$[Cu_2(HF_2)(H_2O)_8][AlF_6]\cdot 2H_2O$

Matthias Weil

Institute for Chemical Technologies and Analytics, Division of Structural Chemistry, Vienna University of Technology, Getreidemarkt 9/164-SC, A-1060 Vienna, Austria
Correspondence e-mail: mweil@mail.zserv.tuwien.ac.at

The title compound, octaaqua(hydrogendifluorido)dicopper(II) hexafluoridoaluminate dihydrate, was obtained under hydrothermal conditions. The structure is isotypic with that of the analogous Fe^{III} compound, $[Cu_2(HF_2)(H_2O)_8][FeF_6]\cdot 2H_2O$. The coordination sphere of the Cu^{II} atom is formed by one F and three water O atoms at short distances < 2 Å and is augmented by two additional water O atoms at significantly longer distances, leading to a considerably distorted octahedral environment. By edge-sharing, these octahedra form dimeric $[Cu_2(HF_2)(H_2O)_8]^{3+}$ units that are bonded to $[AlF_6]^{3-}$ anions ($\bar{1}$ symmetry) and to crystal lattice water molecules via hydrogen bonds. Besides F—H$\cdots$F interactions between the dimeric cationic units, O—H$\cdots$F and O—H$\cdots$O hydrogen bonds (both in part bifurcated) are observed.

Related literature

For the structure of the isotypic Fe^{III} analogue, see: Le Bail & Mercier (2009). For a natural compound in the Cu/Al/F/O/H system, $Cu_4Al_3(OH)_{14}F_3(H_2O)_2$ (mineral name khaidarkanite), see: Rastsvetaeva et al. (1997).

Experimental

Crystal data
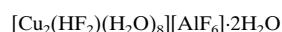
$[Cu_2(HF_2)(H_2O)_8][AlF_6]\cdot 2H_2O$	$\gamma = 94.454\,(1)^\circ$
$M_r = 487.23$	$V = 363.15\,(3)$ Å^3
Triclinic, $P\bar{1}$	$Z = 1$
$a = 6.6119\,(3)$ Å	Mo $K\alpha$ radiation
$b = 7.3410\,(3)$ Å	$\mu = 3.12$ mm^{-1}
$c = 8.3174\,(3)$ Å	$T = 293$ K
$\alpha = 107.336\,(1)^\circ$	$0.18 \times 0.14 \times 0.06$ mm
$\beta = 106.715\,(1)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	3899 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2000)	2013 independent reflections
	1952 reflections with $I > 2\sigma(I)$
$T_{min} = 0.52$, $T_{max} = 0.80$	$R_{int} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.072$	
$S = 1.08$	
2013 reflections	$\Delta\rho_{max} = 0.44$ e Å^{-3}
130 parameters	$\Delta\rho_{min} = -0.54$ e Å^{-3}
10 restraints	

Table 1
Selected bond lengths (Å).

Cu—F4	1.9049 (12)	Cu—O3^i	2.7139 (16)
Cu—O1	1.9441 (14)	Al—F1	1.8001 (10)
Cu—O2	1.9522 (14)	Al—F2	1.8091 (11)
Cu—O3	1.9739 (13)	Al—F3	1.8209 (11)
Cu—O4	2.3463 (15)		

Symmetry code: (i) $-x+1, -y+1, -z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H11$\cdots$F1^{ii}	0.87 (3)	1.74 (3)	2.6042 (17)	171 (4)
O1—H12$\cdots$F2	0.83 (3)	1.86 (3)	2.6899 (18)	176 (4)
O2—H21$\cdots$F1^i	0.81 (3)	1.79 (3)	2.6020 (18)	172 (4)
O2—H22$\cdots$O5^{iii}	0.83 (3)	1.86 (3)	2.684 (2)	178 (4)
O3—H31$\cdots$F3^i	0.77 (3)	1.82 (3)	2.5877 (18)	178 (4)
O3—H32$\cdots$F3^{iv}	0.79 (3)	1.89 (3)	2.6700 (17)	174 (4)
O4—H41$\cdots$F2^v	0.85 (3)	1.95 (3)	2.7840 (19)	169 (4)
O4—H42$\cdots$O4^{vi}	0.67 (3)	2.41 (4)	2.758 (3)	115 (4)
O4—H42$\cdots$O5^{iv}	0.67 (3)	2.41 (4)	2.784 (2)	117 (4)
O5—H51$\cdots$F2^{vii}	0.75 (3)	2.14 (3)	2.8538 (19)	159 (4)
O5—H51$\cdots$F3^{viii}	0.75 (3)	2.50 (3)	3.072 (2)	135 (4)
O5—H52$\cdots$F4	1.04 (3)	1.67 (3)	2.6620 (19)	158 (3)
F4—H6$\cdots$F4^v	0.9031 (13)	1.6945 (13)	2.596 (3)	175.27 (5)

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+1, -y, -z$; (iii) $-x+1, -y+2, -z+1$; (iv) $x+1, y, z$; (v) $-x+1, -y+1, -z+1$; (vi) $-x+2, -y+1, -z+1$; (vii) $x, y+1, z$; (viii) $-x, -y+1, -z$.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ATOMS for Windows (Dowty, 2006); software used to prepare material for publication: SHELXL97.

References

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Dowty, E. (2006). ATOMS for Windows. Shape Software, Kingsport, Tennessee, USA.

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Rastsvetaeva, R. K., Chukanov, N. V. & Karpenko, V. Yu. (1997). Dokl. Akad. Nauk, 353, 354-357.

Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.

supplementary materials

$[Cu_2(HF_2)(H_2O)_8][AlF_6]\cdot 2H_2O$

M. Weil

Comment

The crystal structure (Fig. 1) of the title compound, $[Cu_2(HF_2)(H_2O)_8][AlF_6].2H_2O$), is isotypic with $[Cu_2(HF_2)(H_2O)_8][FeF_6].2H_2O$ (Le Bail & Mercier, 2009). Except the Al—F distances ($\bar{d} = 1.810$ Å *versus* 1.930 Å for the average Fe—F distance), all other interatomic distances, angles and the hydrogen bond geometry are very similar for the two structures. A detailed description of this structure has been given Le Bail & Mercier (2009).

There is one additional compound described in the Cu/Al/F/O/H system, *viz* the mineral khaidarkanite with formula $Cu_4Al_3(OH)_{14}F_3(H_2O)_2$ (Rastsvetaeva *et al.*, 1997). The latter differs from the title compound as its structure contains distorted $[Cu(OH)_5(H_2O)]$ octahedra, and $[Al(OH)_6]$ and $[AlF_4(H_2O)_2]$ octahedra as building units.

Experimental

AlF_3 and $CuSO_4 \cdot 5H_2O$ (both Merck, p.a.) were reacted hydrothermally in a 2 *M* HF solution at 393 K for 4 d. Blue crystals of the title compound with mostly platy habit and up to 0.3 mm in length were obtained.

Refinement

The structure was solved using direct methods. For better comparison with the isotypic Fe[III] analogue (Le Bail & Mercier, 2009), the atomic coordinates of the latter were used for the final refinement cycles. All H atoms were located from difference Fourier maps. The water H atoms were restrained to have O—H distances of 0.85 Å. Their U_{iso} values were refined with one common parameter. The position of the H atom of the disordered HF group (set with a site occupation factor of 1/2) was fixed during refinement, but its U_{iso} value was refined independently.

Figures
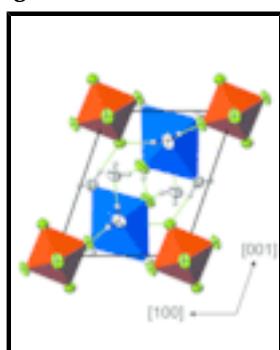
Fig. 1. The crystal structure of $[Cu_2(HF_2)(H_2O)_8][AlF_6](H_2O)_2$ in polyhedral representation projected along [010]. Colour key: O atoms white, F atoms green, H atoms are grey, $[CuO_5F]$ octahedra are blue, $[AlF_6]$ octahedra are red. Displacement ellipsoids are given at the 74% probability level; H atoms are displayed as spheres of arbitrary radius. Hydrogen bonds are indicated with green lines. Note that for clarity only one of the disordered H atoms bonded to the F atom is shown.

octaaqua(hydrogendifluorido)dicopper(II) hexafluoridoaluminate dihydrate

Crystal data

$[Cu_2(HF_2)(H_2O)_8][AlF_6]\cdot 2H_2O$	$Z = 1$
$M_r = 487.23$	$F_{000} = 244$
Triclinic, $P\bar{1}$	$D_x = 2.228$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 6.6119$ (3) Å	Cell parameters from 3443 reflections
$b = 7.3410$ (3) Å	$\theta = 2.7–30.0°$
$c = 8.3174$ (3) Å	$\mu = 3.12$ mm^{-1}
$\alpha = 107.336$ (1)°	$T = 293$ K
$\beta = 106.715$ (1)°	Plate, blue
$\gamma = 94.454$ (1)°	$0.18 \times 0.14 \times 0.06$ mm
$V = 363.15$ (3) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	2013 independent reflections
Radiation source: fine-focus sealed tube	1952 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.019$
$T = 293$ K	$\theta_{max} = 30.0°$
ω scans	$\theta_{min} = 2.7°$
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$h = -9 \rightarrow 9$
$T_{min} = 0.52$, $T_{max} = 0.80$	$k = -10 \rightarrow 10$
3899 measured reflections	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.026$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.072$	$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.1517P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} = 0.001$
2013 reflections	$\Delta\rho_{max} = 0.44$ e Å^{-3}
130 parameters	$\Delta\rho_{min} = -0.54$ e Å^{-3}
10 restraints	Extinction correction: SHELXL97 (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.059 (5)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Cu	0.60564 (3)	0.55637 (3)	0.23399 (2)	0.01836 (10)	
Al	0.0000	0.0000	0.0000	0.01611 (15)	
F1	0.21626 (18)	−0.02274 (17)	−0.09157 (16)	0.0272 (2)	
F2	0.19296 (18)	0.12317 (17)	0.21936 (15)	0.0282 (2)	
F3	−0.02395 (19)	0.23071 (16)	−0.03724 (18)	0.0278 (2)	
F4	0.4323 (2)	0.5863 (2)	0.38450 (18)	0.0354 (3)	
O1	0.5678 (2)	0.2833 (2)	0.2103 (2)	0.0289 (3)	
O2	0.6023 (3)	0.8243 (2)	0.2410 (2)	0.0266 (3)	
O3	0.7505 (2)	0.5080 (2)	0.0522 (2)	0.0248 (3)	
O4	0.9127 (2)	0.6621 (2)	0.4883 (2)	0.0278 (3)	
O5	0.2346 (3)	0.8900 (2)	0.4430 (2)	0.0296 (3)	
H11	0.636 (6)	0.198 (5)	0.160 (5)	0.055 (3)*	
H12	0.456 (5)	0.233 (5)	0.218 (5)	0.055 (3)*	
H21	0.668 (6)	0.881 (5)	0.196 (5)	0.055 (3)*	
H22	0.653 (6)	0.910 (5)	0.340 (4)	0.055 (3)*	
H31	0.833 (6)	0.586 (5)	0.050 (5)	0.055 (3)*	
H32	0.811 (6)	0.421 (5)	0.027 (5)	0.055 (3)*	
H41	0.885 (6)	0.716 (5)	0.583 (4)	0.055 (3)*	
H42	1.009 (5)	0.644 (5)	0.483 (5)	0.055 (3)*	
H51	0.213 (6)	0.925 (5)	0.365 (4)	0.055 (3)*	
H52	0.344 (6)	0.796 (5)	0.435 (5)	0.055 (3)*	
H6	0.4722	0.5226	0.4629	0.026 (12)*	0.50

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.02240 (14)	0.01519 (13)	0.02078 (14)	0.00360 (8)	0.01130 (9)	0.00657 (9)
Al	0.0176 (3)	0.0141 (3)	0.0194 (3)	0.0027 (2)	0.0093 (2)	0.0063 (2)
F1	0.0279 (5)	0.0262 (5)	0.0377 (6)	0.0082 (4)	0.0226 (5)	0.0129 (5)
F2	0.0273 (5)	0.0301 (6)	0.0225 (5)	−0.0007 (4)	0.0070 (4)	0.0049 (4)
F3	0.0304 (5)	0.0188 (5)	0.0424 (6)	0.0066 (4)	0.0175 (5)	0.0161 (5)
F4	0.0481 (7)	0.0379 (7)	0.0378 (7)	0.0205 (6)	0.0281 (6)	0.0211 (5)

O1	0.0280 (7)	0.0161 (6)	0.0471 (8)	0.0040 (5)	0.0213 (6)	0.0084 (6)
O2	0.0394 (7)	0.0176 (6)	0.0273 (6)	0.0042 (5)	0.0164 (6)	0.0091 (5)
O3	0.0284 (6)	0.0189 (6)	0.0333 (7)	0.0049 (5)	0.0200 (6)	0.0079 (5)
O4	0.0262 (6)	0.0276 (7)	0.0280 (6)	0.0050 (5)	0.0086 (5)	0.0073 (5)
O5	0.0379 (7)	0.0279 (7)	0.0266 (6)	0.0090 (6)	0.0134 (6)	0.0108 (5)

Geometric parameters (Å, °)

Cu—F4	1.9049 (12)	Al—F1	1.8001 (10)
Cu—O1	1.9441 (14)	Al—F1^{ii}	1.8001 (10)
Cu—O2	1.9522 (14)	Al—F2^{ii}	1.8091 (11)
Cu—O3	1.9739 (13)	Al—F2	1.8091 (11)
Cu—O4	2.3463 (15)	Al—F3^{ii}	1.8209 (11)
Cu—O3^{i}	2.7139 (16)	Al—F3	1.8209 (11)
Cu—Cu^{i}	3.5440 (4)	F4—F4^{iii}	2.596 (3)
F4—Cu—O1	86.72 (6)	F4^{iii}—F4—O1	75.78 (7)
F4—Cu—O2	90.07 (6)	Cu—F4—O5	120.66 (7)
O1—Cu—O2	172.31 (6)	F4^{iii}—F4—O5	123.74 (8)
F4—Cu—O3	172.54 (6)	O1—F4—O5	159.76 (8)
O1—Cu—O3	91.01 (6)	Cu—F4—O2	45.67 (4)
O2—Cu—O3	91.29 (6)	F4^{iii}—F4—O2	138.16 (10)
F4—Cu—O4	89.18 (6)	O1—F4—O2	92.70 (6)
O1—Cu—O4	97.22 (6)	O5—F4—O2	75.99 (6)
O2—Cu—O4	89.72 (6)	H11—O1—H12	113 (4)
O3—Cu—O4	98.16 (6)	Cu—O2—Cu^{i}	65.57 (4)
F4—Cu—O3^{i}	89.91 (5)	F4—O2—Cu^{i}	93.18 (5)
O1—Cu—O3^{i}	91.35 (6)	Cu—O2—H21	126 (3)
O2—Cu—O3^{i}	81.64 (6)	F4—O2—H21	169 (3)
O3—Cu—O3^{i}	83.04 (5)	Cu^{i}—O2—H21	83 (3)
O4—Cu—O3^{i}	171.31 (5)	Cu—O2—H22	117 (3)
F1—Al—F1^{ii}	180.00 (8)	F4—O2—H22	91 (3)
F1—Al—F2^{ii}	90.44 (5)	Cu^{i}—O2—H22	176 (3)
F1^{ii}—Al—F2^{ii}	89.56 (5)	H21—O2—H22	92 (4)
F1—Al—F2	89.56 (5)	Cu—O3—Cu^{i}	96.96 (5)
F1^{ii}—Al—F2	90.44 (5)	Cu—O3—H31	123 (3)
F2^{ii}—Al—F2	180.0	Cu^{i}—O3—H31	107 (3)
F1—Al—F3^{ii}	89.97 (5)	Cu—O3—H32	125 (3)
F1^{ii}—Al—F3^{ii}	90.03 (5)	Cu^{i}—O3—H32	106 (3)
F2^{ii}—Al—F3^{ii}	90.57 (6)	H31—O3—H32	97 (4)
F2—Al—F3^{ii}	89.43 (6)	Cu—O4—H41	113 (2)
F1—Al—F3	90.03 (5)	F4—O4—H41	75 (3)
F1^{ii}—Al—F3	89.97 (5)	Cu—O4—H42	121 (3)
F2^{ii}—Al—F3	89.43 (6)	F4—O4—H42	156 (3)
F2—Al—F3	90.57 (6)	H41—O4—H42	126 (4)

F3^{ii}—Al—F3	180.00 (8)	F4—O5—H51	110 (3)
Cu—F4—F4^{iii}	109.26 (8)	H51—O5—H52	109 (3)
Cu—F4···O1	47.26 (4)		

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

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H11···F1^{iv}	0.87 (3)	1.74 (3)	2.6042 (17)	171 (4)
O1—H12···F2	0.83 (3)	1.86 (3)	2.6899 (18)	176 (4)
O2—H21···F1^{i}	0.81 (3)	1.79 (3)	2.6020 (18)	172 (4)
O2—H22···O5^{v}	0.83 (3)	1.86 (3)	2.684 (2)	178 (4)
O3—H31···F3^{i}	0.77 (3)	1.82 (3)	2.5877 (18)	178 (4)
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O4—H42···O4^{vii}	0.67 (3)	2.41 (4)	2.758 (3)	115 (4)
O4—H42···O5^{vi}	0.67 (3)	2.41 (4)	2.784 (2)	117 (4)
O5—H51···F2^{viii}	0.75 (3)	2.14 (3)	2.8538 (19)	159 (4)
O5—H51···F3^{ix}	0.75 (3)	2.50 (3)	3.072 (2)	135 (4)
O5—H52···F4	1.04 (3)	1.67 (3)	2.6620 (19)	158 (3)
F4—H6···F4^{iii}	0.9031 (13)	1.6945 (13)	2.596 (3)	175.27 (5)

Symmetry codes: (iv) −x+1, −y, −z; (i) −x+1, −y+1, −z; (v) −x+1, −y+2, −z+1; (vi) x+1, y, z; (iii) −x+1, −y+1, −z+1; (vii) −x+2, −y+1, −z+1; (viii) x, y+1, z; (ix) −x, −y+1, −z.

Fig. 1