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Rubidium potassium hexafluoridozirconate(IV) bis(hydrogen fluoride), $Rb_{2-x}K_xZrF_6\cdot 2HF$ (x = 0.4171)

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Key indicators: single-crystal X-ray study; T = 173 K; mean σ(Zr–F) = 0.001 Å; disorder in main residue; R factor = 0.026; wR factor = 0.061; data-to-parameter ratio = 20.5.

The title compound is built from edge-sharing centrosymmetric dimeric $[Zr_2F_{12}]^{4-}$ complexes, HF molecules, Rb^+ and K^+ cations. Rubidium and potassium ions are statistically disordered on one of the metal positions. The Zr^{IV} coordination polyhedron is a monocapped trigonal prism. The two crystallographically independent Rb(K) ions are coordinated by F atoms and HF molecules with coordination numbers 7 and 9, respectively, for the two sites. In addition, the structure is stabilized by strong F—H···F hydrogen bonds.

Related literature

For related literature, see: Blatov (2004); Gerasimenko *et al.* (2006), Gerasimenko, Didenko & Kavun (2007); Gerasimenko, Kavun *et al.* (2007); Kavun *et al.* (2006); Serezhkin *et al.* (1997).

Experimental

Crystal data

$Rb_{1.58}K_{0.42}ZrF_6\cdot 2HF$
M_r = 396.84
Monoclinic, $P2_1/c$
a = 7.2427 (5) Å
b = 11.7111 (8) Å
c = 9.0742 (6) Å
β = 90.413 (2)°
V = 769.65 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 11.68 mm^{-1}
T = 173 (2) K
0.27 × 0.22 × 0.17 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
Absorption correction: Gaussian (*XPREP*; Bruker, 2003)
T_{min} = 0.176, T_{max} = 0.444
6082 measured reflections
2437 independent reflections
2223 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.061
S = 1.06
2437 reflections
119 parameters
1 restraint
Only H-atom coordinates refined
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.62 e Å^{-3}

Table 1
Selected bond lengths (Å).

Zr—F3	1.9886 (13)	Zr—F6	2.0958 (13)
Zr—F2	1.9919 (12)	Zr—F1	2.1403 (11)
Zr—F5	2.0014 (11)	Zr—F1^{i}	2.1950 (11)
Zr—F4	2.0497 (13)	Zr—Zr^{i}	3.6579 (4)

Symmetry code: (i) $-x, -y+2, -z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
F7—H1···F6^{ii}	0.79 (4)	1.54 (4)	2.326 (2)	176 (4)
F8a—H2···F4	0.79 (4)	1.62 (4)	2.402 (2)	168 (4)
F8b—H2···F4	0.84 (4)	1.62 (4)	2.326 (8)	139 (4)

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FI2047).

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supplementary materials

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Rubidium potassium hexafluoridozirconate(IV) bis(hydrogen fluoride), $Rb_{2-x}K_xZrF_6{\cdot}2HF$ (x = 0.4171)

A. V. Gerasimenko, N. A. Didenko and V. Y. Kavun

Comment

This work is a continuation of the study of the structure and physicochemical properties of zirconium fluoride complexes with homo- and heteroatomic cations (Gerasimenko *et al.*, 2006, 2007*a*, 2007*b*; Kavun *et al.*, 2006) and deals with synthesis and crystal structure of rubidium–potassium hexafluoridozirconate(IV) di(hydrogen fluoride), $Rb_{2-x}K_xZrF_6{\cdot}2HF$ (I) where x=0.4171. The asymmetric unit contains one Zr atom, six fluorine atoms, two sites of rubidium and potassium cations and two hydrogen fluoride molecules. The Zr atoms are coordinated by seven F atoms in a slightly distorted monocapped trigonal prism geometry. Two Zr-centred polyhedra are linked by double F bridges to form a centrosymmetric dimeric $[Zr_2F_{12}]^{4-}$ complex (Fig. 1) with a $Zr\cdots Zr^{i}$ distance of 3.6579 (4) Å. Along to the *c* direction, Zr- polyhedra pack up in columns (Fig. 2).

In this structure, there are two sites in which the outer-sphere rubidium and potassium cations are located. In each site the rubidium cations are statistically substituted by the potassium cations. According to the performed refinement, Rb/K site occupancy factors are equal to 0.8742 (7)/0.1258 for the Rb1/K1 site and 0.7087 (7)/0.2913 for the Rb2/K2 site. The coordination numbers (CN) of these sites were calculated by the method of intersecting spheres (Serezhkin *et al.*, 1997) with use of the program package *TOPOS* (Blatov, 2004). For the first site (Fig. 3a), the CN is 9 (Rb1(K1)–F, 2.7609 (14) – 3.1054 (13) Å) and for the second site (Fig. 3 b), the CN is 7 (Rb2(K2)–F, 2.7584 (14) – 2.9094 (14) Å).

The HF molecules are involved as donors in strong hydrogen bonds (2.326 (2), 2.402 (2) and 2.326 (8) Å) with the $F6^{ii}$ and F4 atoms (Fig. 2). The F8 atom of HF molecule is split on two sites: F8a and F8b (Fig. 2, 3). The refined occupancy of the F8a and F8b sites are 0.790 (4) and 0.210 (4), respectively. Unfortunately, we did not manage to split the position of H2 atom, therefore, the angle of the hydrogen bond F8b–H2···F4 equal to139(4)° is unusual for strong hydrogen bonds.

Experimental

ZrO_2 (6.2 g, 0.05 mol; Reachem(Russia), 99.99% purity) was reacted with RbF (7.8 g, 0.075 mol; Alfa Aesar, 99.7% purity) and $KF{\cdot}2H_2O$ (2.4 g, 0.025 mol; Reachem(Russia), 99.99% purity) in a solution of hydrofluoric acid (40%, 30 ml; Reachem(Russia), 99.99% purity). Upon slow evaporation at room temperature, crystals of $Rb_{5-x}K_xZr_3F_{17}{\cdot}0.5H_2O$ (x =2.0 and 2.25) precipitated first (later we will report about their crystal structures), and after they were separated, crystals of (I) precipitated next.

Refinement

The Rb and K site occupancies were refined together with the refinement of the structural parameters of these atoms, assuming that their positional and thermal parameters were the same. The site-occupancy factors of F8a and F8b atoms were refined by restraining the sum of occupancies to 1.0. Their displacement parameters were constrained to be identical using

the EADP instructions. The H atoms were found in a difference Fourier map and refined with $U_{iso}(H) = 1.5U_{eq}(F)$. The maximum peak and deepest hole are located 0.79 Å and 0.72 Å, respectively, from Zr and F6.

Figures

Fig. 1. A view of the centrosymmetric dimeric $[Zr_2F_{12}]^{4-}$ complex, with displacement ellipsoids drawn at the 50% probability level. Symmetry code as in Table 1.

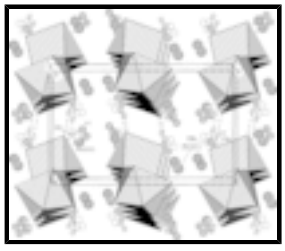


Fig. 2. The structure of (I), viewed along the *c* axis.

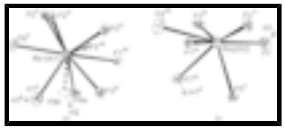


Fig. 3. (*a*) The Rb1(K1) and (*b*) Rb2(K2) coordination polyhedra, with displacement ellipsoids drawn at the 50% probability level. Symmetry codes: ii: $1-x, 1/2+y, 1/2-z$; iv: $1-x, 2-y, -z$; v: $1-x, -1/2+y, 1/2-z$; vi: $1+x, 3/2-y, -1/2+z$; vii: $1+x, y, z$; ix: $x, -1+y, z$; *x*: $1+x, -1+y, z$; xii: $1-x, 1-y, z$.

Rubidium potassium hexafluoridozirconate(IV) bis(hydrogen fluoride)

Crystal data

$Rb_{1.58}K_{0.42}ZrF_6 \cdot 2HF$	$F_{000} = 722$
$M_r = 396.84$	$D_x = 3.425$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 1764 reflections
$a = 7.2427$ (5) Å	$\theta = 2.8$–$31.3°$
$b = 11.7111$ (8) Å	$\mu = 11.68$ mm^{-1}
$c = 9.0742$ (6) Å	$T = 173$ (2) K
$\beta = 90.413$ (2)°	Prism, colourless
$V = 769.65$ (9) Å^3	0.27 × 0.22 × 0.17 mm
$Z = 4$	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	2437 independent reflections
Radiation source: fine-focus sealed tube	2223 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.033$
Detector resolution: 8.33 pixels mm^{-1}	$\theta_{max} = 31.5°$
$T = 173(2)$ K	$\theta_{min} = 2.8°$
ω scans	$h = -10 \rightarrow 10$
Absorption correction: gaussian (SADABS and XPREP; Bruker, 2003)	$k = -17 \rightarrow 16$

T_{min} = 0.176, T_{max} = 0.444
6082 measured reflections

$l = -13 \rightarrow 7$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.061$
$S = 1.06$
2437 reflections
119 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
Only H-atom coordinates refined
$w = 1/[\sigma^2(F_o^2) + (0.0216P)^2 + 0.8571P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.026$
$\Delta\rho_{max} = 0.68$ e Å^{-3}
$\Delta\rho_{min} = -0.62$ e Å^{-3}
Extinction correction: SHELXL, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0034 (3)

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 $F^2 > 2$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)
Zr	0.13506 (2)	0.979721 (14)	0.169058 (18)	0.01248 (4)	
Rb1	0.85934 (3)	0.681632 (16)	−0.00920 (2)	0.01949 (5)	0.8742 (7)
K1	0.85934 (3)	0.681632 (16)	−0.00920 (2)	0.01949 (5)	0.1258
Rb2	0.63267 (3)	0.14738 (2)	0.22385 (2)	0.02009 (6)	0.7087 (7)
K2	0.63267 (3)	0.14738 (2)	0.22385 (2)	0.02009 (6)	0.2913
F2	−0.05205 (17)	1.02431 (10)	0.31821 (13)	0.0210 (3)	
F1	0.05701 (15)	0.91307 (9)	−0.04199 (12)	0.0172 (2)	
F5	0.08382 (18)	0.81754 (10)	0.22501 (13)	0.0232 (3)	
F6	0.2991 (2)	0.97382 (11)	0.36010 (14)	0.0300 (3)	
F3	0.25829 (19)	1.13146 (11)	0.16978 (18)	0.0335 (3)	
F4	0.37882 (18)	0.92093 (14)	0.08435 (16)	0.0360 (4)	
F7	0.5434 (2)	0.17326 (12)	0.52128 (18)	0.0402 (4)	
H1	0.593 (5)	0.121 (3)	0.560 (4)	0.060*	
F8a	0.6904 (3)	0.8804 (2)	0.1602 (3)	0.0417 (6)	0.790 (4)

F8b	0.6467 (11)	0.8442 (8)	0.1869 (10)	0.040 (2)	0.210 (4)
H2	0.586 (5)	0.897 (3)	0.147 (4)	0.060*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zr	0.01345 (7)	0.01337 (7)	0.01059 (7)	0.00168 (6)	−0.00099 (6)	−0.00001 (6)
Rb1	0.02571 (10)	0.01514 (8)	0.01765 (9)	0.00183 (7)	0.00263 (7)	0.00237 (6)
K1	0.02571 (10)	0.01514 (8)	0.01765 (9)	0.00183 (7)	0.00263 (7)	0.00237 (6)
Rb2	0.01561 (10)	0.02453 (11)	0.02013 (11)	0.00128 (8)	0.00099 (8)	−0.00070 (8)
K2	0.01561 (10)	0.02453 (11)	0.02013 (11)	0.00128 (8)	0.00099 (8)	−0.00070 (8)
F2	0.0253 (6)	0.0220 (5)	0.0156 (5)	0.0044 (4)	0.0042 (4)	0.0006 (4)
F1	0.0210 (5)	0.0169 (5)	0.0138 (5)	0.0053 (4)	−0.0029 (4)	−0.0029 (4)
F5	0.0330 (6)	0.0160 (5)	0.0207 (6)	0.0031 (4)	0.0029 (5)	0.0033 (4)
F6	0.0370 (7)	0.0303 (6)	0.0226 (6)	0.0114 (5)	−0.0128 (5)	−0.0042 (5)
F3	0.0259 (6)	0.0244 (6)	0.0501 (8)	−0.0088 (5)	−0.0119 (6)	0.0105 (6)
F4	0.0154 (5)	0.0602 (9)	0.0324 (7)	0.0094 (6)	−0.0016 (5)	−0.0153 (6)
F7	0.0547 (9)	0.0300 (7)	0.0359 (8)	0.0137 (6)	−0.0158 (7)	0.0032 (6)
F8a	0.0205 (8)	0.0497 (12)	0.0547 (13)	0.0074 (8)	−0.0132 (8)	−0.0072 (10)
F8b	0.027 (4)	0.052 (5)	0.040 (4)	0.015 (3)	−0.012 (3)	−0.002 (3)

Geometric parameters (Å, °)

Zr—F3	1.9886 (13)	F1—Zr^{i}	2.1950 (11)
Zr—F2	1.9919 (12)	F1—K2^{xii}	2.8860 (11)
Zr—F5	2.0014 (11)	F1—Rb2^{xii}	2.8860 (11)
Zr—F4	2.0497 (13)	F1—Rb1^{xiv}	3.0806 (11)
Zr—F6	2.0958 (13)	F1—K1^{xiv}	3.0806 (11)
Zr—F1	2.1403 (11)	F5—K2^{ii}	2.8964 (12)
Zr—F1^{i}	2.1950 (11)	F5—Rb2^{ii}	2.8964 (12)
Zr—Zr^{i}	3.6579 (4)	F5—Rb1^{iii}	2.9183 (12)
Zr—K1^{ii}	3.8882 (3)	F5—K1^{iii}	2.9183 (12)
Zr—Rb1^{ii}	3.8882 (3)	F5—Rb1^{xiv}	3.1054 (13)
Zr—K1^{iii}	4.0207 (3)	F5—K1^{xiv}	3.1054 (13)
Zr—Rb1^{iii}	4.0207 (3)	F6—K1^{ii}	3.0156 (13)
Rb1—F3^{iv}	2.7609 (14)	F6—Rb1^{ii}	3.0156 (13)
Rb1—F2^{v}	2.8829 (12)	F6—K2^{xv}	3.3969 (15)
Rb1—F5^{vi}	2.9183 (13)	F6—Rb2^{xv}	3.3969 (15)
Rb1—F7^{ii}	2.9197 (18)	F3—K2^{xv}	2.7584 (14)
Rb1—F2^{vi}	2.9489 (12)	F3—Rb2^{xv}	2.7584 (14)
Rb1—F6^{v}	3.0156 (13)	F3—Rb1^{iv}	2.7609 (14)
Rb1—F8b	3.033 (9)	F3—K1^{iv}	2.7609 (14)
Rb1—F8a	3.051 (2)	F3—K1^{ii}	3.2550 (16)
Rb1—F1^{vii}	3.0806 (11)	F3—Rb1^{ii}	3.2550 (16)

Rb1—F5^{vii}	3.1054 (13)	F4—K2^{xii}	2.9094 (14)
Rb1—F8b^{viii}	3.164 (9)	F4—Rb2^{xii}	2.9094 (14)
Rb1—F3^{v}	3.2550 (16)	F4—Rb2^{xv}	3.4615 (16)
Rb2—F3^{ix}	2.7584 (14)	F7—K2^{xvi}	2.8621 (16)
Rb2—F7	2.7964 (17)	F7—Rb2^{xvi}	2.8621 (16)
Rb2—F2^{x}	2.8278 (12)	F7—Rb1^{v}	2.9197 (18)
Rb2—F7^{xi}	2.8621 (16)	F7—K1^{v}	2.9197 (18)
Rb2—F1^{xii}	2.8860 (11)	F7—H1	0.79 (4)
Rb2—F5^{v}	2.8964 (12)	F8a—F8b	0.583 (9)
Rb2—F4^{xii}	2.9094 (14)	F8a—K2^{xv}	3.207 (2)
Rb2—F8b^{v}	3.176 (9)	F8a—Rb2^{xv}	3.207 (2)
Rb2—F8a^{ix}	3.207 (2)	F8a—Rb1^{xvii}	3.313 (2)
Rb2—F6^{ix}	3.3969 (15)	F8a—K1^{xvii}	3.313 (2)
Rb2—F4^{ix}	3.4615 (16)	F8a—H2	0.79 (4)
Rb2—F8b^{ix}	3.568 (9)	F8b—K1^{xvii}	3.164 (9)
F2—K2^{xiii}	2.8278 (12)	F8b—Rb1^{xvii}	3.164 (9)
F2—Rb2^{xiii}	2.8278 (12)	F8b—K2^{ii}	3.176 (9)
F2—Rb1^{ii}	2.8829 (12)	F8b—Rb2^{ii}	3.176 (9)
F2—K1^{ii}	2.8829 (12)	F8b—Rb2^{xv}	3.568 (9)
F2—K1^{iii}	2.9489 (12)	F8b—H2	0.84 (4)
F2—Rb1^{iii}	2.9489 (12)		
F3—Zr—F2	94.07 (6)	F8b^{v}—Rb2—F6^{ix}	83.42 (16)
F3—Zr—F5	158.63 (6)	F8a^{ix}—Rb2—F6^{ix}	64.92 (4)
F2—Zr—F5	87.03 (5)	F3^{ix}—Rb2—F4^{ix}	50.53 (4)
F3—Zr—F4	85.05 (6)	F7—Rb2—F4^{ix}	108.06 (4)
F2—Zr—F4	159.22 (5)	F2^{x}—Rb2—F4^{ix}	98.39 (3)
F5—Zr—F4	86.46 (6)	F7^{xi}—Rb2—F4^{ix}	102.15 (4)
F3—Zr—F6	77.00 (6)	F1^{xii}—Rb2—F4^{ix}	90.96 (3)
F2—Zr—F6	80.28 (5)	F5^{v}—Rb2—F4^{ix}	163.69 (3)
F5—Zr—F6	82.18 (5)	F4^{xii}—Rb2—F4^{ix}	55.00 (5)
F4—Zr—F6	79.30 (6)	F8b^{v}—Rb2—F4^{ix}	108.15 (15)
F3—Zr—F1	116.39 (6)	F8a^{ix}—Rb2—F4^{ix}	42.00 (4)
F2—Zr—F1	121.80 (5)	F6^{ix}—Rb2—F4^{ix}	45.37 (3)
F5—Zr—F1	80.36 (5)	F3^{ix}—Rb2—F8b^{ix}	86.82 (13)
F4—Zr—F1	76.38 (5)	F7—Rb2—F8b^{ix}	101.86 (15)
F6—Zr—F1	150.76 (5)	F2^{x}—Rb2—F8b^{ix}	59.86 (13)
F3—Zr—F1^{i}	76.90 (5)	F7^{xi}—Rb2—F8b^{ix}	132.56 (15)
F2—Zr—F1^{i}	77.01 (4)	F1^{xii}—Rb2—F8b^{ix}	71.30 (14)
F5—Zr—F1^{i}	123.92 (5)	F5^{v}—Rb2—F8b^{ix}	132.78 (13)
F4—Zr—F1^{i}	122.65 (5)	F4^{xii}—Rb2—F8b^{ix}	68.69 (15)

F6—Zr—F1^{i}	143.78 (5)	F8b^{v}—Rb2—F8b^{ix}	139.89 (13)
F1—Zr—F1^{i}	64.93 (5)	F8a^{ix}—Rb2—F8b^{ix}	7.76 (14)
F3—Zr—Zr^{i}	97.13 (4)	F6^{ix}—Rb2—F8b^{ix}	57.28 (14)
F2—Zr—Zr^{i}	99.99 (4)	F4^{ix}—Rb2—F8b^{ix}	38.61 (13)
F5—Zr—Zr^{i}	103.71 (4)	F3^{ix}—Rb2—H1	94.1 (7)
F4—Zr—Zr^{i}	100.72 (4)	F7—Rb2—H1	14.4 (7)
F6—Zr—Zr^{i}	174.11 (4)	F2^{x}—Rb2—H1	74.3 (7)
F1—Zr—Zr^{i}	32.93 (3)	F7^{xi}—Rb2—H1	133.4 (7)
F1^{i}—Zr—Zr^{i}	32.00 (3)	F1^{xii}—Rb2—H1	128.3 (7)
F3—Zr—K1^{ii}	56.76 (5)	F5^{v}—Rb2—H1	88.8 (7)
F2—Zr—K1^{ii}	45.93 (4)	F4^{xii}—Rb2—H1	157.3 (7)
F5—Zr—K1^{ii}	112.13 (4)	F8b^{v}—Rb2—H1	75.9 (7)
F4—Zr—K1^{ii}	119.86 (4)	F8a^{ix}—Rb2—H1	95.5 (7)
F6—Zr—K1^{ii}	50.27 (4)	F6^{ix}—Rb2—H1	60.6 (7)
F1—Zr—K1^{ii}	158.95 (3)	F4^{ix}—Rb2—H1	103.5 (7)
F1^{i}—Zr—K1^{ii}	94.13 (3)	F8b^{ix}—Rb2—H1	89.9 (7)
Zr^{i}—Zr—K1^{ii}	126.108 (8)	Zr—F2—K2^{xiii}	118.67 (5)
F3—Zr—Rb1^{ii}	56.76 (5)	Zr—F2—Rb2^{xiii}	118.67 (5)
F2—Zr—Rb1^{ii}	45.93 (4)	Zr—F2—Rb1^{ii}	104.31 (5)
F5—Zr—Rb1^{ii}	112.13 (4)	K2^{xiii}—F2—Rb1^{ii}	104.05 (4)
F4—Zr—Rb1^{ii}	119.86 (4)	Rb2^{xiii}—F2—Rb1^{ii}	104.05 (4)
F6—Zr—Rb1^{ii}	50.27 (4)	Zr—F2—K1^{ii}	104.31 (5)
F1—Zr—Rb1^{ii}	158.95 (3)	K2^{xiii}—F2—K1^{ii}	104.05 (4)
F1^{i}—Zr—Rb1^{ii}	94.13 (3)	Rb2^{xiii}—F2—K1^{ii}	104.05 (4)
Zr^{i}—Zr—Rb1^{ii}	126.108 (8)	Zr—F2—K1^{iii}	107.35 (5)
K1^{ii}—Zr—Rb1^{ii}	0.000 (4)	K2^{xiii}—F2—K1^{iii}	113.54 (4)
F3—Zr—K1^{iii}	130.00 (5)	Rb2^{xiii}—F2—K1^{iii}	113.54 (4)
F2—Zr—K1^{iii}	44.43 (3)	Rb1^{ii}—F2—K1^{iii}	108.04 (4)
F5—Zr—K1^{iii}	43.60 (4)	K1^{ii}—F2—K1^{iii}	108.04 (4)
F4—Zr—K1^{iii}	123.24 (5)	Zr—F2—Rb1^{iii}	107.35 (5)
F6—Zr—K1^{iii}	70.46 (4)	K2^{xiii}—F2—Rb1^{iii}	113.54 (4)
F1—Zr—K1^{iii}	110.42 (3)	Rb2^{xiii}—F2—Rb1^{iii}	113.54 (4)
F1^{i}—Zr—K1^{iii}	109.51 (3)	Rb1^{ii}—F2—Rb1^{iii}	108.04 (4)
Zr^{i}—Zr—K1^{iii}	113.868 (8)	K1^{ii}—F2—Rb1^{iii}	108.04 (4)
K1^{ii}—Zr—K1^{iii}	73.249 (7)	Zr—F1—Zr^{i}	115.07 (5)
Rb1^{ii}—Zr—K1^{iii}	73.249 (7)	Zr—F1—K2^{xii}	113.54 (4)
F3—Zr—Rb1^{iii}	130.00 (5)	Zr^{i}—F1—K2^{xii}	109.46 (4)
F2—Zr—Rb1^{iii}	44.43 (3)	Zr—F1—Rb2^{xii}	113.54 (4)
F5—Zr—Rb1^{iii}	43.60 (4)	Zr^{i}—F1—Rb2^{xii}	109.46 (4)
F4—Zr—Rb1^{iii}	123.24 (5)	Zr—F1—Rb1^{xiv}	110.76 (4)
F6—Zr—Rb1^{iii}	70.46 (4)	Zr^{i}—F1—Rb1^{xiv}	105.12 (4)

F1—Zr—Rb1^{iii}	110.42 (3)	K2^{xii}—F1—Rb1^{xiv}	101.76 (3)
F1^{i}—Zr—Rb1^{iii}	109.51 (3)	Rb2^{xii}—F1—Rb1^{xiv}	101.76 (3)
Zr^{i}—Zr—Rb1^{iii}	113.868 (8)	Zr—F1—K1^{xiv}	110.76 (4)
K1^{ii}—Zr—Rb1^{iii}	73.249 (7)	Zr^{i}—F1—K1^{xiv}	105.12 (4)
Rb1^{ii}—Zr—Rb1^{iii}	73.249 (7)	K2^{xii}—F1—K1^{xiv}	101.76 (3)
F3^{iv}—Rb1—F2^{v}	165.97 (4)	Rb2^{xii}—F1—K1^{xiv}	101.76 (3)
F3^{iv}—Rb1—F5^{vi}	74.50 (4)	Zr—F5—K2^{ii}	124.13 (6)
F2^{v}—Rb1—F5^{vi}	103.22 (3)	Zr—F5—Rb2^{ii}	124.13 (6)
F3^{iv}—Rb1—F7^{ii}	72.69 (4)	Zr—F5—Rb1^{iii}	108.18 (5)
F2^{v}—Rb1—F7^{ii}	118.71 (4)	K2^{ii}—F5—Rb1^{iii}	105.57 (4)
F5^{vi}—Rb1—F7^{ii}	122.10 (4)	Rb2^{ii}—F5—Rb1^{iii}	105.57 (4)
F3^{iv}—Rb1—F2^{vi}	115.83 (4)	Zr—F5—K1^{iii}	108.18 (5)
F2^{v}—Rb1—F2^{vi}	71.96 (4)	K2^{ii}—F5—K1^{iii}	105.57 (4)
F5^{vi}—Rb1—F2^{vi}	55.89 (3)	Rb2^{ii}—F5—K1^{iii}	105.57 (4)
F7^{ii}—Rb1—F2^{vi}	100.01 (4)	Zr—F5—Rb1^{xiv}	114.20 (5)
F3^{iv}—Rb1—F6^{v}	139.43 (4)	K2^{ii}—F5—Rb1^{xiv}	97.13 (3)
F2^{v}—Rb1—F6^{v}	53.04 (4)	Rb2^{ii}—F5—Rb1^{xiv}	97.13 (3)
F5^{vi}—Rb1—F6^{v}	126.13 (4)	Rb1^{iii}—F5—Rb1^{xiv}	105.98 (4)
F7^{ii}—Rb1—F6^{v}	66.82 (4)	K1^{iii}—F5—Rb1^{xiv}	105.98 (4)
F2^{vi}—Rb1—F6^{v}	70.32 (3)	Zr—F5—K1^{xiv}	114.20 (5)
F3^{iv}—Rb1—F8b	69.88 (18)	K2^{ii}—F5—K1^{xiv}	97.13 (3)
F2^{v}—Rb1—F8b	107.10 (17)	Rb2^{ii}—F5—K1^{xiv}	97.13 (3)
F5^{vi}—Rb1—F8b	140.44 (18)	Rb1^{iii}—F5—K1^{xiv}	105.98 (4)
F7^{ii}—Rb1—F8b	62.08 (17)	K1^{iii}—F5—K1^{xiv}	105.98 (4)
F2^{vi}—Rb1—F8b	159.74 (18)	Zr—F6—K1^{ii}	97.42 (5)
F6^{v}—Rb1—F8b	92.68 (18)	Zr—F6—Rb1^{ii}	97.42 (5)
F3^{iv}—Rb1—F8a	62.45 (6)	Zr—F6—K2^{xv}	94.57 (5)
F2^{v}—Rb1—F8a	112.27 (5)	K1^{ii}—F6—K2^{xv}	87.38 (3)
F5^{vi}—Rb1—F8a	129.92 (5)	Rb1^{ii}—F6—K2^{xv}	87.38 (3)
F7^{ii}—Rb1—F8a	68.92 (5)	Zr—F6—Rb2^{xv}	94.57 (5)
F2^{vi}—Rb1—F8a	168.91 (5)	K1^{ii}—F6—Rb2^{xv}	87.38 (3)
F6^{v}—Rb1—F8a	103.56 (5)	Rb1^{ii}—F6—Rb2^{xv}	87.38 (3)
F3^{iv}—Rb1—F1^{vii}	52.65 (3)	Zr—F3—K2^{xv}	120.10 (6)
F2^{v}—Rb1—F1^{vii}	113.39 (3)	Zr—F3—Rb2^{xv}	120.10 (6)
F5^{vi}—Rb1—F1^{vii}	69.83 (3)	Zr—F3—Rb1^{iv}	124.75 (6)
F7^{ii}—Rb1—F1^{vii}	119.39 (4)	K2^{xv}—F3—Rb1^{iv}	109.85 (4)
F2^{vi}—Rb1—F1^{vii}	124.42 (3)	Rb2^{xv}—F3—Rb1^{iv}	109.85 (4)
F6^{v}—Rb1—F1^{vii}	158.76 (3)	Zr—F3—K1^{iv}	124.75 (6)
F8b—Rb1—F1^{vii}	75.10 (18)	K2^{xv}—F3—K1^{iv}	109.85 (4)
F8a—Rb1—F1^{vii}	64.26 (5)	Rb2^{xv}—F3—K1^{iv}	109.85 (4)
F3^{iv}—Rb1—F5^{vii}	96.48 (4)	Zr—F3—K1^{ii}	92.52 (5)

F2^{v}—Rb1—F5^{vii}	70.57 (3)	K2^{xv}—F3—K1^{ii}	94.77 (4)
F5^{vi}—Rb1—F5^{vii}	105.77 (4)	Rb2^{xv}—F3—K1^{ii}	94.77 (4)
F7^{ii}—Rb1—F5^{vii}	124.11 (4)	Rb1^{iv}—F3—K1^{ii}	105.93 (4)
F2^{vi}—Rb1—F5^{vii}	131.90 (3)	K1^{iv}—F3—K1^{ii}	105.93 (4)
F6^{v}—Rb1—F5^{vii}	107.80 (3)	Zr—F3—Rb1^{ii}	92.52 (5)
F8b—Rb1—F5^{vii}	62.77 (16)	K2^{xv}—F3—Rb1^{ii}	94.77 (4)
F8a—Rb1—F5^{vii}	58.27 (4)	Rb2^{xv}—F3—Rb1^{ii}	94.77 (4)
F1^{vii}—Rb1—F5^{vii}	51.23 (3)	Rb1^{iv}—F3—Rb1^{ii}	105.93 (4)
F3^{iv}—Rb1—F8b^{viii}	57.94 (17)	K1^{iv}—F3—Rb1^{ii}	105.93 (4)
F2^{v}—Rb1—F8b^{viii}	133.92 (18)	Zr—F4—K2^{xii}	115.73 (6)
F5^{vi}—Rb1—F8b^{viii}	63.29 (16)	Zr—F4—Rb2^{xii}	115.73 (6)
F7^{ii}—Rb1—F8b^{viii}	58.94 (16)	Zr—F4—Rb2^{xv}	93.56 (5)
F2^{vi}—Rb1—F8b^{viii}	64.24 (18)	K2^{xii}—F4—Rb2^{xv}	125.00 (5)
F6^{v}—Rb1—F8b^{viii}	97.44 (16)	Rb2^{xii}—F4—Rb2^{xv}	125.00 (5)
F8b—Rb1—F8b^{viii}	109.0 (2)	Rb2—F7—K2^{xvi}	130.29 (6)
F8a—Rb1—F8b^{viii}	108.51 (18)	Rb2—F7—Rb2^{xvi}	130.29 (6)
F1^{vii}—Rb1—F8b^{viii}	102.92 (16)	Rb2—F7—Rb1^{v}	101.85 (5)
F5^{vii}—Rb1—F8b^{viii}	153.48 (17)	K2^{xvi}—F7—Rb1^{v}	102.74 (5)
F3^{iv}—Rb1—F3^{v}	124.10 (4)	Rb2^{xvi}—F7—Rb1^{v}	102.74 (5)
F2^{v}—Rb1—F3^{v}	56.27 (3)	Rb2—F7—K1^{v}	101.85 (5)
F5^{vi}—Rb1—F3^{v}	159.03 (4)	K2^{xvi}—F7—K1^{v}	102.74 (5)
F7^{ii}—Rb1—F3^{v}	76.19 (4)	Rb2^{xvi}—F7—K1^{v}	102.74 (5)
F2^{vi}—Rb1—F3^{v}	114.48 (3)	Rb2—F7—H1	104 (3)
F6^{v}—Rb1—F3^{v}	47.68 (3)	K2^{xvi}—F7—H1	100 (3)
F8b—Rb1—F3^{v}	54.60 (18)	Rb2^{xvi}—F7—H1	100 (3)
F8a—Rb1—F3^{v}	63.41 (5)	Rb1^{v}—F7—H1	120 (3)
F1^{vii}—Rb1—F3^{v}	112.03 (3)	K1^{v}—F7—H1	120 (3)
F5^{vii}—Rb1—F3^{v}	65.43 (3)	F8b—F8a—Rb1	82.8 (9)
F8b^{viii}—Rb1—F3^{v}	132.73 (15)	F8b—F8a—K2^{xv}	124.3 (9)
F3^{ix}—Rb2—F7	86.85 (5)	Rb1—F8a—K2^{xv}	152.61 (8)
F3^{ix}—Rb2—F2^{x}	144.10 (4)	F8b—F8a—Rb2^{xv}	124.3 (9)
F7—Rb2—F2^{x}	87.41 (4)	Rb1—F8a—Rb2^{xv}	152.61 (8)
F3^{ix}—Rb2—F7^{xi}	73.63 (5)	F8b—F8a—Rb1^{xvii}	70.3 (9)
F7—Rb2—F7^{xi}	119.18 (4)	Rb1—F8a—Rb1^{xvii}	98.15 (6)
F2^{x}—Rb2—F7^{xi}	138.31 (4)	K2^{xv}—F8a—Rb1^{xvii}	95.66 (6)
F3^{ix}—Rb2—F1^{xii}	130.57 (4)	Rb2^{xv}—F8a—Rb1^{xvii}	95.66 (6)
F7—Rb2—F1^{xii}	139.90 (4)	F8b—F8a—K1^{xvii}	70.3 (9)
F2^{x}—Rb2—F1^{xii}	54.38 (3)	Rb1—F8a—K1^{xvii}	98.15 (6)
F7^{xi}—Rb2—F1^{xii}	89.20 (4)	K2^{xv}—F8a—K1^{xvii}	95.66 (6)
F3^{ix}—Rb2—F5^{v}	140.34 (4)	Rb2^{xv}—F8a—K1^{xvii}	95.66 (6)
F7—Rb2—F5^{v}	86.53 (4)	F8b—F8a—H2	74 (3)

F2^{x}—Rb2—F5^{v}	74.46 (4)	Rb1—F8a—H2	120 (3)
F7^{xi}—Rb2—F5^{v}	75.80 (4)	K2^{xv}—F8a—H2	70 (3)
F1^{xii}—Rb2—F5^{v}	72.92 (3)	Rb2^{xv}—F8a—H2	70 (3)
F3^{ix}—Rb2—F4^{xii}	77.83 (4)	Rb1^{xvii}—F8a—H2	123 (3)
F7—Rb2—F4^{xii}	162.24 (5)	K1^{xvii}—F8a—H2	123 (3)
F2^{x}—Rb2—F4^{xii}	99.69 (4)	F8a—F8b—Rb1	86.2 (9)
F7^{xi}—Rb2—F4^{xii}	65.15 (4)	F8a—F8b—K1^{xvii}	99.7 (10)
F1^{xii}—Rb2—F4^{xii}	53.12 (3)	Rb1—F8b—K1^{xvii}	101.8 (2)
F5^{v}—Rb2—F4^{xii}	111.01 (4)	F8a—F8b—Rb1^{xvii}	99.7 (10)
F3^{ix}—Rb2—F8b^{v}	57.80 (15)	Rb1—F8b—Rb1^{xvii}	101.8 (2)
F7—Rb2—F8b^{v}	61.51 (17)	F8a—F8b—K2^{ii}	169.4 (11)
F2^{x}—Rb2—F8b^{v}	143.82 (16)	Rb1—F8b—K2^{ii}	91.2 (2)
F7^{xi}—Rb2—F8b^{v}	59.32 (17)	K1^{xvii}—F8b—K2^{ii}	90.9 (2)
F1^{xii}—Rb2—F8b^{v}	145.50 (16)	Rb1^{xvii}—F8b—K2^{ii}	90.9 (2)
F5^{v}—Rb2—F8b^{v}	84.96 (15)	F8a—F8b—Rb2^{ii}	169.4 (11)
F4^{xii}—Rb2—F8b^{v}	115.52 (16)	Rb1—F8b—Rb2^{ii}	91.2 (2)
F3^{ix}—Rb2—F8a^{ix}	91.79 (5)	K1^{xvii}—F8b—Rb2^{ii}	90.9 (2)
F7—Rb2—F8a^{ix}	108.11 (5)	Rb1^{xvii}—F8b—Rb2^{ii}	90.9 (2)
F2^{x}—Rb2—F8a^{ix}	56.75 (4)	F8a—F8b—Rb2^{xv}	47.9 (9)
F7^{xi}—Rb2—F8a^{ix}	128.97 (5)	Rb1—F8b—Rb2^{xv}	134.0 (3)
F1^{xii}—Rb2—F8a^{ix}	63.57 (4)	K1^{xvii}—F8b—Rb2^{xv}	91.6 (2)
F5^{v}—Rb2—F8a^{ix}	127.33 (4)	Rb1^{xvii}—F8b—Rb2^{xv}	91.6 (2)
F4^{xii}—Rb2—F8a^{ix}	64.00 (5)	K2^{ii}—F8b—Rb2^{xv}	132.8 (3)
F8b^{v}—Rb2—F8a^{ix}	146.87 (16)	Rb2^{ii}—F8b—Rb2^{xv}	132.8 (3)
F3^{ix}—Rb2—F6^{ix}	47.43 (4)	F8a—F8b—H2	65 (3)
F7—Rb2—F6^{ix}	62.84 (4)	Rb1—F8b—H2	118 (3)
F2^{x}—Rb2—F6^{ix}	99.19 (3)	K1^{xvii}—F8b—H2	134 (3)
F7^{xi}—Rb2—F6^{ix}	120.99 (4)	Rb1^{xvii}—F8b—H2	134 (3)
F1^{xii}—Rb2—F6^{ix}	128.33 (3)	K2^{ii}—F8b—H2	108 (3)
F5^{v}—Rb2—F6^{ix}	149.16 (3)	Rb2^{ii}—F8b—H2	108 (3)
F4^{xii}—Rb2—F6^{ix}	99.78 (4)	Rb2^{xv}—F8b—H2	45 (3)

Symmetry codes: (i) −*x*, −*y*+2, −*z*; (ii) −*x*+1, *y*+1/2, −*z*+1/2; (iii) *x*−1, −*y*+3/2, *z*+1/2; (iv) −*x*+1, −*y*+2, −*z*; (v) −*x*+1, *y*−1/2, −*z*+1/2; (vi) *x*+1, −*y*+3/2, *z*−1/2; (vii) *x*+1, *y*, *z*; (viii) *x*, −*y*+3/2, *z*−1/2; (ix) *x*, *y*−1, *z*; (x) *x*+1, *y*−1, *z*; (xi) *x*, −*y*+1/2, *z*−1/2; (xii) −*x*+1, −*y*+1, −*z*; (xiii) *x*−1, *y*+1, *z*; (xiv) *x*−1, *y*, *z*; (xv) *x*, *y*+1, *z*; (xvi) *x*, −*y*+1/2, *z*+1/2; (xvii) *x*, −*y*+3/2, *z*+1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
F7—H1···F6^{xviii}	0.79 (4)	1.54 (4)	2.326 (2)	176 (4)
F8a—H2···F4	0.79 (4)	1.62 (4)	2.402 (2)	168 (4)
F8b—H2···F4	0.84 (4)	1.62 (4)	2.326 (8)	139 (4)

Symmetry codes: (xviii) −*x*+1, −*y*+1, −*z*+1.

Fig. 1

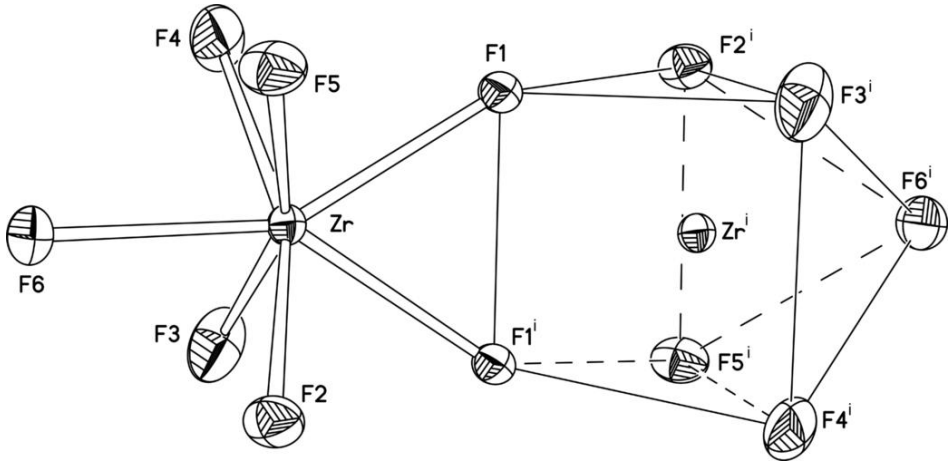


Fig. 2

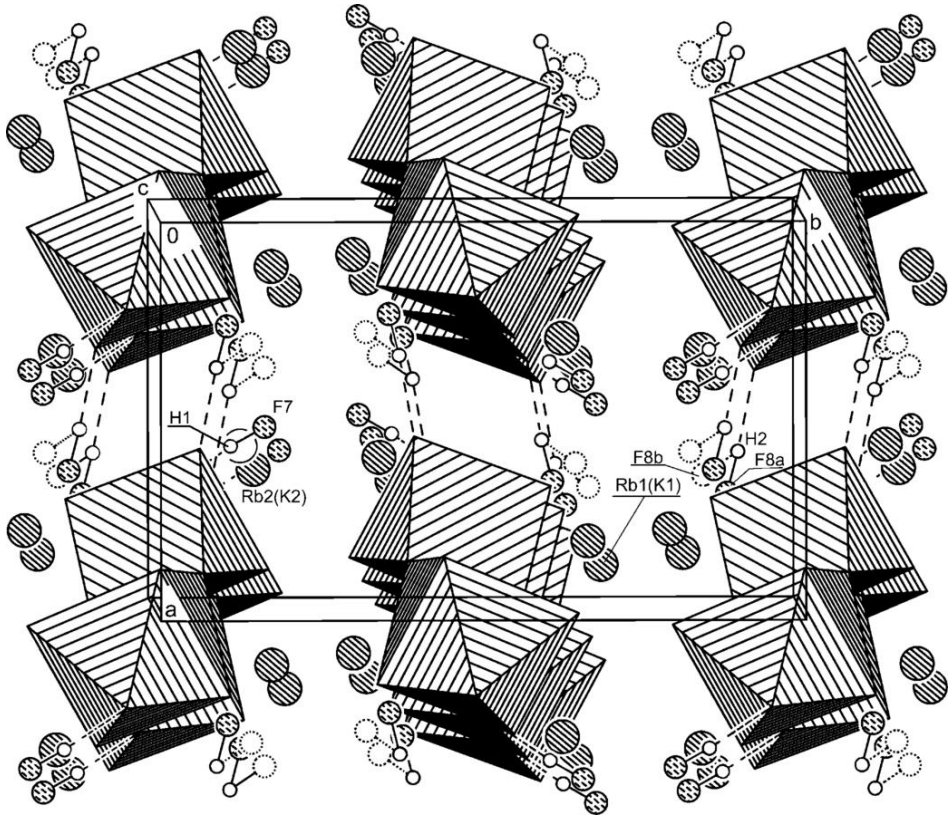
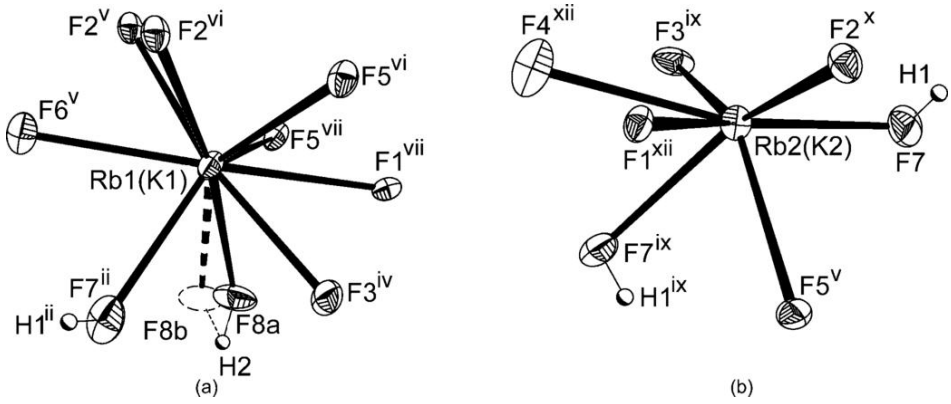


Fig. 3


F2v
F2vi
F5vi
F6v
F5vii
F1vii
Rb1(K1)
F7ii
H1ii
F8b
F8a
H2
F3iv
(a)
F4xii
F3ix
F2x
H1
F1xii
Rb2(K2)
F7
F7ix
H1ix
F5v
(b)