Synthesis and study of tetramethylammonium hexafluoridozirconate and hexafluoridohafnate solvated by $H_2O \cdot HF$ adducts and $[N(CH_3)_4]_2ZrF_6$

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A B S T R A C T

A new type of zirconium and hafnium fluoride complexes of the composition $[N(CH_3)_4]_2AF_6 \cdot (H_2O \cdot HF)$ (A = Zr, Hf) solvated by $H_2O \cdot HF$ adducts and the compound $[N(CH_3)_4]_2ZrF_6$ have been synthesized. The synthesized compounds were studied by X-ray diffraction, vibrational spectroscopy, quantum chemical calculations and differential thermal analysis. The crystal structures of $[N(CH_3)_4]_2AF_6 \cdot (H_2O \cdot HF)$ (A = Zr, Hf) are built up from $N(CH_3)_4^+$ cations, octahedral complex anions $[AF_6]^{2-}$, and solvate adducts $H_2O \cdot HF$ linked by strong hydrogen bonds $F–H \cdots O$. The compound $[N(CH_3)_4]_2ZrF_6$ is built up from $N(CH_3)_4^+$ cations and complex anions $[ZrF_6]^{2-}$. In the investigated structures, the complex anions, cations, and adducts are linked by ionic interactions and a branched system of hydrogen bonds $O–H \cdots F$ and $C–H \cdots F$.

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1. Introduction

Complex fluorides of zirconium and hafnium obtained from hydrofluoric acid solutions crystallize predominantly as water-free compounds or crystal hydrates (see, for example, [1]). From hydrofluoric acid solutions were also obtained a number of complex fluorides of zirconium and hafnium [2–7], as well as aluminum [8] and antimony (III) [9], containing solvate HF molecules. Data are also available on the synthesis of a number of oxygen-containing compounds solvated by HF molecules [10–12].

During a systematic study of the performed systematic studies of the chemistry and structure of complex fluorides of the Periodic Table IV–V groups metals, a new type of zirconium and hafnium fluoride complexes, $[N(CH_3)_4]_2AF_6 \cdot (H_2O \cdot HF)$ (A = Zr (**1**), Hf (**2**)), containing simultaneously H_2O and HF solvate molecules bonded into $H_2O \cdot HF$ adducts, were synthesized for the first time. The compound $[N(CH_3)_4]_2ZrF_6$ (**3**) was also obtained for the first time. A complex study of the synthesized compounds by means of X-ray diffraction, IR and Raman spectroscopy, thermogravimetry and quantum chemistry has been carried out.

2. Results and discussion

The synthesized fluoride complexes **1** and **2** crystallize from the solution as crystals suitable for X-ray diffraction. The compound **3** was obtained through thermal decomposition of **1** and from solution. The compounds **1** and **2** are thermally unstable. At room temperature they decompose emitting an 'acidic' gaseous product that is detected by reddening of the universal litmus paper placed by the crystals. The decomposition of the synthesized crystals is accelerated under the effect of X-ray radiation. Unlike **1** and **2**, the compound **3** is stable in air under regular conditions and upon heating in a relatively broad temperature range.

From the chemical analysis results, the N:Zr(Hf):F ratio is equal to 2.1:1:6.9 in the synthesized fluoride complexes **1** and **2**, in **3** the ratio N:Zr:F is equal to 1.9:1:6.0.

2.1. X-ray study

The compounds **1** and **2** are isostructural and built up from discrete complex anions $[AF_6]^{2-}$, tetramethylammonium, $N(CH_3)_4^+$ (TMA) cations, and H_2O and HF molecules. The coordination of the A atoms by six F atoms results in the formation of slightly distorted octahedra. The distortion of the A-polyhedra is characterized by scattering of A–F bond lengths and *cis* F–A–F angles from 1.9847(5) up to 2.0267(5) Å and from 87.84(2) up to 93.16(2)° for **1**; from

Table 1
Selected geometric parameters (Å) for **1–3**.

[N(CH$_3$)$_4$]$_2$ZrF$_6$·(H$_2$O·HF)		[N(CH$_3$)$_4$]$_2$HfF$_6$·(H$_2$O·HF)		[N(CH$_3$)$_4$]$_2$ZrF$_6$	
Zr(1)–F(5)	1.9847(5)	Hf(1)–F(5)	1.973(1)	Zr(1)–F(1)	1.998(1)
Zr(1)–F(6)	1.9848(5)	Hf(1)–F(6)	1.972(2)	Zr(1)–F(1)^{xiii}	1.998(1)
Zr(1)–F(2)	1.9934(5)	Hf(1)–F(2)	1.983(1)	Zr(1)–F(1)^{xiv}	1.998(1)
Zr(1)–F(3)	1.9981(5)	Hf(1)–F(3)	1.988(1)	Zr(1)–F(1)^{xv}	1.998(1)
Zr(1)–F(1)	2.0267(5)	Hf(1)–F(1)	2.011(1)	Zr(1)–F(1)^{xvi}	1.998(1)
Zr(1)–F(4)	2.0267(5)	Hf(1)–F(4)	2.014(2)	Zr(1)–F(1)^{xvii}	1.998(1)
N(1)–C(1)	1.4939(9)	N(1)–C(1)	1.489(2)	N(1)–C(1)^{xviii}	1.494(2)
N(1)–C(1)^i	1.4939(9)	N(1)–C(1)^i	1.489(2)	N(1)–C(1)	1.494(2)
N(1)–C(2)^i	1.4956(9)	N(1)–C(2)^i	1.495(2)	N(1)–C(1)^{xix}	1.494(2)
N(1)–C(2)	1.4956(9)	N(1)–C(2)	1.495(2)	N(1)–C(2)	1.496(3)
N(2)–C(4)	1.4938(9)	N(2)–C(4)	1.489(2)		
N(2)–C(4)^{ii}	1.4938(9)	N(2)–C(4)^{ii}	1.489(2)		
N(2)–C(3)^{ii}	1.4956(9)	N(2)–C(3)^{ii}	1.499(2)		
N(2)–C(3)	1.4956(9)	N(2)–C(3)	1.499(2)		
N(3)–C(5)^{iii}	1.4972(8)	N(3)–C(5)^{iii}	1.497(2)		
N(3)–C(5)	1.4972(9)	N(3)–C(5)	1.497(2)		
N(3)–C(6)	1.4973(8)	N(3)–C(6)	1.495(2)		
N(3)–C(6)^{iii}	1.4973(8)	N(3)–C(6)^{iii}	1.495(2)		
N(4)–C(7)^{iv}	1.4929(9)	N(4)–C(7)^{iv}	1.493(2)		
N(4)–C(7)	1.4929(9)	N(4)–C(7)	1.493(2)		
N(4)–C(8)	1.4940(9)	N(4)–C(8)	1.496(2)		
N(4)–C(8)^{iv}	1.4940(9)	N(4)–C(8)^{iv}	1.496(2)		

Symmetry codes: (i) −x + 2, y, −z + 3/2; (ii) −x, y, −z + 3/2; (iii) −x + 1, y, −z + 3/2; (iv) −x + 1, y, −z + 1/2; (xiii) y − 1, −x + y, −z; (xiv) −x, −y + 2, −z; (xv) −y + 1, x − y + 2, z; (xvi) x − y + 1, x + 1, −z; (xvii) −x + y − 1, −x + 1, z; (xviii) −x + y + 1, −x + 1, z; (xix) −y + 1, x − y, z.

1.972(2) up to 2.014(2) Å and from 87.77(5) up to 92.82(5)° for **2** (Table 1). The H$_2$O and HF molecules are linked to each other through short hydrogen bonds F–H···O (2.4327(9) and 2.434(2) Å in **1** and **2**, respectively, (Table 2), thus forming H$_2$O·HF adducts (Fig. 1). The formation of strong hydrogen bonds F–H···O (2.356–2.386(3) Å) was revealed by means of the method of neutron diffraction in the structures of adducts CsH$_2$PO$_3$·HF, KH$_2$PO$_4$·HF, and CsH$_2$PO$_4$·HF [10]. The same F–H···O distance value (2.384(5) Å) was found in the crystal structure of adduct (C$_6$H$_5$)$_3$PO·HF [11]. The formation of H$_2$O·HF adducts from H$_2$O and HF molecules linked through hydrogen bonds has been found in the structures of [Cu{NC$_5$H$_4$(NHCOCH$_3$)-4}$_2$(CH$_3$O$_2$)$_2$ (H$_2$O)]·2HF 2H$_2$O [13] and Co$_2$(DH)$_4$O$_2$(H$_2$O)$_2$·2(HF)·0.67(H$_2$O) (DH$^-$– monodeprotonated dimethylglyoxime) [14]. In both structures H$_2$O and HF molecules are disordered while hydrogen atoms are not localized. In the Cu compound, the hydrogen bond length r(F···O) was determined to be equal to 2.749 Å whereas in the case of the Co compounds, it was found to be 2.526 which is close to the values obtained for compounds **1** and **2**. The former bond length is one of the longest observed for F–H···O hydrogen bonds.

In the structures of **1** and **2** H$_2$O·HF adducts are linked through hydrogen bonds O–H···F with fluorine atoms F(1) and F(4) of two octahedra, thus forming supramolecular associates, in which structural units are linked only by strong hydrogen bonds F–H···O and O–H···F (Table 2 and Fig. 1). The A–F(1) and A–F(4) bonds are the longest ones in the A atoms polyhedra.

TMA cations comprise almost regular tetrahedra with C–N bond lengths and C–N–C valence angles ranging from 1.4929(9) up to 1.4973(8) Å and from 108.85(7) up to 109.99(8)° for **1**; from 1.489(2) up to 1.499(2) Å and from 109.0(2) up to 109.9(2)° for **2** (Table 1). Nitrogen atoms are located on twofold rotation axes (Wyckoff positions 4c), so that the asymmetric part of the structures contains four halves of TMA cations. A part of H···F linkages with lengths less than the sum of the van der Waals radii of hydrogen and fluorine atoms (2.67 Å) [15] can be attributed to weak hydrogen bonds C–H···F linking mainly cations and anions of the structures under study [16]. Two C–H···F bonds are linked to the adduct F(7) atom (Table 2). The structural units of the compounds **1** and **2** are linked into a three-dimensional structure by a system of branched hydrogen bonds and ionic interactions (Fig. 2a).

As was mentioned above, the compounds **1** and **2** rapidly decompose in air, are thermally unstable and sensitive to X-ray radiation. Under effect of X-ray radiation the decomposition rate increases dozens-fold. One can see from the diffractograms shown in Fig. 3 that the compounds obtained upon heating **1** up to 250 °C and upon decomposition in air are fully in compliance with the calculated diffractogram made on the basis of the structural determination of the compound **3**.

The compound **3** is isostructural to [N(CH$_3$)$_4$]$_2$OsF$_6$ [17] and [N(CH$_3$)$_4$]$_2$TiF$_6$ [18]. The Zr and N atoms in **3** are located on threefold rotation axes (Wyckoff positions 3a and 6c, respectively) and the octahedron [ZrF$_6$]$^{2-}$ and the tetrahedron N(CH$_3$)$_4$$^+$ are almost regular (Table 1 and Fig. 2b). The Zr-polyhedron distortion in **3** is characterized by cis F–Zr–F equal to 89.95(4) or 90.05(4)° at the same values of Zr–F bond lengths – 1.9989(9) Å. The H···F links with lengths less than the sum of H and F atoms van der Waals radii are attributed to hydrogen bonds C–H···F linking cations and anions in the structure (Table 2).

The structural packing of compound 3 shows the presence of a void of 32 Å^3 with coordinates of the void center $x = 0.0$, $y = 0.0$, $z = 0.5$ [19] in the unit cell (for the void volume calculations, the PLATON default values for atom radii were used). The centers of Zr-octahedra, TMA cations, and voids in the structure are located along the coordinate axis c and "stringed" on threefold rotation axes (Fig. 4a). Similar voids with the same coordinates are present in the structures of trigonal modifications of [N(CH$_3$)$_4$]$_2$OsF$_6$ [17] (32 Å^3) and [N(CH$_3$)$_4$]$_2$TiF$_6$ [18] (24 Å^3) as well as in the tetragonal modification of [N(CH$_3$)$_4$]$_2$PtF$_6$ [20] and the cubic modification of [N(CH$_3$)$_4$]$_2$TiF$_6$ [21] (31 Å^3).

Possible reasons of the void formation in [N(CH$_3$)$_4$]$_2$ZrF$_6$ can be seen from Fig. 4a. Along the threefold rotation axis Zr octahedra and TMA tetrahedra are oriented with respect to each other by mutually parallel trigonal faces (angle between the normals to F(1)F(1)^{xv}F(1)^{xvii} and to C(1)^{xxxvi}C(1)^{xxxvii}C(1)^{xxxviii} planes is equal to 0°). Voids are located between two TMA cations oriented to their direction with C(2) vertices. Thus, along the c axis cations and anions alternate in accordance with the following rule: ...TMA...ZrF$_6$...TMA...void...TMA...ZrF$_6$...TMA...void.... A virtually identical situation takes place in the location of structural units in [N(CH$_3$)$_4$]$_2$AF$_6$·(H$_2$O·HF) along the direction [2 1 2]: the