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# Syntheses, Raman Spectroscopy and Crystal Structures of Alkali Hexa-fluoridorhenates(IV) Revisited

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# Syntheses, Raman spectroscopy and crystal structures of alkali hexafluoridorhenates(IV) revisited

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The $A_2[ReF_6]$ ($A$ = K, Rb and Cs) salts are isotypic and crystallize in the trigonal space group type $P\overline{3}m1$, adopting the $K_2[GeF_6]$ structure type. Common to all $A_2[ReF_6]$ structures are slightly distorted octahedral $[ReF_6]^{2-}$ anions with an average Re—F bond length of 1.951 (8) Å. In those salts, symmetry lowering on the local $[ReF_6]^{2-}$ anions from $O_h$ (free anion) to $D_{3d}$ (solid-state structure) occur. The distortions of the $[ReF_6]^{2-}$ anions, as observed in their Raman spectra, are correlated to the size of the counter-cations.

## 1. Chemical context

The hexafluoridorhenate(IV) anion has been known for 80 years but its chemistry is understudied with respect to the heavier halogen analogs (Ruff & Kwasnik, 1934). The scarcity of $[ReF_6]^{2-}$ salts is attributed to the difficulties in their preparation and purification. $K_2[ReF_6]$ was the first hexafluoridorhenate(IV) salt to be reported; it was prepared from the solid-state melting reaction (SSMR) of $K_2[ReBr_6]$ with $KHF_2$ (Ruff & Kwasnik, 1934). Almost two decades later, ten salts comprising the $[ReF_6]^{2-}$ anion and with different counter-cations ($Rb^+$, $Cs^+$, $PPh_4^+$ (Ph = $C_6H_5$), $[Ni(NH_3)_6]^{2+}$, $[Co(NH_3)_6]^{3+}$, $\{[Co(NH_3)_6](NO_3)\}^{2+}$, $\{[Cr(NH_3)_6](NO_3)\}^{2+}$, $[Co(NH_3)_5Cl]^{2+}$, $[Cr(NH_3)_5Cl]^{2+}$, $[Co(NH_3)_4(CO_3)]^{2+}$) had been reported (Peacock, 1956; Weise, 1956; Pedersen *et al.*, 2014; Brauer & Allardt, 1962). Those salts were prepared by cation metathesis starting from $(NH_4)_2[ReF_6]$ or $K_2[ReF_6]$. However, the synthetic procedure to prepare $(NH_4)_2[ReF_6]$ or $K_2[ReF_6]$ was not explained in detail. To date, only the structures of two $[ReF_6]^{2-}$ salts have been characterized by single crystal X-ray diffraction (SCXRD): $K_2[ReF_6]$ (measured at 292 K) and $(PPh_4)_2[ReF_6]\cdot H_2O$ (measured at 122 K) (Clark & Russell, 1978; Pedersen *et al.*, 2014). Similarly, the synthesis of the $K_2[TcF_6]$ congener, which was reported in 1963, involves the SSMR of $K_2[TcBr_6]$ with $KHF_2$ followed by an aqueous work-up (Schwochau & Herr, 1963). However, $[TcF_6]^{2-}$ salts have been reinvestigated recently (Balasekaran *et al.*, 2013), and various routes for the different salts of $A_2[TcF_6]$ [$A$ = Na, K, Rb, Cs and $N(CH_3)_4$] were reported. These salts were characterized by Raman and IR spectroscopy and by SCXRD. The $A_2[ReF_6]$ salts could serve as suitable precursors to explore the chemistry of rhenium in the oxidation state IV.

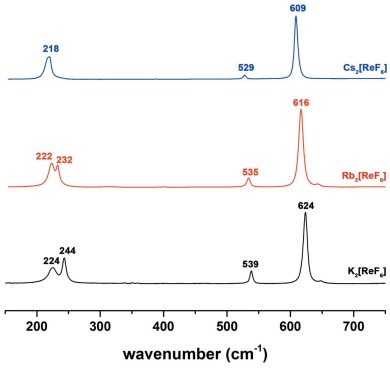

**Table 1**
Structural details (Å, °) of the $[ReF_6]^{2-}$ anion in this study and of the related anion in $[TcF_6]^{2-}$ salts[a].

| | $M$—F, $M$ = Re | F—$M$—F, $M$ = Re | $M$—F, $M$ = Tc | F—$M$—F, $M$ = Tc |
|---|---|---|---|---|
| $K_2[MF_6]$ | 1.948 (3) | 86.08 (12), 93.92 (12), 180 | 1.928 (6) | 86.93 (5), 93.07 (5), 180 |
| $Rb_2[MF_6]$ | 1.945 (7) | 86.5 (3), 93.5 (3), 180 | 1.933 (3) | 87.2 (2), 92.8 (2), 180 |
| $Cs_2[MF_6]$ | 1.9594 (18) | 86.86 (7), 93.14 (7), 180 | 1.935 (5) | 87.8 (2), 92.2 (2), 180 |

Note: (*a*) Balasekaran *et al.* (2013).

Here, we revisited the synthesis of $A_2[ReF_6]$ ($A$ = K, Rb, Cs) salts and report their crystal structures determined from single crystal data, and their Raman spectra.

## 2. Structural commentary

The title alkaline metal salts $A_2[ReF_6]$ ($A$ = K, Rb, Cs) are isotypic. They adopt the $K_2[GeF_6]$ structure type (Hoard & Vincent, 1939) and crystallize in the trigonal space group type $P\overline{3}m1$ (Table 1), just like the related $A_2[TcF_6]$ ($A$ = K, Rb, Cs) compounds (Balasekaran *et al.*, 2013). Selected bond lengths and angles of the series of $[ReF_6]^{2-}$ anions of the present work and the reported $[TcF_6]^{2-}$ salts (Balasekaran *et al.*, 2013) are presented in Table 1. Representative for all other title compounds, the $[ReF_6]^{2-}$ anion of the $Cs_2[ReF_6]$ salt is given in Fig. 1. The $Re^{IV}$ atom is located on a position with site symmetry $\overline{3}m$. (Wyckoff position 1*a*) at the origin of the trigonal unit cell. The six symmetry-related fluorine ligands form a slightly distorted octahedral coordination sphere around the rhenium(IV) atom. The Re—F bond lengths for the K, Rb, and Cs salts of $[ReF_6]^{2-}$, 1.948 (3), 1.945 (7) and 1.9594 (18) Å, respectively, are longer than the Tc—F bond lengths for the congener K, Rb, and Cs salts of $[TcF_6]^{2-}$, 1.928 (1), 1.933 (3), and 1.935 (5) Å, respectively (Balasekaran *et al.*, 2013).

In $A_2[ReF_6]$ ($A$ = $K^+$, $Rb^+$, $Cs^+$), each cation is located on a position with site symmetry 3*m*. (Wyckoff position 2*d*) and is surrounded by twelve neighboring F atoms resulting in a [3 + 6 + 3] arrangement with three groups of fluoride ligands with distances of 3.0955 (19) Å (three of such), 3.1655 (6) Å (six of such), and 3.224 (2) Å (three of such) for the $Cs^+$ salt as a representative of the three $[ReF_6]^{2-}$ salts. These bond-length distributions are also found in the $K^+$ and $Rb^+$ salts of the $[ReF_6]^{2-}$ complexes. This correlates well and confirms that $A_2[ReF_6]$ salts are isotypic with $K_2[GeF_6]$ and the congener $A_2[TcF_6]$ ($A$ = $K^+$, $Rb^+$, $Cs^+$) (Balasekaran *et al.*, 2013; Hoard & Vincent, 1939). In comparison with the previous structure determination of $K_2[ReF_6]$ (Clark & Russell, 1978), the current redetermination resulted in better reliability factors, together with a more precise determination of lattice parameters and atomic coordinates.

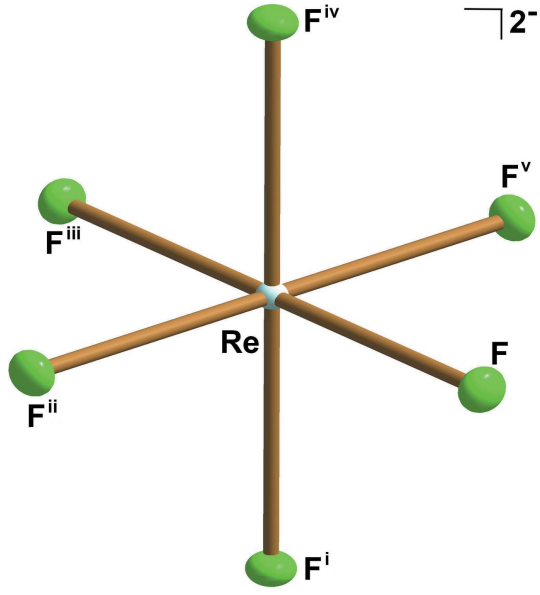


**Figure 1**
Representation of the $[ReF_6]^{2-}$ anion in $Cs_2[ReF_6]$. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x, -y, -z$; (ii) $x-y, x, -z$; (iii) $-x+y, -x, z$; (iv) $-y, x-y, z$; (v) $y, -x+y, -z$.]

## 3. Raman spectroscopy

As reported previously for $K_2[ReF_6]$ and $A_2[TcF_6]$ ($A$ = K, Rb, Cs) (Bettinelli *et al.*, 1987; Balasekaran *et al.*, 2013), the $[ReF_6]^{2-}$ anions are compressed along the crystallographic *c* axis, thus lowering the ideal molecular symmetry of the $[ReF_6]^{2-}$ anions from $O_h$ to $D_{3d}$ in the solid state. The representive unit-cell plot of $Cs_2[ReF_6]$ is given in Fig. 2. The effect of symmetry lowering among the alkali metal salts of $[TcF_6]^{2-}$ and its correlation with the vibrational spectra are

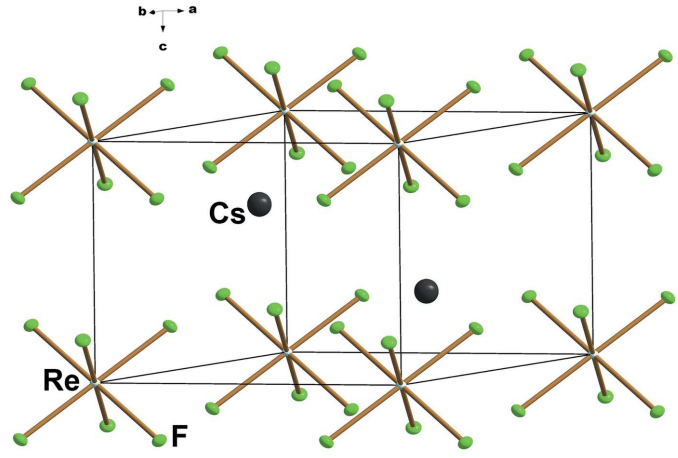


**Figure 2**
A packing diagram of $Cs_2[ReF_6]$. Displacement ellipsoids are drawn at the 50% probability level.

**Table 2**
Experimental details.

| | $K_2[ReF_6]$ | $Rb_2[ReF_6]$ | $Cs_2[ReF_6]$ |
|---|---|---|---|
| Crystal data | | | |
| $M_r$ | 378.40 | 471.14 | 566.02 |
| Crystal system, space group | Trigonal, $P\bar{3}m1$ | Trigonal, $P\bar{3}m1$ | Trigonal, $P\bar{3}m1$ |
| Temperature (K) | 100 | 100 | 100 |
| $a$, $c$ (Å) | 5.834 (2), 4.546 (2) | 5.9926 (13), 4.7177 (10) | 6.268 (1), 4.931 (1) |
| $V$ (Å$^3$) | 134.00 (11) | 146.72 (7) | 167.77 (6) |
| $Z$ | 1 | 1 | 1 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 24.26 | 37.22 | 28.83 |
| Crystal size (mm) | 0.10 × 0.07 × 0.04 | 0.08 × 0.07 × 0.04 | 0.25 × 0.12 × 0.11 |
| Data collection | | | |
| Diffractometer | Bruker D8 QUEST | Bruker D8 QUEST | Bruker D8 QUEST |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2015) | Numerical (*SADABS*; Bruker, 2015) | Multi-scan (*SADABS*; Bruker, 2015) |
| $T_{min}$, $T_{max}$ | 0.14, 0.44 | 0.11, 0.30 | 0.05, 0.15 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 2148, 180, 180 | 1526, 115, 111 | 2683, 218, 218 |
| $R_{int}$ | 0.054 | 0.073 | 0.040 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.714 | 0.593 | 0.713 |
| Refinement | | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.016, 0.041, 1.13 | 0.027, 0.074, 1.30 | 0.013, 0.036, 1.25 |
| No. of reflections | 180 | 115 | 218 |
| No. of parameters | 12 | 12 | 13 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 1.80, −1.37 | 1.91, −1.36 | 0.68, −2.92 |

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXS* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 2007) and *publCIF* (Westrip, 2010).

well described (Balasekaran *et al.*, 2013). Here, a similar trend occurs for the $A_2[ReF_6]$ series ($A$ = K, Rb, Cs; Fig. 3). In the case of $K_2[ReF_6]$, the Raman spectrum exhibits four bands at 624, 539, 244 and 224 cm$^{-1}$. The latter two vibrations correspond to the $F_{2g}$ band split due to the symmetry lowering. In the Raman spectra of $A_2[MF_6]$ complexes ($A$ = K, Rb, Cs; $M$ = Tc, Re), the $F_{2g}$ splitting decreases from $K_2[ReF_6]$ to $Cs_2[ReF_6]$ due to differences in $M$—F bond length. Furthermore, the slight increase of $M$—F bond lengths from $K_2[MF_6]$ to $Cs_2[MF_6]$ are well represented in the Raman spectra which causes the Raman bands to shift to lower wavenumbers.

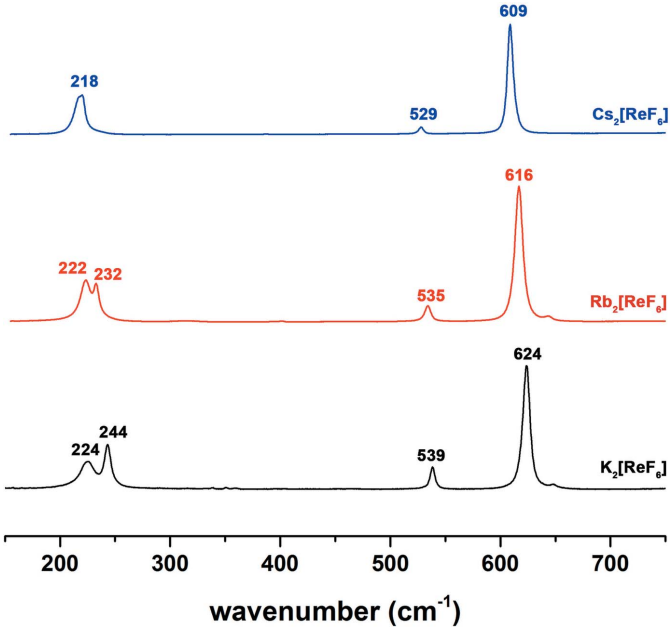


**Figure 3**
Raman spectra of $A_2[ReF_6]$ ($A$ = K, Rb, Cs).

## 4. Synthesis and crystallization

Ammonium perrhenate, ammonium bifluoride, potassium fluoride, rubidium fluoride, cesium fluoride, and hydrobromic acid (48%) were purchased from Sigma Aldrich and used without any further purification. This work was performed in a well-ventilated fume hood due to the corrosive nature of bifluoride. $K_2[ReBr_6]$ was prepared as described in the literature (Watt *et al.*, 1963), and the detailed synthesis of $A_2[ReF_6]$ ($A$ = K, Rb, Cs) is described below. Single crystals of $A_2[ReF_6]$ ($A$ = K, Rb, Cs) were obtained by slow evaporation at room temperature of an aqueous solution of the respective salt.

**Synthesis of $K_2[ReF_6]$**

$K_2[ReF_6]$ was prepared by melting $K_2[ReBr_6]$ (2 g, 2.69 mmol) with excess $KHF_2$ (14 g, 0.18 mol) in a nickel crucible at 673 K for 30 min in a box furnace. The resulting greyish solid product formed was allowed to cool to room temperature and was washed first with MeOH (4 × 10 ml). Subsequently, the product was washed with several aliquots of an $H_2O$/MeOH mixture (3 × 5 ml, 1:4 volume ratios) and centrifuged. The pink solid obtained was dissolved in warm water (5–10 ml, 353 K) and evaporated slowly at room temperature. The resultant pink crystals of $K_2[ReF_6]$ were recrystallized from warm water (5 ml, 353 K) and colorless

crystals of $K_2[ReF_6]$ were obtained. Yield: 661 mg, 1.7 mmol (65%). IR (KBr, $cm^{-1}$): 518, 484 sh (Re—F).

**Syntheses of $A_2[ReF_6]$ ($A$ = Rb, Cs) salts**

$K_2[ReF_6]$ (151 mg, 0.4 mmol) was dissolved in 4 ml of hot water (353 K). $M$F ($M$ = Rb, Cs) (0.8 mmol) dissolved in 1 ml of hot water (353 K) was added dropwise. The solution was allowed to evaporate slowly at room temperature. Crystals of $Rb_2[ReF_6]$ and $Cs_2[ReF_6]$ were formed in 24 h and washed first with cold water (3 × 2 ml) to remove other fluoride impurities followed by isopropanol (3 × 1 ml), and diethyl ether (3 × 1 ml). $Rb_2[ReF_6]$ yield: 156 mg, 0.33 mmol (83%). IR (KBr, $cm^{-1}$): 521 (Re—F). $Cs_2[ReF_6]$ yield: 175 mg, 0.276 mmol (77%). IR (KBr, $cm^{-1}$): 507, 480 sh (Re—F).

IR spectra were measured on a Shimadzu IR Affinity-1 spectrometer between 400 and 4000 $cm^{-1}$. Raman spectra were recorded on a HORIBA T64000 triple spectrometer operating at 30 mW in subtractive mode. The spectra were taken from pure single crystals at room temperature using the 514.5 nm (Kr/Ar) laser line.

## 5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

## Acknowledgements

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# supporting information

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## Syntheses, Raman spectroscopy and crystal structures of alkali hexafluoridorhenates(IV) revisited

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### Computing details

For all structures, data collection: *APEX3* (Bruker, 2015); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2007); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### Dipotassium hexafluoridorhenate(IV) (SMB_K2ReF6_1)

*Crystal data*

$K_2[ReF_6]$
$M_r$ = 378.40
Trigonal, $P\overline{3}m1$
$a$ = 5.834 (2) Å
$c$ = 4.546 (2) Å
$V$ = 134.00 (11) Å$^3$
$Z$ = 1
$F$(000) = 167
$D_x$ = 4.689 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 2236 reflections
$\theta$ = 4.0–30.5°
$\mu$ = 24.26 mm$^{-1}$
$T$ = 100 K
Hexagonal, translucent colourless
0.10 × 0.07 × 0.04 mm

*Data collection*

Bruker D8 QUEST diffractometer
Radiation source: sealed tube, Siemens KFFMo2K-90
Curved graphite monochromator
Detector resolution: 8.3333 pixels mm$^{-1}$
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2015)
$T_{min}$ = 0.14, $T_{max}$ = 0.44
2148 measured reflections
180 independent reflections
180 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.054
$\theta_{max}$ = 30.5°, $\theta_{min}$ = 4.0°
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -6 \rightarrow 6$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.016
$wR(F^2)$ = 0.041
$S$ = 1.13
180 reflections
12 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0194P)^2 + 0.517P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 1.80 e Å$^{-3}$
$\Delta\rho_{min}$ = −1.37 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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Re1 | 0 | 0 | 0 | 0.00863 (14) |
| F1 | 0.3254 (6) | 0.1627 (3) | 0.2299 (6) | 0.0137 (5) |
| K1 | 0.3333 | 0.6667 | 0.2955 (4) | 0.0111 (3) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Re1 | 0.00883 (16) | 0.00883 (16) | 0.0082 (2) | 0.00441 (8) | 0 | 0 |
| F1 | 0.0119 (13) | 0.0162 (10) | 0.0117 (12) | 0.0060 (6) | −0.0012 (10) | −0.0006 (5) |
| K1 | 0.0118 (5) | 0.0118 (5) | 0.0096 (6) | 0.0059 (2) | 0 | 0 |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Re1—F1 | 1.948 (3) | F1—K1$^{viii}$ | 2.9325 (10) |
| Re1—F1$^{i}$ | 1.948 (3) | F1—K1$^{vi}$ | 2.946 (3) |
| Re1—F1$^{ii}$ | 1.948 (3) | K1—F1$^{xi}$ | 2.762 (3) |
| Re1—F1$^{iii}$ | 1.948 (3) | K1—F1$^{x}$ | 2.762 (3) |
| Re1—F1$^{iv}$ | 1.948 (3) | K1—F1$^{xii}$ | 2.762 (3) |
| Re1—F1$^{v}$ | 1.948 (3) | K1—F1$^{xiii}$ | 2.9325 (11) |
| Re1—K1$^{i}$ | 3.6263 (13) | K1—F1$^{xiv}$ | 2.9325 (10) |
| Re1—K1$^{vi}$ | 3.6263 (13) | K1—F1$^{iv}$ | 2.9325 (11) |
| Re1—K1$^{vii}$ | 3.6263 (13) | K1—F1$^{xv}$ | 2.9325 (11) |
| Re1—K1 | 3.6263 (13) | K1—F1$^{xvi}$ | 2.9325 (11) |
| Re1—K1$^{viii}$ | 3.6263 (13) | K1—F1$^{xvii}$ | 2.946 (3) |
| Re1—K1$^{ix}$ | 3.6263 (13) | K1—F1$^{ii}$ | 2.946 (3) |
| F1—K1$^{x}$ | 2.762 (3) | K1—F1$^{vi}$ | 2.946 (3) |
| F1—K1 | 2.9325 (11) | | |
| | | | |
| F1—Re1—F1$^{i}$ | 180.0 | K1—F1—K1$^{viii}$ | 168.22 (13) |
| F1—Re1—F1$^{ii}$ | 86.08 (12) | Re1—F1—K1$^{vi}$ | 93.38 (11) |
| F1$^{i}$—Re1—F1$^{ii}$ | 93.92 (12) | K1$^{x}$—F1—K1$^{vi}$ | 105.55 (10) |
| F1—Re1—F1$^{iii}$ | 93.92 (12) | K1—F1—K1$^{vi}$ | 94.27 (6) |
| F1$^{i}$—Re1—F1$^{iii}$ | 86.08 (12) | K1$^{viii}$—F1—K1$^{vi}$ | 94.27 (6) |
| F1$^{ii}$—Re1—F1$^{iii}$ | 180.00 (19) | F1$^{xi}$—K1—F1$^{x}$ | 65.46 (11) |
| F1—Re1—F1$^{iv}$ | 93.92 (12) | F1$^{xi}$—K1—F1$^{xii}$ | 65.46 (11) |
| F1$^{i}$—Re1—F1$^{iv}$ | 86.08 (12) | F1$^{x}$—K1—F1$^{xii}$ | 65.46 (11) |
| F1$^{ii}$—Re1—F1$^{iv}$ | 86.08 (12) | F1$^{xi}$—K1—F1$^{xiii}$ | 62.44 (10) |
| F1$^{iii}$—Re1—F1$^{iv}$ | 93.92 (12) | F1$^{x}$—K1—F1$^{xiii}$ | 127.81 (6) |
| F1—Re1—F1$^{v}$ | 86.08 (12) | F1$^{xii}$—K1—F1$^{xiii}$ | 95.05 (6) |

| | | | |
|---|---|---|---|
| F1$^{i}$—Re1—F1$^{v}$ | 93.92 (12) | F1$^{xi}$—K1—F1$^{xiv}$ | 62.44 (10) |
| F1$^{ii}$—Re1—F1$^{v}$ | 93.92 (12) | F1$^{x}$—K1—F1$^{xiv}$ | 95.05 (6) |
| F1$^{iii}$—Re1—F1$^{v}$ | 86.08 (12) | F1$^{xii}$—K1—F1$^{xiv}$ | 127.81 (6) |
| F1$^{iv}$—Re1—F1$^{v}$ | 180.00 (7) | F1$^{xiii}$—K1—F1$^{xiv}$ | 58.10 (11) |
| F1—Re1—K1$^{i}$ | 126.206 (14) | F1$^{xi}$—K1—F1$^{iv}$ | 95.05 (6) |
| F1$^{i}$—Re1—K1$^{i}$ | 53.794 (14) | F1$^{x}$—K1—F1$^{iv}$ | 127.81 (6) |
| F1$^{ii}$—Re1—K1$^{i}$ | 125.81 (9) | F1$^{xii}$—K1—F1$^{iv}$ | 62.44 (10) |
| F1$^{iii}$—Re1—K1$^{i}$ | 54.19 (9) | F1$^{xiii}$—K1—F1$^{iv}$ | 61.22 (12) |
| F1$^{iv}$—Re1—K1$^{i}$ | 126.205 (14) | F1$^{xiv}$—K1—F1$^{iv}$ | 118.98 (2) |
| F1$^{v}$—Re1—K1$^{i}$ | 53.795 (14) | F1$^{xi}$—K1—F1$^{xv}$ | 95.05 (6) |
| F1—Re1—K1$^{vi}$ | 54.19 (9) | F1$^{x}$—K1—F1$^{xv}$ | 62.44 (10) |
| F1$^{i}$—Re1—K1$^{vi}$ | 125.81 (9) | F1$^{xii}$—K1—F1$^{xv}$ | 127.81 (6) |
| F1$^{ii}$—Re1—K1$^{vi}$ | 53.794 (14) | F1$^{xiii}$—K1—F1$^{xv}$ | 118.98 (2) |
| F1$^{iii}$—Re1—K1$^{vi}$ | 126.206 (14) | F1$^{xiv}$—K1—F1$^{xv}$ | 61.22 (12) |
| F1$^{iv}$—Re1—K1$^{vi}$ | 126.205 (14) | F1$^{iv}$—K1—F1$^{xv}$ | 168.22 (13) |
| F1$^{v}$—Re1—K1$^{vi}$ | 53.795 (14) | F1$^{xi}$—K1—F1$^{xvi}$ | 127.81 (6) |
| K1$^{i}$—Re1—K1$^{vi}$ | 107.11 (3) | F1$^{x}$—K1—F1$^{xvi}$ | 62.44 (10) |
| F1—Re1—K1$^{vii}$ | 125.81 (9) | F1$^{xii}$—K1—F1$^{xvi}$ | 95.05 (6) |
| F1$^{i}$—Re1—K1$^{vii}$ | 54.19 (9) | F1$^{xiii}$—K1—F1$^{xvi}$ | 168.22 (13) |
| F1$^{ii}$—Re1—K1$^{vii}$ | 126.206 (14) | F1$^{xiv}$—K1—F1$^{xvi}$ | 118.98 (2) |
| F1$^{iii}$—Re1—K1$^{vii}$ | 53.794 (14) | F1$^{iv}$—K1—F1$^{xvi}$ | 118.98 (2) |
| F1$^{iv}$—Re1—K1$^{vii}$ | 53.795 (14) | F1$^{xv}$—K1—F1$^{xvi}$ | 58.10 (11) |
| F1$^{v}$—Re1—K1$^{vii}$ | 126.205 (14) | F1$^{xi}$—K1—F1 | 127.81 (6) |
| K1$^{i}$—Re1—K1$^{vii}$ | 72.89 (3) | F1$^{x}$—K1—F1 | 95.05 (6) |
| K1$^{vi}$—Re1—K1$^{vii}$ | 180.0 | F1$^{xii}$—K1—F1 | 62.44 (10) |
| F1—Re1—K1 | 53.794 (14) | F1$^{xiii}$—K1—F1 | 118.98 (2) |
| F1$^{i}$—Re1—K1 | 126.206 (14) | F1$^{xiv}$—K1—F1 | 168.22 (13) |
| F1$^{ii}$—Re1—K1 | 54.19 (9) | F1$^{iv}$—K1—F1 | 58.09 (11) |
| F1$^{iii}$—Re1—K1 | 125.81 (9) | F1$^{xv}$—K1—F1 | 118.98 (2) |
| F1$^{iv}$—Re1—K1 | 53.794 (14) | F1$^{xvi}$—K1—F1 | 61.22 (11) |
| F1$^{v}$—Re1—K1 | 126.206 (14) | F1$^{xi}$—K1—F1$^{xvii}$ | 105.55 (10) |
| K1$^{i}$—Re1—K1 | 180.0 | F1$^{x}$—K1—F1$^{xvii}$ | 144.70 (4) |
| K1$^{vi}$—Re1—K1 | 72.89 (3) | F1$^{xii}$—K1—F1$^{xvii}$ | 144.70 (4) |
| K1$^{vii}$—Re1—K1 | 107.11 (3) | F1$^{xiii}$—K1—F1$^{xvii}$ | 53.80 (10) |
| F1—Re1—K1$^{viii}$ | 53.795 (14) | F1$^{xiv}$—K1—F1$^{xvii}$ | 53.80 (10) |
| F1$^{i}$—Re1—K1$^{viii}$ | 126.205 (14) | F1$^{iv}$—K1—F1$^{xvii}$ | 85.73 (6) |
| F1$^{ii}$—Re1—K1$^{viii}$ | 126.206 (14) | F1$^{xv}$—K1—F1$^{xvii}$ | 85.73 (6) |
| F1$^{iii}$—Re1—K1$^{viii}$ | 53.794 (14) | F1$^{xvi}$—K1—F1$^{xvii}$ | 114.69 (6) |
| F1$^{iv}$—Re1—K1$^{viii}$ | 125.81 (9) | F1—K1—F1$^{xvii}$ | 114.69 (6) |
| F1$^{v}$—Re1—K1$^{viii}$ | 54.19 (9) | F1$^{xi}$—K1—F1$^{ii}$ | 144.70 (4) |
| K1$^{i}$—Re1—K1$^{viii}$ | 72.90 (3) | F1$^{x}$—K1—F1$^{ii}$ | 144.70 (4) |
| K1$^{vi}$—Re1—K1$^{viii}$ | 72.90 (3) | F1$^{xii}$—K1—F1$^{ii}$ | 105.55 (10) |
| K1$^{vii}$—Re1—K1$^{viii}$ | 107.10 (3) | F1$^{xiii}$—K1—F1$^{ii}$ | 85.73 (6) |
| K1—Re1—K1$^{viii}$ | 107.10 (3) | F1$^{xiv}$—K1—F1$^{ii}$ | 114.69 (6) |
| F1—Re1—K1$^{ix}$ | 126.205 (14) | F1$^{iv}$—K1—F1$^{ii}$ | 53.80 (10) |
| F1$^{i}$—Re1—K1$^{ix}$ | 53.795 (14) | F1$^{xv}$—K1—F1$^{ii}$ | 114.69 (6) |
| F1$^{ii}$—Re1—K1$^{ix}$ | 53.794 (14) | F1$^{xvi}$—K1—F1$^{ii}$ | 85.73 (6) |
| F1$^{iii}$—Re1—K1$^{ix}$ | 126.206 (14) | F1—K1—F1$^{ii}$ | 53.80 (10) |

| | | | |
|---|---|---|---|
| F1$^{iv}$—Re1—K1$^{ix}$ | 54.19 (9) | F1$^{xvii}$—K1—F1$^{ii}$ | 60.91 (10) |
| F1$^{v}$—Re1—K1$^{ix}$ | 125.81 (9) | F1$^{xi}$—K1—F1$^{vi}$ | 144.70 (4) |
| K1$^{i}$—Re1—K1$^{ix}$ | 107.10 (3) | F1$^{x}$—K1—F1$^{vi}$ | 105.55 (10) |
| K1$^{vi}$—Re1—K1$^{ix}$ | 107.10 (3) | F1$^{xii}$—K1—F1$^{vi}$ | 144.70 (4) |
| K1$^{vii}$—Re1—K1$^{ix}$ | 72.90 (3) | F1$^{xiii}$—K1—F1$^{vi}$ | 114.69 (6) |
| K1—Re1—K1$^{ix}$ | 72.90 (3) | F1$^{xiv}$—K1—F1$^{vi}$ | 85.73 (6) |
| K1$^{viii}$—Re1—K1$^{ix}$ | 180.0 | F1$^{iv}$—K1—F1$^{vi}$ | 114.69 (6) |
| Re1—F1—K1$^{x}$ | 161.08 (14) | F1$^{xv}$—K1—F1$^{vi}$ | 53.80 (10) |
| Re1—F1—K1 | 93.79 (6) | F1$^{xvi}$—K1—F1$^{vi}$ | 53.80 (10) |
| K1$^{x}$—F1—K1 | 84.95 (6) | F1—K1—F1$^{vi}$ | 85.73 (6) |
| Re1—F1—K1$^{viii}$ | 93.79 (6) | F1$^{xvii}$—K1—F1$^{vi}$ | 60.91 (10) |
| K1$^{x}$—F1—K1$^{viii}$ | 84.95 (6) | F1$^{ii}$—K1—F1$^{vi}$ | 60.91 (10) |

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

## Dirubidium hexafluoridorhenate(IV) (SMB_Rb2ReF6_j)

*Crystal data*

$Rb_2[ReF_6]$
$M_r$ = 471.14
Trigonal, $P\bar{3}m1$
$a$ = 5.9926 (13) Å
$c$ = 4.7177 (10) Å
$V$ = 146.72 (7) Å$^3$
$Z$ = 1
$F$(000) = 203
$D_x$ = 5.332 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 1612 reflections
$\theta$ = 3.9–28.3°
$\mu$ = 37.22 mm$^{-1}$
$T$ = 100 K
Hexagonal plate, translucent colourless
0.08 × 0.07 × 0.04 mm

*Data collection*

Bruker D8 QUEST diffractometer
Radiation source: sealed tube, Siemens KFFMo2K-90
Curved graphite monochromator
Detector resolution: 8.3333 pixels mm$^{-1}$
$\varphi$ and $\omega$ scans
Absorption correction: numerical (*SADABS*; Bruker, 2015)
$T_{min}$ = 0.11, $T_{max}$ = 0.30
1526 measured reflections
115 independent reflections
111 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.073
$\theta_{max}$ = 24.9°, $\theta_{min}$ = 3.9°
$h = -7 \rightarrow 7$
$k = -7 \rightarrow 7$
$l = -5 \rightarrow 5$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.074
$S$ = 1.30
115 reflections
12 parameters
0 restraints
Primary atom site location: heavy-atom method
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0175P)^2 + 3.5548P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.91 e Å$^{-3}$
$\Delta\rho_{min}$ = −1.36 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)*

| | $x$ | $y$ | $z$ | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Re1 | 0 | 0 | 0 | 0.0157 (5) |
| F1 | 0.3151 (14) | 0.1576 (7) | 0.2231 (15) | 0.0151 (17) |
| Rb1 | 0.3333 | 0.6667 | 0.2971 (4) | 0.0138 (6) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Re1 | 0.0133 (6) | 0.0133 (6) | 0.0205 (8) | 0.0066 (3) | 0 | 0 |
| F1 | 0.015 (4) | 0.017 (3) | 0.012 (3) | 0.0077 (19) | 0.001 (3) | 0.0007 (14) |
| Rb1 | 0.0131 (8) | 0.0131 (8) | 0.0152 (12) | 0.0065 (4) | 0 | 0 |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Re1—F1$^{i}$ | 1.945 (7) | F1—Rb1$^{viii}$ | 3.0181 (11) |
| Re1—F1$^{ii}$ | 1.945 (7) | F1—Rb1$^{vi}$ | 3.058 (7) |
| Re1—F1$^{iii}$ | 1.945 (7) | Rb1—F1$^{xi}$ | 2.907 (7) |
| Re1—F1$^{iv}$ | 1.945 (7) | Rb1—F1$^{x}$ | 2.907 (7) |
| Re1—F1$^{v}$ | 1.945 (7) | Rb1—F1$^{xii}$ | 2.907 (7) |
| Re1—F1 | 1.945 (7) | Rb1—F1$^{xiii}$ | 3.0181 (11) |
| Re1—Rb1$^{i}$ | 3.7330 (10) | Rb1—F1$^{xiv}$ | 3.0181 (11) |
| Re1—Rb1$^{vi}$ | 3.7330 (11) | Rb1—F1$^{v}$ | 3.0181 (11) |
| Re1—Rb1$^{vii}$ | 3.7330 (11) | Rb1—F1$^{xv}$ | 3.0181 (11) |
| Re1—Rb1 | 3.7330 (10) | Rb1—F1$^{xvi}$ | 3.0181 (11) |
| Re1—Rb1$^{viii}$ | 3.7330 (11) | Rb1—F1$^{xvii}$ | 3.058 (7) |
| Re1—Rb1$^{ix}$ | 3.7330 (11) | Rb1—F1$^{ii}$ | 3.058 (7) |
| F1—Rb1$^{x}$ | 2.907 (7) | Rb1—F1$^{vi}$ | 3.058 (7) |
| F1—Rb1 | 3.0181 (11) | | |
| | | | |
| F1$^{i}$—Re1—F1$^{ii}$ | 93.5 (3) | Rb1—F1—Rb1$^{viii}$ | 166.2 (3) |
| F1$^{i}$—Re1—F1$^{iii}$ | 86.5 (3) | Re1—F1—Rb1$^{vi}$ | 93.9 (2) |
| F1$^{ii}$—Re1—F1$^{iii}$ | 180.0 (3) | Rb1$^{x}$—F1—Rb1$^{vi}$ | 104.5 (2) |
| F1$^{i}$—Re1—F1$^{iv}$ | 93.5 (3) | Rb1—F1—Rb1$^{vi}$ | 94.26 (14) |
| F1$^{ii}$—Re1—F1$^{iv}$ | 93.5 (3) | Rb1$^{viii}$—F1—Rb1$^{vi}$ | 94.26 (14) |
| F1$^{iii}$—Re1—F1$^{iv}$ | 86.5 (3) | F1$^{xi}$—Rb1—F1$^{x}$ | 65.8 (2) |
| F1$^{i}$—Re1—F1$^{v}$ | 86.5 (3) | F1$^{xi}$—Rb1—F1$^{xii}$ | 65.8 (2) |
| F1$^{ii}$—Re1—F1$^{v}$ | 86.5 (3) | F1$^{x}$—Rb1—F1$^{xii}$ | 65.8 (2) |
| F1$^{iii}$—Re1—F1$^{v}$ | 93.5 (3) | F1$^{xi}$—Rb1—F1$^{xiii}$ | 62.7 (2) |
| F1$^{iv}$—Re1—F1$^{v}$ | 180.0 | F1$^{x}$—Rb1—F1$^{xiii}$ | 128.31 (8) |
| F1$^{i}$—Re1—F1 | 180.0 | F1$^{xii}$—Rb1—F1$^{xiii}$ | 96.30 (14) |

| | | | |
|---|---|---|---|
| F1$^{ii}$—Re1—F1 | 86.5 (3) | F1$^{xi}$—Rb1—F1$^{xiv}$ | 62.7 (2) |
| F1$^{iii}$—Re1—F1 | 93.5 (3) | F1$^{x}$—Rb1—F1$^{xiv}$ | 96.30 (14) |
| F1$^{iv}$—Re1—F1 | 86.5 (3) | F1$^{xii}$—Rb1—F1$^{xiv}$ | 128.31 (8) |
| F1$^{v}$—Re1—F1 | 93.5 (3) | F1$^{xiii}$—Rb1—F1$^{xiv}$ | 56.0 (3) |
| F1$^{i}$—Re1—Rb1$^{i}$ | 53.64 (2) | F1$^{xi}$—Rb1—F1$^{v}$ | 96.30 (14) |
| F1$^{ii}$—Re1—Rb1$^{i}$ | 125.2 (2) | F1$^{x}$—Rb1—F1$^{v}$ | 128.31 (8) |
| F1$^{iii}$—Re1—Rb1$^{i}$ | 54.8 (2) | F1$^{xii}$—Rb1—F1$^{v}$ | 62.7 (2) |
| F1$^{iv}$—Re1—Rb1$^{i}$ | 53.64 (2) | F1$^{xiii}$—Rb1—F1$^{v}$ | 63.1 (3) |
| F1$^{v}$—Re1—Rb1$^{i}$ | 126.36 (2) | F1$^{xiv}$—Rb1—F1$^{v}$ | 118.68 (6) |
| F1—Re1—Rb1$^{i}$ | 126.36 (2) | F1$^{xi}$—Rb1—F1$^{xv}$ | 96.30 (14) |
| F1$^{i}$—Re1—Rb1$^{vi}$ | 125.2 (2) | F1$^{x}$—Rb1—F1$^{xv}$ | 62.7 (2) |
| F1$^{ii}$—Re1—Rb1$^{vi}$ | 53.64 (2) | F1$^{xii}$—Rb1—F1$^{xv}$ | 128.31 (8) |
| F1$^{iii}$—Re1—Rb1$^{vi}$ | 126.36 (2) | F1$^{xiii}$—Rb1—F1$^{xv}$ | 118.68 (5) |
| F1$^{iv}$—Re1—Rb1$^{vi}$ | 53.64 (2) | F1$^{xiv}$—Rb1—F1$^{xv}$ | 63.1 (3) |
| F1$^{v}$—Re1—Rb1$^{vi}$ | 126.36 (2) | F1$^{v}$—Rb1—F1$^{xv}$ | 166.2 (3) |
| F1—Re1—Rb1$^{vi}$ | 54.8 (2) | F1$^{xi}$—Rb1—F1$^{xvi}$ | 128.31 (8) |
| Rb1$^{i}$—Re1—Rb1$^{vi}$ | 106.77 (3) | F1$^{x}$—Rb1—F1$^{xvi}$ | 62.7 (2) |
| F1$^{i}$—Re1—Rb1$^{vii}$ | 54.8 (2) | F1$^{xii}$—Rb1—F1$^{xvi}$ | 96.30 (14) |
| F1$^{ii}$—Re1—Rb1$^{vii}$ | 126.36 (2) | F1$^{xiii}$—Rb1—F1$^{xvi}$ | 166.2 (3) |
| F1$^{iii}$—Re1—Rb1$^{vii}$ | 53.64 (2) | F1$^{xiv}$—Rb1—F1$^{xvi}$ | 118.68 (6) |
| F1$^{iv}$—Re1—Rb1$^{vii}$ | 126.36 (2) | F1$^{v}$—Rb1—F1$^{xvi}$ | 118.68 (5) |
| F1$^{v}$—Re1—Rb1$^{vii}$ | 53.64 (2) | F1$^{xv}$—Rb1—F1$^{xvi}$ | 56.0 (3) |
| F1—Re1—Rb1$^{vii}$ | 125.2 (2) | F1$^{xi}$—Rb1—F1 | 128.31 (8) |
| Rb1$^{i}$—Re1—Rb1$^{vii}$ | 73.23 (3) | F1$^{x}$—Rb1—F1 | 96.30 (14) |
| Rb1$^{vi}$—Re1—Rb1$^{vii}$ | 180.0 | F1$^{xii}$—Rb1—F1 | 62.7 (2) |
| F1$^{i}$—Re1—Rb1 | 126.36 (2) | F1$^{xiii}$—Rb1—F1 | 118.68 (6) |
| F1$^{ii}$—Re1—Rb1 | 54.8 (2) | F1$^{xiv}$—Rb1—F1 | 166.2 (3) |
| F1$^{iii}$—Re1—Rb1 | 125.2 (2) | F1$^{v}$—Rb1—F1 | 56.0 (3) |
| F1$^{iv}$—Re1—Rb1 | 126.36 (2) | F1$^{xv}$—Rb1—F1 | 118.68 (5) |
| F1$^{v}$—Re1—Rb1 | 53.64 (2) | F1$^{xvi}$—Rb1—F1 | 63.1 (3) |
| F1—Re1—Rb1 | 53.64 (2) | F1$^{xi}$—Rb1—F1$^{xvii}$ | 104.5 (2) |
| Rb1$^{i}$—Re1—Rb1 | 180.0 | F1$^{x}$—Rb1—F1$^{xvii}$ | 144.30 (9) |
| Rb1$^{vi}$—Re1—Rb1 | 73.23 (3) | F1$^{xii}$—Rb1—F1$^{xvii}$ | 144.30 (9) |
| Rb1$^{vii}$—Re1—Rb1 | 106.77 (3) | F1$^{xiii}$—Rb1—F1$^{xvii}$ | 52.0 (2) |
| F1$^{i}$—Re1—Rb1$^{viii}$ | 126.36 (2) | F1$^{xiv}$—Rb1—F1$^{xvii}$ | 52.0 (2) |
| F1$^{ii}$—Re1—Rb1$^{viii}$ | 126.36 (2) | F1$^{v}$—Rb1—F1$^{xvii}$ | 85.74 (14) |
| F1$^{iii}$—Re1—Rb1$^{viii}$ | 53.64 (2) | F1$^{xv}$—Rb1—F1$^{xvii}$ | 85.74 (14) |
| F1$^{iv}$—Re1—Rb1$^{viii}$ | 54.8 (2) | F1$^{xvi}$—Rb1—F1$^{xvii}$ | 114.25 (9) |
| F1$^{v}$—Re1—Rb1$^{viii}$ | 125.2 (2) | F1—Rb1—F1$^{xvii}$ | 114.25 (9) |
| F1—Re1—Rb1$^{viii}$ | 53.64 (2) | F1$^{xi}$—Rb1—F1$^{ii}$ | 144.30 (9) |
| Rb1$^{i}$—Re1—Rb1$^{viii}$ | 73.23 (3) | F1$^{x}$—Rb1—F1$^{ii}$ | 144.30 (9) |
| Rb1$^{vi}$—Re1—Rb1$^{viii}$ | 73.23 (3) | F1$^{xii}$—Rb1—F1$^{ii}$ | 104.5 (2) |
| Rb1$^{vii}$—Re1—Rb1$^{viii}$ | 106.77 (3) | F1$^{xiii}$—Rb1—F1$^{ii}$ | 85.74 (14) |
| Rb1—Re1—Rb1$^{viii}$ | 106.77 (3) | F1$^{xiv}$—Rb1—F1$^{ii}$ | 114.25 (9) |
| F1$^{i}$—Re1—Rb1$^{ix}$ | 53.64 (2) | F1$^{v}$—Rb1—F1$^{ii}$ | 52.0 (2) |
| F1$^{ii}$—Re1—Rb1$^{ix}$ | 53.64 (2) | F1$^{xv}$—Rb1—F1$^{ii}$ | 114.25 (9) |
| F1$^{iii}$—Re1—Rb1$^{ix}$ | 126.36 (2) | F1$^{xvi}$—Rb1—F1$^{ii}$ | 85.74 (14) |
| F1$^{iv}$—Re1—Rb1$^{ix}$ | 125.2 (2) | F1—Rb1—F1$^{ii}$ | 52.0 (2) |

| | | | |
|---|---|---|---|
| F1$^{v}$—Re1—Rb1$^{ix}$ | 54.8 (2) | F1$^{xvii}$—Rb1—F1$^{ii}$ | 62.2 (2) |
| F1—Re1—Rb1$^{ix}$ | 126.36 (2) | F1$^{xi}$—Rb1—F1$^{vi}$ | 144.30 (9) |
| Rb1$^{i}$—Re1—Rb1$^{ix}$ | 106.77 (3) | F1$^{x}$—Rb1—F1$^{vi}$ | 104.5 (2) |
| Rb1$^{vi}$—Re1—Rb1$^{ix}$ | 106.77 (3) | F1$^{xii}$—Rb1—F1$^{vi}$ | 144.30 (9) |
| Rb1$^{vii}$—Re1—Rb1$^{ix}$ | 73.23 (3) | F1$^{xiii}$—Rb1—F1$^{vi}$ | 114.25 (9) |
| Rb1—Re1—Rb1$^{ix}$ | 73.23 (3) | F1$^{xiv}$—Rb1—F1$^{vi}$ | 85.74 (14) |
| Rb1$^{viii}$—Re1—Rb1$^{ix}$ | 180.0 | F1$^{v}$—Rb1—F1$^{vi}$ | 114.25 (9) |
| Re1—F1—Rb1$^{x}$ | 161.6 (3) | F1$^{xv}$—Rb1—F1$^{vi}$ | 52.0 (2) |
| Re1—F1—Rb1 | 95.10 (14) | F1$^{xvi}$—Rb1—F1$^{vi}$ | 52.0 (2) |
| Rb1$^{x}$—F1—Rb1 | 83.70 (14) | F1—Rb1—F1$^{vi}$ | 85.74 (14) |
| Re1—F1—Rb1$^{viii}$ | 95.10 (14) | F1$^{xvii}$—Rb1—F1$^{vi}$ | 62.2 (2) |
| Rb1$^{x}$—F1—Rb1$^{viii}$ | 83.70 (14) | F1$^{ii}$—Rb1—F1$^{vi}$ | 62.2 (2) |

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

## Dicaesium hexafluoridorhenate(IV) (SMB_Cs2ReF6_1a)

### *Crystal data*

$Cs_2[ReF_6]$
$M_r$ = 566.02
Trigonal, $P\bar{3}m1$
$a$ = 6.268 (1) Å
$c$ = 4.931 (1) Å
$V$ = 167.77 (6) Å$^3$
$Z$ = 1
$F$(000) = 239
$D_x$ = 5.602 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 135 reflections
$\theta$ = 3.8–32.6°
$\mu$ = 28.83 mm$^{-1}$
$T$ = 100 K
Hexagonal plate, clear colourless
0.25 × 0.12 × 0.11 mm

### *Data collection*

Bruker D8 QUEST diffractometer
Radiation source: sealed tube, Siemens KFFMo2K-90
Curved graphite monochromator
Detector resolution: 8.3333 pixels mm$^{-1}$
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2015)
$T_{min}$ = 0.05, $T_{max}$ = 0.15
2683 measured reflections
218 independent reflections
218 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.040
$\theta_{max}$ = 30.4°, $\theta_{min}$ = 3.8°
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = -7 \rightarrow 7$

### *Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.013
$wR(F^2)$ = 0.036
$S$ = 1.25
218 reflections
13 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0181P)^2 + 0.1419P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.68 e Å$^{-3}$
$\Delta\rho_{min}$ = −2.92 e Å$^{-3}$
Extinction correction: SHELXL2014 (Sheldrick, 2015)
Extinction coefficient: 0.029 (2)

*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* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Re1 | 0 | 0 | 0 | 0.00427 (15) |
| F1 | 0.3027 (3) | 0.15135 (17) | 0.2165 (4) | 0.0092 (4) |
| Cs1 | 0.3333 | 0.6667 | 0.30027 (9) | 0.00615 (14) |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Re1 | 0.00483 (16) | 0.00483 (16) | 0.0032 (2) | 0.00241 (8) | 0 | 0 |
| F1 | 0.0088 (8) | 0.0107 (6) | 0.0075 (9) | 0.0044 (4) | −0.0023 (6) | −0.0012 (3) |
| Cs1 | 0.00661 (16) | 0.00661 (16) | 0.0052 (2) | 0.00331 (8) | 0 | 0 |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Re1—F1$^{i}$ | 1.9594 (18) | F1—Cs1$^{viii}$ | 3.1655 (6) |
| Re1—F1$^{ii}$ | 1.9594 (18) | F1—Cs1$^{vi}$ | 3.224 (2) |
| Re1—F1$^{iii}$ | 1.9594 (18) | Cs1—F1$^{xi}$ | 3.0955 (19) |
| Re1—F1$^{iv}$ | 1.9594 (18) | Cs1—F1$^{x}$ | 3.0955 (19) |
| Re1—F1$^{v}$ | 1.9594 (18) | Cs1—F1$^{xii}$ | 3.0955 (19) |
| Re1—F1 | 1.9594 (18) | Cs1—F1$^{xiii}$ | 3.1655 (6) |
| Re1—Cs1$^{i}$ | 3.9100 (6) | Cs1—F1$^{xiv}$ | 3.1655 (6) |
| Re1—Cs1$^{vi}$ | 3.9100 (6) | Cs1—F1$^{iii}$ | 3.1655 (6) |
| Re1—Cs1$^{vii}$ | 3.9100 (6) | Cs1—F1$^{xv}$ | 3.1655 (6) |
| Re1—Cs1 | 3.9100 (6) | Cs1—F1$^{xvi}$ | 3.1655 (6) |
| Re1—Cs1$^{viii}$ | 3.9100 (6) | Cs1—F1$^{xvii}$ | 3.224 (2) |
| Re1—Cs1$^{ix}$ | 3.9100 (6) | Cs1—F1$^{iv}$ | 3.224 (2) |
| F1—Cs1$^{x}$ | 3.0955 (19) | Cs1—F1$^{vi}$ | 3.224 (2) |
| F1—Cs1 | 3.1655 (6) | | |
| | | | |
| F1$^{i}$—Re1—F1$^{ii}$ | 93.14 (7) | Cs1—F1—Cs1$^{viii}$ | 163.82 (6) |
| F1$^{i}$—Re1—F1$^{iii}$ | 86.86 (7) | Re1—F1—Cs1$^{vi}$ | 94.78 (7) |
| F1$^{ii}$—Re1—F1$^{iii}$ | 180.00 (4) | Cs1$^{x}$—F1—Cs1$^{vi}$ | 102.55 (5) |
| F1$^{i}$—Re1—F1$^{iv}$ | 93.14 (7) | Cs1—F1—Cs1$^{vi}$ | 94.07 (3) |
| F1$^{ii}$—Re1—F1$^{iv}$ | 93.14 (7) | Cs1$^{viii}$—F1—Cs1$^{vi}$ | 94.07 (3) |
| F1$^{iii}$—Re1—F1$^{iv}$ | 86.86 (7) | F1$^{xi}$—Cs1—F1$^{x}$ | 67.11 (6) |
| F1$^{i}$—Re1—F1$^{v}$ | 86.86 (7) | F1$^{xi}$—Cs1—F1$^{xii}$ | 67.11 (6) |
| F1$^{ii}$—Re1—F1$^{v}$ | 86.86 (7) | F1$^{x}$—Cs1—F1$^{xii}$ | 67.11 (6) |
| F1$^{iii}$—Re1—F1$^{v}$ | 93.14 (7) | F1$^{xi}$—Cs1—F1$^{xiii}$ | 62.38 (6) |
| F1$^{iv}$—Re1—F1$^{v}$ | 180.00 (8) | F1$^{x}$—Cs1—F1$^{xiii}$ | 129.122 (17) |
| F1$^{i}$—Re1—F1 | 180.0 | F1$^{xii}$—Cs1—F1$^{xiii}$ | 97.70 (3) |

| | | | |
|---|---|---|---|
| F1$^{ii}$—Re1—F1 | 86.86 (7) | F1$^{xi}$—Cs1—F1$^{xiv}$ | 62.38 (6) |
| F1$^{iii}$—Re1—F1 | 93.14 (7) | F1$^{x}$—Cs1—F1$^{xiv}$ | 97.70 (3) |
| F1$^{iv}$—Re1—F1 | 86.86 (7) | F1$^{xii}$—Cs1—F1$^{xiv}$ | 129.122 (17) |
| F1$^{v}$—Re1—F1 | 93.14 (7) | F1$^{xiii}$—Cs1—F1$^{xiv}$ | 53.43 (7) |
| F1$^{i}$—Re1—Cs1$^{i}$ | 53.533 (6) | F1$^{xi}$—Cs1—F1$^{iii}$ | 97.70 (3) |
| F1$^{ii}$—Re1—Cs1$^{i}$ | 53.533 (6) | F1$^{x}$—Cs1—F1$^{iii}$ | 129.122 (17) |
| F1$^{iii}$—Re1—Cs1$^{i}$ | 126.467 (6) | F1$^{xii}$—Cs1—F1$^{iii}$ | 62.38 (6) |
| F1$^{iv}$—Re1—Cs1$^{i}$ | 124.74 (6) | F1$^{xiii}$—Cs1—F1$^{iii}$ | 65.44 (7) |
| F1$^{v}$—Re1—Cs1$^{i}$ | 55.26 (6) | F1$^{xiv}$—Cs1—F1$^{iii}$ | 118.323 (15) |
| F1—Re1—Cs1$^{i}$ | 126.467 (6) | F1$^{xi}$—Cs1—F1$^{xv}$ | 97.70 (3) |
| F1$^{i}$—Re1—Cs1$^{vi}$ | 124.74 (6) | F1$^{x}$—Cs1—F1$^{xv}$ | 62.38 (6) |
| F1$^{ii}$—Re1—Cs1$^{vi}$ | 53.533 (6) | F1$^{xii}$—Cs1—F1$^{xv}$ | 129.122 (17) |
| F1$^{iii}$—Re1—Cs1$^{vi}$ | 126.467 (6) | F1$^{xiii}$—Cs1—F1$^{xv}$ | 118.323 (14) |
| F1$^{iv}$—Re1—Cs1$^{vi}$ | 53.532 (6) | F1$^{xiv}$—Cs1—F1$^{xv}$ | 65.44 (7) |
| F1$^{v}$—Re1—Cs1$^{vi}$ | 126.468 (6) | F1$^{iii}$—Cs1—F1$^{xv}$ | 163.82 (6) |
| F1—Re1—Cs1$^{vi}$ | 55.26 (6) | F1$^{xi}$—Cs1—F1 | 129.123 (17) |
| Cs1$^{i}$—Re1—Cs1$^{vi}$ | 106.554 (9) | F1$^{x}$—Cs1—F1 | 97.70 (3) |
| F1$^{i}$—Re1—Cs1$^{vii}$ | 55.26 (6) | F1$^{xii}$—Cs1—F1 | 62.38 (6) |
| F1$^{ii}$—Re1—Cs1$^{vii}$ | 126.467 (6) | F1$^{xiii}$—Cs1—F1 | 118.323 (15) |
| F1$^{iii}$—Re1—Cs1$^{vii}$ | 53.533 (6) | F1$^{xiv}$—Cs1—F1 | 163.82 (6) |
| F1$^{iv}$—Re1—Cs1$^{vii}$ | 126.468 (6) | F1$^{iii}$—Cs1—F1 | 53.43 (7) |
| F1$^{v}$—Re1—Cs1$^{vii}$ | 53.532 (6) | F1$^{xv}$—Cs1—F1 | 118.323 (15) |
| F1—Re1—Cs1$^{vii}$ | 124.74 (6) | F1$^{xi}$—Cs1—F1$^{xvi}$ | 129.122 (17) |
| Cs1$^{i}$—Re1—Cs1$^{vii}$ | 73.446 (9) | F1$^{x}$—Cs1—F1$^{xvi}$ | 62.38 (6) |
| Cs1$^{vi}$—Re1—Cs1$^{vii}$ | 180.0 | F1$^{xii}$—Cs1—F1$^{xvi}$ | 97.70 (3) |
| F1$^{i}$—Re1—Cs1 | 126.467 (6) | F1$^{xiii}$—Cs1—F1$^{xvi}$ | 163.82 (6) |
| F1$^{ii}$—Re1—Cs1 | 126.467 (6) | F1$^{xiv}$—Cs1—F1$^{xvi}$ | 118.323 (15) |
| F1$^{iii}$—Re1—Cs1 | 53.533 (6) | F1$^{iii}$—Cs1—F1$^{xvi}$ | 118.323 (15) |
| F1$^{iv}$—Re1—Cs1 | 55.26 (6) | F1$^{xv}$—Cs1—F1$^{xvi}$ | 53.43 (7) |
| F1$^{v}$—Re1—Cs1 | 124.74 (6) | F1—Cs1—F1$^{xvi}$ | 65.44 (7) |
| F1—Re1—Cs1 | 53.533 (6) | F1$^{xi}$—Cs1—F1$^{xvii}$ | 102.55 (5) |
| Cs1$^{i}$—Re1—Cs1 | 180.0 | F1$^{x}$—Cs1—F1$^{xvii}$ | 143.51 (2) |
| Cs1$^{vi}$—Re1—Cs1 | 73.447 (8) | F1$^{xii}$—Cs1—F1$^{xvii}$ | 143.51 (2) |
| Cs1$^{vii}$—Re1—Cs1 | 106.553 (8) | F1$^{xiii}$—Cs1—F1$^{xvii}$ | 49.86 (5) |
| F1$^{i}$—Re1—Cs1$^{viii}$ | 126.467 (6) | F1$^{xiv}$—Cs1—F1$^{xvii}$ | 49.86 (5) |
| F1$^{ii}$—Re1—Cs1$^{viii}$ | 55.26 (6) | F1$^{iii}$—Cs1—F1$^{xvii}$ | 85.93 (3) |
| F1$^{iii}$—Re1—Cs1$^{viii}$ | 124.74 (6) | F1$^{xv}$—Cs1—F1$^{xvii}$ | 85.93 (3) |
| F1$^{iv}$—Re1—Cs1$^{viii}$ | 126.467 (6) | F1—Cs1—F1$^{xvii}$ | 113.96 (2) |
| F1$^{v}$—Re1—Cs1$^{viii}$ | 53.533 (6) | F1$^{xvi}$—Cs1—F1$^{xvii}$ | 113.96 (2) |
| F1—Re1—Cs1$^{viii}$ | 53.533 (6) | F1$^{xi}$—Cs1—F1$^{iv}$ | 143.51 (2) |
| Cs1$^{i}$—Re1—Cs1$^{viii}$ | 73.447 (8) | F1$^{x}$—Cs1—F1$^{iv}$ | 143.51 (2) |
| Cs1$^{vi}$—Re1—Cs1$^{viii}$ | 73.447 (9) | F1$^{xii}$—Cs1—F1$^{iv}$ | 102.55 (5) |
| Cs1$^{vii}$—Re1—Cs1$^{viii}$ | 106.553 (9) | F1$^{xiii}$—Cs1—F1$^{iv}$ | 85.93 (3) |
| Cs1—Re1—Cs1$^{viii}$ | 106.553 (9) | F1$^{xiv}$—Cs1—F1$^{iv}$ | 113.96 (2) |
| F1$^{i}$—Re1—Cs1$^{ix}$ | 53.533 (6) | F1$^{iii}$—Cs1—F1$^{iv}$ | 49.86 (5) |
| F1$^{ii}$—Re1—Cs1$^{ix}$ | 124.74 (6) | F1$^{xv}$—Cs1—F1$^{iv}$ | 113.96 (2) |
| F1$^{iii}$—Re1—Cs1$^{ix}$ | 55.26 (6) | F1—Cs1—F1$^{iv}$ | 49.86 (5) |
| F1$^{iv}$—Re1—Cs1$^{ix}$ | 53.533 (6) | F1$^{xvi}$—Cs1—F1$^{iv}$ | 85.93 (3) |

| | | | |
|---|---|---|---|
| F1$^{v}$—Re1—Cs1$^{ix}$ | 126.467 (6) | F1$^{xvii}$—Cs1—F1$^{iv}$ | 64.10 (5) |
| F1—Re1—Cs1$^{ix}$ | 126.467 (6) | F1$^{xi}$—Cs1—F1$^{vi}$ | 143.51 (2) |
| Cs1$^{i}$—Re1—Cs1$^{ix}$ | 106.553 (8) | F1$^{x}$—Cs1—F1$^{vi}$ | 102.55 (5) |
| Cs1$^{vi}$—Re1—Cs1$^{ix}$ | 106.553 (9) | F1$^{xii}$—Cs1—F1$^{vi}$ | 143.51 (2) |
| Cs1$^{vii}$—Re1—Cs1$^{ix}$ | 73.447 (9) | F1$^{xiii}$—Cs1—F1$^{vi}$ | 113.96 (2) |
| Cs1—Re1—Cs1$^{ix}$ | 73.447 (9) | F1$^{xiv}$—Cs1—F1$^{vi}$ | 85.93 (3) |
| Cs1$^{viii}$—Re1—Cs1$^{ix}$ | 180.0 | F1$^{iii}$—Cs1—F1$^{vi}$ | 113.96 (2) |
| Re1—F1—Cs1$^{x}$ | 162.67 (9) | F1$^{xv}$—Cs1—F1$^{vi}$ | 49.86 (5) |
| Re1—F1—Cs1 | 96.61 (3) | F1—Cs1—F1$^{vi}$ | 85.93 (3) |
| Cs1$^{x}$—F1—Cs1 | 82.30 (3) | F1$^{xvi}$—Cs1—F1$^{vi}$ | 49.86 (5) |
| Re1—F1—Cs1$^{viii}$ | 96.61 (3) | F1$^{xvii}$—Cs1—F1$^{vi}$ | 64.10 (5) |
| Cs1$^{x}$—F1—Cs1$^{viii}$ | 82.30 (3) | F1$^{iv}$—Cs1—F1$^{vi}$ | 64.10 (5) |

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