
F6—Zr1—F3	178.34 (3)	C4—C3—H3	120.4
F6—Zr1—F4	90.06 (3)	C3—C4—C6	124.33 (9)
F6—Zr1—F5	93.71 (3)	C5—C4—C3	117.02 (9)
O1—Cu1—F1	170.35 (2)	C5—C4—C6	118.65 (9)
O2—Cu1—F1	83.91 (3)	N1—C5—C4	123.31 (9)
O2—Cu1—O1	88.37 (3)	N1—C5—C9	116.59 (8)
O2—Cu1—N1	93.32 (4)	C4—C5—C9	120.10 (8)
O2—Cu1—N2	176.00 (4)	C4—C6—H6	119.4
O3—Cu1—F1	91.52 (3)	C7—C6—C4	121.21 (9)
O3—Cu1—O1	94.18 (3)	C7—C6—H6	119.4
O3—Cu1—O2	89.34 (4)	C6—C7—H7	119.5
O3—Cu1—N1	168.59 (3)	C6—C7—C8	121.05 (9)
O3—Cu1—N2	94.61 (4)	C8—C7—H7	119.5
N1—Cu1—F1	77.75 (3)	C9—C8—C7	118.70 (9)
N1—Cu1—O1	96.98 (3)	C9—C8—C10	117.05 (9)
N1—Cu1—N2	82.69 (3)	C10—C8—C7	124.25 (9)
N2—Cu1—F1	95.36 (3)	N2—C9—C5	116.52 (8)
N2—Cu1—O1	91.94 (3)	N2—C9—C8	123.22 (8)
Zr1—F1—Cu1	132.59 (3)	C8—C9—C5	120.25 (8)
Cu1—O1—H1A	121.0 (13)	C8—C10—H10	120.3

Cu1—O1—H1B	125.9 (14)	C11—C10—C8	119.41 (9)
H1A—O1—H1B	102.0 (18)	C11—C10—H10	120.3
Cu1—O2—H2A	128.2 (14)	C10—C11—H11	120.2
Cu1—O2—H2B	120.1 (13)	C10—C11—C12	119.63 (9)
H2A—O2—H2B	109.8 (19)	C12—C11—H11	120.2
Cu1—O3—H3A	130.1 (13)	N2—C12—C11	122.20 (9)
Cu1—O3—H3B	122.1 (15)	N2—C12—H12	118.9
H3A—O3—H3B	107.6 (19)	C11—C12—H12	118.9
C1—N1—Cu1	129.37 (7)	H4A—O4—H4B	106.4 (19)
C1—N1—C5	118.41 (8)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···F5^{i}	0.794 (18)	1.944 (18)	2.7338 (9)	173.5 (18)
O1—H1*B*···F4^{ii}	0.78 (2)	1.93 (2)	2.7147 (10)	179 (2)
O2—H2*A*···F3^{i}	0.79 (2)	1.85 (2)	2.6324 (10)	171 (2)
O2—H2*B*···F6	0.82 (2)	1.87 (2)	2.6491 (10)	159.2 (19)
O3—H3*A*···F2^{iii}	0.79 (2)	1.85 (2)	2.6327 (10)	177.5 (19)
O3—H3*B*···O4^{iv}	0.79 (2)	1.87 (2)	2.6481 (12)	170 (2)
O4—H4*A*···F3	0.799 (19)	2.002 (19)	2.7691 (10)	160.9 (18)
O4—H4*B*···F5^{v}	0.78 (2)	2.02 (2)	2.7449 (11)	155 (2)

Symmetry codes: (i) *x*−1/2, −*y*+1/2, *z*+1/2; (ii) −*x*+1/2, *y*+1/2, −*z*+1/2; (iii) *x*−1/2, −*y*+1/2, *z*−1/2; (iv) *x*−1, *y*, *z*; (v) *x*+1/2, −*y*+1/2, *z*+1/2.

Triaqua-2κ^3*O*-μ-fluorido-pentafluorido-1κ^5*F*-(1,10-phenanthroline-2κ^2*N*,*N*′)copper(II)hafnium(IV) monohydrate (III)

Crystal data

$[CuHfF_6(C_{12}H_8N_2)(H_2O)_3]\cdot H_2O$
M_r = 608.30
Monoclinic, $P2_1/n$
a = 9.9411 (3) Å
b = 17.2733 (4) Å
c = 9.9972 (2) Å
β = 95.116 (1)°
V = 1709.84 (7) Å^3
Z = 4
$F(000)$ = 1156
D_x = 2.363 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9921 reflections
θ = 2.4–36.4°
μ = 7.39 mm^{-1}
T = 101 K
Rodlike, blue
0.17 × 0.12 × 0.05 mm

Data collection

Bruker Kappa APEX CCD area detector diffractometer
Radiation source: sealed tube
Triumph monochromator
Detector resolution: 8 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
T_{min} = 0.480, T_{max} = 0.747
43322 measured reflections
8248 independent reflections
7980 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 36.4°, θ_{min} = 2.4°
h = −16→16
k = −28→28
l = −13→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.015$
$wR(F^2) = 0.036$
$S = 1.13$
8248 reflections
267 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0108P)^2 + 0.940P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 1.03$ e Å^{-3}
$\Delta\rho_{min} = -0.98$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Hf1	0.52483 (2)	0.82180 (2)	0.31483 (2)	0.00816 (1)
Cu1	0.76520 (2)	0.63146 (2)	0.26150 (2)	0.01043 (2)
F1	0.59437 (9)	0.71639 (5)	0.36048 (9)	0.01579 (14)
F2	0.44315 (10)	0.79101 (5)	0.13341 (9)	0.01846 (15)
F3	0.34510 (8)	0.79333 (5)	0.38379 (9)	0.01545 (13)
F4	0.46393 (9)	0.93051 (5)	0.27960 (10)	0.01710 (15)
F5	0.58415 (8)	0.85522 (5)	0.50333 (8)	0.01413 (13)
F6	0.70198 (9)	0.84641 (5)	0.24732 (9)	0.01652 (14)
O1	0.90410 (10)	0.56191 (6)	0.13766 (11)	0.01534 (16)
H1A	0.952 (3)	0.5850 (18)	0.092 (3)	0.043 (8)*
H1B	0.944 (3)	0.5250 (18)	0.158 (3)	0.038 (8)*
O2	0.77370 (14)	0.71712 (6)	0.13085 (11)	0.0204 (2)
H2A	0.770 (3)	0.7646 (16)	0.155 (3)	0.039 (8)*
H2B	0.794 (3)	0.7190 (18)	0.058 (3)	0.041 (8)*
O3	0.91370 (13)	0.67963 (8)	0.37400 (13)	0.0258 (3)
H3A	0.982 (3)	0.6915 (16)	0.342 (3)	0.036 (8)*
H3B	0.923 (3)	0.6862 (16)	0.451 (3)	0.036 (8)*
N1	0.59097 (11)	0.59097 (6)	0.17348 (10)	0.01118 (15)
N2	0.74478 (10)	0.54241 (6)	0.38597 (10)	0.01065 (14)
C1	0.51346 (13)	0.61947 (7)	0.07036 (13)	0.01500 (19)
H1	0.543886	0.663510	0.024768	0.018*
C2	0.38773 (14)	0.58678 (9)	0.02611 (15)	0.0187 (2)
H2	0.334281	0.608849	−0.047718	0.022*
C3	0.34248 (13)	0.52246 (9)	0.09056 (15)	0.0185 (2)
H3	0.257713	0.499831	0.061741	0.022*
C4	0.42372 (12)	0.49081 (7)	0.19968 (14)	0.01433 (19)
C5	0.38832 (14)	0.42310 (8)	0.27286 (16)	0.0186 (2)
H5	0.305923	0.397016	0.247140	0.022*
C6	0.47075 (14)	0.39590 (8)	0.37801 (15)	0.0175 (2)
H6	0.445833	0.350595	0.423706	0.021*

C7	0.59489 (13)	0.43449 (7)	0.42121 (13)	0.01293 (18)
C8	0.63154 (11)	0.50068 (6)	0.35078 (12)	0.01037 (16)
C9	0.54650 (11)	0.52808 (7)	0.23831 (12)	0.01084 (16)
C10	0.68394 (14)	0.41075 (7)	0.53102 (14)	0.0160 (2)
H10	0.664685	0.365860	0.580801	0.019*
C11	0.79903 (14)	0.45307 (7)	0.56563 (14)	0.0159 (2)
H11	0.859827	0.437608	0.639508	0.019*
C12	0.82601 (12)	0.51916 (7)	0.49119 (13)	0.01334 (18)
H12	0.905102	0.548379	0.516812	0.016*
O4	0.13489 (12)	0.70967 (8)	0.25315 (12)	0.0224 (2)
H4A	0.143 (3)	0.6980 (16)	0.176 (3)	0.030 (7)*
H4B	0.200 (3)	0.7376 (18)	0.269 (3)	0.043 (8)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Hf1	0.00935 (2)	0.00804 (2)	0.00717 (2)	−0.00036 (1)	0.00110 (1)	−0.00014 (1)
Cu1	0.01135 (5)	0.01143 (5)	0.00851 (6)	−0.00251 (4)	0.00096 (4)	0.00007 (4)
F1	0.0220 (4)	0.0106 (3)	0.0152 (3)	0.0038 (3)	0.0040 (3)	0.0018 (2)
F2	0.0247 (4)	0.0205 (4)	0.0095 (3)	−0.0001 (3)	−0.0024 (3)	−0.0022 (3)
F3	0.0121 (3)	0.0211 (4)	0.0134 (3)	−0.0043 (3)	0.0027 (2)	−0.0008 (3)
F4	0.0185 (4)	0.0101 (3)	0.0220 (4)	0.0021 (2)	−0.0022 (3)	0.0012 (3)
F5	0.0138 (3)	0.0182 (3)	0.0101 (3)	0.0009 (2)	−0.0005 (2)	−0.0036 (2)
F6	0.0154 (3)	0.0159 (3)	0.0195 (4)	−0.0027 (3)	0.0086 (3)	−0.0005 (3)
O1	0.0153 (4)	0.0138 (4)	0.0177 (4)	0.0018 (3)	0.0062 (3)	0.0026 (3)
O2	0.0361 (6)	0.0122 (4)	0.0147 (4)	0.0008 (4)	0.0127 (4)	0.0002 (3)
O3	0.0208 (5)	0.0440 (7)	0.0132 (5)	−0.0190 (5)	0.0050 (4)	−0.0095 (4)
N1	0.0121 (4)	0.0118 (4)	0.0094 (4)	0.0016 (3)	−0.0002 (3)	−0.0011 (3)
N2	0.0094 (3)	0.0127 (4)	0.0098 (4)	−0.0003 (3)	0.0005 (3)	0.0000 (3)
C1	0.0168 (5)	0.0155 (5)	0.0120 (5)	0.0052 (4)	−0.0023 (4)	−0.0018 (3)
C2	0.0141 (5)	0.0248 (6)	0.0160 (5)	0.0063 (4)	−0.0045 (4)	−0.0049 (4)
C3	0.0112 (4)	0.0253 (6)	0.0183 (6)	0.0016 (4)	−0.0025 (4)	−0.0082 (4)
C4	0.0103 (4)	0.0164 (5)	0.0162 (5)	−0.0012 (3)	0.0009 (3)	−0.0056 (4)
C5	0.0137 (5)	0.0184 (5)	0.0242 (6)	−0.0060 (4)	0.0052 (4)	−0.0060 (4)
C6	0.0178 (5)	0.0138 (5)	0.0221 (6)	−0.0052 (4)	0.0073 (4)	−0.0030 (4)
C7	0.0152 (4)	0.0100 (4)	0.0143 (5)	−0.0003 (3)	0.0051 (4)	−0.0007 (3)
C8	0.0096 (4)	0.0105 (4)	0.0113 (4)	−0.0008 (3)	0.0025 (3)	−0.0011 (3)
C9	0.0090 (4)	0.0123 (4)	0.0111 (4)	0.0002 (3)	0.0007 (3)	−0.0026 (3)
C10	0.0212 (5)	0.0127 (4)	0.0148 (5)	0.0024 (4)	0.0053 (4)	0.0022 (4)
C11	0.0190 (5)	0.0158 (5)	0.0129 (5)	0.0038 (4)	0.0008 (4)	0.0032 (4)
C12	0.0121 (4)	0.0166 (5)	0.0110 (4)	0.0010 (3)	−0.0004 (3)	0.0012 (3)
O4	0.0190 (4)	0.0316 (6)	0.0167 (5)	−0.0120 (4)	0.0027 (3)	−0.0048 (4)

Geometric parameters (Å, º)

Hf1—F1	1.9863 (8)	C1—H1	0.9500
Hf1—F2	1.9922 (9)	C1—C2	1.4065 (19)
Hf1—F3	2.0320 (8)	C2—H2	0.9500

Hf1—F4	1.9946 (8)	C2—C3	1.380 (2)
Hf1—F5	2.0085 (8)	C3—H3	0.9500
Hf1—F6	1.9873 (8)	C3—C4	1.409 (2)
Cu1—F1	2.5130 (9)	C4—C5	1.440 (2)
Cu1—O1	2.2776 (10)	C4—C9	1.4033 (16)
Cu1—O2	1.9804 (11)	C5—H5	0.9500
Cu1—O3	1.9597 (11)	C5—C6	1.358 (2)
Cu1—N1	1.9979 (11)	C6—H6	0.9500
Cu1—N2	2.0002 (10)	C6—C7	1.4348 (18)
O1—H1A	0.80 (3)	C7—C8	1.4076 (17)
O1—H1B	0.77 (3)	C7—C10	1.4085 (19)
O2—H2A	0.86 (3)	C8—C9	1.4259 (17)
O2—H2B	0.77 (3)	C10—H10	0.9500
O3—H3A	0.81 (3)	C10—C11	1.376 (2)
O3—H3B	0.77 (3)	C11—H11	0.9500
N1—C1	1.3256 (16)	C11—C12	1.4016 (18)
N1—C9	1.3590 (16)	C12—H12	0.9500
N2—C8	1.3565 (15)	O4—H4A	0.81 (3)
N2—C12	1.3298 (16)	O4—H4B	0.81 (3)

F1—Hf1—F2	94.00 (4)	C9—N1—Cu1	112.08 (8)
F1—Hf1—F3	89.93 (4)	C8—N2—Cu1	112.04 (8)
F1—Hf1—F4	175.95 (4)	C12—N2—Cu1	129.51 (8)
F1—Hf1—F5	88.90 (4)	C12—N2—C8	118.43 (10)
F1—Hf1—F6	88.47 (4)	N1—C1—H1	118.9
F2—Hf1—F3	86.85 (4)	N1—C1—C2	122.28 (13)
F2—Hf1—F4	89.88 (4)	C2—C1—H1	118.9
F2—Hf1—F5	173.04 (4)	C1—C2—H2	120.2
F4—Hf1—F3	91.46 (4)	C3—C2—C1	119.61 (12)
F4—Hf1—F5	87.38 (4)	C3—C2—H2	120.2
F5—Hf1—F3	86.83 (3)	C2—C3—H3	120.5
F6—Hf1—F2	92.84 (4)	C2—C3—C4	119.07 (12)
F6—Hf1—F3	178.34 (4)	C4—C3—H3	120.5
F6—Hf1—F4	90.17 (4)	C3—C4—C5	124.03 (12)
F6—Hf1—F5	93.57 (4)	C9—C4—C3	117.37 (12)
O1—Cu1—F1	170.30 (3)	C9—C4—C5	118.61 (12)
O2—Cu1—F1	83.89 (4)	C4—C5—H5	119.4
O2—Cu1—O1	88.40 (4)	C6—C5—C4	121.10 (12)
O2—Cu1—N1	93.29 (5)	C6—C5—H5	119.4
O2—Cu1—N2	175.97 (5)	C5—C6—H6	119.5
O3—Cu1—F1	91.55 (5)	C5—C6—C7	121.04 (12)
O3—Cu1—O1	94.23 (5)	C7—C6—H6	119.5
O3—Cu1—O2	89.26 (6)	C8—C7—C6	118.74 (12)
O3—Cu1—N1	168.66 (5)	C8—C7—C10	116.98 (11)
O3—Cu1—N2	94.73 (5)	C10—C7—C6	124.28 (12)
N1—Cu1—F1	77.76 (4)	N2—C8—C7	123.21 (11)
N1—Cu1—O1	96.88 (4)	N2—C8—C9	116.62 (10)
N1—Cu1—N2	82.69 (4)	C7—C8—C9	120.16 (10)

N2—Cu1—F1	95.41 (4)	N1—C9—C4	123.19 (11)
N2—Cu1—O1	91.87 (4)	N1—C9—C8	116.50 (10)
Hf1—F1—Cu1	132.71 (4)	C4—C9—C8	120.31 (11)
Cu1—O1—H1A	118 (2)	C7—C10—H10	120.3
Cu1—O1—H1B	128 (2)	C11—C10—C7	119.48 (12)
H1A—O1—H1B	104 (3)	C11—C10—H10	120.3
Cu1—O2—H2A	121 (2)	C10—C11—H11	120.2
Cu1—O2—H2B	133 (2)	C10—C11—C12	119.57 (12)
H2A—O2—H2B	104 (3)	C12—C11—H11	120.2
Cu1—O3—H3A	120 (2)	N2—C12—C11	122.31 (12)
Cu1—O3—H3B	131 (2)	N2—C12—H12	118.8
H3A—O3—H3B	109 (3)	C11—C12—H12	118.8
C1—N1—Cu1	129.31 (9)	H4A—O4—H4B	101 (3)
C1—N1—C9	118.46 (11)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···F5^{i}	0.80 (3)	1.94 (3)	2.7359 (13)	172 (3)
O1—H1*B*···F4^{ii}	0.77 (3)	1.95 (3)	2.7135 (13)	176 (3)
O2—H2*A*···F6	0.86 (3)	1.85 (3)	2.6456 (14)	154 (3)
O2—H2*B*···F3^{i}	0.77 (3)	1.87 (3)	2.6362 (14)	171 (3)
O3—H3*A*···O4^{iii}	0.81 (3)	1.85 (3)	2.6529 (17)	173 (3)
O3—H3*B*···F2^{iv}	0.77 (3)	1.86 (3)	2.6330 (15)	176 (3)
O4—H4*A*···F5^{v}	0.81 (3)	2.00 (3)	2.7429 (15)	154 (3)
O4—H4*B*···F3	0.81 (3)	2.01 (3)	2.7702 (14)	156 (3)

Symmetry codes: (i) *x*+1/2, −*y*+3/2, *z*−1/2; (ii) −*x*+3/2, *y*−1/2, −*z*+1/2; (iii) *x*+1, *y*, *z*; (iv) *x*+1/2, −*y*+3/2, *z*+1/2; (v) *x*−1/2, −*y*+3/2, *z*−1/2.

Bis[diaquafluorido(1,10-phenanthroline-κ^2N,N')copper(II)] hexafluoridohafnate(IV) dihydrate (IV)

Crystal data

$[CuF(C_{12}H_8N_2)(H_2O)_2]_2[HfF_6]\cdot 2H_2O$
M_r = 926.07
Monoclinic, $P2_1/n$
a = 13.6451 (2) Å
b = 7.1161 (1) Å
c = 15.7457 (3) Å
β = 99.691 (1)°
V = 1507.09 (4) Å^3
Z = 2
$F(000)$ = 900
D_x = 2.041 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9864 reflections
θ = 3.2–31.6°
μ = 4.93 mm^{-1}
T = 100 K
Block, blue
0.16 × 0.16 × 0.10 mm

Data collection

Bruker Kappa APEX CCD area detector diffractometer
Radiation source: sealed tube
Triumph monochromator
Detector resolution: 8 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
T_{min} = 0.489, T_{max} = 0.746
123138 measured reflections
5034 independent reflections
4982 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 31.6°, θ_{min} = 1.8°
h = −20→20
k = −10→10
l = −23→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.014$
$wR(F^2) = 0.035$
$S = 1.15$
5034 reflections
230 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0117P)^2 + 1.360P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.67$ e Å^{-3}
$\Delta\rho_{min} = -0.70$ e Å^{-3}
Extinction correction: SHELXL2018/3 (Sheldrick 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00177 (14)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.62127 (2)	0.64187 (2)	0.68925 (2)	0.01005 (3)
F1	0.76115 (6)	0.65941 (11)	0.70156 (5)	0.01498 (14)
O1	0.62607 (8)	0.45374 (15)	0.78219 (7)	0.01690 (18)
H1A	0.624 (2)	0.491 (3)	0.8306 (18)	0.038 (7)*
H1B	0.6623 (18)	0.375 (4)	0.7848 (15)	0.031 (6)*
O2	0.61132 (8)	0.88111 (16)	0.76902 (8)	0.0210 (2)
H2A	0.5660 (19)	0.907 (4)	0.7866 (16)	0.035 (6)*
H2B	0.6525 (18)	0.961 (3)	0.7795 (15)	0.028 (6)*
N1	0.47279 (8)	0.62122 (15)	0.66010 (7)	0.01255 (18)
N2	0.60647 (8)	0.72932 (15)	0.56647 (7)	0.01210 (18)
C1	0.40802 (10)	0.5731 (2)	0.71056 (9)	0.0173 (2)
H1	0.431969	0.536685	0.768377	0.021*
C2	0.30508 (11)	0.5746 (2)	0.68062 (10)	0.0229 (3)
H2	0.260252	0.542670	0.718419	0.027*
C3	0.26932 (10)	0.6223 (2)	0.59655 (11)	0.0227 (3)
H3	0.199828	0.621543	0.575619	0.027*
C4	0.33664 (10)	0.67219 (19)	0.54175 (9)	0.0169 (2)
C5	0.43786 (9)	0.67246 (17)	0.57741 (8)	0.0125 (2)
C6	0.30786 (11)	0.7249 (2)	0.45299 (10)	0.0218 (3)
H6	0.239621	0.721580	0.427555	0.026*
C7	0.37640 (12)	0.7791 (2)	0.40497 (9)	0.0212 (3)
H7	0.355271	0.814434	0.346577	0.025*
C8	0.48019 (11)	0.78432 (18)	0.44052 (8)	0.0161 (2)
C9	0.51006 (9)	0.72954 (17)	0.52666 (8)	0.0122 (2)
C10	0.55590 (12)	0.84042 (19)	0.39478 (9)	0.0204 (3)
H10	0.539638	0.879121	0.336361	0.024*
C11	0.65340 (12)	0.8386 (2)	0.43549 (9)	0.0206 (3)
H11	0.704981	0.875387	0.405306	0.025*

C12	0.67606 (10)	0.78186 (19)	0.52197 (8)	0.0162 (2)
H12	0.743579	0.781115	0.549530	0.019*
Hf1	0.500000	0.500000	1.000000	0.01221 (3)
F2	0.41065 (9)	0.67878 (17)	0.92652 (8)	0.0399 (3)
F3	0.54442 (8)	0.69971 (16)	1.08602 (7)	0.0347 (3)
F4	0.61050 (7)	0.56285 (16)	0.93645 (6)	0.0286 (2)
O3	0.44170 (9)	0.97485 (17)	0.82435 (8)	0.0211 (2)
H3A	0.4338 (19)	0.893 (4)	0.8558 (17)	0.044 (7)*
H3B	0.4502 (18)	1.063 (4)	0.8509 (16)	0.034 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.00921 (6)	0.01226 (7)	0.00874 (6)	0.00025 (5)	0.00170 (5)	0.00021 (5)
F1	0.0105 (3)	0.0159 (4)	0.0182 (4)	0.0005 (3)	0.0014 (3)	−0.0001 (3)
O1	0.0223 (5)	0.0169 (4)	0.0126 (4)	0.0065 (4)	0.0061 (4)	0.0035 (3)
O2	0.0179 (5)	0.0181 (5)	0.0301 (5)	−0.0050 (4)	0.0127 (4)	−0.0111 (4)
N1	0.0116 (4)	0.0135 (5)	0.0128 (4)	−0.0001 (4)	0.0027 (3)	−0.0023 (4)
N2	0.0146 (4)	0.0112 (4)	0.0107 (4)	−0.0009 (4)	0.0028 (3)	−0.0007 (3)
C1	0.0155 (5)	0.0213 (6)	0.0166 (6)	−0.0021 (5)	0.0070 (4)	−0.0041 (5)
C2	0.0147 (6)	0.0280 (7)	0.0281 (7)	−0.0020 (5)	0.0099 (5)	−0.0065 (6)
C3	0.0117 (5)	0.0253 (7)	0.0305 (7)	0.0023 (5)	0.0024 (5)	−0.0074 (6)
C4	0.0136 (5)	0.0146 (5)	0.0210 (6)	0.0034 (4)	−0.0014 (4)	−0.0046 (5)
C5	0.0127 (5)	0.0107 (5)	0.0134 (5)	0.0020 (4)	0.0001 (4)	−0.0026 (4)
C6	0.0203 (6)	0.0179 (6)	0.0230 (6)	0.0072 (5)	−0.0084 (5)	−0.0047 (5)
C7	0.0291 (7)	0.0151 (6)	0.0157 (6)	0.0074 (5)	−0.0075 (5)	−0.0020 (5)
C8	0.0256 (6)	0.0104 (5)	0.0108 (5)	0.0033 (5)	−0.0008 (4)	−0.0006 (4)
C9	0.0161 (5)	0.0089 (5)	0.0109 (5)	0.0014 (4)	0.0004 (4)	−0.0012 (4)
C10	0.0371 (8)	0.0129 (5)	0.0112 (5)	0.0010 (5)	0.0044 (5)	0.0012 (4)
C11	0.0323 (7)	0.0161 (6)	0.0156 (6)	−0.0021 (5)	0.0104 (5)	0.0006 (5)
C12	0.0206 (6)	0.0149 (5)	0.0144 (5)	−0.0029 (5)	0.0064 (4)	−0.0013 (4)
Hf1	0.01420 (4)	0.01322 (4)	0.01094 (4)	−0.00344 (2)	0.00713 (2)	−0.00266 (2)
F2	0.0325 (6)	0.0375 (6)	0.0482 (7)	0.0045 (5)	0.0029 (5)	0.0185 (5)
F3	0.0321 (5)	0.0372 (6)	0.0387 (6)	−0.0155 (4)	0.0174 (4)	−0.0263 (5)
F4	0.0268 (5)	0.0418 (6)	0.0213 (4)	−0.0156 (4)	0.0165 (4)	−0.0086 (4)
O3	0.0212 (5)	0.0188 (5)	0.0250 (5)	−0.0002 (4)	0.0093 (4)	−0.0061 (4)

Geometric parameters (Å, º)

Cu1—F1	1.8899 (8)	C5—C9	1.4279 (18)
Cu1—O1	1.9763 (10)	C6—H6	0.9500
Cu1—O2	2.1335 (11)	C6—C7	1.354 (2)
Cu1—N1	2.0060 (11)	C7—H7	0.9500
Cu1—N2	2.0085 (11)	C7—C8	1.433 (2)
O1—H1A	0.81 (3)	C8—C9	1.4042 (17)
O1—H1B	0.74 (3)	C8—C10	1.413 (2)
O2—H2A	0.74 (3)	C10—H10	0.9500
O2—H2B	0.80 (3)	C10—C11	1.376 (2)

N1—C1	1.3290 (16)	C11—H11	0.9500
N1—C5	1.3588 (16)	C11—C12	1.4039 (19)
N2—C9	1.3586 (16)	C12—H12	0.9500
N2—C12	1.3254 (16)	Hf1—F2	1.9922 (11)
C1—H1	0.9500	Hf1—F2^{i}	1.9921 (11)
C1—C2	1.4044 (19)	Hf1—F3	1.9863 (10)
C2—H2	0.9500	Hf1—F3^{i}	1.9863 (10)
C2—C3	1.374 (2)	Hf1—F4	1.9957 (9)
C3—H3	0.9500	Hf1—F4^{i}	1.9957 (9)
C3—C4	1.408 (2)	O3—H3A	0.78 (3)
C4—C5	1.4006 (17)	O3—H3B	0.75 (3)
C4—C6	1.436 (2)		

F1—Cu1—O1	93.54 (4)	C4—C6—H6	119.5
F1—Cu1—O2	92.88 (4)	C7—C6—C4	121.08 (13)
F1—Cu1—N1	172.75 (4)	C7—C6—H6	119.5
F1—Cu1—N2	90.83 (4)	C6—C7—H7	119.4
O1—Cu1—O2	95.86 (5)	C6—C7—C8	121.29 (13)
O1—Cu1—N1	91.49 (5)	C8—C7—H7	119.4
O1—Cu1—N2	155.24 (5)	C9—C8—C7	118.50 (13)
N1—Cu1—O2	91.79 (4)	C9—C8—C10	116.91 (13)
N1—Cu1—N2	82.44 (4)	C10—C8—C7	124.59 (13)
N2—Cu1—O2	108.26 (5)	N2—C9—C5	116.56 (11)
Cu1—O1—H1A	118.1 (17)	N2—C9—C8	123.16 (12)
Cu1—O1—H1B	119.3 (18)	C8—C9—C5	120.27 (12)
H1A—O1—H1B	109 (2)	C8—C10—H10	120.2
Cu1—O2—H2A	124 (2)	C11—C10—C8	119.50 (12)
Cu1—O2—H2B	125.3 (17)	C11—C10—H10	120.2
H2A—O2—H2B	110 (3)	C10—C11—H11	120.3
C1—N1—Cu1	129.04 (9)	C10—C11—C12	119.49 (13)
C1—N1—C5	118.73 (11)	C12—C11—H11	120.3
C5—N1—Cu1	112.17 (8)	N2—C12—C11	122.24 (13)
C9—N2—Cu1	112.16 (8)	N2—C12—H12	118.9
C12—N2—Cu1	129.15 (9)	C11—C12—H12	118.9
C12—N2—C9	118.69 (11)	F2^{i}—Hf1—F2	180.0
N1—C1—H1	119.1	F2—Hf1—F4	90.34 (5)
N1—C1—C2	121.71 (13)	F2—Hf1—F4^{i}	89.66 (5)
C2—C1—H1	119.1	F2^{i}—Hf1—F4^{i}	90.34 (5)
C1—C2—H2	120.1	F2^{i}—Hf1—F4	89.66 (5)
C3—C2—C1	119.88 (13)	F3^{i}—Hf1—F2^{i}	91.48 (6)
C3—C2—H2	120.1	F3^{i}—Hf1—F2	88.52 (6)
C2—C3—H3	120.3	F3—Hf1—F2^{i}	88.52 (6)
C2—C3—C4	119.36 (13)	F3—Hf1—F2	91.48 (6)
C4—C3—H3	120.3	F3^{i}—Hf1—F3	180.0
C3—C4—C6	124.23 (13)	F3—Hf1—F4	90.69 (4)
C5—C4—C3	117.12 (13)	F3^{i}—Hf1—F4^{i}	90.69 (4)
C5—C4—C6	118.64 (13)	F3^{i}—Hf1—F4	89.31 (4)
N1—C5—C4	123.15 (12)	F3—Hf1—F4^{i}	89.31 (4)

N1—C5—C9	116.67 (11)	F4^{i}—Hf1—F4	180.0
C4—C5—C9	120.18 (12)	H3A—O3—H3B	107 (3)

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···F4	0.81 (3)	1.78 (3)	2.5926 (14)	176 (3)
O1—H1*B*···F1^{ii}	0.74 (3)	1.85 (3)	2.5861 (13)	172 (3)
O2—H2*A*···O3	0.74 (3)	1.95 (3)	2.6906 (15)	176 (3)
O2—H2*B*···F1^{iii}	0.80 (3)	1.83 (3)	2.6255 (13)	175 (2)
O3—H3*A*···F2	0.78 (3)	1.94 (3)	2.7270 (17)	176 (3)
O3—H3*B*···F3^{iv}	0.75 (3)	1.96 (3)	2.7020 (15)	173 (3)

Symmetry codes: (ii) −*x*+3/2, *y*−1/2, −*z*+3/2; (iii) −*x*+3/2, *y*+1/2, −*z*+3/2; (iv) −*x*+1, −*y*+2, −*z*+2.