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Crystal structures of dioxonium lanthanoid(III) pentakis (tetrafluoridoborates) of lanthanum and cerium

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ABSTRACT

The fluoropolymers as FEP and PFA are widely used materials for making reaction vessels applied to experiments involving liquid anyhdrous HF, elemental F_2 and various inorganic fluorides and fluoro-organic compounds. However, due to their permeability to gases and liquids, crystals of unexpected compounds can be sometimes grown during extended durations of the crystallizations. One of such examples is the growth of single crystals of $(H_3O)_2Ce(BF_4)_5$, which were grown unintentionally from the CeF_3/BF_3/aHF solution after five months of crystallization. Reaction between the La_2O_3 and excess of BF_3 in anhydrous HF yielded a similar compound, i.e., $(H_3O)_2La(BF_4)_5$ upon crystallization. The attempts to prepare single crystals of analogous compounds of Nd and Sm failed. $(H_3O)_2Ce(BF_4)_5$ crystallizes in the monoclinic $P2_1/n$ space group (No. 14) with $a = 11.9160(14)$ Å, $b = 9.1551(12)$ Å, $c = 14.5290(14)$ Å, $\beta = 94.929(5)^\circ$, $V = 1579.1(3)$ Å^3, and $Z = 4$ at 200 K. The crystal structure of $(H_3O)_2La(BF_4)_5$ is isotypic with cerium compound. Corresponding unit cell is monoclinic, $P2_1/n$ space group (No.14), with $a = 12.004(10)$ Å, $b = 9.197(2)$ Å, $c = 14.577(7)$ Å, $\beta = 94.459(9)^\circ$, $V = 1604.5(17)$ Å^3 and $Z = 4$ at 100 K. The crystal structures of $(H_3O)_2Ln(BF_4)_5$ (Ln = La, Ce) consist of slabs formed from the Ln^{3+} cations interconnected with the $[BF_4]^-$anions. The oxonium cations are located in the space between the slabs. Ln^{3+} cations are nine-fold coordinated with a tricapped trigonal prismatic arrangement of F ligands.

1. Introduction

The translucent fluorocarbon polymers FEP (fluorethylenpropylen: hexafluoropropylene-tetrafluoroethylene copolymer) and PFA (perfluoro alkoxy: tetrafluoroethylene-perfluoroether copolymer) have remarkable kinetical stability to elemental fluorine. Reaction vessels made of such materials provide the possibility for low temperature synthesis of various fluoro-compounds and nonmetal and metal fluorides, especially in the highest oxidation states, in liquid hydrogen fluoride (aHF) [1]. Both, FEP and PFA, materials are transparent to the visible light providing us the possibility to visually follow what is happening during the synthesis. One of the obstacles of these materials is their permeability to gases and liquids. The permeability or transmission of gases and vapors is dependent upon the solubility of the gas or vapor (in the polymer) and the rate of diffusion through the polymer [2]. The former is dependent upon the chemical relationship between permeant molecule and the polymer and the latter is dependent upon the size of permeant molecule and the amorphous configuration of the polymer [2]. For chemical reactions, which proceed in aHF for a short time, the permeability of FEP and PFA materials doesn't represent any important disadvantage. However, in the case of some long-lasting crystallizations, which can take place few moths, the diffusion of water vapour through the FEP or PFA walls of the reaction vessel causes crystal growth of unexpected phases [3–6]. One of such examples, i.e., the growth of single crystals of $(H_3O)_2Ce(BF_4)_5$, is described in the present paper. Additionally, the crystal structure of the isotypic $(H_3O)_2La(BF_4)_5$ is reported.

2. Experimental

CAUTION: Anhydrous HF and some fluorides are highly toxic and must be handled in a well-ventilated hood and protective clothing must be worn at all times! It is not recommended to touch FEP and PFA reaction and crystallization vessels with bare hands, especially in the case of long-lasting synthesis or crystallizations.

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2.1. Apparatus, techniques and reagents

The volatile materials (anhydrous HF, F_2, BF_3) were handled in a nickel vacuum line and an all-PTFE vacuum system equipped with PTFE valves [7]. The non-volatile materials were manipulated in a dry-box (M. Braun, Germany) in which the residual water in the atmosphere never exceeded <0.5 ppm. The reactions were carried out in FEP (Polytetra GmbH, Germany) reaction vessels (height 250–300 mm, i.d. of 16 mm, o.d. 19 mm) equipped with PTFE valves [8] and PTFE-coated stirring bars. Prior to their use, all the reaction vessels were passivated with elemental fluorine (Solvay, 99.98%). Anhydrous HF (Linde AG, Pullach, Germany, 99.995%) was treated with K_2NiF_6 (Advance Research Chemicals Inc, 99.9%) for several hours prior to its use. La_2O_3 (Koch Light Laboratories Ltd., 99.9% (REO)), Nd_2O_3 (Koch Light Laboratories Ltd., 99.5% (REO)), Sm_2O_3 (Ventron, Alfa Products, 99.9% (REO)) were heated prior use at 1373 K for two hours on air to remove absorbed H_2O and CO_2 [9]. CeF_3 (Johnson Matthey GmbH, Alfa Products, 99.9% (REO), and BF_3 (Union Carbide Austria, GmbH, 99.5%) were used as supplied.

X-ray powder diffraction patterns were obtained by the Debye-Scherrer method using CuKα radiation. Samples were loaded into quartz capillaries (0.3 mm) in a dry box. Intensities were estimated visually. Infrared spectra were recorded on a Perkin-Elmer Spectrum GX FTIR spectrometer on powdered samples between AgCl windows in a leak–proof brass–cell.

2.2. Attempted syntheses of $(H_3O)_2La(BF_4)_5$

La_2O_3 (1.11 mmol) and H_2O (1.11 mmol) were loaded into reaction vessel and aHF (6 ml) was condensed onto La_2O_3/H_2O at 77 K on a vacuum system. The reaction vessel was warmed up and BF_3 was added till the pressure in the reaction vessel reached 4 bar. The supernatant solution above an insoluble solid was colourless. After ten days of the extensive stirring at ambient temperature, the excess of BF_3 and aHF were pumped away at room temperature. Mass of isolated solid was 0.969 g; predicted for $(H_3O)_2La(BF_4)_5$: 1.356 g and for $La(BF_4)_3$: 0.886 g.

2.3. Crystal growth of $(H_3O)_2Ln(BF_4)_5$ (Ln = La, Ce)

Single crystals of $(H_3O)_2La(BF_4)_5$ were grown in T-shaped crystallization vessel comprised of two FEP tubes (one 16 mm i.d. × 19 mm o.d. and the other 4 mm i.d. × 6 mm o.d.). Each tube was heat-sealed on one end and joined at 90° through a Teflon T-connector (Fig. S1). A Teflon valve was connected at 180° to the 19-mm o.d. tube. Before use, the above-mentioned crystallization vessel was passivated with elemental fluorine. The product of reaction between La_2O_3 (0.61 mmol), large excess of BF_3 and aHF (5 ml), was loaded (approximately 150 mg) into the wider arm of the crystallization vessel in a dry-box. The aHF (4 ml) was then condensed onto the starting material at 77 K. The crystallization mixture was brought up to ambient temperature and the clear colorless solution that had developed above insoluble solid, was decanted into the narrower arm. Evaporation of the solvent from this solution was carried out by maintaining a temperature gradient of ca. 15 °C between the 6-mm o.d. tube and the 19-mm o.d. tube) by continous flow of tap water for several days (Fig. S1). When the HF level in the smaller diameter vessel ceased to further decrease, it was necessary to increase the temperature gradient. This was accomplished by slowly cooling the larger vessel in a cryostat from +12 °C to −30 °C and to induce crystallization (Fig. S1). During one month, the slow distillation of aHF from the 6-mm o.d. tube into the 19-mm o.d. tube resulted in crystal growth of $(H_3O)_2La(BF_4)_5$ inside the 6-mm o.d. tube.

Three similar attempts, to prepare single crystals of the unknown $(H_3O)_2Nd(BF_4)_5$ by slow crystallization (3 months) from the violet solutions of Nd_2O_3 (0.3/0.06/0.15 mmol) and large excess of BF_3 in aHF (6/6/12 ml), resulted only in a few single crystals of $NdF(HF)(BF_4)_2$ [10], which were found between the powdered material.

Only an unidentified powdered material was observed after three months long crystallization of Sm_2O_3 (0.07 mol)/large excess of BF_3/aHF (20 ml) colorless solution.

Single crystals of $(H_3O)_2Ce(BF_4)_5$ were grown five months during the attempt to prepare the single crystals of $CeF(HF)(BF_4)_2$ [10] from colorless solution of CeF_3 (0.5 mmol) in aHF (6 ml) acidified with large excess of BF_3.

2.4. Crystal structure determination of $(H_3O)_2Ln(BF_4)_5$ (Ln = La, Ce)

Crystals were immersed in perfluorodecalin (ABCR, 98%) inside a dry box, selected under a microscope, and mounted on the goniometer head of the diffractometer in a cold nitrogen stream. Data were collected at 100 K (La) and 200 K (La, Ce) on a Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector using graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). Data were treated using the Rigaku Crystal Clear software suite package [11]. The solutions were obtained by direct methods using the SIR-92 [12] (as implemented in the program package TeXan [13]) program. All further solution refinements were performed using the SHELXL-2014 [14] program implemented in the program package WinGX [15]. Hydrogen atoms were placed on ideal positions and refined as riding atoms with relative isotropic displacement parameters. The figures were prepared using the DIAMOND 3.1 software [16].

More details about the crystal-structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz.karlsruhe.de by quoting the deposition numbers CSD 431267 H3O 2La BF4 5, and CSD 431268 H3O 2Ce BF4 5

3. Results and discussion

3.1. Attempted synthesis and crystal growths of $(H_3O)_3Ln(BF_4)_5$ compounds

Previously reported crystal structures of $La(BF_4)_3$ and $PrF(HF)BF_4$ were determined on single crystals grown from clear saturated solutions of LnF_3 dissolved in aHF acidified with large excess of BF_3 (4 bar) [10]. The growths were carried out in a double T − shaped apparatus consisting of two FEP tubes (wall thickness 1.5 mm) and took place for 4 − 5 months. The attempt to prepare single crystals of $Ce(BF_4)_3$ and/or $CeF(HF)BF_4$ resulted in the growth of $(H_3O)_2Ce(BF_4)_5$. This was apparently resulting from slow diffusion of water vapour through the thin wall of the FEP reaction vessel during five months of crystallization. Such diffusion of water vapour was observed before and it led to the formation of oxonium salts [3], to the reduction of transition metals to lower oxidation states [4,6] or to partial hydrolysis of the main-group-element fluoro-compounds [5]. Reaction between La_2O_3 and excess of BF_3 in anhydrous HF yielded compound with unspecified composition (X-ray powder diffraction data are given in Table S1), which finally resulted in the $(H_3O)_2La(BF_4)_5$ upon crystallization. The fact that the $n(\text{oxygen}):n(La^{3+}) = 2:1$ molar ratio in the $(H_3O)_2La(BF_4)_5$ is higher than the $n(\text{oxygen}):n(La^{3+}) = 1.5:1$ molar ratio in the starting La_2O indicates that either some $La(BF_4)_3$ [10] or $LaF(HF)(BF_4)_2$ [10] were also formed, or either that the additional oxygen could arise from H_2O diffusion. The attempt to synthesize pure $(H_3O)_2La(BF_4)_5$ compound by reaction between La_2O_3, H_2O, $10BF_3$ and 10HF in liquid aHF failed. The infrared spectrum (Fig. S2) of isolated solid shows very broad bands at around 1650 cm^{-1} and 3500 cm^{-1}

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