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[Cu₂(HF₂)(H₂O)₈][AlF₆]·2H₂O

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{Cu}-\text{O}) = 0.002$ Å; R factor = 0.026; wR factor = 0.072; data-to-parameter ratio = 15.5.

The title compound, octaaqua(hydrogendifluorido)dicopper(II) hexafluoroaluminate dihydrate, was obtained under hydrothermal conditions. The structure is isotopic with that of the analogous Fe^{III} compound, [Cu₂(HF₂)(H₂O)₈][FeF₆]·2H₂O. 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 [Cu₂(HF₂)(H₂O)₈]³⁺ units that are bonded to [AlF₆]³⁻ anions ($\bar{1}$ symmetry) and to crystal lattice water molecules *via* hydrogen bonds. Besides F—H···F interactions between the dimeric cationic units, O—H···F and O—H···O hydrogen bonds (both in part bifurcated) are observed.

Related literature

For the structure of the isotopic Fe^{III} analogue, see: Le Bail & Mercier (2009). For a natural compound in the Cu/Al/F/O/H system, Cu₄Al₃(OH)₁₄F₃(H₂O)₂ (mineral name khaidarkanite), see: Rastsvetaeva *et al.* (1997).

Experimental

Crystal data

[Cu₂(HF₂)(H₂O)₈][AlF₆]·2H₂O $\gamma = 94.454$ (1)[°]
 $M_r = 487.23$ $V = 363.15$ (3) Å³
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)[°] $0.18 \times 0.14 \times 0.06$ mm
 $\beta = 106.715$ (1)[°]

Data collection

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.072$
 $S = 1.08$
2013 reflections
130 parameters
10 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.44$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.54$ e Å⁻³

Table 1

Selected bond lengths (Å).

Cu—F4	1.9049 (12)	Cu—O ³ⁱ	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···F1 ⁱⁱ	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 ⁱⁱⁱ	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)
O3—H32···F3 ^{iv}	0.79 (3)	1.89 (3)	2.6700 (17)	174 (4)
O4—H41···F2 ^v	0.85 (3)	1.95 (3)	2.7840 (19)	169 (4)
O4—H42···O4 ^{vi}	0.67 (3)	2.41 (4)	2.758 (3)	115 (4)
O4—H42···O5 ^{iv}	0.67 (3)	2.41 (4)	2.784 (2)	117 (4)
O5—H51···F2 ^{vii}	0.75 (3)	2.14 (3)	2.8538 (19)	159 (4)
O5—H51···F3 ^{viii}	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 ^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.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2101).

References

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supporting information

Acta Cryst. (2009). E65, i29 [doi:10.1107/S1600536809009702]

[Cu₂(HF₂)(H₂O)₈][AlF₆]·2H₂O**Matthias Weil****S1. Comment**

The crystal structure (Fig. 1) of the title compound, [Cu₂(HF₂)(H₂O)₈][AlF₆].2H₂O, is isotypic with [Cu₂(HF₂)(H₂O)₈][FeF₆].2H₂O (Le Bail & Mercier, 2009). Except the Al—F distances ($\bar{d} = 1.810 \text{ \AA}$ 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 Cu₄Al₃(OH)₁₄F₃(H₂O)₂ (Rastsvetaeva *et al.*, 1997). The latter differs from the title compound as its structure contains distorted [Cu(OH)₅(H₂O)] octahedra, and [Al(OH)₆] and [AlF₄(H₂O)₂] octahedra as building units.

S2. Experimental

AlF₃ and CuSO₄·5H₂O (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.

S3. 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.

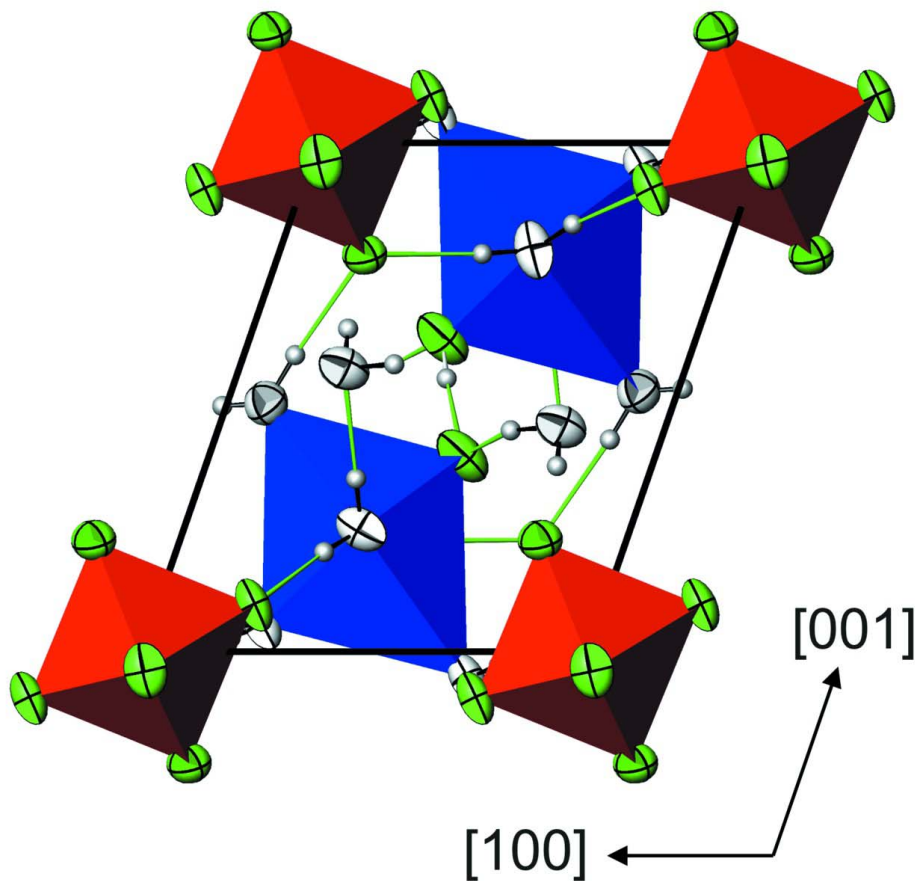


Figure 1

The crystal structure of $[\text{Cu}_2(\text{HF}_2)(\text{H}_2\text{O})_8][\text{AlF}_6](\text{H}_2\text{O})_2$ in polyhedral representation projected along $[010]$. Colour key: O atoms white, F atoms green, H atoms are grey, $[\text{CuO}_5\text{F}]$ octahedra are blue, $[\text{AlF}_6]$ 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) hexafluoroaluminate dihydrate

Crystal data

$[\text{Cu}_2(\text{HF}_2)(\text{H}_2\text{O})_8][\text{AlF}_6] \cdot 2\text{H}_2\text{O}$

$M_r = 487.23$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 6.6119(3)\ \text{\AA}$

$b = 7.3410(3)\ \text{\AA}$

$c = 8.3174(3)\ \text{\AA}$

$\alpha = 107.336(1)^\circ$

$\beta = 106.715(1)^\circ$

$\gamma = 94.454(1)^\circ$

$V = 363.15(3)\ \text{\AA}^3$

$Z = 1$

$F(000) = 244$
 $D_x = 2.228 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 3443 reflections
 $\theta = 2.7\text{--}30.0^\circ$

$\mu = 3.12 \text{ mm}^{-1}$
 $T = 293 \text{ K}$
 Plate, blue
 $0.18 \times 0.14 \times 0.06 \text{ mm}$

Data collection

Bruker SMART CCD area-detector
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2000)
 $T_{\min} = 0.52$, $T_{\max} = 0.80$

3899 measured reflections
 2013 independent reflections
 1952 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$
 $\theta_{\max} = 30.0^\circ$, $\theta_{\min} = 2.7^\circ$
 $h = -9 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = -11 \rightarrow 11$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.072$
 $S = 1.08$
 2013 reflections
 130 parameters
 10 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.1517P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.44 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.54 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick,
 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	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 (Å²)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H11 \cdots F1 ^{iv}	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 ^v	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 ^{vi}	0.79 (3)	1.89 (3)	2.6700 (17)	174 (4)
O4—H41 \cdots F2 ⁱⁱⁱ	0.85 (3)	1.95 (3)	2.7840 (19)	169 (4)
O4—H42 \cdots O4 ^{vii}	0.67 (3)	2.41 (4)	2.758 (3)	115 (4)
O4—H42 \cdots O5 ^{vi}	0.67 (3)	2.41 (4)	2.784 (2)	117 (4)
O5—H51 \cdots F2 ^{viii}	0.75 (3)	2.14 (3)	2.8538 (19)	159 (4)
O5—H51 \cdots F3 ^{ix}	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 ⁱⁱⁱ	0.9031 (13)	1.6945 (13)	2.596 (3)	175.27 (5)

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