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CONCERNING XENON DIFLUORIDE INTERACTIONS WITH $XeF_5^+MF_6^-$, THE EXISTENCE OF $XeF_2.XeF_5^+RuF_6^-$ AND THE ABSENCE OF $XeF_2.XeF_5^+NbF_6^-$[a]

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During the interactions of XeF_2 with $XeF_5^+MF_6^-$ (M=Ru and Nb), the adduct $XeF_2.XeF_5^+RuF_6^-$ was formed but not the adduct $XeF_2.XeF_5^+NbF_6^-$, which is in accordance with the different fluoride ion donor abilities of NbF_6^-, RuF_6^- and XeF_2. The crystal structure of $XeF_5^+NbF_6^-$ was determined. It is orthorhombic and isostructural with $XeF_5^+RuF_6^-$.

INTRODUCTION

The first interactions of XeF_2 with XeF_5^+ salts were studied in the system XeF_2 - $XeF_5^+AsF_6^-$ (1). During this study two adducts $XeF_2.XeF_5^+AsF_6^-$ and $XeF_2(XeF_5^+AsF_6^-)_2$ were isolated and their possible structures proposed. When the

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[a] Dedicated to the late Prof. Jože Slivnik

system XeF_2 - $XeF_5^+AsF_6^-$ was reinvestigated, an additional adduct, $2XeF_2.XeF_5^+AsF_6^-$, was isolated and the structures of all three (2:1, 1:1 and 1:2) were determined (2), confirming the structures already proposed by Bartlett (1).

Recently, a systematic study of the interactions of XeF_2 with a whole series of XeF_5^+ and some $Xe_2F_{11}^+$ salts was initiated (3), in order to gain more information about the mechanism of these interactions. So far, only the adduct, $XeF_2.XeF_5^+RuF_6^-$, has been isolated. Interestingly enough, the adduct $XeF_2.XeF_5^+NbF_6^-$ was not obtained, although $XeF_5^+NbF_6^-$ and $XeF_5^+RuF_6^-$ are isostructural.

RESULTS AND DISCUSSION

During the interaction of XeF_2 with XeF_5^+ salts it was not expected that XeF_2 could replace XeF_6 in its salts because XeF_6 is a much stronger fluoride ion donor than XeF_2. However, it was expected that the highly polarizing XeF_5^+ cation would tend to remove a fluoride ion from the XeF_2 molecule (1). There is, however, competition between the Lewis acid which forms the salt with XeF_5^+ and XeF_2 in the donation of a fluoride ion to XeF_5^+. It could be expected that strong Lewis acids like AsF_5 would form corresponding $XeF_2.XeF_5^+MF_6^-$ adducts, because their ability to donate a fluoride ion to XeF_5^+ is weaker than that of XeF_2. In contrast, weak Lewis acids would compete successfully with a XeF_2 molecule in the donation of a fluoride ion to XeF_5^+. The fluoride ion donor ability of the Lewis acid and XeF_2 is only one of the factors which govern the formation of XeF_2 adducts with XeF_5^+ salts; there are also some others such as the structure of the XeF_5^+ salts, the coordination of XeF_5^+, etc.

In order to elucidate the fluoride ion donor effect on the formation of $XeF_2.XeF_5^+MF_6^-$ adducts, the two systems XeF_2 - $XeF_5^+RuF_6^-$ and XeF_2 - $XeF_5^+NbF_6^-$ were investigated.

The structure of $XeF_5^+RuF_6^-$ was determined by Bartlett et al (4), while the structure of $XeF_5^+NbF_6^-$ was refined during this study. The two salts are close to being isostructural, with slight differences in bond lengths and angles, which are evident from Table 1. (See also Figure 1).

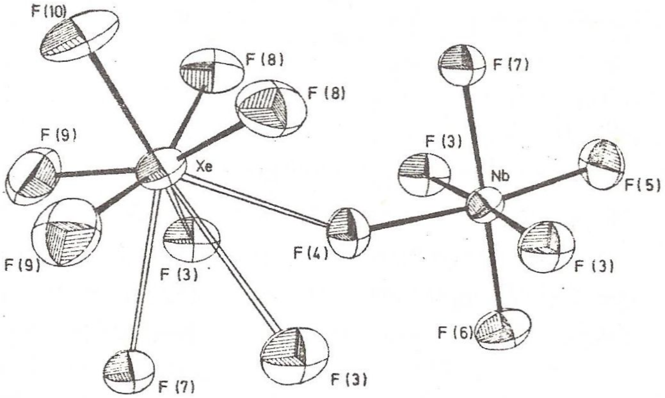

Fig. 1: XeF_5^+ and NbF_6^- structural units and the coordination of XeF_5^+

It should be noted here that the XeF_5^+ cation occurring in the $XeF_5^+NbF_6^-$ structure is similar in shape to that seen in other XeF_5^+ structures such as $XeF_5^+RuF_6^-$ (4), $(XeF_5^+)_2PdF_6^{2-}$ (5) and $XeF_5^+AsF_6^-$ (6), in which the coordination of the cation is often different. The NbF_6^- anion is a slightly distorted octahedron. The XeF_5^+ and NbF_6^- groups are arranged so that each XeF_5^+ group is nearly equidistant from four NbF_6^- groups and such that one F^- atom from each MF_6^- group is less than 0.3 nm distant from the xenon atom. In order to make an adduct, a fluoride ion from XeF_2 should displace with XeF_5^+ interacting fluoride ion from NbF_6^-. During the study of the reaction systems XeF_2 - $XeF_5^+RuF_6^-$ and XeF_2 - $XeF_5^+NbF_6^-$, the adduct $XeF_2.XeF_5^+RuF_6^-$ was isolated but not the adduct $XeF_2.XeF_5^+NbF_6^-$, thus suggesting that

Table 1: Interatomic distances (nm) and angles (deg) for $XeF_5^+RuF_6^-$ and $XeF_5^+NbF_6^-$

	$XeF_5^+RuF_6^-$ a)	$XeF_5^+NbF_6^-$ b)
M - F (3)	0.1850 (7) c)	0.1880 (4)
M - F (4)	0.1876 (11)	0.1925 (6)
M - F (5)	0.1820 (12)	0.1846 (6)
M - F (6)	0.1827 (10)	0.1840 (6)
M - F (7)	0.1867 (9)	0.1933 (5)
Xe - F (3)	0.2924 (7)	0.2963 (4)
Xe - F (4)	0.2552 (11)	0.2546 (6)
Xe - F (7)	0.2601 (9)	0.2551 (5)
Xe - F (8)	0.1848 (8)	0.1842 (5)
Xe - F (9)	0.1841 (8)	0.1842 (5)
Xe - F (10)	0.1793 (8)	0.1814 (6)
F (4) - M - F (7)	87.76 (53)	84.40 (23)
F (4) - M - F (6)	91.40 (61)	94.41 (28)
F (5) - M - F (6)	91.36 (56)	92.97 (28)
F (5) - M - F (7)	89.48 (61)	88.22 (24)
F (6) - M - F (7)	179.16 (81)	178.81 (27)
F (4) - M - F (5)	177.25 (79)	172.62 (25)
F (3) - Xe - F (10)	129.59 (30)	128.57 (80)
F (8) - Xe - F (8)	87.78 (25)	87.90 (21)
F (8) - Xe - F (9)	88.44 (41)	87.99 (22)
F (8) - Xe - F (10)	78.59 (43)	79.09 (24)
F (9) - Xe - F (10)	79.43 (51)	79.10 (23)
F (7) - Xe - F (10)	140.57 (65)	141.13 (29)
F (4) - Xe - F (10)	142.26 (69)	141.78 (29)
M - F (7) - Xe	154.86 (29)	157.74 (27)
M - F (3) - Xe	139.91 (22)	141.16 (20)
M - F (4) - Xe	144.26 (34)	150.44 (28)

a) Reference 4 b) This work c) Estimated standard deviations in parentheses fluoride ion donor ability decreases in the sequence $NbF_6^- > XeF_2 > RuF_6^-$.

The slight differences in bond lengths which are evident from Table 1 (compare the distances Xe - F (3), Xe - F (7), M - F (4), M - F (3) and M - F (7) for the two compounds) support the fact that NbF_6^- is a better fluoride ion donor than RuF_6^-. The fact that the fluoride ion donor ability of XeF_2 is somewhere between the two Lewis acids is in agreement with the distance of 0.247 nm of the terminal fluorine of XeF_2 from XeF_5^+ in $XeF_2.XeF_5^+AsF_6^-$ (2).

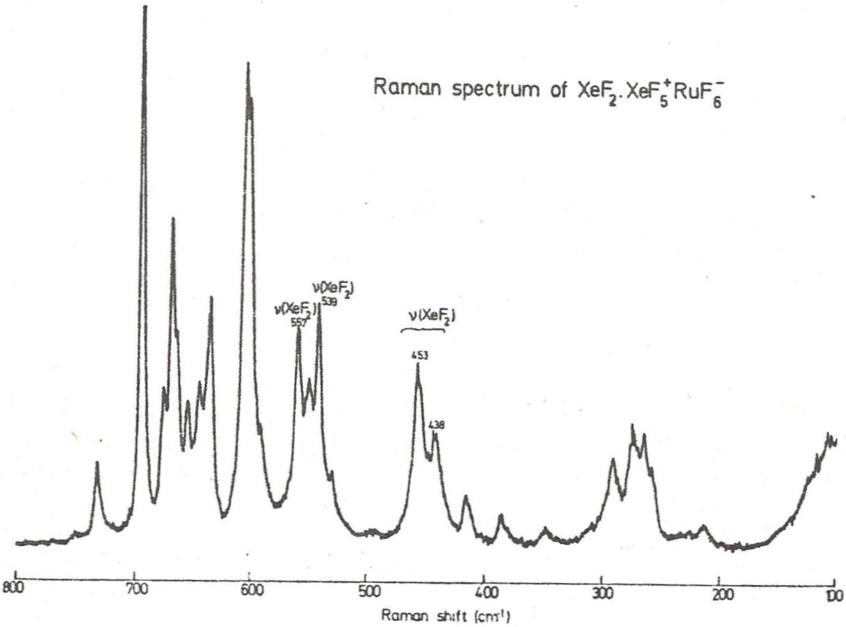

Fig. 2: Raman spectrum of $XeF_2.XeF_5^+RuF_6^-$

In the Raman spectrum of $XeF_2.XeF_5^+RuF_6^-$ (Figure 2) there is no peak at 497 cm^{-1} corresponding to the symmetric stretching frequency of molecular XeF_2. However, there are two new pairs of bands at 438, 453 cm^{-1} and 539, 557 cm^{-1} which do not have counterparts in $XeF_5^+RuF_6^-$. It may be significant that the mean frequency for these two pairs of bands is 496 cm^{-1}, which coincides almost exactly with the symmetric stretching frequency of molecular XeF_2. We believe that linear distortion is present here. The distortion is approximately of the same order as in $XeF_2.XeF_5^+AsF_6^-$ (2).

The other features of the spectrum of $XeF_2.XeF_5^+RuF_6^-$ are attributable to $(XeF_5)^+$ and $(RuF_6)^-$ species. The same $(XeF_5)^+$ and $(RuF_6)^-$ fundamentals occur as in the spectrum of $(XeF_5)^+(RuF_6)^-$ itself (although slightly modified) (7).

EXPERIMENTAL

General apparatus and techniques

The initial products ($XeF_5^+RuF_6^-$ and $XeF_5^+NbF_6^-$) were synthesized in argon arc welded nickel pressure and weighing vessels, equipped with Teflon packed nickel valves. The volume of the reaction vessels was about 10^{-4} m^3. The vessels which were designed for manipulating solid materials were tested hydrostatically up to 20 MPa. The reaction between XeF_2 and the XeF_5^+ salts were carried out in quartz tubes (ø 8 mm) equipped with Teflon packed nickel valves. The glass tube was joined to the metal system by means of a tightened cone fitted with a Teflon gasket.

Transfer of all materials was carried out either in the atmosphere of a dry box or by distillation under vacuum in well dried apparatus.

Raman spectra were recorded using a Spex 1401 double monochromator instrument. As exciting radiation, the 514.5 nm line of an Ar^+ laser (Coherent Radiation) was used. Powdered samples were loaded into quartz capillaries in a dry box and temporarily plugged with Kel-F grease. They were sealed with a small flame outside the dry box.

X-Ray measurements

Single crystals of $XeF_5^+NbF_6^-$ for X-Ray work were grown by sublimation of small samples of the powder sealed under argon in thin-walled quartz X-Ray capillaries. The capillaries were placed in an electrically heated tube which provided for a temperature gradient along the capillary of 1 or 2°C at a temperature of 50°C. The capillaries were left in this heater for some days and were then inspected for single crystal development using a polarizing microscope.

Precise unit cell dimensions /a=1.6964 (3), b=0.8390 (2), c=0.5621 (1) nm, V=0.8000 (5) nm^3, Z=4 and d_c=3.569 Mg/m^3/ were obtained by the least squares procedure from the θ values of 45 moderately high order reflexions measured on a CAD-4 diffractometer ($MoK\alpha_1$; λ=0.070926 nm).

Intensities were collected with graphite - monochromated MoK_α radiation (λ=0.071069 nm) in the ω -2θ mode with varying scan speeds.

Details of data collection and reduction are given in Table 2. Precise absorption correction was performed (12 faces, grid: 10 x 10 x 10). The structure was refined using the model of Bartlett (4) using 1234 reflexions to an R-value of 3.5%.

Table 2: Data - collection Summary

Temperature (K)	293 (1)
Diffractometer	CAD-4-automatic four circle
Scan method	$\omega - 2\theta$
2θ scan width ($^\circ$)	$0.60 + 0.2 \, tg \, \theta$
Aperture (mm)	$2.4 + 0.87 \, tg \, \theta$
Radiation (nm)	MoK$_\alpha$ (λ=0.071069)
Monochromator	Graphite crystal
Scan rate ($^\circ$min^{-1})	min.: 1.7 max.: 20.1
Maximum scan time (s)	40
2θ max ($^\circ$)	60
Intensity control	after each 72 reflexions
Orientation control	after each 144 reflexions
Background	1/4 of the scan time at each of the scan limits
Size of crystal (mm)	0.10 x 0.11 x 0.13
Reference reflexions	040; 211; 801
Intensity decrease (%)	3
Measured reflexions	1297 (+h, +k, +l)
Unique reflexions	1234
Observed reflexions/$I_o > 2\sigma(I_o)$/	709
Unobserved reflexions	525
σ (I) based on	Counting statistics
μ (mm^{-1})	5.76
Transmittance	min.: 0.662, max.: 0.632

The empirical weighting function $w = w_F \times w_s$, where

$w_F(|F_o| < 20.0) = (|F_o|/20.0)^3$

$w_F(|F_o| > 80.0) = (80.0/|F_o|)^3$

$w_F(20.0 < |F_o| < 80.0) = 1.0$

$w_s(\sin\Theta < 0.24) = (\sin\Theta/0.24)^2$

$w_s(\sin\Theta > 0.36) = (0.36/\sin\Theta)^2$

$w_s(0.24 < \sin\Theta < 0.36) = 1.0$,

was used to keep $\sum w(\Delta F)^2$ uniform over the ranges of $(\sin\Theta)/\lambda$ and $|F_o|$. Scattering factors from Cromer and Mann (8), and anomalous - dispersion corrections from Cromer and Liberman (9) were used in the calculation, together with an isotropic extinction correction after Larson (10). Final refinement parameters are given in Table 3.

All calculations were carried out on the CDC - Cyber 72 computer at RRC Ljubljana using the X-Ray-72 system of crystallographic programs (11).

Table 3: Refinement Summary

Scale factor	3.85
Extinction coefficient	0.55
$R = \sum\|\Delta F\| / \sum\|F_o\|$	0.035
$R_w = [\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$	0.037
Average shift/error	0.085
Maximum shift/error	1.68 (u_{22}-F (10))
Data (m)-to-variable (n) ratio	14.4
$[\sum w(\Delta F)^2/(m-n)]^{1/2}$	0.341
Number of contributing reflexions	1023

REAGENTS

Xenon difluoride was prepared by photosynthesis using a near UV lamp (12), and xenon hexafluoride was prepared by the reaction between xenon and fluorine in the presence of nickel difluoride at 120°C (13). $XeF_5^+NbF_6^-$ was prepared by the reaction between XeF_6 and NbF_5 at 90°C and removal of excess of XeF_6 by pumping at 60°C (14). $XeF_5^+RuF_6^-$ was prepared by fluorinating a sample of the 1:1 XeF_2 - RuF_5 complex with excess of gaseous fluorine at 350°C overnight (4).

PREPARATIONS

Stoichiometric amounts of XeF_2 and XeF_5^+ salt were weighed into a quartz tube in the dry box. XeF_2 was placed on the bottom of the tube in order to minimize the sublimation of XeF_2 during the fusion of both components. Sometimes 101 KPa of fluorine was also added to minimize sublimation of XeF_2 from the hot zone. The melt was left to crystallize and was checked by Raman spectroscopy.

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POVZETEK

Pri študiju interakcij med XeF_2 in solmi tipa $XeF_5^+MF_6^-$ (M=Ru in Nb) nam je uspelo izolirati adukt $XeF_2.XeF_5^+RuF_6^-$. Analognega adukta $XeF_2.XeF_5^+NbF_6^-$ nismo zasledili, kar pripisujemo različni donorski sposobnosti F^- iona, ki jo kažejo NbF_6^-, RuF_6^- in XeF_2. Določili smo strukturo $XeF_5^+NbF_6^-$, za katerega se je izkazalo, da je izostrukturen s $XeF_5^+RuF_6^-$.

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