Contents lists available at ScienceDirect



Journal of Fluorine Chemistry



journal homepage: www.elsevier.com/locate/fluor

Short Communication

(N₂H₆)₃TaF₈TaF₇HF₂ and **Na₇TaF₈(TaF₇)₂**: Novel fluoride tantalates with different isolated anionic polyhedra



E. Goreshnik

Department of Inorganic Chemistry and Technology, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

ARTICLE INFO

ABSTRACT

Article history: Received 14 December 2016 Received in revised form 4 January 2017 Accepted 6 January 2017 Available online 13 January 2017

Keywords: Heptafluorotantalate Octafluorotantalate Crystal structure Raman spectra

1. Introduction

Tantalum pentahalides because of its Lewis acidity and partial coordination unsaturation form various adducts with O-donors [1,2], *N*-heterocyclic carbenes [3], diphosphine and diarsine [4] etc. Tantalum pentafluoride can also accept fluorine anions, resulting in the formation of $[TaF_6]^-$, $[TaF_7]^{2-}$, and $[TaF_8]^{3-}$ complex anions. Increasing the acidity of the solution promotes the formation of hexafluoridotantalate-anion, whereas solution dilution or adding alkali metal fluorides shifts the equilibriums towards [TaF₇]²⁻ and $[TaF_8]^{3-}$ [5]. The lower solubility of MTaF₇ compounds (in comparison with $M(TaF_6)_2$ ones) is an important reason of the crystallization of alkaline earth metals heptafluoridotantalates(V) even from anhydrous HF [6]. The most widely studied are salts of inorganic cations and protonated organic amines containing octahedral complex [TaF₆]⁻anion. Heptafluoridotantalates(V) appear much rarely. Industrially important K₂TaF₇ salt is well studied and structurally characterized [7,8,]. The crystal structures of Rb_2TaF_7 [9], $MTaF_7$ (M = Ca, Sr, Ba, Pb) [6], (enH₂)TaF₇ [10], $(C_4H_{10}N_2H_2)TaF_7$ [11], $(trenH_4)(TaF_7)_2$ and $(trenH_4)(TaF_7)_2 \cdot H_2O$ [12], $(trenH_3)TaF_7 \cdot F$ [13], $(C_2H_5N_4)_2TaF_7$, $(C_2H_6N_4)TaF_7 \cdot H_2O$ [14] have been reported. The primary crystallographic information, i.e. crystal symmetry and unit cell parameters, for the Na₂TaF₇, $Na_2TaF_7 H_2O$ [15], $Li_2TaF_7 H_2O$, M_2TaF_7 (M=, Cs, NH₄) [16] $MTaF_7 \cdot 6H_2O$ (M = Mn, Co, Ni, Zn, and Cd) compounds was also published [17]. Octafluoridotantalate(V) anions were found in only two compounds, Na₃TaF₈ [18] and Ba₅F(TaF₈)(TaF₆O)₂ [19]. X-ray

The reaction of hydrazinium difluoride and TaF₅ in 66% hydrofluoric acid water solution resulted in the formation of rather unusual (N_2H_6)₃TaF₈TaF₇HF₂ compound. Similar procedure started from a TaF₅—NaF mixture performed in 35% HF water solution resulted in the formation of a Na₇TaF₈(TaF₇)₂ compound. Synthesis, crystal structures and Raman spectra of these new compounds are reported in this communication. The main feature of both compounds is the presence of discrete TaF₈^{3–} and TaF₇^{2–} anions in their crystal structures, which was also confirmed by Raman spectroscopy.

© 2017 Elsevier B.V. All rights reserved.

structural study reveals that the salt with K₃TaF₈ chemical formula is a double salt K₂TaF₇·KF [20], similarly to that in the case of (trenH₃)TaF₇·F [13]. Synthesis and characterization of hydrazinium fluoridotantalates(V) were reported many years ago [21]. The compound crystallized with N₂H₆F₂: TaF₅ ratio of 1.5:1 from 45% hydrofluoric acid water solution was identified, basing on vibrational spectroscopy and mass balance, as (N₂H₆)₃(TaF₈)₂H₂O. As authors [21] concluded: "The investigation of the formation conditions of hydrazinium fluorotantalates posed more questions than were answered mainly because the ionic equilibria in the solutions containing tantalum, hydrofluoric acid and hydrazine are very complex". Furthermore, structural data of the isolated hydrazinium fluorotantalates were absent, their X-ray powder diffraction patterns were complicated and indexing of them was not attempted. Reaction of hydrazinium difluoride and TaF₅ in 66% HF water solution resulted in the formation of rather unusual (N₂H₆)₃TaF₈TaF₇HF₂ compound. An intention to grow Na₃TaF₈ crystals for comparison of its Raman spectrum and the spectrum of $(N_2H_6)_3$ TaF₈TaF₇HF₂ resulted in the formation of Na₇TaF₈(TaF₇)₂ compound. Synthesis, crystal structures and Raman spectra of these new compounds are reported in this communication.

2. Results and discussion

2.1. Crystal structure

The crystal structure of $(N_2H_6)_3$ TaF₈TaF₇HF₂ compound consists of discrete TaF₈³⁻, TaF₇²⁻ and HF₂⁻ anions, bound with the N₂H₆²⁺ cations via N—H···F hydrogen bonds (Fig. 1). The presence of both seven- and eight-coordinated tantalum centrum was reported

E-mail address: evgeny.goreshnik@ijs.si (E. Goreshnik).



Fig. 1. Crystallographically independent part of the structure of $(N_2H_6)_3$ TaF₈. TaF₇HF₂ salt. Thermal ellipsoids are drawn at 50% probability.

earlier for a Ba₅F(TaF₈)(TaF₆O)₂ [19] compound. The Ta1 atom from TaF₈³⁻ anion possesses a square-antiprismatic surrounding. Such a geometry agrees well with a Raman spectrum (see below). Eight Ta—F bonds lengths vary from 1.943(3) to 2.111(3) Å. Similar tantalum atom coordination sphere with the Ta—F distances of 1.981(3) – 2.439(3) Å (153 K) was observed in recently redetermined structure of Na₃TaF₈ salt [22]. In above mentioned Ba₅F(TaF₈)(TaF₆O)₂ corresponding values were 1.941–2.040 Å [19]. Two shortest Ta1–F distances, namely 1.943(3) and 1.951(3) Å, correspond to terminal fluorine atoms, whereas other six participate in a formation of rather strong N—H…F hydrogen bonds, connecting TaF₈³⁻ anion with eight N₂H₆²⁺ cations.

The TaF₇ anion adopts a shape of distorted pentagonal bipyramide, with two closer located axial fluorine ligands (Ta2– F_{ax} 1.888(4)–1.894(4) Å) and five slightly removed from the central atom equatorial F centers (Ta2– F_{ax} 1.930(4)–2.002(3) Å). Four equatorial fluorine atoms form hydrogen bonds with six cations. Similar surrounding of the Ta ion was found earlier in CaTaF₇ with the 1.878(14)–2.044(13) Å Ta—F bonds lengths. One may note that in all other structurally characterized metal heptafluoridotantalates the TaF₇ polyhedron may be described as a mono-capped trigonal prism, whereas in hybrid salts with organic cations monocapped trigonal prismatic and pentagonal bi-pyramidal TaF₇²⁻ geometry appears nearly evenly (Table 1.) The flexibility of sevencoordination in general [23] and in particular for tantalates is generally well known. As K.O. Christe [24] has noted, "heptacoordinated structures exhibit fluxionality and are readily deformed from the idealized 1/3/3, 1/5/1, or 1/4/2 arrangements by the presence of polyatomic ligands, solid-state and packing effects, or the influence of counterions". One may also add, that in metal salts cation - anion interactions are probably more susceptible to packing, whereas in the case of hybrid organic-inorganic compounds the geometry of organic cations influences on hydrogen bonds direction and, in turn, could be responsible for the formation of definite shape of TaF_7^{2-} polyhedron.

The HF_2^- anion appears to be a little bit asymmetric, with the F—H distances of 1.08(8)–1.18(8) Å. The F…F distance of 2.264(5) Å is practically the same length as those in structures of [Cu(HF₂) (pyz)₂]SbF₆ (2.286(2) Å), [Cu₂F(HF)(HF₂)(pyz)₄](SbF₆)₂ (2.281(4) Å) at 150 K [25], a little bit longer than that in the crystal structure of [N(CH₃)₄][HF₂] (2.213(4) Å) [26], but shorter than those in Ba₄F₄HF₂(PF₆)₃ (2.28(2) Å), Pb₂F₂(HF₂)(PF₆) (2.32(4) Å), Ca(HF₂)₂ (2.283(2) Å) [27] and KHF₂ (2.277(6) Å) [28]. Each F atom forms rather strong hydrogen bonds with two cations.

There are four crystallographically independent hydrazinium cations in structure discussed. Two of them are built from two pairs of symmetrically generated (axis 2) atoms. The N—N distances form a narrow range of 1.422(9)–1.441(9) Å. Each of N₂H₆²⁺ moieties demonstrate a unique anionic surrounding despite a formation of equal (six) amount of N—H···F hydrogen bonds. The N1—N1 molecule is bound to four TaF₈³⁻ and two HF₂⁻ units. The N2—N2 is surrounded by four TaF₈³⁻ and two TaF₇²⁻ anions. The N3—N4 is bonded to three pairs of HF₂⁻, TaF₈³⁻ and TaF₇²⁻ anions respectively. The last one, N5—N6 cation is linked to one HF₂⁻, two TaF₈³⁻ and three TaF₇²⁻ units. Mentioned above hydrogen bonds connect anions and cations into three-dimensional network. Hydrogen bonds in this structure appear to be rather strong, with

Table 1				
Observed geor	metry in struct	urally characterize	d heptafluoridotant	alate

Compound	Polyhedron	Т, К	Ta—F distances	Ref.
K ₂ TaF ₇	CTP [*] dist	RT	1.918-1.975	[7,8]
K ₂ TaF ₇ ·KF	CTP dist	RT	1.9643(1)-1.9953(1)	[19]
Rb ₂ TaF ₇	CTP	RT	1.940(5)-1.945(2), 2.013(3)	[9]
Rb ₂ TaF ₇	CTP	123	1.933(3)-1.941(4), 1.997(3)	[9]
CaTaF ₇	BP dist	200	1.878(14)-1.894(12), 1.940(16)-2.044(13)	[6]
SrTaF7	CTP	200	1.908(16)-2.019(12)	[6]
BaTaF7	CTP	200	1.916(5)-2.004(5)	[6]
PbTaF7	CTP	200	1.868(3)-1.982(3)	[6]
(enH ₂)TaF ₇	BP	100	1.900(1), 1.961(5)-2.005(2)	[10]
(pipH ₂)TaF ₇	BP	RT	1.906(2), 1.949(2)-1.996(2)	[11]
[H4tren](TaF7)2·2H2O	CTP dist	RT	1.894(7)-1.969(7), 2.019(7)	[12]
[H4tren](TaF7)2·2H2O	CTP dist	RT	1.914(7)-1.988(5), 1.990(5)	[12]
[H ₄ tren](TaF ₇) ₂	CTP dist	RT	1.86(2)-1.96(2), 2.00(2)	[12]
[H4tren](TaF7)2	BP	RT	1.89(2)-1.90(2), 1.93(1)-2.01(1)	[12]
[H3tren][TaF7]F	CTP dist	RT	1.932(7)-1.966(6)	[13]
(C ₂ H ₅ N ₄) ₂ TaF ₇	CTP	RT	1.859(2)-1.999(1), 2.024(2)	[14]
$(C_2H_6N_4)T_aF_7 \cdot H_2O$	BP dist	RT	1.890(3)-1.895(3),	[14]
			1.914(7)-2.001(9)	
$(N_2H_6)_3(TaF_8)(TaF_7)HF_2$	BP dist	150	1.888(4)-1.894(4),	This work
			1.930(4)-2.002(3)	
Na7TaF8(TaF7)2	CTP dist	150	1.926(5)-1.961(4),	This work
			2.011(4)-2.018(4)	

^{*} CTP – mono-capped trigonal prism, BP – pentagonal bi-pyramide, dist – distorted geometry, for BP geometry the shortest distances to F atoms at apical positions are typed first and separated by commas, for CTP distances to the "capped" fluorine atoms are printed at the end and separated by commas (if distinguishable). For [H₄tren](TaF₇)₂·2H₂O and [H₄tren](TaF₇)₂ parameters for each Ta center are shown in separate row.



Fig. 2. Crystallographically independent part of the structure of $Na_7TaF_8(TaF_7)_2$ salt. Thermal ellipsoids are drawn at 50% probability. Na—F bonds are omitted for clarity.

H···F distances of 1.77–2.05 Å and N–H···F angles varying from 141.4 to 173.7°.

The structure of compound **II** is comprised from two pairs of crystallographically independent TaF_7^{2-} and TaF_8^{3-} anions and eight independent Na cations (Fig. 2). Both TaF_8^{3-} anions demonstrate, similarly to that in compound I, square-antiprismatic geometry. The Ta1, F11 and F12 atoms from Ta(1)F₈ unit occupy special positions at mirror plane. Similarly, the Ta2, F22 and F24 atoms are located at mirror plane in the case of Ta(2)F₈ moiety. The Ta-F distances vary from 1.962(7) to 2.021(5) Å similarly to those in (N₂H₆)₃TaF₈TaF₇HF₂. Both TaF₇²⁻ anions possess mono-capped trigonal prismatic shape with Ta-F bonds lengths of 1.926(5)-1.961(4) Å within trigonal prism and noticeably elongated distances to capped fluorine center of 2.011(4)–2.018(4) Å. Such a shape differs from that in (N₂H₆)₃TaF₈TaF₇HF₂ and much more similar to the coordination polyhedron of tantalum atom in mentioned above BaTaF₇ [6].

Sodium ions in Na₇TaF₈(TaF₇)₂ possess unusually high coordination numbers. The Na1, Na2, Na3 and Na6 centers possess coordination number 8, whereas coordination environment of Na4, Na5, Na7 and Na8 ions comprise from 7 fluorine atoms. The Na—F distances are in the range of 2.163(8)–2.979(6) Å.

2.2. Raman spectroscopy

Raman spectrum of $(N_2H_6)_3$ TaF₈TaF₇HF₂ appears to be rather complicated, as one may expect regarding the presence of four spectroscopically distinguishable moieties (Fig. 3). Strong split peak at 1060 cm⁻¹ could be attributed to N—N vibration [29]. A pair of strong peaks at 2905 and 2964 cm⁻¹ represent *sym* and *asym* modes of N—H vibrations. The peak at 656.6 cm⁻¹ appears exactly as the same position as it was found in Raman spectrum of BaTaF₇ [6] and, consequently, belongs to TaF₇^{2–} anion. Also peak at 387.7 could be attributed to TaF₇^{2–} moiety, correspondingly to similar position in BaTaF₇.

Peak at 614.7 cm⁻¹ could be assigned to the anion HF_2^- . In [N (CH₃)₄]HF₂ the peak at 576 cm⁻¹ [26], in NaHF₂ the peak at 630 cm⁻¹ [30], in Sr₂(H₂F₃)(HF₂)₂(AsF₆) the peak at 620 cm⁻¹ [31] and the peak at 592 cm⁻¹ in Ba₄F₄(HF₂)(PF₆)₃ [27] were assigned to the symmetric HF₂⁻ anion.

On the other hand, mentioned peaks observed in $Sr_2(H_2F_3)$ $(HF_2)_2(AsF_6)$ and $Ba_4F_4(HF_2)(PF_6)_3$ were relatively weak, whereas a peak found at 620 cm⁻¹ in Raman spectrum of Na₃TaF₈ and assigned to TaF₈³⁻ vibration, was reported as a very strong [32].



Fig. 3. Raman spectra of $(N_2H_6)_3$ TaF₈TaF₇HF₂ and Na₇TaF₈(TaF₇)₂ compounds. Raman spectrum of Na₃TaF₈ has shown for comparison. Marked by asterisks two peaks at 500 and 710 cm⁻¹ in spectrum of $(N_2H_6)_3$ TaF₈TaF₇HF₂ belong to silicon grease, used for crystal mounting on a glass capillary for previously performed XRD experiment.

Moreover, in $Ca(HF_2)_2$ we did not find (possibly because of the weakness) corresponding to HF₂⁻ anion Raman mode. One may conclude, that observed in Raman spectrum of $(N_2H_6)_3TaF_8TaF_7HF_2$ at 614.7 $\rm cm^{-1}$ peak belongs to $\rm TaF_8$ unit, and peak from $\rm HF_2^-$ anion is invisible (or appears as a very small shoulder on the lower frequency side of mentioned peak). The Raman spectrum of $Na_7TaF_8(TaF_7)_2$ appears, as could be expected, much simpler and easier for assignment than that for $(N_2H_6)_3TaF_8TaF_7HF_2$. Peaks at 285, 343, and 651 cm⁻¹ basing on similarity with the Raman spectra of MTaF₇ (M=Ca, Sr, Pb, Ba) [6], originate from TaF_7^{2-} anion. Weak doublet at 382/394 cm⁻¹, observed in the Raman spectrum of K₂TaF₇ [8] at 377/390 cm⁻¹, also belongs therefore to TaF_7^{2-} unit. The strongest peak from TaF_8 moiety, found in the Raman spectrum of Na_3TaF_8 at 616 cm⁻¹, appears in the spectrum of Na₇TaF₈(TaF₇)₂ at 620 cm⁻¹. Basing on rather low intensity of this band comparatively to those from TaF_7^{2-} , one may assume that weak peaks, visible in the spectrum of Na₃TaF₈ at 372 and 410 cm⁻¹ respectively, are invisible because too low intensity.

3. Conclusions

First time compounds containing both TaF_8^{3-} and TaF_7^{2-} discrete anions were obtained and characterized. One may emphasize, that the only two compounds (namely Na₃TaF₈ and Ba₅F(TaF₈)(TaF₆O)₂) containing TaF₈³⁻ anion were earlier structurally characterized. The appearance of both – pentagonal bipyramidal and mono-capped trigonal prismatic – TaF₇²⁻ polyhedra

Table 2

Crystallographic data for (N₂H₆)₃TaF₈TaF₇ (HF₂) and Na₇TaF₈(TaF₇)₂ compounds.

Empirical formula	$F_{17}H_{19}N_6Ta_2$	F ₂₂ Na ₇ Ta ₃
Formula weight	788.06	1121.78
Crystal system	orthorhombic	monoclinic
Space group	Pbcm (#60)	$P2_{1}/m$ (#11)
T, K	150	150
a, Å	11.4019(4)	7.66154(16)
b, Å	11.6967(4)	26.4269(6)
c, Å	22.1807(7)	7.83676(19)
α	90	90
β	90	92.757(2)
γ	90	90
V, Å ³	2958.09(18)	92.757(2)
Z	8	4
Dcalc., g/cm ³	3.539	4.701
F(000)	2880	1976
Radiation	ΜοΚα	ΜοΚα
μ , mm ⁻¹	14.983	21.086
Goodness-of-fit on F ²	1.280	1.124
R ^a	0.0263	0.034
wR ^b	0.0600	0.0637

 $\overset{a}{} \frac{R = \sum (||F_0| - |F_c||) / \sum |F_0|.}{\omega R} = \left(\sum \omega \left(|F_0|^2 - |F_c|^2 \right) / \sum \omega |F_0|^2 \right)^{1/2}, \\ \omega = 1 / \left[\sigma^2 \left(F_0^2 \right) + (0.0898P)^2 + 0.7472P \right], \\ where P = \left(F_0^2 + 2F_c^2 \right) / 3.$

confirms well known flexibility of seven-coordinated tantalum coordination environment. The formation of these new compound emphasizes once more how complicated are ionic equilibria in the solutions containing tantalum and hydrofluoric acid.

4. Experimental part

4.1. Synthesis

4.1.1. Starting materials

HF (Riedek-de Haen AG, 66%), $N_2H_6F_2$ (Alfa Aesar, 99%), NaF (Merck, 99%) were used as supplied. TaF₅ was prepared by fluorination of tantalum powder under high-pressure as previously described [33].

4.1.2. (N₂H₆)₃TaF₈TaF₇HF₂

A mixture of hydrazinium hydrofluoride and TaF₅ (molar ratio 1:1) was dissolved in 66% hydrofluoric acid water solution. After short heating in a water base and slow cooling crystals of $(N_2H_6)_3$ TaF₈TaF₇HF₂ compound were found. Crystals of unreacted $(N_2H_6)F_2$ and TaF₅ (identified by single crystal X-ray diffraction) were also observed.

4.1.3. $Na_7TaF_8(TaF_7)_2$

First this compound was obtained occasionally during an attempt to grow crystals of Na₃TaF₈. Unattended heating of the NaF and TaF₅ mixture (3 to 1 molar ratio) dissolved in 5% water solution of hydrofluoric acid has led to full solvent evaporation and appearance of Na₇TaF₈(TaF₇)₂ crystals. The rest of the polycrystallinic substance was not analysed. For intentional preparation a mixture of NaF and TaF₅ in a 7:3 molar ratio has been recrystallized from 35% water solution of HF (such a concentration has been chosen as a concentration of azeotropic HF—H₂O mixture). Crystals of desired compound, contaminated by crystals of NaHF₂ by-product (identified by single crystal X-ray diffraction), were grown. Additional crystallizations of the same NaF—TaF₅ mixture from 5% and from 66% water solution of HF were performed. Plate-like crystals of Na₃TaF₈ in the first case and cubic crystals of NaTaF₆ in the last case were found.

4.2. Crystallography

Single-crystal data for both compound were collected on a Gemini A diffractometer equipped with an Atlas CCD detector, using graphite monochromated MoKαradiation. The data were treated using the CrysAlisPro software suite program package [34]. Analytical absorption correction has been applied to all data sets. Structures were solved with charge-flipping method using the Superflip program (Olex crystallographic software [35]). The electron density map, obtained by Superflip software, was analysed by EDMA program [36], which gave initial models of structures. Structure refinement has been performed with the SHELXL-2014 [37] software, implemented in the program package WinGX [38] (Table 2). Figures were prepared using Diamond 3.2 software [39]. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe. 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49 7247 808 666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe. de/request for deposited data.html) on quoting the depository numbers CSD-432011 $((N_2H_6)_3TaF_8TaF_7HF_2)$ and -432010 $(Na_7TaF_8(TaF_7)_2).$

4.3. Raman spectroscopy

A Raman spectrum was measured with a Horiba Jobin–Yvon LabRAM HR spectrometer using the 632.81-nm excitation line of a He–Ne laser with a power of 17 mW. To avoid decomposition of the sample, a density filter was applied to reduce the power of the laser to 1.7 mW. An Olympus ×50 long-distance lens was used. The spectra were obtained by accumulating 50 scans with an integration time of 5 s directly in the air at room temperature. Prior to recording, the spectrometer was calibrated using a Si polycrystalline plate as a standard with a characteristic band at 520.6 cm⁻¹.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. jfluchem.2017.01.006.

References

- [1] F. Marchetti, G. Pampaloni, Chem. Commun. 48 (2012) 635-653.
- [2] M. Bortoluzzi, N. Guazzelli, F. Marchetti, G. Pampaloni, S. Zacchini, Dalton Trans. 41 (2012) 12898–12906.
- [3] M. Bortoluzzi, E. Ferretti, F. Marchetti, G. Pampaloni, S. Zacchini, Dalton Trans. 45 (2016) 6939–6948.
- [4] W. Levason, M.E. Light, G. Reid, W. Zhang, Dalton Trans. 43 (2014) 9557–9566.
- [5] A. Agulyansky, The Chemistry of Tantalum and Niobium Fluoride Compounds, Elsevier Amsterdam, 2004.
- [6] T. Bunič, M. Tramšek, E. Goreshnik, B. Žemva, Solid State Sci. 9 (2007) 88–94.
- [7] C.C. Torardi, L.H. Brixner, G. Blasse, J. Solid State Chem. 67 (1987) 21–25.
- [8] R.B. English, A.M. Heyns, E.C. Reynhardt, J. Phys. C: Solid State Phys. 16 (1983) 829–840.
- [9] N.M. Laptash, A.A. Udovenko, T.B. Emelina, J. Fluor. Chem. 132 (2011) 1152– 1158.
- [10] H. Lu, R. Gautier, M.D. Donakowski, L. Fuoco, Z. Liu, K.R. Poeppelmeier, Cryst. Growth Des. 14 (2014) 844–850.
- [11] Y. Feng, Z. Meng, Q. Huang, D. Qiu, H. Shi, Inorg. Chem. Commun. 13 (2010) 1118–1121.
- [12] M.A. Saada, A. Hémon-Ribaud, L.S. Smiri, M. Leblanc, V. Maisonneuve, J. Fluor. Chem. 126 (2005) 1246–1251.
- [13] E. Goreshnik, M. Leblanc, V. Maisonneuve, J. Solid State Chem. 177 (2004) 4023–4030.
- [14] A.A. Udovenko, R.L. Davidovich, V.B. Logvinova, J. Struct. Chem. 56 (2015) 1623-1628.
- [15] R.E. Eberts, F.X. Pink, J. Inorg. Nucl. Chem. 30 (1968) 457-462.
- [16] R.L. Davidovich, T.A. Kaidalova, T.F. Levchishina, B.I. Sergienko, Atlas of Infra-Red Absorption Spectra and X-ray Data of Complex Fluorides of IV and V Groups [in Russian], Nauka, Moscow, 1972.
- [17] R.L. Davidovich, T.F. Levchishina, T.A. Kaidailova, V.I. Sergienko, J. Less-Common Met. 27 (1972) 35–43.
- [18] J.L. Hoard, W.J. Martin, M.E. Smith, J.F. Whitney, J. Am. Chem. Soc. 76 (1954) 3820-3823.

- [19] F. Averdunk, R. Hoppe, J. Fluor. Chem. 42 (1989) 413-427.
- [20] L. Smrčok, R. Černý, M. Boča, I. Macková, B. Kubiková, Acta Crystalogr. C 66 (2010) i16-i18.
- [21] B. Frlec, M. Vilhar, J. Inorg. Nucl. Chem. 33 (1971) 4069-4076.
- [22] V. Langer, L. Smrčok, M. Boča, Acta Cryst. C 66 (2010) i85-i86.
- [23] R. Hoffmann, B.F. Beier, E.L. Muetterties, A.R. Rossi, Inorg. Chem. 16 (1977) 511– 522.
- [24] R. Haiges, J.A. Boatz, M. Yousufuddin, K.O. Christe, Angew. Chem. Int. Ed. 46 (2007) 2869–2874.
- [25] J.L. Manson, J.A. Schlueter, K.A. Funk, H.I. Southerland, B. Twamley, T. Lancaster, S.J. Blundell, P.J. Baker, F.L. Pratt, J. Singleton, R.D. McDonald, P.A. Goddard, P. Sengupta, C.D. Batista, L. Ding, C. Lee, M.-H. Whangbo, I. Franke, S. Cox, C. Baines, D. Trial, J. Am. Chem. Soc. 131 (2009) 6733–6747.
- [26] W.W. Wilson, K.O. Christe, J. Feng, R. Bau, Can. J. Chem. 67 (1989) 1898–1901.
 [27] T. Bunič, M. Tramšek, E. Goreshnik, B. Žemva, J. Solid State Chem. 181 (2008)
- 2318-2324.
- [28] J.A. Ibers, Journal de Physique (Paris) 25 (1964) 474-477.
- [29] A. Ouasri, A. Rhandour, M.-C. Dhamelincourt, P. Dhamelincourt, A. Mazzah, J. Raman Spectr. 33 (2002) 726–729.
- [30] J.J. Rush, W. Schroeder, A.J. Melveger, J. Chem. Phys. 56 (1972) 2793-2800.
- [31] M. Tramšek, G. Tavčar, T. Bunič, P. Benkič, B. Žemva, J. Fluor. Chem. 126 (2005) 1088–1094.
- [32] K.O. Hartman, F.A. Miller, Spectrochim. Acta 24 (1968) 669-684.
- [33] B. Frlec, Vest. Slov. Kem. Drus. 16 (1969) 47.
- [34] Rigaku Oxford Diffraction, CrysAlis PRO, Version 38.41, Rigaku Corporation, Tokyo, Japan, 2015.
- [35] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H.J. Puschmann, Appl. Cryst. 42 (2009) 339–341.
- [36] L. Palatinus, S.J. Prathapa, S. van Smaalen, J. Appl. Cryst. 45 (2012) 575-580.
- [37] G.M. Sheldrick, Acta Cryst. C 71 (2015) 3-8.
- [38] L.J. Farrugia, J. Appl. Cryst. 45 (2012) 849-854.
- [39] Crystal Impact GbR, DIAMOND v3.1, Crystal Impact GbR, Bonn, Germany, 2004–2005.