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Synthesis and Characterization of Barium Hexafluoridoosmates

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Abstract: Two barium hexafluoridoosmates, Ba(OsF$_6$)$_2$ and BaOsF$_6$, were synthesized and were characterized for the first time using X-ray powder and single crystal diffraction, IR spectroscopy, as well as NMR spectroscopy in anhydrous hydrogen fluoride. Ba(OsF$_6$)$_2$ crystallizes in the space group type $P2_1/c$ with the cell parameters $a = 6.4599(4)$, $b = 10.7931(8)$, $c = 14.7476(10)$ Å, $\beta = 115.195(5)^\circ$, $V = 930.42(12)$ Å$^3$, $Z = 4$ at 293 K. BaOsF$_6$ crystallizes in the space group type $R3$ with the cell parameters $a = 7.3286(10)$, $c = 7.2658(15)$ Å, $V = 337.95(12)$ Å$^3$, $Z = 3$ at 100 K. Additionally, we have obtained the compounds Ba(OsF$_6$)$_2$·3BrF$_3$, Ba(OsF$_6$)$_2$·HF, Ba(OsF$_6$)$_2$·6H$_2$O from the respective solvents, and Ba(OsF$_6$)$_2$.

Keywords: osmium; fluorides; bromine trifluoride; crystal structure

1. Introduction

The fluoroanions of osmium, OsF$_6^-$ and OsF$_6^{2-}$, are known since the 1950s. The first compounds containing these species were prepared by Hepworth and coworkers [1]: MOsF$_6$ ($M = $ Li, K, Rb, Cs, Ag) and $M_2$OsF$_6$ ($M = $ K, Cs), and were later characterized by various techniques, such as IR spectroscopy [2–6] and X-ray diffraction [7–9]. Both anions can be of relevance for the urban mining processes [10,11] and the analytical chemistry of osmium [12,13]. Furthermore, the recent investigations showed that both species can be treated as model systems for investigating spin-orbit entangled phenomena in complexes with Os$^{4+}$ and Os$^{5+}$ atoms [14].

To the best of our knowledge, no alkaline-earth metal compounds with hexafluoridoosmate ions have been synthesized so far. Here, we present our results on the syntheses and characterization of the two barium hexafluoridoosmates: BaOsF$_6$ and Ba(OsF$_6$)$_2$. Also, we briefly report three derivatives of barium hexafluoridoosmate(V), which are solvates: “Ba(OsF$_6$)$_2$·nBrF$_3$”, “Ba(OsF$_6$)$_2$·nHF”, and Ba(OsF$_6$)$_2$·6H$_2$O.

2. Materials and Methods

General: All of the operations with the compounds were carried out in an atmosphere of dry and purified argon (Westfalen AG, Münster, Germany), so that a possible contact of the substance with moisture or air was minimized ($O_2 < 1$ ppm, $H_2O < 1$ ppm). BrF$_3$ was synthesized by slowly passing gaseous fluorine through liquid bromine in an FEP U-tube reactor. Anhydrous HF was additionally dried by storing it over K$_2$NiF$_6$. BaF$_2$ and Os were used without additional purification.
Preparation of Ba(OsF₆)₂: BaF₂ (0.1137 g, 0.65 mmol, 1.00 equiv.) and Os (0.2466 g, 1.30 mmol, 1.00 equiv.) were placed in an FEP tube and were layered with large excess of bromine trifluoride (1 mL, 2.8 g, 20.45 mmol, 69.13 equiv.). The FEP tube was closed with a PFA valve and was allowed to stay for 24 h at 120 °C with occasional shaking. After that the excess of BrF₃ was pumped off at room temperature, the tube was flushed with argon several times and the compound was stored in a glove box with an inert atmosphere in a Teflon container. The total yield of dry product was 0.463 g (0.62 mmol, 95.7% of theory).

Preparation of Ba(OsF₆)₃: Ba(OsF₆)₂ (0.1334 g, 0.65 mmol, 1.00 equiv.) was placed in an Teflon beaker and was dissolved in ~5 mL of H₂O (5 g, 277 mmol, 517 equiv.). The beaker was left on a hot plate set up to 80 °C. After complete evaporation of water, the product was transferred into a Teflon container and further handled on air. The total yield of the dry product was 0.080 g (80.9% of theory), which corresponds to 0.064 g of BaOsF₆ and 0.016 g of OsO₂, according to Reaction 2.

Preparation of Ba(OsF₆)₂·3BrF₃: Ba(OsF₆)₂ (0.05 g, 0.067 mmol) was placed in an FEP tube and covered with a small amount of BrF₃ (~0.1 mL). The FEP tube was heated to 120 °C and then allowed to cool down to room temperature on air. Upon cooling the crystals of the target product were formed in the tube and were then picked directly out of BrF₃. The mass of the product was not determined due to the presence of the excess solvent.

Preparation of Ba(OsF₆)₂·HF: Ba(OsF₆)₂ (0.05 g, 0.067 mmol) was placed in an FEP tube. A small amount of HF (~0.1 mL) was distilled at −196 °C into the tube and then was heated up to 50 °C in order to dissolve the hexafluoridoosmate. Then, the FEP tube was allowed to cool down to room temperature on air. Upon cooling the crystals of the target product were formed in the tube and were then picked directly out of HF. The mass of the product was not determined due to the presence of the excess solvent.

Preparation of Ba(OsF₆)₂·6H₂O: Ba(OsF₆)₂ (0.05 g, 0.067 mmol) was placed on an FEP plate. A few droplets of water were placed on the substance. Then, the plate was allowed to stay in the air flow of the laboratory ventilation to facilitate the drying process without heating. When a significant amount of water was evaporated and the crystals of the target compound appeared, the plate was transferred into a refrigerator and was kept there at −35 °C. Storage at room temperature leads eventually to the decomposition of the product into BaOsF₆ and the black powder. The mass of the product was not determined due to the presence of the excess solvent.

Density Measurement Details: The density of Ba(OsF₆)₂ was measured using the automated gas displacement pycnometry system AccuPyc II 1340 (Micromeritics, Aachen, Germany) using a calibrated 0.1 cm³ sample holder and helium as the gas being displaced. The number of preliminary purges was set to 30, while the subsequent density measurements were done 50 times with further averaging.

Single Crystal X-ray Diffraction: Structure analysis was carried out using a Stoe IPDS2 (Stoe, Darmstadt, Germany) or IPDS2T diffractometer IPDS2 (Stoe, Darmstadt, Germany) with monochromated molybdenum radiation (Mo-Kα, λ = 0.71073 Å, a plane graphite monochromator) and an image plate detector. Evaluation and integration of the diffraction data was carried out using the Stoe X-Area software suite (v1.69) [15], and an empirical absorption correction was applied. The structure was solved using direct methods (SHELXT, 2014/4) [16] and refined against F² (SHELXL) [17]. All of the atoms were located by Difference Fourier synthesis. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/requestfordepositeddata.html) on quoting the depository numbers Ba(OsF₆)₂: CSD-433821, BaOsF₆: CSD-433819, Ba(OsF₆)₂·6H₂O: CSD-433821.

X-ray Powder Diffractometry: Powder X-ray diffraction patterns were obtained with a Stadi-MP diffractometer (Stoe, Darmstadt, Germany) using Cu-Kα1 radiation, a germanium monochromator, and a Mythen1K detector (the resolution is 0.015 Å). A sample of Ba(OsF₆)₂ was filled into a flame-dried quartz capillary (Ø 0.3 mm) inside a glove box, and then sealed. The measurement was carried out in the 2θ range from 10 to 75° with a detector step of 0.3° and collection time of 250 s. The data
were handled and indexed using the WinXPOW software (v3.07) [18]. Le Bail profile fitting, space group assignment and Rietveld refinement were done in the Jana2006 software [19]. The structure solution prior to the Rietveld refinement was done using the SUPERFLIP algorithm [20] implemented in Jana2006. Barium and osmium atoms were refined isotropic, whereas the displacement parameters of the fluorine atoms were fixed.

**NMR spectroscopy:** $^1$H and $^{19}$F NMR spectra were recorded on a Bruker Avance III HD 300 NMR spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany). $^1$H NMR spectroscopy (300 MHz, Bruker BioSpin GmbH, Rheinstetten, Germany) used SiMe$_4$ and $^{19}$F NMR spectroscopy (293 MHz) used neat CFCI$_3$ as an external reference, respectively. Samples were prepared by condensing liquid anhydrous hydrogen fluoride onto Ba(OsF$_6$)$_2$ at −196 °C in 3 mm FEP tubes, which were sealed with a heat gun and these were subsequently placed in standard 5 mm glass NMR tubes. Chemical shifts are given for 300 K at 1.31 bar hydrogen fluoride vapor pressure. Ba(OsF$_6$)$_2$: $^{19}$F (aHF): $\delta = 149.03$ (OsF$_6^−$).

**IR Spectroscopy:** The IR spectra of BaOsF$_6$ were recorded using a Bruker Alpha FTIR spectrometer (Bruker Optik GmbH, Rosenheim, Germany) under an Ar atmosphere. The data were handled in the OPUS software package [21].

**Computational Details:** The structural and spectroscopic properties of Ba(OsF$_6$)$_2$ and BaOsF$_6$ were investigated using the CRYSTAL14 program package (CRYSTAL14) [22,23]. Both the atomic positions and the lattice parameters were fully optimized using the PBE0 hybrid density functional method [24,25]. Split-valence + polarization (SVP) level basis sets, as derived from the molecular Karlsruhe basis sets [26], were applied for all the atoms (see Supporting information for additional basis set details). The reciprocal space was sampled using a compound-dependent Monkhorst-Pack-type k-point grid: $6 \times 4 \times 2$ for Ba(OsF$_6$)$_2$ and $8 \times 8 \times 8$ for BaOsF$_6$ [27]. For the evaluation of the Coulomb and exchange integrals (TOLINTEG), tight tolerance factors of 8, 8, 8, 8, and 16 were used. Default optimization convergence thresholds and DFT integration grids were applied in all calculations. For Ba(OsF$_6$)$_2$, we carried out spin-polarized calculations. We set the spin orientations for the crystallographically inequivalent osmium atoms so that we obtained an antiferromagnetic ordering. The harmonic vibrational frequencies [28,29] and IR intensities [30] were obtained by using the computational schemes that were implemented in CRYSTAL. The IR spectrum of BaOsF$_6$ was broadened by using Lorenzian peak profile and FWHM of 8 cm$^{-1}$.

3. Results

3.1. Synthesis of Barium Hexafluoridoosmate(V)

We used bromine trifluoride as the oxidizing and fluorinating medium for the synthesis of Ba(OsF$_6$)$_2$ [1]. A stoichiometric mixture of BaF$_2$ and osmium metal was loaded into a vessel made of FEP (perfluorinated ethylene-propylene copolymer) and covered with an excess of BrF$_3$. The tightly closed vessel was heated up to 120 °C and kept at this temperature for 24 h. Under these conditions, the oxidation of osmium slowly proceeds, according to the following Equation (1):

$$3 \text{BaF}_2 + 6 \text{Os} + 10 \text{BrF}_3 \rightarrow 3 \text{Ba(OsF}_6\text{)_2} + 5 \text{Br}_2.$$

After cooling down to room temperature the FEP vessel contained a clear green-brown solution. The excess of bromine trifluoride was pumped off yielding a fine pale-pink powder with a mass corresponding to the composition of Ba(OsF$_6$)$_2$ (see experimental details).

3.2. Synthesis of Barium Hexafluoridoosmate(IV)

BaOsF$_6$ was obtained by dissolving Ba(OsF$_6$)$_2$ in water and evaporating the solution at 80 °C. Upon the addition of water the solution became pale yellow and small gas bubbles appeared, which was reported to be OsO$_4$ [1]. When the water was completely evaporated, a mixture of a black powder with colorless crystals was obtained. The nature of the black powder is yet unclear, however, the experimental data indicate that osmium(IV) dioxide formed due to the disproportionation
of the OsF$_6^-$ anion in aqueous solution. The tentative reaction can be described by the following Equation (2):

$$2 \text{Ba(OsF}_6^2\text{)}_2 + 6 \text{H}_2\text{O} \rightarrow 2 \text{BaOsF}_6 + \text{OsO}_4 + \text{OsO}_2 + 12 \text{HF}$$  (2)

3.3. Attempts to Grow Single Crystals of Ba(OsF$_6^2$)$_2$

As no single crystals of barium hexafluoridoosmate(V) were obtained after evaporation of bromine trifluoride, we attempted to grow them using the following solvents: BrF$_3$, HF, and H$_2$O. However, in all of the cases, solvent molecules were retained in the crystal lattice forming solvates.

3.3.1. Bromine Trifluoride

If BrF$_3$ is not evaporated completely, the growth of large prismatic light-green crystals can be observed. The compound was identified as a BrF$_3$ solvate of Ba(OsF$_6^2$)$_2$. However, we faced certain difficulties with the structure elucidation (see Section 3.3). Thus, details on this compound will be reported elsewhere.

3.3.2. Anhydrous Hydrogen Fluoride (aHF)

Ba(OsF$_6^2$)$_2$ was found to be well soluble in aHF forming a reddish solution and yielding pink crystals after evaporation. However, the resulting compound seems to retain at least one molecule of HF, and can be described with a preliminary formula “Ba(OsF$_6^2$)$_2$·HF”.

3.3.3. Water

It was noticed that during the synthesis of BaOsF$_6$, the hydrolysis of Ba(OsF$_6^2$)$_2$ does not happen immediately. If water is quickly evaporated from a large surface of the solution without heating, the residue is a thin colorless film consisting of small crystals. According to single crystal diffraction data, they belong to another compound: Ba(OsF$_6^2$)$_2$·6H$_2$O.

4. Discussion

4.1. Barium Hexafluoridoosmate(V)

No single crystals of Ba(OsF$_6^2$)$_2$ have been obtained so far. Despite that it was possible to successfully solve its crystal structure on the basis of powder X-ray diffraction data. The powder diffraction pattern of Ba(OsF$_6^2$)$_2$ recorded in a sealed quartz capillary is shown in Figure 1. The structure solution was carried out using the SUPERFLIP algorithm [31] and implemented in the Jana2006 software [32]. Due to the instability of the Rietveld refinement only the Os and the Ba atoms could be refined isotropic. The thermal displacement parameters of the fluorine atoms had to be fixed.

Barium bis(hexafluoroosmate(V)) crystallizes in the monoclinic primitive space group type $P2_1/c$ (No. 14) with the cell parameters $a = 6.4599(4)$, $b = 10.7931(8)$, $c = 14.7476(10)$ Å, $\beta = 115.195(5)^\circ$, $V = 930.42(12)$ Å$^3$, and $Z = 4$ at 293 K. The pycnometric density equals 5.20 ± 0.04 g/cm$^3$, which is sufficiently close to the theoretical value of 5.3236 g/cm$^3$. The crystal structure of Ba(OsF$_6^2$)$_2$ is shown in Figure 2; its asymmetric unit is shown in Figure 3.

All atoms in the crystal lattice of Ba(OsF$_6^2$)$_2$ occupy the general 4e Wyckoff position. The barium cation is coordinated by nine fluorine atoms belonging to nine different OsF$_6^-$ anions resulting in a tricapped trigonal prismatic coordination sphere.
Figure 1. Powder X-ray diffraction pattern (at 293 K) of Ba(OsF$_6$)$_2$: the experimental data (black crosses), the Rietveld profile (red), and the differential profile (bottom, black). The calculated reflection positions for Ba(OsF$_6$)$_2$ are shown as black ticks. $R_p = 0.0343$, $wR_p = 0.0492$.

Figure 2. The crystal structure of Ba(OsF$_6$)$_2$ (projection along $a$-axis). Atoms are shown with isotropic displacement parameters, F atoms with fixed ones.

Figure 3. Asymmetric unit of Ba(OsF$_6$)$_2$. Atoms are shown with isotropic displacement parameters, F atoms with fixed ones.
Due to the low precision in the determination of the bond lengths and angles, it was not possible to carry out a detailed analysis of the structural features in Ba(OsF$_6$)$_2$. For further information, we also optimized the structure with quantum chemical methods (DFT-PBE0/SVP level of theory). Some selected experimental and calculated values are given in Table 1, together with the corresponding values in KOsF$_6$, which is a well characterized compound with the OsF$_6^-$ anion [8]. The experimental and theoretical lattice constants are in good agreement (differences less than 1.3%). The calculated bond lengths and angles correspond to the experimental values within the 3σ criterion. The crystallographic details of Ba(OsF$_6$)$_2$ are given in Table 2.

| Table 1. Selected crystallographic data for Ba(OsF$_6$)$_2$ and KOsF$_6$ [8]. |
|-----------------|-----------------|-----------------|
| Value           | Ba(OsF$_6$)$_2$ | KOsF$_6$       |
|                 | Exp.           | DFT-PBE0        |
| $a$, Å          | 6.4599(4)      | 6.46           |
| $b$, Å          | 10.7931(8)     | 10.65          |
| $c$, Å          | 14.7476(10)    | 14.55          |
| β, °            | 115.195(5)     | 114.8          |
| V, Å$^3$        | 930.42(12)     | 908.38         |
| $M_{\cdot}\cdot\cdot F$ | 2.64(11) | 2.61           |
| Os–F            | 1.72(9)        | 1.87           |
| F–Os–F#         | 2.08(10)       | 1.92           |
| F–Os–F#         | 82(4)          | 86(1)          |

| Table 2. Crystallographic details of the characterized compounds. |
|-----------------|-----------------|-----------------|
| Parameter       | Ba(OsF$_6$)$_2$ | BaOsF$_6$      |
|                 |                 | BaOsF$_6$·6H$_2$O |
| Empirical formula | BaF$_{12}$Os$_2$ | BaF$_6$Os       |
| Color and appearance | Pale-pink powder | Colorless needles |
| Crystal system  | Monoclinic      | Triclinic       |
| Space group     | $P2_1/c$ (No. 14) | R$\bar{3}$ (No. 148) |
| $a$, Å          | 6.4599(4)       | 7.3286(10)      |
| $b$, Å          | 10.7931(8)      | 7.6258(15)      |
| $c$, Å          | 14.7476(10)     | 90.0            |
| $\alpha$, °     | 90              | 90              |
| $\beta$, °      | 115.195(5)      | 90              |
| $\gamma$, °     | 90.195(5)       | 90              |
| V, Å$^3$        | 930.42(12)      | 337.95(12)      |
| Z                | 4               | 3               |
| $\rho$ calc/g cm$^{-3}$ | 5.324 | 6.509           |
| $\mu$/mm$^{-1}$ | 85.272         | 36.892          |
| Size/mm$^3$     |                | 19.869          |
| $\lambda$, Å    | 1.540598 (Cu-K$\alpha$) | 0.71073 (Mo-K$\alpha$) |
| $T$, K          | 293             | 100             |
| $R_{wp}$, $R_p$ | –               | 0.0343, 0.0492  |
| $\omega$R$_p$, $\omega$R$_p$ | 0.0365, 0.0468 | 0.0199, 0.0390 |
| $R(I^2)$ (all data), $\omega$R($I^2$) (all data) | 0.0336, 0.0383 | 0.0336, 0.0383 |
| $S$ (all data)  | 4.736           | 1.344           |
| No. of data points, parameters, constraints, restraints | 4356, 85, 0, 0 | 5088, 227, 0, 0 |
| 20 range measured (min; max; increment) | 10, 75.325, 0.015 | 4.44, 63.80, – |
| 20 range refined (min; max) | 10, 75.325, 0.015 | 4.44, 63.80, – |
| $\Delta$min/\Delta$\max$, e Å$^{-1}$ | – | 1.323, –1.195 |

We recorded the IR spectrum of Ba(OsF$_6$)$_2$ in the range from 4000 to circa 360 cm$^{-1}$. We observe no vibrations in the range down to 1500 cm$^{-1}$, which shows the purity of the compound. For further details of the band assignment in the region from 1500 to 360 cm$^{-1}$, see the Supporting Information, Figure S1 and Table S1.
Additionally, we measured the $^1$H and $^{19}$F NMR spectra (Figure S2) of the compound dissolved in anhydrous hydrogen fluoride at room temperature. Due to the paramagnetic properties of osmium(V), the signals are broadened and the chemical shift is unpredictable in NMR spectroscopy [31]. The paramagnetic shift of the solvent additionally gives information on the interaction of Ba(OsF$_6$)$_2$ with the solvent.

The proton signal of HF in the $^1$H NMR spectrum of a Ba(OsF$_6$)$_2$ solution in anhydrous hydrogen fluoride (Figure 4) was observed at 19.93 ppm ($\omega_{1/2} = 12.6$ Hz). This is a downfield shift of 10.55 ppm when compared to neat anhydrous hydrogen fluoride which we observed at 8.38 ppm ($\omega_{1/2} = 2.9$ Hz). This trend is also observed in the $^{19}$F NMR spectrum (Figure 5) where the fluorine signal of HF was observed at $-176.32$ ppm ($\omega_{1/2} = 79.0$ Hz), which is a downfield shift of 22 ppm as compared to neat hydrogen fluoride ($-198.32$ ppm, $\omega_{1/2} = 12.0$ Hz). This distinct paramagnetic down field shift is indicative for a considerable interaction of the paramagnetic OsF$_6^{-}$-moiety with the solvent, and it is expected if the osmium(V)-anion is in solution. The observed chemical shift of neat anhydrous hydrogen fluoride in the $^1$H and $^{19}$F NMR spectra are in good agreement with literature values [32].

![Figure 4](image-url)  
Figure 4. $^1$H NMR spectra of neat anydrous HF (top) and anhydrous HF with Ba(OsF$_6$)$_2$ (bottom).

![Figure 5](image-url)  
Figure 5. $^{19}$F NMR spectrum of anhydrous HF (top) and Ba(OsF$_6$)$_2$ in anhydrous HF (bottom).

While in the $^1$H NMR spectrum of Ba(OsF$_6$)$_2$ solutions in HF, no further signal was observed—as would be expected—one additional signal at 149.03 ppm, with a very broad line width ($\omega_{1/2} = 131.6$ Hz) was observed in the $^{19}$F NMR spectrum (Figure 6). This signal is assigned to the OsF$_6^{-}$-anion and indicates that only one species is present in solution. Therefore, the anions are solvent separated and do not interact with each other.
4.2. Barium Hexafluoridoosmate(IV)

As mentioned above, we obtained BaOsF$_6$ in the form of colorless crystals with an impurity of the yet unidentified black powder. One of the crystals was selected under perfluorinated oil and was mounted on the goniometer using the MiTeGen MicroLoops$^\text{TM}$ system.

By single crystal X-ray diffraction we observed that barium hexafluoridoosmate(IV) crystallizes in the trigonal centered space group type $R\overline{3}$ (No. 148) with the cell parameters $a = 7.3286(10)$, $c = 7.2658(15)$ Å, $V = 337.95(12)$ Å$^3$, $Z = 3$ at 100 K and, therefore, isotypic to BaRuF$_6$ [8,33] and BaIrF$_6$ [8,34]. The crystal structure of BaOsF$_6$ is shown in Figure 7. A section of its crystal structure showing one formula unit is given in Figure 8.

![Figure 7](image1.png)  
Figure 7. The crystal structure of BaOsF$_6$ (projection along c-axis). Displacement ellipsoids are shown at 70% probability level at 100 K.

![Figure 8](image2.png)  
Figure 8. Formula unit of BaOsF$_6$. Displacement ellipsoids are shown at 70% probability at 100 K.
The barium ion occupies the special $3b$ Wyckoff position and is coordinated by twelve fluorine atoms, which stem from eight OsF$_6^{2-}$ anions. The resulting coordination polyhedron is close to a cuboctahedron. The Ba⋯F distances are 2.773(3) and 2.870(3) Å.

Each osmium atom resides on the special $3a$ Wyckoff position ($3$) and is coordinated by six fluorine atoms (each on the general $18f$ position), resulting in an arrangement that is very similar to an octahedron ($S_6$-symmetry). The Os–F bond length is 1.937(3) Å, the F–Os–F# angles are 85.68(12), and 94.32(12)$°$. Similar values are reported for the isotypic BaIrF$_6$ with the Ir–F bond being 1.936(4) Å and F–Ir–F# angles of 85.93(17) and 94.07(16)$°$. The experimentally determined and calculated cell parameters, bond lengths, and angles of BaOsF$_6$ are given in Table 2. As to the best of our knowledge, no other compound containing a OsF$_6^{2-}$ anion has been structurally characterized so far, we compare distances and angles with the isotypic BaIrF$_6$ (Table 3).

<table>
<thead>
<tr>
<th>Value</th>
<th>BaOsF$_6$ Exp.</th>
<th>BaOsF$_6$ DFT-PBE0</th>
<th>BaIrF$_6$ Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$, Å</td>
<td>7.3286(10)</td>
<td>7.21</td>
<td>7.3965(5)</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>7.2658(15)</td>
<td>7.33</td>
<td>7.2826(7)</td>
</tr>
<tr>
<td>$V$, Å$^3$</td>
<td>337.95(12)</td>
<td>330.21</td>
<td>345.04(6)</td>
</tr>
<tr>
<td>Ba⋯F</td>
<td>2.773(3)</td>
<td>2.6</td>
<td>2.800(4)</td>
</tr>
<tr>
<td>$M$–F</td>
<td>2.870(3)</td>
<td>2.98</td>
<td>2.882(4)</td>
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<td>1.936(4)</td>
</tr>
<tr>
<td>$F$–M–F#</td>
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<td></td>
<td>94.07(16)</td>
<td>97.3</td>
<td>94.1(2)</td>
</tr>
</tbody>
</table>

In order to identify the nature of the black powder that accompanies the formation of BaOsF$_6$, we collected a powder X-ray diffraction pattern of the mixture. However, as it is seen from Figure 9, the pattern contains only the reflections of barium hexafluoroosmate(IV), indicating an amorphous nature of the other phase.

![Figure 9](image)

**Figure 9.** Powder X-ray diffraction pattern (at 293 K) of BaOsF$_6$: the experimental data (black crosses), the Le Bail profile (red), and the differential profile (bottom, black). The calculated reflection positions for BaOsF$_6$ are shown as black ticks. $R_F = 0.0189$, $wR_F = 0.0264$. 

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**Table 3.** Selected crystallographic data for BaOsF$_6$ and BaIrF$_6$ [34].
An additional investigation by means of IR spectroscopy (Figure 10) did not show the presence of any characteristic vibrational modes, e.g., of the OH\(^{-}\) group, indicating that the black powder is a relatively simple compound. The investigations on the identification of this phase are ongoing. Currently, we think that the phase may be osmium dioxide (see Reaction 2), which is known to be formed in amorphous state from the reduction of aqueous solutions of OsO\(_4\) [35].

![Figure 10. IR spectra of BaOsF\(_6\): experimentally observed (black) and calculated with DFT-PBE0 (red).](image)

Unfortunately, the compound is insoluble in anhydrous HF, so no solution NMR spectrum could be obtained.

**4.3. A barium Hexafluoridoosmate(V) Solvate of BrF\(_3\)**

In an attempt to grow single crystals of Ba(OsF\(_6\))\(_2\), we tried to use bromine trifluoride as a solvent. Upon partial evaporation of BrF\(_3\) and the subsequent cooling of the resulting solution down to room temperature, big pale-green prismatic crystals were obtained. One crystal was selected under perfluorinated oil using a polarizing light-optical microscope and mounted on the goniometer.

The obtained compound crystallizes in a primitive monoclinic cell with the cell parameters

\[
\begin{align*}
a &= 15.539(3), \\
b &= 37.029(7), \\
c &= 15.722(3) \text{ Å,} \\
\beta &= 90.10(3)°, \\
V &= 9046(3) \text{ Å}^3 \text{ at 100 K. }
\end{align*}
\]

The tentative space group type is \(P2_1/n\) (No. 14). The structure solution and refinement did not lead to a chemically plausible model. Due to the \(\beta\)-angle being so close to 90\(^°\), we also attempted structure solutions in the orthorhombic crystal system and then using various twin refinements. However, the structure models obtained were not satisfactory. The refinement of the structure in one of the maximal \(\text{translationengleiche}\) subgroups of \(P2_1/n\), namely \(Pn, P2_1,\) and \(PT\), led to no substantial improvement of the structural model. The investigations on the crystal structure of this solvate are ongoing and the results will be reported elsewhere.

**4.4. A Barium Hexafluoridoosmate(V) Solvate of Hydrogen Fluoride**

Anhydrous hydrogen fluoride (aHF) was used as the next solvent to obtain single crystals of Ba(OsF\(_6\))\(_2\). Upon dissolving Ba(OsF\(_6\))\(_2\) in aHF, a clear red solution was obtained. When the solvent was partially evaporated, red-pink crystals were formed. The crystals were selected directly out of aHF and mounted under perfluorinated oil. After solving the crystal structure, we identified this new compound preliminary as “Ba(OsF\(_6\))\(_2\)∙HF”.

Barium bis(hexafluoridoosmate(V))—hydrogen fluoride (1/1) crystallizes in the orthorhombic crystal system. First, we obtained the lattice parameters

\[
\begin{align*}
a &= 10.9127(12), \\
b &= 11.5853(11), \\
c &= 15.900(2) \text{ Å,} \\
V &= 2010.2(4) \text{ Å}^3 \text{ at 100 K, and the space group type } Pbcn \text{ (No. 60) was established. }
\end{align*}
\]

However, the structure model showed rather large displacement parameters for the fluorine ligands bound to the Os atom. As we could not resolve the disorder, we checked the reciprocal space for additional information and observed statistically significant superstructure reflections leading to
the lattice parameters $a = 21.8173(7)$, $b = 31.7637(15)$, $c = 11.8742(3)$ Å, and $V = 8020.9(4) \text{ Å}^3$ at 100 K. However, all of our refinements in the larger unit cell led to unsatisfactory results. Currently, the crystal structure of the compound is still under investigation and will be reported elsewhere.

4.5. Barium Hexafluoridoosmate(V) Hexahydrate

We used water as the last choice of solvents in this study. Despite that Ba(OsF$_6$)$_2$ is hydrolyzed in water, this process is not instantaneous giving the chance to recrystallize the substance. However, the obtained crystals belong to another new compound: barium hexafluoridoosmate(V) hexahydrate, Ba(OsF$_6$)$_2$$\cdot$6H$_2$O.

Barium bis(hexafluoridoosmate(V)) hexahydrate crystallizes in the triclinic space group type $P\overline{1}$ (No. 2) with cell parameters $a = 8.9967(5)$, $b = 9.9840(6)$, $c = 10.2088(6)$ Å, $\alpha = 84.653(5)^\circ$, $\beta = 64.629(4)^\circ$, $\gamma = 64.273(4)^\circ$, $V = 741.55(8) \text{ Å}^3$, and $Z = 2$ at 100 K. The crystal structure of Ba(OsF$_6$)$_2$$\cdot$6H$_2$O is shown in Figure 11; a section of the crystal structure showing the surroundings of the barium cation is shown in Figure 12.

**Figure 11.** The crystal structure of Ba(OsF$_6$)$_2$$\cdot$6H$_2$O (projection along c-axis). Displacement ellipsoids are shown at 70% probability level at 100 K. All the non-hydrogen atoms are shown anisotropic, hydrogen atoms are shown with arbitrary radii.

**Figure 12.** Fragment of the crystal structure of Ba(OsF$_6$)$_2$$\cdot$6H$_2$O showing the coordination of OsF$_6$$^-$ and H$_2$O around Ba$^{2+}$. Displacement ellipsoids are shown at 70% probability level at 100 K. All non-hydrogen atoms are shown anisotropic, hydrogen atoms are shown with arbitrary radii.
All atoms in Ba(OsF$_6$)$_2$·6H$_2$O occupy the general 2$i$ Wyckoff position. The barium cation has the coordination number 10 and is coordinated by six oxygen atoms and four fluorine atoms. The resulting coordination polyhedron is a bicapped square antiprism. The Ba···O distances lie within the internal of 2.7249(2) to 2.8313(2) Å. The Ba···F distances are slightly longer and they lie in the range of 2.7823(1) to 2.9324(2) Å.

The OsF$_6$~ anions are very close to the octahedral geometry: the Os–F bond lengths are 1.8607(1) to 1.8823(1) Å and F–Os–F# angles are 88.876(4) to 90.924(4)°. The neighboring anions are linked together through the water molecules by weak hydrogen bonds: the shortest O···F distance equals 2.8069(1) Å. The crystallographic details of Ba(OsF$_6$)$_2$·6H$_2$O are given in Table 2.

5. Conclusions

In this work, we have synthesized and structurally characterized for the first time two alkaline-earth metal hexafluoroosmates: Ba(OsF$_6$)$_2$ and BaOsF$_6$. The compounds contain spatially isolated OsF$_6$~ (or OsF$_6^{2-}$ respectively) anions with their symmetry close to O$_h$. In an attempt to grow single crystals of Ba(OsF$_6$)$_2$, we obtained three new solvates depending on the used solvent: Ba(OsF$_6$)$_2$·3BrF$_3$, Ba(OsF$_6$)$_2$·HF, and Ba(OsF$_6$)$_2$·6H$_2$O, which were also characterized.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4352/8/1/11/s1: Figure S1: IR spectra of Ba(OsF$_6$)$_2$: experimentally observed (black) and calculated with DFT-PBE0 (red), Figure S2: $^{19}$F NMR spectrum of Ba(OsF$_6$)$_2$ in anhydrous HF, Table S1: Region assignment for the theoretical IR spectrum of Ba(OsF$_6$)$_2$, Basis sets.

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Author Contributions: Sergei I. Ivlev, Roman V. Ostvald and Florian Kraus conceived and designed the experiments; Sergei I. Ivlev performed the experiments; Sergei I. Ivlev and Antti J. Karttunen performed the calculations; Magnus R. Buchner measured the NMR spectra; Sergei I. Ivlev, Antti J. Karttunen, Magnus R. Buchner, Roman V. Ostvald and Florian Kraus analyzed the data; Sergei I. Ivlev and Florian Kraus wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References


