

## Three hexafluoridoiridates(IV), Ca[ $\text{IrF}_6$ ] $\cdot 2\text{H}_2\text{O}$ , Sr[ $\text{IrF}_6$ ] $\cdot 2\text{H}_2\text{O}$ and Ba[ $\text{IrF}_6$ ]

Anton I. Smolentsev,<sup>a\*</sup> Alexander I. Gubanov<sup>b,a</sup> and  
Andrey M. Danilenko<sup>a</sup>

<sup>a</sup>Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, Akademian Lavrentiev Prospekt 3, Novosibirsk 90, 630090 Russian Federation, and <sup>b</sup>Novosibirsk State University, Pirogova Street 2, Novosibirsk 90, 630090 Russian Federation

Correspondence e-mail: smolentsev@ngs.ru

Received 26 July 2007

Accepted 9 September 2007

Online 13 October 2007

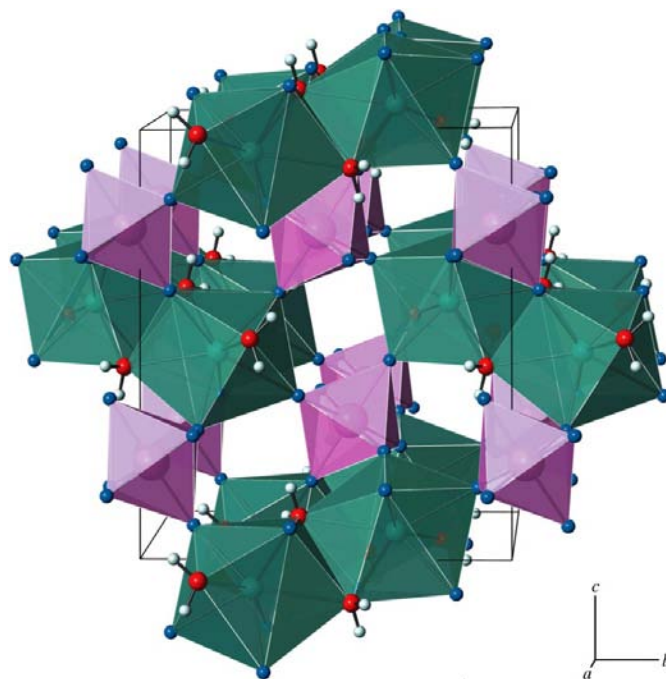
The structures of the hexafluoridoiridates(IV) of calcium, Ca[ $\text{IrF}_6$ ] $\cdot 2\text{H}_2\text{O}$  [calcium hexafluoridoiridate(IV) dihydrate], strontium, Sr[ $\text{IrF}_6$ ] $\cdot 2\text{H}_2\text{O}$  [strontium hexafluoridoiridate(IV) dihydrate], and barium, Ba[ $\text{IrF}_6$ ] [barium hexafluoridoiridate(IV)], have been determined by single-crystal X-ray analysis. The first two compounds are isomorphous. Their metal cations are eight-coordinated in a distorted square-antiprismatic coordination environment, and their anions are represented by an almost ideal octahedron. These two structures can be described as frameworks in which all atoms occupy general positions. Sr[ $\text{RhF}_6$ ] and Ba[ $\text{RhF}_6$ ] have a different space group ( $R\bar{3}m$ , from powder diffraction data) but similar cell dimensions. The structures are very close to that of Ba[ $\text{IrF}_6$ ]. The cation is in a cuboctahedral coordination. The metal atoms are located on special positions of  $\bar{3}$  symmetry, while the F atoms are in general positions.

### Comment

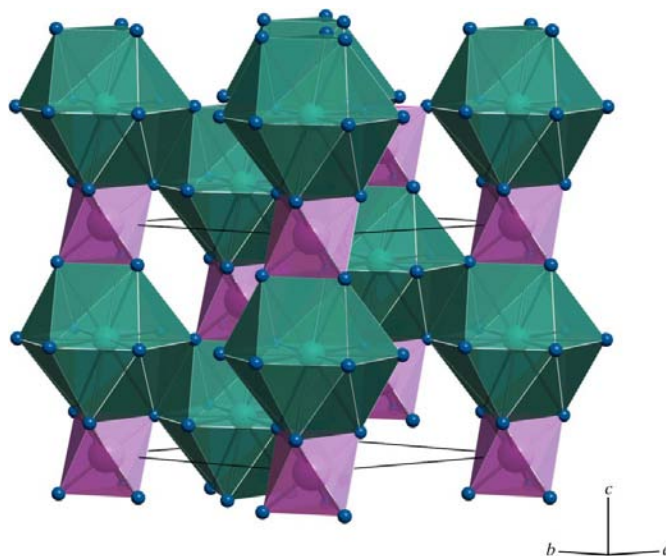
Fluorine-containing complexes of noble metals attract attention in various areas of chemistry, such as chemical analysis, electrochemistry and applied chemistry (Mitkin, 2001). In particular, this concerns hexafluoridometallates. However, structure determination using single-crystal X-ray analysis for many of these compounds has not been carried out yet. Among the complexes of  $\text{Ir}^{\text{IV}}$ , several have been characterized by X-ray powder diffraction (Babel, 1967), but only one structure solved by the single-crystal method ( $\text{K}_2[\text{IrF}_6]$ ; Fitz *et al.*, 2002) is currently available. A new contribution to the crystal chemistry of these compounds seemed useful. We focused our attention on the investigation of alkali and alkaline earth metal hexafluoridoiridates. In this paper, the syntheses and structures of three complexes, namely

Ca[ $\text{IrF}_6$ ] $\cdot 2\text{H}_2\text{O}$  (I), Sr[ $\text{IrF}_6$ ] $\cdot 2\text{H}_2\text{O}$  (II), and Ba[ $\text{IrF}_6$ ] (III), are reported.

The first two title compounds, (I) and (II), are isostructural. The coordination environment of the alkaline earth metal cations includes five F atoms and three  $\text{H}_2\text{O}$  molecules, forming a distorted square antiprism (Fig. 1). The complex anion,  $[\text{IrF}_6]^{2-}$ , has the shape of an almost ideal octahedron, with average Ir–F distances of 1.934 (7) and 1.913 (10) Å for



**Figure 1**  
A packing diagram for the Ca[ $\text{IrF}_6$ ] $\cdot 2\text{H}_2\text{O}$  and Sr[ $\text{IrF}_6$ ] $\cdot 2\text{H}_2\text{O}$  structures, viewed along  $[100]$ . Hydrogen bonds have been omitted for clarity.



**Figure 2**  
A packing diagram for the Ba[ $\text{IrF}_6$ ] structure, viewed along  $[\bar{1}10]$ .

the Ca and Sr compounds, respectively. In each anion, five F atoms coordinate to the metal cation and one is involved in hydrogen bonding. There are two types of H<sub>2</sub>O molecules, each with a different function. The molecules of one type bridge two cations, while molecules of the other type coordinate only to single cations. Both types also form strong hydrogen bonds with each other and with the F atoms. In addition, there are longer O—H...F contacts, with distances of about 3.4 Å.

The barium compound, (III), is isostructural with the Sr[RhF<sub>6</sub>] and Ba[RhF<sub>6</sub>] complexes (Wilhelm & Hoppe, 1974). They all belong to the Ba[GeF<sub>6</sub>] structural type. The coordination environment of the Ba<sup>2+</sup> cation includes 12 equidistant F atoms, forming a slightly distorted cuboctahedron. Each F atom is shared between two cuboctahedra and forms one vertex of the [IrF<sub>6</sub>]<sup>2-</sup> octahedron. Thus, the anion interconnects eight Ba<sup>2+</sup> cations. The Ba and Ir atoms form two rhombohedral sublattices separated by *c*/2 (Fig. 2).

## Experimental

The title compounds were synthesized by the following method. Firstly, K<sub>2</sub>[IrCl<sub>6</sub>] was obtained by reaction between IrCl<sub>4</sub>·4H<sub>2</sub>O dissolved in concentrated HCl and KCl solution in a K:Ir ratio of 2:1. In the second stage, K<sub>2</sub>[IrF<sub>6</sub>] was obtained by the interaction of K<sub>2</sub>[IrCl<sub>6</sub>] with gaseous F<sub>2</sub> at atmospheric pressure and 573 K in a flow reactor. An aqueous solution of K<sub>2</sub>[IrF<sub>6</sub>] was then treated with ion-exchange resin in the H form for one day. The mixture was filtered and a solution of H<sub>2</sub>[IrF<sub>6</sub>] acid was collected. Concentration by evaporation at room temperature yielded a solution of 0.11 M. Ca[IrF<sub>6</sub>]·2H<sub>2</sub>O, Sr[IrF<sub>6</sub>]·2H<sub>2</sub>O and Ba[IrF<sub>6</sub>] were prepared by the reaction between 0.11 M H<sub>2</sub>[IrF<sub>6</sub>] (5 ml) and the corresponding reagent, viz. CaO (56 mg), SrCO<sub>3</sub> (74 mg) or BaCO<sub>3</sub> (99 mg). Crystals suitable for X-ray analysis were obtained, in each case, by slow evaporation at room temperature.

### Compound (I)

#### Crystal data

Ca[IrF <sub>6</sub> ]·2H <sub>2</sub> O	<i>V</i> = 612.22 (3) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 382.31	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 5.9055 (2) Å	<i>μ</i> = 22.72 mm <sup>-1</sup>
<i>b</i> = 9.5369 (3) Å	<i>T</i> = 296 (2) K
<i>c</i> = 11.0140 (3) Å	0.10 × 0.06 × 0.04 mm
<i>β</i> = 99.2620 (10)°	

#### Data collection

Bruker Nonius X8 APEX CCD area-detector diffractometer	5426 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2004)	1790 independent reflections
<i>T</i> <sub>min</sub> = 0.210, <i>T</i> <sub>max</sub> = 0.464 (expected range = 0.182–0.403)	1688 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R</i> <sub>int</sub> = 0.028

#### Refinement

<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.021	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.056	<i>Δρ</i> <sub>max</sub> = 0.94 e Å <sup>-3</sup>
<i>S</i> = 1.25	<i>Δρ</i> <sub>min</sub> = -2.84 e Å <sup>-3</sup>
1790 reflections	
107 parameters	
6 restraints	

**Table 1**  
Selected bond lengths (Å) for (I).

Ir1—F5	1.926 (2)	Ca1—F3 <sup>ii</sup>	2.306 (3)
Ir1—F1	1.929 (3)	Ca1—F6 <sup>iii</sup>	2.313 (3)
Ir1—F4	1.931 (3)	Ca1—F2 <sup>iv</sup>	2.326 (3)
Ir1—F6	1.937 (3)	Ca1—F1	2.402 (3)
Ir1—F3	1.937 (2)	Ca1—O1	2.464 (4)
Ir1—F2	1.947 (2)	Ca1—O2 <sup>v</sup>	2.540 (4)
Ca1—F5 <sup>i</sup>	2.281 (3)	Ca1—O2	2.607 (3)

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (iv)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (v)  $-x + 1, -y, -z + 1$ .

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1B...F4 <sup>vi</sup>	0.81 (4)	1.96 (5)	2.736 (4)	159 (8)
O2—H2B...F4 <sup>iii</sup>	0.78 (4)	2.07 (4)	2.777 (5)	152 (6)
O2—H2A...O1 <sup>vii</sup>	0.83 (4)	2.14 (4)	2.966 (5)	175 (5)

Symmetry codes: (iii)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (vi)  $x + 1, y, z$ ; (vii)  $x - 1, y, z$ .

### Compound (II)

#### Crystal data

Sr[IrF <sub>6</sub> ]·2H <sub>2</sub> O	<i>V</i> = 655.82 (5) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 429.85	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>	Mo <i>K</i> α radiation
<i>a</i> = 6.0328 (2) Å	<i>μ</i> = 28.47 mm <sup>-1</sup>
<i>b</i> = 9.8264 (4) Å	<i>T</i> = 296 (2) K
<i>c</i> = 11.2123 (5) Å	0.18 × 0.08 × 0.04 mm
<i>β</i> = 99.3630 (10)°	

#### Data collection

Bruker Nonius X8 APEX CCD area-detector diffractometer	5732 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2004)	1895 independent reflections
<i>T</i> <sub>min</sub> = 0.080, <i>T</i> <sub>max</sub> = 0.336	1753 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R</i> <sub>int</sub> = 0.018

#### Refinement

<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.019	H atoms treated by a mixture of independent and constrained refinement
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.052	<i>Δρ</i> <sub>max</sub> = 2.33 e Å <sup>-3</sup>
<i>S</i> = 1.12	<i>Δρ</i> <sub>min</sub> = -1.25 e Å <sup>-3</sup>
1895 reflections	
107 parameters	
6 restraints	

**Table 3**  
Selected bond lengths (Å) for (II).

Ir1—F5	1.903 (3)	Sr1—F2 <sup>ii</sup>	2.454 (3)
Ir1—F1	1.907 (3)	Sr1—F3 <sup>iii</sup>	2.453 (3)
Ir1—F4	1.909 (3)	Sr1—F6 <sup>iv</sup>	2.461 (3)
Ir1—F3	1.910 (3)	Sr1—F1	2.515 (3)
Ir1—F6	1.919 (3)	Sr1—O1	2.610 (4)
Ir1—F2	1.930 (3)	Sr1—O2 <sup>v</sup>	2.700 (4)
Sr1—F5 <sup>i</sup>	2.421 (3)	Sr1—O2	2.704 (4)

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (iv)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (v)  $-x + 1, -y, -z + 1$ .

**Table 4**  
Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1B...F4 <sup>vi</sup>	0.81 (4)	1.97 (4)	2.784 (6)	175 (7)
O2—H2B...F4 <sup>iv</sup>	0.73 (4)	2.11 (4)	2.788 (5)	154 (6)
O2—H2A...O1 <sup>vii</sup>	0.80 (4)	2.29 (5)	3.002 (6)	149 (6)

Symmetry codes: (iv)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (vi)  $x + 1, y, z$ ; (vii)  $x - 1, y, z$ .

**Compound (III)***Crystal data*

Ba[IrF <sub>6</sub> ]	Z = 3
M <sub>r</sub> = 443.54	Mo K $\alpha$ radiation
Trigonal, R $\bar{3}$	$\mu$ = 37.44 mm <sup>-1</sup>
a = 7.3965 (5) Å	T = 293 (2) K
c = 7.2826 (7) Å	0.12 × 0.04 × 0.04 mm
V = 345.04 (5) Å <sup>3</sup>	

*Data collection*

Bruker Nonius X8 APEX CCD area-detector diffractometer	889 measured reflections 182 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 2004)	182 reflections with I > 2 $\sigma$ (I) R <sub>int</sub> = 0.037
T <sub>min</sub> = 0.178, T <sub>max</sub> = 0.216	

*Refinement*

R[F <sup>2</sup> > 2 $\sigma$ (F <sup>2</sup> )] = 0.024	15 parameters
wR(F <sup>2</sup> ) = 0.066	$\Delta\rho_{\max}$ = 1.91 e Å <sup>-3</sup>
S = 1.22	$\Delta\rho_{\min}$ = -2.46 e Å <sup>-3</sup>
182 reflections	

**Table 5**

Selected bond lengths (Å) for (III).

Ir1—F1	1.935 (4)	Ba1—F1	2.800 (4)
--------	-----------	--------	-----------

The H atoms were located in difference electron-density maps and refined with O—H distances restrained to 0.82 (5) Å and H···H

distances restrained to 1.30 (5) Å (to obtain H—O—H angles of about 105°).

For all compounds, data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2004); program(s) used to refine structure: *SHELXTL*; molecular graphics: *BS* (Ozawa & Kang, 2004); software used to prepare material for publication: *SHELXTL*.

The authors thank Dr D. Yu. Naumov for helpful comments.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3025). Services for accessing these data are described at the back of the journal.

**References**

- Babel, D. (1967). *Structure and Bonding*, Vol. 3, pp. 1–87. Berlin, Heidelberg, New York: Springer-Verlag.
- Bruker (2004). *APEX2* (Version 1.08), *SAINT* (Version 7.03), *SADABS* (Version 2.11) and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.
- Fitz, H., Muller, B. G., Graudejus, O. & Bartlett, N. (2002). *Z. Anorg. Allg. Chem.* **628**, 133–137.
- Mitkin, V. N. (2001). *Spectrochim. Acta B*, **56**, 137–175.
- Ozawa, T. C. & Kang, S. J. (2004). *Balls & Sticks (BS)*. Version 1.51. URL: <http://www.softbug.com/toycrate/bs>.
- Wilhelm, V. & Hoppe, R. (1974). *Z. Anorg. Allg. Chem.* **407**, 13–22.