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XeF_2·$2CrF_4$ and $XeF_5^+CrF_5^-$: Syntheses, Crystal Structures, and Some Properties[†]

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XeF_2·$2CrF_4$ was prepared by solvolysis of XeF_2·CrF_4 in anhydrous hydrogen fluoride (aHF) and subsequent decantation of the majority of dissolved XeF_2 in aHF. Remaining XeF_2 and a large excess of CrF_4 form XeF_2·$2CrF_4$ after aHF is removed. Ruby-red single crystals were obtained either by heating the sample in a thermal gradient or by recrystallization in supercritical SF_6. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 855.1(3)$ pm, $b = 922.1(3)$ pm, $c = 1043.8(3)$ pm, $\alpha = 76.02(2)°$, $\beta = 81.36(2)°$, $\gamma = 88.08(3)°$, and $Z = 4$ at 293 K. The basic structural unit is formed by four independent Cr atoms, each octahedrally coordinated by six F atoms. Two fluorine ligands are provided by two different XeF_2 molecules. The distorted octahedra are connected via common F atoms to form a three-dimensional network. $XeF_5^+CrF_5^-$ was prepared from XeF_6 and CrF_4 at room temperature or by the reaction of XeF_6 and CrF_5 at 333 K. Red single crystals were grown from the solution of $XeF_5^+CrF_5^-$ in aHF. The compound crystallizes in the orthorhombic space group *Pbca* with $a = 1828.1(13)$ pm, $b = 842.9(7)$ pm, $c = 1852.1(12)$ pm, and $Z = 16$ at 268 K. The main structural feature is formed by an infinite chain of distorted CrF_6 octahedra joined via cis vertexes, while XeF_5^+ cations compensate the negative charge of each octahedron.

Introduction

Reactions between chromium fluorides and xenon fluorides have been extensively studied in the past.[1−3] During these investigations the following compounds were synthesized: XeF_2·nCrF_4 ($n = 1, 2$), $XeF_5^+CrF_5^-$, and its XeF_4 adduct $(XeF_5^+CrF_5^-)_4$·XeF_4. In pure form only XeF_2·CrF_4 and $(XeF_5^+CrF_5^-)_4$·XeF_4 were prepared and their crystal structures determined.[3] By solvolysis of XeF_2·CrF_4 in anhydrous HF, very pure CrF_4 was obtained for the first time.[3] As indicated by its powder diffraction pattern, it has a different structure than the CrF_4 isolated and structurally characterized by Müller.[4] In the systems of xenon fluorides—chromium fluorides, major questions were still open. Concerning the reaction between XeF_2 and CrF_4, we were interested in the preparation of pure XeF_2·$2CrF_4$ to determine its structure. In the system XeF_6/CrF_4 we wanted to prepare pure $XeF_5^+CrF_5^-$ to compare its structure with that of $XeF_5^+GeF_5^-$.[5] The latter represented by then the only known structure of an XeF_5^+ salt of a polymeric fluorometalate(IV). The present studies include synthetic work, determination of the crystal structures and some properties of the compounds XeF_2·$2CrF_4$ and $XeF_5^+CrF_5^-$.

Experimental Section

1. Apparatus and Reagents. A nickel vacuum line with a mechanical pump, a mercury diffusion pump, and soda lime scrubbers for removal of volatile fluorides were used. The part of the vacuum line used for transfer of aHF, CrF_5, XeF_6, and KrF_2 was made entirely from Teflon, FEP, or PFA to avoid the formation of H_2 or to prevent reduction of reagents. This part of the line was equipped with a Monel Helicoid pressure gauge (0−1500 Torr (±0.3%), Bristol Babcock Inc.) connected via a Teflon valve. Teflon−FEP (17.46 mm i.d. × 19.05 mm o.d.) or −PFA (16 mm i.d. × 19 mm o.d.) reaction vessels equipped with Teflon valves, and Teflon-covered mixing bars were used for all experiments. Chromium metal (BDH, technical powder), chromium difluoride (Merck), and chromium trifluoride (Johnson Matthey, anhydrous, 98%) were used as supplied. Chromium pentafluoride was prepared from lower chromium fluorides under pressure of elemental fluorine.[1] Xenon (99.99%) and krypton (99.99%) were used as supplied by Messer Griesheim. Xenon difluoride was prepared by irradiating a gaseous mixture of xenon and fluorine at room temperature.[6,7] Krypton difluoride was prepared photochemically from krypton in liquid fluorine at 77 K.[8,9] Xenon hexafluoride was synthesized from xenon and fluorine in the presence of nickel difluoride at 393 K.[10] Fluorine (99%, Solvay) was used as supplied. For special purposes fluorine was additionally purified by photochemical means.[11] Anhydrous hydrogen fluoride (99.8%, UCAR) was purified by treatment with K_2NiF_6 for several days.

2. Instrumentation. Nonvolatile materials and single crystals were manipulated in a glovebox (MBraun). The residual of water in the atmosphere within the glovebox never exceeded 1 ppm. Infrared spectra were recorded on a PE FTIR-1710 instrument. For volatile materials a 10 cm nickel cell with AgCl windows was used. Raman spectra were taken on a Renishaw Ramascope dispersive instrument. A 25 mW He−Ne laser with $\lambda = 632.8$ nm was used for excitation.

3. Preparation of Single Crystals of XeF_2·$2CrF_4$. XeF_2·CrF_4 (12.04 mmol) prepared according to ref 3 was loaded into one leg of a T-shaped apparatus made from two PFA tubes (16 × 19 mm), and

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[†] Dedicated to Professor Neil Bartlett on occasion of the official close of his distinguished academic career.

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about 8 mL of aHF was condensed onto the solid at 77 K. At room-temperature solvolysis of $XeF_2 \cdot CrF_4$ took place (see under synthesis of CrF_4[3]). The supernatant solution was thoroughly decanted once from the precipitate before the remaining aHF was pumped away. The mixture of CrF_4 (large excess) and XeF_2 left behind, reacted immediately to $XeF_2 \cdot 2CrF_4$. About half of the resulting mixture of $XeF_2 \cdot 2CrF_4$ with excess CrF_4 was put into a brass reaction vessel (tube 8 mm i.d. × 10 mm o.d., length 100 mm) connected to a nickel valve. This reaction vessel was mounted on a hot plate (333 K) so that a temperature gradient of about 35−40 K between the lower and upper part of the vessel was maintained over the period of 2 months. Ruby-red single crystals of $XeF_2 \cdot 2CrF_4$ were easily separated from noncrystalline powder. Structural data given in the current paper are from one of these crystals. The other half of the above mixture was loaded into a nickel reaction vessel designed for work with binary fluorides as supercritical media.[12] Single crystals of $XeF_2 \cdot 2CrF_4$ were obtained under supercritical conditions in SF_6 within 2 days.

4. Preparation of Single Crystals of $XeF_5^+CrF_5^-$. From the reaction between CrF_5 and excess XeF_6 a sample of $XeF_5^+CrF_5^-$ (∼5 mmol) was prepared as already described.[3] The IR spectrum of the XeF_6 used did not show any bands due to XeF_4 and/or XeF_2. Red single crystals of $XeF_5^+CrF_5^-$ were obtained from the supersaturated aHF solution in the apparatus described elsewhere.[13]

5. Reaction of Cr with XeF_6 and KrF_2 in aHF. Chromium metal (1.94 mmol) was weighed into a PFA reaction vessel. About 7 mL of aHF, 10.19 mmol of XeF_6, and 20.53 mmol of KrF_2 were added subsequently at 77 K. After 1 h at room temperature the solution was slightly colored (reddish to yellow). During the reaction the intensity of the red color was increasing and, when all chromium was dissolved (∼12 h), the solution was intensely red. At this stage KrF_2 was still present. The course of the reaction was followed by taking in-line Raman spectra. While all volatile components were pumped off at room temperature, it became obvious that the color was due to CrF_5 dissolved in aHF. As majority of CrF_5 could be pumped off, the reaction between CrF_5 and XeF_6 in aHF has to be rather slow at room temperature. However, when aHF was removed, some of the CrF_5 and XeF_6 reacted to fluorine and $XeF_5^+CrF_5^-$ as revealed from Raman spectra.[14]

6. Reaction of Cr with KrF_2 in aHF. Chromium metal (1.94 mmol) was weighed into a PFA reaction vessel. About 5 mL of aHF and 16.42 mmol of KrF_2 were added. The only reaction product was CrF_5 which was completely dissolved in aHF.

7. Reaction of CrF_3 with XeF_6 in aHF. A 1.28 mmol amount of CrF_3 was weighed into a PFA reaction vessel; aHF (∼5 mL) and XeF_6 (∼10 mmol) were added. Raman spectra of the red solution as well as of the precipitate showed that $(XeF_5^+CrF_5^-)_4 \cdot XeF_4$ had formed.[14]

8. Structural Investigations. Crystals of $XeF_2 \cdot 2CrF_4$ as well as $XeF_5^+CrF_5^-$ are very sensitive even to traces of moisture. Therefore, they were selected in a glovebox using a surgical microscope ($f = 300$ mm, Opton) and loaded into 0.5 mm quartz glass capillaries which were temporarily closed by Kel-F grease and later flame-sealed outside the glovebox. Numerous attempts were necessary until a crystal of reasonable quality was found for $XeF_5^+CrF_5^-$ (see Discussion). Single-crystal data for both compounds were collected on a diffractometer with an area detector based on an imaging plate (Stoe IPDS). Details of the diffraction experiments are given in Table 1 and in the Supporting Information. For crystallographic calculations the program systems SHELXTL-Plus[15] and SHELXL-97[16] were used.

Table 1. Crystal Data and Structure Refinement for $XeF_2 \cdot 2CrF_4$ and $XeF_5^+CrF_5^-$

empirical formula	$XeF_2 \cdot 2CrF_4$	$XeF_6 \cdot CrF_4$
fw	425.30	373.30
temp (K)	293 ± 2	268 ± 2
wavelength (pm)	71.073	
space group	$P\bar{1}$ (No. 2)	$Pbca$ (No. 61)
a (pm)	855.1(3)	1828.1(13)
b (pm)	922.1(3)	842.9(7)
c (pm)	1043.8(3)	1852.1(12)
α (deg)	76.02(2)	90
β (deg)	81.36(2)	90
γ (deg)	88.08(3)	90
V (nm^3)	0.7897(4)	2.854(4)
formula units, Z	4	16
d(calc) (g/cm^3)	3.577	3.475
abs coeff (mm^{-1})	7.099	6.411
F(000)	768	2688
$2\theta_{max}$ (deg)	52.0	46.0
no. of reflcns collcd	6651	7486
no. of indepdt reflcns	2801	1863
R_{int}	0.0620	0.1594
refinement method	full-matrix least-squares on F^2	
no. of params	235	217
goodness-of-fit (GOF) on F^2	1.125	1.100
R indices R_1, wR_2 (all data)[a]	0.0311, 0.0825	0.0906, 0.1957

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. w$R_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. GOF $= \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n = no. of reflcns and p = no. of refined params.

Table 2. Final Positional and Displacement Parameters for $XeF_2 \cdot 2CrF_4$

atom	x	y	z	U_{eq} (pm^2)[a]
Xe1	0.07633(3)	0.51251(3)	−0.27736(3)	290(1)
Xe2	0.19745(3)	1.12090(3)	0.06581(3)	241(1)
Cr1	0.21368(6)	0.91703(6)	−0.37672(6)	169(2)
Cr2	0.29141(6)	0.75020(6)	−0.02771(6)	168(2)
Cr3	0.41787(7)	0.66387(6)	0.28895(6)	169(2)
Cr4	0.39844(6)	0.25759(6)	0.43981(6)	155(2)
F1	0.0785(4)	0.3001(3)	−0.2408(4)	551(9)
F2	0.0689(3)	0.7565(3)	−0.3206(3)	322(6)
F3	0.0790(3)	1.0282(3)	−0.3106(3)	341(6)
F4	0.3668(3)	1.0715(2)	−0.4288(2)	222(5)
F5	0.3750(2)	0.7823(2)	−0.4206(3)	246(5)
F6	0.1672(3)	0.9511(3)	−0.5327(3)	316(6)
F7	0.2849(3)	0.8560(3)	−0.2080(3)	333(6)
F8	0.1055(3)	0.6700(3)	−0.0195(3)	283(5)
F9	0.4043(3)	0.6147(3)	−0.0767(3)	380(6)
F10	0.4364(3)	0.8741(3)	−0.0221(3)	287(5)
F11	0.1503(3)	0.9097(3)	0.0311(3)	314(6)
F12	0.2245(4)	1.3156(3)	0.0967(4)	477(8)
F13	0.2920(3)	0.6550(3)	0.1558(3)	269(5)
F14	0.5911(3)	0.6554(3)	0.1797(3)	276(5)
F15	0.5485(3)	0.6569(2)	0.4247(2)	234(5)
F16	0.2508(3)	0.6117(3)	0.4092(3)	292(5)
F17	0.3983(3)	0.8525(3)	0.2623(3)	327(6)
F18	0.4424(3)	0.4389(2)	0.3205(2)	225(5)
F19	0.3894(3)	0.1698(3)	0.3159(3)	285(5)
F20	0.2038(3)	0.3000(3)	0.4741(3)	290(5)

[a] U_{eq} defined as $^1/_3$ of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensors.

9. Description of the $XeF_2 \cdot 2CrF_4$ Structure. $XeF_2 \cdot 2CrF_4$ crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with four formula units in the unit cell and one in the asymmetric unit, respectively. Pertinent crystallographic data are given in Table 1, positional and isotropic displacement parameters of the atoms in Table 2, and interatomic distances in Table 3. A complete list of bond angles is available in the Supporting Information, and the labeling scheme is given in Figure 1. The basic structural unit is formed by four independent Cr atoms each being octahedrally coordinated by six F atoms. For each of two of the Cr atoms one F ligand is provided by a different XeF_2 molecule (Figure 1). The distorted octahedra are connected via common F atoms to finally form a rather complicated network. Nevertheless, the four

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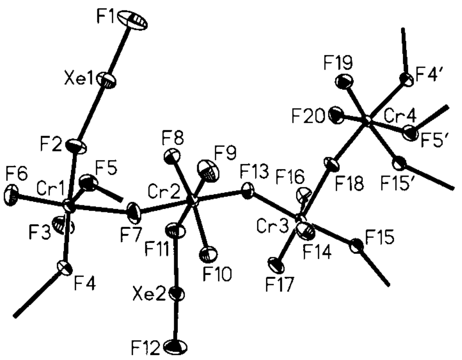

Figure 1. Basic structural unit in $XeF_2{\cdot}2CrF_4$ showing the labeling scheme. The ellipsoids are drawn at the 50% probability level.

Table 3. Selected Interatomic Distances (pm) for $XeF_2{\cdot}2CrF_4$

Xe1−F1	190.3(3)	Xe2−F12	192.7(3)
Xe1−F2	218.6(3)	Xe2−F11	212.7(3)
Cr1−F2	188.5(2)	Cr2−F7	190.7(3)
Cr1−F3	169.6(3)	Cr2−F8	175.7(2)
Cr1−F4	189.1(2)	Cr2−F9	168.3(3)
Cr1−F5	190.5(2)	Cr2−F10	173.1(2)
Cr1−F6	168.7(3)	Cr2−F11	202.3(3)
Cr1−F7	190.0(3)	Cr2−F13	190.5(3)
Cr3−F13	189.9(3)	Cr4−F18	183.9(2)
Cr3−F14	174.0(2)	Cr4−F19	169.6(3)
Cr3−F15	192.0(2)	Cr4−F20	170.2(2)
Cr3−F16	175.0(2)	Cr4−F4′	191.9(2)
Cr3−F17	170.1(2)	Cr4−F5′	194.9(2)
Cr3−F18	202.9(2)	Cr4−F15′	189.3(2)

CrF_6 units may be differentiated into two groups. Cr1 and Cr4 are connected to two nonbridging and four bridging fluorine ligands, while Cr2 and Cr3 show three nonbridging besides three bridging fluorine atoms. For the first group (Cr1, Cr4) the nonbridging fluorines are in both cases in cis arrangement with rather short Cr−F distances of about 169 pm. Accordingly, the respective angles are opened up by almost 10° compared to 90° in a regular octahedron. Although for Cr1 one ligand (F2) is provided by an XeF_2 molecule, the distances of the four bridging ligands are very similar, ranging from 188.5 to 190.5 pm. However, within the unit around Cr4 only two distances are very close to these values while the remaining two are considerably shortened (F18) or elongated (F5′) by about 5 pm. This represents different functionalities, as will be discussed later. Most of the bond angles show only slight deviations from a right angle. Only those angles opposite the ones opened up by about 10° are closed in to a very similar extent. For Cr2 and Cr3 the three nonbridging ligands are arranged in what might be considered the square plane of each elongated octahedron. The distances of the central fluorines (F9 and F17) are again close to 169 pm. The distances of the remaining two terminal ligands (F8, F10 and F14, F16) for each octahedron are elongated by about 5 pm. As expected the similar arrangement of the bridging fluorines is also reflected in the bond distances. While the apical distances are again close to 191 pm, the distances opposite to the shortest nonbridging ligands are considerably longer than all other Cr−F bonds. In one case this particular ligand (F11) is provided by a second XeF_2 molecule, while for F18 this influence leads to exceptional Cr−F distances. Cr3−F18 is the longest while Cr4−F18 is the shortest of all bridging distances. Accordingly F18 forms a very asymmetric Cr−F−Cr bridge with the two distances differing by 19 pm.

10. Description of the $XeF_5^+CrF_5^-$ Structure. The compound $XeF_5^+CrF_5^-$ was found to crystallize in the orthorhombic space group *Pbca* (No. 61) with two formula units in the asymmetric unit (Table 1). Respective data are listed in Tables 4 and 5 with the labeling scheme indicated in Figure 2. The main structural feature is an infinite chain of distorted CrF_6 octahedra joined via shared cis vertexes. Each octahedron is carrying a negative charge which is compensated by an XeF_5^+ cation. Accordingly, the compound should be described as $XeF_5^+CrF_5^-$. The cations show the characteristic square pyramidal shape with the Xe atoms slightly below the square plane. Each Xe atom is forming three additional contacts at about 260 pm to fluorine ligands of the anionic chain (Figure 3). The differences in these interactions are responsible for the formation of two crystallographically distinguished cations and CrF_6 octahedra, respectively. The cation formed by Xe1 is connected to two fluorine atoms bonded to Cr1 and to one fluorine from the second type of octahedron. This way edge-sharing of the Xe1 polyhedron with the Cr1 octahedron besides a common vertex with a Cr2 octahedron is achieved. In contrast Xe2 is interacting with three F atoms from three different CrF_6 octahedra, two of type Cr2 and one of type Cr1. The differences in functionality of the Cr−F bonds are reflected in the interatomic distances as expected. The bond lengths for terminal fluorine ligands are at 169 pm identical to those in $XeF_2{\cdot}2CrF_4$. All Cr−F bonds involved in interactions with

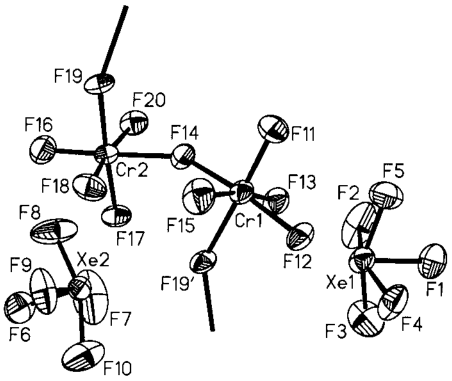

Figure 2. Basic structural unit in $XeF_5^+CrF_5^-$ including labeling scheme and with ellipsoids drawn at the 50% probability level.

Table 4. Final Positional and Displacement Parameters for $XeF_5^+CrF_5^-$

atom	*x*	*y*	*z*	U_{eq} (pm^2)[a]
Xe1	0.40015(7)	0.27199(15)	0.77642(6)	424(5)
Xe2	0.12143(7)	0.25118(14)	0.46564(6)	434(5)
Cr1	0.33542(16)	−0.0570(3)	0.66982(15)	356(7)
Cr2	0.16972(15)	−0.1806(3)	0.56833(14)	314(7)
F1	0.4403(8)	0.3491(16)	0.8583(6)	719(39)
F2	0.3180(8)	0.300(2)	0.8320(9)	1015(62)
F3	0.3948(10)	0.4871(15)	0.7611(8)	850(49)
F4	0.4969(7)	0.2770(15)	0.7492(7)	609(32)
F5	0.4138(9)	0.0920(15)	0.8270(6)	742(42)
F6	0.0725(8)	0.2654(17)	0.3814(8)	800(42)
F7	0.0544(13)	0.401(2)	0.4845(10)	1407(92)
F8	0.0520(8)	0.1064(19)	0.4788(10)	1050(63)
F9	0.1750(10)	0.117(2)	0.4106(7)	962(54)
F10	0.1682(11)	0.415(2)	0.4205(12)	1439(99)
F11	0.3455(8)	−0.1958(14)	0.7338(6)	609(34)
F12	0.4231(5)	0.0375(11)	0.6890(5)	389(23)
F13	0.2959(7)	0.0899(13)	0.7295(5)	481(27)
F14	0.2402(6)	−0.1320(12)	0.6451(5)	435(25)
F15	0.3768(7)	−0.1723(13)	0.5998(6)	574(31)
F16	0.1061(7)	−0.2263(13)	0.5048(7)	550(30)
F17	0.1646(6)	0.0283(11)	0.5487(6)	476(27)
F18	0.2484(6)	−0.2028(12)	0.5120(5)	468(26)
F19	0.1793(5)	−0.3983(10)	0.5931(5)	372(23)
F20	0.1050(6)	−0.1579(12)	0.6396(6)	452(26)

[a] U_{eq} defined as $^1/_3$ of the trace of the $\mathbf{U}_{ij}$ tensors.

Table 5. Selected Interatomic Distances (pm) for $XeF_5^+CrF_5^-$

Xe1−F1	180.5(11)	Xe2−F6	180.2(13)
Xe1−F2	183.7(13)	Xe2−F7	179.3(15)
Xe1−F3	183.8(13)	Xe2−F8	177.8(13)
Xe1−F4	183.9(13)	Xe2−F9	181.1(15)
Xe1−F5	180.1(13)	Xe2−F10	182.7(16)
Cr1−F11	167.5(11)	Cr2−F14	196.2(10)
Cr1−F12	182.5(10)	Cr2−F16	169.9(11)
Cr1−F13	181.1(11)	Cr2−F17	180.0(9)
Cr1−F14	190.8(10)	Cr2−F18	178.6(10)
Cr1−F15	178.9(11)	Cr2−F19	190.0(9)
Cr1−F19′	197.1(10)	Cr2−F20	178.3(10)

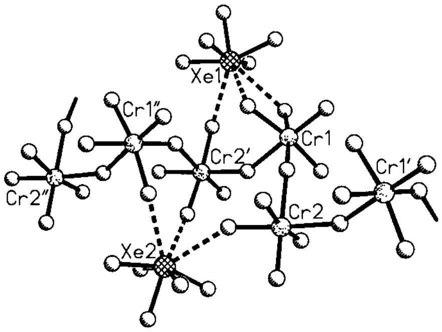

Figure 3. Interaction of XeF_5^+ cations with the chain of CrF_6 octahedra in $XeF_5^+CrF_5^-$.

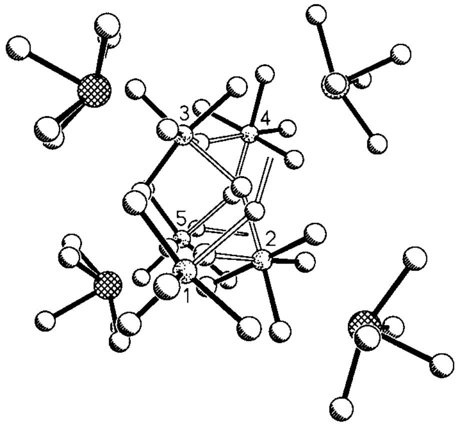

Figure 4. Part of the helical chain of CrF_6 octahedra in $XeF_5^+CrF_5^-$ surrounded by XeF_5^+ cations. The connecting bonds in the chain are given as open lines and the sequence is indicated by numbering the Cr atoms from 1 in front to 5 in the back.

the cations are between 179 and 182 pm, with those that are edge-sharing being the marginally longer ones. Both Cr−F−Cr bridges are very similar but asymmetric and kinked with angles at 146° and distances of 191 and 196 pm, respectively. The view of the structure along the *b* axis (Figure 4) shows the helix-like chains of CrF_6 octahedra, separated by XeF_5^+ cations, and finally forming a hexagonal rod packing.

Results and Discussion

$XeF_2 \cdot 2CrF_4$. Xenon(II) fluoride oxidizes either chromium metal or CrF_2 only to CrF_3. For the preparation of xenon(II) fluorochromates(IV) it is therefore necessary to react XeF_2 with CrF_4 or CrF_5. Because the best method for isolating pure CrF_4 is using $XeF_2 \cdot CrF_4$ as a starting material,[3] it is obvious that Xe(II) fluorochromates(IV) could be prepared only by the reaction between CrF_5 and excess XeF_2 at 323−333 K. CrF_5 is reduced to CrF_4, while XeF_2 is oxidized to XeF_4. After removal of excess XeF_2 and XeF_4, the final product is blue $XeF_2 \cdot CrF_4$. The use of excess XeF_2 is important as otherwise a black wax melting below 323 K is obtained.[3] Very likely, this black wax is a mixture of different chains of vertex-sharing CrF_6 octahedra arising from $XeF_2 \cdot CrF_4$ and unreacted CrF_5. CrF_5 seems to crystallize in the VF_5 type structure[17] containing infinite chains of octahedra, while $XeF_2 \cdot CrF_4$ shows XeF_2 molecules engaged in the formation of chains built from CrF_6 octahedra. Varying mixtures of such different chains seem to be not able to arrange in long-range order which would finally result in crystallization. However, if during preparation a more than 5-fold excess of XeF_2 over CrF_5 is present, all CrF_5 will be reduced to form $XeF_2 \cdot CrF_4$.

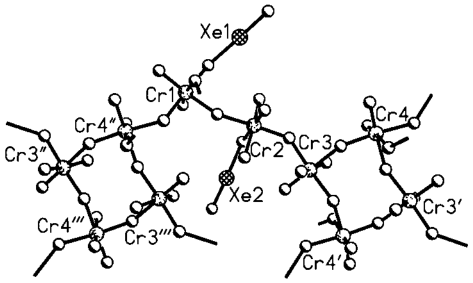

Figure 5. Selected part of the structure of $XeF_2 \cdot 2CrF_4$ showing the centrosymmetric rings and part of their connectivity.

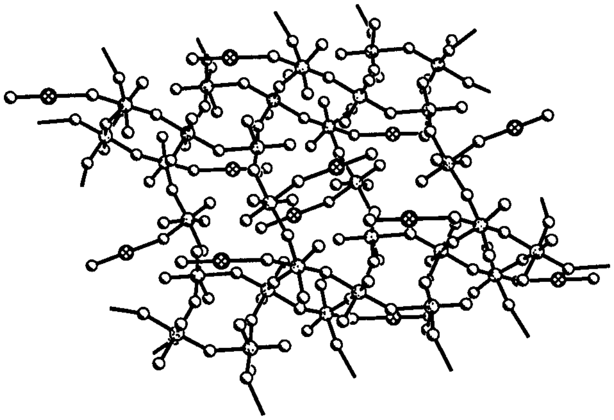

Figure 6. Impression of the infinite network in $XeF_2 \cdot 2CrF_4$

$XeF_2 \cdot 2CrF_4$ cannot be prepared from $XeF_2 \cdot CrF_4$ by thermal decomposition at higher temperatures, because besides XeF_2 evolution XeF_4 is also obtained at temperatures as low as 333 K. The nonvolatile product of the thermal decomposition is CrF_3. Obviously, under these conditions CrF_4 can still oxidize XeF_2 to XeF_4.

The best synthetic route for $XeF_2 \cdot 2CrF_4$ is solvolysis of $XeF_2 \cdot CrF_4$ in aHF, followed by the subsequent decantation of most of the dissolved XeF_2. When aHF is distilled away, the remaining XeF_2 and the large excess of CrF_4 form $XeF_2 \cdot 2CrF_4$. Single crystals of $XeF_2 \cdot 2CrF_4$ may be obtained by two different methods, either by heating the solid for 2 months using a thermal gradient or by recrystallization in supercritical SF_6.

A selected part of the structure is depicted in Figure 5 showing the main features of connectivity. Four octahedra are arranged in centrosymmetric rings resembling rather closely the RuF_5 type structure.[18] However, as Cr in this case is only tetravalent, six fluorine bridges to other units are formed. As can also be seen from Figure 5, these rings are connected through a chain of two octahedra each carrying an XeF_2 molecule. One vertex of the octahedron around Cr1 is also connecting further. The chain like arrangement is very similar to the chains in the structure of $XeF_2 \cdot CrF_4$.[3] Moreover, the XeF_2CrF_4 unit involving Cr2 is identical to the building block in the crystal structure of the compound $XeF_2 \cdot CrF_4$. The final structure consists of a rather complicated network as shown in Figure 6. The crystallographically distinguished units resemble different functionalities as briefly mentioned above. One may start with the crude assumption that each nonbridging fluorine ligand contributes a bond order of 1 to the Cr center while the bridging ones are contributing a bond order of $^1/_2$ to each Cr center. For Cr1 and Cr4 this results in a bond order of 4, in perfect agreement with tetravalent Cr ions. For Cr2 and Cr3, however,

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this simple model results in bond order of 4.5. Clearly, the observed elongation of two nonbridging and one bridging Cr−F distances are the result of the necessary reduction of the Cr bond orders to 4.0. It seems very remarkable that in one case this leads to a very asymmetric Cr−F−Cr bridge, while in the second case this is achieved by a rather weak coordination of an XeF_2 molecule. In contrast, the second XeF_2 molecule is more strongly connected to Cr1 which shows four bridging and two nonbridging ligands. As the XeF_2 molecules provide major contributions to the metal coordination, they are not easily replaced by other fluorine ligands or removed. The asymmetry of the almost linear XeF_2 molecules, together with their particular differences, is well in accord with distinguished stages on the ionization pathway from F−Xe−F to $F{-}Xe^+{-}F^-$, as described in detail earlier.[19]

$XeF_5^+CrF_5^-$. Although in a melt of XeF_6 chromium in lower chromium fluorides is oxidized to Cr^{4+}, this reaction is not useful for the preparation of pure $XeF_5^+CrF_5^-$. During the oxidation of chromium, the XeF_4 formed is always leading to the formation of very stable $(XeF_5^+CrF_5^-)_4{\cdot}XeF_4$. To prepare pure $XeF_5^+CrF_5^-$ only CrF_4 or CrF_5 can be used besides very pure XeF_6 (without traces of XeF_4). The reaction between CrF_4 and XeF_6 proceeds at room temperature in aHF. The resulting $XeF_5^+CrF_5^-$ is also soluble in aHF, giving an orange-red solution from which single crystals were grown. At room temperature the reaction between CrF_5 and XeF_6 proceeds very slowly either without a solvent or in aHF, while at 333 K the reaction of the neat compounds is very fast. During the reaction with CrF_5 elemental fluorine is liberated. The reaction probably proceeds via thermal decomposition of CrF_5 to CrF_4 and fluorine. The formation of solid $XeF_5^+CrF_5^-$ removes CrF_4 from the equilibrium this way accelerating the decomposition. The thermal decomposition of CrF_5 was corroborated in a separate experiment in which CrF_5 was kept at 333 K for some time and elemental fluorine was obtained. CrF_5 is a very strong oxidizer that can even oxidize xenon to XeF_2 or XeF_4 at 333 K. On the other hand, it is not too unusual that even in strongly oxidizing xenon hexafluoride Cr^{4+} is formed from Cr^{5+}. In analogous experiments attempts to fluorinate Os(VIII) compounds at higher temperatures were leading to Os(VI).[20] We were always puzzled by our failure to synthesize an XeF_5^+ salt of Cr^{5+}. When chromium metal was treated with a large excess of KrF_2 in aHF at room temperature, even in the presence of excess XeF_6 only CrF_5 was formed in a first step. Although CrF_5 and the moderately strong fluoro base XeF_6 were both dissolved in aHF no reaction took place as long as KrF_2 was still present. After KrF_2 decomposed, the reaction slowly proceeded to $XeF_5^+CrF_5^-$. This seems to indicate that the large asymmetric cation XeF_5^+ is not contributing enough stabilizing lattice energy as is achieved by smaller cations such as Cs^+ in the rather easy formation of $M^+CrF_6^-$. However, XeF_5^+ salts are obtained with Cr^{4+}. The same situation is observed in the case of palladium where $(XeF_5^+)_2PdF_6^{2-}$ is formed[21] but not $XeF_5^+PdF_6^-$ or $Xe_2F_{11}^+PdF_6^-$, although $CsPdF_6$[22] is easily prepared in the presence of KrF_2.

To our knowledge the structures of only three compounds containing an MF_5^- type anion have been determined. Like in $XeF_5^+CrF_5^-$ all three structures are characterized by infinite chains formed from apex-sharing MF_6 octahedra. In $XeF_5^+GeF_5^-$ the anionic chain is formed by GeF_6 octahedra sharing trans vertexes and the XeF_5^+ cation shows four interactions with the chain. In the closely related $ClO_2^+GeF_5^-$ the GeF_6 octahedra are sharing cis vertexes. The cation/anion interactions are not comparable to those of XeF_5^+. Finally, the more complex compound $(XeF_5^+CrF_5^-)_4{\cdot}XeF_4$ shows alternation of cis and trans vertexes shared between CrF_6 octahedra. As with $XeF_5^+GeF_5^-$ in the “trans part” four cation/anion interactions are observed while for the “cis part” three respective contacts including edge-sharing are observed as is also seen for one cation in the current structure of $XeF_5^+CrF_5^-$. From the comparison of these structures one may conclude that the differences in stability between cis and trans chains have to be rather subtle, although at first sight the trans arrangement should be more favorable, in particular due to the additional cation/anion interaction. On the other side, effective packing is certainly more important for the stability of the whole structure and mainly based on the sizes of the particular atoms or structural units involved. The packing requirements are also reflected in the slightly different interactions which lead to crystallographically distinguished units of the same type. Very clearly, this is reflected in the structure of $(XeF_5^+CrF_5^-)_4{\cdot}XeF_4$ where the alternation of cis and trans connections leads to a rather open framework. However, the voids in the framework are filled very effectively by XeF_4 molecules, as is demonstrated by the chemical behavior of $XeF_5^+CrF_5^-$. The latter compound is very difficult to crystallize and acts as the most effective scavenger for XeF_4, while the XeF_4 adduct crystallizes very easily.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, is available. Access and ordering information is given on any current masthead page.

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