Scientific paper

Hydrogen Fluoride Adducts with the Strontium Cation: $Sr(HF)_3(TaF_6)_2$ and $Sr(HF)(BF_4)_2$

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Dedicated to the memory of Professor Ljubo Golič

Abstract

By slow crystallization from anhydrous HF solution crystals of two new HF adducts with the composition $Sr(HF)_3(TaF_6)_2$ and $Sr(HF)(BF_4)_2$ were obtained and investigated by X-ray single crystal technique and Raman spectroscopy. $Sr(HF)_3(TaF_6)_2$ (**I**) crystallizes in a monoclinic $P2_1/c$ space group, $a = 8.663(17)$ Å, $b = 12.714(5)$ Å, $c = 10.759(10)$ Å, $\beta = 94.24(2)°$, $V = 1181.77(300)$ Å^3, $Z = 4$. The metal coordination sphere consists of nine fluorine atoms and adopts the shape of tri-capped trigonal prism. Six F atoms belong to six TaF_6^- anions and 3 fluorine atoms are from three terminal HF molecules. Owing to the bridging function of TaF_6^- anions infinite double layers lying in *bc* plane appear. These layers are interconnected into 3-D structure by F–H…F(Ta) hydrogen bonds. $Sr(HF)(BF_4)_2$ (**II**) crystallizes in an orthorhombic $Pmn2_1$ space group with $a = 5.1566(17)$ Å, $b = 9.637(3)$ Å, $c = 6.900(2)$ Å, $V = 342.89(18)$ Å^3, $Z = 2$. Seven F atoms from BF_4^- anions and two F atoms from two bridging HF molecules form tri-capped trigonal prismatic surrounding of Sr cation. One of BF_4^- anions is connected to 4 metal centres, another one to 3 Sr cations and H atom of HF molecule. Owing to bridging function of both HF and BF_4^- moieties the complex 3-D structure appears.

Keywords: Strontium, weakly bonded anion, HF adduct, TaF_6^-, BF_4^-

1. Introduction

Salts containing hexafluorometalate anions have rather low lattice energies as a consequence of the anion volume (>100 Å^3).[1] Most of these anions, AF_6^-, where A is As, Sb, Bi, Ta, Nb, are poor Lewis bases, so that even anhydrous HF which has extremely low basicity can provide sufficient solvation energy to bring about dissolution of $M(AF_6)_x$ salts. The cations in these solutions are solvated forming $M^{n+}(HF)_x$ species.[2] After the solvent was removed only non-solvated $M(AF_6)_x$ salts were isolated. HF functioning as a ligand was not observed until 1998 when the first compound $[La(HF)_2](AsF_6)_3$,[3] in which HF was introduced in the metal coordination sphere, was isolated. Later many new coordination compounds with HF molecules interacting directly with the metal centre were isolated and structurally characterized: $[Pb(HF)](AsF_6)_2$,[4] $[Ca(HF)_2](AsF_6)_2$,[5] $[Cd(HF)](AsF_6)_2$,[6] $[M(HF)_2](SbF_6)_2$ (M = Mg, Ca),[7] $[Ca(HF)_6](AsF_6)_2$,[8] $[Au(HF)_2](SbF_6)_2 \cdot 2HF$,[9] $[OsO_3F(HF)_2](AsF_6)_2$ and $[OsO_3F(HF)](SbF_6)_2$,[10] $K_2(HF)_2CrF_6$, $K_3(HF)_2Cr_2F_{11}$, $Na_2(HF)_2CrF_6$[11] Even in the presence of covalently bonded fluoride-anion in the metal environment, the HF molecule can form direct bond to the metal centre as it was observed, for example, in $BaF(HF_2)$[12] and $Ba(H_3F_4)_2$[13] compounds. High absolute electronegativity of Sr^{2+} (27.3 eV)[14] is an important factor in the process of the formation of the coordination compounds with HF. The solubility of strontium difluoride in anhydrous HF is much higher (14.83(9) g/100 g HF) than in the case of other MF_2 compounds, what makes the syntheses with SrF_2 easier.[15] The strontium hexafluorophosphate forms in the presence of HF an unique compound $Sr_2[HF_2][H_2F_3][PF_6]_2$[16] where all F atoms are involved in bonding with the metal cation. One may expect that the strontium salts with other weakly bonded large anions could form adducts with HF. In this paper the synthesis and the characterization of two new compounds $Sr(HF)_3(TaF_6)_2$ and $Sr(HF)(BF_4)_2$ are described.

2. Results and Discussion

2. 1. Description of the Crystal Structures

In the structure of $Sr(HF)(BF_4)_2$ nine fluorine atoms form coordination surrounding of strontium atom in the shape of tri-capped trigonal prism (Fig. 1). Seven Sr – F(B) bonds appear to be equal to 2.453(4)–2.483(8) Å, whereas two Sr – F(H) bonds are strongly elongated to 2 x 2.871(3) Å. Each HF molecule acts as a bridge, being bound *via* F atom to two metal centres. Additionally H atom is involved in a formation of strong F–H…F(B) hydrogen bond (H…F 1.6(2) Å, F…F 2.47(1) Å). The surrounding of each of two crystallographically independent BF_4^- units differs: $B(1)F_4^-$ is connected to 4 Sr atoms, $B(2)F_4^-$ to 3 Sr atoms and one H atom of HF molecule. Owing to bridging function of both HF and BF_4^- moieties the complex 3-D structure appears (Fig. 2).

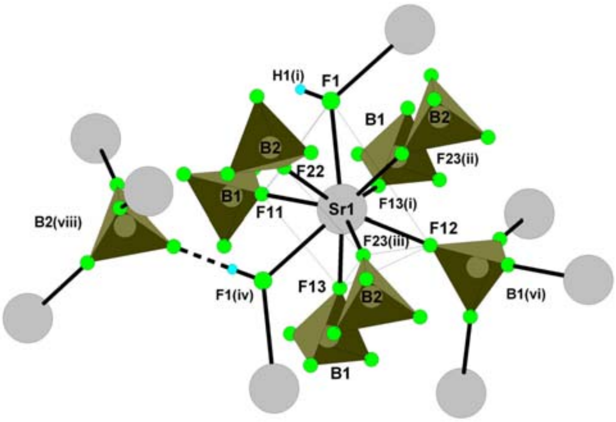

Fig. 1. The Sr atom surrounding and the bridging function of BF_4^- anions in $Sr(HF)(BF_4)_2$

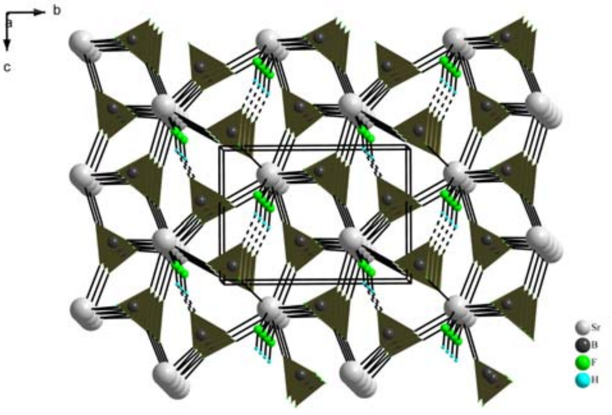

Fig. 2. Packing diagram of $Sr(HF)(BF_4)_2$

In the structure of $Sr(HF)_3(TaF_6)_2$ compound the coordination sphere of Sr atom also adopts the shape of a tri-capped trigonal prism. But contrary to $Sr(HF)(BF_4)_2$ the metal environment includes only six F atoms from six TaF_6^- anions and 3 fluorine atoms from three HF molecules (Fig. 3). All three F(H) centres are located on the same triangular face, and the Sr–F(H) distances lie in a rather narrow range of 2.51(2)–2.55(2) Å, while the Sr–F(Ta) bond lengths vary from 2.48(2) to 2.61(2) Å. The shortest metal – capping fluorine atom bond length of 2.51(2) Å is slightly longer than the shortest distance from strontium atom to the fluorine atom at the corner of trigonal prism 2.48(2) Å. Both crystallographically independent TaF_6^- units play the same μ_3-*cis*-bridging function, i.e. all three F bridges belong to one triangular face of TaF_6 octahedron. The distances from Ta atom to terminal (1.83(2)–1.89(3) Å) and bridging (1.89(2)–1.93(2) Å) fluorine atoms differ slightly. Owing to above mentioned bridging function of TaF_6^- anions infinite double layers lying in *bc* plane appear. These layers are interconnected into 3-D

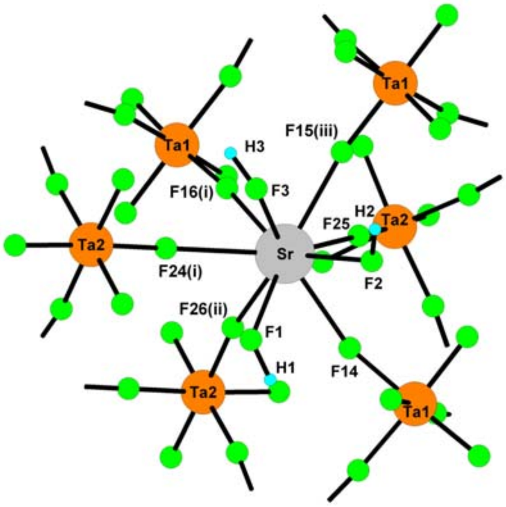

Fig. 3. The surrounding of Sr atom in $Sr(HF)_3(TaF_6)_2$

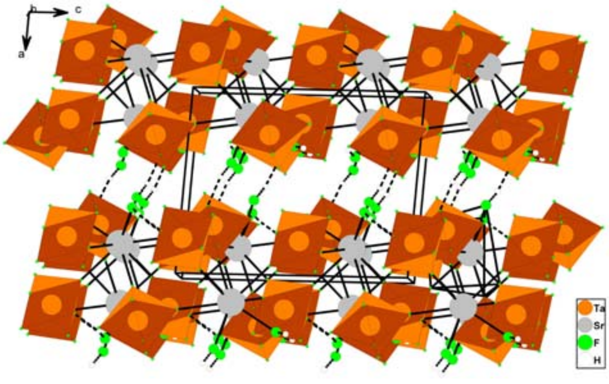

Fig. 4. Packing diagram of $Sr(HF)_3(TaF_6)_2$

structure by F–H…F(Ta) hydrogen bonds with F…H distances of 1.69 – 1.88 Å (Fig. 4).

2. 2. Raman Spectra

The Raman spectra of $Sr(HF)_3(TaF_6)_2$ and $Sr(HF)(BF_4)_2$ show only bands which could be attributed to the anions. Vibrational bands at frequencies higher than 1000 cm^{-1} which could be most probably associated with the HF bridges,[10] were not observed. The octahedral TaF_6^- anion (O_h symmetry) has three Raman active fundamental vibrations ν_1, ν_2 and ν_5 which are expected at 692, 581 and 272 cm^{-1}, respectively.[17,18] The Raman spectrum of the compound $Sr(HF)_3(TaF_6)_2$ is shown on Fig. 5. In this compound TaF_6^- octahedra are deformed due to interactions with strontium cations and therefore the vibrational bands appear at higher frequencies at 716, 664 and 289 cm^{-1}.

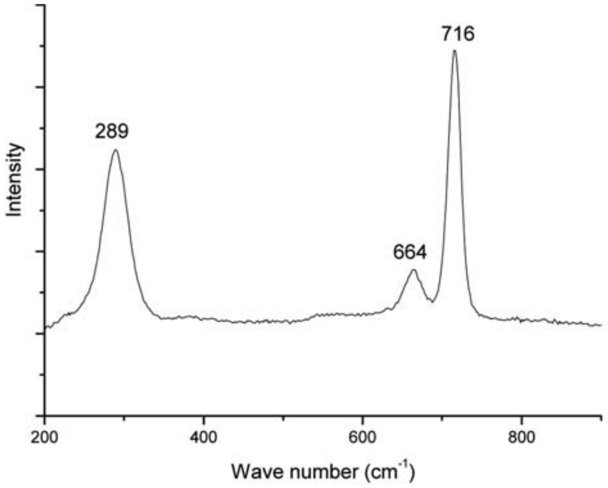

Fig. 5. Raman spectrum of $Sr(HF)_3(TaF_6)_2$ in a capillary.

In the case of the compound $Sr(HF)(BF_4)_2$ again only the bands of the BF_4^- anion are seen. T_d symmetry of the BF_4^- anion has vibrational bands ν_1 at 777, ν_2 at 360, ν_3 at 1070 cm^{-1} and ν_4 at 533 cm^{-1}.[18] In the Raman spectrum of $Sr(HF)(BF_4)_2$ these bands appear at 792, 354, and at 532 cm^{-1}. The Raman band at around 1000 cm^{-1} was not seen due to a high fluorescence of the sample in this region.

3. Conclusions

Because HF is extremely weak base no coordination compounds with HF acting as a ligand to metal ion were discovered before 1998. Already in the late seventies it was proven by spectroscopic methods that salts $M^{n+}(AF_6)_n$ or $M^{n+}(BF_4)_n$ dissolve in anhydrous HF yielding solvated cations of the type $[M(HF)_6]^{n+}$.[19] When the solvent HF is slowly removed the coordination compounds of the type $[M^{n+}(HF)_m](AF_6)_n$ or $[M^{n+}(HF)_m](BF_4)_n$ are formed. These compounds are usually not stable at room temperature. They are loosing HF and yielding non-solvated salts. Therefore, if the preparation of coordination compounds with HF ligands to the metal centre is desired the isolation should be performed at low temperature. Using this synthetic approach two new coordination compounds $Sr(HF)_3(TaF_6)_2$ and $Sr(HF)(BF_4)_2$ with HF as a ligand to metal cation were isolated and structurally characterized.

4. Experimental Section

4. 1. General Experimental Procedures

A nickel vacuum line and Teflon vacuum system were used as previously described.[20] Volatile material (aHF, BF_3) was manipulated in an all-Teflon vacuum line equipped with Teflon valves. Non-volatile materials (SrF_2, Ta) that were 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 stirring bar was used for syntheses. A T-shaped FEP reaction vessel constructed from one large FEP tube (16 mm i.d.) and a smaller FEP tube (4 mm i.d.) joint at right angle and equipped with Teflon valve was used for crystallization.

4. 2. Reagents

SrF_2 (Alfa Aesar, 99.99%), tantalum (BDH, 99.5%) and fluorine (Solvay, 99.98%) were used as purchased. Boron trifluoride (Union Carbide, 99.5%) was used as supplied. Anhydrous HF (Fluka, purum) was treated with K_2NiF_6 (Ozark-Mahoning, 99%) for several days prior to use. Caution: Anhydrous hydrogen fluorine must be handled in a well-ventilated hood and protective clothing must be worn all the times! The experimentalist must become familiar with these reagents and the hazards associated with them. Fresh tubes of calcium gluconate gel should always be on hand for the fast treatment of skin exposed to these reagents. For treatment of HF injuries see reference.[21]

4. 2. 1. Synthesis of $Sr(HF)_3(TaF_6)_2$

SrF_2 (0.159 g, 1.26 mmol) and Ta (0.458 g, 2.53 mmol) were weighed into reaction vessel inside the dry box. Anhydrous HF was added by sublimation at –196 °C. Then the reaction vessel was warmed up to room temperature and after two days hydrogen was pumped out at –196 °C. The procedure was repeated until there was no hydrogen in the reaction vessel. At the next stage the fluorine (approximately 2–4 mmol) was added to the reaction mixture. Reaction was left to proceed for one additional day.

The excess of F_2 was pumped off from the reaction vessel at –196 °C and "fresh" F_2 was added again. At the end of the reaction F_2 was pumped off at –196 °C and HF at –23 °C. The reaction vessel was warmed to room temperature and weighed: the mass of the product $Sr(HF)_3(TaF_6)_2$ was 0.944 g (1.28 mmol).

4. 2. 2. Synthesis of $Sr(HF)(BF_4)_2$

SrF_2 (0.106 g, 0.842 mmol) was weighed into reaction vessel inside the dry box. The reaction vessel was cooled with liquid nitrogen and anhydrous HF was added by sublimation at –196 °C. Then the reaction vessel was warmed up to room temperature and weighed. The reaction vessel was cooled again at –196 °C and BF_3 (0.308g, 4.55 mmol) was added to the reaction vessel. Reaction proceeded at room temperature for 24 hours. From the solution the product was isolated by pumping off the solvent and excessive BF_3 at –23 °C. The reaction vessel was warmed to room temperature and weighed: the mass of the product was 0.241 g i.e. 0.857 mmol as calculated for $Sr(HF)(BF_4)_2$.

4. 2. 3. Preparation of Single Crystals

Small amounts of compounds obtained (189 mg of $Sr(HF)_3(TaF_6)_2$ and 166 mg of $Sr(HF)(BF_4)_2$) were transferred in the dry box into the crystallization PFA vessel. Anhydrous HF was added on the vacuum line and a saturated solution was prepared. This solution was decanted into narrower part of the reaction vessel, which was left at room temperature while the wider part was slightly cooled to generate a small temperature gradient. The crystallization proceeded for several days. Colourless crystals were isolated by pumping off the aHF at –15 °C for $Sr(HF)_3(TaF_6)_2$ and at –21 °C for $Sr(HF)(BF_4)_2$. Inside the dry box they were put in perfluoronated oil (ABCR, FO5960), selected under the microscope and transferred into cold nitrogen stream at the X-ray diffractometer.

4. 2. 4. Crystallography

Single-crystal data were collected on a Mercury CCD area detector coupled to a Rigaku AFC7S diffractometer using monochromatized MoKα radiation. Data were corrected for Lorentz, polarization, and absorption effects and processed using Rigaku CrystalClear software suite program package.[22] Both structures were solved by direct methods using SIR-92 program,[23] and refined with SHELXL-97 software,[24] implemented in program package WinGX.[25] Because of poor quality of diffraction array in the case of $[Sr(HF)_3](TaF_6)_2$ compound fluorine atoms were refined in isotropic mode. The figures were prepared using DIAMOND 3.1 software.[26] The crystal data and the details of structure refinement for both compounds are given in Table 1.

Table 1 Details of experimental and crystallographic data for **I** and **II** compounds

Compound	I	II
Empirical formula	$H_3F_{15}SrTa_2$	B_2HF_9Sr
Formula weight	737.54	281.25
Crystal size, mm	0.12 × 0.1 × 0.08	0.12 × 0.1 × 0.04
Temperature, K	200	200
Radiation	MoKα	MoKα
Color, shape	Colorless, chunk	Colorless, chunk
Space group	$P2_1/c$	$Pmn2_1$
Unit cell dimensions		
a, Å	8.6642(12)	5.1566(17)
b, Å	12.7256(14)	9.637(3)
c, Å	10.7687(14)	6.900(2)
β, °	*94.201(8)*	
V, Å^3	1184.1(3)	342.89(18)
Z	4	2
D_c, g/cm^3	4.137	2.724
μ, mm^{-1}	*23.10*	*7.98*
F(000)	1288	260
Scan range *θ*,°	1.9-29.1	2.1-28.7
Measured reflections	4710	1518
Used ($I > 2\sigma(I)$)	1200	757
Parameters refined	164	72
R (F)	0.088	0.039
R (F)^2	0.198	0.093
Goodness-of-fit	0.95	1.11

4. 2. 5. Raman Spectroscopy

Raman spectra of the powdered samples in sealed quartz capillaries were collected on a Renishaw Raman Imaging Microscope System 1000 with the exciting line at 632.8 nm of a He–Ne laser. The geometry for all the Raman experiments was 180° back scattering with laser power 25 mW.

5. Acknowledgements

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Povzetek

S počasno kristalizacijo iz brezvodnega HF smo izolirali dva nova HF adukta s sestavo $Sr(HF)_3(TaF_6)_2$ in $Sr(HF)(BF_4)_2$, ki smo ju raziskovali z rentgensko tehniko za mono kristale in z ramansko spektroskopijo. $Sr(HF)_3(TaF_6)_2$ (**I**) kristalizira v monoklinski prostorski skupini $P2_1/c$, a = 8.663(17) Å, b = 12.714(5) Å, c = 10.759(10) Å, β = 94.24(2)°, V=1181.77(300) Å^3, Z=4. V koordinacijski sferi kovine se nahaja devet fluorovih atomov v obliki trigonalne prizme s tremi kapami na pravokotnih ploskvah. Šest F atomov pripada šestim TaF_6^- anionom, tri F atome pa prispevajo tri terminalne HF molekule. Glede na to, da so TaF_6^- anioni mostovni dobimo neskončne dvojne plasti, ki ležijo v *bc* ravnini. Te plasti so med seboj povezane v 3-D strukturo z F–H…F(Ta) vodikovimi vezmi. $Sr(HF)(BF_4)_2$ (**II**) kristalizira v ortorombski $Pmn2_1$ prostorski skupini z a = 5.1566(17) Å, b = 9.637(3) Å, c = 6.900(2) Å, V=342.89(18) Å^3, Z=2. Sedem F atomov od BF_4^- anionov in dva F atoma od dveh mostovnih HF molekul tvori okrog Sr kationa trigonalno prizmo s tremi kapami na pravokotnih ploskvah. Eden od BF_4^- anionov je povezan s štirimi kovinskimi centri, medtem ko je drugi BF_4^- povezan le s tremi Sr kationi in H atomom od HF molekule. Glede na to, da je tako HF kot BF_4^- skupina mostovna, dobimo 3-D strukturo.