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The Structures of Barium Hexafluorosilicate and Cesium Hexafluororhenate(V)

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The crystal structure of $CsReF_6$, together with a reinvestigation of that of $BaSiF_6$, is reported. Both have been determined from single crystal three-dimensional X-ray diffraction data. The structure of $BaSiF_6$ has been found to conform to the initially assigned space group $R\bar{3}m$, *contrary to the suggesttions of other workers. The unit cell of $BaSiF_6$ has the dimensiona a_{hex} 7.189(1), c_{hex} 7.015(1) Å; Z = 3. Refinement by a least squares method gave* R *0.0079 and* R_w *0.0077. Crystals of $CsReF_6$ belong to the lower symmetry rhombohedral space group* $R\bar{3}$. *The unit cell has the dimensions a_{hex} 7.853(1), c_{hex} 8.140(1) Å; Z = 3. Refinement gave* R *0.031 and* R_w *0.030. The lowering of symmetry is caused by rotation of the ReF_6^- octahedra about the 3-fold axis through each Re atom, causing $CsReF_6$ to have the $KOsF_6$ structure.*

Introduction

Although structures of the complex fluorides of general formula $A^IB^VF_6$ have been extensively studied by X-ray powder photography, [1] single crystal X-ray diffraction has been employed to a much lesser extent. Of the 80 or so complexes which have been studied, there appear to be only five basic structural types. The major factor controlling the lattice type is the ionic radius of the cation, A^+. Complex fluorides containing the largest cations Tl^+, Rb^+, and Cs^+, and some potassium salts have the rhombohedral $KOsF_6$ structure described by Hepworth, Jack and Westland [2].

In 1940, Hoard and Vincent [3] investigated the structure of the related compound $BaSiF_6$ using oscillation photographs of single crystals. They deduced that $BaSiF_6$ has the rhombohedral space group $R\bar{3}m$, and a number of other compounds have subsequently been assigned this structure [4]. The $KOsF_6$ structure, however, has the slightly lower symmetry space group $R\bar{3}$. It has been suggested [1] that the lowering of symmetry is associated with a distortion of the OsF_6^- octahedron by contraction along a 3-fold axis, and that such a lowering of symmetry could not be ruled out for $BaSiF_6$. Presumably the contraction would be along a non-crystallographic 3-fold axis, since a contraction along the crystallographic 3-fold axis does not lower the symmetry.

Wyckoff [4] in his review of structures of this class has indicated that a few compounds give results which leave uncertainty as to whether they belong to the $BaSiF_6$ or $KOsF_6$ structural types. He also suggested that the $BaSiF_6$ structure could have the lower symmetry. In view of the importance of this structure as an architype in general descriptions of structural chemistry we have repeated the structural determination of $BaSiF_6$, using single crystal X-ray diffraction in an attempt to determine whether the true space group is $R\bar{3}$ or $R\bar{3}m$. We have also determined the structure of $CsReF_6$ which had previously been assigned to the $KOsF_6$ structural type, on the basis of powder photography, [1] to see whether it would be better described by the $R\bar{3}m$ space group.

Experimental

Preparation

BaSiF₆

Powdered silica (1 g) was dissolved in 10 cm^3 50% aqueous hydrofluoric acid and added to a solution of barium nitrate (3 g) in 35 cm^3 water. The resultant white precipitate was filtered, washed with water and dried at 150 °C.

Small colourless needle crystals were obtained by slow evaporation from freshly prepared dilute hydrochloric acid solutions. A crystal of dimensions 0.03 × 0.03 × 0.20 mm was mounted on a glass fibre for X-ray structural analysis.

CsReF₆

Initially, ReF_5 was prepared by reduction of ReF_6 by PF_3, which were obtained from Ozark-Mahoning. Volatile materials were handled in a passivated stainless steel vacuum line. Excess ReF_6 was condensed onto PF_3 (4 mmol) at −196 °C in a Kel-F tube and the tube was allowed to warm slowly to room temperature. After 24 hours the excess ReF_6, together with PF_5, was pumped out leaving a pale green solid. Anhydrous hydrogen fluoride (10 cm^3) was distilled onto the solid, and the resulting yellow green solution was filtered through a Teflon filter medium in a Kel-F cartridge, to remove insoluble impurities.

An excess of CsF solution was added to part of the above solution of ReF_5 to give a very pale blue solution of $CsReF_6$. Small colourless rhombohedral crystals were obtained by slow vacuum distillation of the hydrogen fluoride from the solution held in a synthetic sapphire reaction tube. After decanting the solution and pumping off excess HF vapour, a crystal suitable for X-ray structural determination (0.24 × 0.30 × 0.19 mm) was transferred and sealed in a Lindemann glass capillary (~0.3 mm) in a dry atmosphere glove box.

Crystal Data

$BaSiF_6$, M = 279.4, rhombohedral, a_{hex} = 7.189(1), c_{hex} = 7.015(1) Å, U = 314.0 $Å^3$, Z = 3, D_c = 4.43 Mg m^{-3}, $F(000)$ = 366.02, space group $R\bar{3}m$ (No. 166), MoKα (graphite-monochromated) radiation, λ = 0.71069 Å, μ = 98.09 cm^{-1}, absorption corrections applied, max. and min. transmission factors 0.799, 0.668.

$CsReF_6$, M = 433.1, rhombohedral, a_{hex} = 7.853(1), c_{hex} = 8.140(1) Å, U = 434.8 $Å^3$, Z = 3, D_c = 4.96 Mg m^{-3}, $F(000)$ = 548.9, space group $R\bar{3}$ (No. 148), MoKα (graphite-monochromated) radiation, λ = 0.71069 Å, μ = 273.7 cm^{-1}, absorption corrections applied, max. and min. transmission factors 0.0597, 0.0134.

The density of the $CsReF_6$ crystal could not be measured due to the very high reactivity of the compound towards moisture. Even when sealed in a capillary the crystal surfaces turned black within several hours.

Data Collection

$BaSiF_6$

A preliminary X-ray (CuKα, nickel-filtered) photographic investigation of the $BaSiF_6$ crystal was consistent with the findings of Hoard and Vincent [3]. The crystal was mounted in an arbitrary orientation on an Enraf-Nonius, four-circle, CAD-4F diffractometer controlled by a PDP/8A computer. The Enraf-Nonius procedure SEARCH was used to obtain 25 accurately centred reflections which were then used in the program INDEX to obtain an orientation matrix and approximate cell dimensions. Accurate cell dimensions and their estimated standard deviations together with an accurate orientation matrix were obtained by least squares refinement of the setting angles obtained for 25 reflections that were accurately centred by the SETANG procedure. It was established that $BaSiF_6$ was rhombohedral with cell dimensions in close agreement with those of Hoard and Vincent.

Intensity data were collected at room temperature (293 K) using MoKα radiation (0.71069 Å, graphite-monochromated) and the $\omega:2\theta$ scan technique over the range $0.5° \leqslant \theta \leqslant 30.0°$. With the crystal indexed in the hexagonal setting, all reflections over the range h(−10 → 10), k(−10 → 10), l(−9 → 9) that satisfied the condition $-h + k + l = 3n$, and were within the θ limits, were measured. The measurement of approximately 150 reflections that were expected to be systematically absent confirmed that the diffraction spectra conformed to the rhombohedral condition. The net intensity (NI) was calculated as NI = INT − 2(BGL + BGR), where INT is the estimated peak density and BGR and BGL are the estimated background intensities. The estimated standard deviation of the net intensity was calculated as $\sigma(I) = [\mathrm{INT} + 4(\mathrm{BGL} + \mathrm{BGR})]^{1/2}$. During the data collection four reference reflections, monitored every 5000 seconds of X-ray exposure time, showed no significant decrease in intensity during the analysis. The intensities were corrected for Lorentz, polarisation and absorption effects [5a]. All of the 1228 measured reflections were considered observed ($I \geqslant 2\sigma(I)$).

$CsReF_6$

A preliminary X-ray photographic analysis of the $CsReF_6$ crystal indicated a rhombohedral unit cell in accordance with the powder data of Peacock [6]. The crystal was subjected to a similar analysis to that used for $BaSiF_6$ with the following modifications. The intensity data were collected with the crystal indexed in the rhombohedral setting. Within the θ limits, all reflections over the range h(−2 → 7), k(−7 → 7), l(−7 → 7) were measured. During the data collection four reference reflections, monitored every 3000 seconds of X-ray exposure time, indicated an average decrease in intensity of 27% during the analysis. The intensities were corrected for this deterioration, Lorentz, polarisation and absorption effects. All of the 1303 measured reflections were considered observed ($I \geqslant 2\sigma(I)$).

Solution and Refinement of Structures

Structure determination and refinement were performed using the SHELX-76 program system [7] and the University of Melbourne's Cyber 170–730 computer system. The scattering factors used for silicon and fluorine were those collected by Sheldrick, [7] while the atomic scattering factors and anomalous dispersion terms for Cs, Re and Ba were those given in references [5b] and [5c], respectively.

$BaSiF_6$

Following absorption corrections the intensity data were amalgamated in both the $R\bar{3}$ and $R\bar{3}m$

TABLE I. Atomic Positional and Thermal Parameters for $BaSiF_6$ with Estimated Standard Deviations in Parentheses.[a]

Atom	x/a	y/b	z/c
Ba	0	0	0.5
Si	0	0	0
F	0.1096(1)	−0.1096(1)	0.1419(2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ba	0.0108(1)	0.0108(1)	0.0088(2)	0	0	0.0054(1)
Si	0.0087(3)	0.0087(3)	0.0080(5)	0	0	0.0043(1)
F	0.0186(4)	0.0186(4)	0.0150(4)	0.0022(2)	−0.0022(2)	0.0126(4)

[a] For Tables I and II the form of the anisotropic temperature factor is: $T = \exp\{-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})\}$.

space groups. In $R\bar{3}$ there were 207 unique reflections and R_{amal} 0.0288, where:

$$R_{\text{amal}} = [\Sigma(N\Sigma w(F_{\text{mean}} - F)^2)/\Sigma((N-1)\Sigma wF^2)]^{1/2}$$

in which the inner summations are over N equivalent reflections averaged to give F_{mean}, the outer summations are over all unique reflections and the weight, w, is taken as $(\sigma(F))^{-2}$. In $R\bar{3}m$ there were 129 unique reflections with R_{amal} 0.0280. The similarity of the values for R_{amal} suggests that $R\bar{3}m$ is the correct space group.

Working in both space groups the position of the barium atom was determined from a three dimensional Patterson map, while the remaining atoms were located in subsequent difference maps. The structure was refined using a full-matrix least squares method in which the function $\Sigma w\Delta^2$ was minimised, where $\Delta = \|Fo| - |Fc\|$ and w was the weight applied to each reflection. Refinement of atomic positions including isotropic thermal factors for all atoms yielded R 0.024 and 0.026 in the space groups $R\bar{3}$ and $R\bar{3}m$ respectively, where $R = \Sigma\Delta/\Sigma|Fo|$.

In the space group $R\bar{3}$, the F atom was found to be sitting in a position corresponding to a special position of site symmetry m in the space group $R\bar{3}m$. Subsequent refinement was performed using the space group $R\bar{3}m$ only. Further cycles of refinement using anisotropic thermal parameters for all atoms reduced R to 0.017. Final cycles of refinement employed a weighting scheme were w was modified according to the expression $w = [k/\sigma^2(F) + |g|F^2]$, and an isotropic extinction parameter, x, where $Fc = F(1 - 0.0001xF^2/\sin\theta)$. At convergence the values of k, g and x were 1.000, 0.00184 and 0.0043 respectively, and the final R and R_w were 0.0079 and 0.0077 respectively, where $R_w = [\Sigma w\Delta^2/\Sigma w|Fo|^2]^{1/2}$. The maximum parameter shift in the final refinement cycle was 0.02σ, while the highest residual peak was 0.35 e Å^{-3}, in the vicinity of the barium atom. The analysis of variance showed no special features, an indication that the weighting scheme was satisfactory.

$CsReF_6$

After absorption corrections the intensity data were transformed to the hexagonal setting. The amalgamation of the data in the space group $R\bar{3}$ gave 281 unique reflections with R_{amal} 0.068, while amalgamation in $R\bar{3}m$ gave 171 unique reflections with R_{amal} 0.125. Such a difference between the two R_{amal} values indicates that $R\bar{3}m$ is probably not the correct space group. The $CsReF_6$ structure was then refined in both space groups in analogous manner to $BaSiF_6$. The cesium and rhenium atoms were found in a Patterson map while the fluorine atoms were located from subsequent difference maps. Since the fluorine atoms were not found in a position which would correspond to that on a mirror plane of the space group $R\bar{3}m$, refinement was continued in $R\bar{3}$ only. Refinement of atomic positions including anisotropic thermal parameters for all atoms yielded R 0.044. After a weighting scheme was introduced R and R_w were 0.040 and 0.034 respectively. Reflection −1 2 0 was omitted due to a large deviation of Fo from Fc for this reflection, and an isotropic extinction parameter was employed. At convergence the values of k, g and x were 1.000, 0.00430 and 0.0020 respectively, and the final R and R_w were 0.031 and 0.030 respectively. The maximum parameter shift in the final cycle of refinement was 0.01σ, while the highest residual peak in the difference map was 1.7 e Å^{-3}, in the vicinity of the rhenium atom. The analysis of variance showed no special features, an indication that the weighting scheme was satisfactory.

The final atomic parameters for $BaSiF_6$ and $CsReF_6$, together with their estimated standard deviations, are given in Tables I and II respectively. Tables of calculated and observed structure factors for these compounds have been deposited with the Editors.

TABLE II. Atomic Positional and Thermal Parameters for $CsReF_6$ with Estimated Standard Deviations in Parentheses.

Atom	x/a	y/b	z/c
Cs	0	0	0.5
Re	0	0	0
F	0.0582(7)	−0.1561(6)	0.1344(5)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs	0.0307(4)	0.0307(4)	0.0375(6)	0	0	0.0153(2)
Re	0.0205(3)	0.0205(3)	0.0323(4)	0	0	0.0103(1)
F	0.049(2)	0.046(2)	0.060(2)	0.013(2)	−0.003(2)	0.031(2)

Results and Discussion

We were interested in redetermining the structure of $BaSiF_6$ to decide whether the correct space group was $R\bar{3}m$ as assigned by Hoard and Vincent, [3] or the lower symmetry space group $R\bar{3}$. The position of the fluorine atoms in the structure determines which symmetry is correct. In order to belong to the space group $R\bar{3}m$ the fluorine atoms must fall on a mirror plane, and so reduce the 12 general positions to 6 special positions, thus defining the octahedron about the silicon atoms. Should the F atoms not fall on a mirror plane, then the structure probably has the lower symmetry, $R\bar{3}$, which has only 6 general positions around the central atom. Otherwise the placement of one fluorine atom in the structure would generate 12 others and require the introduction of disorder in the crystal to account for the structure.

The special position on a mirror plane (18h) in $R\bar{3}m$ has site symmetry m and is characterised by the co-ordinates $x, \bar{x}, z$ [5d]. The intensity data for $BaSiF_6$ were initially amalgamated on the space group $R\bar{3}$. After locating the Ba and Si atoms, a subsequent difference map showed a fluorine atom in the position 0.11, −0.11, 0.14. When this position was assigned and refined as a general position with isotropic thermal parameters, the refined co-ordinates (with estimated standard deviations in brackets) were 0.1098(5), −0.1097(5), 0.1421(4). This position is clearly of the type $x, \bar{x}, z$ and so falls on the mirror plane of the space group $R\bar{3}m$. Therefore this gives us further justification for amalgamating the data on the space group of higher symmetry without having to introduce disorder to account for the atoms generated, and the original assignment of Hoard and Vincent is vindicated.

The bond lengths and non-bonded distances are shown in Table III, and are compared to the distances given by Hoard and Vincent. Their results, obtained from early single crystal techniques, are in excellent agreement with the results of this investigation. Axial distances refer to those along the 3-fold axis, while girdle distances refer to distances from each barium ion to atoms of the six SiF_6^{2-} groups arranged close to the xy plane around the barium ion.

TABLE III. Interatomic Distances (Å) and Angles (°) for $BaSiF_6$ with Estimated Standard Deviations in Parentheses.

	This work	Hoard and Vincent[a]
Si--F	1.685(1)	1.71
$F\cdots F^{I}$	2.363(1)	
$F\cdots F^{II}$	2.403(2)	
$F\cdots F^{II'}$	2.809(1)	2.77
$Ba\cdots F$ (axial)	2.864(1)	2.88
$Ba\cdots F^{I'}$ (girdle)	2.7925(6)	2.75
$Ba\cdots Si$ (axial)	3.5075	3.495
$Ba\cdots Si'$ (girdle)	4.3133	4.30
$F{-}{-}Si{-}{-}F^{I}$	89.03(5)	
$F{-}{-}Si{-}{-}F^{II}$	90.97(5)	

Atoms with Roman numerals as superscripts refer to atoms in the following positions relative to the co-ordinates x, y, z:

I $y - x, y, z$
II $y, y - x, -z$

Primed atoms have the translation (2/3, 1/3, 1/3)

[a] Ref. [3].

The SiF_6^{2-} anions are not perfect octahedra, but are slightly elongated along the 3-fold axis. Such a stretch does not destroy the $\bar{3}m$ symmetry, since the mirror planes are parallel to the 3-fold axis. This distortion is comparatively small, the fluorine–fluorine distances parallel to the z-axis being only 0.04 Å longer than those in the xy plane. The co-ordination of Ba^{2+} ions is nearly completely regular since the three fluorine atoms above and three below each barium ion are only 0.07 Å further away than the six fluorine atoms forming a staggered ring about the cation.

In refining the structure of $CsReF_6$, the intensity data were again initially amalgamated in the space group $R\bar{3}$. After defining the positions of the cesium and rhenium atoms, a difference map revealed that

TABLE IV. Interatomic Distances (A) and Angles (°) for $CsReF_6$ with Estimated Standard Deviations in Parentheses.

Re--F	1.863(4)
$F\cdots F^{I}$	2.612(5)
$F\cdots F^{II}$	2.657(6)
$F\cdots F^{II'}$	3.144(5)
$Cs\cdots F$ (axial)	3.336(4)
$Cs\cdots F^{I'}$ (girdle)	3.111(4)
$Cs\cdots Re$ (axial)	4.070
$Cs\cdots Re'$ (girdle)	4.732
$F\text{--}Re\text{--}F^{I}$	89.0(2)
$F\text{--}Re\text{--}F^{II}$	91.0(2)

Atoms with Roman numerals as superscripts refer to atoms in the following positions:

I $y - x, y, z$
II $y, y - x, -z$

Primed atoms have the transition (2/3, 1/3, 1/3)

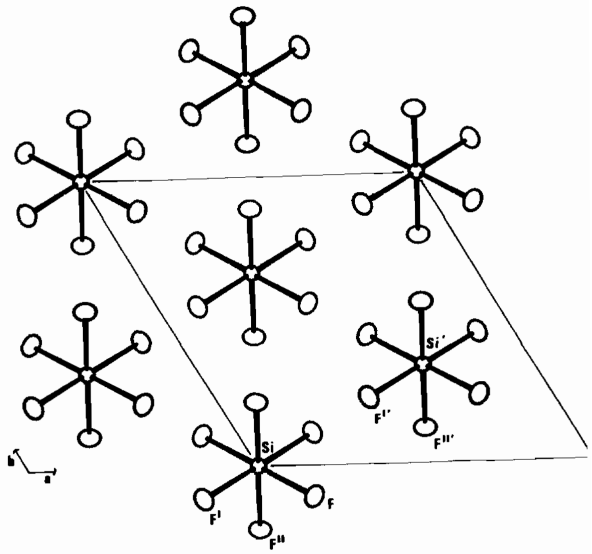

Fig. 1. A projection of $BaSiF_6$ onto (001). The Ba^{2+} ions *which lie directly above each Si atom, have been omitted for* clarity.

the fluorine atoms did not fall on a position of the type $x, \bar{x}, z$ (or its related positions), so that it was not possible to refine this structure in the space group $R\bar{3}m$. The loss of symmetry is due to a small rotation of the ReF_6^- octahedron about the 3-fold axis through the rhenium atom in the centre of each octahedron, thus destroying the mirror symmetry. Disorder was unlikely since a satisfactory refinement of the structure was obtained using the space group $R\bar{3}$.

In an attempt to refine the $CsReF_6$ structure in the space group $R\bar{3}m$ two factors indicated that this was the incorrect space group. Firstly in amalgamating the data a large number of inconsistencies arose as a result of trying to merge reflections which proved to be non-equivalent. Such inconsistencies did not occur when the data were merged in $R\bar{3}$. Secondly, during refinement in the space group $R\bar{3}$m, after placing fluorine atoms on the mirror plane a difference map revealed large peaks nearby, but not on the mirror planes. Therefore, forcing the structure into $R\bar{3}m$ symmetry did not satisfy the observed data, and the use of the space group $R\bar{3}$ provided the only reasonable solution.

The bond lengths and non-bonded distances are shown in Table IV. The increase in all distances compared to those in $BaSiF_6$ are due to the larger size of both the cesium ions and rhenium atoms. The stretching of the ReF_6^- octahedra along the 3-fold axis is much the same in magnitude as for SiF_6^{2-}. There is, however, a much larger difference (0.22 Å) between the cesium–fluorine axial distance and the cesium–fluorine girdle distance. This can probably be attributed to larger coulombic repulsions between cesium ions and the rhenium atoms in adjacent complex anions, compared to the corresponding Ba–Si interactions in $BaSiF_6$. The distance from a cesium ion to a rhenium atom along the 3-fold axis is 0.66 Å shorter than the distance from the cesium to rhenium atoms associated with the fluorine atoms forming the girdle. Thus a significant repulsion would be expected to take place between the cesium ions and the axial ReF_6^- complex anions, causing the longer Cs–F axial distances. Although the corresponding difference in Ba–Si distances is 0.81 Å, the smaller core charge of Si would cause less repulsion between Ba^{2+} and the SiF_6^{2-} complex anions, resulting in a smaller difference between Ba–F axial and girdle distances.

The lowering of symmetry in $CsReF_6$ is probably brought about by the large size of the Cs^+ cation. Structures of this type can be described as a cubic close packed lattice of F^- and A ions (A = Cs^+, Ba^{2+}, Tl^+, Rb^+) with octahedral sites being occupied by B atoms (B = Si, Re, *etc.*) in such a manner as to keep A ions separated in an AF_{12} co-ordination. In the case where the ionic radii of A and F are nearly identical, the cubic close packed AF_{12} lattice will be very stable and regular. This is the case with barium and fluorine ($r_{Ba^{2+}}$ = 1.35 Å; r_{F^-} = 1.33 Å), and little distortion would be expected for compounds such as $BaSiF_6$.

Where the cation A is much smaller than F^-, the cubic close packed array is no longer stable and other cubic, rhombohedral or tetragonal structures result [1] in which the co-ordination number of A is less than twelve.

If the cation A becomes larger than F^-, the ten-

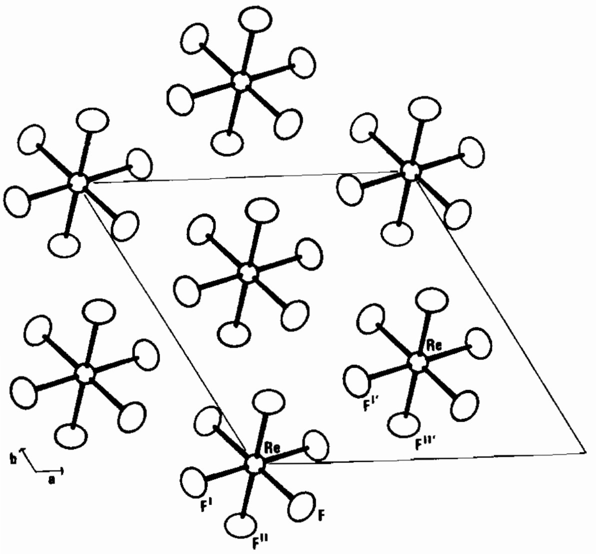

Fig. 2. A projection of $CsReF_6$ onto (001). The Cs^+ ions, which lie directly above each Re atom, have been omitted for clarity.

dency will be for the cubic close packed array to open up. This is the case for $CsReF_6$ where Cs^+ with an ionic radius of 1.69 Å, is much larger than the F^- radius. The effect of the larger cation is to push the surrounding six fluorine atoms of the girdle out in a hinge fashion, where the hinge axis is the atom in the octahedral site, in this case the Re atom. This hinging rotates the ReF_6^- octahedron about its 3-fold axis and lowers the symmetry for $\bar{3}m$ to $\bar{3}$. The effect of this rotation can be seen by comparing Figs. 1 and 2.

Kemmitt, Russell and Sharp [1] have found that a large number of ABF_6 compounds have the rhombohedral $KOsF_6$ structure when the radius ratio for A:F is greater than or equal to one. This is the case for $CsReF_6$ which, we have confirmed, does have the $KOsF_6$ structure. In the light of the above observations it could be suggested that most compounds of this type would fall into the space group $R\bar{3}$, especially when the A:F radius ratio is greater than one, causing distortion of the cubic close packed lattice. It is likely that the $R\bar{3}m$ structure is only feasible when the radius ratio is very close to unity as in $BaSiF_6$, and the lattice is not forced into distortion by the larger A cations. However, it is interesting to note that not all compounds with an A:F radius ratio of unity necessarily have the $R\bar{3}m$ symmetry, since $KOsF_6$ itself, which is $R\bar{3}$, has a K:F radius ratio of 1.0.

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