

## XeF<sub>2</sub>.CrF<sub>4</sub> and (XeF<sub>5</sub><sup>+</sup>CrF<sub>5</sub><sup>-</sup>)<sub>4</sub>.XeF<sub>4</sub>: Syntheses, crystal structures and some properties

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**ABSTRACT.** - XeF<sub>2</sub>.CrF<sub>4</sub> (I) has been prepared by the reaction between CrF<sub>5</sub> and excess of XeF<sub>2</sub> at 50°C. The blue solid quickly interacts with liquid anhydrous HF (AHF) at room temperature yielding amethyst CrF<sub>4</sub>. XeF<sub>2</sub>.CrF<sub>4</sub> crystallizes in the monoclinic space group P2<sub>1</sub>/n with  $a = 7.666(2)$ ,  $b = 7.268(5)$ ,  $c = 9.901(3)$  Å,  $\beta = 91.25(2)^\circ$ ,  $V = 551.5$  Å<sup>3</sup>,  $Z = 4$  and  $d_c = 3.581$  gcm<sup>-3</sup>. (XeF<sub>5</sub><sup>+</sup>CrF<sub>5</sub><sup>-</sup>)<sub>4</sub>.XeF<sub>4</sub> (II) has been prepared by the reaction between CrF<sub>2</sub> and excess of XeF<sub>6</sub> at 120°C. Red solid dissolves in liquid AHF at room temperature. (XeF<sub>5</sub><sup>+</sup>CrF<sub>5</sub><sup>-</sup>)<sub>4</sub>.XeF<sub>4</sub> crystallizes in the orthorhombic space group Pbca with  $a = 11.988(6)$ ,  $b = 15.862(2)$ ,  $c = 16.538(2)$  Å,  $V = 3144.8$  Å<sup>3</sup>,  $Z = 4$  and  $d_c = 3.592$  gcm<sup>-3</sup>. The structures were solved by Patterson method using diffractometer data sets and refined to conventional  $R = 0.068$  for 741 reflexions (I) and to  $R = 0.052$  for 2850 reflexions (II). The main feature of the XeF<sub>2</sub>.CrF<sub>4</sub> structure is the infinite chain of distorted CrF<sub>6</sub> octahedra that share trans vertices. The Xe-F species are arranged alternately to left and right along the chain with the distance Xe-F(2) being 1.93(2) Å and the bridging distance Xe-F(1) being 2.13(2) Å. (XeF<sub>5</sub><sup>+</sup>CrF<sub>5</sub><sup>-</sup>)<sub>4</sub>.XeF<sub>4</sub> structure consists of infinite chain of distorted CrF<sub>6</sub> octahedra that alternately share trans and cis vertices, being the first known example of this kind. There are two crystallographically distinguishable XeF<sub>5</sub><sup>+</sup> cations: XeF<sub>5</sub><sup>+</sup>(Xe-1) is distorted with equatorial distances in the range 1.80(1) to 1.87(1) Å and axial distance 1.830(9) Å, while XeF<sub>5</sub><sup>+</sup>(Xe-2) has dimensions as already known. XeF<sub>4</sub> is situated between two chains in such a way that the closest contacts of xenon (Xe-3) to fluorine ligands in both chains are at the distance 3.126(7) Å.

### INTRODUCTION

The system chromium fluorides - xenon fluorides was investigated in the past [1,2]. It was found that chromium(V) fluoride oxidizes xenon to xenon difluoride and xenon tetrafluoride at 120°C, while it is reduced to chromium(III) fluoride.

Further it was found that during the reaction between chromium(V) fluoride and excess of xenon difluoride at 60°C a brown solid with negligible vapour pressure at room temperature was isolated. The chemical composition of this product was close to  $\text{XeF}_2 \cdot 2\text{CrF}_4$  [1]. The reaction between lower chromium fluorides ( $\text{CrF}_2$ ,  $\text{CrF}_3$ ) and the melt of xenon hexafluoride gives red solid [2] with the composition  $n\text{XeF}_6 \cdot \text{CrF}_4$  where  $n$  was varying in the range 1.00 to 1.15. In all cases it was proven by magnetic susceptibility measurements that chromium is in 4+ valence state [1,2]. The system chromium fluorides - xenon fluorides was reinvestigated in order to obtain structural information about xenon(II) and xenon(VI) fluorochromates(IV) and to test the possibility of using these compounds as starting materials for the preparation of very pure  $\text{CrF}_4$ .

## EXPERIMENTAL

**1. Apparatus.** - Volatile materials were manipulated in nickel vacuum system equipped with nickel valves. Nonvolatile materials were handled in the dry argon atmosphere of a glove box with maximum content of 0.2 ppm of water vapour (M. Braun, Garching, FRG). The reactions were carried out in a 100 cm<sup>3</sup> nickel reaction vessels equipped with nickel valves or in FEP ampoules (18 mm o.d.), equipped with Teflon valves.

**2. Technique.** - Infrared spectra were taken on FTIR spectrometer (Perkin-Elmer 1710) over the range 250-1500 cm<sup>-1</sup>. Nonvolatile materials were sandwiched between two AgCl windows sealed in the dry box in the brass holder. For volatile materials a 10 cm nickel cell with AgCl windows was used. Raman spectra were obtained with Spex 1401 double monochromator. A detection system utilising photon-counting techniques was used in conjunction with a variety of laser lines (Coherent Radiation). Powdered samples were filled in a dry box in 1 mm i.d. quartz capillaries which were provisionally closed with Kel-F grease in the dry box and sealed in a small flame outside the dry box. X-ray powder diffraction patterns of solid samples were obtained with Enraf apparatus (Delft, Holland), using graphite-monochromatized  $\text{CuK}\alpha$  radiation. Finely powdered samples were filled into 0.5 mm quartz capillaries as described for Raman spectroscopy.

**3. Reagents.** - Xenon (99.99 %) and krypton (99.99 %) were used as supplied by Messer Griesheim (Austria). Fluorine from a cylinder (96-98%), produced in this laboratory, was additionally purified by photochemical method [3] to a purity of more than 99.9 %. Anhydrous hydrogen fluoride (AHF), 99.8% (UCAR, Oevel, Belgium) was treated prior use by  $\text{K}_2\text{NiF}_6$  for several hours, and in some cases with krypton difluoride (1 g  $\text{KrF}_2$ /10 g HF) at room temperature, and finally at 50°C. Xenon difluoride was prepared by irradiating gaseous mixture of xenon and fluorine at room temperature [4]. Xenon hexafluoride was prepared by the reaction between xenon and fluorine in the presence of nickel difluoride at 120°C

[5]. Krypton difluoride was prepared by the irradiation of liquefied mixture of krypton and fluorine at -196°C by UV light [6]. Chromium difluoride (Merck, Darmstadt, FRG) and chromium(III) fluoride (Ozark Mahoning, South Boulder, USA) were used as supplied. Chromium(V) fluoride was prepared by fluorination with elemental fluorine under pressure [1].

**4. Synthesis of  $\text{XeF}_2 \cdot \text{CrF}_4$ .** - Xenon difluoride (40.44 mmol) was loaded into FEP ampoule with all Teflon valve in the dry box. The ampoule was connected to the vacuum line and  $\text{CrF}_5$  (7.97 mmol) was added by sublimation into ampoule cooled to -196°C. The reaction vessel was left to warm up to room temperature. The reaction between  $\text{CrF}_5$  and  $\text{XeF}_2$  is quick although it took several hours at 50°C before it was completed. The unreacted  $\text{XeF}_2$  and the formed  $\text{XeF}_4$  were pumped out of the ampoule at room temperature and checked by recording their infrared spectra. In the reaction vessel an unvolatile blue solid was left (2.392 g). The weight calculated for 7.97 mmol of  $\text{CrF}_5$  is 2.370 g. Chem. Anal.: Calcd. for  $\text{XeF}_2 \cdot \text{CrF}_4$ : Xe, 44.16; Cr, 17.49; F, 38.35%. Found: Xe, 43.7; Cr, 17.0; F, 38.2%.

**5. Synthesis of  $\text{XeF}_5^+ \text{CrF}_5^-$ .** - Xenon hexafluoride (24.00 mmol) was sublimed into FEP ampoule with all Teflon valve.  $\text{CrF}_5$  (6.71 mmol) was added by sublimation and the ampoule was warmed up to room temperature. The reaction did not proceed at room temperature. The reaction vessel was held at 60°C for three days. Evolved fluorine (cca 3.30 mmol) and excessive xenon hexafluoride were pumped away. Red solid (2.363 g) with negligible vapour pressure at room temperature was isolated. The weight calculated for 6.71 mmol of  $\text{CrF}_5$  is 2.504g. Chem. Anal.: Calcd. for  $\text{XeF}_5^+ \text{CrF}_5^-$ : Xe, 35.17; Cr, 13.93; F, 50.90%. Found: Xe, 34.6 ; Cr, 13.1; F, 50.3%.

The same compound could be synthesized also by the reaction between  $\text{CrF}_4$  (2.99 mmol) prepared as described in paragraph 8 and excess of  $\text{XeF}_6$  (7.84 mmol) at room temperature.  $\text{CrF}_4$  was weighed into FEP ampoule in the dry box and  $\text{XeF}_6$  was added by sublimation to -196°C. The reaction vessel was warmed up to room temperature, where reaction started immediately what was seen by the colour change. The reaction vessel was left at room temperature for 16 hours before excess of  $\text{XeF}_6$  was pumped away at the same temperature. In the reaction vessel red solid was left (1.052 g). The weight calculated for 2.99 mmol of  $\text{CrF}_4$  is 1.116 g. The hydrolysis of  $\text{XeF}_5^+ \text{CrF}_5^-$  is very vigorous accompanied with flashes. Chem. Anal.: Found: Xe, 34.8; Cr, 13.3; F, 50.9%.

**6. Synthesis of  $(\text{XeF}_5^+ \text{CrF}_5^-)_4 \cdot \text{XeF}_4$ .** -  $\text{CrF}_2$  (14.40 mmol) was loaded into 100 ml nickel reactor equipped with nickel valve. Then excess of  $\text{XeF}_6$  (37.00 mmol) was added by sublimation to -196°C. The reaction vessel was held at 120°C for ten days. Then excess of formed  $\text{XeF}_4$  and excess of  $\text{XeF}_6$  were pumped away at room temperature. The nonvolatile red solid  $(\text{XeF}_5^+ \text{CrF}_5^-)_4 \cdot \text{XeF}_4$  (6.117 g) was obtained. Calculated weight for 14.40 mmol of  $\text{CrF}_2$  is 6.122 g. Chem. Anal.:

Calcd. for  $(\text{XeF}_5^+\text{CrF}_5^-)_4\cdot\text{XeF}_4$ : Xe, 38.61; Cr, 12.23; F, 49.16%. Found: Xe, 36.9; Cr, 12.4; F, 49.8%.

**7. Thermal stability of  $\text{XeF}_2\cdot\text{CrF}_4$  and  $(\text{XeF}_5^+\text{CrF}_5^-)_4\cdot\text{XeF}_4$ .** -  $\text{XeF}_2\cdot\text{CrF}_4$  starts to lose  $\text{XeF}_2$  already at 40°C in a dynamic vacuum. At 100°C beside of  $\text{XeF}_2$  also  $\text{XeF}_4$  was obtained thus showing that  $\text{CrF}_4$  was reduced to  $\text{CrF}_3$ .

$(\text{XeF}_5^+\text{CrF}_5^-)_4\cdot\text{XeF}_4$  starts to lose  $\text{XeF}_6$  already at 35°C ( $\sim 0.5 \text{ mg min}^{-1}$   $\text{XeF}_6$ ) in a dynamic vacuum. At 50°C in the volatile products beside  $\text{XeF}_6$  also  $\text{XeF}_4$  was detected by infrared spectroscopy. After pumping  $(\text{XeF}_5^+\text{CrF}_5^-)_4\cdot\text{XeF}_4$  (3.85 mmol) at 50°C for more than 70 hours the compound  $\text{XeF}_6\cdot 2\text{CrF}_4$  (3.84 mmol) was obtained. This compound does not decompose further but it sublimes out from the hot zone at 140°-160°C.

**8. Preparation of  $\text{CrF}_4$ .** - 10 ml of AHF were added to  $\text{XeF}_2\cdot\text{CrF}_4$  (3.36 mmol) by sublimation to -196°C. The mixture was stirred. The solvolysis of  $\text{XeF}_2\cdot\text{CrF}_4$  took place immediately when the temperature of the reaction vessel was close to 0°C. The blue colour of  $\text{XeF}_2\cdot\text{CrF}_4$  changed to amethyst colour of  $\text{CrF}_4$  which was washed from  $\text{XeF}_2$  by many (up to 10) washings of the precipitate with AHF. The weight of  $\text{CrF}_4$  calculated for 3.36 mmol of  $\text{XeF}_2\cdot\text{CrF}_4$  is 0.430 g; obtained 0.423 g. Chem. Anal.: Calcd. for  $\text{CrF}_4$ : Cr, 40.62; F, 59.38%. Found: Cr, 40.8; F, 58.9%. Infrared spectrum of  $\text{CrF}_4$ : 530(vs,br), 753(s), 807(s)  $\text{cm}^{-1}$ , Raman spectrum of  $\text{CrF}_4$  770(33), 792 sh, 797(100), 829(10)  $\text{cm}^{-1}$ .

**9. Preparation of single crystals of  $\text{XeF}_2\cdot\text{CrF}_4$  and  $(\text{XeF}_5^+\text{CrF}_5^-)_4\cdot\text{XeF}_4$ .** - Single crystals of  $\text{XeF}_2\cdot\text{CrF}_4$  suitable for crystal structure analysis were obtained directly during the synthesis of the compound from  $\text{CrF}_5$  and excess of  $\text{XeF}_2$  at 50°C in nickel reactor. Time of the reaction was 12 hours. The proper crystals were chosen in a dry-box by the use of the microscope (Opton, Oberkochen, FRG).

The compound  $(\text{XeF}_5^+\text{CrF}_5^-)_4\cdot\text{XeF}_4$  was weighed into FEP apparatus and AHF was added by sublimation to -196°C. After AHF was saturated with salt by dissolving it at room temperature, the solution was decanted. Crystallization of  $(\text{XeF}_5^+\text{CrF}_5^-)_4\cdot\text{XeF}_4$  occurred as the solvent evaporated. This was achieved by small thermal gradient to a colder trap (20 to 14°C) over a period of some hours. Red crystals were loaded in 0.5 mm quartz capillaries in a dry-box using the microscope.

The capillaries filled with crystals were sealed temporarily with a plug of Kel-F grease, and drawn down in a small flame outside the dry-box.

**10. Structural determination of  $\text{XeF}_2\cdot\text{CrF}_4$  and  $(\text{XeF}_5^+\text{CrF}_5^-)_4\cdot\text{XeF}_4$ .** - The irregularly shaped crystals were very sensitive to moisture. Several crystals were mounted in specially prepared quartz capillaries and tested on CAD-4 automated diffractometer. From the previous experiences very fast data collection was applied. This was justified by considerable decay of the crystals during data

collection. Details of data collection and processing are given in Table I. Cell dimensions were determined by least-squares fit of the setting angles of 25 reflections with  $\theta$  in the range 7-10°.

TABLE I - Crystal Data and Details of Structure Determination and Refinement for  
 $\text{XeF}_2 \cdot \text{CrF}_4$  (I) and  $(\text{XeF}_5^+ \text{CrF}_5^-)_4 \cdot \text{XeF}_4$  (II)

	I	II
formula	$\text{XeCrF}_6$	$\text{Xe}_3\text{Cr}_4\text{F}_{44}$
mol wt	297.3	1700.5
space group	P2 <sub>1</sub> /n	Pbca
cryst system	monoclinic	orthorhombic
a, Å	7.666(2)	11.988(6)
b	7.268(5)	15.862(2)
c	9.901(3)	16.538(2)
$\beta$ , deg	91.25(2)	-
vol, Å <sup>3</sup>	551.5	3144.8
Z	4	4
d <sub>c</sub> , gcm <sup>-3</sup>	3.581	3.592
shape od crystal	irregular	prismatic
dimensions, mm	0.41x0.22x0.05	0.4x0.4x0.7
colour	light blue	dark red
diffractometer	CAD-4 Enraf Nonius	
data collected	asymmetric set only	
radiation	MoK $\alpha$	
monochromator (angle, deg)	graphite (12.1)	
temp, K	293(1)	
scan technique	$\omega - 2\theta$	
2 $\theta$ scan width, deg	2.40 + 0.9 tan $\theta$	
scan rate, deg/min	8.24 - 16.48	
bkgd	0.25 of scan time at each of scan limits	
2 $\theta_{\max}$ , deg	30	30
max scan time,s	10	10
reference reflcns	3 after each hour	
orient reflcns	3 after 500 refls	
intensity decrease, %	18	22
observed reflcns	741	2850
criterion	$I > 2.5 \sigma(I)$	
lin abs coeff, cm <sup>-1</sup>	81.11	68.79
absorption correction	none	
program used	SHELX76, GX, ORTEP	
scattering factors	neutral atoms	
R, wR factors	0.068; 0.076	0.052; 0.0587
max shift/error	0.055	0.060

Lists of calculated and observed amplitudes of structure factors could be obtained on request from the authors.

**11. Description of the  $\text{XeF}_2\text{CrF}_4$  structure.** - Atomic coordinates and temperature factors for  $\text{XeF}_2\text{CrF}_4$  are given in Table II, selected bond lengths and angles are given in Table III. The structure of  $\text{XeF}_2\text{CrF}_4$  is shown in Fig. 1. It consists of infinite chain of  $\text{CrF}_6$  octahedra that share trans vertices. The angle  $\text{Cr}-\text{F}(3)-\text{Cr}^{\text{ii}}$  is  $147.3(8)^\circ$ . The interatomic distance  $\text{Xe}-\text{F}(2)$  is  $1.93(2)$  Å and  $\text{Xe}-\text{F}(1)$  is  $2.13(2)$  Å. The angle  $\text{F}(1)-\text{Xe}-\text{F}(2)$  is  $176.2(1)^\circ$ .  $\text{CrF}_6$  octahedron has three terminal fluorines with the distances  $\text{Cr}-\text{F}$  in the range  $1.71(2)[\text{Cr}-\text{F}(6)]-1.75(2)[\text{Cr}-\text{F}(4)]$  Å and three bridging fluorines with the distances  $\text{Cr}-\text{F}$  in the range  $1.88(2)[\text{Cr}-\text{F}(3)]-2.00(2)[\text{Cr}-\text{F}(1)]$  Å. The cis angles in  $\text{CrF}_6$  octahedron are in the range  $79.8(7)^\circ$  for  $\text{F}(1)-\text{Cr}-\text{F}(5)$  to  $100.1(8)^\circ$  for  $\text{F}(5)-\text{Cr}-\text{F}(6)$ .

TABLE II - Fractional Atomic Coordinates and Isotropic Temperature Factors ( $\text{\AA}^2$ )  
(With standard deviations in the least significant digits in parentheses. For anisotropic atoms, the equivalent isotropic temperature factors are shown.)

	$x/a$	$y/b$	$z/c$	$U$
Xe	0.7715(2)	0.1559(2)	0.3836(1)	0.031
Cr	0.7480(5)	0.0859(4)	0.7573(3)	0.024
F1	0.8723(19)	0.1308(18)	0.5852(14)	0.039
F2	0.6929(23)	0.1681(25)	0.1974(19)	0.062
F3	0.7290(19)	-0.1634(15)	0.6983(13)	0.034
F4	0.5650(17)	0.1373(18)	0.6564(16)	0.040
F5	0.9609(19)	0.0485(19)	0.8109(15)	0.040
F6	0.6420(20)	0.0471(21)	0.9048(14)	0.044

TABLE III - Selected Bond Lengths (Å) and Angles (°) for  $\text{XeF}_2\text{CrF}_4$

Xe - F1	2.13(2)	Xe - F2	1.93(2)	Cr - F1	2.00(2)	Cr - F3	1.91(2)
Cr - F3 <sup>i</sup>	1.88(2)	Cr - F4	1.75(2)	Cr - F5	1.73(2)	Cr - F6	1.71(2)

F1 - Xe - F2	176.2(1)	F3 - Cr - F3 <sup>i</sup>	175.6(1)	F3 <sup>i</sup> - Cr - F6	90.2(7)
F1 - Cr - F3	85.9(6)	F3 - Cr - F4	88.4(7)	F4 - Cr - F5	162.3(3)
F1 - Cr - F3 <sup>i</sup>	89.8(6)	F3 - Cr - F5	90.6(7)	F4 - Cr - F6	97.6(8)
F1 - Cr - F4	82.5(7)	F3 - Cr - F6	94.0(7)	F5 - Cr - F6	100.1(8)
F1 - Cr - F5	79.8(7)	F3 <sup>i</sup> - Cr - F4	89.8(7)	Cr - F3 - Cr <sup>ii</sup>	147.3(8)
F1 - Cr - F6	179.9(1)	F3 <sup>i</sup> - Cr - F5	89.9(7)		

Symmetry code:  
i)  $3/2-x, 1/2+y, 3/2-z$   
ii)  $3/2-x, -1/2+y, 3/2-z$

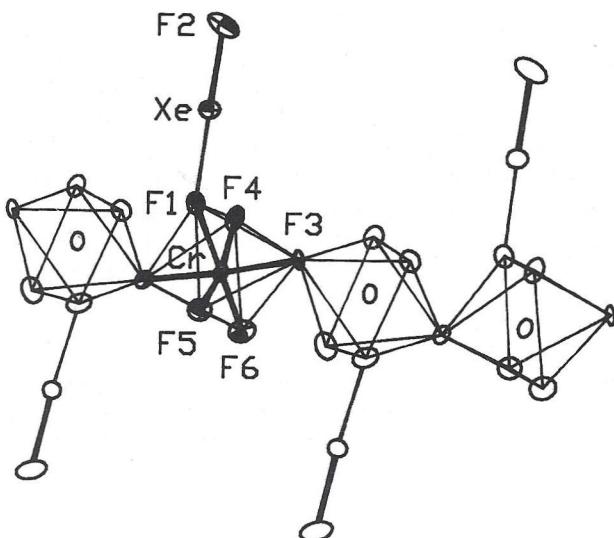


Fig.1.  $\text{XeF}_2 \cdot \text{CrF}_4$  structure

**12. Description of the  $(\text{XeF}_5^+ \text{CrF}_5^-)_4 \cdot \text{XeF}_4$  structure.** - Atomic coordinates and temperature factors for  $(\text{XeF}_5^+ \text{CrF}_5^-)_4 \cdot \text{XeF}_4$  are given in Table IV, selected bond lengths and angles are given in Table V. The structure of  $(\text{XeF}_5^+ \text{CrF}_5^-)_4 \cdot \text{XeF}_4$  is illustrated in Figures 2, 3 and 4. The anion consists of infinite chain of  $\text{CrF}_6$  octahedra that alternately share trans and cis vertices. The interatomic distances between chromium atoms and fluorine atoms are in the range from 1.701(8), to 1.895(7) for terminal fluorines and from 1.890(6) to 1.961(7) for bridging fluorines. The angle  $\text{Cr}(1)\text{-F}(6)\text{-Cr}(2)$  is  $142.3(4)^\circ$  and the angle  $\text{Cr}(1)\text{-F}(4)\text{-Cr}(2)^i$  is  $136.6(4)^\circ$ . The cations  $\text{XeF}_5^+$  are arranged alternately above and below the chain. There are two kinds of  $\text{XeF}_5^+$ : one (Xe-2) has close contacts to four fluorine atoms of two neighbouring fluorine bridged  $\text{CrF}_6$  octahedra in the chain, in the range 2.591(7)-2.854(7) Å while the second one (Xe-1) has only three close contacts to fluorine atoms of two neighbouring fluorine bridged  $\text{CrF}_6$  octahedra in the range 2.580(7)-2.676(7) Å. The coordination of the xenon atom (Xe-2) is nearly that of a capped square antiprism of  $C_{4v}$  symmetry like in  $\text{XeF}_5^+ \text{GeF}_5^-$  [7]. The dimensions of this cation (Xe-2) are close to those reported previously [8-11] for  $\text{XeF}_5^+$  salts, while the dimensions of the other cation (Xe-1) are different from known  $\text{XeF}_5^+$  species. The main difference is the distance Xe-

$F_{eq}$  which is usually in the range 1.83-1.86 Å and longer than  $Xe-F_{ax}$ . In the cation ( $Xe\text{-}1$ ) there is axial distance [ $Xe(1)\text{-}F(11)$ ] 1.830(9) Å while two equatorial distances [ $Xe(1)\text{-}F(12)$ ,  $Xe(1)\text{-}F(14)$ ] are 1.80(1) and 1.87(1) Å respectively. Xenon tetrafluoride is situated, as illustrated in Fig. 5, between two chains in such a way that the closest contacts of xenon ( $Xe\text{-}3$ ) to neighbouring fluorine ligands are above and below the  $XeF_4$  plane at the distance 3.126(7) Å. The angle  $F(32)\text{-}Xe(3)\text{-}F(8)^{iii}$  is 84.5(5)° and the angle  $F(31)\text{-}Xe(3)\text{-}F(8)^{iii}$  is 115.9(4)°. Planar molecule of xenon tetrafluoride is slightly deformed so that there are two interatomic distances 1.90(2) Å [ $Xe(3)\text{-}F(31), F(31)^{ii}$ ] and two distances 1.97(2) Å [ $Xe(3)\text{-}F(32), F(32)^{ii}$ ].  $Xe\text{-}3$  is the center of inversion.

TABLE IV - Fractional Atomic Coordinates and Isotropic Temperature Factor (Å<sup>2</sup>)  
(With standard deviations in the least significant digits in parentheses. For anisotropic atoms, the equivalent isotropic temperature factors are shown.)

	x/a	y/b	z/c	U
Xe1	0.16704(6)	0.41805(4)	0.26931(5)	0.029
F11	0.1385(8)	0.3078(5)	0.2945(7)	0.062
F12	0.1480(9)	0.3760(5)	0.1689(6)	0.067
F13	0.3094(7)	0.3756(5)	0.2728(7)	0.070
F14	0.1764(8)	0.4228(5)	0.3821(6)	0.058
F15	0.0147(6)	0.4232(5)	0.2839(6)	0.049
Xe2	0.61447(6)	0.66741(4)	0.04592(5)	0.030
F21	0.6945(8)	0.6973(6)	-0.0418(5)	0.061
F22	0.6641(7)	0.5639(5)	0.0133(6)	0.051
F23	0.5088(8)	0.6626(6)	-0.0344(5)	0.056
F24	0.5957(8)	0.7825(5)	0.0475(6)	0.058
F25	0.7522(6)	0.6858(5)	0.0918(5)	0.045
Xe3	0.00000	0.50000	0.00000	0.050
F31	-0.0954(9)	0.4632(10)	0.0846(7)	0.100
F32	-0.0856(12)	0.6052(10)	-0.0132(10)	0.112
Cr1	0.3436(1)	0.6057(1)	0.1361(1)	0.021
F1	0.2575(6)	0.5949(5)	0.0538(4)	0.041
F2	0.4619(5)	0.5592(4)	0.0853(4)	0.029
F3	0.3036(5)	0.5092(4)	0.1843(5)	0.033
F4	0.2255(5)	0.6641(4)	0.1933(4)	0.029
F5	0.3994(5)	0.7043(4)	0.1109(4)	0.033
F6	0.4325(5)	0.6176(4)	0.2349(4)	0.025
Cr2	0.5791(1)	0.6390(1)	0.2717(1)	0.020
F7	0.5905(5)	0.7214(4)	0.1997(4)	0.030
F8	0.5808(5)	0.5393(4)	0.3243(4)	0.032
F9	0.6392(5)	0.5727(4)	0.1869(4)	0.025
F10	0.5265(6)	0.6947(5)	0.3509(5)	0.043

TABLE V - Selected Bond Lengths (Å) and Angles (°) for (XeF<sub>5</sub><sup>+</sup>CrF<sub>5</sub><sup>-</sup>)<sub>4</sub>.XeF<sub>4</sub>

Xe1 - F11	1.830(9)	Xe2 - F24	1.840(8)	Cr1 - F3	1.792(7)
Xe1 - F12	1.80(1)	Xe2 - F25	1.840(8)	Cr1 - F4	1.939(7)
Xe1 - F13	1.836(9)	Xe2 - F2	2.591(7)	Cr1 - F5	1.750(7)
Xe1 - F14	1.87(1)	Xe2 - F5	2.854(7)	Cr1 - F6	1.961(7)
Xe1 - F15	1.844(8)	Xe2 - F7	2.699(7)	Cr2 - F6	1.891(6)
Xe1 - F3	2.597(7)	Xe2 - F9	2.789(7)	Cr2 - F7	1.773(7)
Xe1 - F8 <sup>i</sup>	2.676(7)	Xe3 - F31,F31 <sup>ii</sup>	1.90(2)	Cr2 - F8	1.805(7)
Xe1 - F9 <sup>i</sup>	2.580(7)	Xe3 - F32,F32 <sup>ii</sup>	1.97(2)	Cr2 - F9	1.895(7)
Xe2 - F21	1.802(9)	Xe3 - F8,F8 <sup>iii</sup>	3.126(7)	Cr2 - F10	1.701(8)
Xe2 - F22	1.828(9)	Cr1 - F1	1.716(8)	Cr2 - F4 <sup>iv</sup>	1.890(6)
Xe2 - F23	1.838(9)	Cr1 - F2	1.805(7)		
F11 - Xe1 - F12	80.4(5)			F11 - Xe1 - F13	79.4(4)
F11 - Xe1 - F14	79.8(5)			F11 - Xe1 - F15	80.1(4)
F12 - Xe1 - F13	90.6(5)			F12 - Xe1 - F14	160.2(2)
F12 - Xe1 - F15	90.7(5)			F13 - Xe1 - F14	85.9(5)
F13 - Xe1 - F15	158.9(2)			F14 - Xe1 - F15	85.8(5)
F21 - Xe2 - F22	80.0(5)			F21 - Xe2 - F23	78.2(4)
F21 - Xe2 - F24	79.4(5)			F21 - Xe2 - F25	79.2(4)
F22 - Xe2 - F23	88.5(5)			F22 - Xe2 - F24	159.3(2)
F22 - Xe2 - F25	88.4(4)			F23 - Xe2 - F24	88.1(5)
F23 - Xe2 - F25	157.4(2)			F24 - Xe2 - F25	86.9(4)
F31 - Xe3 - F32	91.6(7)			F31 - Xe3 - F8 <sup>iii</sup>	115.9(4)
F32 - Xe3 - F8 <sup>iii</sup>	84.5(5)				
F1 - Cr1 - F2	93.6(4)			F1 - Cr1 - F3	96.0(4)
F1 - Cr1 - F4	89.7(4)			F1 - Cr1 - F5	97.5(4)
F1 - Cr1 - F6	175.9(1)			F2 - Cr1 - F3	93.9(3)
F2 - Cr1 - F4	174.8(1)			F2 - Cr1 - F5	87.4(3)
F2 - Cr1 - F6	90.0(3)			F3 - Cr1 - F4	89.7(3)
F3 - Cr1 - F5	166.3(1)			F3 - Cr1 - F6	81.7(4)
F4 - Cr1 - F5	88.2(3)			F4 - Cr1 - F6	86.8(3)
F5 - Cr1 - F6	84.6(3)				
F4 <sup>iv</sup> - Cr2 - F6	178.0(1)			F4 <sup>iv</sup> - Cr2 - F7	88.8(3)
F4 <sup>iv</sup> - Cr2 - F8	91.5(3)			F4 <sup>iv</sup> - Cr2 - F9	89.5(3)
F4 <sup>iv</sup> - Cr2 - F10	89.9(4)			F6 - Cr2 - F7	89.3(3)
F6 - Cr2 - F8	90.5(3)			F6 - Cr2 - F9	90.9(3)
F6 - Cr2 - F10	89.8(4)			F7 - Cr2 - F8	165.6(1)
F7 - Cr2 - F9	83.3(3)			F7 - Cr2 - F10	99.3(4)
F8 - Cr2 - F9	82.3(3)			F8 - Cr2 - F10	95.1(4)
F9 - Cr2 - F10	177.3(1)				
Cr1 - F4 - Cr2 <sup>i</sup>	136.6(4)			Cr1 - F6 - Cr2	142.3(4)

Symmetry code: i) -1/2+x, y, 1/2-z  
 ii) -x, 1-y, -z  
 iii) 1/2-x, 1-y, -1/2+z  
 iv) 1/2+x, y, 1/2-z

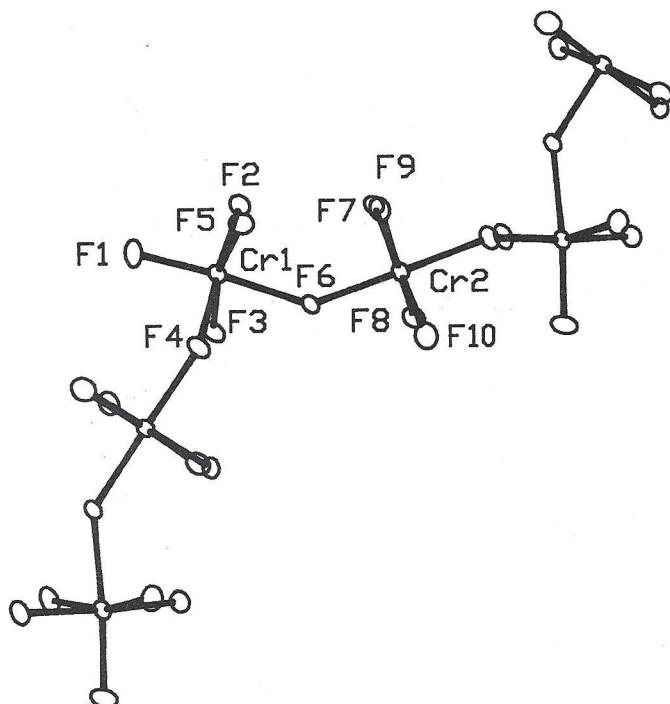


Fig. 2. Chain of  $\text{CrF}_6$  octahedra in  $(\text{XeF}_5^+\text{CrF}_5^-)_4\text{XeF}_4$

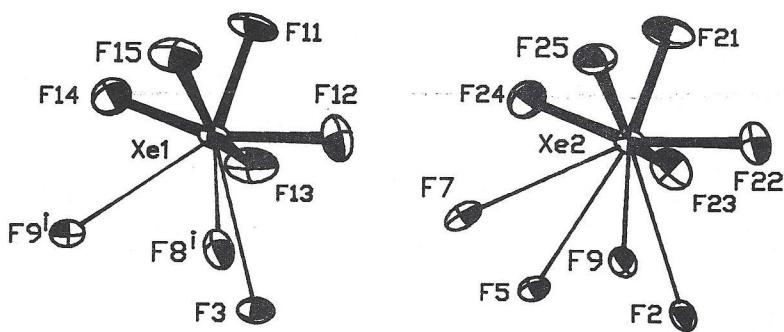


Fig. 3. ORTEP diagram of  $\text{XeF}_5^+$  ions in  $(\text{XeF}_5^+\text{CrF}_5^-)_4\text{XeF}_4$

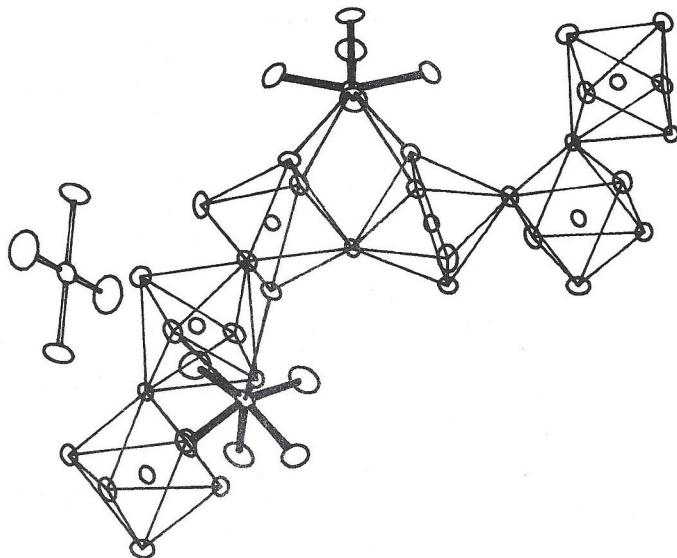


Fig. 4.  $(\text{XeF}_5^+ \text{CrF}_5^-)_4 \cdot \text{XeF}_4$  structure

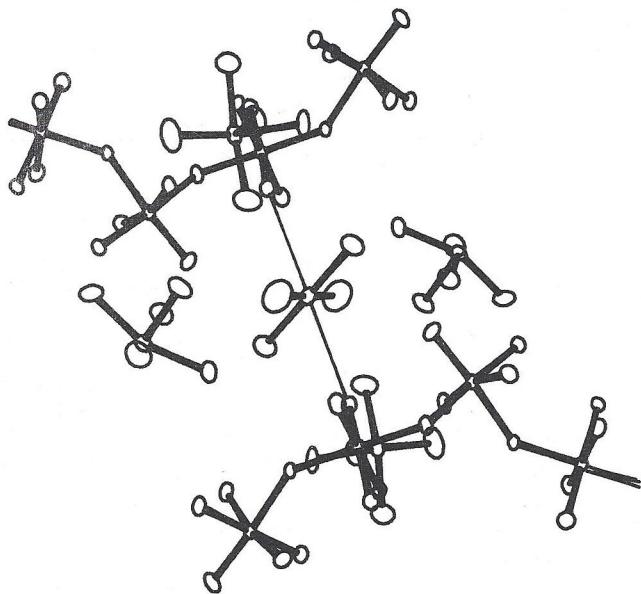
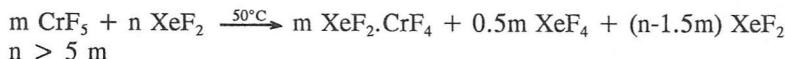


Fig. 5.  $\text{XeF}_4$  environment in  $(\text{XeF}_5^+ \text{CrF}_5^-)_4 \cdot \text{XeF}_4$

## RESULTS AND DISCUSSION

### Synthesis, Crystal Structure and Some Properties of $\text{XeF}_2\text{CrF}_4$

Xenon difluoride is capable to oxidize chromium only to 3+. Therefore  $\text{XeF}_2\text{CrF}_4$  could be prepared either by a direct reaction between  $\text{CrF}_4$  and  $\text{XeF}_2$  at room temperature or by the reaction between  $\text{CrF}_5$  and  $\text{XeF}_2$ . For the latter reaction a big excess of  $\text{XeF}_2$  is necessary.



Chromium(V) fluoride oxidizes xenon difluoride to xenon(IV) fluoride and reduces to chromium(IV) fluoride which reacts with excess of xenon(II) fluoride to a blue solid  $\text{XeF}_2\text{CrF}_4$ . If the excess of xenon difluoride is too small a product looking as black wax is obtained with the melting point below 50°C. This is probably polymeric chains of  $\text{CrF}_6$  octahedra formed from  $(\text{F}\cdots\text{CrF}_4)_n$  and  $(\text{CrF}_5)_n$  octahedra.

The reaction in AHF is not possible because  $\text{XeF}_2\text{CrF}_4$  itself is not stable in AHF, where solvolysis took place and very pure  $\text{CrF}_4$  is precipitated. It is of amethyst colour. There are many reports about the synthesis of  $\text{CrF}_4$  [12-14]. No one of these samples seems to be pure although the sample made by Christe [14] has very similar IR and Raman spectra to our sample. An alternative method for the preparation of pure  $\text{CrF}_4$  is the reduction of  $\text{CrF}_5$  in AHF solution at temperatures below 0°C by stoichiometric amount of  $\text{XeF}_2$ .

$\text{XeF}_2\text{CrF}_4$  is a deep blue, crystalline solid, stable in a dynamic vacuum to about 40°C, where it starts to decompose slowly losing  $\text{XeF}_2$ . At higher temperatures (100°C) beside  $\text{XeF}_2$  also  $\text{XeF}_4$  is obtained. The final product of decomposition is  $\text{CrF}_3$ . It looks that  $\text{CrF}_4$  is still enough strong oxidizing agent to convert  $\text{XeF}_2$  to  $\text{XeF}_4$  at a little higher temperatures.

$\text{CrF}_4$ , as poor fluoroacid, in reaction with  $\text{XeF}_2$ , as a weak fluoride-ion donor, will not form ionic compound e.g.  $\text{XeF}^+\text{CrF}_5^-$  but compound e.g.  $\text{F-Xe}\cdots\text{F-CrF}_4$  which is at the beginning of the ionization pathway  $\text{XeF}_2 \rightarrow \text{XeF}^+ + \text{F}^-$ . The Xe-F distance 1.93(2) Å is shorter than in  $\text{XeF}_2$  itself (Xe-F=2.01(1) Å) [15] but longer than in  $\text{XeF}^+$  species (Xe-F+=1.82(3)-1.90(3) Å) [11,16-18].  $\text{XeF}^+$  is characterized by strong band or pair of bands in the region 598 to 621 cm<sup>-1</sup> in Raman [19] and in the region 600-626 cm<sup>-1</sup> in the infrared spectrum [20]. In the Raman and infrared spectra of  $\text{XeF}_2\text{CrF}_4$  the bands which could be assigned to Xe-F stretching vibrations are 584 cm<sup>-1</sup> and 577 cm<sup>-1</sup> respectively. The shortest Cr-F bond [ $\text{Cr-F}(6)=1.71(2)$  Å] is trans to the bridging fluorine atom of  $\text{XeF}_2$ . Fluorine ligand F(6) is so close to chromium that neighbouring fluorine ligands F(4) and F(5) are pushed towards F(1) because of fluorine-

fluorine repulsions so that the angle F(4)-Cr-F(5) is only 162.3(3) $^\circ$ . Because of all this CrF<sub>6</sub> octahedra are very distorted.

From X-ray powder data, chromium pentafluoride [21] has the same structure as vanadium pentafluoride, for which a full single-crystal analysis has been reported [22]. The structure of VF<sub>5</sub> consists of infinite chains of molecules linked by cis-bridging fluorine atoms, with an approximately octahedral arrangement of fluorine atoms around the vanadium atom. The structure of XeF<sub>2</sub>.CrF<sub>4</sub> consists of an infinite chain of distorted CrF<sub>6</sub> octahedra linked by trans-bridging fluorine atoms. The angle Cr-F-Cr [147.3(8) $^\circ$ ] is nearly the same as V-F-V angle in VF<sub>5</sub> [149.7(1.0) $^\circ$ ].

### Synthesis, Crystal Structure and Some Properties of $(\text{XeF}_5^+ \text{CrF}_5^-)_4 \cdot \text{XeF}_4$

Xenon(VI) fluorochromates(IV) could be synthesized using different synthetic routes. Chromium(II) fluoride or chromium(III) fluoride could be converted to the xenon(VI) complex using excess of XeF<sub>6</sub> and temperatures between 60°C and 120°C. XeF<sub>6</sub> is capable to oxidize chromium to 4+ valence state while XeF<sub>6</sub> is reduced to XeF<sub>4</sub>. During these synthetic routes the complex  $(\text{XeF}_5^+ \text{CrF}_5^-)_x \cdot \text{XeF}_4$ , where  $x \geq 4$ , is prepared because formed XeF<sub>4</sub> is bonded between two infinite chains of CrF<sub>6</sub> octahedra. The amount of bonded XeF<sub>4</sub> varies from the experiment to experiment. The maximum amount of bonded XeF<sub>4</sub> obtained up to now, during growing crystals in AHF solution, was one XeF<sub>4</sub> per four XeF<sub>5</sub><sup>+</sup>CrF<sub>5</sub><sup>-</sup> groups. Undoubtedly, we have here XeF<sub>4</sub> molecular complex which owes its existence to appreciable Coulombic interactions between positive Xe atom (Xe-3) and highly negative fluorine ligands of CrF<sub>6</sub> octahedra. In the case that XeF<sub>5</sub><sup>+</sup>CrF<sub>5</sub><sup>-</sup> should be prepared, only direct reaction between XeF<sub>6</sub>, free of XeF<sub>4</sub>, and CrF<sub>4</sub> at room temperature, or the reaction between CrF<sub>5</sub> and XeF<sub>6</sub> at higher temperature (60°C), should be used. In the latter reaction elemental fluorine is evolved. The reaction proceeds because CrF<sub>5</sub> is thermodynamically unstable and it decomposes at temperatures above 60°C to CrF<sub>4</sub> and elemental fluorine. The equilibrium is not achieved because CrF<sub>4</sub> is immediately reacting further to XeF<sub>5</sub><sup>+</sup>CrF<sub>5</sub><sup>-</sup>. Although CrF<sub>4</sub> is a poor fluoroacid in the reaction with XeF<sub>6</sub>, as moderately strong fluorobase, forms XeF<sub>5</sub><sup>+</sup> salt which could be crystallized from AHF solution without solvolysis. Thus CrF<sub>4</sub> nicely discriminates between the basicity of XeF<sub>2</sub> and XeF<sub>6</sub>.

The anion consists of infinite chain of distorted CrF<sub>6</sub> octahedra that alternately share cis and trans vertices. Evidently, choice of cis vs. trans bridging for polymerized (CrF<sub>5</sub>)<sub>n</sub> is one of energetic and/or packing subtlety. There are two crystallographically distinct XeF<sub>5</sub><sup>+</sup> cations, XeF<sub>5</sub>(Xe-1) is the first example of the structure of XeF<sub>5</sub> which differs from the usual shape. The axial Xe-F interatomic distance in the cation XeF<sub>5</sub><sup>+</sup> is in all cases, where anion is octahedron, shorter than the equatorial, the difference ranging from 0.03-0.06 Å, and the axial Xe-F distance is close to 1.80 Å. All Xe-F equatorial distances are rather similar. In XeF<sub>5</sub> (Xe-1) the interatomic distance Xe(1)-F(12) is only 1.80(1) and trans

situated Xe(1)-F(14) is 1.87(1) Å. The possible reasons for this are that  $\text{XeF}_5$  is squashed between  $\text{XeF}_4$  and the chain, and because of packing considerations, since the volume per fluorine atom in the structure, of 17.87 Å<sup>3</sup>, is low for an arrangement which does not correspond to close packing.  $\text{XeF}_5$  (Xe-2) has the usual shape and dimensions. It seems that the coordination geometry of  $\text{XeF}_5$  groups and their bridging fluorine ligands is determined by simple Coulombic interactions. These involve the negatively charged bridging fluorines, the somewhat negative equatorial ligands of the  $\text{XeF}_5$  group, and the positive charge on the xenon atom. The latter is shielded on the pseudo 4-fold axis by the non-bonding xenon valence-electron pair. The observed geometry nicely conforms to the balance of these repulsive and attractive interactions. Xenon(1) has close interactions with three fluorine ligands like in  $(\text{XeF}_5^+)_2\text{PdF}_6^{2-}$  [23], and xenon(2) with four fluorine ligands from  $\text{CrF}_6$  octahedra like in  $\text{XeF}_5^+\text{GeF}_5^-$  [7].

Coulombic interactions between positive charge Xe(3) and negative fluorine ligands from  $(\text{CrF}_5^-)_n$  chain are responsible for the molecular complex of  $\text{XeF}_4$  with  $\text{XeF}_5^+\text{CrF}_5^-$  polymer. In the solid reaction the amount of bonded  $\text{XeF}_4$  is lower than when the crystals are grown from the saturated AHF solution. Because of two nonbonding xenon valence-electron pairs above and below  $\text{XeF}_4$  plane the approach of fluorine ligands is not on the octahedral positions but between lone pairs and equatorial fluorines at the distance 3.126(7) Å in such a way that repulsion between fluorine ligands and nonbonding xenon valence-electron pairs is minimal.  $\text{XeF}_4$  is slightly distorted with two Xe-F distances 1.90(2) Å and two Xe-F distances 1.97(2) Å, while Xe-F bond length in the solid  $\text{XeF}_4$  is 1.953(2) Å [23].

The Raman spectra of  $(\text{XeF}_5^+\text{CrF}_5^-)_4\text{XeF}_4$  show bands at 545 cm<sup>-1</sup> and 504 cm<sup>-1</sup>, which are practically identical with the strongest bands of solid  $\text{XeF}_4$   $\nu_1$  (543 cm<sup>-1</sup>) and  $\nu_4$  (502 cm<sup>-1</sup>) [24]. Also in the infrared spectra there is the strong band at 563 cm<sup>-1</sup> which is in accord with  $\nu_6$  band of solid  $\text{XeF}_4$  at 561 cm<sup>-1</sup> [25]. In the vibrational spectra of  $\text{XeF}_5^+\text{CrF}_5^-$  these  $\text{XeF}_4$  bands are missing. The structure  $\text{XeF}_5^+\text{CrF}_5^-$  probably consists of trans bridged  $\text{CrF}_6$  octahedra with  $\text{XeF}_5^+$  cations alternately on left and right side of the  $(\text{CrF}_5^-)_n$  chain like in  $\text{XeF}_5^+\text{GeF}_5^-$  [7].

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## REFERENCES

- [1] J. Slivnik and B. Žemva, *Z. anorg. allg. Chem.*, 1971, 385, p. 137.
- [2] B. Žemva, J. Zupan and J. Slivnik, *J. inorg. nucl. Chem.*, 1973, 35, p. 3941.
- [3] A. Šmalc, K. Lutar and J. Slivnik, *J. Fluorine Chem.*, 1975, 6, p. 287.
- [4] K. Lutar, A. Šmalc and J. Slivnik, *Vestn. Slov. Kem. Drus.*, 1979, 26, p. 435.
- [5] B. Žemva and J. Slivnik, *Vestn. Slov. Kem. Drus.*, 1972, 19, p. 43.
- [6] J. Slivnik, A. Šmalc, K. Lutar, B. Žemva and B. Frlec, *J. Fluorine Chem.*, 1975, 5, p. 273.
- [7] T.E. Mallouk, B. Desbat and N. Bartlett, *Inorg. Chem.*, 1984, 23, p. 3160.
- [8] N. Bartlett, F. Einstein, D.F. Stewart and J. Trotter, *J. Chem. Soc., Chem. Commun.*, 1966, p. 550; *J. Chem. Soc., A*, 1967, p. 1190.
- [9] N. Bartlett, M. Gennis, D.D. Gibler, B.K. Morrell and A. Zalkin, *Inorg. Chem.*, 1973, 12, p. 1717.
- [10] K. Leary, D.H. Templeton, A. Zalkin and N. Bartlett, *Inorg. Chem.*, 1973, 12, p. 1726.
- [11] N. Bartlett, B.G. DeBoer, F.J. Hollander, F.O. Sladky, D.H. Templeton, and A. Zalkin, 1974, 13, p. 780.
- [12] H.V. Wartenberg, *Z. anorg. allg. Chem.*, 1941, 247, p. 135.
- [13] H.C. Clark and Y.N. Sadana, *Can. J. Chem.*, 1964, 42, p. 50.
- [14] R. Bougon, W.W. Wilson and K.O. Christe, *Inorg. Chem.*, 1985, 24, p. 2286.
- [15] H.A. Levy and P.A. Agron, In Noble Gas Compounds; H.H. Hyman Ed., The University of Chicago Press, Chicago and London, 1963, p. 221.
- [16] J. Burgess, C.J.W. Fraser, V.M. Mc Rae, R.D. Peacock, D.R. Russell, *J. inorg. nucl. Chem., H.H. Hyman Mem. Vol.*, 1976, p. 183.
- [17] A. Zalkin, D.L. Ward, R.N. Biagioli, D.H. Templeton and N. Bartlett, *Inorg. Chem.*, 1978, 17, p. 1318.
- [18] B. Žemva, A. Jesih, D.H. Templeton, A. Zalkin, A.K. Cheetham and N. Bartlett, *J. Am. Chem. Soc.*, 1987, 109, p. 7420.
- [19] F.O. Sladky, P.A. Bulliner and N. Bartlett, *J. Chem. Soc., A*, 1969, p. 2179.
- [20] B. Frlec and J.H. Holloway, *J. Chem. Soc., Dalton Trans.*, 1975, p. 535.
- [21] A.J. Edwards, *Proc. Chem. Soc.*, 1963, p. 205.
- [22] A.J. Edwards and G.R. Jones, *J. Chem. Soc., A*, 1969, p. 1651.
- [23] J.H. Burns, P.A. Agron and H.A. Levy, *Science*, 1963, 139, p. 1208.
- [24] H.H. Claassen, C.L. Chernick and J.G. Malm, *J. Am. Chem. Soc.*, 1963, 85, p. 1927.
- [25] T. Ogrin, private communication.