ELSEVIER

Journal of Fluorine Chemistry 112 (2001) 173–183

JOURNAL OF FLUORINE CHEMISTRY

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Novel oxonium compounds of lanthanoids: synthesis of $(H_3O)_3La_2F(AsF_6)_8$, and syntheses and crystal structures of $(H_3O)_8La_2F(AsF_6)_{13}$ and $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$

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Received 15 June 2001; accepted 31 August 2001

Dedicated to K.O. Christe on the occasion of his 65th birthday

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Abstract

Reactions of Ln_2O_3 with AsF_5 in aHF (Ln = La–Lu, aHF = anhydrous hydrogen fluoride) yield solutions of H_3O^+, solvated Ln^{3+} and AsF_6^- ions. Very similar solutions of these ions may be obtained from combination of various other starting materials, e.g. LnF_3–H_2O–AsF_5–aHF, $LnF_x(AsF_6)_{3-x}$–H_3OAsF_6–aHF. From such solutions a new type of oxonium compounds with general formula $(H_3O)_xLn_yF_z(AsF_6)_{x+3y-z}$ have been isolated at ambient temperature. $(H_3O)_3La_2F(AsF_6)_8$ was obtained as a white powder from the solution of La_2O_3 dissolved in AsF_5–aHF after pumping off all volatiles at room temperature. Colourless crystals of $(H_3O)_8La_2F(AsF_6)_{13}$ were prepared by slow static evaporation from a solution obtained after solvolysis of solid $(H_3O)_3La_2F(AsF_6)_8$ in aHF at ambient conditions. Colourless crystals of $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$ were prepared by the reaction of La_2O_3 with AsF_5 and aHF under solvothermal conditions above the critical temperature of AsF_5. Similar reactions of other oxides Ln_2O_3 (Ln = Nd, Sm, Gd, Dy, Ho, Tm) have also been studied. $(H_3O)_8La_2F(AsF_6)_{13}$ crystallises in the monoclinic space group $P2_1/c$ (no. 14) with $a = 1079.3(3)$ pm, $b = 2859.0(7)$ pm, $c = 1068.0(3)$ pm, $\beta = 109.310(8)^\circ$, and $Z = 2$. $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$ crystallises in the triclinic space group $P\bar{1}$ (no. 2) with $a = 1064.8(3)$ pm, $b = 1073.3(4)$ pm, $c = 1213.9(3)$ pm, $\alpha = 75.53(2)^\circ$, $\beta = 64.79(2)^\circ$, $\gamma = 70.07(2)^\circ$, and $Z = 1$. Both structures are closely related with zig-zag chains of alternating La_2F and AsF_6 units resembling the main feature. Oxonium ions are arranged among such anionic chains. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Oxonium salts; Lanthanoid(III) hexafluoroarsenates; Anhydrous HF; Lewis acids

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1. Introduction

In 1975, Christe et al. reported about the synthesis of H_3O^+ salts containing AsF_6^- and SbF_6^- anions. H_3OAsF_6 and H_3OSbF_6 were prepared as crystalline solids from the H_2O–HF–AsF_5 and the H_2O–HF–SbF_5 system, respectively [1]. Both salts possess unusual thermal stability. H_3OAsF_6 and H_3OSbF_6 decompose at about 466 and 630 K, respectively. Nine years later, Christe et al. reported about characterisation of H_3OAsF_6 and H_3OSbF_6 by X-ray and neutron diffraction techniques, DSC measurements, and vibrational spectroscopy [2].

H_3OAsF_6 reacts with $M(AsF_6)_2$ (M = divalent metal) in anhydrous hydrogen fluoride (aHF) at room temperature yielding novel oxonium salts $H_3OM(AsF_6)_3$ (M = Mn [3], Fe [4], Co [3], Ni [3]). Analogous reactions in the systems $Ln(AsF_6)_3$–H_3OAsF_6–aHF or Ln_2O_3–AsF_5–aHF (Ln = La–Lu) are yielding new oxonium salts of lanthanoids with general formula $(H_3O)_xLn_yF_z(AsF_6)_{x+3y-z}$. The present paper describes the synthesis of three lanthanum compounds $(H_3O)_3La_2F(AsF_6)_8$, $(H_3O)_8La_2F(AsF_6)_{13}$ and $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$, including crystal structures of the latter two compounds. Results of reactions between some other Ln_2O_3 (Ln = Nd, Sm, Gd, Dy, Ho, Tm) and AsF_5 in aHF are also presented.

2. Results and discussion

2.1. Reactions of Ln_2O_3 with AsF_5 in aHF

Reactions of Ln_2O_3 in the superacidic medium AsF_5–aHF at 298 K proceed according to the formal equation:

$$Ln_2O_3 + nAsF_5 + mHF \rightarrow (H_3O^+)_3[Ln(HF)_x{}^{3+}]_2(AsF_6^-)_9 + (n-9)AsF_5 + (m-9-2x)HF, \quad n \geq 9, \quad m > 300 \qquad (1)$$

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PII: S0022-1139(01)00508-5

In clear solutions obtained from such reactions, solvated lanthanoid cations $Ln(HF)_x^{3+}$ [5], H_3O^+ cations and AsF_6^- anions are formed. This is well in agreement with the literature data [6] derived from CeO_2 dissolved in aHF and acidified with SbF_5, where authors anticipated solvated Ce^{4+}, H_3O^+ and SbF_6^- ions. In solutions of AsF_5 in anhydrous hydrogen fluoride H_2F^+ along with AsF_5, AsF_6^- and $As_2F_{11}^-$ species form in an equilibrium [7]. Water may be synthesised in situ from Ln_2O_3 and aHF. In AsF_5–aHF systems, water behaves as a very strong base and consequently displaces the weaker base HF from H_2F^+, thus forming H_3O^+ ions directly in solution [1]. The rate of reaction between Ln_2O_3 and liquid aHF at room temperature rapidly diminishes along the lanthanoid series of elements. Stronger bases at the beginning of the series (e.g. La_2O_3, Sm_2O_3) react quickly and pure trifluorides are obtained within a few days. The approach using aHF as a reaction medium proved very convenient also in the syntheses of some other binary fluorides in pure form [8]. The reactions of more acidic Ln_2O_3 (e.g. Gd_2O_3, Dy_2O_3) are rather slow, as within of time required to complete formation of LaF_3 or SmF_3, only about 15% of GdF_3 or DyF_3 are formed. Even after 35 days, only about 30% of the starting Gd_2O_3 or Dy_2O_3 had been converted to GdF_3 or DyF_3, respectively. However, in the presence of strong Lewis acids reaction of any Ln_2O_3 in aHF proved much quicker, the more basic representatives were completely dissolved within a few minutes, and even the slowest reaction was finished within 30 min. Similar observations were obtained at reactions of Ln_2O_3 with elemental fluorine [9], e.g. La_2O_3 reacts violently at room temperature to LaF_3, Nd_2O_3, Sm_2O_3 and Eu_2O_3 start to react at 533 K and reactions are completed at 823 K, while Ln_2O_3 (Ln = Gd, Dy, Ho, Er, Tm, Yb, Lu) are not completely transformed to corresponding trifluorides even at 823 K. Further, decreasing basicity of lanthanoid metals along the series is well established in many systems. Reactions of the same acid or base along the series frequently show the borderline of basic/acidic properties in the series, e.g. reactions of medium strong base XeF_6 do not proceed from LaF_3 to GdF_3. The required acidity of LnF_3 is achieved with DyF_3, $3XeF_6{\cdot}DyF_3$ and $6XeF_6{\cdot}LnF_3$, (Ln = Ho–Lu) were isolated [10].

The stoichiometric ratio $Ln_2O_3{:}AsF_6 = 1{:}9$ given in Eq. (1) for the aHF solution was confirmed by titration. The last traces of La_2O_3 dissolved in aHF when exactly the molar ratio $La_2O_3{:}AsF_5 = 1{:}9$ had been reached. In the Raman spectrum of such solution, only a broad peak around 685 cm^{-1} was observed, indicating the presence of AsF_6^- anions [11]. Of course, combinations of H_3O^+, $Ln(HF)_x^{3+}$ and AsF_6^- ions in aHF solution are also obtained from other starting mixtures, e.g. LnF_3–H_2O–AsF_5–aHF and $LnF_x(AsF_6)_{3-x}$–H_3OAsF_6–aHF.

2.2. Isolation of $(H_3O)_3La_2F(AsF_6)_8$

Up to now, we did not succeed to isolate the compound $[H_3O^+]_3[Ln(HF)_x^{3+}]_2[AsF_6^-]_9$ which represents the main product in above-mentioned equation. After the solvent aHF together with excess AsF_5 have been condensed off respective solutions at room temperature, the solid residue slowly releases some gaseous material in vacuum. In case of La, this process stops precisely after one mole of AsF_5 per formula unit has been released, yielding $(H_3O)_3La_2F(AsF_6)_8$. As will be shown later, changes of reaction conditions at the step of product isolation give rise to variety of compositions of the particular product.

2.3. Isolation of reaction products with Ln = Nd, Sm, Gd, Dy, Ho, Tm

In the case of less basic representatives of lanthanoid series, much longer times of pumping are required than with La to reach products stable at room temperature (several 10 h versus few hours). Fine powders of typical but faint colour for the particular Ln^{3+} ion are obtained. Necessity of more extended pumping is associated with release of more than just one molecule of AsF_5 per formula unit. In the case of Nd and Sm, two additional molecules of AsF_5 were released, resulting in formation of compounds $(H_3O)_3Ln_2F_3(AsF_6)_6$. However, while for Nd isolation proceeded at room temperature, 273 K had to be maintained in the case of Sm (Fig. 1). This is again in agreement with decreasing basicity of LnF_3 type materials along the series. Weight balance and chemical analyses of Gd, Dy, Ho and Tm reaction products (Table 1) indicate that not only AsF_5 is released during pumping under dynamic vacuum. Respective IR-spectra suggest evaporation of H_2O and/or H_3OAsF_6. So far, it has to remain open if isolated products from these reactions are single phase and what may be their precise composition. However, below 253 K, all products completely

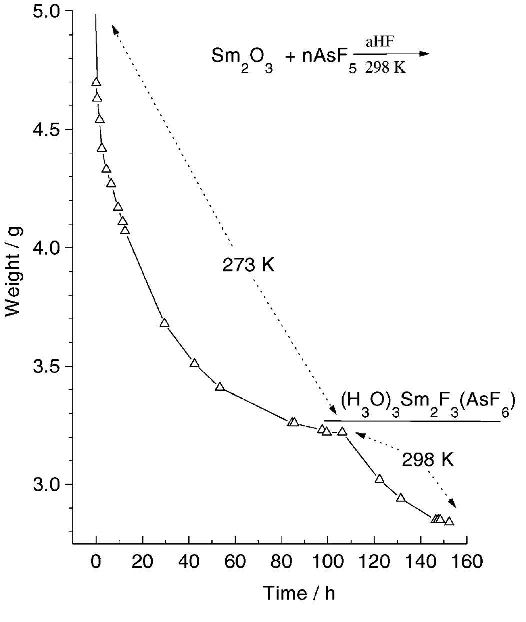

Fig. 1. Pumping curve in the course of isolation of $(H_3O)_3Sm_2F_3(AsF_6)_6$ at 273 K.

Table 1
Reactions between Ln_2O_3 and AsF_5 in aHF (Ln = Gd, Dy, Ho, Tm)

Starting compound	Weight of product (g)	Chemical analysis			
		Ln (%)	F (%)	As (%)	H_2O (%)
Gd_2O_3	2.9730	28.5	40.1	24.7	3.0
Dy_2O_3	2.0420	29.8	39.4	24.3	–
Ho_2O_3	2.1190	29.7	39.8	26.7	3.0
Tm_2O_3	3.1962	31.3	38.1	26.9	–[a]

[a] Product was insoluble in organic solvent.

dissolve in aHF without solvolysis. This also proves that materials insoluble under these conditions like LnF_3, Ln_2O_3 or LnOF are definitely not among reaction products.

2.4. Solvolysis of $(H_3O)_3La_2F(AsF_6)_8$ in aHF

$(H_3O)_3La_2F(AsF_6)_8$ is solvolysed in aHF at room temperature (like $LnF_x(AsF_6)_{3-x}$ [13]), according to following equation:

$$6(H_3O)_3La_2F(AsF_6)_8 \overset{aHF, 298\,K}{\rightarrow} 5(H_3O)_3[La(HF)_x]_2(AsF_6)_9 + 3H_3OAsF_6 + 2LaF_3 \qquad (2)$$

While the X-ray powder diffraction (XRD) pattern of the precipitate showed only characteristic lines of LaF_3, respective pattern of the solid recovered from the supernatant solution showed only the diagram of $(H_3O)_3La_2F(AsF_6)_8$.

2.5. Crystallisation from aHF solutions containing H_3O^+, La^{3+} and AsF_6^- ions at room temperature, and crystallisation using solvothermal conditions of AsF_5

As the XRD pattern of $(H_3O)_3La_2F(AsF_6)_8$ is quite a complicated one (Section 4.5), numerous attempts were made to grow single crystals from various solutions in aHF. In all cases, single crystals of $(H_3O)_8La_2F(AsF_6)_{13}$ among white powder material were isolated. The largely different molar ratio of H_3O to La in the crystals as compared to the starting solutions indicates that the powder phase most likely is not homogeneous. In general, crystal growth in these systems is slow. Close to the end of such a process, the very viscous, honey-like material has to sit for several weeks, before finally crystals start to develop.

The attempt was made to synthetise $(H_3O)_8La_2F(AsF_6)_{13}$ compound in a bulk quantities (see Section 4.10). Though corresponding molar ratio of H_3O:LaF_3 (4:1) was used the $(H_3O)_3La_2F(AsF_6)_8$ compound was synthesised, however, in the mixture with H_3OAsF_6. Therefore, the kinetic reasons are the most probable for obtaining the phase $(H_3O)_8La_2F(AsF_6)_{13}$ in the crystalline form. This and previous results (Section 2.3) show that from the solutions in which H_3O^+, solvated Ln^{3+} and AsF_6^- ions are present the whole set of different compounds of the type $(H_3O)_xLn_yF_z(AsF_6)_{x+3y-z}$ is possible to isolate under different conditions, e.g. $(H_3O)_3La_2F(AsF_6)_8$, $(H_3O)_8La_2F(AsF_6)_{13}$, $(H_3O)_3Ln_2F_3(AsF_6)_6$, Ln = Nd, Sm. Phases which can adopt the chain structure of $(H_3O)_8La_2F(AsF_6)_{13}$ or $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$ are energetically favourable (see Section 2.6).

The synthesis of these compounds is possible also at higher temperatures. The solvothermal conditions of AsF_5 above its critical temperature (337 K [12]) are suitable for the preparation of single crystals. In the described experiment, the phase $(H_3O)_4La_2F(AsF_6)_9$ was stabilised with additional ligand AsF_3. The most probable way for the formation of AsF_3 is reduction of some AsF_5 on the wall of protective metal vessel of the Teflon liner due to permanent diffusion of AsF_5 through the Teflon.

Finally, Fig. 2 shows the scheme of the reactions initiated by the reaction of La_2O_3 with AsF_5 in aHF, and which were discussed in above items. Owing to clarity the stoichiometry of equations is omitted.

2.6. Crystal structures of $(H_3O)_8La_2F(AsF_6)_{13}$ and $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$

$(H_3O)_8La_2F(AsF_6)_{13}$ crystallises in the monoclinic space group $P2_1/c$ (no. 14) with two formula units in the unit cell. Pertinent crystallographic data are given in Table 2 and selected interatomic distances and angles in Table 3. The labelling scheme is given in Fig. 3a. The basic unit of the structure is formed by one fluorine atom (F1) located at a centre of symmetry and connecting two lanthanum atoms. This arrangement is bridged by four AsF_6^- anions (As3, As5) with bridging fluorines of each anion in *cis*-position. Coordination of each La atom is further extended by three additional, non-bridging, AsF_6 units (As2, As4, As6). The environment of each La atom is completed by a

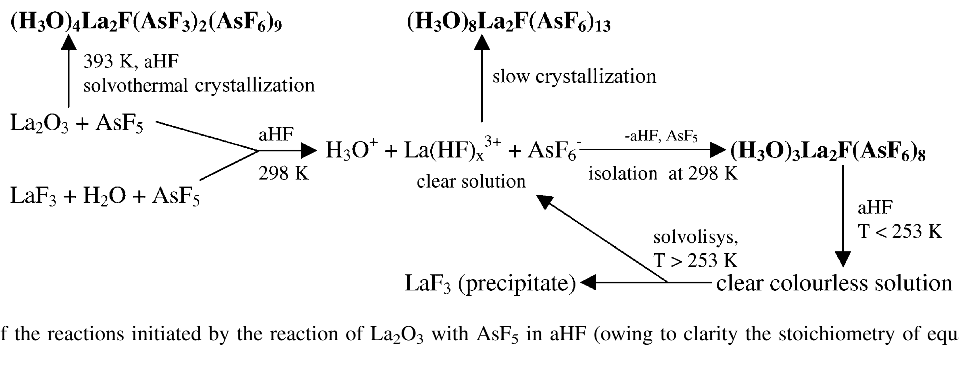

Fig. 2. Scheme of the reactions initiated by the reaction of La_2O_3 with AsF_5 in aHF (owing to clarity the stoichiometry of equations is omitted).

Table 2
Crystal data and structure refinement for $(H_3O)_8La_2F(AsF_6)_{13}$ and $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$

Empirical formula	$(H_3O)_8La_2F(AsF_6)_{13}$	$(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$
Formula weight	2904.97	2337.04
Temperature (K)	293	293
Wavelength (pm)	71.07	71.07
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
Unit cell dimensions		
a (pm)	1079.3(3)	1064.8(3)
b (pm)	2859.0(7)	1073.3(4)
c (pm)	1068.0(3)	1213.9(3)
α (°)	90	75.53(2)
β (°)	109.310(8)	64.79(2)
γ (°)	90	70.07(2)
Volume (nm^3)	3.1101(15)	1.1711(6)
Z	2	1
Density (calculated) (Mg/m^3)	3.102	3.314
Absorption coefficient (mm^{-1})	8.489	9.777
Theta range for data collection (°)	1.42–27.99	2.03–30.00
Index ranges	$-12 \leq h \leq 14$, $-28 \leq k \leq 38$,$-8 \leq l \leq 14$	$-14 \leq h \leq 14$, $-17 \leq k \leq 17$, $-17 \leq l \leq 17$
Reflections collected	12219	14136
Independent reflections	7136 ($R_{int} = 0.026$)	6819 ($R_{int} = 0.054$)
Absorption correction	Multi-scan	ψ-scan
Maximum and minimum transmission	0.183, 0.122	0.231, 0.106
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5308/0/464	5374/0/356
Goodness-of-fit on F^2	1.143	1.081
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0546$, $wR2 = 0.1166$	$R1 = 0.0417$, $wR2 = 0.1023$
R indices (all data)	$R1 = 0.0773$, $wR2 = 0.1291$	$R1 = 0.0748$, $wR2 = 0.1085$
Extinction coefficient	0.00071(9)	0.0022(2)
Largest diffraction peak and hole (electron nm^{-3})	2211, −2159	1354, −1491

trans-bridging AsF_6 anion (As1), finally leading to a *trans* zig-zag chain of alternating La_2F and AsF_6 units. The chains are running along [1 0 0] direction, respective view down the *a*-axis exhibits the typical rod packing (Fig. 4). Four H_3O^+ cations and one non-coordinating AsF_6^- anion (As7) per La atom supplement the chains in formation of the entire structure. Lanthanum is nine coordinated with fluorine atoms F31, F41, F51, and F32′, F52′, F61 at the apexes of a trigonal prism (Fig. 5). Three additional ligands F1, F11 and F21 are capping the rectangular faces of the prism.[2]

The structure of $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$ is closely related to the structure of $(H_3O)_8La_2F(AsF_6)_{13}$. It crystallises in the triclinic space group $P\bar{1}$ (no. 2) with one formula unit within the cell. Pertinent crystallographic data are given in Table 2, and selected interatomic distances and bond angles in Table 4. The labelling scheme is given in Fig. 3b. As emphasised in Fig. 3b, the main difference within the basic structural unit, as compared to $(H_3O)_8La_2F(AsF_6)_{13}$, is represented by the replacement of one particular AsF_6 unit (As2 and As2′) by an AsF_3 molecule. Furtheron, there are no non-coordinating AsF_6 units incorporated in the structure. Accordingly, only two H_3O^+ cations per La atom are needed to compensate negative charges (Fig. 6). The coordination of La is similar as in the case of $(H_3O)_8La_2F(AsF_6)_{13}$ with slight differences in F–La–F angles caused by different steric activity of AsF_3 unit compared to AsF_6 unit in $(H_3O)_8La_2F(AsF_6)_{13}$.

As mentioned above, both structures are characterised by very similar chain-like arrangement. A single fluoride ion (F1) is located on a centre of symmetry. The La–F1 distances are almost identical in both structures (222.03(7) and 222.36(7) pm, respectively). This particular distance is considerably shorter than all other La–F distances within these two structures. It is also shorter than La–F distances in LaF_3 (242–264 pm) [15] or those in other lanthanum hexafluoroarsenates like in $La(HF)_2(AsF_6)_3$ (243.3–282.6 pm) [16]. On the other hand, all other eight distances in the coordination sphere of La are comparable to these compounds, 240.7–272.7 pm in the case of $(H_3O)_8La_2F(AsF_6)_{13}$, and 242.5–274.0 pm for $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$. La–F–La bridges were also found in recently described structures of $La_2F(AuF_4)_5$ [17], and $LaFSnF_6$ [18]. In $La_2F(AuF_4)_5$, bridging distance is 229.5(8) pm and the bridging angle is 160°. In the structures of $(H_3O)_8La_2F(AsF_6)_{13}$ and $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$, the La–F–La linkages are bridged by four AsF_6 units, while in $La_2F(AuF_4)_5$, only three AuF_4 units are in bridging position. In contrast, however, the AuF_4 units

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[2] Preliminary results about $(H_3O)_8La_2F(AsF_6)_{13}$ and $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$ were presented at *The International Conference on Fluorine Chemistry'99* in Yokohama [13] and later published in special issue of *Journal of Fluorine Chemistry* [14], where some figures of the crystal structures are already available.

Table 3
Selected interatomic distances (pm) and bond angles (°) for $(H_3O)_8La_2F(AsF_6)_{13}$[a]

La(1)–F(1)	222.03(7)
La(1)–F(11)	248.4(5)
La(1)–F(21)	247.6(6)
La(1)–F(31)	272.7(7)
La(1)–F(32)′	251.6(6)
As(1)–F(11)	175.9(5)
As(2)–F(21)	176.0(6)
As(3)–F(31)	174.5(7)
As(3)′–F(32)′	175.9(6)
As(4)–F(41)	177.2(6)
As(5)–F(51)	173.9(6)
As(5)′–F(52)′	173.8(6)
As(6)–F(61)	171.0(8)
La(1)–F(41)	241.8(6)
La(1)–F(51)	254.2(6)
La(1)–F(52)′	260.9(6)
La(1)–F(61)	240.7(9)
La(1)–F(1)–La(1)′	180
La(1)–F(11)–As(1)	166.6(3)
La(1)–F(21)–As(2)	167.1(4)
La(1)–F(31)–As(3)	157.8(3)
La(1)–F(32)′–As(3)′	156.4(3)
La(1)–F(41)–As(4)	162.2(4)
La(1)–F(51)–As(5)	149.2(3)
La(1)–F(52)′–As(5)′	149.8(4)
La(1)–F(61)–As(6)	154.3(9)
F(51)–As(5)–F(52)	89.2(3)
F(31)–As(3)–F(32)	87.8(3)

[a] Symmetry operations used to generate equivalent atoms: *-x*, *-y*, *-z*.

Table 4
Selected interatomic distances (pm) and bond angles (°) for $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$[a]

La(1)–F(1)	222.36(7)
La(1)–F(11)	245.4(5)
La(1)–F(21)	249.8(5)
La(1)–F(31)	274.0(6)
La(1)–F(32)′	253.6(5)
As(1)–F(11)	176.2(5)
As(3)–F(31)	174.5(5)
As(3)′–F(32)′	176.3(5)
As(4)–F(41)	178.2(5)
As(5)–F(51)	174.9(6)
As(5)′–F(52)′	176.9(5)
As(6)–F(61)	173.0(7)
As(2)–F(21)	177.6(5)
As(2)–F(25)	168.2(6)
As(2)–F(26)	168.3(7)
La(1)–F(41)	242.5(5)
La(1)–F(51)	254.0(6)
La(1)–F(52)′	258.6(5)
La(1)–F(61)	250.3(9)
La(1)–F(1)–La(1)′	180
La(1)–F(11)–As(1)	161.9(3)
La(1)–F(21)–As(2)	167.0(3)
La(1)–F(31)–As(3)	158.9(3)
La(1)–F(32)′–As(3)′	152.2(3)
La(1)–F(41)–As(4)	159.3(3)
La(1)–F(51)–As(5)	148.7(3)
La(1)–F(52)′–As(5)′	147.4(3)
La(1)–F(61)–As(6)	131.6(7)
F(51)–As(5)–F(52)	88.7(3)
F(31)–As(3)–F(32)	87.4(2)

[a] Symmetry operations used to generate equivalent atoms: *-x*, *-y*, *-z*.

form a three-dimensional network via additional connectivity. Flexibility of such bridges is indicated in the case of $LaFSnF_6$ [18], where the distance La–F of 230.7 pm is comparable to La–F distance in $La_2F(AuF_4)_5$ while the bridging angle La–F–La is much smaller (143.8°).

Comparison of bond distances and angles in AsF_6 units in $(H_3O)_8La_2F(AsF_6)_{13}$ show that they are distorted, due to their different functions in the structure. There are four different kinds of AsF_6 units: AsF_6 units (As3, As5) are bridging two La atoms, AsF_6 units (As1) are connecting La_2F units into chain, AsF_6 units (As2, As4, As6) are connected only to one La atom and are without further connections, and AsF_6 units (As7) which lie between the chains without any connections. As expected, distances between As and bridging F atoms in all three groups are longer (171.0(8)–177.2(6) pm) than respective distances to terminal fluorines (163.7(8)–170.7(8) pm).

In the case of $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$, there are only three different kinds of AsF_6 units: AsF_6 units (As3, As5) are bridging two La atoms, AsF_6 units (As1) are connecting La_2F units into chain, and AsF_6 units (As4, As6) are connected only to one La atom and are without further connections. Distances between As atoms and bridging F atoms in all three groups are in the range of 173.0(7)–178.2(5) pm. Distances to terminal fluorines are in the range of 162.7(8)–170.9(8) pm.

Non-bridging distances in AsF_3 unit are 168.2(6) and 168.3(7) pm what is close to distances in AsF_3 (169.9–172.1 pm) [19] and comparable to terminal distances in some other compounds, e.g. in $M(AsF_6)_2 \cdot 2AsF_3$, (M = Fe, Co, Ni), (169.1(4) pm for Ni compound, 168.8(4) pm for Co compound and 169.3(4) pm for Fe compound) [20]. The dramatic change of bridging distance in AsF_3 (177.6(5) pm) shows that the bonding is rather strong. In accordance with this is also the distance $La{-}F(21)AsF_2 = 249.8(5)$ pm which is in the range of distances to $La{-}FAsF_5$. This shows that the bonding of AsF_3 units is not weaker than the bonding of AsF_6 units.

3. Concluding remarks

Results of reactions in the system Ln_2O_3–AsF_5–aHF indicated that a variety of phases are formed. They can be written with general formula $(H_3O)_xLn_yF_z(AsF_6)_{x+3y-z}$. At the moment, only $(H_3O)_3La_2F(AsF_6)_8$, $(H_3O)_8La_2F(AsF_6)_{13}$, and $(H_3O)_3Ln_2F_3(AsF_6)_6$ (Ln = Nd, Sm) have been isolated. Additionally AsF_3 can be bonded to these

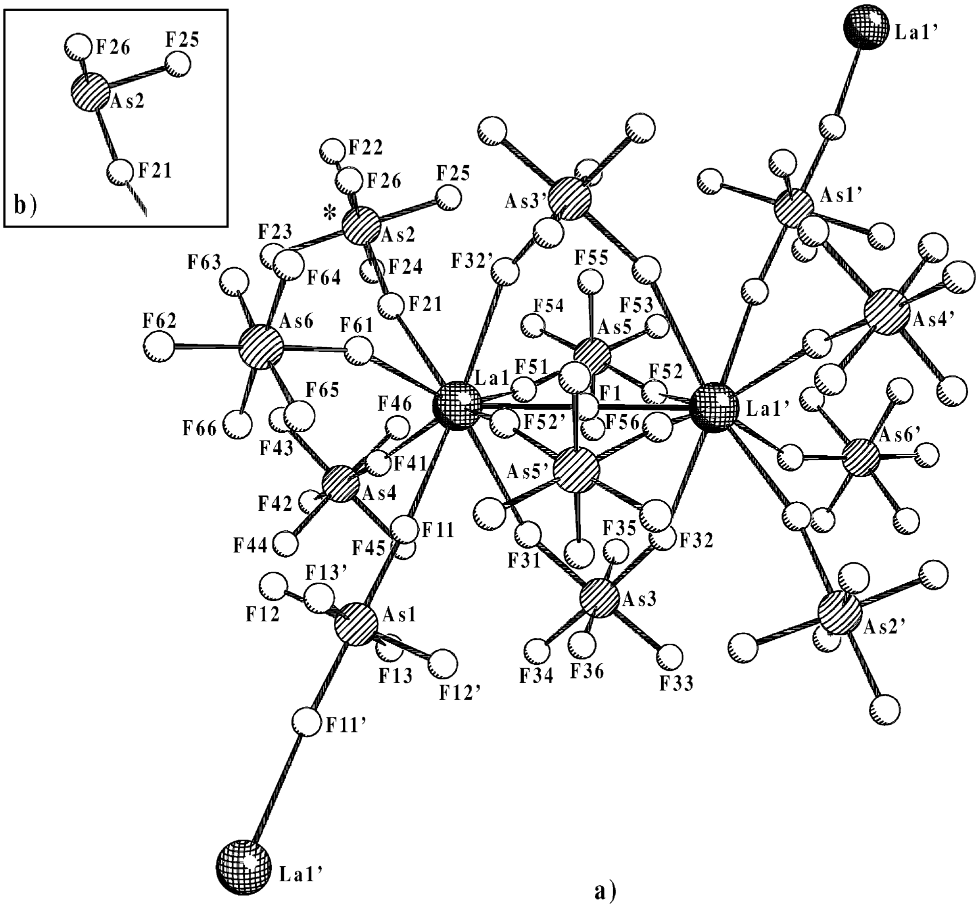

Fig. 3. Basic structural unit in (a) $(H_3O)_8La_2F(AsF_6)_{13}$ and (b) $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$ (two AsF_6 units marked with asterisk are replaced by AsF_3 molecules) showing the labelling scheme.

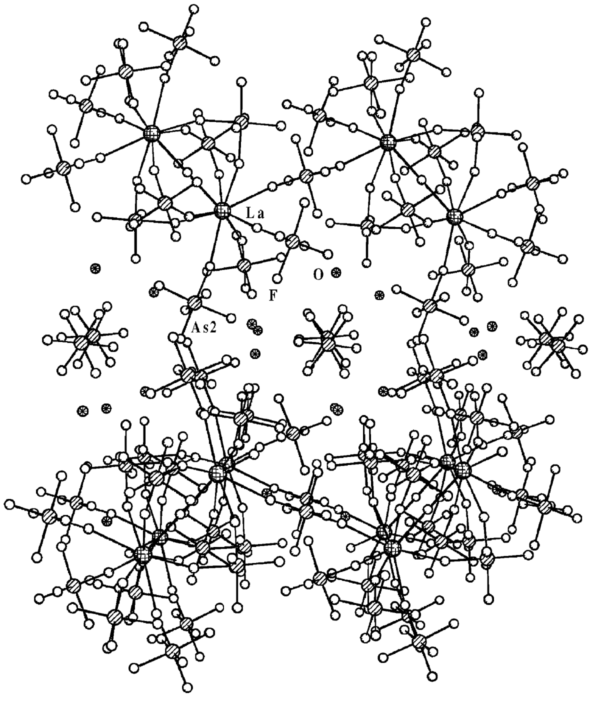

Fig. 4. Formation of chains in the crystal structure of the $(H_3O)_8La_2F(AsF_6)_{13}$.

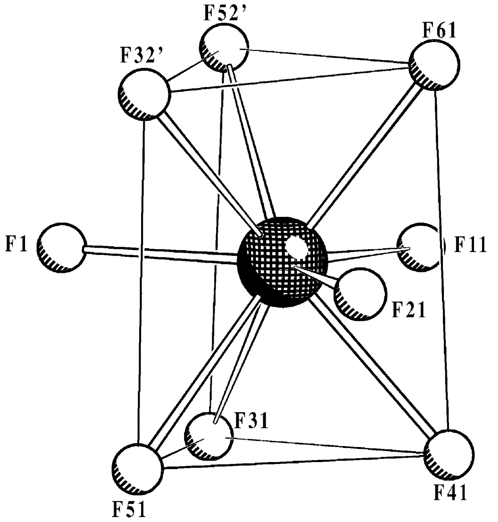

Fig. 5. Coordination of La atom in $(H_3O)_8La_2F(AsF_6)_{13}$.

products yielding a new type of compounds, e.g. $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$. In these systems, the preparation of pure compounds and their characterisation only by mass balance, chemical analysis and spectroscopic methods is almost impossible. The most prospective way to elucidate these

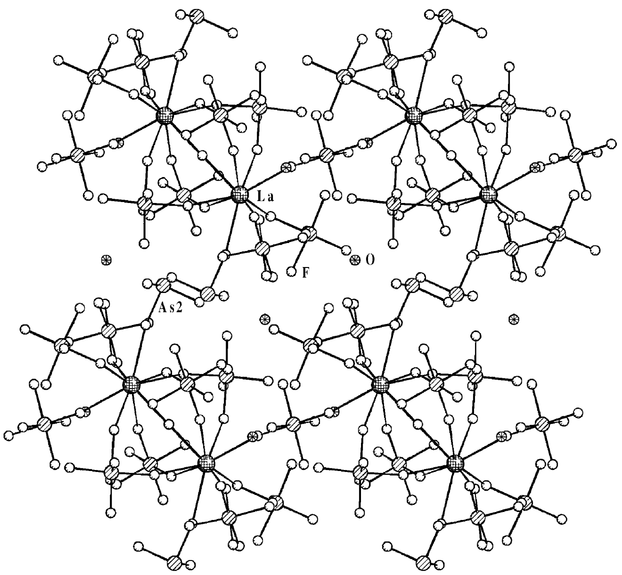

Fig. 6. Formation of chains in the crystal structure of the $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$.

systems is the preparation of single crystals of different phases. This work is now in progress.

4. Experimental

4.1. Apparatus and reagents

A nickel vacuum line with a mechanical pump, a mercury diffusion pump, and soda lime scrubbers for removal of volatile fluorides were used. The part of the vacuum line used for transfer of aHF and AsF_5 was entirely made from Teflon, FEP or PFA in order to diminish corrosion and to avoid associated formation of hydrogen. This part of the line was equipped with a Monel Helicoid pressure gauge (0–1500 Torr (±0.3%), Bristol Babcock Inc.) connected via a Teflon valve. PFA reaction vessels (16 mm i.d. × 19 mm o.d.) equipped with Teflon valves, and Teflon-coated mixing bars were used in all experiments. La_2O_3 (Koch Light Laboratories Ltd., 99.9 (REO)), Nd_2O_3 (Koch Light Laboratories Ltd., 99.5 (REO)) and Sm_2O_3 (Ventron, Alfa Products, 99.9 (REO)) were heated prior use at 1373 K for 2 h in the air to remove adsorbed H_2O and CO_2 [21]. Chemical analyses after the heating gave the following metal content: La_2O_3: found: 85.4, calcd.: 85.27; Nd_2O_3: found: 85.8, calcd.: 85.73; Sm_2O_3: found: 86.1, calcd.: 86.23. Gd_2O_3 (Ventron Alfa Products, 99.9 (REO)), Dy_2O_3 (Rare Earth Products Ltd., 99.9 (REO)), Ho_2O_3 (Rare Earth Products Ltd., 99.9 (REO)) and Tm_2O_3 (Ventron Alfa Products, 99.9 (REO)) were used as supplied. Chemical analyses of metal content: Gd_2O_3: found: 86.6, calcd.: 86.76; Dy_2O_3: found: 87.1; calcd.: 87.13; Ho_2O_3: found: 87.2, calcd: 87.30; Tm_2O_3: found: 87.3, calcd.: 87.56. LaF_3 (Ventron Alfa Products, 99.9 (REO)) was used as supplied. Chemical analysis of LaF_3 showed: La, found: 70.4, calcd.: 70.91; F, found: 28.3, calcd.: 29.09. All lanthanoid compounds used as starting materials were also checked by XRD methods. AsF_5 was synthesised by pressure fluorination of As_2O_3 (Johnson Matthey GmbH) as previously described for PF_5 [22]. Anhydrous hydrogen fluoride (aHF) (Praxair, 99.9) was treated with K_2NiF_6 for several days prior to use.

4.2. Instrumentation

Non-volatile materials and single crystals were manipulated in a glove box (MBraun). The residual of water in the atmosphere within the glove box never exceeded 1 ppm. XRD patterns were obtained by the Debye–Scherrer method with Straumanis loading using Cu Kα radiation. Powder samples and selected single crystals were enclosed in 0.3 mm thin-walled quartz glass capillaries.

4.3. Chemical analysis

Lanthanoid ions were determined by complexometric titration; [23–25] total fluoride ion content was determined with an ion selective electrode [26,27]; AsF_6^- species were determined gravimetrically as insoluble tetraphenylarsonium salt [28,29]; arsenic was determined by the ICP method [30]; and the content of H_2O in the H_3O^+ salts was determined by dissolving a known amount in methanol before titrating evolved H_2O with Karl Fischer reagent. The water content determined this way is systematically lower than the calculated one. This is due to the fact that all samples incompletely dissolve in methanol. However, up to now we have not been able to find a better organic solvent.

4.4. Reactions of Ln_2O_3 with aHF ($Ln = La, Sm, Gd, Dy$)

Onto about 0.200 g of particular Ln_2O_3 (Ln = La, Sm, Gd, Dy), about 5 ml aHF was condensed and the mixture was stirred for 4 days at room temperature (Table 5). Weight balance, chemical analysis and XRD patterns of the insoluble reaction products showed in the case of La and Sm total transformation to corresponding LnF_3. In the case of Gd and Dy, only about 15% LnF_3 was isolated after 4 days. Therefore, reactions were continued for additional 4 weeks, after which period another 15% of Gd_2O_3 and Dy_2O_3 had been transformed to respective trifluorides.

4.5. Synthesis of $(H_3O)_3La_2F(AsF_6)_8$

In a glove box, 0.775 g (2.38 mmol) La_2O_3 was loaded into a PFA reaction vessel. Then aHF (∼6 ml) was condensed onto La_2O_3 and excess AsF_5 (La_2O_3: AsF_5 = 1:12) was added, both at 77 K. While warming to room temperature the solid phase immediately dissolved and a clear colourless solution was obtained. The solution was stirred for few hours before it was cooled again to 77 K. Pressure measurement at this temperature proved that no oxygen had

Table 5
Reactions between Ln_2O_3 and aHF (Ln = La, Sm, Gd, Dy) at room temperature

Compound	Ln_2O_3 (g)	Ln_2O_3 (mmol)	LnF_3		Chemical analysis			
			Calculated (g)	Obtained (g)	Calculated for LnF_3 (g)		Obtained for products (g)	
					Ln (%)	F (%)	Ln (%)	F (%)
La_2O_3	0.2064	0.63	0.2468	0.2471	70.91	29.09	70.6	29.0
Sm_2O_3	0.2158	0.62	0.2571	0.2752	72.50	27.50	72.2	27.5
Gd_2O_3	0.2286	0.63	0.2704	0.2355	73.40	26.60	–	4.8
Dy_2O_3	0.2358	0.63	0.2766	0.2425	74.03	25.97	–	4.4

been evolved. Subsequently, aHF and AsF_5 were pumped away at 293 K. Before the solvent was finally removed, a very dense liquid with low vapour pressure was obtained from which suddenly a solid product precipitated. During pumping, weight loss was carefully recorded, and pumping was continued at 293 K until the product was loosing <8 mg ($\sim$0.05 mmol) of AsF_5 per mmol h. This was reached after several hours, at which point the product was without vapour pressure at 273 K. Then 4.438 g of a white solid were isolated, corresponding to 2.38 mmol $(H_3O)_3La_2F(AsF_6)_8$. Chemical analysis: found (calcd.): H_2O, 2.7 (2.90); La, 14.6 (14.90); AsF_6, 80.9 (81.03); F, 49.8 (49.91). XRD pattern of the compound with *d*-values and intensities is in Table 7.

4.6. Reactions of Ln_2O_3 with AsF_5 in aHF, Ln = Nd, Sm, Gd, Dy, Ho, Tm

Reactions of Ln_2O_3 (Ln = Nd, Sm, Gd, Dy, Ho, Tm) with AsF_5 in aHF were carried out similarly as described for La_2O_3. Reaction conditions are shown in Table 6. In all cases, clear solutions with typical colour of the particular Ln^{3+} element were obtained. Reaction time depended on excess of AsF_5 used, and on the position of the element in the lanthanoid series. Ln_2O_3 at the end of the series and, therefore, with lower basicity react slower, but all reactions were finished within 30 min. Pressure measurements at 77 K showed that there were not any volatiles present at this temperature. Isolation of products always proceeded through a step of highly viscous solution, an indication of very large solubility in aHF. In the case of Nd, the weight of isolated product was 4.022 g; calculated weight for $(H_3O)_3Nd_2F_3(AsF_6)_6$ is 4.084 g. Chemical analysis of the product showed: Nd (19.3), F (46.9), As (29.5), H_2O (2.7); calcd. for $(H_3O)_3Nd_2F_3(AsF_6)_6$: Nd (18.78), F (48.24), As (29.26), H_2O (3.52). In the case of Sm, the pumping was carried out at 273 K (Fig. 1). The weight of isolated product was 3.217 g; calculated weight for $(H_3O)_3Sm_2F_3(AsF_6)_6$ is 3.282 g. In the case of Gd, Dy, Ho and Tm, reaction products were isolated at room temperature. Weight and chemical analyses of the products are given in Table 1. All these products turned out to be amorphous in XRD experiments.

Table 6
Starting conditions for reactions between Ln_2O_3 and AsF_5 in aHF (Ln = Nd, Sm, Gd, Dy, Ho, Tm)

Ln_2O_3	Ln_2O_3 (g)	Ln_2O_3 (mmol)	AsF_5 (g)	AsF_5 (mmol)	aHF (ml)
Nd_2O_3	0.8948	2.66	7.65	45.03	6
Sm_2O_3	0.7405	2.12	5.70	33.55	9
Gd_2O_3	0.9696	2.67	7.10	41.79	7
Dy_2O_3	0.6999	1.88	4.99	29.37	7
Ho_2O_3	0.7279	1.93	5.32	31.31	7
Tm_2O_3	0.9315	2.42	8.60	50.62	7

4.7. Titration of La_2O_3 with AsF_5 in aHF

In additional experiments at 293 K, the exact amount of AsF_5 required for complete dissolution of La_2O_3 in excess aHF was determined. Onto La_2O_3 (0.755 g, 2.38 mmol), 5 ml of aHF was condensed at 77 K. Small portions of AsF_5 gas, monitored by measuring pressure and weight, were added stepwise to the suspension of La_2O_3 (which quickly became a suspension of La_2O_3–LaF_3–aHF mixture, see Section 4). In the first step, 14.79 mmol of AsF_5 was added, corresponding to molar ratio La_2O_3:AsF_5 = 1:6.22. After 3 days of stirring, there was still quite large amount of solid in the reaction mixture. Then the next two metering of AsF_5 which corresponded to the total molar ratio La_2O_3:AsF_5 = 1:7.95 (reaction time was 3 h) and La_2O_3:AsF_5 = 1:8.43 (reaction time was 24 h) were performed. After these two additions, the small amount of undissolved material was still observed. When the last portion of AsF_5 (1.37 mmol) was added and the molar ratio La_2O_3:AsF_5 = 1:9 was reached within 1 h all remaining solid was dissolved and clear solution was obtained.

4.8. Solvolysis of $(H_3O)_3La_2F(AsF_6)_8$ in aHF

The reaction was carried out in a double T-shaped reaction vessel. Then 5 ml of aHF was condensed onto 1.914 g (1.03 mmol) of $(H_3O)_3La_2F(AsF_6)_8$ at 77 K. After warming up to 253 K, a clear solution was obtained, which remained completely clear till 259 K. Above this temperature, precipitation started to occur, the amount of precipitate increasing with rising temperature. Finally, the sample was left at room temperature for 2 days. After separating precipitate and solution by decantation, XRD pattern of the precipitate

Table 7
X-ray powder diffraction (XRD) data for $(H_3O)_3La_2F(AsF_6)_8$[a]

	d (pm)	2θ	I/I_0
1	1466.286	6.023	6.47
2	1192.035	7.410	17.43
3	1155.911	7.642	13.44
4	1079.770	8.182	4.95
5	897.211	9.850	100.00
6	862.292	10.250	18.26
7	810.046	10.913	30.96
8	766.965	11.528	5.26
9	707.793	12.496	10.90
10	678.390	13.040	1.92
11	648.064	13.653	12.81
12	612.710	14.445	12.06
13	595.080	14.875	3.44
14	574.362	15.415	4.35
15	540.518	16.386	7.68
16	512.607	17.285	28.69
17	484.506	18.296	15.43
18	475.306	18.653	4.95
19	462.324	19.182	18.19
20	446.187	19.883	21.71
21	429.935	20.642	23.00
22	422.787	20.995	20.76
23	415.335	21.376	31.64
24	409.660	21.676	12.23
25	401.334	22.131	21.43
26	392.300	22.648	26.77
27	388.644	22.864	26.17
28	383.289	23.187	73.44
29	378.082	23.511	92.23
30	369.385	24.073	70.83
31	362.001	24.572	53.68
32	351.766	25.298	97.60
33	345.402	25.772	46.86
34	341.111	26.102	33.44
35	338.361	26.312	32.53
36	329.725	27.020	25.09
37	323.995	27.508	10.92
38	317.448	28.086	21.72
39	303.064	29.449	7.68
40	295.652	30.204	5.86
41	290.583	30.744	6.17
42	286.656	31.176	6.47
43	283.782	31.500	7.07
44	278.210	32.148	4.65
45	272.862	32.795	3.44
46	269.414	33.227	3.44
47	263.594	33.983	3.44
48	258.810	34.631	6.47
49	255.721	35.062	12.23
50	251.967	35.602	5.56
51	250.497	35.818	4.65
52	246.195	36.466	5.26
53	241.369	37.222	9.80
54	235.449	38.193	5.86
55	232.916	38.625	6.47
56	228.618	39.381	4.04
57	225.651	39.920	6.47
58	222.196	40.568	3.44
59	219.955	41.000	3.44
60	216.147	41.756	7.98
61	214.034	42.188	5.86
62	212.478	42.511	7.07
63	210.441	42.943	9.20
64	206.858	43.725	24.17
65	203.749	44.427	16.52
66	200.856	45.102	4.95
67	198.605	45.642	7.98
68	195.976	46.290	9.20
69	195.116	46.506	10.11
70	193.546	46.905	25.55
71	192.398	47.205	24.28
72	190.532	47.693	6.17
73	189.322	48.017	7.07
74	186.631	48.754	14.88
75	185.472	49.079	18.46
76	184.269	49.420	11.01
77	183.145	49.744	13.74
78	182.036	50.068	11.92
79	179.862	50.716	11.01
80	177.052	51.580	7.07
81	175.666	52.017	12.56
82	173.673	52.659	5.56
83	170.754	53.631	5.26
84	168.250	54.494	4.95
85	166.126	55.250	4.65
86	162.056	56.761	4.65
87	159.831	57.625	4.65
88	158.476	58.165	5.86
89	157.147	58.705	3.14

[a] XRD pattern of $(H_3O)_3La_2F(AsF_6)_8$ was taken by Dr. H. Borrmann, Max-Planck Institut für Chemische Physik fester Stoffe, Dresden, Germany.

showed only the characteristic lines of LaF_3, while the solid isolated from the solution showed only lines of $(H_3O)_3La_2F(AsF_6)_8$.

4.9. Preparation of single crystals of $(H_3O)_8La_2F(AsF_6)_{13}$

This experiment was carried out in a double T-shaped apparatus made of two PFA tubes (19 mm o.d. and 6 mm o.d.). About 0.500 g (0.27 mmol) $(H_3O)_3La_2F(AsF_6)_8$ was loaded inside the glove box into the wider tube. Later on aHF (~5 ml) was condensed at 77 K and the mixture was warmed up to room temperature. After solvolysis had taken place (see Section 4.8), the clear solution was poured into the narrower tube. The solvent was slowly evaporated from this solution by maintaining a temperature gradient of about 10 K between wider and narrower tube for 6 months. Colourless single crystals of $(H_3O)_8La_2F(AsF_6)_{13}$ were found among white powder material.

4.10. Reactions between LaF_3, H_2O and AsF_5 in aHF

LaF_3 and H_2O were loaded into the PFA reaction vessel before about 5 ml of aHF and excess AsF_5 were condensed on top at 77 K. The reaction mixture was allowed to warm up to room temperature and a clear solution was obtained within a few minutes. In a first reaction, H_2O and LaF_3

were used in molar ratio 3:2; H_2O (0.046 g, 2.55 mmol); LaF_3 (0.316 g, 1.61 mmol) and AsF_5 (1.600 g, 9.42 mmol). The XRD pattern of isolated compound showed only *d*-values of $(H_3O)_3La_2F(AsF_6)_8$ (Table 7). In a second reaction, molar ratio of H_2O:LaF_3 was 4:1; H_2O (0.124 g, 6.90 mmol); LaF_3 (0.320 g, 1.63 mmol) and AsF_5 (2.571 g, 15.13 mmol). The XRD pattern of isolated solid product showed a mixture of $(H_3O)_8La_2F(AsF_6)_8$ and H_3OAsF_6.

4.11. Preparation of single crystals of $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$

The reaction between La_2O_3 (0.150 g, 0.46 mmol), AsF_5 (0.200 g, 11.80 mmol) and aHF (0.040 g, 2.00 mmol) was carried out in a special stainless steel autoclave with a Teflon liner ($V = 6$ ml). After metering all reactants into the autoclave, it was heated to 393 K for 4 months. After cooling to ambient temperature all volatiles were pumped away. Colourless single crystals of $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$ were found among amorphous white powder.

4.12. Structural investigations

Crystals of $(H_3O)_8La_2F(AsF_6)_{13}$ as well as of $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$ are very sensitive even to traces of moisture. Therefore, they were selected in a glove box using a surgical microscope (Opton, $f = 300$ mm) and mounted into 0.3 mm quartz glass capillaries which were temporarily closed by Kel-F grease and later flame-sealed outside the glove box. Single-crystal data of $(H_3O)_8La_2F(AsF_6)_{13}$ were collected on Mercury CCD area detector coupled with a Rigaku AFC7S diffractometer and of $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$ on Rigaku AFC7S Four Circle diffractometer, both using monochromatised Mo Kα radiation. Date were processed using Rigaku Crystalclear software suite [31] and teXan for Windows program package [32]. Details of the diffraction experiments are given in Table 2. Both structures were solved using direct and successive Fourier difference methods. Although several crystals were investigated, it was not possible to clearly localise hydrogen atoms of the oxonium ions, main reasons being the fair quality and high sensitivity of all crystals as well-probable disorder of H_3O^+ cations. For all crystallographic calculations program systems WinGX [33] and SHELXL-97 [34] were used. Further details of the crystal-structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-411956, the name of the authors and citation of the paper.[3]

Acknowledgements

The authors gratefully acknowledge Prof. T.A. O'Donnell for helpful discussions on chemistry in superacids and B. Sedej for chemical analysis. Financial support from the Slovenian–German Joint Fund and the Ministry of Education, Science and Sport of the Republic of Slovenia is also acknowledged.

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[3] Crystal structures of $(H_3O)_8La_2F(AsF_6)_{13}$ and $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$ were first determined on our single crystals with the help of Dr. H. Borrmann, Max-Planck Institut für Chemische Physik fester Stoffe, Dresden, Germany. To obtain better data, the determination of crystal structures of $(H_3O)_8La_2F(AsF_6)_{13}$ and $(H_3O)_4La_2F(AsF_3)_2(AsF_6)_9$ was later repeated on new crystals. All crystallographic data presented in this paper are from new batch of crystals.

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