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SCIENCE DIRECT
Solid State Sciences 8 (2006) 927–931
Solid State Sciences
www.elsevier.com/locate/ssscie

Barium trihydrogen tetrafluoride of the composition $Ba(H_3F_4)_2$: The first example of homoleptic HF metal environment

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Received 9 February 2006; accepted 21 February 2006

Available online 2 May 2006

Dedicated to Prof. Dr. Reint Eujen on the occasion of his 60th birthday

Abstract

Single crystals of the composition $Ba(H_3F_4)_2$ were obtained from an anhydrous hydrogen fluoride (aHF) solution of BaF_2, in the presence of XeF_2 and excessive PF_5. The compound crystallizes in a hexagonal $P\bar{6}2c$ space group with $a = 7.7756(12)$ Å, $c = 12.650(3)$ Å, $V = 662.4(2)$ Å^3 and $Z = 4$. The coordination sphere of barium atom consists of twelve fluorine atoms from HF molecules forming regular icosahedra. Metal and fluorine atoms form infinite three-dimensional network. HF molecules are bonded via F^- anions to $H_3F_4^-$ anions. The $Ba(H_3F_4)_2$ compound represents the first known example of homoleptic HF environment of the metal cation.

Keywords: Poly(hydrogen fluorides); Hydrogen bond; Crystal structure; Barium fluoride

1. Introduction

Hydrogen fluoride can be added in excess to many bases, proton acceptors as well as fluoride ion donors, to yield compounds with H_nF_{n+1} anions, formed by strong F(H)···F hydrogen bonds. The hydrogen difluoride anion ($n = 1$) and the series of compounds containing this anion were well characterized by several examples and by various methods. The compounds with $n > 1$ are usually described as poly(hydrogen fluorides) [1,2]. The existence of barium fluoride adduct with HF of the composition $BaF_2{\cdot}5.95HF$ was reported more than forty years ago [3]. Also the structure of non-stable $BaF_2{\cdot}HF$ (or $BaF(HF_2)$) compound has been described [4]. The existence of different poly-hydrogen-fluoride anions, such as chair-like $H_3F_4^-$ in $KF{\cdot}2.5HF$ and trigonal $H_3F_4^-$ in $KF{\cdot}3HF$ [1], $H_2F_3^-$ in $KF{\cdot}2HF$ and $H_4F_5^-$ in $KF{\cdot}4HF$ adduct [5], have been proved by X-ray crystal structure investigations.

In the recent years we have synthesized compounds with polyhydrogen anions bonded as a ligand to the metal cation: $M_2(H_2F_3)(HF_2)_2(AF_6)$ (M = Ca, A = As; M = Sr, A = As, P) [2]. In the polymeric compounds $H_2F_3^-$ and HF_2^- anions bridge metal centers forming close packed three-dimensional networks. Various compounds with HF bonded directly on the metal center of the general formula $[M^{n+}(HF)_x](AF_6)_n$ are also known: $[La(HF)_2](AsF_6)_3$ [6], $[Pb(HF)](AsF_6)_2$ [7], $[Cd(HF)](AsF_6)_2$ [8], $[M(HF)_2](SbF_6)_2$ (M = Mg, Ca) [9], $[Ca(HF)_6](AsF_6)_2$ and $[Ca(HF)](AsF_6)_2$ [10], $[Au(HF)_2]{\cdot}(SbF_6)_2{\cdot}2HF$ [11].

In the present paper the crystal structure of the compound with the formula $BaF_2{\cdot}6HF$ is described. This is to our knowledge the first example of a metal center in a homoleptic environment of HF molecules.

2. Experimental section

2.1. General experimental procedures

A nickel vacuum line and Teflon vacuum system were used as previously described [12]. Volatile materials (aHF, PF_5) were manipulated in an all-Teflon vacuum line equipped with Teflon

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1293-2558/$ – see front matter
doi:10.1016/j.solidstatesciences.2006.02.045

valves. Non-volatile materials sensitive to traces of moisture were handled in the dry argon atmosphere in a glove box with maximum content of 0.1 ppm of water vapour (Mbraun, Garching, Germany). A FEP reaction vessel equipped with a Teflon valve and a Teflon-covered mixing bar were used for the syntheses. The crystals were grown in a crystallization vessel made from a T-shaped FEP reaction vessel, constructed from one 16-mm i.d. FEP tubing. A ∼30 cm length of 4-mm i.d. FEP tube connected by a Teflon valve provided the flexibility for decanting the aHF solution from one leg of the T-reactor to the other.

2.2. Reagents

BaF_2 (Alfa Aesar, 99.99%) and fluorine (Solvay, 99.98%) were used as purchased. PF_5 was prepared by fluorination by P_2O_5 powder under high-pressure as previously described [13]. Its purity was checked by IR spectroscopy. XeF_2 was prepared by the photochemical reaction between xenon and fluorine at room temperature [14]. Anhydrous HF (Fluka, purum) was treated with K_2NiF_6 (Ozark-Mahoning, 99%) for several days prior to use.

2.3. Synthesis of $Ba(H_3F_4)_2$

In order to perform the direct synthesis of $Ba(H_3F_4)_2$, BaF_2 (0.5418 g, 3.09 mmol) was dissolved in aHF (9.089 g). In the case of the isolation in the dynamic vacuum at −5 °C the weight of the product was lower as expected (0.7600 g, calc.: 0.912 g). Than the synthesis was repeated and the product was isolated in a dynamic vacuum at lower temperature (−18 °C). The weight of the product (0.9091 g, i.e., 3.08 mmol) corresponded to the composition $Ba(H_3F_4)_2$. From this solution we were not able to obtain single crystals of the reasonable quality. Because of the thermal instability of the product the other characterization methods were not applicable.

2.4. Preparation of single crystals of $Ba(H_3F_4)_2$

Single crystals of $Ba(H_3F_4)_2$ were found after long time crystallization of $[Ba(XeF_2)_n](PF_6)_2$. This coordination compound was prepared by the reaction of BaF_2 (0.3672 g, 2.09 mmol) and XeF_2 (1.809 g, 10.69 mmol) and excessive PF_5 in aHF. The product (2.5914 g) with $n \approx 4$ was isolated under dynamic vacuum. Methods of the synthesis and crystallization of this type of compounds are described in the literature [15]. Colourless crystals, isolated by a removal of aHF on the vacuum line, were immersed in a perfluoronated oil (ABCR, FO5960) in the dry box, selected under the microscope and transferred into cold nitrogen stream on the X-ray diffractometer.

2.5. Crystal structure determination

Single crystal data were collected using a Mercury CCD area detector coupled to a Rigaku AFC7 diffractometer with graphite monochromated Mo K_α radiation at 200 K. The data were corrected for Lorentz and polarization effects. A multi-scan absorption correction was applied to data sets. Data were processed using the CrystalClear software suite [16]. Structure was solved using direct methods by SIR-92 program [17] implemented in program package TeXsan [18] and expanded by Fourier techniques. Full-matrix least squares refinement of F^2 against all reflections was performed using the SHELXL 97 program [19].

The positions of all hydrogen atoms were found on difference Fourier maps. Those positional and thermal parameters were not refined. The figures were prepared using DIAMOND 3.1 software [20]. The crystal data and the details of structure refinement for $Ba(H_3F_4)_2$ are given in Table 1, atomic coordinates and equivalent displacement parameters are placed in Table 2.

Table 1
Crystal data and structure refinement for $Ba(H_3F_4)_2$

Empirical formula	BaF_8H_6
Fw	295.39
T (K)	200
Space group	$P\bar{6}2c$ (no. 190)
a (Å)	7.7756(12)
c (Å)	12.650(3)
volume (Å^3)	662.4(2)
Z value	4
$D_{calculated}$ (g/cm^3)	2.962
λ (Å)	0.71069
μ (mm^{-1})	6.079
$R1$;[a] $wR2$	0.0243; 0.0468
GOF	1.198

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [(w(F_o^2 - F_c^2)^2)/\sum w(F_o^2)^2]^{1/2}$, GOF $= [\sum(w(F_o^2 - F_c^2)^2)/(N_o - N_p)]^{1/2}$, where N_o = no. of reflns and N_p = no. of refined parameters.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters U_{eq} in $Ba(H_3F_4)_2$

Atom	x	y	z	U_{eq} (Å^2)
Ba1	2/3	1/3	0.56311(3)	0.01414(16)
F1	0.4372(5)	0.0657(5)	0.3984(2)	0.0307(7)
F2	0.7274(5)	0.1647(5)	3/4	0.0225(10)
F3	0.0000	0.7012(5)	1/2	0.0319(11)
F11	0.3399(6)	0.1767(15)	1/4	0.0355(10)
F12	0.0000	0.0000	1/2	0.079(3)
H1	0.4228	0.1038	1/3	0.015
H2	0.8084	0.0853	3/4	0.015
H3	0.0000	0.8125	1/2	0.015

3. Results and discussion

In the structure of the $Ba(H_3F_4)_2$ the central Ba atom is coordinated to twelve HF molecules. The Ba–F distances lie in a narrow range of 2.830(3)–2.855(2) Å and form nearly regular icosahedra (Fig. 1, Table 3). Each HF moiety acts as bridge between two metal centers (Fig. 2) with the shortest Ba···Ba distances of 4.765 Å. The barium atom has four closest metal neighbours located on tetrahedral manner. Each of the mentioned "the closest neighbours" is bonded to the barium atom via three HF bridges. Thus, $Ba(HF)_{12}$ icosahedra are joined to infinite three-dimensional network with two kinds of the infinite