

Scientific paper

# Synthesis and Crystal Structures of Lanthanoid(III) Hexafluoroarsenates with AsF<sub>3</sub> Ligands

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Dedicated to Prof. Dr. Boris Žemva on the occasion of receiving the Zois Award for lifetime achievements.

## Abstract

Lanthanoid(III) hexafluoroarsenates with AsF<sub>3</sub> as a ligand were prepared with the reactions of solutions of Ln(AsF<sub>6</sub>)<sub>3</sub> in anhydrous hydrogen fluoride and AsF<sub>3</sub>. Solid products with composition Ln(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub> (Ln = La, Nd, Sm, Eu, Gd, Tb, Er, Tm) were isolated at 233 K. The attempt to prepare corresponding Yb and Lu compounds failed. Single crystals of Ln(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub> (Ln = Ce, Pr) were prepared by the reaction of LnF<sub>3</sub> (Ln = Ce, Pr) with AsF<sub>5</sub> and aHF under solvothermal conditions above critical temperature of AsF<sub>5</sub>. During the crystallization the reduction of some AsF<sub>5</sub> occurred and AsF<sub>3</sub> was formed. Compounds crystallize in a hexagonal crystal system, space group P  $\bar{6}$  2c (*a* = 10.6656(7) Å (Ce); 10.6383(7) Å (Pr); *c* = 10.9113(9) Å (Ce), 10.878(2) Å (Pr); *V* = 1074.9(1) Å<sup>3</sup> (Ce), 1066.2(2) Å<sup>3</sup> (Pr); *Z* = 2). Ln atoms are coordinated by nine fluorine atoms in the shape of the tri-capped trigonal prism and are further connected in three-dimensional framework *via* trans bridging AsF<sub>6</sub> units. Three fluorine atoms are provided by AsF<sub>3</sub> (capped positions) and six by AsF<sub>6</sub> units. X-ray powder analysis of Ln(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub> (Ln = La, Nd, Sm, Eu, Gd, Tb, Er, Tm) show that they are isostructural with corresponding Ce and Pr compounds.

**Keywords:** Lanthanoid metals, hexafluoroarsenates, arsenic trifluoride

## 1. Introduction

Lanthanoid trifluorides are insoluble in aHF, but are readily dissolved in aHF acidified with AsF<sub>5</sub>. LnF<sub>3</sub> dissolves when mole ratio of Ln to AsF<sub>5</sub> is 1:3 or higher. If isolation of lanthanoid(III) fluoroarsenates(V) from aHF/AsF<sub>5</sub> is performed at ambient temperature, products, with the exception of La(AsF<sub>6</sub>)<sub>3</sub>, readily lose AsF<sub>5</sub>. Compounds with compositions LnF(AsF<sub>6</sub>)<sub>2</sub> (Ln = Ce–Er) and Ln<sub>2</sub>F<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub> (Ln = Tm–Lu) were isolated.<sup>1</sup> This behaviour perfectly reflects the increased fluoroacidity of lanthanoid centers along the series. Lanthanoid hexafluoroarsenates are convenient precursors for the preparation of many coordination compounds with various ligands such as HF<sup>2</sup>, SO<sub>2</sub><sup>3</sup>, OPF<sub>3</sub>, NSF<sub>3</sub>,<sup>4</sup> XeF<sub>2</sub><sup>5</sup> and also AsF<sub>3</sub>. The Ln(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub> (Ln = Ce, Pr) compounds and their structures have been first mentioned briefly more than a decade ago,<sup>6</sup> but details of their syntheses and crystal structures are given here for the first time. The paper is also dealing with the selected examples of other elements of the lanthanoid series in order to study the stability of the Ln(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub> compounds along the series.

AsF<sub>3</sub> can act as a ligand to metal ions in two different ways: either by coordination through its fluorine ligands or by coordination through its electron lone pair on arsenic. Examples of AsF<sub>3</sub> coordination to a metal centre through fluorine atom are: M(AsF<sub>3</sub>)<sub>2</sub>(AsF<sub>6</sub>)<sub>2</sub> (M = Fe, Co, Ni),<sup>7–8</sup> (H<sub>3</sub>O)<sub>4</sub>La<sub>2</sub>F(AsF<sub>3</sub>)<sub>2</sub>(AsF<sub>6</sub>)<sub>9</sub>,<sup>9</sup> Sn(AsF<sub>3</sub>)<sub>2</sub>(SbF<sub>6</sub>)<sub>2</sub><sup>10</sup> and Ca(AsF<sub>3</sub>)<sub>2</sub>(AsF<sub>6</sub>)<sub>2</sub>.<sup>11</sup> Interesting cases of coordination of the AsF<sub>3</sub> *via* electron lone pair on arsenic were found in the F<sub>3</sub>As–AuSbF<sub>6</sub> and [(F<sub>3</sub>As)AuXe][Sb<sub>2</sub>F<sub>11</sub>].<sup>12–13</sup>

## 2. Experimental

### 2.1. General Experimental Procedure and Reagents

Volatile materials (anhydrous HF, AsF<sub>5</sub>, AsF<sub>3</sub>, F<sub>2</sub>) were handled in an all PTFE vacuum line equipped with PTFE (polytetrafluoroethylene) valves. The manipulations of the non-volatile materials were carried out 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 FEP (tetrafluoroethylene-hexafluoropropylene; Polytetra GmbH, Germany) reaction vessels (height 250–300 mm with inner diameter 15.5 mm and outer diameter 18.75 mm) equipped with PTFE valves and PTFE coated stirring bars. Prior to their use all reaction vessels were passivated with elemental fluorine. Fluorine was used as supplied (Solvay Fluor and Derivate GmbH, Germany). Anhydrous HF (Linde, 99.995 %) was treated with  $K_2NiF_6$  (Advance Research Chemicals, Inc.) for several hours prior to use. Arsenic pentafluoride was prepared by high-pressure fluorination of  $As_2O_3$ .<sup>14</sup> Arsenic trifluoride was prepared according to a modified literature procedure by the reaction of  $As_2O_3$  with aHF in a nickel reaction vessel at 493 K.<sup>15</sup> The purity of  $AsF_3$  was checked by IR spectroscopy. Lanthanoid trifluorides purchased from Johnson Matthey GmbH, Alfa Products, 99.9% (REO) or Wako Chemicals (99.5%) were used as supplied. **Caution:** aHF,  $AsF_5$  and  $AsF_3$  must be handled in a well-ventilated fume hood, and protective clothing must be worn at all times.

## 2. 2. Synthesis and Characterization Procedures

The  $Ln(AsF_3)_3(AsF_6)_3$  ( $Ln = La, Nd, Sm, Eu, Gd, Tb, Er, Tm$ ) compounds were prepared by the following procedure.  $LnF_3$  (from 200 to 250 mg) was weighted into reaction vessel. Anhydrous hydrogen fluoride (approx. 2 to 3 ml) and  $AsF_5$  (molar ratio between  $LnF_3$  and  $AsF_5$  must be higher than 1:3) were condensed onto the reaction vessel with  $LnF_3$  at 77 K and the reaction vessel was warmed to ambient temperature. After one day of intense stirring, clear solutions of  $Ln(AsF_6)_3$  in aHF/ $AsF_5$  were cooled in liquid nitrogen and  $AsF_3$  was added (the molar ratio between  $Ln$  and  $AsF_3$  was higher than 1:3). The reaction vessel was warmed again to ambient temperature and left 24 hours. The products were isolated by pumping away the solvent and excessive  $AsF_5$  and  $AsF_3$  at 233 K. The processes of isolation at such low temperature lasted at least several weeks (from 3 to 14 weeks).

Products were characterized by X-ray powder diffraction. Experimental X-ray powder patterns of  $Ln(AsF_3)_3(AsF_6)_3$  ( $Ln = La, Nd, Sm, Eu, Gd, Tb, Er, Tm$ ) matched the X-ray powder patterns calculated from the crystal structures of  $Ln(AsF_3)_3(AsF_6)_3$  ( $Ln = Ce, Pr$ ).  $Tb(AsF_3)_3(AsF_6)_3$  was characterized also by chemical analysis (Calcd. for  $Tb(AsF_3)_3(AsF_6)_3$ :  $Tb, 14.2$ ;  $As, 40.1$ ;  $F, 45.8$ ;  $AsF_6^-, 50.5$ ; Found:  $Tb, 14.8$ ;  $As, 39.2$ ;  $F, 45.0$ ;  $AsF_6^-, 49.2$ ). The content of terbium was determined by complexometric titration.<sup>16</sup> The content of fluorine (F) was determined by direct potentiometry using fluoride ion selective electrode after preceding total decomposition with  $NaKCO_3$ .<sup>17–19</sup> The total arsenic content was determined after preceding fusion with  $NaKCO_3$  with iodometric titration and of  $AsF_6^-$  gravimetrically.<sup>20</sup>

The volume of low-temperature-isolated solid products of the heavier lanthanoid elements (Tm, Yb, Lu) expanded immediately after warming to ambient temperature. This effect was less visible in the case of Tm and the most visible in the case of Lu. This indicates the release of gases ( $AsF_3, AsF_5$ ) and partial (Tm) or complete decomposition (Yb, Lu) of solids isolated at 233 K. Thulium compound still gave the X-ray pattern which was in agreement with  $Ln(AsF_3)_3(AsF_6)_3$ , meanwhile attempts to get X-ray powder patterns of Yb and Lu compounds failed.

Single crystals of  $Ln(AsF_3)_3(AsF_6)_3$  ( $Ln = Ce, Pr$ ) were prepared with the same procedure as used for preparation of single crystals  $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$ <sup>9</sup> and  $La(HF)(AsF_6)_3$ .<sup>2</sup> Approximately, 1 mmol of  $LnF_3$  ( $Ln = Ce, Pr$ ) was loaded in the dry-box into a stainless steel autoclave with a Teflon liner.  $AsF_5$  (approx. 15 mmol) and aHF (approx. 3 mmol) were added at 77 K. The autoclave was heated at 398 K for several months. During the crystallization the reduction of some  $AsF_5$  occurred and  $AsF_3$  was formed. The most probable way for the formation of  $AsF_3$  is reduction of some  $AsF_5$  on the wall of protective metal vessel on the Teflon liner due to permanent diffusion of  $AsF_5$  through the Teflon. After all volatiles were pumped away, only few single crystals were found between powdered materials. Selected ones were mounted in quartz glass capillaries (0.3 mm). Preparations of single crystals from saturated aHF solutions failed.

The crystallographic parameters and summaries of data collection for both compounds are presented in Table 1. Single-crystal data were collected on a Rigaku AFC7 diffractometer using graphite monochromatized  $MoK\alpha$  radiation at room temperature from crystals sealed in glass capillary. An empirical absorption correction based on azimuthal scans of several reflections was applied. Both structures were solved by direct methods using SIR-92<sup>21</sup> and SHELXS-97 programs (teXan crystallographic software package of Molecular Structure Corporation<sup>22</sup>) and refined with SHELXL-97<sup>23</sup> software, implemented in program package WinGX<sup>24</sup>. Full-matrix least-squares refinements based on  $F^2$  were carried out for the positional and thermal parameters for all non-hydrogen atoms. Determined crystal structure demonstrated satisfactory geometry but show huge thermal ellipsoids of terminal fluorine atoms belonging to  $AsF_3$  group. In order to improve the structural model, the position of F4 terminal fluorine atom was split on two positions (F41, F42) resulting in lower R-value and slightly smaller thermal ellipsoids but in some inadequate As–F bond lengths. Attempts to find better models in space group with lower symmetry were unsuccessful. To resolve these problems crystal of  $Ce(AsF_3)_3(AsF_6)_3$  was re-measured at 200 K and at 100 K. Since no real improvement was achieved only unit cell dimensions, determined at these temperatures, are listed in Table 1. The figures were prepared using DIAMOND 3.1 software.<sup>25</sup> Further details of the crystal-structure investigation may be obtained from the Fachin-

**Table 1.** Crystal data and structure refinement for Ce(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub> (I) and Pr(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub> (II) compounds.

	I	II
Empirical formula	CeAs <sub>6</sub> F <sub>27</sub>	PrAs <sub>6</sub> F <sub>27</sub>
Formula weight	1102.64	1103.43
Wavelength	0.71069 Å	0.71069 Å
Crystal system, space group	hexagonal, $P\bar{6} 2c$	hexagonal, $P\bar{6} 2c$
Temperature, K	293(2)	293(2)
Unit cell dimensions, Å		
<i>a</i> , Å	10.6656(7)	10.6383(7)
	10.6495(7) <sup>a</sup>	
	10.6329(7) <sup>b</sup>	
<i>c</i> , Å	10.9113(9)	10.878(2)
	10.8971(9) <sup>a</sup>	
	10.8677(9) <sup>b</sup>	
<i>V</i> , Å <sup>3</sup>	1074.9(1)	1066.2(2)
	1070.3(1) <sup>a</sup>	
	1064.1(1) <sup>b</sup>	
<i>Z</i>	2	2
Calculated density, g/cm <sup>3</sup>	3.407	3.437
Absorption coeff., mm <sup>-1</sup>	11.5	11.745
<i>F</i> (000)	998	1000
Crystal size, mm	0.11 × 0.06 × 0.06	0.03 × 0.03 × 0.02
Colour	colourless	green
Theta range for data collection, deg	2.2 – 29.97	2.21 – 29.97
Limiting indices	0 ≤ <i>h</i> ≤ 12, 0 ≤ <i>k</i> ≤ 12, 0 ≤ <i>l</i> ≤ 15	0 ≤ <i>h</i> ≤ 14, -14 ≤ <i>k</i> ≤ 12, -15 ≤ <i>l</i> ≤ 15
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Measured reflections	630	1233
Used in refinement	630	797
Free parameters	65	66
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.865	0.834
<i>R</i> indices	<i>R</i> <sub>1</sub> = 0.0364, <i>wR</i> <sub>1</sub> = 0.088	<i>R</i> <sub>1</sub> = 0.0386, <i>wR</i> <sub>1</sub> = 0.0839
Largest diff. peak and hole	0.961 and -1.248 e Å <sup>-3</sup>	0.942 and -1.153 e Å <sup>-3</sup>

<sup>a</sup> at 200 K, <sup>b</sup> at 100 K.

formationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number: CSD-424853 (Ce(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub>), CSD-424852 (Pr(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub>).

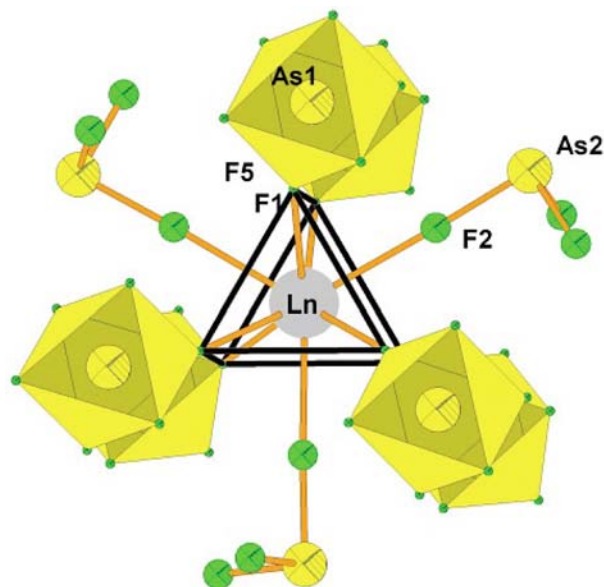
### 3. Results and Discussion

The Ln(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub> compounds can be prepared by the reaction between corresponding aHF solutions of Ln(AsF<sub>6</sub>)<sub>3</sub> and AsF<sub>3</sub>. Isolated solids are less stable in dynamic vacuum at room temperature as similar compounds with XeF<sub>2</sub> as a ligand.<sup>26</sup> Several experiments with the isolation of the desired compounds (Ln = Nd, Sm, Gd) at room temperature were done. The final masses of the products isolated at room temperature were significantly lower than the calculated for Ln(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub>. The products become both AsF<sub>3</sub> and AsF<sub>5</sub> deficient. Additionally, it was found that the stability of Ln(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub> compounds decreases from La to Tm. For that reason, Ln(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub> prepared in aHF should be isolated at low temperature. When the Ln(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub> compounds are completely dry, they are stable at room temperature

however, they should be kept in the inert atmosphere since they readily react with moisture. The results of chemical analysis in the case of Tb confirmed the composition Tb(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub>. Additionally, the X-ray powder patterns obtained from the bulk reaction products (Ln = La, Nd, Sm, Eu, Gd, Tb, Er, Tm) are identical to the simulated X-ray powder patterns calculated from the single crystal structure of Ln(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub> (Ln = Ce, Pr). X-ray powder patterns of solid products, which were isolated at room temperature, also show the presence of Ln(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub> phases. Yb and Lu products, which were isolated at low temperature, decomposed immediately after warming to ambient temperature.

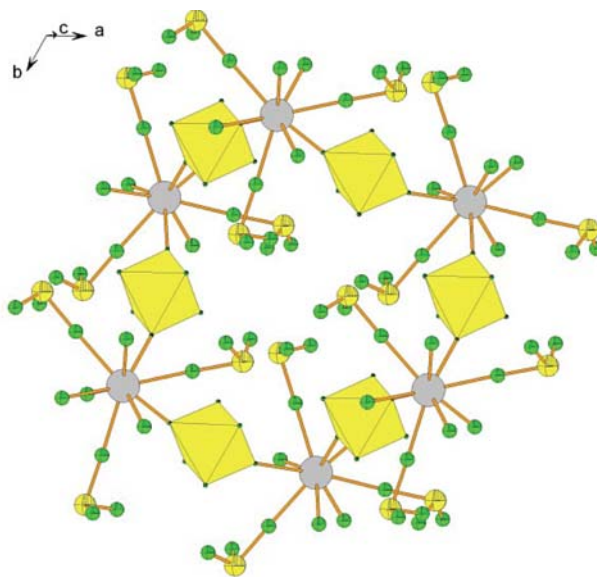
In the crystal structure of Ln(AsF<sub>3</sub>)<sub>3</sub>(AsF<sub>6</sub>)<sub>3</sub> the lanthanoid atom is coordinated to nine fluorine atoms in the form of tri-capped trigonal prism (Figure 1). Six fluorine atoms provided from six AsF<sub>6</sub><sup>-</sup> anions are located at the corners of the trigonal prism and three additional fluorine atoms belong to three AsF<sub>3</sub> units. The Ln–F(AsF<sub>6</sub>) distances are shorter than Ln–F(AsF<sub>3</sub>) ones (2.421(7) versus 2.47(1) Å in the case of Ce, 2.415(6) versus 2.435(7) Å for Pr, respectively). The lanthanoid atom is located at the special 2*d* crystallographic position (at  $\bar{6}$ ), therefore all six

$\text{Ln}-\text{F}(\text{AsF}_6)$  distances are equal, as well as all three  $\text{Ln}-\text{F}(\text{AsF}_3)$  distances.



**Figure 1.** Nine-fold coordination of Ln (Ln = Ce, Pr) atom in the crystal structure of  $\text{Ln}(\text{AsF}_3)_3(\text{AsF}_6)_3$ . Fluorine atoms of  $\text{AsF}_3$  units are presented in non-split isotropic mode for clarity.

$\text{AsF}_6$  units connect Ln atoms *via* trans-bridges. The  $\text{As}-\text{F}_{\text{bridge}}$  distances are longer than  $\text{As}-\text{F}_{\text{terminal}}$  (1.765(6) vs 1.67(1) Å in Ce compound, 1.761(5) vs 1.665(9) Å in Pr derivative). The  $\text{As}-\text{F}$  distances are listed in Table 2. Twenty-four member zigzag rings of Ln atoms, As atoms and F atoms from  $\text{AsF}_6$  units are found. Every second Ln atom of this 24-member ring is in the same plane.  $\text{AsF}_3$  moieties are located inside these channels of approx. 4 Å radii without any further interactions (Figure 2). Due to the trans-bridging role of  $\text{AsF}_6$  units, Ln centres with attached  $\text{AsF}_3$  units are interconnected into three-dimensional framework. Two of bridging  $\text{AsF}_6$  units are involved in a formation of above mentioned rings, next two associate these rings into infinite channels (bonding along 001 crystallographic direction), and the last two  $\text{AsF}_6$  units are responsible for a bonding in 100 and 010 directions. (Figure 3).



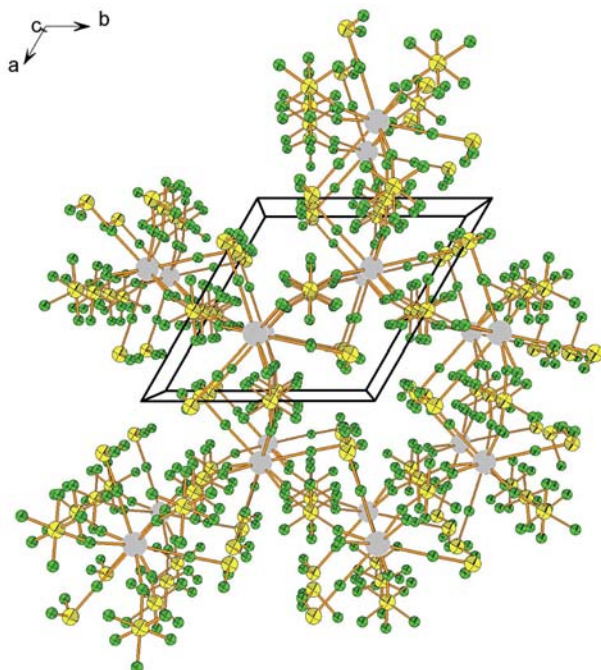
**Figure 2.** Twenty-four member ring of Ln (Ln = Ce, Pr) atoms, As atoms and F atoms from  $\text{AsF}_6$  units, forming channels along *c*-axis. All fluorine atoms are shown in isotropic mode for clarity.

In the case of  $\text{AsF}_6$  units, shape and orientation of the thermal ellipsoids describe librational motions of terminal fluorine atoms around  $\text{F}_b-\text{As}-\text{F}_b$  axis. The  $\text{AsF}_3$  units are bound to the Ln centres *via* only one fluorine bridge and, therefore, possess higher “degree of freedom”. To overcome the problem with librational (roughly around  $\text{Ln}-\text{F}_b-\text{As}$  axis) disorder, positions of both terminal fluorine atoms in  $\text{AsF}_3$  moiety were split into two positions (Figure 4). Unfortunately, even such approach results in large thermal parameters for each terminal F atom and inadequate  $\text{As}-\text{F}$  bond lengths. In the crystal structure of  $\text{Ce}(\text{AsF}_3)_3(\text{AsF}_6)_3$  the length of the terminal  $\text{As2}-\text{F42}$  bond is practically the same as bridging  $\text{As2}-\text{F2}$  distance, whereas the  $\text{As2}-\text{F41}$  distance is shorter. The data obtained by a low-temperature single-crystal X-ray diffraction has led to a practically identical model as at room temperature. Although the shapes of thermal ellipsoids are smaller at 100 K, splitting of two fluorine positions was still observed. The situation with  $\text{As}-\text{F}$  bond lengths became even worse, because at 100 K the terminal  $\text{As2}-\text{F42}$  di-

**Table 2.** Interatomic distances (Å) of  $\text{AsF}_6$  and  $\text{AsF}_3$  moieties in  $\text{Ce}(\text{AsF}_3)_3(\text{AsF}_6)_3$  (I) and  $\text{Pr}(\text{AsF}_3)_3(\text{AsF}_6)_3$  (II)

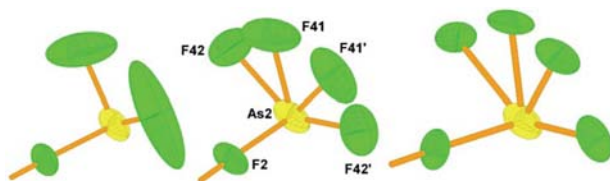
I			
$\text{As1}-\text{F1}, \text{As1}-\text{F1}^{\text{ii}}$	1.765(6)	$\text{As2}-\text{F2}$	1.78(1)
$\text{As1}-\text{F3}, \text{As1}-\text{F3}^{\text{ii}}$	1.67(1)	$\text{As2}-\text{F41}, \text{As2}-\text{F41}^{\text{i}}$	1.69(2) <sup>a)</sup>
$\text{As1}-\text{F5}, \text{As1}-\text{F5}^{\text{ii}}$	1.68(1)	$\text{As2}-\text{F42}, \text{As2}-\text{F42}^{\text{i}}$	1.767(2) <sup>a)</sup>
II			
$\text{As1}-\text{F1}, \text{As1}-\text{F1}^{\text{ii}}$	1.761(5)	$\text{As2}-\text{F2}$	1.800(8)
$\text{As1}-\text{F3}, \text{As1}-\text{F3}^{\text{ii}}$	1.652(8)	$\text{As2}-\text{F41}, \text{As2}-\text{F41}^{\text{i}}$	1.76(2) <sup>a)</sup>
$\text{As1}-\text{F5}, \text{As1}-\text{F5}^{\text{ii}}$	1.665(9)	$\text{As2}-\text{F42}, \text{As2}-\text{F42}^{\text{i}}$	1.67(2) <sup>a)</sup>

<sup>a)</sup> Due to the huge thermal ellipsoids the positions of terminal F4 atoms belonging to  $\text{AsF}_3$  were split on two sites (F41, F42). Symmetry codes: (i)  $x, y, -z+3/2$ ; (ii)  $y, x, -z+1$ .



**Figure 3.** Part of the three-dimensional framework in the crystal structure of  $\text{Ln}(\text{AsF}_3)_3(\text{AsF}_6)_3$ . All fluorine atoms are shown in isotropic mode for clarity.

stance is longer than the bridging As2–F2 one. Careful examination of thermal ellipsoids of As2 and its fluorine neighbours shows that fluorine ellipsoids become noticeably smaller with decrease of temperature, whereas the ellipsoid of As2 is large even at 100 K. Based on that observations, and taking into account the direction of the main axis of the As2 ellipsoid (Figure 4) it could be concluded that at 293 K there is a combination of librational motion of terminal fluorine atoms in the  $\text{AsF}_3$  group and the disordering of the whole  $\text{AsF}_3$  unit in both structures. Lowering the temperature (200 K and 100 K) decreases thermal motion of atoms, but does not influence the disorder of atoms. X-ray diffraction experiments give us an average (in manifold unit cells) atomic coordinates and, consequently, average interatomic distances. Because of that, the observed As–F<sub>terminal</sub> bond lengths of disordered  $\text{AsF}_3$  units are not realistic. It could be concluded that a weak fixation of the  $\text{AsF}_3$  group and rather low (71%) packing index of the structure promotes disorder of  $\text{AsF}_3$  groups.



**Figure 4.** Large thermal ellipsoids of fluorine atoms in  $\text{AsF}_3$  unit at 293 K (left), model with split fluorine positions at 293 K (centre), model with split fluorine positions at 100 K (right).

## 4. Conclusions

$\text{Ln}(\text{AsF}_3)_3(\text{AsF}_6)_3$  (Ln = La, Nd, Sm, Eu, Gd, Tb, Er, Tm) compounds can be prepared by the reaction of  $\text{LnF}_3$ ,  $\text{AsF}_5$  and  $\text{AsF}_3$  in aHF as solvent. Isolation of the products from corresponding solutions must be performed at low temperature. Compounds, with exception of Tm, are stable at room temperature when dry, but they are moisture sensitive. Attempts to prepare corresponding Yb and Lu compounds failed.

Isolated solids give similar X-ray powder diffraction patterns, which match the X-ray powder diffraction data calculated from the crystal structures of  $\text{Ln}(\text{AsF}_3)_3(\text{AsF}_6)_3$  (Ln = Ce, Pr). On the basis of this data it could be concluded that all  $\text{Ln}(\text{AsF}_3)_3(\text{AsF}_6)_3$  compounds are isostructural. In the crystal structure of  $\text{Ln}(\text{AsF}_3)_3(\text{AsF}_6)_3$  (Ln = Ce, Pr) compounds Ln atoms are nine-fold coordinated by fluorine atoms in the shape of the tri-capped trigonal prism. Three fluorine atoms are provided by three  $\text{AsF}_3$  groups (capped positions) and six fluorine atoms are provided by six  $\text{AsF}_6$  units. The latter further connect Ln atoms in three-dimensional framework. At 293 K there is a combination of librational motions of terminal fluorine atoms of  $\text{AsF}_3$  group and the disordering of the whole  $\text{AsF}_3$  units. Lowering the temperature (200 and 100 K) decreases thermal motions of atoms, but does not influence the disordering of atoms.

## 5. Acknowledgement

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## 6. References

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## Povzetek

Z reakcijami med lantanoidnimi(III) heksafluoroarzenati(V) in  $\text{AsF}_3$  v brezvodnem HF kot topilu smo sintetizirali spojine s sestavo  $\text{Ln}(\text{AsF}_3)_3(\text{AsF}_6)_3$  ( $\text{Ln} = \text{La, Nd, Sm, Eu, Gd, Tb, Er, Tm}$ ). Spojineje potrebno izolirati pri 233 K. Poskusi priprave spojin Yb in Lu niso bili uspešni. Monokristale  $\text{Ln}(\text{AsF}_3)_3(\text{AsF}_6)_3$  ( $\text{Ln} = \text{Ce, Pr}$ ) smo pripravili z reakcijo  $\text{LnF}_3$  ( $\text{Ln} = \text{Ce, Pr}$ ) in  $\text{AsF}_5$  in HF pri 393 K, nad kritično temperaturo  $\text{AsF}_5$ . Med procesom kristalizacije se je del  $\text{AsF}_5$  reduciralv  $\text{AsF}_3$ . Spojine kristalizirajo v heksagonalnem kristalnem sistemu, prostorski skupini  $P\bar{6}2c$  ( $a = 10.6656(7) \text{ \AA}$  (Ce);  $10.6383(7) \text{ \AA}$  (Pr);  $c = 10.9113(9) \text{ \AA}$  (Ce),  $10.878(2) \text{ \AA}$  (Pr);  $V = 1074.9(1) \text{ \AA}^3$  (Ce),  $1066.2(2) \text{ \AA}^3$  (Pr);  $Z = 2$ ). Atomi Ln so koordinirani z devetimi fluorovimi atomi. Šest fluorovih atomov, ki jih prispevajo  $\text{AsF}_6$  enote, tvori pravilno trigonalno prizmo okoli atoma Ln. Nad stranskimi ploskvami prizme so trije fluorovi atomi, ki pripadajo  $\text{AsF}_3$  molekulam. Atomi Ln so preko  $\text{AsF}_6$  enot povezani v tridimenzionalno kristalno mrežo. Podatki rentgenske praškovne analize spojin  $\text{Ln}(\text{AsF}_3)_3(\text{AsF}_6)_3$  ( $\text{Ln} = \text{La, Nd, Sm, Eu, Gd, Tb, Er, Tm}$ ) kažejo, da so spojine izostrukturne s spojinama Ce in Pr.