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CRYSTAL STRUCTURE OF $(Xe_2F_{11}^+)(VF_6^-)$ [†]

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Abstract

Single crystal of $(Xe_2F_{11}^+)(VF_6^-)$ has been prepared. Compound crystallises in monoclinic space group $P2_1/n$ (No.14) with a =8 55.1(1) pm, b = 889.6(1) pm, c = 1570.3(1) pm, β = 93.31(2)°, V = 1.1925(9) nm^3, Z = 4 and ρ_c = 3.545 Mg/m^3. A structure determination using three-dimensional MoK_α X-ray data resulted in conventional R and wR factors of 0.046 and 0.066 respectively, for 2217 unique reflections for which $I \geq 3\sigma(I)$. The structure shows two groups; the essentially octahedral VF_6^- anion and $Xe_2F_{11}^+$ cation, which consists of two XeF_5 units bridged by additional common fluorine atom. Calculation of Mulliken charges for structural units $Xe_2F_{11}VF_6$ and $Xe_2F_{11}AuF_6$ has been performed.

Introduction

The system vanadium pentafluoride – xenon fluorides has been extensively investigated in the past [1], [2], [3], [4], [5]. $2XeF_6{\cdot}VF_6$ was the first compound prepared in this system [4]. VF_5 is strong enough fluoro acid to form adducts not only with medium strong fluoro bases like XeF_6, but also with weak fluoro bases like XeF_2 [2], [3] and KrF_2 [6]. Later the system XeF_6-VF_5 was reinvestigated and two new adducts $XeF_6{\cdot}VF_5$ and $XeF_6{\cdot}2VF_5$ have been isolated [7]. Since there are only two known crystal structures of the cation $Xe_2F_{11}^+$ ($Xe_2F_{11}AuF_6$ [8] and $(Xe_2F_{11})_2NiF_6$

[†] Dedicated to the memory of Prof. Dr. Jože Šiftar

[9]), it was decided to prepare single crystal of $Xe_2F_{11}VF_6$ and determine its crystal structure. For comparison quantum-mechanical calculations on neutral structural units of $Xe_2F_{11}MF_6$ with M = Au and V were also performed.

Experimental

1. Apparatus

The preparation of $Xe_2F_{11}VF_6$ was carried out in FEP reaction vessel with Teflon valve. For the manipulation of the reactants and products a nickel vacuum line was used. It was equipped with mechanical pump connected to the system cross soda lime scrubbers for removal of fluorine, hydrogen fluoride and volatile oxidising fluorides, and mercury diffusion pump to achieve high vacuum in the system. Monitoring of pressure was done with Monel Helicoid pressure gauges.

2. Reagents

XeF_6 was prepared by the reaction between xenon (L'Air Liquide, 99.5%) and fluorine (Solvay, 98-99%) in the presence of nickel difluoride (Alfa Ventron, 99.5%) at 393 K [10]. Traces of XeF_4 that might be still present in XeF_6 were not problematic, since XeF_4 is much weaker fluoride ion donor as XeF_6 [11].

Vanadium pentafluoride was prepared by fluorination of pure vanadium metal (Alfa Ventron, 99.7%) with step-by-step fluorination at temperature 523 K in a nickel reaction vessel [12]. Quality of the product was tested with IR spectroscopy showing only bands of VF_5 with some traces of VOF_3.

3. Preparation of $Xe_2F_{11}VF_6$

649.9 mg (4.45 mmol) of vanadium pentafluoride was condensed in FEP reaction vessel. Then excess of XeF_6 (15.90 mmol) were introduced in the vessel with condensation. At room temperature mixture looked like yellowish mash. The vessel was kept at 313 K for one day.

When reaction was finished, excess of XeF_6 was pumped out, while the reaction vessel was kept at temperatures between 248 to 258 K till constant weight (2.913 g) was reached (Figure 1). This weight is in experimental error limits of theoretical yield for $Xe_2F_{11}VF_6$ (2.832g). The compound was identified with Raman spectrum (Renishaw Raman Imaging Microscope, System 1000, wavelength 623.8 pm, 25 mW) of the solid product. It was identical with Raman spectrum of $(Xe_2F_{11}^+)(VF_6^-)$, known from the literature [7]. The compound is white crystalline material well soluble in anhydrous HF (aHF). Raman spectrum of the solution was also recorded (Figure 2). The compound does not decompose in aHF, since Raman spectrum of the recrystallised compound is identical with Raman spectrum of the compound before recrystallisation.

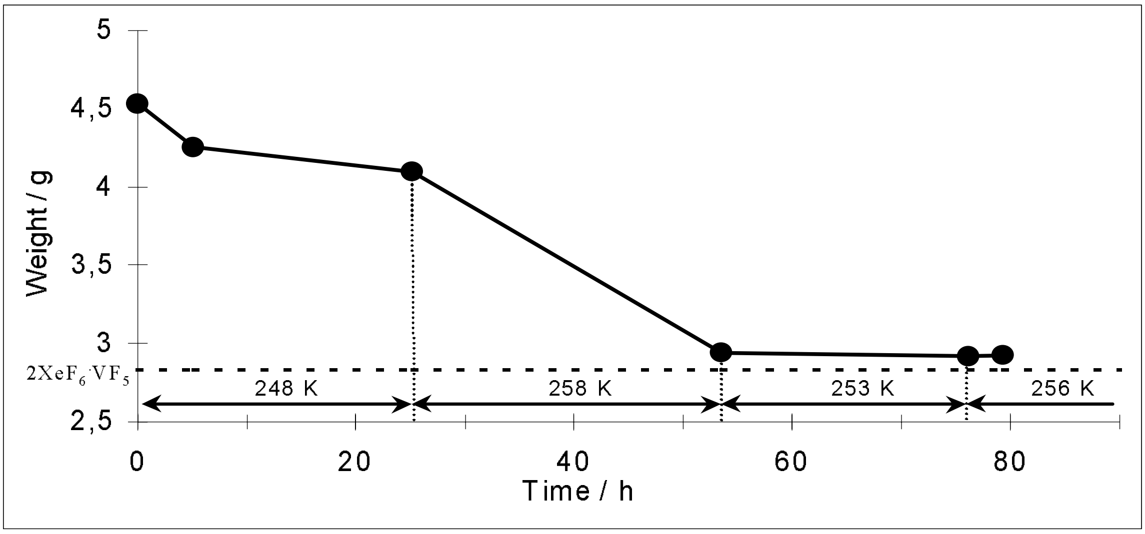

Figure 1: Pumping curve during the preparation of $Xe_2F_{11}VF_6$ compound.

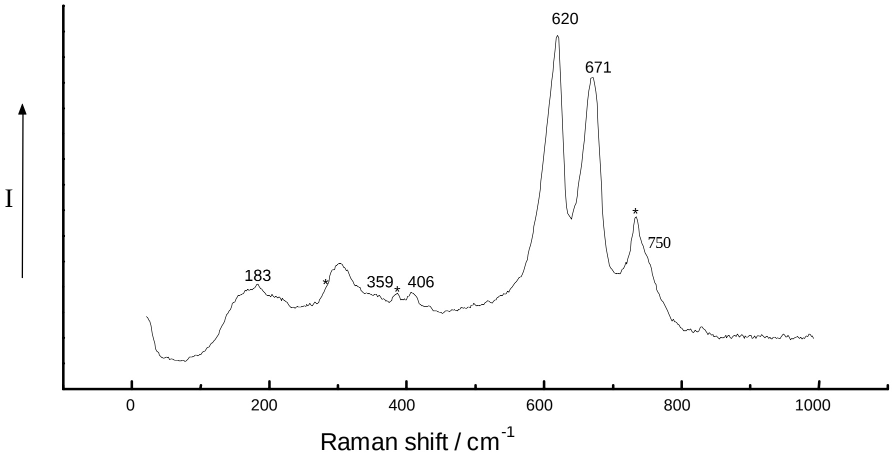

Figure 2: Raman spectrum of 0.4 mmol ($Xe_2F_{11}^+$)(VF_6^-) dissolved in 1 ml of aHF in FEP vessel (Asterisks denote lines arising from the FEP material).

4. Preparation of single crystal

On the top of reaction vessel colourless needle like crystals were found, but they were quickly disappearing in a dry box (MBraun, Garching). Reason for this was complete dissociation of compound's vapours on volatile molecules of XeF_6 and VF_5 what has been already shown with IR spectroscopy [4].

Because of the problem with vanishing crystals, powdered solid compound was packed in 7-10 cm long fluorinated thin walled quartz capillaries (0.5 mm inner diameter) in dry box. Capillaries were temporarily closed with Kel-F grease and flame sealed outside the drybox. Powdered compound was pressed to the bottom of sealed capillaries by throwing the capillary down the 30-cm long vertical tube. Then capillaries were kept in a vertical position and lower part of capillaries was warmed up between 308 and 318 K. On the walls of the capillaries needle like crystals were formed. Raman spectrum of the group of grown crystals in the capillary showed that the compound is still the same as was synthesised. Some of the crystals decomposed in the capillaries because of the reaction of the compound with quartz forming colourless droplets. It was shown by Raman spectroscopy that these droplets are $XeOF_4$ [13].

5. Structure determination

Out of 30 crystals prepared in capillaries only two of them had appropriate diffractive properties for structure determination. One of them showed properties of twin crystal with common b axis and opposite a and c axis (probably coincidentally orientated two crystals in the capillary). Other crystal showed similar feature, but it was possible to separate reflections of the individual crystal. Single crystal data were collected on an ENRAF-NONIUS CAD4 diffractometer at 296(1) K using the ω-2θ scan technique to a maximum 2θ value of 60.0°. Scans of $(0.5+2\cdot\tan\theta)°$ were made with maximal counting time of 10 s. Profiles of reflections were recorded for all data. The counter aperture consisted of a variable horizontal slit with a width range of $(2.7+0.4\cdot\tan\theta)$ mm and a vertical slit set to 2.0 mm. The smallest necessary set of diffraction data was collected. Further details are given in Table 1.

Table 1: Crystal Data and Structure Refinement.

Empirical formula	Xe_2VF_{17}
Molecular weight	636.51 g/mol
λ	71.069 pm
Space group	$P2_1/n$ (No.14)
$a = 855.1(1)$ pm ;	$\alpha = 90°$
$b = 889.6(1)$ pm ;	$\beta = 93.31(2)°$
$c = 1570.3(1)$ pm ;	$\gamma = 90°$
Volume of unit cell	1.1925(9) nm^3
Z	4
ρ_{calc}	3.545 Mg/m^3
μ	6.60 mm^{-1}
F(000)	284
Crystal dimension	0.45 mm × 0.14 mm × 0.19 mm
Index range	$0 \leq h \leq 12$ $0 \leq k \leq 12$ $-21 \leq l \leq 21$
Number of independent data	3460
Number of observed ($I > 3\sigma_I$)	2217
$R(F_0) = 0.046$ ($I > 3\sigma_I$)	$wR(F_0) = 0.066$ ($I > 3\sigma_I$)
$R(F_0) = 0.083$ (all data)	$wR(F_0) = 0.173$ (all data)

The structure was solved using Patterson and Fourier methods and refined with Xtal 3.4 system of programs [14]. There was no absorption correction done, because size of the crystal was close to 2/μ and not commercial capillary was used. Details of the structure refinement are given in Table 2.

Table 2: Final Positional and Displacement Parameters.

Atom	x	y	z	U_{eq} (pm^2) [a]
Xe1	0.73359(9)	0.28654(8)	0.62091(4)	386(2)
Xe2	0.75264(8)	0.20082(7)	0.34200(4)	361(2)
V	0.7499(2)	-0.1636(2)	0.5227(1)	351(5)
F1	0.5716(13)	0.2050(11)	0.6788(7)	800(40)
F2	0.8809(15)	0.1886(12)	0.6933(7)	910(40)
F3	0.7351(14)	0.4097(11)	0.7128(6)	780(40)
F4	0.8946(11)	0.4153(11)	0.5994(7)	760(40)
F5	0.5939(10)	0.4310(9)	0.5812(6)	640(30)
F6	0.7570(9)	0.2695(8)	0.4785(5)	503(23)
F7	0.8962(10)	0.3524(9)	0.3442(5)	566(25)
F8	0.6043(11)	0.3482(10)	0.3445(6)	660(30)
F9	0.7353(11)	0.2595(11)	0.2313(5)	610(30)
F10	0.5881(11)	0.0799(11)	0.3009(6)	690(30)
F11	0.8983(11)	0.0751(10)	0.2940(5)	620(30)
F12	0.7264(12)	0.0094(9)	0.5828(5)	660(30)
F13	0.7571(11)	-0.0434(8)	0.4300(5)	556(25)
F14	0.5471(10)	-0.1691(10)	0.5063(7)	710(30)
F15	0.7673(14)	-0.3199(9)	0.4599(7)	770(40)
F16	0.7403(12)	-0.2670(10)	0.6152(6)	670(30)
F17	0.9503(10)	-0.1452(12)	0.5373(7)	780(40)

[a] U_{eq} is defined as one-third of the trace of U_{ij} tensors.

Supplemental material is available from authors.

6. Quantum-mechanical calculations

Mulliken charges [15] on the smallest neutral part of $Xe_2F_{11}AuF_6$ and $Xe_2F_{11}VF_6$ structures were calculated with Gaussian 94 program system [16]. LanL2MB (5D, 7F) [17] basis set has been used. Results are given in Table 3.

Table 3: Calculated Mulliken Charges (in units e_0) of Structural Units $Xe_2F_{11}AuF_6$ and $Xe_2F_{11}VF_6$.

$Xe_2F_{11}VF_6$				$Xe_2F_{11}AuF_6$			
Xe_2F_{11} group	**XeF_5 units**	***Atom***	***Charge***	**Xe_2F_{11} group**	**XeF_5 units**	***Atom***	***Charge***
+0.930	**+0.748**	**F3**	-0.315	**+0.931**	**+0.752**	**F4**	-0.317
		F5	-0.309			**F6**	-0.315
		F4	-0.305			**F6'**	-0.315
		F2	-0.296			**F5'**	-0.302
		F1	-0.314			**F5**	-0.302
		Xe1	2.287			**Xe2**	2.303
		F6	**-0.548**			**F7**	**-0.549**
	+0.730	**Xe2**	2.299		**+0.728**	**Xe1**	2.277
		F7	-0.316			**F2**	-0.310
		F8	-0.314			**F2'**	-0.310
		F10	-0.304			**F3**	-0.310
		F11	-0.316			**F3'**	-0.310
		F9	-0.319			**F1**	-0.309
VF_6 group	**-0.930**	**V**	0.744	**AuF_6 group**	**-0.931**	**Au**	0.742
		F12	-0.362			**F12**	-0.364
		F13	-0.354			**F8**	-0.355
		F14	-0.251			**F9**	-0.202
		F15	-0.227			**F11**	-0.209
		F16	-0.232			**F10**	-0.272
		F17	-0.248			**F9'**	-0.271

[*] Each line of table represents 'equivalently' positioned atoms in both structures.

7. Description of structure

Structure analysis defined the VF_6 and Xe_2F_{11} groups as shown in Figure 3. Some distances and angles are given in Table 4. Xe_2F_{11} group is composed of two XeF_5 units connected by additional bridging fluorine atom.

The VF_6 group is approximately octahedral with quite different V-F distances (Table 4). Cis angels are close to 90°, the greatest deviations being for F12-V-F13 = 85.8(4)° and F15-V-F16 = 93.5°.

Each XeF_5 unit approximates to a square-based pyramid, with xenon atom placed bellow the base. The F_{ax}-Xe-F_{eq} angles are close to 79°, while cis F_{eq}-Xe-F_{eq} angles are not equivalent (Table 4). Both XeF_5 units forming a Xe_2F_{11} group are crystallographically distinct, and the bridge bonding by the shared fluorine atom (F6) is slightly asymmetric. Bridging distances Xe1-F6 and Xe2-F6 (226.2(8) pm and 222.7(8) pm respectively) are short enough to justify the identification of Xe_2F_{11} group, since other intergroup distances are longer. Present structure is closely comparable to structure of $Xe_2F_{11}AuF_6$ (space group Pnma, No. 62), where major differences in crystallographic sense arise because of mirror plane perpendicular to b axis that is not present in structure of $Xe_2F_{11}VF_6$ (atoms Xe1, Xe2, Au and some fluorine atoms have to be placed on mentioned mirror plane). Asymmetric units are packed in the crystal lattice as layers with approximately parallel (Xe, V, Xe) planes. (Figure 4).

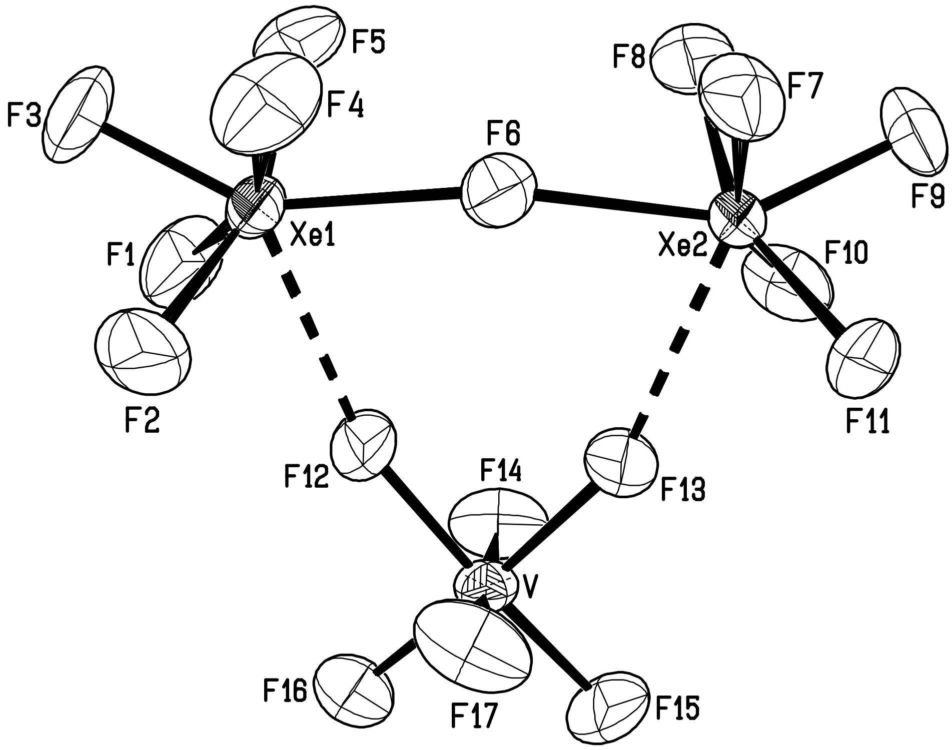

Figure 3: ORTEP [18] view of structural unit $(Xe_2F_{11}^{+})(VF_6^{-})$.

Table 4: Interatomic Distances and Angles for $Xe_2F_{11}VF_6$ compound

$Xe_2F_{11}^+$ CATION:

Distances (pm)			
Xe1-F1	185(1)	Xe2-F10	185.7(9)
Xe1-F2	186(1)	Xe2-F11	186.5(9)
Xe1-F3	181.2(9)	Xe2-F9	181.2(7)
Xe1-F4	184(1)	Xe2-F7	182.3(8)
Xe1-F5	183.8(8)	Xe2-F8	182.6(9)
Xe1-F6	226.2(8)	Xe2-F6	222.7(8)
Xe1-F12	253.7(8)	Xe2-F13	257.4(7)

Angles (Deg)			
Axial			
F3-Xe1-F1	79.4(5)	F9-Xe2-F10	79.3(4)
F3-Xe1-F2	79.8(5)	F9-Xe2-F11	78.7(4)
F3-Xe1-F4	78.4(5)	F9-Xe2-F7	79.8(4)
F3-Xe1-F5	79.8(4)	F9-Xe2-F8	78.2(4)
F6-Xe1-F3	146.2(4)	F6-Xe2-F9	147.1(4)
Cis-equatorial			
F1-Xe1-F2	90.9(5)	F10-Xe2-F11	91.3(4)
F2-Xe1-F4	85.2(5)	F11-Xe2-F7	89.2(4)
F4-Xe1-F5	88.9(4)	F7 –Xe2-F8	86.4(4)
F5-Xe1-F1	87.2(4)	F8 –Xe2-F10	84.8(4)

VF_6^- ANION:

Distances (pm)		**Cis Angles (deg)**	
V-F12	182.2(8)	F12-V-F13	85.8(4)
V-F13	181.1(8)	F12-V-F14	87.8(5)
V-F14	174.0(9)	F12-V-F16	90.2(4)
V-F15	171.6(9)	F12-V-F17	89.4(5)
V-F16	172.5(9)	F13-V-F14	88.7(5)
V-F17	172.3(9)	F13-V-F15	90.5(4)
		F13-V-F17	88.4(5)
		F14-V-F15	90.6(5)
		F14-V-F16	90.8(5)
		F15-V-F16	93.5(3)
		F15-V-F17	92.0(6)
		F16-V-F17	92.0(5)

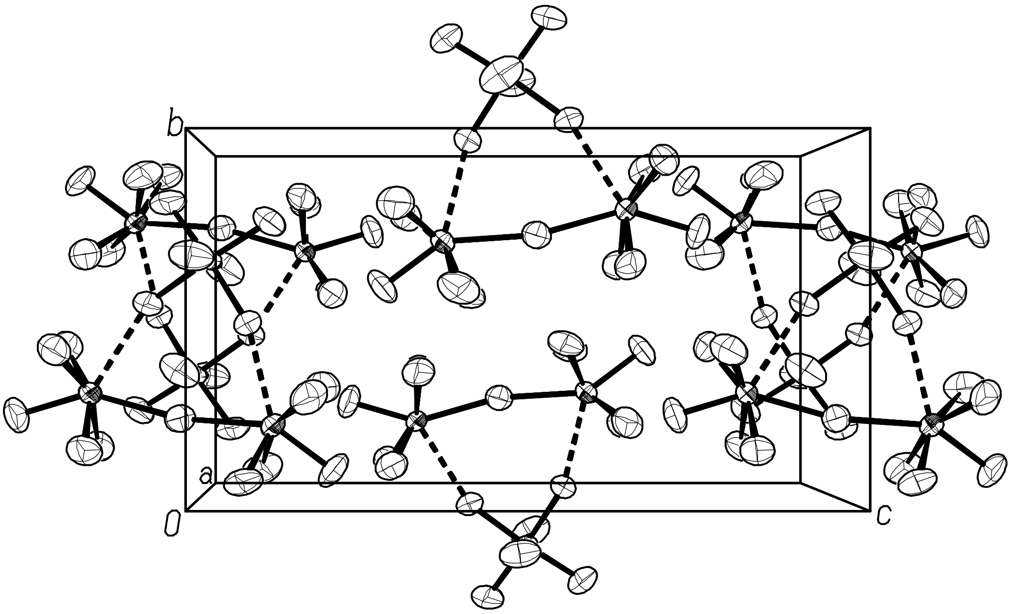

Figure 4: Projection of Unit Cell Packing down the a Axis.

Results and discussion

The cation $Xe_2F_{11}^+$ was first crystallographically defined in the compound $Xe_2F_{11}AuF_6$ [8] and latter in $(Xe_2F_{11})_2NiF_6$ [9]. Interaction between $Xe_2F_{11}^+$ and anion (AuF_6^- and NiF_6^{2-} respectively) was considered as Coulombic interaction.

In agreement with mentioned model, Raman spectrum of $(Xe_2F_{11}^+)(VF_6^-)$ compound dissolved in aHF (0.4 mmol $Xe_2F_{11}VF_6$ in 1ml of aHF) clearly shows dissociation of compound and further dissociation of $Xe_2F_{11}^+$ species resembling the tautomerism of XeF_6 solutions [19] (Figure 2). Strong lines at 671 cm^{-1} and 620 cm^{-1} indicate presence of XeF_5^+ ions. Lines at 406 cm^{-1}, 359 cm^{-1} and around 200 cm^{-1} indicate presence of $Xe_2F_{11}^+$, XeF_5^+ ions and tetrameric clusters of $[(XeF_5^+)F^-]_4$. The shoulder at approximately 750 cm^{-1} might be assigned to ν_1 (a_{1g}) of VF_6^-.

Because of vanadium (V) electron configuration (no electrons in 3d-orbitals) there are no Jahn-Teller distortions of VF_6^- species, so regular octahedral geometry of VF_6^-

anion is favourable. Any departures of octahedral symmetry, in this structure, can be interpreted as a consequence of interaction with the $Xe_2F_{11}^+$ cations. So V-F distances of bridging fluorine atoms F12 and F13 are considerable elongated in comparison with other nonbridging fluorines on VF_6^- species. Consequence of bonding interaction with positive $Xe_2F_{11}^+$ species are also calculated higher negative Mulliken charges on mentioned atoms (Table 3), what is due to the delocalization of charge from negatively charged VF_6^- species to positive $Xe_2F_{11}^+$ cation, and indicate ionic character of interaction. The situation with $Xe_2F_{11}AuF_6$ compound is very similar. It should be mentioned here, that LanL2MB (5D, 7F) basis set is not considered as very precise one, but is good enough for at least some of qualitative comparisons, especially because it supports wave functions of heavier atoms down to the bismuth.

In $Xe_2F_{11}^+$ species close approach of bridging F6 atom to each Xe atom and the departure of Xe-F-Xe angle from linearity suggest that a measure of covalence should be incorporated into bond description, what was already noticed by $(Xe_2F_{11}^+)(AuF_6^-)$ compound [8]. The bond in $Xe_2F_{11}^+$ can be described as a resonance hybrid of canonical forms $[XeF_5^+XeF_6]\leftrightarrow[XeF_6XeF_5^+]$ with unequal weights [8], [9], and comparable contribution of ionic canonical form $[XeF_5^+F^-XeF_5^+]$. That is also evident from distribution of Mulliken charges on $Xe_2F_{11}^+$ species (Table 3). Bridging F6 atom in vanadium compound is carrying negative charge ($-0.548e_0$), with unequally distributed positive charges on XeF_5 units ($0.748e_0$ on unit with Xe1 atom and $0.730e_0$ on unit with Xe2). That is in accordance with asymmetric bridging Xe1-F6-Xe2 distances. The same is true for $Xe_2F_{11}^+$ species in gold compound (Table 3).

In vanadium compound there is also indication of steric activity of nonbonding lone electron pair as noticed in some already known structures [8], [20], [21]. Close approach of bridging F6 atom to Xe1 and Xe2 could deflect nonbonding lone electron pair from its axial position. Because of repulsion of F1 and F2 atoms on Xe1, and F10 and F11 on Xe2 with lone electron pair there is increase of angles F1-Xe1-F2 and F10-Xe2-F11 and lengthening of corresponding atomic distances. VF_6 group is slightly tilted from (Xe1, V, Xe2) plane (Table 5) what can give additional insight in distortions of XeF_5 unit from C_{4v} symmetry.

Table 5: Distances of some Atoms from (Xe1, V, Xe2) Plane in Structural Unit $Xe_2F_{11}VF_6$.

Atom	**F3**	**F6**	**F9**	**F12**	**F13**	**F15**	**F16**
Distance (pm)	8.49	12.21	-19.36	-13.54	3.57	8.44	-5.41

In both, gold and vanadium compound Xe-F-Xe angles are close to 170° (169.2(2)° and 166.5(4)° respectively) and calculated total charges on VF_6 and AuF_6 groups are practically the same ($-0.930e_0$ and $-0.931e_0$ respectively). So the most probable reason for mentioned tilt of VF_6 group, which is not property of $Xe_2F_{11}AuF_6$ structure, is packing of asymmetric units in unit cell (Figure 4). With such tilt probably stronger interaction of smaller VF_6^- anion with $Xe_2F_{11}^+$ cation is achieved, since steric activity of nonbonding valence pair on Xe atoms is weaker, if interacting fluorine atoms approach little off the plane (Xe1, V, Xe2).

In $(Xe_2F_{11}^+)(VF_6^-)$ more steric freedom by interaction of F12 and F13 ligands with Xe1 and Xe2 atoms respectively is also indicated by quite large reduction of angle F12-V-F13 (85.8(4)°) on VF_6^- group from 90°. The reduction of the analogous angle in AuF_6^- group is smaller (F8-Au-F12 = 88.0(5)°) [8].

Conclusion

An usual way of understanding the structure is its comparison with similar structures. In case of compounds with $Xe_2F_{11}^+$ cation now only three crystal structures are known. Since there are many compounds with different anions, which compositions suggest they contain $Xe_2F_{11}^+$ cation [22], it would be of great interest to compare their structures, charges, molecular electrostatic potential and lattice energies. Unfortunately preparation of suitable single crystal is difficult. Some efforts have been done in the past with $2XeF_6 \cdot AsF_6$ compound [23] and $Xe_2F_{11}RuF_6$ compound [24], but they failed because all crystals showed disorder or gross twinning features and were not suitable for an X-ray structure determination.

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Povzetek

Pripravljen je bil monokristal spojine ($Xe_2F_{11}^+$)(VF_6^-). Spojina kristalizira v monoklinski prostorski skupini $P2_1/n$ (No.14) z a =855.1(1) pm, b = 889.6(1) pm, c = 1570.3(1) pm, β = 93.31(2)°, V = 1.1925(9) nm^3, Z = 4 in ρ_c = 3.545 Mg/m^3. Struktura analiza, narejena na 2217 neodvisnih uklonov z $I \geq 3\sigma(I)$ zbranih na štirikrožnem difraktometru z MoK_α svetlobo, je dala rezultat z R = 0.046 in wR = 0.066. Dobljeno strukturo sestavljata dve skupini; približno oktaedralni anion VF_6^- in kation $Xe_2F_{11}^+$, ki je sestavljen iz dveh enot XeF_5 povezanih preko dodatnega mostovnega fluorovega atoma. Narejen je bil tudi izračun Mullikenovih nabojev za strukturni enoti $Xe_2F_{11}VF_6$ in $Xe_2F_{11}AuF_6$.