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Binary Lead Fluoride Pb$_3$F$_8$

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Abstract: The binary lead fluoride Pb$_3$F$_8$ was synthesized by the reaction of anhydrous HF with PbF$_4$ or by the reaction of BrF$_3$ with PbF$_2$. The compound was characterized by single-crystal and powder X-ray diffraction, IR, Raman, and solid-state MAS $^{19}$F NMR spectroscopy, as well as thermogravimetric analysis, XP and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. Solid-state quantum-chemical calculations are provided for the vibrational analyses and band assignments. The electronic band structure offers an inside view of the mixed valence compound.

Introduction

The binary lead fluorides PbF$_2$ and PbF$_4$ are well established compounds.$^{[1,2]}$ Their first lab synthesis dates back to the first half of the 19th century and the determination of their crystal structures to 1944 and 1962, respectively.$^{[1-10]}$ In addition, PbF$_5$, which is better described as Pb$_2$F$_4$ containing Pb$^{II}$ and Pb$^{IV}$ atoms, was reported.$^{[5]}$ While for Sn and Ge also the mixed valence compounds M$_2$F$_8$ ($M =$ Sn, Ge), and even Ge$_2$F$_{12}$ and Ge$_3$F$_{13}$ are known, only the three binary lead fluorides mentioned above are unambiguously known.$^{[6-9]}$ Therefore, the existence of a mixed valence compound of the composition Pb$_3$F$_8$ appears to be likely. For lead, mixed valence compounds are nothing special and the well-characterized compound Pb$_2$O$_4$ (latin: Minium), which was used as a pigment in ancient Rome and in anti-corrosion coatings, or which is even today in usage for charlatanism, comes to the mind.$^{[10-13]}$ A compound of the average chemical composition (Pb$_3$F$_8$)$_n$ was mentioned only twice in the literature. Nothing besides this average composition has been reported. Pb$_3$F$_8$ was first mentioned in 1972 by Banner and co-workers as a result of the reaction of Pb$_2$O$_4$ with gaseous HF on a thermogravimetric scale.$^{[14]}$ In their search for Pb$_3$F$_8$, Charpin and co-workers described reactions leading to Pb$_2$F$_6$ as a product or side product. Again, no details on Pb$_3$F$_8$ were given, even not how the compound was identified as Pb$_3$F$_8$.$^{[15]}$ Herein, we present the synthesis and characterization of the binary lead(II/IV) fluoride Pb$_3$F$_8$.

Results and Discussion

The formation of the title compound can be envisaged by the following stoichiometric Equation (1).

\[ \text{Pb}_2\text{O}_4 + 8\text{HF} \rightarrow \text{Pb}_3\text{F}_8 + 4\text{H}_2\text{O} \]  

(1)

Pb$_2$O$_4$ is reacted with an excess of anhydrous HF (aHF) at room temperature, so that the equilibrium of the reaction is shifted to the product side. After a few minutes of reaction time the deep-orange color of Pb$_2$O$_4$ is already gone and the reaction is complete within one hour at room temperature. After the removal of the volatiles (HF and H$_2$O), the product is obtained as a slightly beige powder (Figure S1, Supporting Information) that is easily ground. The dry powder of Pb$_3$F$_8$ is stable for several hours in air. The compound prepared in this way always contains small amounts of PbF$_2$ (typically 5–8%), as evidenced by Rietveld analysis (Table S1, Figure S2, Supporting Information) on powder X-ray diffraction patterns. The obtained lattice parameters are $a = 8.8434(1)$ Å, $b = 7.5427(1)$ Å, $c = 10.2339(1)$ Å, $\beta = 98.810(1)^\circ$, $V = 672.3(3)$ Å$^3$ at $T = 298$ K. They agree well with those obtained from single-crystal X-ray diffraction, see below. To suppress the back reaction by hydrolysis, a large excess of circa 100 equivalents of aHF is needed. If the reaction mixture is allowed to stand for three days at room temperature, or, if an excess of aHF is used that is too small, a
product is obtained that always contains larger amounts of PbF₃ than mentioned above. To obtain phase pure PbF₃ we attempted to oxidize PbF₂ using an excess of BrF₅ under warming up to 130 °C. However, after evaporation of the residual BrF₅, the remaining colorless powder consists of PbF₃ and small amounts of PbF₂ (circa 3%). Thermogravimetric investigations (Figures S3, S4, Supporting Information, and for further details see the Supporting Information) indicate that the thermal decomposition of PbF₃ is complex. The decomposition under loss of fluorine gas starts roughly around 80 °C. After thermal decomposition, pure PbF₃ is obtained as evidenced by powder XRD (Figure S5, Supporting Information). The overall mass loss during this procedure has been determined twice, once to 5.2 and once to 4.7%. Both values are in reasonably good agreement with the theoretically expected mass loss of 4.9%. Thus, Pb₂F₆ decomposes thermally to three equivalents of PbF₂ and one equivalent of F₂. Further details will be reported elsewhere. Helium pycnometric density determination (see the Supporting Information) yields a density of circa 7.68 g cm⁻³ for the used sample of PbF₆. Due to the presence of circa 15% PbF₃ (ρ = 8.44 g cm⁻³) in the sample used for density determination, a value of 7.74 g cm⁻³ is to be expected from the measurements. Thus, the experimentally determined density is in very good agreement with the measurement and with the crystallographic density of PbF₆ of circa 7.61 g cm⁻³.

Single-crystal X-ray diffraction shows Pb₂F₆ to crystallize in the monoclinic space group I2/a (No. 15, mS44, 15eF3) with the lattice parameters a = 8.7800(18), b = 7.4927(15), c = 10.1965(6) Å; β = 98.78(3)°; V = 662.9(4) Å³; Z = 4, at T = 100 K, while at room temperature lattice parameters of a = 8.8400(5), b = 7.5398(5), c = 10.2297(7) Å, β = 98.82(2)°, V = 673.77(8) Å³ are obtained. The latter agree well with the values determined from powder X-ray diffraction at room temperature. No phase change was observed upon cooling from room temperature to 100 K and Table S2, Supporting Information, holds details of the single crystal structure determination. Surprisingly, Pb₂F₆ is not isotypic to the compounds M₂F₆ (M = Ge, Sn) but, to the best of our knowledge, represents a novel structure type.⁶⁻⁷ As the crystal structure of Pb₂F₆ is complicated we will start from Pb(1)–F distances, we assign oxidation state +II to the Pb(2) atoms. Charge distribution (CHARDI) calculations²¹ (Table S3, Supporting Information) agree with the description of Pb₂F₆ as a mixed valence compound as charges of +4.12 and +1.94 are calculated for the Pb(1) and Pb(2) atoms, respectively. Thus, the assignment of the oxidation states is supported.

One Pb(2)–F(4) distance within the pentagonal pyramid is shortest with 2.330(3) Å, and represents the “tip” of the pyramid pointing to the bottom in Figure 1. The other two Pb(2)–F(4) distances are longer and equal within the standard uncertainty (2.446(3) and 2.449(3) Å). The other Pb(2)–F(4) distances are significantly longer and range from 2.505(3) to 2.651(3) Å. As can be seen in Figure 1, the Pb(2) atom is not located in the center of the coordination polyhedron but resides close to the pentagonal face. Such a coordination polyhedron is reminiscent of the text-book anion [XOF₄]₆⁻⁻²⁴ and the peculiar location and coordination sphere of the Pb(2) atom is attributed to an accumulation of electron density in real space as shown in the quantum chemical calculations below. Due to the chemical hardness of the fluoride anion and its extremely low polarizability, its electron density leads to repulsion and deformation of the electron density at the Pb atom. Some call this effect the “sterically active lone-pair” and its influence on local as well as crystal structure is known for example from α- and β-PbO, or from the black and pigeon blood red modifications of SnO.⁵⁻³⁻²⁷ However, above the “lone-pair” of the Pb⁴⁺ atom there are three additional F atoms with Pb–F distances of 2.851(4), 2.874(3), and 3.051(3) Å. According to the distance histogram one could count those three F atoms to the coordination sphere of Pb(2) leading to coordination number 6 + 3. The coordination polyhedron around Pb(2) is then irregular with ten triangles and one tetragon as the faces. Also, the calculated effective coordination number (ECoN) of 6.9 hints to a small contribution of the three next-nearest fluoride atoms to its coordination sphere, whereas the calculated ECoN for Pb(1) agrees well with C. N. = 6 as assigned by our structure analysis.

We now come to the global structure description by explaining how the coordination polyhedra are interconnected. The F(4) atoms are μ₁₂-bridging between Pb(2) atoms and that leads to the formation of a 1D infinite zigzag ladder shown in Figure 2a. Two longer Pb(2)–F(4) distances form the stringers of the ladder, while the short Pb(2)–F(4) distances represent

![Figure 1. The coordination spheres of the two lead atoms of Pb₂F₆. The Pb(1) atom is coordinated octahedron-like, the Pb(2) atom like a pentagonal pyramid. Pb atoms are shown in grey, F atoms in yellow. Displacement ellipsoids at 70% probability at 100 K.](image)

From 2.330(3) to 2.651(3) Å. As they are clearly longer than the Pb(1)–F distances, we assign oxidation state +II to the Pb(2) atoms. Charge distribution (CHARDI) calculations²¹ (Table S3, Supporting Information) agree with the description of Pb₂F₆ as a mixed valence compound as charges of +4.12 and +1.94 are calculated for the Pb(1) and Pb(2) atoms, respectively. Thus, the assignment of the oxidation states is supported.
the rungs of the ladder (Figure 2a). Thus, the “lone-pairs” on the Pb(2) atoms point to the left and right in Figure 2a.

The topside and underside of the infinite ladder are coordinated by [Pb(1)F$_6$]$_2^-$ octahedra as shown in Figure 2b. The ladders are sandwiched between the octahedra and vice versa, leading to a 2D infinite layer of ladders interconnected by octahedra. A section is shown in Figure 3a.

Figure 2. a) Ladder-like connection of the Pb(2) atoms (grey) via μ$_2$-bridging F(4) atoms (yellow). b) Connection of the Pb(2) containing ladder to the Pb(1) containing octahedra. Displacement ellipsoids shown with 70% probability at 100 K.

Thus, the “stERICALLY active lone-pairs” of the Pb(2) atoms point out of the topside and underside of these layers (Figure 3b) separating them from each other. Figure 3b shows a section of the crystal structure of PbF$_3$ with the 2D infinite layers parallel to the ab plane stacked along the c axis. The Niggli formula indicates the coordination number and environment of the Pb atoms nicely. For the Pb$^{1+}$ atom [PbF$_{32}$F$_3$] and for the Pb$^{2+}$ atom [PbF$_{32}$] is obtained. Thus, PbF$_3$ can be described by the Niggli formula $\frac{2}{3}$[PbF$_{32}$F$_3$]$_{1/2}$[PbF$_{32}$]. The Pb atoms are hexagonally packed and each is anticuboctahedrally surrounded by twelve Pb atoms. Thus, the arrangement of the Pb atoms of PbF$_3$ corresponds to the simple Mg structure type. However, the F atoms neither fill the octahedral nor the tetrahedral voids of the sphere packing.

Raman spectroscopic investigations have been carried out on PbF$_3$ and on PbF$_2$ for comparison. For experimental details see the Supporting Information. The experimentally obtained spectra were then compared with ones obtained from DFT-PBE0/TZVP calculations based on the crystal structures of PbF$_3$ and PbF$_2$. The most striking difference between the Raman spectrum of PbF$_3$ and the spectrum of PbF$_2$ (see Figures S6 and S7, Supporting Information) is the strong vibrational band at 531 cm$^{-1}$ that is only present in the Raman spectrum of PbF$_2$. This band is well reproduced by our theoretical findings and can be attributed to a symmetric stretching of the Pb$^{2+}$-F bonds, which explains the absence of this band in PbF$_2$. PbF$_3$ is also clearly identified by the lattice vibrational bands around 100 cm$^{-1}$ as this frequency region corresponds to a minimum in Raman intensity in the spectrum of PbF$_2$. The two peaks at around 250 cm$^{-1}$ and the two peaks at around 200 cm$^{-1}$ belong to a symmetric stretching of the Pb$^{2+}$-F bonds and bending modes of the Pb$^{2+}$-F bonds, respectively. In summary, the Raman spectrum supports our classification of PbF$_3$ as a mixed valence compound. Full band assignments are available from Tables S4 to S6, Supporting Information.

An IR spectroscopic investigation of PbF$_3$ powder in the range from 4000 to 450 cm$^{-1}$ (Figure S8) shows only a single broader band at 466 cm$^{-1}$, which is comprised of intense Pb$^{2+}$-F stretch and weaker Pb$^{2+}$-F scissoring and rocking modes. For Li$_2$PbF$_4$, which contains [PbF$_3$]$_{3/2}$ octahedra, a band at 475 cm$^{-1}$ has been observed.$^{[18]}$ This agrees well considering the different connectivity of the [PbF$_{32}$]$_{1/2}$ octahedra in the two compounds. The experimentally determined band position of PbF$_3$ agrees well with the quantum chemically calculated bands at 493, 470, and 456 cm$^{-1}$. The complete assignment of IR bands is given in Table S5, Supporting Information. The obtained PbF$_3$ is essentially free of impurities such as H$_2$O, OH$^-$, or HF, as no bands in the range from 4000 to circa 450 cm$^{-1}$ are present.

Solid-state $^{19}$F MAS NMR experiments (Figure 4 and Table 1) of PbF$_3$ were performed to further corroborate the crystal structure model. The $^{19}$F DEPTH MAS NMR spectrum shows four resonances, one occurring at $\delta = -18.2$ ppm and a group of three overlapping signals at $\delta = -40.0, -48.5$, and $-56$ ppm. All four resonances have peak areas including spinning side-bands of 1:0.4:1.03:0.90. The spectrum also contains a fifth peak at $\delta = -24.2$ ppm with a lower intensity which is likely to originate from the PbF$_2$ impurity.$^{[19]}$ These observations are expected for F atoms which do not have fast ion-dynamics on
A tentative peak assignment of the \(^{19}\text{F}\) resonances follows the idea that neighboring cations contribute to the \(^{19}\text{F}\) chemical shift according to their coordination number and distance to \(\text{F}\) atoms in ionic fluorides. Consequentially, \(\text{F}\) atoms with a similar bonding situation should feature similar isotropic and anisotropic chemical shift values. In the present case (Table 1) the group of three resonances has an anisotropic chemical shift which is larger by about a factor of two compared to the peak which appears at the highest ppm values. In the structure three \(\text{F}\) atoms are coordinated to two \(\text{Pb}\) atoms, one \(\text{F}\) atom is coordinated to three. Therefore, the resonance at \(-18.2\) ppm is assigned to the three-fold coordinated fluorine site (F(4)) and the three signals at \(-40, -48.5,\) and \(-56\) ppm are assigned to the fluorine atoms F(1), F(2), and F(3) coordinated by the two lead Pb(1) and Pb(2) atoms.

We have performed X-ray photoelectron spectroscopy (XPS) as well as near-edge X-ray absorption fine structure (NEXAFS) measurements to get information about the electronic structure of \(\text{PbF}_3\). The survey XP spectrum of \(\text{PbF}_3\) on carbon tape is presented in Figure 5a. The spectrum only shows contributions from \(\text{Pb}\) and \(\text{F}\) atoms, besides minor C 1s and O 1s peaks from the carbon tape.

Another sample that was studied with hard X-ray photoelectron spectroscopy (HAXPES, Figure S9 in the Supporting Information) shows the same features and even less contributions from the carbon tape. During the XPS and HAXPES measurements, the sample exhibits substantial photoemission-induced charging, which results in peak shifts and broadening. For this reason, a refined analysis of the XPS peak shapes with a discrimination between \(\text{Pb}^0\) and \(\text{Pb}^+\) contributions is not possible. Instead, we performed NEXAFS spectroscopy measurements on the \(\text{Pb}\) M\(_\text{II}\)-edge to gain further insight into the electronic structure of \(\text{PbF}_3\) (Figure 5c). As a reference, we also studied \(\text{PbF}_2\) and \(\text{Pb}_2\text{O}_4\). Between 2490 and 2495 eV, a pre-edge feature is observed, which is followed by the M\(_\text{II}\)-edge for all three species. \(\text{PbF}_2\) shows a sharp peak at 2490 eV with a minimum at 2495 eV. In contrast, there is only a broad feature between 2490 and 2495 eV for \(\text{Pb}_2\text{O}_4\). The \(\text{PbF}_3\) spectrum resembles a mixture of both reference samples. A peak at 2490 eV is observed, whereas there is no minimum at 2495 eV like for \(\text{PbF}_2\).

Table 1. Estimates for the \(^{19}\text{F}\) solid-state NMR chemical shift parameters for \(\text{PbF}_3\) obtained by a least-square fit of the experimentally obtained spectrum (Figure 4) with SIMPSON version 3.1.2\(^{[30,31]}\) simulations of the used version of the DEPTH\(^{[29]}\) experiment.

<table>
<thead>
<tr>
<th>Site</th>
<th>(\delta_{\text{iso}}) (ppm)</th>
<th>(\delta_{\text{aniso}}) (ppm)</th>
<th>(\eta)</th>
<th>(\delta_{\text{a}}) (ppm)</th>
<th>(\delta_{\text{b}}) (ppm)</th>
<th>(\delta_{\text{c}}) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(4)</td>
<td>-18.2</td>
<td>66.1</td>
<td>0.60</td>
<td>47.9</td>
<td>-31.5</td>
<td>-71.2</td>
</tr>
<tr>
<td>F(1)–F(3)</td>
<td>-40.0</td>
<td>-111.8</td>
<td>0.61</td>
<td>50.5</td>
<td>-18.5</td>
<td>-151.7</td>
</tr>
<tr>
<td>F(1)–F(3)</td>
<td>-48.5</td>
<td>-121.0</td>
<td>0.65</td>
<td>51.5</td>
<td>-27.4</td>
<td>-169.5</td>
</tr>
<tr>
<td>F(1)–F(3)</td>
<td>-56.0</td>
<td>-119.2</td>
<td>0.47</td>
<td>31.6</td>
<td>-24.5</td>
<td>-175.2</td>
</tr>
</tbody>
</table>

The NMR timescale, as four symmetry-in equivalent \(\text{F}\) atoms (F(1) to F(4)) with the same site multiplicity are present in the crystal structure.

Figure 4. \(^{19}\text{F}\) DEPTH MAS NMR spectrum (experimental: solid line, simulated: dashed line) of \(\text{PbF}_3\) at 20 kHz spinning frequency. The spinning side bands are marked with asterisks. The simulation includes a version of the DEPTH\(^{[29,31]}\) sequence with four \(\pi\)-pulses: \(\pi/2-\pi-\pi-\pi-\text{detour}-\text{FID}\). The DEPTH experiment results in MAS NMR spectra free of probe head background. The simulation includes the effect of the deadtime delay and excitation profile of the DEPTH sequences which causes the baseline rolling. Zeroth and first order phase correction are included as variable parameters in the least-square fit.

Figure 5. (a) Survey XP spectrum of \(\text{PbF}_3\) on carbon tape, taken with monochromatic Al K\(_\text{α}\) radiation. (b) Valence band spectrum of \(\text{PbF}_3\) measured with Al K\(_\text{α}\) radiation in comparison to DFT calculations (PBE0/NCPW). A Shirley background was subtracted from the experimental data to compare it to the theoretical results. The contribution of the Pb 6s orbitals to the total calculated DOS is highlighted. Further details concerning the data treatment are given in the Supporting Information. (c) Pb M\(_\text{II}\)-edge NEXAFS spectra of \(\text{PbF}_2\), \(\text{PbF}_3\), and \(\text{Pb}_2\text{O}_4\) measured by the X-ray fluorescence yield. Inset: Zoom-in of the pre-edge feature.
Instead, there is a broad feature similar to the case of PbO₂. This is in line with the presence of both Pb²⁺ and Pb⁴⁺ species in the PbF₅ sample and with a small contamination of PbF₂ as stated above. The differences in the M₄-edge itself are more complicated as there are nearly no similarities between the three compounds. In the range from 2500 to 2510 eV, PbF₂ and PbF₅ show similar spectral features, but above that range PbF₂ exhibits a local minimum, whereas PbF₅ shows a peak. A similar peak is observed in the PbO₂ spectrum but shifted by nearly 10 eV to higher energies.

We have calculated the electronic structure of PbF₅ by DFT methods using the hybrid functional PBE0 and fully relativistic pseudopotentials. To estimate the accuracy of our calculations we compared the experimentally determined valence band XP spectrum with the calculated partial density of states (pDOS) that is corrected by background and cross-section effects (see the Supporting Information). The results are shown in Figure 5b. The valence band width as well as its three-peaked shape are well reproduced by the DFT calculations.

In the following, we investigate the electronic structure of PbF₅ in more detail by calculating its band structure and charge distribution. The band structure as well as the total DOS are given in Figure 6.

The band structure calculations show PbF₅ to be an insulator with a band gap of approximately 4.5 eV in line with its off-white color. The DOS of the valence band is dominated by F 2p states that range from −1 eV to 2 eV. At about 4 eV the top of the valence band consists of four bands with only a small amount of dispersion that can be attributed to the filled Pb⁶ 6s bands. The conduction band is located at about 9 eV and consists of two bands. Both show nearly exclusive Pb⁴⁺ 6s character as illustrated by the pDOS in the right of Figure 6. A small amount of the Pb⁴⁺ 6s states is located at the bottom of the valence band at about −4 eV due to some covalent Pb⁴⁺–F bond character. For the same reason Pb⁴⁺ 6s states are present at about −2 eV. The band structure of the mixed valence compound PbO₂ shows similar characteristics. We thus conclude that like PbO₂ also PbF₅ is a mixed valence compound with the lead atoms in the oxidation states +II and +IV.

The crystal structure of PbF₅ indicates that the Pb³⁺ atoms feature “sterically active lone-pairs”. We calculated electron-density difference maps of PbF₅ which display the difference of the electron density of the compound compared to a superposition of the electron density of free atoms, yielding information where electron density is accumulated or depleted. The electron-density difference map of PbF₅ is shown in Figure 7. It is drawn in a view perpendicular to the ladder-like connection of the Pb(2) atoms and the F(4) atoms, compare Figure 2a.

The map displays a strong polarization of the electron density around the Pb³⁺ atoms. The electron density along the Pb–F bonds is minimized (brownish colors) in line with the expected high amount of ionic bonding character. Moreover, there is an accumulation of electron density (in blue colors) besides the Pb³⁺ atoms, pointing to the left and right side of the depicted ladder. Therefore, the electron density at the Pb³⁺ atoms is “pushed” away from the fluorine atoms inside the ladder. This effect is often referred to “sterically active lone-pairs” of the Pb³⁺ atoms. The electron density around the fluorine atoms (in yellow color) is strongly and nearly spherically increased as is expected for F⁻ anions due to the high electronegativity of the F atom.

Conclusions

The binary lead(II/IV) fluoride PbF₅ was synthesized from PbO₂ in anhydrous HF at room temperature. The bulk phase appears off-white while single crystals are colorless. It is thermally stable up to circa 80 °C and then decomposes to PbF₂ under loss of F₂. The compound crystallizes in the monoclinic space group I2/a (No. 15) with the lattice parameters a = 8.7800(18), b = 7.4927(17), c = 10.196(5) Å; β = 98.78(3)°; V =
The authors declare no conflict of interest.