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Crystal structures of two copper(I)–6,6′-dimethyl-2,2′-bipyridyl (dmbpy) compounds, $[Cu(dmbpy)_2]_2[MF_6]\cdot xH_2O$ (M = Zr, Hf; x = 1.134, 0.671)

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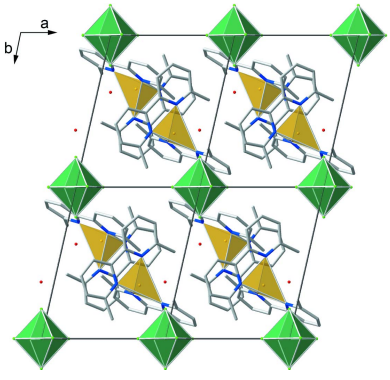
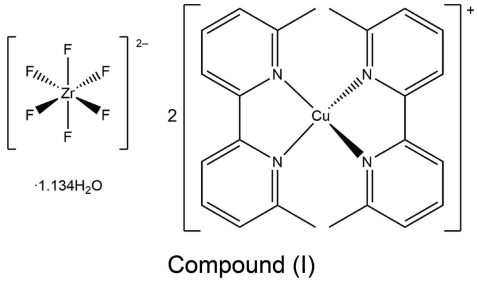
The syntheses and crystal structures of two bimetallic molecular compounds, namely, bis[bis(6,6′-dimethyl-2,2′-bipyridine)copper(I)] hexafluoridozirconate(IV) 1.134-hydrate, $[Cu(dmbpy)_2]_2[ZrF_6]\cdot 1.134H_2O$ (dmbpy = 6,6′-dimethyl-2,2′-bipyridyl, $C_{12}H_{12}N_2$), (I), and bis[bis(6,6′-dimethyl-2,2′-bipyridine)copper(I)] hexafluoridohafnate(IV) 0.671-hydrate, $[Cu(dmbpy)_2]_2[HfF_6]\cdot 0.671H_2O$, (II), are reported. Apart from a slight site occupany difference for the water molecule of crystallization, compounds (I) and (II) are isostructural, featuring isolated tetrahedral cations of copper(I) ions coordinated by two dmbpy ligands and centrosymmetric, octahedral anions of fluorinated early transition metals. The tetrahedral environments of the copper complexes are distorted owing to the steric effects of the dmbpy ligands. The extended structures are built up through Coulombic interactions between cations and anions and π–π stacking interactions between heterochiral Δ- and Λ-$[Cu(dmbpy)_2]^+$ complexes. A comparison between the title compounds and other $[Cu(dmbpy)_2]^+$ compounds with monovalent and bivalent anions reveals a significant influence of the cation-to-anion ratio on the resulting crystal packing architectures, providing insights for future crystal design of distorted tetrahedral copper compounds.

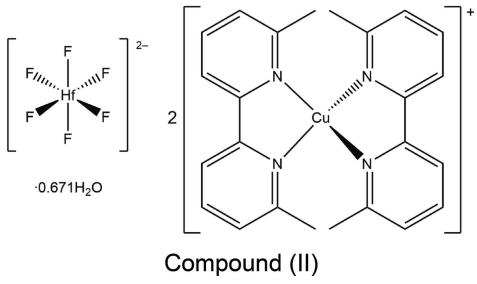
1. Chemical context

Copper(I) complexes with distorted tetrahedral environments have been studied as catalytic active sites in electron-transfer reactions and are found in a number of proteins that contain copper (Vallee & Williams, 1968; Colman *et al.*, 1978; Adman *et al.*, 1978). The realization of significantly distorted tetrahedral geometry requires sufficient steric hindrance between the ligands. The methyl groups of the 6,6′-dimethyl-2,2′-bipyridyl ($C_{12}H_{12}N_2$; dmbpy) ligand create a large steric hindrance upon coordination, and, consequently, a common strategy to form distorted tetrahedral complexes is to use dmbpy or its derivatives as ligands (McKenzie *et al.*, 1971; Burke *et al.*, 1980). Previously, compounds with distorted tetrahedral $[Cu(dmbpy)_2]^+$ cations have been reported, namely $[Cu(dmbpy)_2]X$ (X = $[BF_4]^-$, $[ClO_4]^-$, $[PF_6]^-$), $[Cu(dmbpy)_2][C_{16}H_9O_8]\cdot H_2O$ ($C_{16}H_9O_8$ = 2′,3,3′-tricarboxybiphenyl-2-carboxylate) and $[Cu(dmbpy)_2]X_2$ (X = $[BF_4]^-$, $[ClO_4]^-$). (Burke *et al.*, 1980; Cui *et al.*, 2005; Itoh *et al.*, 2005; Mei *et al.*, 2011; Bozic-Weber *et al.*, 2012; Li *et al.*, 2017) Here, we report two structures with $[MF_6]^{2-}$ (M = Zr, Hf), which are the first known distorted tetrahedral copper compounds with bivalent anions.





Compound (I)



Compound (II)

2. Structural commentary

Compound (I) has the formula $[Cu(dmbpy)_2]_2[ZrF_6]\cdot 1.134H_2O$ and crystallizes in the triclinic space group $P\overline{1}$ (Fig. 1). The structure of compound (I) features isolated tetrahedral $[Cu(dmbpy)_2]^+$ cations and octahedral ZrF_6^{2-} anions (Zr site symmetry $\overline{1}$). The coordination geometry of Cu1 and its donor N atoms deviates from an ideal tetrahedron, as demonstrated by the 83.33 (10)° angle between the least squares planes containing Cu1 and each ligand (Table 1). To quantify the deviation from T_d symmetry in $[Cu(dmbpy)_2]^+$ cations, the τ_4' parameter is employed and it gives a value of 0.66 for compound (I) (Okuniewski *et al.*, 2015). The distorted tetrahedral geometry of $[Cu(dmbpy)_2]^+$ in compound (I) is consistent with other reported compounds containing $[Cu(dmbpy)_2]^+$ cations (Burke *et al.*, 1980; Cui *et al.*, 2005; Mei *et al.*, 2011; Bozic-Weber *et al.*, 2012). Moreover, the dmbpy ligands in (I) are non-planar and are slightly twisted on the 2,2′ carbon bond to give a dihedral angle of 8.68 (10)° between the N1/C1–C5 and N2/C6–C10 rings and 7.44 (11)° between the N3/C13–C17 and N4/C18–C22 rings. The distorted tetrahedral environment and non-planar ligand geometry give the $[Cu(dmbpy)_2]^+$ cations a C_2 symmetry, and enantiomeric Δ- and Λ-$[Cu(dmbpy)_2]^+$ pairs are related across inversion centers. The octahedral coordination environment of Zr1 is slightly distorted, with Zr1—F bond lengths ranging from 1.9955 (13) to 2.0183 (12) Å (Table 1). The minor distortion of the ZrF_6^{2-} anion may arise due to hydrogen-bonding interactions between water molecules of crystallization and fluorine atoms on the *trans* position of the ZrF_6^{2-} anions [see O1—H1*B*···F2 (Table 2)].

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1—N1	2.0208 (16)	Zr1—F1	2.0113 (15)
Cu1—N2	2.0348 (17)	Zr1—F2	2.0183 (12)
Cu1—N3	2.0123 (17)	Zr1—F3	1.9955 (13)
Cu1—N4	2.0616 (18)		
N1—Cu1—N2	81.40 (7)	N3—Cu1—N1	136.29 (7)
N1—Cu1—N4	116.24 (7)	N3—Cu1—N2	126.16 (7)
N2—Cu1—N4	120.45 (7)	N3—Cu1—N4	81.05 (7)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*B*···F2	0.87	1.47	2.337 (4)	177

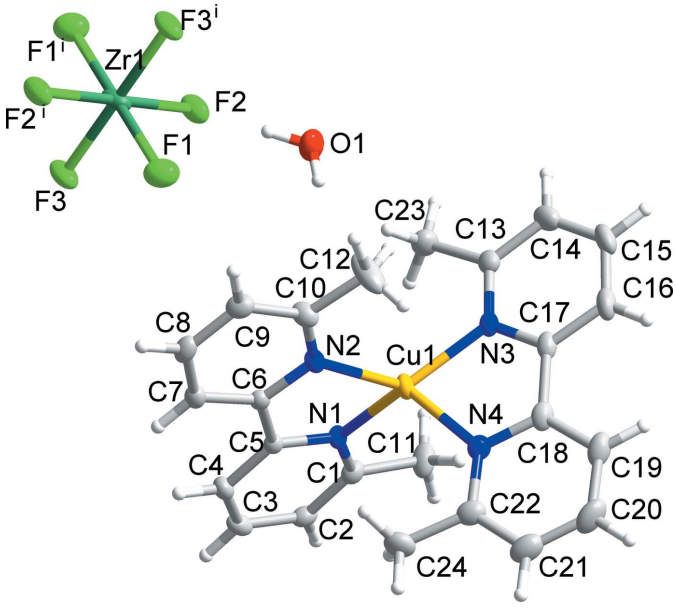


Figure 1
The molecular structure of (I) showing 50% displacement ellipsoids. Symmetry code: (i) $-x, 2-y, 2-z$.

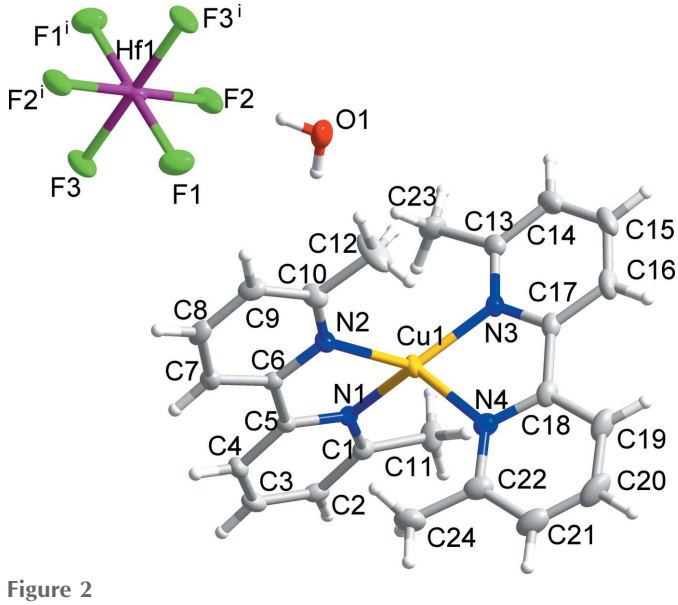


Figure 2
The molecular structure of (II) showing 50% displacement ellipsoids. Symmetry code: (i) (i) $-x, 2-y, 2-z$.

Table 3
Selected geometric parameters (Å, °) for (II).

Cu1—N1	2.0229 (12)	Hf1—F1	2.0111 (11)
Cu1—N2	2.0414 (12)	Hf1—F2	2.0033 (9)
Cu1—N3	2.0121 (12)	Hf1—F3	1.9945 (10)
Cu1—N4	2.0659 (13)		
N1—Cu1—N2	81.22 (5)	N3—Cu1—N1	136.20 (5)
N1—Cu1—N4	116.52 (5)	N3—Cu1—N2	126.39 (5)
N2—Cu1—N4	120.35 (5)	N3—Cu1—N4	80.94 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1B—H1*B*···F2	0.87	1.50	2.328 (4)	156

Compound (II) has the formula $[Cu(dmbpy)_2]_2[HfF_6]\cdot 0.671H_2O$ and crystallizes in the triclinic space group $P\overline{1}$ (Fig. 2). Compound (II) is isostructural to compound (I), therefore, the $[Cu(dmbpy)_2]^+$ cations also have C_2 symmetry, with the angle between the least squares planes containing Cu1 and each ligand being 84.14 (8)° (Table 3) and the τ_4' parameter being 0.66, and the dmbpy ligands are slightly twisted on the 2,2′ carbon bond to give an angle of 9.69 (7)° between the N1/C1–C5 and N2/C6–C10 rings and 7.97 (8)° between the N3/C13–C17 and N4/C18–C22 rings. Moreover, the octahedral coordination environment of Hf1 is also slightly distorted, with Hf1—F bond lengths ranging from 1.9945 (10) to 2.0111 (11) Å. Like in compound (I), hydrogen-bonding interactions are present between the water molecule of crystallization and fluorine atoms on the *trans* position of HfF_6^{2-} anions, but the geometry of the hydrogen bond is slightly different from that in compound (I) [see O1—H1*B*···F2 (Table 4)].

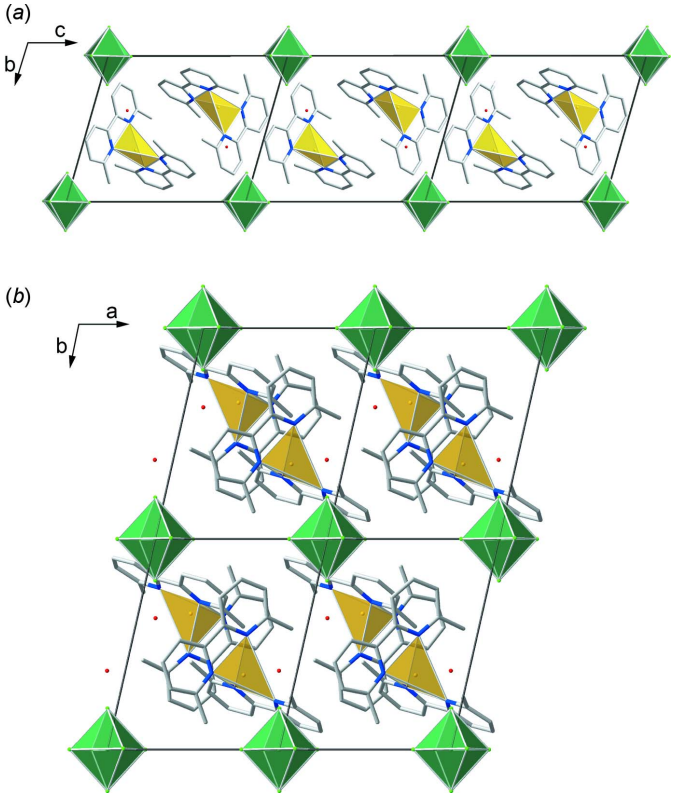


Figure 3
The packing for (I) viewed (*a*) down [100] and (*b*) down [001], with the copper and zirconium coordination environments represented by yellow/orange and green polyhedra, respectively.

Table 5
Aromatic π–π stacking interactions (Å, °) in (I).

Description	type	d_{py-py}	interplanar angle	interplanar distance
Heterochiral	face-to-face	3.6967 (12)	0	3.347
Heterochiral	parallel displaced	5.3726 (13)	0	3.708

Table 6
Aromatic π–π stacking interactions (Å, °) in (II).

Description	type	d_{py-py}	interplanar angle	interplanar distance
Heterochiral	face-to-face	3.7016 (8)	0	3.355
Heterochiral	parallel displaced	5.3777 (11)	0	3.678

3. Supramolecular features

In the extended structures of compounds (I) and (II), the $[Cu(dmbpy)_2]^+$ cations and octahedral MF_6^{2-} anions are closely packed *via* Coulombic interactions (Fig. 3). The Δ/Λ-$[Cu(dmbpy)_2]^+$ cations stack into racemic pairs along the *c*-axis direction *via* a heterochiral face-to-face π–π interaction between the N1/C1–C5 and N2/C6–C10 rings with an interplanar angle of 0°, interplanar distances of 3.347 and 3.355 Å, and centroid–centroid distances (d_{py-py}) of 3.6967 (12) and 3.7016 (8) Å, for compounds (I) and (II), respectively (Tables 5 and 6). Next, Δ/Λ-$[Cu(dmbpy)_2]^+$ pairs pack into racemic chains along the *c*-axis direction with heterochiral parallel displaced π–π interactions between the N3/C13–C17 and N4/C18–C22 rings with an interplanar angle of 0°, interplanar distances of 3.708 and 3.678 Å, and centroid–centroid distances (d_{py-py}) of 5.3726 (13) and 5.3777 (11) Å, for compounds (I) and (II), respectively. The MF_6^{2-} anions with hydrogen-bonded water molecules are interlaced between the racemic chains to form the extended three-dimensional structure. Compared to other molecular compounds with MF_6^{2-} anions in an extended and complicated hydrogen network (Gautier *et al.*, 2012; Nisbet *et al.*, 2020, 2021), the MF_6^{2-} anions in (I) and (II) experience less distortion because the hydrogen-bonding contacts are less extensive and only occur along the same axis due to the site symmetry of hydrogen-bonding interactions (Kunz & Brown, 1995; Halasyamani, 2004).

4. Database survey

A survey of compounds related to compounds (I) and (II) reported in the Cambridge Structural Database (CSD version

Table 7
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$[Cu(C_{12}H_{12}N_2)_2]_2[ZrF_6]\cdot 1.134H_2O$	$[Cu(C_{12}H_{12}N_2)_2]_2[HfF_6]\cdot 0.671H_2O$
M_r	1089.61	1168.58
Crystal system, space group	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$
Temperature (K)	100	100
a, b, c (Å)	8.6219 (3), 10.8064 (3), 12.9992 (4)	8.5737 (1), 10.7967 (2), 13.0183 (2)
α, β, γ (°)	103.078 (2), 104.013 (3), 98.863 (2)	103.273 (1), 103.662 (1), 98.785 (1)
V (Å^3)	1116.33 (6)	1112.07 (3)
Z	1	1
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.25	3.35
Crystal size (mm)	0.98 × 0.13 × 0.05	0.3 × 0.17 × 0.08
Data collection		
Diffractometer	Rigaku Saturn724+ (2x2 bin mode)	Rigaku Saturn724+ (2x2 bin mode)
Absorption correction	Gaussian (*CrysAlis PRO*; Rigaku OD, 2020)	Gaussian (*CrysAlis PRO*; Rigaku OD, 2020)
T_{min}, T_{max}	0.376, 1.000	0.433, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16573, 5673, 4588	40796, 8003, 7235
R_{int}	0.039	0.032
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.722	0.784
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.088, 1.07	0.023, 0.056, 1.08
No. of reflections	5673	8003
No. of parameters	312	312
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.59, −0.54	0.48, −0.73

Computer programs: *CrysAlis PRO* (Rigaku OD, 2020), *SHELXT2014/5* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), and *OLEX2* (Dolomanov *et al.*, 2009).

2020.1 from April 2020; Groom *et al.*, 2016) produced four other compounds based on $[Cu(dmbpy)_2]^+$ complexes: $[Cu(dmbpy)_2][BF_4]$ (CSD refcode: MPYRCU; Burke *et al.*, 1980), $[Cu(dmbpy)_2][PF_6]$ (REFSUS; Bozic-Weber *et al.*, 2012), $[Cu(dmbpy)_2][ClO_4]$ (FAXLAS; Cui *et al.*, 2005), and $[Cu(dmbpy)_2][C_{16}H_9O_8]\cdot H_2O$ ($C_{16}H_9O_8$ = 2′,3,3′-tricarboxybiphenyl-2-carboxylate) (ABIYER; Mei *et al.*, 2011). All these structures have distorted tetrahedral $[Cu(dmbpy)_2]^+$ cations with C_2 symmetry, with a range of the angle between the least-squares planes containing the metal ion and each ligand being from 75.06 to 86.74°. Moreover, τ_4' parameters for these structures range from 0.70 to 0.74, whereas for both compound (I) and (II) the parameter is 0.66 (Okuniewski *et al.*, 2015).

Unlike compound (I) and (II), which have bivalent anions MF_6^{2-}, the compounds reported in the CSD are charge-balanced by monovalent anions and display two different types of packing architectures distinct from those of the title compounds: $[Cu(dmbpy)_2][BF_4]$, $[Cu(dmbpy)_2][PF_6]$, and $[Cu(dmbpy)_2][ClO_4]$ are isostructural, crystallizing in space group $P2_1/c$. Compared to compounds (I) and (II), the ratio of cations-to-anions is smaller in these monovalent-anion compounds. Instead of racemic chains, homochiral chains are observed with homochiral displaced π–π interactions between the ligands with an interplanar angle of around 30°. No local or extended hydrogen-bond networks are observed because these structures do not contain water molecules of crystallization.

Another type of packing architecture is found in $[Cu(dmbpy)_2][C_{16}H_9O_8]\cdot H_2O$, which crystallizes in space group $P\overline{1}$. Unlike the aforementioned five compounds with $[Cu(dmbpy)_2]^+$ cations, π–π interactions in the compound $[Cu(dmbpy)_2][C_{16}H_9O_8]\cdot H_2O$ are dominant between $[Cu(dmbpy)_2]^+$ cations and $[C_{16}H_9O_8]^-$ anions instead of between $[Cu(dmbpy)_2]^+$ cations. In this compound, the $[Cu(dmbpy)_2]^+$ cations and $[C_{16}H_9O_8]^-$ anions are packed into charge-neutral chains *via* Coulombic interactions and π–π interactions along *c* axis and inversion centers are present between the chains. Additionally, the $[C_{16}H_9O_8]^-$ anions and free water molecules generate a three-dimensional network *via* O—H···O hydrogen bonding interactions, resulting in a different architecture.

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 45 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}. Orangish red solid products were recovered by vacuum filtration with a moderate yield. Compound (I) was synthesized in a pouch containing 0.4195 mmol of CuO, 0.4195 mmol of ZrO_2, 0.835 mmol of 6,6′-dimethyl-2,2′-bipyridyl, 0.15 ml (4.14 mmol) of HF (aq) (48%), and 0.1 ml (5.5 mmol) of deionized H_2O. Compound (II) was synthesized in a pouch containing 0.4195 mmol of

CuO, 0.4195 mmol of HfO_2, 0.835 mmol of 6,6′-dimethyl-2,2′-bipyridyl, 0.05 ml (1.38 mmol) of HF (aq) (48%), and 0.2 ml (11 mmol) of deionized H_2O.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 7. Hydrogen-atom positions were assigned from difference map peaks with the exception of the C—H hydrogen atoms of dmbpy, 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). The water occupancies in both structures are refined freely. Four reflections showing very poor agreement were omitted from the final refinement for compound (I).

Acknowledgements

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supporting information

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Crystal structures of two copper(I)–6,6′-dimethyl-2,2′-bipyridyl (dmbpy) compounds, $[Cu(dmbpy)_2]_2[MF_6]\cdot xH_2O$ (M = Zr, Hf; x = 1.134, 0.671)

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Computing details

For both structures, data collection: *CrysAlis PRO* (Rigaku OD, 2020); cell refinement: *CrysAlis PRO* (Rigaku OD, 2020); data reduction: *CrysAlis PRO* (Rigaku OD, 2020); program(s) used to solve structure: *SHELXT2014/5* (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).

Bis[bis(6,6′-dimethyl-2,2′-bipyridine)copper(I)] hexafluoridozirconate(IV) 1.134-hydrate (I)

Crystal data

$[Cu(C_{12}H_{12}N_2)_2]_2[ZrF_6]\cdot 1.134H_2O$
M_r = 1089.61
Triclinic, $P\overline{1}$
a = 8.6219 (3) Å
b = 10.8064 (3) Å
c = 12.9992 (4) Å
α = 103.078 (2)°
β = 104.013 (3)°
γ = 98.863 (2)°
V = 1116.33 (6) Å^3
Z = 1
$F(000)$ = 555
D_x = 1.621 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 10429 reflections
θ = 2.2–30.6°
μ = 1.25 mm^{-1}
T = 100 K
Needle, clear orangish red
0.98 × 0.13 × 0.05 mm

Data collection

Rigaku Saturn724+ (2x2 bin mode) diffractometer
Radiation source: Rotating Anode, Rotating Anode
Confocal monochromator
Detector resolution: 28.5714 pixels mm^{-1}
profile data from ω–scans
Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2020)
T_{min} = 0.376, T_{max} = 1.000
16573 measured reflections
5673 independent reflections
4588 reflections with $I > 2\sigma(I)$
R_{int} = 0.039
θ_{max} = 30.9°, θ_{min} = 2.0°
h = −11→11
k = −14→15
l = −16→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.088
S = 1.07
5673 reflections
312 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0397P)^2 + 0.3898P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 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}	Occ. (<1)
Cu1	0.30548 (3)	0.35420 (2)	0.69756 (2)	0.02018 (8)	
N1	0.4953 (2)	0.36543 (16)	0.82845 (13)	0.0174 (3)	
C1	0.5623 (3)	0.26739 (19)	0.85293 (17)	0.0207 (4)	
N2	0.3424 (2)	0.54652 (16)	0.77601 (14)	0.0195 (3)	
C2	0.7120 (3)	0.2905 (2)	0.93235 (17)	0.0212 (4)	
H2	0.756689	0.219858	0.948974	0.025*	
N3	0.0873 (2)	0.23159 (15)	0.61598 (14)	0.0190 (3)	
C3	0.7947 (3)	0.4174 (2)	0.98671 (17)	0.0230 (4)	
H3	0.898128	0.435022	1.040244	0.028*	
N4	0.3423 (2)	0.29725 (16)	0.54450 (14)	0.0211 (4)	
C4	0.7257 (2)	0.5187 (2)	0.96256 (17)	0.0210 (4)	
H4	0.780962	0.606656	0.999235	0.025*	
C5	0.5745 (2)	0.48980 (18)	0.88392 (16)	0.0160 (4)	
C6	0.4869 (2)	0.59134 (18)	0.85644 (16)	0.0166 (4)	
C7	0.5450 (3)	0.72317 (19)	0.91116 (17)	0.0202 (4)	
H7	0.649798	0.753655	0.964086	0.024*	
C8	0.4472 (3)	0.8091 (2)	0.88699 (18)	0.0237 (4)	
H8	0.484553	0.899537	0.923175	0.028*	
C9	0.2955 (3)	0.7627 (2)	0.81024 (19)	0.0251 (4)	
H9	0.224458	0.819860	0.796195	0.030*	
C10	0.2476 (3)	0.6306 (2)	0.75341 (19)	0.0247 (4)	
C11	0.4653 (3)	0.1315 (2)	0.7923 (2)	0.0325 (5)	
H11A	0.374488	0.110516	0.822909	0.049*	
H11B	0.536537	0.069734	0.800414	0.049*	
H11C	0.421624	0.125560	0.713932	0.049*	
C12	0.0897 (3)	0.5747 (3)	0.6624 (3)	0.0505 (8)	
H12A	0.113803	0.542757	0.592501	0.076*	
H12B	0.027094	0.642511	0.656716	0.076*	
H12C	0.025358	0.502569	0.678793	0.076*	
C13	−0.0357 (3)	0.20374 (19)	0.65956 (18)	0.0222 (4)	
C14	−0.1902 (3)	0.1331 (2)	0.5926 (2)	0.0299 (5)	
H14	−0.276649	0.114742	0.624100	0.036*	
C15	−0.2168 (3)	0.0899 (2)	0.4802 (2)	0.0331 (6)	
H15	−0.322268	0.042926	0.433723	0.040*	
C16	−0.0896 (3)	0.1152 (2)	0.43557 (19)	0.0286 (5)	
H16	−0.105281	0.084169	0.358515	0.034*	
C17	0.0622 (3)	0.18722 (18)	0.50567 (17)	0.0209 (4)	
C18	0.2076 (3)	0.2182 (2)	0.46677 (17)	0.0228 (4)	
C19	0.2083 (3)	0.1682 (2)	0.35859 (18)	0.0297 (5)	

H19	0.112010	0.114338	0.304771	0.036*	
C20	0.3513 (4)	0.1981 (2)	0.3308 (2)	0.0356 (6)	
H20	0.354850	0.164937	0.257431	0.043*	
C21	0.4888 (3)	0.2767 (2)	0.4105 (2)	0.0344 (5)	
H21	0.588640	0.296366	0.392590	0.041*	
C22	0.4816 (3)	0.3270 (2)	0.51691 (19)	0.0260 (5)	
C23	0.0017 (3)	0.2514 (2)	0.78169 (19)	0.0308 (5)	
H23A	0.106137	0.232552	0.816790	0.046*	
H23B	−0.085860	0.207350	0.805470	0.046*	
H23C	0.009325	0.345593	0.803131	0.046*	
C24	0.6265 (3)	0.4151 (2)	0.6065 (2)	0.0325 (5)	
H24A	0.593595	0.492033	0.643469	0.049*	
H24B	0.713290	0.442318	0.574399	0.049*	
H24C	0.667181	0.368394	0.660221	0.049*	
Zr1	0.000000	1.000000	1.000000	0.02476 (9)	
F1	0.09081 (18)	0.99518 (14)	0.87082 (13)	0.0384 (3)	
F2	−0.05473 (16)	0.80350 (12)	0.95926 (12)	0.0322 (3)	
F3	0.22027 (15)	1.00042 (12)	1.09456 (13)	0.0346 (3)	
O1	−0.1062 (4)	0.6247 (3)	0.8061 (3)	0.0369 (11)	0.567 (6)
H1A	−0.045474	0.641036	0.764081	0.055*	0.567 (6)
H1B	−0.087438	0.692874	0.861724	0.055*	0.567 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.02111 (14)	0.01747 (13)	0.01614 (13)	0.00081 (10)	−0.00092 (10)	0.00225 (9)
N1	0.0200 (8)	0.0173 (8)	0.0128 (8)	0.0026 (7)	0.0022 (6)	0.0033 (6)
C1	0.0253 (10)	0.0205 (10)	0.0184 (10)	0.0078 (8)	0.0073 (8)	0.0065 (8)
N2	0.0193 (8)	0.0167 (8)	0.0198 (9)	0.0029 (7)	0.0016 (7)	0.0051 (6)
C2	0.0232 (10)	0.0255 (10)	0.0205 (10)	0.0114 (8)	0.0095 (8)	0.0100 (8)
N3	0.0226 (9)	0.0142 (8)	0.0175 (8)	0.0038 (7)	0.0022 (7)	0.0029 (6)
C3	0.0168 (9)	0.0325 (11)	0.0204 (10)	0.0052 (8)	0.0036 (8)	0.0109 (9)
N4	0.0251 (9)	0.0206 (8)	0.0191 (9)	0.0049 (7)	0.0066 (7)	0.0082 (7)
C4	0.0180 (10)	0.0206 (10)	0.0203 (10)	0.0007 (8)	0.0023 (8)	0.0039 (8)
C5	0.0165 (9)	0.0167 (9)	0.0148 (9)	0.0033 (7)	0.0051 (7)	0.0040 (7)
C6	0.0169 (9)	0.0174 (9)	0.0160 (9)	0.0031 (7)	0.0058 (7)	0.0048 (7)
C7	0.0211 (10)	0.0188 (9)	0.0194 (10)	0.0008 (8)	0.0064 (8)	0.0043 (8)
C8	0.0334 (12)	0.0168 (9)	0.0224 (11)	0.0039 (9)	0.0123 (9)	0.0048 (8)
C9	0.0289 (11)	0.0222 (10)	0.0311 (12)	0.0102 (9)	0.0128 (9)	0.0131 (9)
C10	0.0223 (10)	0.0231 (10)	0.0293 (12)	0.0045 (8)	0.0037 (9)	0.0125 (9)
C11	0.0456 (14)	0.0190 (10)	0.0265 (12)	0.0104 (10)	−0.0010 (10)	0.0033 (9)
C12	0.0333 (14)	0.0281 (13)	0.073 (2)	0.0029 (11)	−0.0190 (14)	0.0192 (13)
C13	0.0230 (10)	0.0173 (9)	0.0245 (11)	0.0053 (8)	0.0055 (8)	0.0031 (8)
C14	0.0234 (11)	0.0204 (10)	0.0428 (14)	0.0019 (9)	0.0087 (10)	0.0057 (10)
C15	0.0247 (12)	0.0217 (11)	0.0382 (14)	0.0006 (9)	−0.0059 (10)	−0.0017 (10)
C16	0.0335 (12)	0.0195 (10)	0.0227 (11)	0.0050 (9)	−0.0054 (9)	0.0007 (8)
C17	0.0276 (11)	0.0148 (9)	0.0170 (10)	0.0062 (8)	−0.0007 (8)	0.0044 (7)
C18	0.0315 (11)	0.0196 (10)	0.0166 (10)	0.0070 (9)	0.0021 (8)	0.0077 (8)

C19	0.0473 (14)	0.0226 (11)	0.0180 (11)	0.0090 (10)	0.0056 (10)	0.0065 (9)
C20	0.0602 (17)	0.0319 (12)	0.0245 (12)	0.0163 (12)	0.0222 (12)	0.0118 (10)
C21	0.0465 (15)	0.0345 (13)	0.0357 (14)	0.0170 (11)	0.0239 (12)	0.0178 (11)
C22	0.0304 (11)	0.0239 (10)	0.0310 (12)	0.0107 (9)	0.0132 (9)	0.0137 (9)
C23	0.0309 (12)	0.0341 (12)	0.0278 (12)	0.0045 (10)	0.0122 (10)	0.0068 (10)
C24	0.0258 (12)	0.0367 (13)	0.0384 (14)	0.0034 (10)	0.0134 (10)	0.0147 (11)
Zr1	0.01462 (14)	0.02394 (15)	0.03837 (19)	0.00405 (11)	0.00458 (12)	0.01715 (13)
F1	0.0390 (8)	0.0355 (8)	0.0507 (9)	0.0129 (6)	0.0198 (7)	0.0209 (7)
F2	0.0256 (7)	0.0188 (6)	0.0479 (9)	0.0022 (5)	0.0034 (6)	0.0104 (6)
F3	0.0207 (6)	0.0230 (6)	0.0511 (9)	0.0052 (5)	−0.0042 (6)	0.0081 (6)
O1	0.041 (2)	0.0389 (19)	0.0244 (17)	0.0009 (14)	0.0117 (14)	0.0001 (13)

Geometric parameters (Å, º)

Cu1—N1	2.0208 (16)	C12—H12B	0.9800
Cu1—N2	2.0348 (17)	C12—H12C	0.9800
Cu1—N3	2.0123 (17)	C13—C14	1.392 (3)
Cu1—N4	2.0616 (18)	C13—C23	1.490 (3)
N1—C1	1.346 (3)	C14—H14	0.9500
N1—C5	1.354 (2)	C14—C15	1.379 (4)
C1—C2	1.390 (3)	C15—H15	0.9500
C1—C11	1.502 (3)	C15—C16	1.379 (4)
N2—C6	1.355 (2)	C16—H16	0.9500
N2—C10	1.346 (3)	C16—C17	1.392 (3)
C2—H2	0.9500	C17—C18	1.481 (3)
C2—C3	1.380 (3)	C18—C19	1.390 (3)
N3—C13	1.344 (3)	C19—H19	0.9500
N3—C17	1.356 (3)	C19—C20	1.379 (4)
C3—H3	0.9500	C20—H20	0.9500
C3—C4	1.385 (3)	C20—C21	1.377 (4)
N4—C18	1.355 (3)	C21—H21	0.9500
N4—C22	1.347 (3)	C21—C22	1.388 (3)
C4—H4	0.9500	C22—C24	1.500 (3)
C4—C5	1.388 (3)	C23—H23A	0.9800
C5—C6	1.485 (3)	C23—H23B	0.9800
C6—C7	1.391 (3)	C23—H23C	0.9800
C7—H7	0.9500	C24—H24A	0.9800
C7—C8	1.384 (3)	C24—H24B	0.9800
C8—H8	0.9500	C24—H24C	0.9800
C8—C9	1.378 (3)	Zr1—F1	2.0113 (15)
C9—H9	0.9500	Zr1—F1^{i}	2.0113 (15)
C9—C10	1.396 (3)	Zr1—F2^{i}	2.0183 (12)
C10—C12	1.503 (3)	Zr1—F2	2.0183 (12)
C11—H11A	0.9800	Zr1—F3	1.9955 (13)
C11—H11B	0.9800	Zr1—F3^{i}	1.9955 (13)
C11—H11C	0.9800	O1—H1A	0.8699
C12—H12A	0.9800	O1—H1B	0.8703

N1—Cu1—N2	81.40 (7)	H12B—C12—H12C	109.5
N1—Cu1—N4	116.24 (7)	N3—C13—C14	120.9 (2)
N2—Cu1—N4	120.45 (7)	N3—C13—C23	116.93 (18)
N3—Cu1—N1	136.29 (7)	C14—C13—C23	122.2 (2)
N3—Cu1—N2	126.16 (7)	C13—C14—H14	120.2
N3—Cu1—N4	81.05 (7)	C15—C14—C13	119.6 (2)
C1—N1—Cu1	127.37 (14)	C15—C14—H14	120.2
C1—N1—C5	119.06 (17)	C14—C15—H15	120.2
C5—N1—Cu1	112.61 (13)	C14—C15—C16	119.7 (2)
N1—C1—C2	121.76 (18)	C16—C15—H15	120.2
N1—C1—C11	116.67 (19)	C15—C16—H16	120.7
C2—C1—C11	121.55 (19)	C15—C16—C17	118.7 (2)
C6—N2—Cu1	112.50 (13)	C17—C16—H16	120.7
C10—N2—Cu1	128.32 (14)	N3—C17—C16	121.5 (2)
C10—N2—C6	119.07 (17)	N3—C17—C18	115.35 (18)
C1—C2—H2	120.5	C16—C17—C18	123.1 (2)
C3—C2—C1	119.10 (19)	N4—C18—C17	115.47 (18)
C3—C2—H2	120.5	N4—C18—C19	121.7 (2)
C13—N3—Cu1	125.56 (14)	C19—C18—C17	122.8 (2)
C13—N3—C17	119.66 (18)	C18—C19—H19	120.6
C17—N3—Cu1	114.36 (14)	C20—C19—C18	118.8 (2)
C2—C3—H3	120.3	C20—C19—H19	120.6
C2—C3—C4	119.43 (19)	C19—C20—H20	120.3
C4—C3—H3	120.3	C21—C20—C19	119.4 (2)
C18—N4—Cu1	113.01 (14)	C21—C20—H20	120.3
C22—N4—Cu1	127.62 (15)	C20—C21—H21	120.0
C22—N4—C18	119.34 (19)	C20—C21—C22	119.9 (2)
C3—C4—H4	120.5	C22—C21—H21	120.0
C3—C4—C5	118.94 (18)	N4—C22—C21	120.8 (2)
C5—C4—H4	120.5	N4—C22—C24	116.8 (2)
N1—C5—C4	121.67 (18)	C21—C22—C24	122.3 (2)
N1—C5—C6	115.42 (17)	C13—C23—H23A	109.5
C4—C5—C6	122.90 (17)	C13—C23—H23B	109.5
N2—C6—C5	115.28 (16)	C13—C23—H23C	109.5
N2—C6—C7	121.72 (18)	H23A—C23—H23B	109.5
C7—C6—C5	122.97 (18)	H23A—C23—H23C	109.5
C6—C7—H7	120.6	H23B—C23—H23C	109.5
C8—C7—C6	118.70 (19)	C22—C24—H24A	109.5
C8—C7—H7	120.6	C22—C24—H24B	109.5
C7—C8—H8	120.1	C22—C24—H24C	109.5
C9—C8—C7	119.71 (19)	H24A—C24—H24B	109.5
C9—C8—H8	120.1	H24A—C24—H24C	109.5
C8—C9—H9	120.5	H24B—C24—H24C	109.5
C8—C9—C10	119.0 (2)	F1^{i}—Zr1—F1	180.00 (9)
C10—C9—H9	120.5	F1—Zr1—F2^{i}	89.69 (6)
N2—C10—C9	121.56 (19)	F1—Zr1—F2	90.31 (6)
N2—C10—C12	116.3 (2)	F1^{i}—Zr1—F2	89.69 (6)
C9—C10—C12	122.1 (2)	F1^{i}—Zr1—F2^{i}	90.31 (6)

C1—C11—H11A	109.5	F2—Zr1—F2^{i}	180.0
C1—C11—H11B	109.5	F3^{i}—Zr1—F1	89.90 (6)
C1—C11—H11C	109.5	F3—Zr1—F1^{i}	89.90 (6)
H11A—C11—H11B	109.5	F3—Zr1—F1	90.10 (6)
H11A—C11—H11C	109.5	F3^{i}—Zr1—F1^{i}	90.10 (6)
H11B—C11—H11C	109.5	F3^{i}—Zr1—F2^{i}	89.43 (5)
C10—C12—H12A	109.5	F3—Zr1—F2	89.43 (5)
C10—C12—H12B	109.5	F3—Zr1—F2^{i}	90.57 (5)
C10—C12—H12C	109.5	F3^{i}—Zr1—F2	90.57 (5)
H12A—C12—H12B	109.5	F3^{i}—Zr1—F3	180.0
H12A—C12—H12C	109.5	H1A—O1—H1B	109.5

Cu1—N1—C1—C2	166.88 (15)	C5—N1—C1—C2	−1.0 (3)
Cu1—N1—C1—C11	−14.7 (3)	C5—N1—C1—C11	177.37 (19)
Cu1—N1—C5—C4	−167.35 (15)	C5—C6—C7—C8	−173.85 (19)
Cu1—N1—C5—C6	14.0 (2)	C6—N2—C10—C9	0.5 (3)
Cu1—N2—C6—C5	−9.8 (2)	C6—N2—C10—C12	179.4 (2)
Cu1—N2—C6—C7	172.18 (15)	C6—C7—C8—C9	0.2 (3)
Cu1—N2—C10—C9	−175.40 (16)	C7—C8—C9—C10	−3.8 (3)
Cu1—N2—C10—C12	3.4 (3)	C8—C9—C10—N2	3.6 (3)
Cu1—N3—C13—C14	170.26 (16)	C8—C9—C10—C12	−175.2 (2)
Cu1—N3—C13—C23	−10.0 (3)	C10—N2—C6—C5	173.65 (18)
Cu1—N3—C17—C16	−171.70 (16)	C10—N2—C6—C7	−4.4 (3)
Cu1—N3—C17—C18	9.7 (2)	C11—C1—C2—C3	−179.0 (2)
Cu1—N4—C18—C17	−0.4 (2)	C13—N3—C17—C16	1.3 (3)
Cu1—N4—C18—C19	−179.26 (16)	C13—N3—C17—C18	−177.34 (18)
Cu1—N4—C22—C21	177.41 (16)	C13—C14—C15—C16	1.1 (4)
Cu1—N4—C22—C24	−1.9 (3)	C14—C15—C16—C17	−1.7 (3)
N1—C1—C2—C3	−0.7 (3)	C15—C16—C17—N3	0.5 (3)
N1—C5—C6—N2	−2.7 (3)	C15—C16—C17—C18	179.0 (2)
N1—C5—C6—C7	175.24 (18)	C16—C17—C18—N4	175.31 (19)
C1—N1—C5—C4	2.3 (3)	C16—C17—C18—C19	−5.9 (3)
C1—N1—C5—C6	−176.43 (18)	C17—N3—C13—C14	−1.9 (3)
C1—C2—C3—C4	1.2 (3)	C17—N3—C13—C23	177.87 (19)
N2—C6—C7—C8	4.0 (3)	C17—C18—C19—C20	−177.4 (2)
C2—C3—C4—C5	0.0 (3)	C18—N4—C22—C21	−0.7 (3)
N3—C13—C14—C15	0.7 (3)	C18—N4—C22—C24	179.95 (19)
N3—C17—C18—N4	−6.1 (3)	C18—C19—C20—C21	−0.2 (3)
N3—C17—C18—C19	172.72 (19)	C19—C20—C21—C22	−1.4 (4)
C3—C4—C5—N1	−1.7 (3)	C20—C21—C22—N4	1.8 (3)
C3—C4—C5—C6	176.86 (19)	C20—C21—C22—C24	−178.8 (2)
N4—C18—C19—C20	1.3 (3)	C22—N4—C18—C17	177.93 (18)
C4—C5—C6—N2	178.58 (18)	C22—N4—C18—C19	−0.9 (3)
C4—C5—C6—C7	−3.4 (3)	C23—C13—C14—C15	−179.0 (2)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*B*···F2	0.87	1.47	2.337 (4)	177

Bis[bis(6,6′-dimethyl-2,2′-bipyridine)copper(I)] hexafluoridohafnate(IV) 0.671-hydrate (II)

Crystal data

$[Cu(C_{12}H_{12}N_2)_2]_2[HfF_6]\cdot 0.671H_2O$
M_r = 1168.58
Triclinic, $P\overline{1}$
a = 8.5737 (1) Å
b = 10.7967 (2) Å
c = 13.0183 (2) Å
α = 103.273 (1)°
β = 103.662 (1)°
γ = 98.785 (1)°
V = 1112.07 (3) Å^3
Z = 1
$F(000)$ = 583
D_x = 1.745 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 31642 reflections
θ = 2.2–33.9°
μ = 3.35 mm^{-1}
T = 100 K
Plate, clear orangish red
0.3 × 0.17 × 0.08 mm

Data collection

Rigaku Saturn724+ (2x2 bin mode) diffractometer
Radiation source: Rotating Anode, Rotating Anode
Confocal monochromator
Detector resolution: 28.5714 pixels mm^{-1}
profile data from ω–scans
Absorption correction: gaussian (CrysAlisPro; Rigaku OD, 2020)
T_{min} = 0.433, T_{max} = 1.000
40796 measured reflections
8003 independent reflections
7235 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 33.9°, θ_{min} = 2.0°
h = −13→13
k = −16→16
l = −19→19

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.056
S = 1.08
8003 reflections
312 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.029P)^2 + 0.1688P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.73 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}	Occ. (<1)
Cu1	0.30255 (2)	0.35382 (2)	0.69812 (2)	0.01849 (4)	
N1	0.49323 (15)	0.36487 (11)	0.82812 (9)	0.0157 (2)	
C1	0.55897 (18)	0.26589 (14)	0.85279 (11)	0.0184 (3)	
N2	0.33991 (15)	0.54691 (12)	0.77752 (10)	0.0187 (2)	

C2	0.70930 (18)	0.28901 (15)	0.93195 (12)	0.0200 (3)
H2	0.752847	0.218202	0.949428	0.024*
N3	0.08393 (15)	0.23090 (11)	0.61730 (10)	0.0173 (2)
C3	0.79431 (18)	0.41592 (16)	0.98475 (12)	0.0218 (3)
H3	0.898138	0.433093	1.037654	0.026*
N4	0.33880 (17)	0.29739 (13)	0.54432 (11)	0.0211 (2)
C4	0.72716 (18)	0.51810 (15)	0.96003 (12)	0.0206 (3)
H4	0.784176	0.605989	0.995319	0.025*
C5	0.57452 (16)	0.48929 (13)	0.88246 (11)	0.0157 (2)
C6	0.48691 (17)	0.59126 (13)	0.85563 (11)	0.0159 (2)
C7	0.54737 (18)	0.72313 (14)	0.90906 (12)	0.0196 (3)
H7	0.653940	0.753278	0.959803	0.024*
C8	0.4488 (2)	0.81009 (14)	0.88679 (13)	0.0222 (3)
H8	0.487246	0.900700	0.922570	0.027*
C9	0.2948 (2)	0.76402 (15)	0.81239 (13)	0.0240 (3)
H9	0.223979	0.821769	0.799097	0.029*
C10	0.24454 (19)	0.63174 (15)	0.75708 (14)	0.0247 (3)
C11	0.4606 (2)	0.13042 (15)	0.79400 (14)	0.0287 (3)
H11A	0.374850	0.108709	0.829125	0.043*
H11B	0.533164	0.068661	0.797454	0.043*
H11C	0.409525	0.125179	0.716942	0.043*
C12	0.0821 (3)	0.5765 (2)	0.6712 (2)	0.0523 (7)
H12A	0.100542	0.546189	0.599023	0.078*
H12B	0.017881	0.644134	0.669871	0.078*
H12C	0.021671	0.503124	0.688661	0.078*
C13	−0.03848 (19)	0.20159 (14)	0.66175 (13)	0.0217 (3)
C14	−0.1938 (2)	0.13117 (16)	0.59615 (16)	0.0294 (3)
H14	−0.279577	0.111864	0.628577	0.035*
C15	−0.2222 (2)	0.08956 (17)	0.48344 (16)	0.0331 (4)
H15	−0.328350	0.042958	0.437675	0.040*
C16	−0.0952 (2)	0.11615 (16)	0.43760 (14)	0.0279 (3)
H16	−0.112119	0.086313	0.360420	0.034*
C17	0.05785 (19)	0.18743 (14)	0.50662 (12)	0.0196 (3)
C18	0.2030 (2)	0.21916 (14)	0.46699 (12)	0.0215 (3)
C19	0.2026 (3)	0.16910 (16)	0.35783 (13)	0.0293 (3)
H19	0.105673	0.115925	0.304363	0.035*
C20	0.3465 (3)	0.19880 (19)	0.32964 (15)	0.0370 (4)
H20	0.349867	0.165652	0.256178	0.044*
C21	0.4854 (3)	0.27688 (19)	0.40872 (16)	0.0348 (4)
H21	0.585269	0.296727	0.390165	0.042*
C22	0.4786 (2)	0.32667 (16)	0.51629 (14)	0.0265 (3)
C23	0.0002 (2)	0.24806 (18)	0.78440 (14)	0.0296 (3)
H23A	0.107943	0.232844	0.818103	0.044*
H23B	−0.084204	0.200229	0.808740	0.044*
H23C	0.002281	0.341524	0.806634	0.044*
C24	0.6249 (2)	0.41315 (19)	0.60455 (16)	0.0332 (4)
H24A	0.593380	0.490705	0.642476	0.050*
H24B	0.711624	0.439691	0.571619	0.050*

H24C	0.665684	0.365753	0.657414	0.050*	
Hf1	0.000000	1.000000	1.000000	0.02373 (3)	
F1	0.09274 (14)	0.99551 (11)	0.87132 (10)	0.0369 (2)	
F2	−0.05307 (12)	0.80472 (9)	0.95921 (9)	0.0312 (2)	
F3	0.22038 (12)	1.00043 (10)	1.09439 (10)	0.0341 (2)	
O1	−0.1061 (5)	0.6264 (4)	0.8063 (3)	0.0338 (12)	0.336 (5)
H1A	−0.014695	0.600372	0.823726	0.051*	0.336 (5)
H1B	−0.097233	0.702606	0.850509	0.051*	0.336 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01904 (8)	0.01683 (8)	0.01581 (8)	0.00282 (6)	−0.00052 (6)	0.00350 (6)
N1	0.0167 (5)	0.0146 (5)	0.0154 (5)	0.0047 (4)	0.0031 (4)	0.0040 (4)
C1	0.0211 (6)	0.0187 (6)	0.0178 (6)	0.0077 (5)	0.0063 (5)	0.0067 (5)
N2	0.0177 (5)	0.0158 (5)	0.0213 (6)	0.0045 (4)	0.0018 (4)	0.0058 (4)
C2	0.0208 (6)	0.0249 (7)	0.0215 (7)	0.0115 (5)	0.0098 (5)	0.0119 (5)
N3	0.0197 (5)	0.0142 (5)	0.0161 (5)	0.0046 (4)	0.0013 (4)	0.0035 (4)
C3	0.0148 (6)	0.0293 (7)	0.0227 (7)	0.0063 (5)	0.0039 (5)	0.0105 (6)
N4	0.0247 (6)	0.0214 (6)	0.0215 (6)	0.0094 (5)	0.0074 (5)	0.0106 (5)
C4	0.0159 (6)	0.0207 (7)	0.0214 (7)	0.0025 (5)	0.0015 (5)	0.0032 (5)
C5	0.0144 (6)	0.0165 (6)	0.0169 (6)	0.0044 (4)	0.0051 (5)	0.0044 (5)
C6	0.0159 (6)	0.0154 (6)	0.0180 (6)	0.0043 (4)	0.0063 (5)	0.0054 (5)
C7	0.0200 (6)	0.0163 (6)	0.0220 (7)	0.0022 (5)	0.0071 (5)	0.0041 (5)
C8	0.0320 (8)	0.0141 (6)	0.0246 (7)	0.0061 (5)	0.0142 (6)	0.0061 (5)
C9	0.0280 (7)	0.0199 (7)	0.0328 (8)	0.0125 (6)	0.0136 (6)	0.0145 (6)
C10	0.0219 (7)	0.0203 (7)	0.0332 (8)	0.0067 (5)	0.0037 (6)	0.0125 (6)
C11	0.0364 (9)	0.0170 (7)	0.0280 (8)	0.0082 (6)	−0.0004 (7)	0.0053 (6)
C12	0.0307 (10)	0.0317 (10)	0.0783 (16)	0.0056 (8)	−0.0207 (10)	0.0220 (10)
C13	0.0216 (7)	0.0166 (6)	0.0263 (7)	0.0054 (5)	0.0059 (6)	0.0049 (5)
C14	0.0206 (7)	0.0206 (7)	0.0439 (10)	0.0028 (6)	0.0077 (7)	0.0053 (7)
C15	0.0228 (7)	0.0220 (8)	0.0402 (10)	0.0018 (6)	−0.0064 (7)	−0.0012 (7)
C16	0.0306 (8)	0.0215 (7)	0.0219 (7)	0.0053 (6)	−0.0062 (6)	0.0012 (6)
C17	0.0249 (7)	0.0149 (6)	0.0167 (6)	0.0070 (5)	0.0000 (5)	0.0041 (5)
C18	0.0308 (8)	0.0182 (6)	0.0162 (6)	0.0092 (6)	0.0036 (6)	0.0071 (5)
C19	0.0483 (10)	0.0248 (8)	0.0169 (7)	0.0136 (7)	0.0084 (7)	0.0073 (6)
C20	0.0652 (13)	0.0345 (9)	0.0250 (8)	0.0232 (9)	0.0248 (9)	0.0139 (7)
C21	0.0474 (11)	0.0339 (9)	0.0380 (10)	0.0185 (8)	0.0264 (9)	0.0177 (8)
C22	0.0308 (8)	0.0270 (8)	0.0318 (8)	0.0131 (6)	0.0155 (7)	0.0162 (6)
C23	0.0297 (8)	0.0349 (9)	0.0272 (8)	0.0077 (7)	0.0141 (7)	0.0077 (7)
C24	0.0258 (8)	0.0366 (9)	0.0427 (10)	0.0071 (7)	0.0154 (7)	0.0154 (8)
Hf1	0.01372 (4)	0.02043 (5)	0.04096 (6)	0.00568 (3)	0.00576 (3)	0.01683 (4)
F1	0.0372 (6)	0.0331 (6)	0.0534 (7)	0.0157 (5)	0.0229 (5)	0.0215 (5)
F2	0.0218 (5)	0.0179 (4)	0.0518 (6)	0.0039 (3)	0.0038 (4)	0.0125 (4)
F3	0.0193 (4)	0.0218 (5)	0.0541 (7)	0.0064 (4)	−0.0039 (4)	0.0100 (4)
O1	0.036 (2)	0.035 (2)	0.0227 (19)	0.0034 (16)	0.0075 (15)	−0.0029 (15)

Geometric parameters (Å, º)

Cu1—N1	2.0229 (12)	C12—H12B	0.9800
Cu1—N2	2.0414 (12)	C12—H12C	0.9800
Cu1—N3	2.0121 (12)	C13—C14	1.391 (2)
Cu1—N4	2.0659 (13)	C13—C23	1.497 (2)
N1—C1	1.3487 (17)	C14—H14	0.9500
N1—C5	1.3548 (18)	C14—C15	1.382 (3)
C1—C2	1.393 (2)	C15—H15	0.9500
C1—C11	1.497 (2)	C15—C16	1.384 (3)
N2—C6	1.3558 (18)	C16—H16	0.9500
N2—C10	1.3476 (19)	C16—C17	1.392 (2)
C2—H2	0.9500	C17—C18	1.479 (2)
C2—C3	1.381 (2)	C18—C19	1.399 (2)
N3—C13	1.344 (2)	C19—H19	0.9500
N3—C17	1.3607 (19)	C19—C20	1.381 (3)
C3—H3	0.9500	C20—H20	0.9500
C3—C4	1.386 (2)	C20—C21	1.380 (3)
N4—C18	1.356 (2)	C21—H21	0.9500
N4—C22	1.347 (2)	C21—C22	1.399 (2)
C4—H4	0.9500	C22—C24	1.495 (3)
C4—C5	1.3915 (19)	C23—H23A	0.9800
C5—C6	1.4845 (19)	C23—H23B	0.9800
C6—C7	1.389 (2)	C23—H23C	0.9800
C7—H7	0.9500	C24—H24A	0.9800
C7—C8	1.390 (2)	C24—H24B	0.9800
C8—H8	0.9500	C24—H24C	0.9800
C8—C9	1.380 (2)	Hf1—F1^{i}	2.0111 (11)
C9—H9	0.9500	Hf1—F1	2.0111 (11)
C9—C10	1.392 (2)	Hf1—F2^{i}	2.0033 (9)
C10—C12	1.500 (2)	Hf1—F2	2.0033 (9)
C11—H11A	0.9800	Hf1—F3^{i}	1.9945 (10)
C11—H11B	0.9800	Hf1—F3	1.9945 (10)
C11—H11C	0.9800	O1—H1A	0.8700
C12—H12A	0.9800	O1—H1B	0.8699

N1—Cu1—N2	81.22 (5)	H12B—C12—H12C	109.5
N1—Cu1—N4	116.52 (5)	N3—C13—C14	121.15 (15)
N2—Cu1—N4	120.35 (5)	N3—C13—C23	116.98 (14)
N3—Cu1—N1	136.20 (5)	C14—C13—C23	121.87 (15)
N3—Cu1—N2	126.39 (5)	C13—C14—H14	120.3
N3—Cu1—N4	80.94 (5)	C15—C14—C13	119.42 (17)
C1—N1—Cu1	127.24 (10)	C15—C14—H14	120.3
C1—N1—C5	119.15 (12)	C14—C15—H15	120.2
C5—N1—Cu1	112.66 (9)	C14—C15—C16	119.63 (15)
N1—C1—C2	121.40 (13)	C16—C15—H15	120.2
N1—C1—C11	116.99 (13)	C15—C16—H16	120.6
C2—C1—C11	121.58 (13)	C15—C16—C17	118.80 (15)

C6—N2—Cu1	112.15 (9)	C17—C16—H16	120.6
C10—N2—Cu1	128.64 (10)	N3—C17—C16	121.28 (15)
C10—N2—C6	119.08 (13)	N3—C17—C18	115.28 (13)
C1—C2—H2	120.3	C16—C17—C18	123.44 (14)
C3—C2—C1	119.31 (13)	N4—C18—C17	115.53 (13)
C3—C2—H2	120.3	N4—C18—C19	121.93 (16)
C13—N3—Cu1	125.50 (10)	C19—C18—C17	122.51 (15)
C13—N3—C17	119.68 (13)	C18—C19—H19	120.8
C17—N3—Cu1	114.43 (10)	C20—C19—C18	118.41 (17)
C2—C3—H3	120.2	C20—C19—H19	120.8
C2—C3—C4	119.57 (13)	C19—C20—H20	120.2
C4—C3—H3	120.2	C21—C20—C19	119.67 (16)
C18—N4—Cu1	113.01 (10)	C21—C20—H20	120.2
C22—N4—Cu1	127.54 (11)	C20—C21—H21	120.1
C22—N4—C18	119.43 (14)	C20—C21—C22	119.72 (18)
C3—C4—H4	120.7	C22—C21—H21	120.1
C3—C4—C5	118.63 (13)	N4—C22—C21	120.82 (17)
C5—C4—H4	120.7	N4—C22—C24	117.38 (15)
N1—C5—C4	121.89 (13)	C21—C22—C24	121.80 (16)
N1—C5—C6	115.22 (12)	C13—C23—H23A	109.5
C4—C5—C6	122.86 (13)	C13—C23—H23B	109.5
N2—C6—C5	115.48 (12)	C13—C23—H23C	109.5
N2—C6—C7	121.72 (13)	H23A—C23—H23B	109.5
C7—C6—C5	122.77 (13)	H23A—C23—H23C	109.5
C6—C7—H7	120.7	H23B—C23—H23C	109.5
C6—C7—C8	118.65 (14)	C22—C24—H24A	109.5
C8—C7—H7	120.7	C22—C24—H24B	109.5
C7—C8—H8	120.2	C22—C24—H24C	109.5
C9—C8—C7	119.60 (14)	H24A—C24—H24B	109.5
C9—C8—H8	120.2	H24A—C24—H24C	109.5
C8—C9—H9	120.5	H24B—C24—H24C	109.5
C8—C9—C10	119.06 (14)	F1^{i}—Hf1—F1	180.00 (7)
C10—C9—H9	120.5	F2^{i}—Hf1—F1	89.79 (5)
N2—C10—C9	121.66 (14)	F2—Hf1—F1	90.21 (5)
N2—C10—C12	116.62 (15)	F2—Hf1—F1^{i}	89.79 (5)
C9—C10—C12	121.71 (15)	F2^{i}—Hf1—F1^{i}	90.21 (5)
C1—C11—H11A	109.5	F2—Hf1—F2^{i}	180.0
C1—C11—H11B	109.5	F3—Hf1—F1	90.15 (5)
C1—C11—H11C	109.5	F3—Hf1—F1^{i}	89.85 (5)
H11A—C11—H11B	109.5	F3^{i}—Hf1—F1^{i}	90.15 (5)
H11A—C11—H11C	109.5	F3^{i}—Hf1—F1	89.85 (5)
H11B—C11—H11C	109.5	F3—Hf1—F2	89.27 (4)
C10—C12—H12A	109.5	F3^{i}—Hf1—F2^{i}	89.26 (4)
C10—C12—H12B	109.5	F3^{i}—Hf1—F2	90.74 (4)
C10—C12—H12C	109.5	F3—Hf1—F2^{i}	90.73 (4)
H12A—C12—H12B	109.5	F3—Hf1—F3^{i}	180.0
H12A—C12—H12C	109.5	H1A—O1—H1B	109.5

Cu1—N1—C1—C2	167.25 (11)	C5—N1—C1—C2	−0.7 (2)
Cu1—N1—C1—C11	−14.69 (19)	C5—N1—C1—C11	177.33 (13)
Cu1—N1—C5—C4	−167.08 (11)	C5—C6—C7—C8	−173.20 (13)
Cu1—N1—C5—C6	14.67 (15)	C6—N2—C10—C9	1.4 (2)
Cu1—N2—C6—C5	−11.14 (15)	C6—N2—C10—C12	−178.95 (17)
Cu1—N2—C6—C7	171.02 (11)	C6—C7—C8—C9	−0.3 (2)
Cu1—N2—C10—C9	−173.90 (12)	C7—C8—C9—C10	−3.1 (2)
Cu1—N2—C10—C12	5.7 (2)	C8—C9—C10—N2	2.6 (2)
Cu1—N3—C13—C14	170.17 (12)	C8—C9—C10—C12	−176.97 (18)
Cu1—N3—C13—C23	−9.84 (19)	C10—N2—C6—C5	172.79 (13)
Cu1—N3—C17—C16	−171.27 (11)	C10—N2—C6—C7	−5.1 (2)
Cu1—N3—C17—C18	9.88 (15)	C11—C1—C2—C3	−179.25 (14)
Cu1—N4—C18—C17	−1.01 (15)	C13—N3—C17—C16	2.0 (2)
Cu1—N4—C18—C19	−179.23 (12)	C13—N3—C17—C18	−176.87 (12)
Cu1—N4—C22—C21	177.63 (12)	C13—C14—C15—C16	1.3 (3)
Cu1—N4—C22—C24	−2.0 (2)	C14—C15—C16—C17	−1.6 (2)
N1—C1—C2—C3	−1.3 (2)	C15—C16—C17—N3	0.0 (2)
N1—C5—C6—N2	−2.27 (18)	C15—C16—C17—C18	178.70 (15)
N1—C5—C6—C7	175.55 (13)	C16—C17—C18—N4	175.36 (14)
C1—N1—C5—C4	2.6 (2)	C16—C17—C18—C19	−6.4 (2)
C1—N1—C5—C6	−175.69 (12)	C17—N3—C13—C14	−2.3 (2)
C1—C2—C3—C4	1.5 (2)	C17—N3—C13—C23	177.72 (13)
N2—C6—C7—C8	4.5 (2)	C17—C18—C19—C20	−176.75 (14)
C2—C3—C4—C5	0.3 (2)	C18—N4—C22—C21	−0.3 (2)
N3—C13—C14—C15	0.6 (2)	C18—N4—C22—C24	−179.92 (14)
N3—C17—C18—N4	−5.82 (18)	C18—C19—C20—C21	−0.4 (3)
N3—C17—C18—C19	172.39 (13)	C19—C20—C21—C22	−0.9 (3)
C3—C4—C5—N1	−2.3 (2)	C20—C21—C22—N4	1.3 (3)
C3—C4—C5—C6	175.77 (13)	C20—C21—C22—C24	−179.15 (16)
N4—C18—C19—C20	1.4 (2)	C22—N4—C18—C17	177.22 (13)
C4—C5—C6—N2	179.49 (13)	C22—N4—C18—C19	−1.0 (2)
C4—C5—C6—C7	−2.7 (2)	C23—C13—C14—C15	−179.34 (16)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1B—H1*B*···F2	0.87	1.50	2.328 (4)	156

Coordination geometry (Å, °) of Cu(dmbpy)$^{2+}$ cations in (I)

N—Cu—N	N—Cu	Cu—N	N—Cu—N
N1—Cu1—N2	2.0208 (16)	2.0348 (17)	81.40 (7)
N1—Cu1—N3		2.0123 (17)	136.29 (7)
N1—Cu1—N4		2.0616 (18)	116.24 (7)
N2—Cu1—N3			126.17 (7)
N2—Cu1—N4			120.45 (7)
N3—Cu1—N4			81.05 (7)

Bond distances (Å) of ZrF_6^{2-} in (I)

Zr—F	Distance (Å)
Zr—F1	2.0113 (15)
Zr—F2	2.0183 (12)
Zr—F3	1.9955 (13)

Hydrogen-bond geometry (Å, °) for (I)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1B···F2	0.870 (3)	1.4674 (14)	2.337 (3)	177.1 (2)

Coordination geometry (Å, °) of $Cu(dmbpy)^{2+}$ cations in (II)

N—Cu—N	N—Cu	Cu—N	N—Cu—N
N1—Cu1—N2	2.0229 (12)	2.0414 (12)	81.22 (5)
N1—Cu1—N3		2.0121 (12)	136.20 (5)
N1—Cu1—N4		2.0659 (13)	116.52 (5)
N2—Cu1—N3			126.39 (5)
N2—Cu1—N4			120.35 (5)
N3—Cu1—N4			80.94 (5)

Bond distances (Å) of HfF_6^{2-} in (II)

Hf—F	Distance (Å)
Hf—F1	2.0111 (11)
Hf—F2	2.0033 (9)
Hf—F3	1.9945 (10)

Hydrogen-bond geometry (Å, °) for (II)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1B···F2	0.870 (4)	1.5048 (11)	2.328 (4)	156.4 (3)