DOI: 10.1002/ejic.200900628

# Synthesis and Characterisation of $[XeF_5]_3[Ti_4F_{19}]$ Containing a Discrete $[Ti_4F_{19}]^{3-}$ Anion

**Zoran Mazej*[a] and Evgeny Goreshnik[a]**

**Keywords:** Titanium / Xenon / Fluorine / Structure elucidation / Vibrational spectroscopy

The complex $[XeF_5]_3[Ti_4F_{19}]$ was prepared by reaction of $XeF_2$, $TiF_4$ and UV-irradiated elemental fluorine in anhydrous hydrogen fluoride as the solvent. The crystal structure of $[XeF_5]_3[Ti_4F_{19}]$ consists of $[XeF_5]^+$ cations and discrete $[Ti_4F_{19}]^{3-}$ anions. The $[XeF_5]$ units have usual slightly distorted pseudo-octahedral symmetry. Contrary to the previously reported $[Ti_4F_{18}]^{2-}$ anion, where each $TiF_6$ octahedron shares three apexes with three other octahedra, in $[Ti_4F_{19}]^{3-}$, only two $\mu_3$-$[TiF_6]$ octahedra share three apexes with three other $[TiF_6]$ units. Each of the remaining two $\mu_2$-$[TiF_6]$ octahedra shares only two vertices with two of the above-mentioned $\mu_3$-$[TiF_6]$ moieties. The Raman spectrum of $[XeF_5]_3$-$[Ti_4F_{19}]$ is in agreement with the presence of $[XeF_5]^+$ cations and $[Ti_4F_{19}]^{3-}$ anions.

## Introduction

The reaction between $TiF_4$ and an excess amount of $XeF_6$ at ambient temperature yields $(XeF_6)_4{\cdot}TiF_4$.[1] The latter releases $XeF_6$ under dynamic vacuum at 40 °C to give $XeF_6{\cdot}TiF_4$, which decomposes further at 65 °C into $XeF_6$ and $XeF_6{\cdot}2TiF_4$.[1] The compositions of the obtained phases were determined by elemental chemical analysis.[1] Their infrared spectra and magnetic susceptibilities were also reported.[1] Because no structural data on these compounds is known, a systematic study was undertaken to achieve a better understanding of the possible phases in the $XeF_6/TiF_4$ system and to investigate the nature of the isolated products {i.e., $[XeF_5]^+$, $[Xe_2F_{11}]^+$ or mixed $[XeF_5]^+$-$[Xe_2F_{11}]^+$ salts and the composition of the anionic part: $[Ti_nF_{4n+x}]^{x-}$ $(n, x \geq 1)$}.

## Results and Discussion

Instead of $XeF_6$, we used $XeF_2$ as a starting material and as precursor for the in situ preparation of $XeF_6$. The $XeF_2/TiF_4$ mixtures could be prepared in the requested molar ratios and loaded into reaction vessels in a dry box; meanwhile, $XeF_6$ could be added onto $TiF_4$ only by condensation in a vacuum system.[2] $XeF_2$ was converted into $XeF_6$ by photochemical reaction with UV-irradiated elemental fluorine in anhydrous hydrogen fluoride (aHF) as a solvent. This method is very convenient for the preparation of some binary and ternary fluorides in which the transition metal is in the highest oxidation state.[3–8] Reactions between different starting mol ratios of $XeF_2$ and $TiF_4$ were investigated [$n(XeF_2)/n(TiF_4)$ = 4:1, 3:1, 2:1, 1:1, 1:2, 1:3]. To obtain a definitive answer as to whether the isolated products are single phases or mixtures of different ones, the isolated solids were dissolved in aHF and recrystallised. Although different kinds of crystals were observed, all attempts resulted so far only in the determination of the crystal structure of $3XeF_6{\cdot}4TiF_4$. The synthesis of $3XeF_6{\cdot}4TiF_4$ was later achieved by the photochemical fluorination of a $XeF_2/TiF_4$ mixture with a mol ratio of $XeF_2/TiF_4$ = 3:4 in aHF.

The crystal structure of $3XeF_6{\cdot}4TiF_4$ consists of $[XeF_5]^+$ cations and previously unknown discrete $[Ti_4F_{19}]^{3-}$ anions. The compound $3XeF_6{\cdot}4TiF_4$ is therefore formulated as $[XeF_5]_3[Ti_4F_{19}]$. There are three crystallographically nonequivalent $[XeF_5]^+$ cations in the crystal structure of $[XeF_5]_3$-$[Ti_4F_{19}]$. All three $[XeF_5]$ units have well-known, slightly distorted pseudo-octahedral symmetry,[9] where the axial Xe–$F_{ax}$ distances [Xe1–F13 1.820(5) Å, Xe2–F23 1.811(5) Å, Xe3–F33 1.822(5) Å] are slightly shorter than the equatorial [Xe1–$F_{eq}$ 1.834(5)–1.847(5) Å, Xe2–$F_{eq}$ 1.826(5)–1.852(5) Å, Xe3–$F_{eq}$ 1.838(5)–1.849(5) Å] distances. Each of the $[XeF_5]$ units makes further contacts with the fluorine atoms of three $[Ti_4F_{19}]^{3-}$ anions, where Xe1···F 2.568, 2.664, 2.694 and 2.812 Å; Xe3···F 2.559, 2.594 and 2.610 Å and Xe2···F 2.470, 2.707 and 2.712 Å, with the next closest F(–Xe2) being at 3.146 Å. The sum of the Xe···F van der Waals radii is 3.63 Å.[10] Although the number and strength of these contacts is not the same for all three $[XeF_5]$ units, they all show the same feature. The anionic fluorine atoms involved in these contacts are arranged symmetrically around the pseudo-fourfold axis of the $[XeF_5]$ unit (i.e., around the sterically active nonbonding valence-electron pair of Xe).

---

[a] Jožef Stefan Institute,
Jamova 39, SI-1000 Ljubljana, Slovenia
Fax: +386-1-477-3155,
E-mail: zoran.mazej@ijs.si

The most interesting feature of the determined crystal structure of $[XeF_5]_3[Ti_4F_{19}]$ is the presence of $[Ti_4F_{19}]^{3-}$ anions. The compounds containing isolated $[TiF_6]^{2-}$,[11] $[Ti_2F_{11}]^{3-}$,[12] $[Ti_2F_{10}]^{2-}$[13,14] and $[Ti_4F_{18}]^{2-}$[15,16] or polymeric $([Ti_7F_{30}]^{2-})_n$,[17] $([Ti_8F_{33}]^{-})_n$,[18] $([TiF_5]^{-})_n$[19] and $([Ti_2F_9]^{-})_n$[16] anions are known. Contrary to a literature statement,[15] the discrete $[TiF_7]^{3-}$ anion is not known. Fluorides of the type $A_3TiF_7$ ($A = Rb^+, Cs^+, [NH_4]^+$)[20] contain $[TiF_6]^{2-}$ anions and "free" fluoride ions[21] and are better formulated as $A_3F(TiF_6)$.[22]

The previously known $[Ti_4F_{18}]^{2-}$ anion[15,16] consists of four $[TiF_6]$ octahedra that are associated by corners in order to built a tetrahedron of octahedra. In this way, Ti atoms are situated at the vertices of a tetrahedron (with nonbonding Ti···Ti distances in the 3.829–3.875 Å range and Ti···Ti···Ti angles around 60°),[15,16] connected by six bridging fluorine atoms and capped by three terminal fluorine atoms each (Figure 1a).

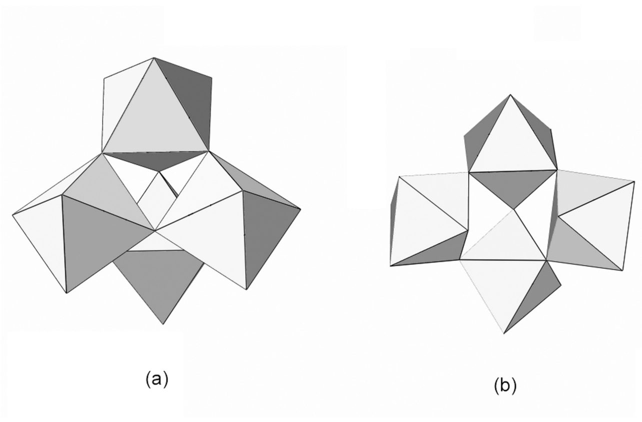

Figure 1. $[Ti_4F_{18}]^{2-}$ (a) and $[Ti_4F_{19}]^{3-}$ (b) anions, each comprising four $[TiF_6]$ octahedra.

The $[Ti_4F_{19}]^{3-}$ anion also consists of four $[TiF_6]$ octahedra that are associated in a manner different from that in $[Ti_4F_{18}]^{2-}$. Two $\mu_3$-$[TiF_6]$ octahedra sharing a joint apex (Figure 1b, octahedra in the middle) are additionally bridged by two $\mu_2$-$[TiF_6]$ units. The nonbonding Ti···Ti distances (3.791–3.865 Å) are in the same range as those in $[Ti_4F_{18}]^{2-}$. Only the Ti···Ti distance between the Ti atoms belonging to the two $\mu_2$-$[TiF_6]$ units is much longer (4.946 Å). The $[Ti_4F_{19}]^{3-}$ anion and three crystallographically independent $[XeF_5]^+$ cations and numbering scheme adopted are given in Figure 2. The packing diagram is depicted in Figure 3.

The Ti–$F_t$ [$F_t$: terminal fluorine atom; 1.747(5)–1.839(5) Å] and Ti–$F_b$ [$F_b$: bridging fluorine atom; 1.935(4)–2.044(4) Å] bond lengths in $[XeF_5]_3[Ti_4F_{19}]$ are comparable to those found for $[Ti_4F_{18}]^{2-}$ salts [Ti–$F_t$ 1.752(4)–1.783(4) Å; Ti–$F_b$ 1.959(4)–2.019(4) Å],[15,16] and both sets of distances are in agreement with those previously observed in various $Ti^{IV}$ fluoride complexes.[23,24] Some of the Ti–$F_t$ distances (1.795–1.839 Å) are slightly elongated due to weak $F_t$···Xe interactions (2.470–2.721 Å).

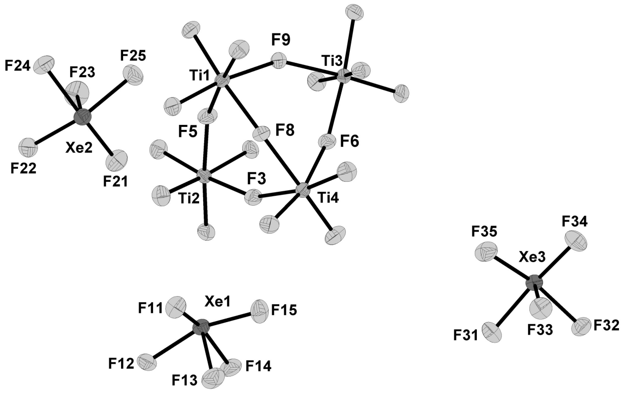

Figure 2. The $[Ti_4F_{19}]^{3-}$ anion and three crystallographically independent $[XeF_5]^+$ cations (ellipsoids are drawn at 40% probability). Selected distances [Å] and angles [°], cations: Xe–$F_{ax}$, Xe1–F13 1.820(5), Xe2–F23 1.811(5), Xe3–F33 1.822(5); Xe–$F_{eq}$, Xe1–F14 1.834(5), Xe1–F15 1.841(5), Xe1–F12 1.841(5), Xe1–F11 1.847(5), Xe2–F21 1.826(5), Xe2–F22 1.839(5), Xe2–F25 1.849(5), Xe2–F24 1.852(5), Xe3–F34 1.838(5), Xe3–F32 1.843(5), Xe3–F35 1.844(5), Xe3–F31 1.849(5); anions: av Ti–$F_t$ 1.742 Å, av Ti–$F_b$ 1.975 Å; Ti2–F3–Ti4 155.8(2), Ti1–F5–Ti2 152.7(3), Ti3–F6–Ti4 147.8(2), Ti1–F8–Ti4 150.4(2), Ti1–F9–Ti3 149.1(3).

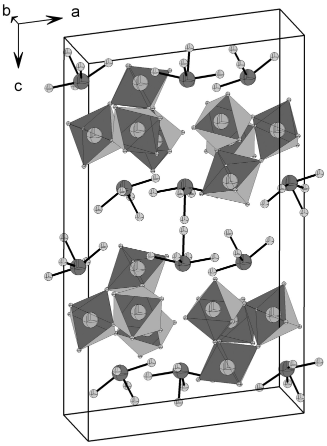

Figure 3. Packing diagram of $[XeF_5]_3[Ti_4F_{19}]$.

## Vibrational Spectra

The Raman spectrum of $[XeF_5]_3[Ti_4F_{19}]$ is shown in Figure 4 with additional details given in Table 1.

The Raman spectra recorded for the powdered sample obtained by synthesis and the Raman spectra recorded for the single crystals of $[XeF_5]_3[Ti_4F_{19}]$ were essentially identical. The bands above $700\ cm^{-1}$ could be readily assigned to the vibration of the anion. The band at $742\ cm^{-1}$ belongs to the symmetric in-phase terminal Ti–F stretching mode, where the frequency of the band increases with increasing content of $TiF_4$ and decreasing charge of the anion {i.e., $[TiF_6]^{2-}$ ≈600,[27] $[Ti_2F_{10}]^{2-}$ 703,[27] $([TiF_5]^{-})_n$ 724,[19] $[Ti_4F_{18}]^{2-}$ ≈746,[15,16] $([Ti_2F_9]^{-})_n$ ≈753,[16] $([Ti_7F_{30}]^{2-})_n$ 765,[17] $[Ti_3F_{13}]^{-}$ 770,[27] $[Ti_6F_{25}]^{-}$ 784[27] and $([TiF_4])_n$ $807\ cm^{-1}$[27]}. The assignments below $700\ cm^{-1}$ were done by comparison with the literature data for the $[XeF_5]^+$ cat-

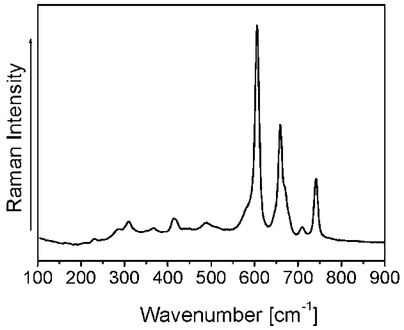

Figure 4. Raman spectrum of $[XeF_5]_3[Ti_4F_{19}]$.

Table 1. Raman data [cm$^{-1}$] of $[XeF_5]_3[Ti_4F_{19}]$ together with literature data for $[XeF_5][AsF_6]$, $[XeF_5]_2[PdF_6]$ and $[XeF_5][RuF_6]$.[25,26]

| $[XeF_5]_3[Ti_4F_{19}]$ | $[XeF_5][AsF_6]$ | $[XeF_5]_2[PdF_6]$ | $[XeF_5][RuF_6]$ | Assignments |
|---|---|---|---|---|
| 742(30) | | | | $[Ti_4F_{19}]^{3-}$ |
| 710(5) | | | | $[Ti_4F_{19}]^{3-}$ |
| 680(sh.)[a] | 664(5), sh. | 676(3) | 677(9) | $[XeF_5]^+$, $\nu_7(E)$ |
| 670(25, sh.) | 661(30) | 660(5), sh. | 664(1), sh. | $[XeF_5]^+$, $\nu_7(E)$ |
| 659(58) | 671(29) | 653(100) | 670(22) | $[XeF_5]^+$, $\nu_1(A_1)$ |
| 606(100) | 629(100) | 590(71) | 606(68) | $[XeF_5]^+$, $\nu_2(A_1)$ |
| | 623(5), sh. | 606(20) | 600(10), sh. | $[XeF_5]^+$, $\nu_4(B_1)$ |
| 582(12, sh.) | | | | $[Ti_4F_{19}]^{3-}$ |
| 516(2, sh.) | | | | $[Ti_4F_{19}]^{3-}$ |
| 489(4) | | | | $[Ti_4F_{19}]^{3-}$ |
| 418(5) | 412(6) | 425(3) | 416(4) | $[XeF_5]^+$, $\nu_8(E)$ |
| 412(6) | 407(6) | 396(3) | 416(4) | $[XeF_5]^+$, $\nu_8(E)$ |
| 368(3) | | | | $[Ti_4F_{19}]^{3-}$ |
| 310(8) | 296(15) | 309(10) | 312(2) | $[XeF_5]^+$, $\nu_3(A_1)$ |
| 284(5) | | | | $[Ti_4F_{19}]^{3-}$ |
| 250(<1) | 255(1) | | | $[XeF_5]^+$, $\nu_6(B_2)$ |
| 231(2) | 240(0+) | 230(4) | 236(1) | $[XeF_5]^+$, $\nu_5(B_1)$ |
| | 214(4) | [230] | 215(2) | $[XeF_5]^+$, $\nu_9(B)$ |

[a] sh. = shoulder.

ion. The possibility that some of the cation vibrational bands overlap with the anionic ones could not be completely excluded.

## Conclusions

In spite of a large number of existing compounds in the $XeF_6/MF_4$ (M = transition element) system,[28] reports about the crystal structures of the corresponding $[XeF_5]^+$ salts are limited to M = Pd, Ni and Cr. The crystal structure of $[XeF_5]_2[MF_6]$ (M = Pd,[29] Ni[30]) consists of $[XeF_5]^+$ and $[MF_6]^{2-}$ entities. The main structural features of $XeF_5CrF_5$ are infinite $[CrF_5]^-$ chains of $[CrF_6]$ octahedra and $[XeF_5]^+$ cations[31] {the crystal structure of $(XeF_5CrF_5)_4{\cdot}XeF_4$ was also reported[32]}. The crystal structure of $[XeF_5]_3[Ti_4F_{19}]$ differs from the previously described ones and represents a unique case containing discrete $[M_4F_{19}]^{3-}$ anions.

## Experimental Section

**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! $XeF_6$ and all of its products are susceptible to moisture and react with water to form $XeO_3$, a compound that easily detonates.[33] For treatment of HF injuries see reference.[34]

**Reagents:** The compound $TiF_4$ was synthesised by the reaction of $TiCl_3$ (Aldrich, 99.999%) and elemental fluorine in aHF. The X-ray powder diffraction pattern and Raman spectrum of isolated $TiF_4$ were in agreement with the literature data.[35,36] Xenon difluoride was prepared by the photochemical reaction between Xe and $F_2$ at ambient temperature.[37]

**Raman Spectroscopy:** Raman spectra were recorded with a Renishaw Raman Imaging Microscope System 1000 by using a He–Ne laser with a wavelength of 632.8 nm.

**X-ray Powder Diffraction Patterns:** X-ray powder diffraction patterns were obtained by using the Debye–Scherrer technique with Ni-filtered Cu-$K_\alpha$ radiation. Samples were loaded into quartz capillaries (0.3 mm) in a dry box. Intensities were estimated visually.

**Synthesis of $[XeF_5]_3[Ti_4F_{19}]$:** In a dry-box, a sample of $XeF_2$ (1.20 mmol) and $TiF_4$ (1.60 mmol) were loaded into a FEP (tetrafluoroethylene–hexafluoropropylene) reaction vessel. aHF (8 mL) was condensed onto the solid at 77 K, and the reaction mixture was brought to ambient temperature. Fluorine was slowly added at ambient temperature to a pressure of 6 bar in the reaction vessel. A 400 W medium pressure mercury lamp (Baird and Tatlock, London, Type 400 LQ) was used as the UV source. After 6 d, volatiles were pumped off at 77 K and a new portion of fluorine was added. The reaction mixture was left stirring for 22 d at ambient temperature. A clear yellowish solution was obtained above an insoluble material. Volatiles were slowly pumped off at ambient temperature for 2 h, leaving behind a colourless solid. The final mass of the isolated solid was 0.501 mg (calcd. for $[XeF_5]_3[Ti_4F_{19}]$ 0.500 mg). The Raman spectrum was recorded, the X-ray powder diffraction diagram was taken and a chemical analysis was obtained {$[XeF_5]_3[Ti_4F_{19}]$ (1231.35): calcd. for Ti 15.56; found Ti 15.0}.

**Crystal Growth of $[XeF_5]_3[Ti_4F_{19}]$:** Single crystals growth of $[XeF_5]_3[Ti_4F_{19}]$ was carried out in a T-shaped apparatus consisting of two FEP tubes (19 mm. o.d., and 6 mm. o.d.). $[XeF_5]_3[Ti_4F_{19}]$ (approximately 150 mg) was loaded into the wider arm of the crystallisation vessel in the dry box. aHF (≈3 mL) was then condensed onto the starting material at 77 K. The crystallisation mixture was brought up to ambient temperature, and the clear colourless solution was decanted into the narrower arm. Evaporation of the solvent from this solution was carried out by maintaining a temperature gradient corresponding to about 10 K between both tubes for 5 weeks. The result of this treatment was to slowly condense the aHF from the narrower tube into the wider tube, leaving behind the crystals. Selected single crystals of $[XeF_5]_3[Ti_4F_{19}]$ were placed inside 0.3-mm quartz capillaries in a dry box and their Raman spectra recorded.

**Crystal Structure Determination:** Crystals were immersed in perfluorinated oil (Perfluorodecalin, ABCR, 98%) in the dry box, selected under a microscope and transferred into the cold nitrogen stream of the diffractometer. Crystal data for $[XeF_5]_3[Ti_4F_{19}]$: $M_t$ = 1231.4 g mol$^{-1}$, space group $P2_1/c$ (No. 14), crystal system monoclinic, $a$ = 12.0866(5) Å, $b$ = 9.5615(3) Å, $c$ = 21.0377(8) Å, $\beta$ = 96.301(2)°, $V$ = 2416.6(2) Å$^3$, $Z$ = 4, $\rho_{calcd.}$ = 3.385 g cm$^{-3}$, $T$ = 200 K. Data collection: Rigaku AFC7S diffractometer equipped with a Mercury CCD area detector by using graphite monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71069). Reflections collected: 19129, independent reflections: 5533 ($R_{int}$ = 0.0463), observed reflections [$I > 2\sigma(I)$]: 4846, $\mu$ = 5.663 mm$^{-1}$. Structural analysis and refinement: The structure was solved by direct methods with the use of the SIR-92[38] program (program package TeXsan[39]) and refined with SHELXL-97[40] software, implemented in the program package WinGX.[41] The figures were prepared using DIAMOND 3.1[42] and Balls & Sticks.[43] Refinement method: Full matrix least-squares on $F^2$. Data-to-parameter ratio: 5533:371. Final $R$ indices: $R_1 = 0.0543$ [$I > 2\sigma(I)$], $wR_2 = 0.1417$ [$I > 2\sigma(I)$], $R_1 = 0.0615$ (all data), $wR_2 = 0.1539$ (all data), GOF on $F^2 = 1.2$, largest difference peak/hole: 2.992/–1.984 e Å$^{-3}$. Further details of the crystal-structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-420743.

## Acknowledgments

The authors gratefully acknowledge the Slovenian Research Agency (ARRS) for financial support of the present study within the research program P1-0045 Inorganic Chemistry and Technology.

---

[1] B. Žemva, J. Slivnik, M. Bohinc, *J. Inorg. Nucl. Chem.* **1976**, *38*, 73–74.

[2] Using $XeF_2$ or $XeF_6$ is a matter of choice. The use of $XeF_2$, which also requires the accompaniment of elemental fluorine and repeated UV photolyses, instead of $XeF_6$ results in longer reaction times.

[3] O. Graudejus, S. H. Elder, G. M. Lucier, C. Shen, N. Bartlett, *Inorg. Chem.* **1999**, *38*, 2503–2509.

[4] G. M. Lucier, J. M. Whalen, N. Bartlett, *J. Fluorine Chem.* **1998**, *89*, 101–104.

[5] J. M. Whalen, G. M. Lucier, L. Chacón, N. Bartlett, *J. Fluorine Chem.* **1998**, *88*, 107–110.

[6] Z. Mazej, *J. Fluorine Chem.* **2002**, *114*, 75–80.

[7] Z. Mazej, *J. Fluorine Chem.* **2002**, *118*, 127–129.

[8] Z. Mazej, E. Goreshnik, *Eur. J. Inorg. Chem.* **2008**, 1795–1812.

[9] H. Selig, J. H. Holloway, *Top. Curr. Chem.* **1984**, *124*, 33–90.

[10] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.

[11] R. J. H. Clark, D. C. Bradley, P. Thornton, "The Chemistry of Titanium, Zirconium and Hafnium" in *Comprehensive Inorganic Chemistry* (Eds.: J. C. Bailar Jr, H. J. Emeléus, Sir R. Nyholm, A. F. Trotman-Dickenson), Pergamon Press, Oxford, **1973**, pp. 415–416.

[12] L. Q. Tang, M. S. Dadachov, X. D. Zou, *Z. Kristallogr. New Cryst. Struct.* **2001**, *216*, 387–388.

[13] M. S. Dadachov, L. Q. Tang, X.-D. Zou, *Z. Kristallogr. New Cryst. Struct.* **2000**, *215*, 605–606.

[14] H. Akutsu, K. Ozeki, T. Ozaki, K. Nozawa, M. Kinoshita, K. Kozawa, T. Uchida, *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1869–1873.

[15] A. Decken, H. D. B. Jenkins, C. Knapp, G. B. Nikiforov, J. Passmore, J. M. Rautiainen, *Angew. Chem. Int. Ed.* **2005**, *44*, 7958–7961.

[16] Z. Mazej, E. Goreshnik, *Inorg. Chem.* **2009**, *48*, 6918–6923.

[17] B. G. Müller, *J. Fluorine Chem.* **1981**, *17*, 489–499.

[18] H. Bialowons, B. G. Müller, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1223–1226.

[19] S. Cohen, H. Selig, *J. Fluorine Chem.* **1982**, *20*, 349–356.

[20] B. Hofmann, R. Hoppe, *Z. Anorg. Allg. Chem.* **1979**, *458*, 151–162.

[21] D. Babel, A. Tressaud, "Crystal Chemistry of Fluorides" in *Inorganic Solid Fluorides, Chemistry and Physics* (Ed.: P. Hagenmuller), Academic Press, Orlando, **1985**, pp. 175–178.

[22] R. Hoppe, *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 63–87.

[23] H. W. Roesky, I. Haiduc, *J. Chem. Soc., Dalton Trans.* **1999**, 2249–2264.

[24] E. F. Murphy, R. Murugavel, H. W. Roesky, *Chem. Rev.* **1997**, *97*, 3425–3468.

[25] C. J. Adams, N. Bartlett, *Isr. J. Chem.* **1978**, *17*, 114–125.

[26] Sh. Sh. Nabiev, *Russ. J. Inorg. Chem.* **1995**, *40*, 1936–1943.

[27] K. O. Christe, C. J. Schack, *Inorg. Chem.* **1977**, *16*, 353–359.

[28] B. Žemva in *Encyclopedia of Inorganic Chemistry* (Eds.: R. B. King), John Wiley & Sons, Chichester, **1994**, vol. 5, pp. 2660–2680.

[29] K. Leary, D. H. Templeton, A. Zalkin, N. Bartlett, *Inorg. Chem.* **1973**, *12*, 1726–1730.

[30] A. Jesih, K. Lutar, I. Leban, B. Žemva, *Eur. J. Solid State, Inorg. Chem.* **1991**, *28*, 829–840.

[31] K. Lutar, H. Borrmann, B. Žemva, *Inorg. Chem.* **1998**, *37*, 3002–3006.

[32] K. Lutar, I. Leban, T. Ogrin, B. Žemva, *Eur. J. Solid State, Inorg. Chem.* **1992**, *29*, 713–727.

[33] S. M. Williamson, C. W. Koch, *Science* **1963**, *139*, 1046–1047.

[34] D. Peters, R. Miethchen, *J. Fluorine Chem.* **1996**, *79*, 161–165.

[35] K. O. Christe, C. J. Schack, *Inorg. Chem.* **1977**, *16*, 353–359.

[36] H. Bialowons, M. Müller, B. G. Müller, *Z. Anorg. Allg. Chem.* **1995**, *621*, 1227–1231.

[37] A. Šmalc, K. Lutar in *Inorganic Syntheses* (Ed.: R. N. Grimes), Wiley, New York, **1992**, vol. 29, p. 1.

[38] A. Altomare, M. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350.

[39] Molecular Structure Corporation, *teXsan for Windows: Single Crystal Structure Analysis Software*, version 1.06, The Woodlands, TX, USA, **1997–1999**.

[40] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.

[41] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

[42] *DIAMOND* v3.1, Crystal Impact GbR, Bonn, Germany, **2004–2005**.

[43] T. C. Ozawa, S. J. Kang, *J. Appl. Crystallogr.* **2004**, *37*, 679; *Balls & Sticks: Easy-to-Use Structure Visualization and Animation Creating Program* (http://www.softbug.com/toycrate/bs/).

Received: August 5, 2009