

Received 23 December 2020

Accepted 19 January 2021

Edited by B. Therrien, University of Neuchâtel, Switzerland

Keywords: crystal structures; lambda (Λ)-shapes; d^0 early transition metals; hydrothermal synthesis.

CCDC references: 2045776; 2045775; 2045774; 2045773

Supporting information: this article has supporting information at journals.iucr.org/e

Crystal structures of $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3(\text{MF}_6)] \cdot \text{H}_2\text{O}$ ($M = \text{Ti}, \text{Zr}, \text{Hf}$) and $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_2\text{F}]_2[\text{HfF}_6] \cdot \text{H}_2\text{O}$

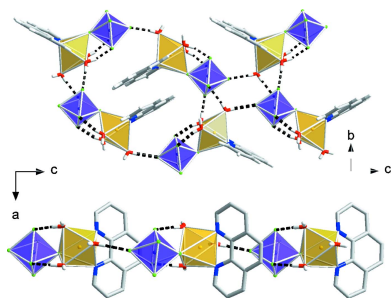
Matthew L. Nisbet and Kenneth R. Poeppelmeier*

2145 Sheridan Road, Evanston, IL 60208, USA. *Correspondence e-mail: krp@northwestern.edu

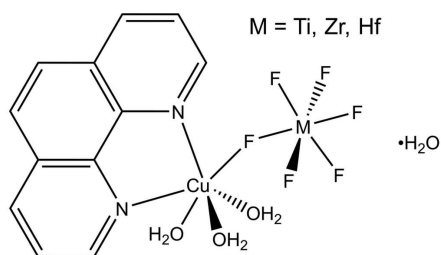
The crystal structures of three bridged bimetallic molecular compounds, namely, triaqua- $2\kappa^3O$ - μ -fluorido-pentafluorido- $1\kappa^5F$ -(1,10-phenanthroline- $2\kappa^2N,N'$)-copper(II)titanium(IV) monohydrate, $[\text{Cu}(\text{TiF}_6)(\text{phen})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ (phen is 1,10-phenanthroline, $\text{C}_{12}\text{H}_8\text{N}_2$), (I), triaqua- $2\kappa^3O$ - μ -fluorido-pentafluorido- $1\kappa^5F$ -(1,10-phenanthroline- $2\kappa^2N,N'$)-copper(II)zirconium(IV) monohydrate, $[\text{Cu}(\text{ZrF}_6)(\text{phen})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$, (II), and triaqua- $2\kappa^3O$ - μ -fluorido-pentafluorido- $1\kappa^5F$ -(1,10-phenanthroline- $2\kappa^2N,N'$)-copper(II)hafnium(IV) monohydrate, $[\text{Cu}(\text{HfF}_6)(\text{phen})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$, (III), and one molecular salt, bis[diaqua-fluorido(1,10-phenanthroline- κ^2N,N')-copper(II)] hexafluoridohafnate(IV) dihydrate, $[\text{CuF}(\text{phen})(\text{H}_2\text{O})_2]_2[\text{HfF}_6] \cdot 2\text{H}_2\text{O}$, (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 $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_2\text{F}]_2[\text{HfF}_6] \cdot \text{H}_2\text{O}$ displays an isolated square-pyramidal $\text{Cu}(\text{phen})(\text{H}_2\text{O})_2\text{F}^+$ complex linked to other cationic complexes and isolated HfF_6^{2-} anions through intermolecular hydrogen-bonding interactions.

1. Chemical context

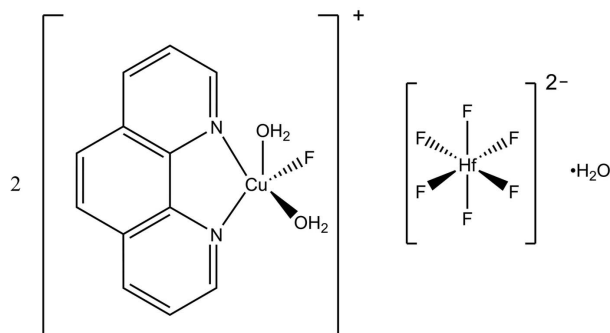
Lambda (Λ)-shaped molecules have been demonstrated as efficient building blocks in the synthesis of non-centrosymmetric (NCS) materials *via* arrangement into head-to-tail and accordion (head-to-head, tail-to-tail) structures (Yamamoto *et al.*, 1992; Tao *et al.*, 1994, 1995; Ostroverkhov *et al.*, 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 $\text{K}_{10}(\text{Mo}_2\text{O}_4\text{F}_7)_3\text{X}$ ($\text{X} = \text{Cl}, ([\text{Br}_3][\text{Br}])_{1/2}, ([\text{I}_3][\text{I}])_{1/2}$), $\text{K}_{10}(\text{Nb}_2\text{O}_2\text{F}_9)_3\text{X}$ ($\text{X} = \text{Br}, ([\text{Br}_3][\text{Br}])_{1/2}, ([\text{I}_3][\text{I}])_{1/2}$), and $[\text{Cu}(\text{H}_2\text{O})_5(\text{VOF}_4(\text{H}_2\text{O}))] \cdot \text{H}_2\text{O}$ (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 $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3(\text{MF}_6)] \cdot \text{H}_2\text{O}$ ($M = \text{Ti}, \text{Zr}, \text{Hf}$; 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 $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_2\text{F}]_2[\text{HfF}_6] \cdot \text{H}_2\text{O}$ provides a point of comparison as an unbridged analogue of $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3(\text{HfF}_6)] \cdot \text{H}_2\text{O}$.



OPEN ACCESS



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



Compound (IV)

2. Structural commentary

Compound (I) has the formula $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3(\text{TiF}_6)] \cdot \text{H}_2\text{O}$ 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

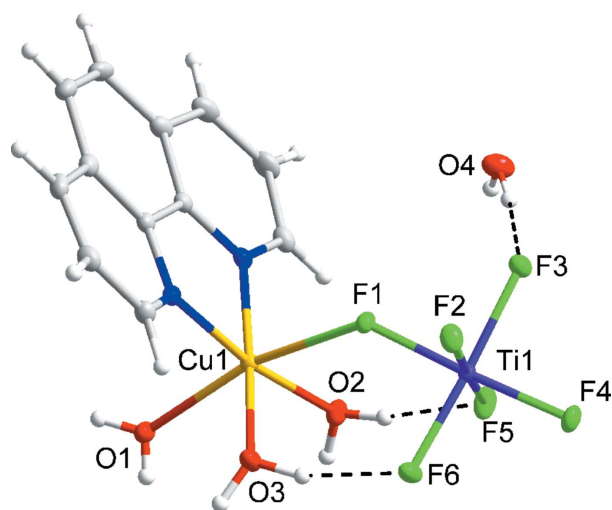


Figure 1
Molecular structure of compound (I), $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3(\text{TiF}_6)] \cdot \text{H}_2\text{O}$. Ellipsoids of non-H atoms are drawn at 50% probability. H atoms are drawn with an atomic radius of 0.135 Å.

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1-H1A \cdots F2^i$	0.70 (4)	2.08 (4)	2.775 (2)	175 (4)
$O1-H1B \cdots F4^{ii}$	0.77 (4)	1.96 (4)	2.726 (2)	174 (3)
$O2-H2A \cdots O4$	0.83 (3)	1.83 (3)	2.654 (2)	175 (3)
$O2-H2B \cdots F5$	0.83 (4)	1.85 (4)	2.666 (2)	167 (3)
$O3-H3A \cdots F3^i$	0.84 (4)	1.85 (4)	2.683 (2)	171 (4)
$O3-H3B \cdots F6$	0.90 (4)	1.81 (4)	2.683 (2)	163 (3)
$O4-H4A \cdots F3^{iii}$	0.75 (4)	2.00 (4)	2.718 (2)	163 (4)
$O4-H4B \cdots F2^i$	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) $-x+\frac{3}{2}, y+\frac{1}{2}, z$.

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 $O2-H2B \cdots F5$ and $O3-H3B \cdots F6$ hydrogen bonds (Table 1).

Compound (II) has the formula $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3(\text{ZrF}_6)] \cdot \text{H}_2\text{O}$ 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 Cu1—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 $O2-H2B \cdots F6$ hydrogen bond (Table 2). The single intramolecular hydrogen bond in compound (II) tilts the ZrF_6^{2-} group significantly relative to

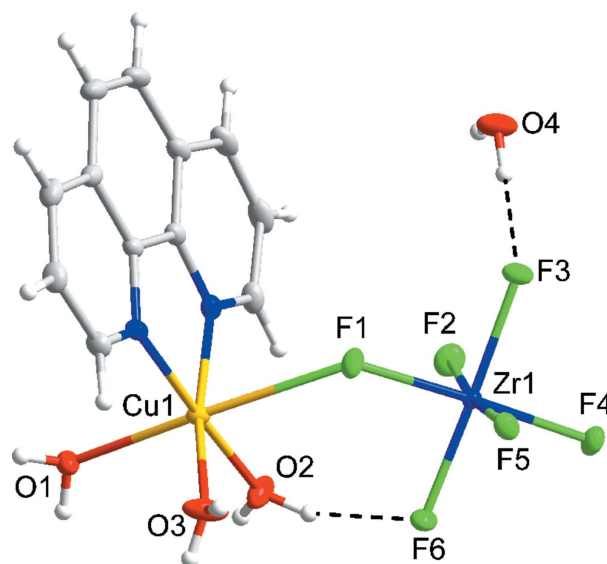


Figure 2
Molecular structure of compound (II), $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3(\text{ZrF}_6)] \cdot \text{H}_2\text{O}$. Ellipsoids of non-H atoms are drawn at 50% probability. H atoms are drawn with an atomic radius of 0.135 Å.

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
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).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
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 $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3(\text{HfF}_6)] \cdot \text{H}_2\text{O}$ and crystallizes in the monoclinic space group $P2_1/n$ (Fig. 3). Compound (III) is isostructural to compound (II).

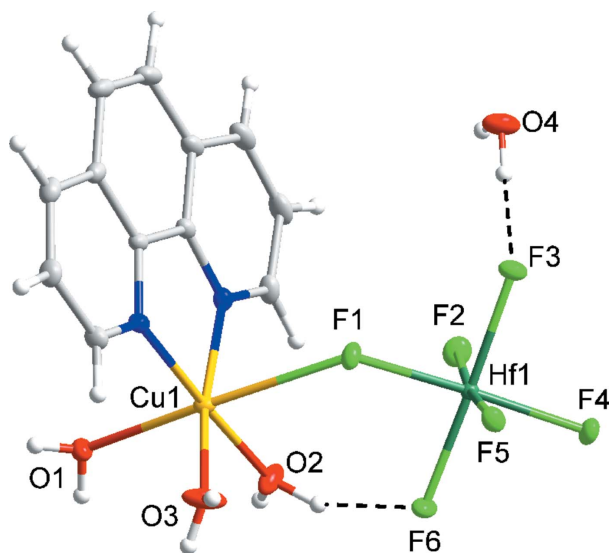


Figure 3
Molecular structure of compound (III), $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3(\text{HfF}_6)] \cdot \text{H}_2\text{O}$. Ellipsoids of non-H atoms are drawn at 50% probability. H atoms are drawn with an atomic radius of 0.135 Å.

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
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 $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_2\text{F}]_2 \cdot [\text{HfF}_6] \cdot \text{H}_2\text{O}$ and crystallizes in the monoclinic space group $P2_1/n$ (Fig. 4). The structure of compound (IV) features isolated square pyramidal $\text{Cu}(\text{phen})(\text{H}_2\text{O})_2\text{F}^+$ 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

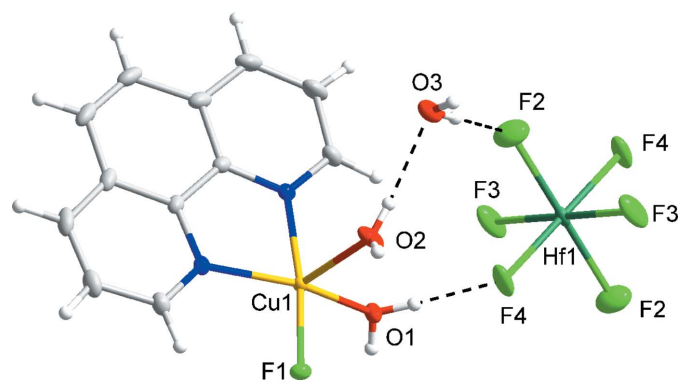


Figure 4
Molecular structure of compound (IV), $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_2\text{F}]_2[\text{HfF}_6] \cdot \text{H}_2\text{O}$. Ellipsoids of non-H atoms are drawn at 50% probability. H atoms are drawn with an atomic radius of 0.135 Å.

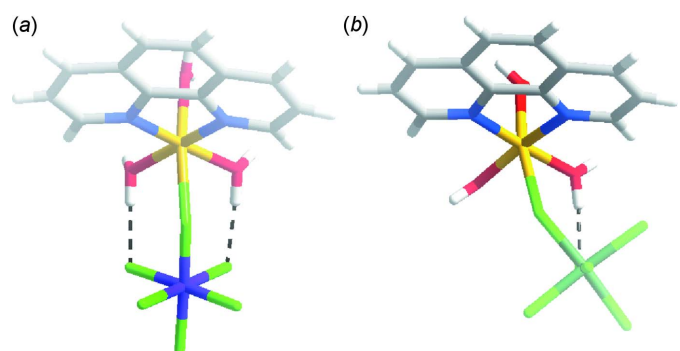


Figure 5
Comparison of the molecular structures of (a) compound (I) and (b) compound (III).

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

Compound number	type	$d_{\text{phenyl-pyridine}}$	$d_{\text{pyridine-pyridine}}$	$d_{\text{phenyl-phenyl}}$	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 $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3(\text{TiF}_6)]$ complex in compound (I) participates in hydrogen bonding with four other $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3(\text{TiF}_6)]$ 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 $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3(\text{MF}_6)]$ ($M = \text{Zr}, \text{Hf}$) units in compound (II) and compound (III) are involved in five hydrogen-bonding contacts to adjacent $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3(\text{MF}_6)]$ complexes and three contacts to hydrating water molecules (Fig. 7, Table 2, and Table 3). The $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3(\text{MF}_6)]$ 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 $\text{Cu}(\text{phen})(\text{H}_2\text{O})_2\text{F}^+$ complexes (Fig. 8). The equatorial water ligands form $\text{O1} \cdots \text{H1A} \cdots \text{F1}$ hydrogen bonds with adjacent $\text{Cu}(\text{phen})(\text{H}_2\text{O})_2\text{F}^+$ complexes and $\text{O1} \cdots \text{H1B} \cdots \text{F4}$ hydrogen bonds with HfF_6^{2-} groups (Table 4). The apical water molecule forms an $\text{O2} \cdots \text{H2B} \cdots \text{F1}$ hydrogen bond to an adjacent $\text{Cu}(\text{phen})(\text{H}_2\text{O})_2\text{F}^+$

complex and a $\text{O2} \cdots \text{H2A} \cdots \text{O3}$ hydrogen bond with a free water molecule (Table 4). Each MF_6^{2-} group forms hydrogen bonds with four free water molecules and two $\text{Cu}(\text{phen})(\text{H}_2\text{O})_2\text{F}^+$ complexes. The $\text{Cu}(\text{phen})(\text{H}_2\text{O})_2\text{F}^+$ 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 $[\text{Cu}(\text{H}_2\text{O})_5(\text{VO}(\text{H}_2\text{O})\text{F}_4)] \cdot \text{H}_2\text{O}$ (Donakowski *et al.*, 2012) is the only example of a molecular inorganic Λ -shape known to the authors. $[\text{Cu}(\text{H}_2\text{O})_5(\text{VOF}_4(\text{H}_2\text{O}))] \cdot \text{H}_2\text{O}$ contains a molecular Λ -shaped $[\text{Cu}(\text{H}_2\text{O})_5(\text{VOF}_4(\text{H}_2\text{O}))]$ molecule that is bridged *via* the $\text{Cu1} \cdots \text{O8} \cdots \text{V1}$ 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-

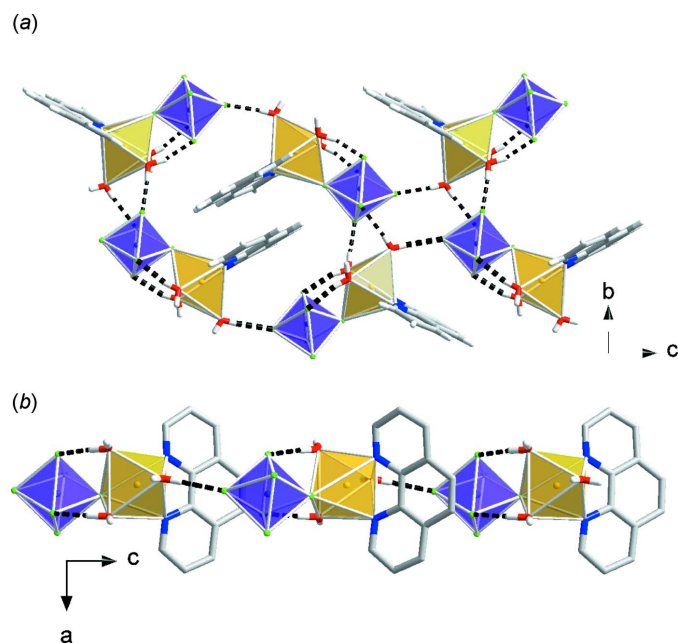


Figure 6
Packing diagrams of compound (I), $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3(\text{TiF}_6)] \cdot \text{H}_2\text{O}$. Yellow polyhedra represent $\text{Cu}(\text{phen})(\text{H}_2\text{O})_3^{2+}$ cations and purple polyhedra represent TiF_6^{2-} anions.

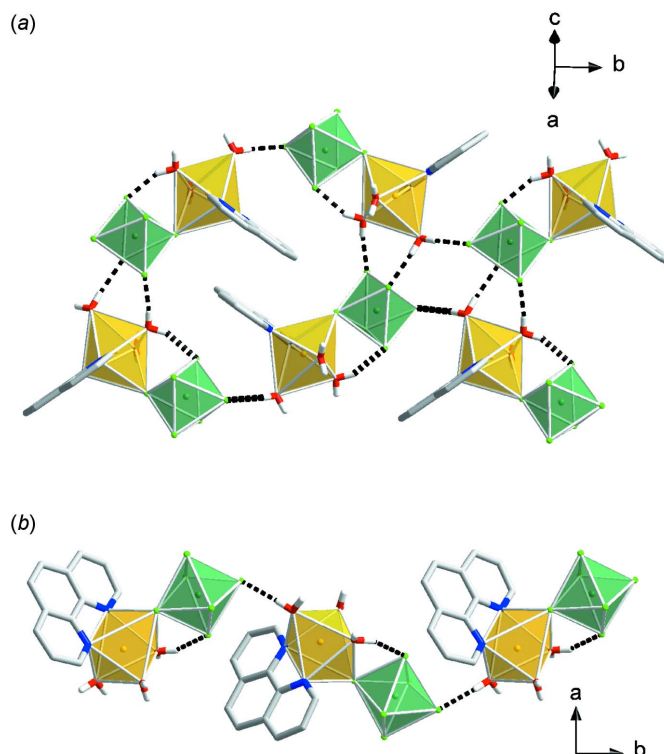


Figure 7
Packing diagrams of compound (II), $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3(\text{ZrF}_6)] \cdot \text{H}_2\text{O}$, and compound (III), $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_3(\text{HfF}_6)] \cdot \text{H}_2\text{O}$. Yellow polyhedra represent $\text{Cu}(\text{phen})(\text{H}_2\text{O})_3^{2+}$ cations and green polyhedra represent ZrF_6^{2-} or HfF_6^{2-} anions.

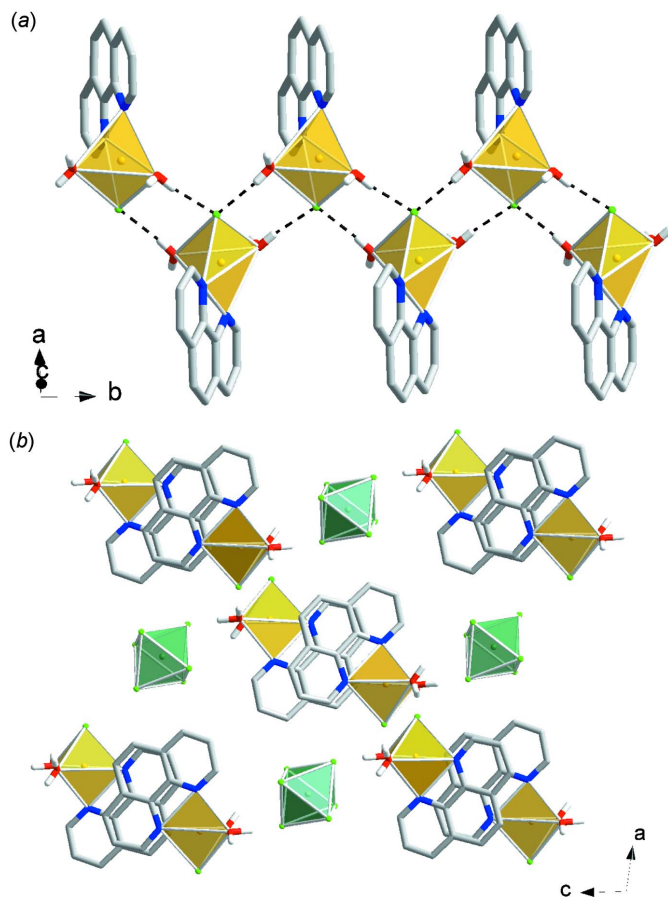


Figure 8

Packing diagrams of compound (IV), $[\text{Cu}(\text{phen})(\text{H}_2\text{O})_2\text{F}][\text{HfF}_6] \cdot \text{H}_2\text{O}$. Yellow polyhedra represent $\text{Cu}(\text{phen})(\text{H}_2\text{O})_2\text{F}^+$ 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 $\text{O8}-\text{Cu}-\text{O}$ bond angle in $[\text{Cu}(\text{H}_2\text{O})_5(\text{VOF}_4(\text{H}_2\text{O}))] \cdot \text{H}_2\text{O}$ is 88.42° , meaning that the complex has a small tilt similar to compound (I).

The Λ -shapes in $[\text{Cu}(\text{H}_2\text{O})_5(\text{VO}(\text{H}_2\text{O})\text{F}_4)] \cdot \text{H}_2\text{O}$ 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 $\text{HF}(\text{aq})$ (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 $\text{HF}(\text{aq})$ (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 $\text{HF}(\text{aq})$ (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 $\text{HF}(\text{aq})$ (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 $0.95 \text{ \AA}$ from the associated C atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ within *OLEX2* (Dolomanov *et al.*, 2009).

Acknowledgements

Single-crystal X-ray diffraction data were acquired at IMISRC at Northwestern University, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205), the State of Illinois, and the International Institute for Nanotechnology (IIN).

Funding information

Funding for this research was provided by: National Science Foundation (award No. DMR-1904701).

References

- Bruker (2016). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2017). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Chang, P.-H., Chen, J.-Y., Tsai, H.-C. & Hsiue, G.-H. (2009). *J. Polym. Sci. A Polym. Chem.* **47**, 4937–4949.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Donakowski, M. D., Gautier, R., Yeon, J., Moore, D. T., Nino, J. C., Halasyamani, P. S. & Poeppelmeier, K. R. (2012). *J. Am. Chem. Soc.* **134**, 7679–7689.
- Harrison, W. T. A., Nenoff, T. M., Gier, T. E. & Stucky, G. D. (1993). *Inorg. Chem.* **32**, 2437–2441.
- Holland, M., Donakowski, M. D., Pozzi, E. A., Rasmussen, A. M., Tran, T. T., Pease-Dodson, S. E., Halasyamani, P. S., Seideman, T.,

Table 6
Experimental details.

	(I)	(II)	(III)	(IV)
Crystal data				
Chemical formula	[CuTiF ₆ (C ₁₂ H ₈ N ₂)-(H ₂ O) ₃]·H ₂ O	[CuZrF ₆ (C ₁₂ H ₈ N ₂)-(H ₂ O) ₃]·H ₂ O	[CuHfF ₆ (C ₁₂ H ₈ N ₂)-(H ₂ O) ₃]·H ₂ O	[CuF(C ₁₂ H ₈ N ₂)-(H ₂ O) ₂] ₂ [HfF ₆]·2H ₂ O
<i>M_r</i>	477.71	521.03	608.30	926.07
Crystal system, space group	Orthorhombic, <i>Pbca</i>	Monoclinic, <i>P2₁/n</i>	Monoclinic, <i>P2₁/n</i>	Monoclinic, <i>P2₁/n</i>
Temperature (K)	100	100	101	100
<i>a</i> , <i>b</i> , <i>c</i> (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
<i>V</i> (Å ³)	3360.34 (13)	1714.64 (12)	1709.84 (7)	1507.09 (4)
<i>Z</i>	8	4	4	2
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
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 (<i>SADABS</i> ; Bruker, 2016)	Multi-scan (<i>SADABS</i> ; Bruker, 2016)	Multi-scan (<i>SADABS</i> ; Bruker, 2016)	Multi-scan (<i>SADABS</i> ; Bruker, 2016)
<i>T_{min}</i> , <i>T_{max}</i>	0.668, 0.746	0.683, 0.747	0.480, 0.747	0.489, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	36860, 4534, 3928	87607, 7546, 7052	43322, 8248, 7980	123138, 5034, 4982
<i>R_{int}</i>	0.043	0.031	0.026	0.033
(sin θ /λ) _{max} (Å ⁻¹)	0.686	0.807	0.835	0.737
Refinement				
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	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
Δρ _{max} , Δρ _{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, 2015a), *SHELXL* (Sheldrick, 2015b), and *OLEX2* (Dolomanov *et al.*, 2009).

- Van Duyne, R. P. & Poeppelmeier, K. R. (2014). *Inorg. Chem.* **53**, 221–228.
- Ostroverkhov, V., Petschek, R. G., Singer, K. D. & Twieg, R. J. (2001). *Chem. Phys. Lett.* **340**, 109–115.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Tao, X. T., Watanabe, T., Shimoda, S., Zou, D. C., Sato, H. & Miyata, S. (1994). *Chem. Mater.* **6**, 1961–1966.
- Tao, X. T., Watanabe, T., Zou, D. C., Shimoda, S., Usui, H., Sato, H. & Miyata, S. (1995). *J. Polym. Sci. B Polym. Phys.* **33**, 2205–2210.
- Yamamoto, H., Katogi, S., Watanabe, T., Sato, H., Miyata, S. & Hosomi, T. (1992). *Appl. Phys. Lett.* **60**, 935–937.

supporting information

Acta Cryst. (2021). E77, 165-170 [https://doi.org/10.1107/S2056989021000645]

Crystal structures of [Cu(phen)(H₂O)₃(MF₆)]·H₂O (*M* = Ti, Zr, Hf) and [Cu(phen)(H₂O)₂F]₂[HfF₆]·H₂O

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).

Triqua-2κ³O-μ-fluorido-pentafluorido-1κ⁵F-(1,10-phenanthroline-2κ²N,N')copper(II)titanium(IV) monohydrate (I)

Crystal data

[CuTiF₆(C₁₂H₈N₂)(H₂O)₃]·H₂O

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) Å³

Z = 8

F(000) = 1912

D_x = 1.889 Mg m⁻³

Mo *Kα* 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* > 2σ(*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 > 2σ(*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/[σ²(*F*_o²) + (0.0163*P*)² + 6.5495*P*]

where *P* = (*F*_o² + 2*F*_c²)/3

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.45 \text{ e } \text{\AA}^{-3}$$

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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 ($\text{\AA}^2$)

	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 ($\text{\AA}$, $^\circ$)

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, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H1A $\cdots$ F2 ⁱ	0.70 (4)	2.08 (4)	2.775 (2)	175 (4)
O1—H1B $\cdots$ F4 ⁱⁱ	0.77 (4)	1.96 (4)	2.726 (2)	174 (3)
O2—H2A $\cdots$ O4	0.83 (3)	1.83 (3)	2.654 (2)	175 (3)
O2—H2B $\cdots$ F5	0.83 (4)	1.85 (4)	2.666 (2)	167 (3)
O3—H3A $\cdots$ F3 ⁱ	0.84 (4)	1.85 (4)	2.683 (2)	171 (4)
O3—H3B $\cdots$ F6	0.90 (4)	1.81 (4)	2.683 (2)	163 (3)
O4—H4A $\cdots$ F3 ⁱⁱⁱ	0.75 (4)	2.00 (4)	2.718 (2)	163 (4)
O4—H4B $\cdots$ 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-2 κ^3 O- μ -fluorido-pentafluorido-1 κ^5 F-(1,10-phenanthroline-2 κ^2 N,N')copper(II)zirconium(IV) monohydrate (II)

Crystal data

[CuZrF₆(C₁₂H₈N₂)(H₂O)₃] $\cdot$ H₂O

$M_r = 521.03$

Monoclinic, $P2_1/n$

$a = 9.9486$ (4) Å

$b = 17.3006$ (7) Å

$c = 10.0022$ (4) Å

$\beta = 95.1335$ (18)°

$V = 1714.64$ (12) Å³

$Z = 4$

$F(000) = 1028$

$D_x = 2.018$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9425 reflections

$\theta = 3.0\text{--}34.9^\circ$

$\mu = 1.93$ mm⁻¹

$T = 100$ K

Cuboid, blue

$0.24 \times 0.12 \times 0.11$ 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)

$T_{\min} = 0.683$, $T_{\max} = 0.747$

87607 measured reflections

7546 independent reflections

7052 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 35.0^\circ$, $\theta_{\min} = 2.4^\circ$

$h = -15 \rightarrow 16$

$k = -27 \rightarrow 27$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.018$

$wR(F^2) = 0.047$

$S = 1.04$

7546 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

$$w = 1/[\sigma^2(F_o^2) + (0.0222P)^2 + 0.6601P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.57 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.67 \text{ e } \text{\AA}^{-3}$

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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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, °)

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 ($\text{\AA}$, $^\circ$)

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
O1—H1A $\cdots$ F5 ⁱ	0.794 (18)	1.944 (18)	2.7338 (9)	173.5 (18)
O1—H1B $\cdots$ F4 ⁱⁱ	0.78 (2)	1.93 (2)	2.7147 (10)	179 (2)
O2—H2A $\cdots$ F3 ⁱ	0.79 (2)	1.85 (2)	2.6324 (10)	171 (2)
O2—H2B $\cdots$ F6	0.82 (2)	1.87 (2)	2.6491 (10)	159.2 (19)
O3—H3A $\cdots$ F2 ⁱⁱⁱ	0.79 (2)	1.85 (2)	2.6327 (10)	177.5 (19)
O3—H3B $\cdots$ O4 ^{iv}	0.79 (2)	1.87 (2)	2.6481 (12)	170 (2)
O4—H4A $\cdots$ F3	0.799 (19)	2.002 (19)	2.7691 (10)	160.9 (18)
O4—H4B $\cdots$ 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) $x+1/2, -y+1/2, z+1/2$.

Triqua- $2\kappa^3O$ - μ -fluorido-pentafluorido- $1\kappa^5F$ -(1,10-phenanthroline- $2\kappa^2N,N'$)copper(II)hafnium(IV) monohydrate (III)

Crystal data

$[\text{CuHfF}_6(\text{C}_{12}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$

$M_r = 608.30$

Monoclinic, $P2_1/n$

$a = 9.9411$ (3) $\text{\AA}$

$b = 17.2733$ (4) $\text{\AA}$

$c = 9.9972$ (2) $\text{\AA}$

$\beta = 95.116$ (1) $^\circ$

$V = 1709.84$ (7) $\text{\AA}^3$

$Z = 4$

$F(000) = 1156$

$D_x = 2.363$ Mg m^{-3}

Mo $K\alpha$ radiation, $\lambda = 0.71073$ $\text{\AA}$

Cell parameters from 9921 reflections

$\theta = 2.4\text{--}36.4^\circ$

$\mu = 7.39$ mm^{-1}

$T = 101$ K

Rodlike, blue

$0.17 \times 0.12 \times 0.05$ 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 $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 36.4^\circ$, $\theta_{\min} = 2.4^\circ$

$h = -16 \rightarrow 16$

$k = -28 \rightarrow 28$

$l = -13 \rightarrow 16$

*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 $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.005$ $\Delta\rho_{\max} = 1.03 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.98 \text{ e } \text{\AA}^{-3}$ *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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 ($\text{\AA}^2$)

	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 ($\text{\AA}$, $^\circ$)

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, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H1A $\cdots$ F5 ⁱ	0.80 (3)	1.94 (3)	2.7359 (13)	172 (3)
O1—H1B $\cdots$ F4 ⁱⁱ	0.77 (3)	1.95 (3)	2.7135 (13)	176 (3)
O2—H2A $\cdots$ F6	0.86 (3)	1.85 (3)	2.6456 (14)	154 (3)
O2—H2B $\cdots$ F3 ⁱ	0.77 (3)	1.87 (3)	2.6362 (14)	171 (3)
O3—H3A $\cdots$ O4 ⁱⁱⁱ	0.81 (3)	1.85 (3)	2.6529 (17)	173 (3)
O3—H3B $\cdots$ F2 ^{iv}	0.77 (3)	1.86 (3)	2.6330 (15)	176 (3)
O4—H4A $\cdots$ F5 ^v	0.81 (3)	2.00 (3)	2.7429 (15)	154 (3)
O4—H4B $\cdots$ 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(C₁₂H₈N₂)(H₂O)₂]₂[HfF₆] $\cdot$ 2H₂O

$M_r = 926.07$

Monoclinic, $P2_1/n$

$a = 13.6451$ (2) Å

$b = 7.1161$ (1) Å

$c = 15.7457$ (3) Å

$\beta = 99.691$ (1)°

$V = 1507.09$ (4) Å³

$Z = 2$

$F(000) = 900$

$D_x = 2.041$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9864 reflections

$\theta = 3.2\text{--}31.6^\circ$

$\mu = 4.93$ mm⁻¹

$T = 100$ K

Block, blue

$0.16 \times 0.16 \times 0.10$ 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 $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 31.6^\circ$, $\theta_{\min} = 1.8^\circ$

$h = -20 \rightarrow 20$

$k = -10 \rightarrow 10$

$l = -23 \rightarrow 23$

*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 $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.002$ $\Delta\rho_{\max} = 0.67 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.70 \text{ e } \text{\AA}^{-3}$

Extinction correction: SHELXL2018/3

(Sheldrick 2015b),

 $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

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 ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 ($\text{\AA}^2$)

	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 ($\text{\AA}$, $^\circ$)

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 ($\text{\AA}$, $^\circ$)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H1A $\cdots$ F4	0.81 (3)	1.78 (3)	2.5926 (14)	176 (3)
O1—H1B $\cdots$ F1 ⁱⁱ	0.74 (3)	1.85 (3)	2.5861 (13)	172 (3)
O2—H2A $\cdots$ O3	0.74 (3)	1.95 (3)	2.6906 (15)	176 (3)
O2—H2B $\cdots$ F1 ⁱⁱⁱ	0.80 (3)	1.83 (3)	2.6255 (13)	175 (2)
O3—H3A $\cdots$ F2	0.78 (3)	1.94 (3)	2.7270 (17)	176 (3)
O3—H3B $\cdots$ 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) $-x+1, -y+2, -z+2$.