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Metal Coordinated HF−A Unique Case

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From stoichiometric amounts of LaF_3 and anhydrous hydrogen fluoride $La(HF)_2(AsF_6)_3$ was prepared under solvothermal conditions in AsF_5 above its critical temperature. The compound crystallizes in space group *Pnma* (No. 62) with $a = 1060.9(2)$ pm, $b = 1726.2(5)$ pm, $c = 770.0(2)$ pm, and $Z = 4$ at 293 K. The structure was determined from single-crystal data and shows 10 fluorine atoms connected to the La center. Two of these ligands are provided by HF molecules, a connectivity that was never observed before. All other fluorine ligands are provided by AsF_6 units which are bridging between La atoms. In this way infinite slabs are formed which are connected via hydrogen bonds only.

Introduction

Besides water, HF is one of the most generally useful solvents, although it is very corrosive and reacts with glass and other materials in conventional vacuum systems. Its particular properties make it an excellent solvent for a wide variety of compounds in inorganic and organic chemistry and, nowadays, is extensively used in biochemical research. Anhydrous HF (aHF) is very versatile as solvent for the generation and study of very strong oxidants but also for very strong reductants. Many fluorides of d and f transition metals are not very soluble in aHF, however, solubility is generally increased by addition of strong Lewis acids. It was shown that cations of d and f block metals are solvated by HF molecules within such solutions.[1a] In course of our ongoing efforts to prepare new compounds of the lanthanides with weakly coordinating fluoro anions, we isolated $La(HF)_2(AsF_6)_3$ as the first compound showing HF bonded to a metal center.

Table 1. Crystal Data and Structure Refinement

empirical formula	$La(HF)_2(AsF_6)_3$
fw	745.69
T	293 K
λ	71.073 pm
space group	*Pnma* (No. 62)
a	1060.9(2) pm
b	1726.2(5) pm
c	770.0(2) pm
V	1410.2(6) nm^3
Z	4
ρ_{calcd}	3.512 $g \cdot cm^{-3}$
μ	10.238 mm^{-1}
$R1(F_o)^a$	0.0226 (all data)
$wR2(F_o^2)^b$	0.0523 (all data)

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Final Positional and Displacement Parameters

atom	x	y	z	U_{eq} (pm^2)[a]
La	0.43971(3)	0.75	0.06436(3)	155.7(12)
F1	0.4004(3)	0.62462(18)	−0.0794(3)	389(7)
H1[b]	0.383(7)	0.591(4)	−0.073(8)	561(226)
As1	0.56153(5)	0.75	−0.38566(6)	200.9(16)
F2	0.4115(4)	0.75	−0.3005(5)	380(8)
F3	0.6110(3)	0.75	−0.1674(4)	347(8)
F4	0.7192(3)	0.75	−0.4570(4)	343(8)
F5	0.5113(4)	0.75	−0.5977(4)	443(10)
F6	0.5659(3)	0.65344(15)	−0.3845(3)	423(7)
As2	0.22952(4)	0.58873(2)	0.34659(4)	202.3(14)
F7	0.3211(3)	0.66586(15)	0.2602(3)	394(6)
F8	0.1781(3)	0.57115(16)	0.1443(3)	413(7)
F9	0.3500(3)	0.52705(18)	0.3236(3)	507(8)
F10	0.2742(3)	0.61510(18)	0.5464(3)	417(7)
F11	0.1057(3)	0.65812(14)	0.3643(3)	357(6)
F12	0.1290(3)	0.52033(15)	0.4306(3)	440(7)

[a] U_{eq} is defined as one-third of the trace of the $\mathbf{U}_{ij}$ tensors. [b] H1 was refined with isotropic displacement parameter only.

Experimental Section

Volatile materials were manipulated in a nickel vacuum line, solids in a drybox (MBraun, Garching, Germany).[2] For preparation of single crystals LaF_3 was used as purchased from Johnson Matthey, Alfa Products, 99.9% (REO) (chemical analysis of LaF_3: La, 70.4; F, 28.3. Calcd: La, 70.9; F, 29.1). A 509 mg (2.6 mmol) amount of LaF_3 was loaded in the drybox into a special nickel autoclave with a Teflon liner (V = 6 mL). At the vacuum system 106 mg (5.3 mmol) of aHF (Praxair, 99.9%, treated with K_2NiF_6 for several days prior to use) was condensed onto the LaF_3, and excess (17 mmol) AsF_5 was added, both at 77 K. AsF_5 had been prepared by fluorination of As_2O_3, a procedure previously described for PF_5.[3] (**Caution!** *aHF and AsF_5 should only be handled in a well-ventilated hood, and protective clothing should be worn at all times!*) The autoclave was heated to 393 K for 14 days. After all volatiles were pumped away, white single crystals were isolated, and selected ones were mounted in 0.3 mm thin-walled quartz glass capillaries. Single-crystal data were collected on a Stoe-IPDS diffractometer; further details are given in Table 1. The structure was solved using Patterson and Fourier difference methods. After refinement of all other atoms including anisotropic displacement parameters, the position of the hydrogen atom was localized in a difference map and finally refined without any restraints being applied (Table 2). The F−H interatomic distance shows the usual systematic shortening as observed by X-ray methods. Accordingly the associated hydrogen bond is longer than the distance between the nuclear centers. As detailed information is not available about the interplay of both bonding schemes for the hydrogen atom, no corrections were applied. For all crystal-

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(1) (a) O'Donnell, T. A. *Superacids and Acidic Melts as Inorganic Chemical Reaction Media*; VCH Publishers: New York, 1993. (b) Ibid., p 136.

(2) Borrmann, H.; Lutar, K.; Žemva, B. *Inorg. Chem.* **1997**, *36*, 880−882.

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Table 3. Selected Distances (pm) and Angles (deg)[a]

La−F1[b]	246.6(3)	As1−F2	172.2(4)
La−F2	282.6(4)	As1−F3	176.0(3)
La−F3	254.7(3)	As1−F4	176.0(3)
La−F4″	248.2(3)	As1−F5	171.8(3)
La−F5$^{\mathrm{V}}$	271.1(3)	As1−F6	166.7(3)
La−F7[b]	244.3(2)	As2−F7	177.7(2)
La−F11‴ [b]	243.3(2)	As2−F8	167.8(2)
F1−H1	61(7)	As2−F9	167.3(3)
		As2−F10	167.3(2)
F1−La−F1′	122.7(1)	As2−F11	178.3(2)
F7−La−F7′	73.0(1)	As2−F12	171.7(3)

[a] Symmetry codes used to generate equivalent atoms: ′, x, $^3/_2 - y$, z; ″, $-^1/_2 + x$, y, $-^1/_2 - z$; ‴, $^1/_2 + x$, y, $^1/_2 - z$; $^{\mathrm{V}}$, x, y, $1 + z$. [b] Due to the mirror symmetry the coordination of La is completed by one additional ligand of types F1, F7, and F11, respectively.

lographic calculations the program systems SHELXTL-Plus[4] and SHELXL-97[5] were used.

Discussion

Recently we prepared a new family of compounds synthesized from rare earth trifluorides and arsenic pentafluoride in aHF. Based on their characterization by gravimetry and chemical analysis three different types of compounds were isolated at 298 K: $La(AsF_6)_3$, $LnF(AsF_6)_2$ (Ln = Ce to Er and Y), and $Ln_2F_3(AsF_6)_3$ (Ln = Tm, Yb, Lu).[6] Although we tried very hard to grow single crystals from respective solutions, we always ended up with amorphous powders. Therefore we decided to use our recent experience with solvothermal reaction conditions.[7] As the basicity of LnF_3 decreases along the lanthanide series, LaF_3 as the strongest base with the largest Ln^{3+} ion seemed to be most promising in forming a stable compound. As solvent we used AsF_5 slightly above its critical temperature[7] adding stoichiometric amounts of aHF. This approach proved immediately successful as well-developed single crystals were isolated. The X-ray structure determination revealed the composition $La(HF)_2(AsF_6)_3$ for the selected colorless crystal, its composition reflecting precisely the La/HF ratio of the reaction mixture. Results of the structure determination are listed in Tables 1−3, the basic structural unit with the labeling scheme is depicted in Figure 1. As the compound crystallizes in space group *Pnma* with $Z = 4$, the La atom had to be placed on a center of symmetry or on a mirror plane. The latter choice proved to be correct in course of the structure refinement. The polyhedron about the metal center is basically a tetracapped trigonal prism, whose triangular faces are formed by two fluorine ligands (F7, F11) provided by AsF_6 units and one by HF molecules. All rectangular faces of the prism are capped by fluorine ligands who are like the La ion within the crystallographic mirror plane. However, while F4 and F5 type ligands provide common apexes with AsF_6 octahedra, F2 and F3 provide a common edge, respectively. This way coordination number 10 is finally achieved for the La atom. As all four fluorine atoms capping are bonded to As1 type atoms which are also within the mirror plane, an infinite net is formed, while nonbridging F6 type atoms complete the octahedron around As1. Although the As1−F6 distance is typical for such an arrangement and considerably shorter than those to bridging fluorine atoms, the latter again split into two groups. As1−(F2,F5) are significantly shorter than As1−(F3,F4), however, this difference is balanced by respective distances to the La atom as La−(F2,F5) are considerably longer than La−(F3,F4). The structure is completed by AsF_6 units of type As2 bridging all La−La distances within the plane above as well as below the mirror plane. The bridging fluorine atoms F7 and F11 are in cis-arrangement with As−F and La−F bond distances very similar to those for F3 and F4, respectively. In contrast to the octahedron designated As1, those labeled As2 exhibit four instead of two nonbridging F ligands. However, As2−F12 is considerably longer than respective distances for all other nonbridging F atoms. This elongation is due to hydrogen bonding to an HF molecule in the next slab. With the distance F12−H1 at 192(7) pm and the angle F12−H1−F1 at 166(9)°, the hydrogen bonding has to be quite strong as these values are very similar to those in crystalline HF.[8] Another indication of the hydrogen bonding is the angle between the two HF molecules (F1−La−F1′) opened up as compared to other ligands in the triangular faces of the prism about La. In turn this leads to one triangular face being tilted by 32° with respect to the other one. However, the most remarkable feature of this particular structure is definitely the HF molecules connected to a metal ion. To our knowledge this is an unprecedented bonding situation, while hydrogen bonding to fluoride ions is well established.[9,10] Although, HF is certainly coordinating to metal centers in respective solutions, attempts to isolate such species had failed so far,[1b] probably because HF is quite a weak ligand. Keeping this in mind it is rather surprising that the F(H)−La distance is equal to most other La−F bonds in the present structure, but also to those in LaF_3.[11] The weakness of HF coordination as well as the strong preference of hydrogen bonding to metal-coordinated fluorine was independently approved even very recently.[12,13] In view of the vast number of

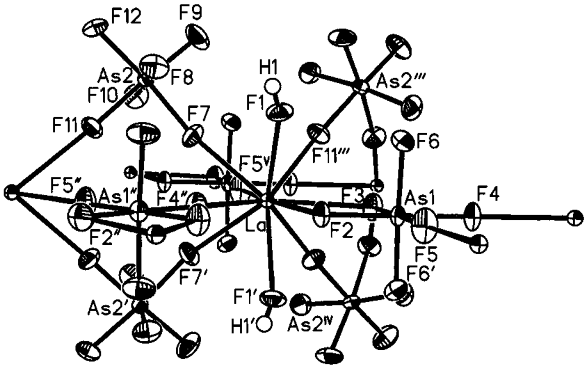

Figure 1. Part of a slab in the structure of $La(HF)_2(AsF_6)_3$ showing the coordination of the La atom with further connectivity and the horizontal mirror plane. The ellipsoids are drawn at the 40% probability level, and the H atoms at arbitrary size.

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(10) **Note Added in Proofs**: During editorial processing of our paper we learned about an earlier paper describing a Nb complex in which HF connectivity was observed as part of HF_2^- ions bridging two Nb atoms: Roesky, H. W.; Sotoodeh, M.; Xu, Y. M.; Schrumpf, F.; Noltemeyer, M. *Z. Anorg. Allg. Chem.* **1990**, *580*, 131−138.

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systems binary fluoride/Lewis acid studied in aHF,[14] it will be interesting to watch out for exciting new compounds involving HF. Currently it seems difficult to predict another system which promises another example combining well-established hydrogen bonding of HF with its newly observed coordination to a metal ion. The importance of our different synthetic approach under solvothermal conditions is also not yet clear.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, is available on the Internet only. Access information is given on any current masthead page.

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