

Indium(I) Hexafluoropnictates (InPnF₆; Pn = P, As, Sb)

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Keywords: Fluorides / Indium / Pnictides / Raman spectroscopy / Structure elucidation

The colourless compounds InPnF₆ (Pn = P, As, Sb), with In^I in a solely fluorine environment, were prepared by reacting In metal with PnF₅ (Pn = P) and displacement of the weaker Lewis acid BF₃ from InBF₄ by a stronger one, PnF₅ (Pn = As, Sb), in anhydrous hydrogen fluoride (aHF). The X-ray powder diffraction analyses show that InPF₆ crystallises in cubic unit cell with $a = 8.07(2)$ Å, while InAsF₆ crystallises in a rhombohedral unit cell with $a = 7.58(2)$ and $c = 7.90(1)$ Å. The

Raman spectra of InPnF₆ (Pn = P, As, Sb) confirm the formation of PnF₆[−] salts. An attempt to prepare InF and In₂F₄ (In^IIn^{III}F₄) by reaction of CsF with InSbF₆ in aHF or by metathetical reaction of InSbF₆ with CsInF₄ in aHF, respectively, failed. Instead of InF and In₂F₄, respectively, a mixture of In and InF₃ was obtained.

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Introduction

The main oxidation state of group 13 elements (B, Al, Ga, In, Tl) is trivalent, although on going from lighter to heavier elements the univalent state becomes more stable. The occurrence of the latter is often described as an inert-pair effect.^[1] In contrast to thallium, univalent indium compounds are not common. All thallium monohalides are well characterised, whereas only InCl, InBr and InI are known in the condensed phase.^[2] Unstable InF has only been observed in the gas phase.^[2–5] Furthermore, reports of complex fluorides with In⁺ in a solely fluorine environment are also scarce.^[6,7] One rare example is InBF₄, which has been prepared by reaction of elemental In with BF₃ in anhydrous hydrogen fluoride (aHF).^[6] In the second case the authors erroneously claimed that they made InBF₄ for the first time.^[7]

In the present work, two aims were followed: to prepare and characterise new ternary compounds with In⁺ in a solely fluorine environment and to exploit the possibility of preparing indium(I) fluoride (InF) and a mixed-valence In^I/In^{III} fluoride (In^IIn^{III}F₄).

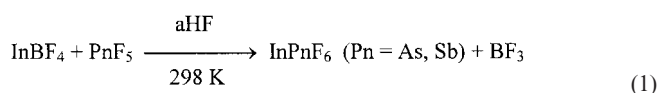
Discussion

Synthesis

The previously known BF₄[−] salt of In⁺ was prepared by the reaction of In metal with an excess of BF₃ in anhydrous hydrogen fluoride (aHF).^[6] The same approach is not applicable to other Lewis acids (i.e., AsF₅, SbF₅) because they

oxidize elemental In to In³⁺ to yield InF₃ (with AsF₅) or a mixture of InF₃·3SbF₅^[8] and SbF₃·nSbF₅ (with SbF₅). For that reason, a different approach has to be used.

The displacement of the weaker Lewis acid BF₃ from InBF₄ by the stronger acid, AsF₅ or SbF₅, in the highly acidic solvent aHF, was successful. When a stoichiometric amount of Lewis acid (AsF₅, SbF₅) was added to a colourless solution of InBF₄ in aHF, a colourless precipitate formed immediately. Colourless InAsF₆ and InSbF₆ were obtained after decanting the liquid phase and removing the remaining traces of volatiles under vacuum at ambient temperature, see Equation (1).



Use of an excess of AsF₅ or SbF₅ caused oxidation of In⁺ to In³⁺ to give InF₃ or a mixture of InF₃·3SbF₅/SbF₃·nSbF₅, respectively. In the course of this study it was also found that InAsF₆, prepared by the reaction of InBF₄ with AsF₅ in aHF [Equation (1)], should be isolated immediately after its precipitation. When the reaction was left to proceed for a longer time, In⁺ was slowly oxidized to In³⁺ to give InAsF₆ contaminated with InF₃. Its oxidation was complete in a few days and only InF₃ was recovered from the reaction mixture.

Compared with AsF₅ or SbF₅, PF₅ and BF₃ are weak Lewis acids (MF_x; $x = 4$ when M = B and $x = 6$ when M = P, As, Sb). A good measure of the strength of their Lewis acidity is the reaction enthalpy $\Delta H(\text{MF}_x + \text{F}^- = [\text{MF}_{x+1}]^-)$, i.e. fluoride ion affinity (FIA).^[9] The main driving forces for the formation of InPnF₆ compounds [Equation (1)] are the difference in fluoride ion affinities (FIA) of BF₃ (347.7 kJ mol^{−1})^[9] and PnF₅ (Pn = P: 397.1 kJ mol^{−1}; As =

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443.1 kJ mol⁻¹; Sb = 503.3 kJ mol⁻¹)^[9] and the lattice energy differences between the starting InBF₄ and the resulting InPnF₆ salts. The lattice potential energies of InMF_x salts have been estimated by Jenkins and Passmore et al. from a generalized volume-based Kapustinskii equation, see Equation (2).^[10,11]

$$U_{\text{TOT}}(\text{InMF}_x) = 2I[a \cdot V_m(\text{InMF}_x)^{-1/3} + \beta] \quad (2)$$

where $a = 117.3 \text{ kJ mol}^{-1} \text{ nm}$, $\beta = 51.9 \text{ kJ mol}^{-1}$ and the lattice ionic strength, I , is 1 for InMF_x salts. Using values of $V_m(\text{InMF}_x) = V_{\text{unit cell}}/Z$ from the crystallographic data of InBF₄^[6] and InPnF₆ (Pn = P, As), their lattice potential energies were estimated to be 616 kJ mol⁻¹ (InBF₄) and about 566 kJ mol⁻¹ (InPF₆, InAsF₆). The smaller lattice energy of InAsF₆ in comparison to InBF₄ is offset by a better fluoride ion acceptor ability of AsF₅ against BF₃, which makes the reaction InBF₄ + AsF₅ thermodynamically more favourable. In the contrast to AsF₅, the FIA of PF₅ is insufficient to compensate the poorer lattice energy of InPF₆ in comparison to InBF₄ and the reaction with the latter does not proceed.

As mentioned previously, In metal is oxidized to In³⁺ by the excess of AsF₅ or SbF₅ in aHF. However, the reaction between In metal and an excess of PF₅ in aHF proceeded in a different manner. Indium metal was slowly oxidized to In⁺ to yield a colourless powder and cubic-shaped single crystals of InPF₆. Even after several days the reaction was not completed. During the isolation the powdery InPF₆ material turned grey and the smooth transparent surface of the crystals became rough and opaque.

The attempt to prepare In^I hexafluorobismuthate by the reaction of InBF₄ with BiF₅ in aHF failed. The yellowish solid isolated immediately after its precipitation was found to consist of InF₃ and BiF₃·*n*BiF₅.^[12]

Crystal Structures

Hexafluoropnictates (MPnF₆, Pn = As, Sb, Bi) of the heavier univalent metals (M = Tl, Rb, Cs) crystallise in a rhombohedral unit cell with the KOsF₆ structure type.^[13] The only exceptions are hexafluorophosphates, which have cubic lattices at room temperature.^[14] The expectation that PnF₆⁻ salts of In⁺ should crystallise in a similar manner were confirmed by X-ray powder analyses.

The X-ray powder data of InPF₆, obtained at 298 K, were indexed with the DicoVol91 program^[15] as a cubic unit cell (Table 1) with $a = 8.07(2) \text{ \AA}$ and $V = 524.9 \text{ \AA}^3$. The isomorphous CsPF₆ has a cubic unit cell with $a = 8.228(5) \text{ \AA}$, $V = 557(1) \text{ \AA}^3$ and $Z = 4$.^[14,16]

The X-ray powder pattern of InAsF₆ obtained at 298 K is very similar to that of CsAsF₆. The isostructurality of both compounds was confirmed after indexing the X-ray powder data of InAsF₆ in a rhombohedral unit cell (Table 2) with $a = 7.58(2) \text{ \AA}$, $c = 7.90(1) \text{ \AA}$ and $V = 393.3 \text{ \AA}^3$. Isomorphous CsAsF₆ has a rhombohedral unit cell with $a = 7.723(1) \text{ \AA}$, $c = 8.0503(10) \text{ \AA}$, $V = 415.8 \text{ \AA}^3$ and $Z = 3$.^[17]

Table 1. X-ray powder data for InPF₆ with a cubic unit cell.^[a]

hkl	d (obsd.)	d (calcd.)	h	k	l
1	4.685	4.657	1	1	1
10	4.030	4.033	2	0	0
9	2.848	2.852	2	2	0
9	2.432	2.432	3	1	1
5	2.324	2.329	2	2	2
1	2.020	2.017	4	0	0
2	1.851	1.851	3	3	1
5	1.805	1.804	4	2	0
5	1.645	1.647	4	2	2
2	1.552	1.552	3	3	3
		1.552	5	1	1
1	1.427	1.426	4	4	0
2	1.345	1.344	4	4	2
		1.344	6	0	0
1	1.274	1.275	6	2	0
1	1.215	1.216	6	2	2

[a] $a = 8.07(2) \text{ \AA}$ and $V = 524.9 \text{ \AA}^3$.

Table 2. X-ray powder data for InAsF₆ with a rhombohedral unit cell.^[a]

hkl	d (obsd.)	d (calcd.)	h	k	l
10	3.772	3.791	1	1	0
10	3.373	3.385	1	0	2
1	2.624	2.633	0	0	3
4	2.521	2.525	2	0	2
4	2.355	2.368	2	1	1
4	2.190	2.189	3	0	0
9	2.100	2.101	2	1	2
5	1.891	1.891	1	0	4
2	1.692	1.692	2	0	4
2	1.653	1.654	3	1	2
2	1.548	1.545	2	1	4
2	1.517	1.516	4	0	2
2	1.437	1.433	4	1	0
2	1.406	1.407	3	2	2
1	1.339	1.339	3	1	4
1	1.264	1.264	3	3	0

[a] $a = 7.58(2) \text{ \AA}$, $c = 7.90(1) \text{ \AA}$ and $V = 393.3 \text{ \AA}^3$.

In the case of InSbF₆ the obtained X-ray powder photographs showed no lines, thereby indicating that the isolated InSbF₆ was of very low crystallinity. This couldn't be improved even after recrystallisation of InSbF₆ from its saturated solution in aHF.

Vibrational Spectra

The Raman spectra of InPnF₆ (Pn = P, As, Sb) are shown in Figure 1 and given in Table 3. They are in agreement with the presence of regular PnF₆⁻ octahedra.

Attempted Synthesis of InF and InInF₄

Preparation of InF has previously been attempted by thermal decomposition of InBF₄ at 373 K.^[6] On the basis of the results of X-ray powder analysis, it was claimed that the grey product contains, along with In metal, another phase which couldn't be identified. However, the X-ray

Table 3. Raman spectra of InPnF_6 ($\text{Pn} = \text{P}, \text{As}, \text{Sb}$) and the literature data for corresponding Cs^+ salts.

InPF_6	CsPF_6 [14,16]	InAsF_6	CsAsF_6 [18]	InSbF_6	CsSbF_6 [19]	Assignment ^[a]
738(100)	744(100)	677(100)	685(100)	641(100)	650(100)	ν_1
568(5)	578(5)	561(20)	576(30)	555(20)	570(13)	ν_2
470(5)	476(16)	365(25)	372(30)	283(15)	283(40)	ν_5
				272(15)	276(26)	ν_5

[a] Assignments are made for octahedral symmetry although in the solid state the actual symmetry could be lower.

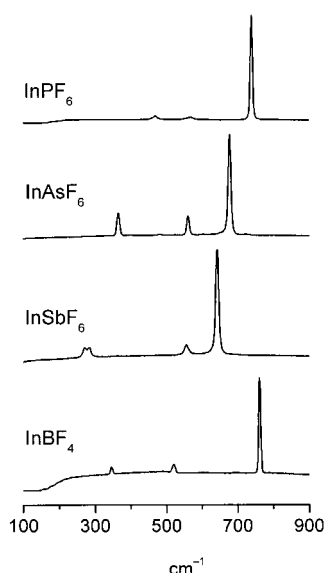


Figure 1. Raman spectra of indium(I) hexafluoropnictates and Raman spectrum of InBF_4 [761(100), 519(10), 346(10)].

powder diffraction pattern of this phase didn't match that of InF_3 nor could it be assigned to a high-ordered room-temperature form of TlF or to the NaCl structural type which is expected for InF .^[6]

Our attempt to prepare InF slightly above the melting point of aHF (189.4 K) by reaction between InSbF_6 and CsF in aHF , expecting that the CsSbF_6 would precipitate and leave InF dissolved in aHF , failed. At this temperature all the insoluble solid was greyish. Colourless CsF reacted with InSbF_6 to form a mixture of colourless CsSbF_6 and InF_3 and finely powdered grey In metal.

Several phases have been isolated and characterised in the TlF/TlF_3 system (i.e., $\text{Tl}_2\text{F}_3 \equiv \text{Tl}^{\text{I}}_3 \text{Tl}^{\text{III}}\text{F}_6$, $\text{Tl}_3\text{F}_5 \equiv \text{Tl}^{\text{I}}_2 \text{Tl}^{\text{III}}\text{F}_5$, $\text{TlF}_2 \equiv \text{Tl}^{\text{I}}\text{Tl}^{\text{III}}\text{F}_4$, $\text{Tl}_3\text{F}_7 \equiv \text{Tl}^{\text{I}}\text{Tl}^{\text{III}}_2\text{F}_7$).^[20,21] An attempt to prepare the indium analogue of TlF_2 (i.e., $\text{InF}_2 \equiv \text{In}^{\text{I}}\text{In}^{\text{III}}\text{F}_4$) by a metathetical reaction between InSbF_6 and CsInF_4 in aHF failed. Nothing happened at 243 K, and when the reaction mixture was brought to ambient temperature and left for one hour, a dark solid formed. This insoluble dark solid was separated from the colourless solution. The former consisted of a mixture of In and InF_3 still contaminated with CsSbF_6 , while the colourless solid isolated from the decanted solution corresponded to CsSbF_6 .

Experimental Section

CAUTION: Anhydrous HF and some of the fluorides below are highly toxic and must be handled using appropriate apparatus and protective gear.

Apparatus and Reagents: Volatile materials (PF_5 , AsF_5 , SbF_5 , BF_3 , aHF) were manipulated in an all-PTFE vacuum line equipped with PTFE valves. Non-volatile materials were manipulated in a dry box (M. Braun). The residual water in the atmosphere within the dry box never exceeded 1 ppm. The reactions were carried out in translucent fluorocarbon polymer (FEP, tetrafluoroethylene-hexafluoropropylene copolymer) reaction vessels (height 250–300 mm with inner diameter 15.5 mm and outer diameter 18.75 mm) equipped with PTFE body valves and PTFE-coated stirring bars. Reaction vessels made from two FEP tubes in a T-shape manner and equipped with PTFE body valves were used in some experiments. Each reaction vessel was pre-treated with F_2 (to about 1 bar) for several hours before use.

Pieces of In metal (Alfa Aesar, 99.99%) were treated with concentrated HCl prior to use to remove the oxide layer. BF_3 (Union Carbide Austria GmbH, 99.5%), CsF (Ventron, 99.9%) and InF_3 (Aldrich, 99.9) were used as supplied. Anhydrous HF (Praxair, 99.9%) was treated with K_2NiF_6 (Ozark-Mahoning, 99%) for several hours prior to use. PF_5 , AsF_5 , SbF_5 and BiF_5 were synthesised by pressure fluorination of phosphorus pentoxide (Aldrich, 99.99%), arsenic trioxide (Fluka, 99.5%), antimony trifluoride (Alfa Aesar, 99%) or bismuth trifluoride (ABCR, 99.5%), respectively, with elemental fluorine in a nickel reactor at 573 K.^[22]

InBF_4 was synthesised from In metal and BF_3 in aHF as described.^[6] CsInF_4 was prepared by annealing a stoichiometric mixture of CsF and InF_3 .^[23]

Instrumentation: Raman spectra were recorded with a Renishaw Raman Imaging Microscope System 1000, with He-Ne laser with wavelength 632.8 nm. X-ray powder diffraction photographs were obtained using the Debye-Scherrer technique with Ni-filtered Cu-K_α radiation. The positions of the lines were measured by visual inspection. Samples were loaded into 0.3-mm i.d. quartz capillaries in a dry-box, which were temporarily stoppered with halocarbon grease and sealed outside in the H_2/O_2 flame.

Chemical Analyses: The amount of total fluoride ion was determined after total decomposition of the sample using a fluoride ion selective electrode.^[24,25] The amount of indium was determined by complexometric titration with EDTA,^[26] the amount of antimony by redox titration,^[27] and the amount of AsF_6^- ion gravimetrically by precipitation with tetraphenylarsonium chloride.^[28,29] The results of chemical analyses are given in mass percents.

Syntheses – General Procedure: Nonvolatile reactants were loaded into FEP reaction vessels in a glove box. Anhydrous hydrogen fluoride (aHF) and, when necessary, PF_5 , AsF_5 or SbF_5 were con-

densed onto the solid reactants at 77 K. The reaction vessels were brought to ambient temperature. The reaction mixtures were vigorously agitated and, after some time, the volatiles were pumped off. Isolated products were characterised by mass balance, chemical analysis, vibrational spectroscopy and/or X-ray powder diffraction analyses.

Reaction Between InBF_4 and PF_5 in aHF: Reaction mixture: 0.544 g (2.70 mmol) of InBF_4 and 0.340 g (2.70 mmol) of PF_5 in 2 mL aHF. After 2 d only a colourless clear solution was visible. An excess of PF_5 (ca. 1.00 g) was then added. The Raman spectrum of the isolated solid showed only bands which could be assigned to InBF_4 (Figure 1).

Synthesis of InPF_6 : Reaction mixture: 0.340 g (2.96 mmol) of In metal and approximately 1.00 g of PF_5 in 4 mL of aHF. After 7 d pieces of In metal were still present. Cubic shaped crystals and a colourless powdered solid were observed beside unreacted In metal. After isolation the colourless powdered solid turned grey. Under microscopic observation it was found that single crystals also decomposed on the surface.

Synthesis of InAsF_6 : Reaction mixture: 0.443 g (2.32 mmol) of InBF_4 and 0.480 g (2.44 mmol) of AsF_5 in 6 mL of aHF. A white precipitate formed immediately and the reaction was left to proceed for 10 min. To decrease the loss of InAsF_6 because of its solubility in aHF the reaction vessel was cooled to 243 K and, whilst cold, the solution was decanted to remove any possible traces of InBF_4 . Yield of InAsF_6 : 0.706 g (100% based on InBF_4). InAsF_6 (303.74): calcd. In 37.80, F 37.53, AsF₆ 62.20; found In 37.6, F 37.1, AsF₆ 62.5. X-ray powder diffraction analysis and Raman spectroscopy excluded the presence of InBF_4 or InF_3 .

When the reaction mixture was left for a longer time the isolated product consisted of InAsF_6 and InF_3 (after 2 d) or only InF_3 (after 9 d).

When In metal or InBF_4 were treated with an excess of AsF_5 in aHF the final product consisted only of InF_3 .

Synthesis of InSbF_6 : Reaction mixture: 0.450 g (2.23 mmol) of InBF_4 and 0.398 g (2.23 mmol) of SbF_5 in 5 mL of aHF. A white precipitate formed immediately. After 1 d the volatiles were pumped off. Yield of InSbF_6 : 0.794 g (100% based on InBF_4). InSbF_6 (350.56): calcd. In 32.75, F 32.52, Sb 34.73; found In 33.0, F 32.1, Sb 34.5.

The reaction between In metal or InBF_4 and an excess of SbF_5 in aHF yielded a mixture of $\text{InF}_3 \cdot 3\text{SbF}_5$ ^[8] and $\text{SbF}_3 \cdot n\text{SbF}_5$, as found by Raman spectroscopy. A detailed characterisation of the latter is beyond the scope of this study.

Reaction Between InBF_4 and BiF_5 in aHF: Reaction mixture: 0.569 g (2.82 mmol) of InBF_4 and 0.857 g (2.82 mmol) of BiF_5 in 10 mL of aHF. A white, very dense suspension was obtained. The liquid phase was decanted away and the remaining volatile components pumped off. The isolated solid was yellowish. The Raman spectrum [587 (100), 570 (sh), 535 (20), 493 (10), 231 (5) 125 (5)] indicated the formation of $\text{BiF}_3 \cdot n\text{BiF}_5$.^[12] A detailed characterisation of this adduct is beyond the scope of this study.

Attempt to Prepare InF : A mixture of InSbF_6 (0.84 mmol) and CsF (0.84 mmol) was loaded into the double T-shaped apparatus. After condensation of aHF onto the sample at 77 K, the reaction vessel was warmed slightly to the melting point of aHF (ca. 190 K). At that temperature the insoluble solid was greyish in aHF. The reaction vessel was allowed to reach room temperature and left for 0.5 h. The colourless liquid was decanted and aHF condensed back onto the insoluble solid. After repeating this procedure several

times, the volatile materials were pumped off at ambient temperature. The X-ray powder diffraction pattern of the grey isolated solid showed lines that could be assigned to InF_3 still contaminated with CsSbF_6 , while the Raman spectrum of the colourless solid isolated from the decanted solution corresponded to that of CsSbF_6 .

Attempt to Prepare In_2F_4 : A mixture of InSbF_6 (0.239, 0.68 mmol) and CsInF_4 (0.221 g, 0.68 mmol) was loaded into the double T-shaped apparatus. After condensation of aHF onto the sample at 77 K, the reaction vessel was warmed to 243 K. A clear solution was visible above the insoluble colourless solid. Since no visible change was observed after 1 h, the reaction vessel was brought to ambient temperature and left for 0.5 h. The colour of the insoluble solid turned to grey-black. The colourless liquid was decanted and aHF condensed back onto the insoluble solid. After repeating this procedure several times, the volatile materials were pumped off at ambient temperature. The X-ray powder diffraction pattern of the grey isolated solid showed lines which could be assigned to InF_3 , while the Raman spectrum of the colourless solid isolated from the decanted solution corresponded to CsSbF_6 .

Acknowledgments

The author gratefully acknowledges the Slovenian Research Agency (ARRS) for the financial support of the present study within the research program: P1-0045 Inorganic Chemistry and Technology. I am also grateful to Dr. Maja Ponikvar for the chemical analysis.

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Received: May 27, 2005

Published Online: August 24, 2005