$[Ba(XeF_2)_5](AF_6)_2$, A = Ru, Nb – SYNTHESIS, CRYSTAL STRUCTURE AND RAMAN SPECTRA

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Dedicated to our colleague and friend Professor Oldřich Paleta on the occasion of his 70th birthday.

The reaction of $Ba(NbF_6)_2$ and excess XeF_2 in anhydrous HF at room temperature yields $[Ba(XeF_2)_5](NbF_6)_2$. This is the first example of the coordination compound with XeF_2 molecule as a ligand and NbF_6^- anion. It crystallizes in the orthorhombic space group *Fmmm*, with $a = 12.084(6)$ Å, $b = 13.646(7)$ Å, $c = 13.927(7)$ Å, $V = 2297(2)$ Å^3, and $Z = 4$. The reaction of $XeF_2 \cdot Xe_2F_3 \cdot RuF_6$ and BaF_2 in anhydrous HF yields $[Ba(XeF_2)_5](RuF_6)_2$ – the first example of the coordination compound containing RuF_6^- anion and XeF_2 molecules. It appears to be isostructural with $[Ba(XeF_2)_5](NbF_6)_2$, with $a = 11.9510(14)$ Å, $b = 13.5174(14)$ Å, $c = 13.8488(12)$ Å, $V = 2237.2(4)$ Å^3, and $Z = 4$. The Raman spectra of both compounds prove that all the XeF_2 molecules are symmetrical. Four XeF_2 molecules per formula unit act as bridges between Ba centres, while one molecule is held in the structure by electrostatic forces. In the series of compounds $[Ba(XeF_2)_5](AF_6)_2$ with A = As, Sb, Ru, Nb, the influence of the anions AF_6^- was analyzed.
Keywords: XeF_2 as a ligand; Crystal structure determination; Raman spectroscopy; Hexafluorometalate anions; Barium salts; Xenon; Barium complexes.

BaF_2 reacts with Lewis acids AF_5, A being Sb, As, Ru and Nb, in anhydrous hydrogen fluoride (aHF) yielding $Ba(AF_6)_2$. Salts containing hexafluorometalate anions have rather low lattice energy as a consequence of the anion volume (from 110 Å^3 in the case of AsF_6^- to 125 Å^3 in the case of NbF_6^-)[1]. Anions AF_6^-, where A is Sb, As, Ru and Nb, are poor Lewis bases so that even a poor base like aHF can provide sufficient solvation energy to dissolve $Ba(AF_6)_2$ salts yielding the $[Ba(HF)_m]^{2+}$ solvated cations and AF_6^- anions. Addition of XeF_2 to such solution introduces a stronger Lewis base than HF, yielding coordination compounds of the type $[Ba(XeF_2)_5](AF_6)_2$. All four compounds $[Ba(XeF_2)_5](AF_6)_2$ (A = Sb, As, Ru and Nb) are iso-

structural. In this paper, the synthesis, Raman spectra and crystal structures of the two newly isolated compounds $[Ba(XeF_2)_5](AF_6)_2$ with A = Ru and Nb are described. Our intention was also to compare all four compounds in order to establish how different properties of these anions like size, Lewis basicity and negative charge on the fluorine ligands influence the bonds in these compounds. All details of the compounds $[Ba(XeF_2)_5](AF_6)_2$ with A = Ru and Nb are given in this paper while the compounds with A = Sb and As were described elsewhere[2,3].

RESULTS AND DISCUSSION
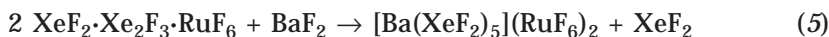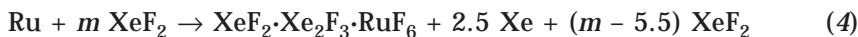
Synthesis

The compound $[Ba(XeF_2)_5](NbF_6)_2$ could be prepared using different synthetic routes. BaF_2 reacts with NbF_5 in the mole ratio 1:2 in aHF at room temperature yielding $Ba(NbF_6)_2$ which reacts further with added Lewis base, XeF_2, to form the title compound. The reaction must be carried out in two steps: first $Ba(NbF_6)_2$ is synthesized and then XeF_2 is coordinated to the Ba centre. The reason is that XeF_2 would otherwise react with the Lewis acid NbF_5 yielding $XeFNbF_6$ or $XeFNb_2F_{11}$, depending on the amount of XeF_2 present in solution.

A more elegant synthetic method is the reaction of BaF_2 with NbF_5 formed in situ by the reaction of Nb metal first with aHF and then with elemental fluorine. After removal of F_2, XeF_2 could be added to the solution of $Ba(NbF_6)_2$ in aHF.

$$BaF_2 + 2\ Nb + m\ HF \rightarrow BaF_2 + 2\ NbF_3 + 3\ H_2 + (m-6)\ HF \qquad (1)$$

$$BaF_2 + 2\ NbF_3 + z\ F_2 \rightarrow Ba(NbF_6)_2 + (z-2)\ F_2 \qquad (2)$$

$$Ba(NbF_6)_2 + n\ XeF_2 \rightarrow [Ba(XeF_2)_5](NbF_6)_2 + (n-5)\ XeF_2 \quad n > 6 \qquad (3)$$

The compound $[Ba(XeF_2)_5](RuF_6)_2$ could be prepared by the reaction between BaF_2 and RuF_5 in aHF and subsequent addition of XeF_2. A smarter synthetic method is the reaction of Ru metal with XeF_2 in aHF yielding first $XeF_2 \cdot Xe_2F_3RuF_6$ which reacts with the added BaF_2 yielding the title compound.

$$Ru + m\ XeF_2 \rightarrow XeF_2 \cdot Xe_2F_3 \cdot RuF_6 + 2.5\ Xe + (m - 5.5)\ XeF_2 \qquad (4)$$

$$2\ XeF_2 \cdot Xe_2F_3 \cdot RuF_6 + BaF_2 \rightarrow [Ba(XeF_2)_5](RuF_6)_2 + XeF_2 \qquad (5)$$

Comparison of Crystal Structures

X-ray crystal structures of [Ba(XeF$_2$)$_5$](AF$_6$)$_2$, A = As, Sb, Ru and Nb, are isotypical. They crystallize in the orthorhombic space group *Fmmm*. The details of X-ray structure experiment and crystallographic data for [Ba(XeF$_2$)$_5$](AF$_6$) compounds are given in Table I, selected bond distances

TABLE I
Details of experimental and crystallographic data for [Ba(XeF$_2$)$_5$](AF$_6$) compounds

Parameter	Atoms A			
	As[3]	Sb[2,3]	**Ru**[a]	**Nb**[a]
Radiation	Mo*K*α	Mo*K*α	**Mo*K*α**	**Mo*K*α**
Space group	*Fmmm*	*Fmmm*	***Fmmm***	***Fmmm***
a, Å	11.6604	12.0985	**11.9510(14)**	**12.084(6)**
b, Å	13.658	13.6072	**13.5174(14)**	**13.646(7)**
c, Å	13.7802	13.9437	**13.8488(12)**	**13.927(7)**
V, Å^3	2194.5	2295.5	**2237.2(4)**	**2297(2)**
Z	4	4	**4**	**4**
μ, mm^{-1}	12.555	11.452	**10.685**	**10.090**
F(000)	2360	2504	**2448**	**2424**
Scan range θ, °	2.96–28.89	3.37–30.05	**2.71–29.18**	**2.68–29.09**
Measured reflections	711	765	**752**	**793**
Used ($I > 2\sigma(I)$)	377	575	**689**	**473**
Parameters refined	51	51	**51**	**51**
R (*F*)	0.0350	0.0498	**0.0491**	**0.0575**
R (*F*)^2; $F > 4\sigma(F)$	0.0828	0.1346	**0.1628**	**0.1981**
Goodness-of-fit	0.922	1.094	**1.151**	**1.237**

[a] Data for new compounds are given in bold.

for all four compounds are placed in Table II. Ba atom has coordination number 12, being surrounded by four symmetry-related sets of three fluorine atoms: F2, F3, both from XeF_2 molecules and F11 from the anion. The 12 fluorine atoms around Ba form a nearly regular icosahedron (Fig. 1). The unit cell of $[Ba(XeF_2)_5](AF_6)_2$ contains three crystallographically different XeF_2 molecules. Two of them ($Xe(2)F_2$ and $Xe(3)F_2$) act as bridging ligands between two Ba^{2+} cations, while $Xe(1)F_2$ is held in the structure only by electrostatic forces between positive Xe2 atoms and negative F1 atoms of $Xe(1)F_2$ molecule (Fig. 2). Only one crystallographically independent AF_6^- anion is found in the unit cell. It exhibits tetragonal distortion with elongated *trans*-located A–F(bridging) bonds in comparison with four shorter A–F(terminal) bonds.

Because in all four compounds only the anions are different, the comparative analysis of all four structures could be of interest. The bond length Ba–F11 should be the most interesting because it shows different Lewis basicities of the AF_6^- anions. If the As compound is not taken into consideration because its anion is much smaller than the other three (the volumes of the unit cells are 2194.5(5), 2237.2(4), 2295.5(3) and 2297(2) $Å^3$ for As, Ru, Sb and Nb compounds, respectively), a small, not significant trend of increasing Lewis basicity is observed going from Sb and Ru to Nb compound.

TABLE II
Selected interatomic distances in $[Ba(XeF_2)_5](AF_6)_2$ (A = As, Sb, Ru, Nb) compounds

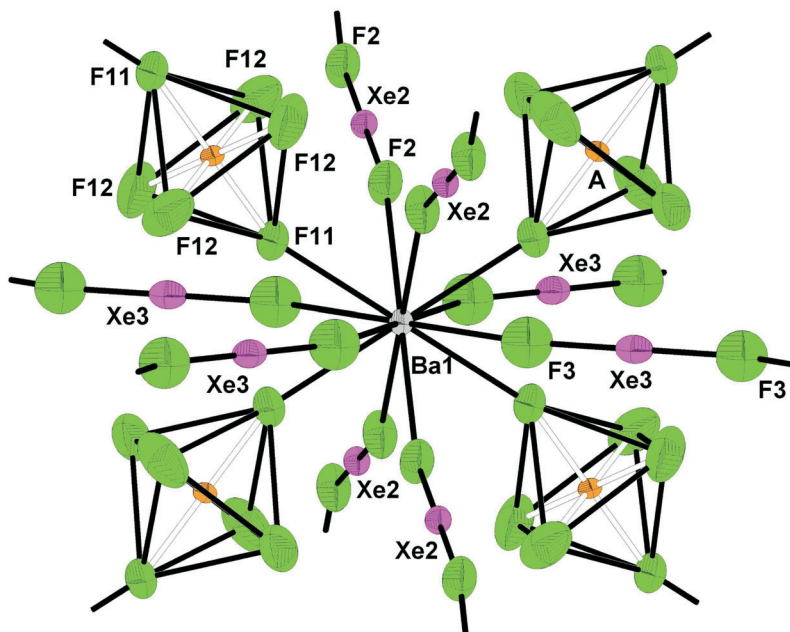| Bond	Atoms A			
	As	Sb	Ru	Nb
Ba–F2	2.700(5)	2.728(6)	2.716(5)	2.740(9)
Ba–F3	2.973(6)	3.018(9)	2.978(6)	3.025(13)
Ba–F11	2.868(4)	2.818(5)	2.810(4)	2.791(8)
A–F11	1.724(4)	1.881(5)	1.853(4)	1.896(8)
A–F12	1.686(4)	1.831(6)	1.810(4)	1.874(8)
F12···Xe2	3.410(4)	3.318(7)	3.295(6)	3.298(10)
F12···Xe3	3.296(4)	3.253(8)	3.239(6)	3.229(10)
F1···Xe2	3.243(4)	3.340(6)	3.300(3)	3.337(7)

FIG. 1
Metal environment in structures of $[Ba(XeF_2)_5](AF_6)_2$ (40% probability displacement ellipsoids)
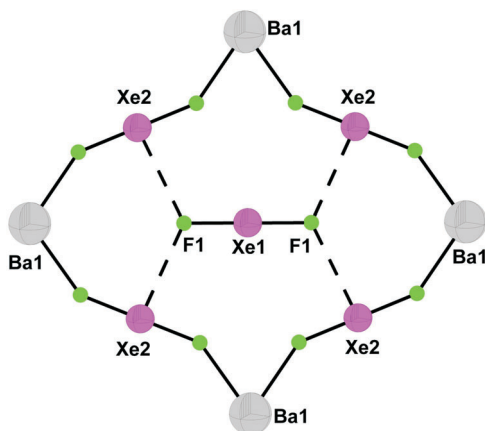

FIG. 2
The "free" $Xe(1)F_2$ molecule and weak intermolecular interactions in structures of $[Ba(XeF_2)_5](AF_6)_2$

The distances Ba–F (F2 and F3) of the bridging XeF_2 molecules are in the As–Nb series practically the same but they differ significantly between $Xe(2)F_2$ and $Xe(3)F_2$ molecules, being shorter with $Xe(2)F_2$ and longer with $Xe(3)F_2$ molecules. The reason is a relatively strong interaction of negative fluorine atoms of $Xe(1)F_2$ molecule with the positive Xe centres of $Xe(2)F_2$ molecules at the distances ranging from 3.234(4) Å for As to 3.340(6) Å for Sb. These electrostatic forces hold the "free" $Xe(1)F_2$ molecule in the crystal structure. It should be mentioned here that these distances in the XeF_2 crystal are 3.42 Å [4]. It is evident from the packing arrangement in the crystals that the region close to the equatorial plane of each $Xe(2)F_2$ molecule is avoided by neighbouring fluorine atoms. This indicates that the non-bonding valence electrons of xenon provide a very effective shielding of the positive charge in that direction. Besides very strong interactions between F1 and Xe2 there are also strong interactions between F12 and Xe2. All these interactions diminish the positive charge on Xe2 and, therefore, the negative charge on F2 atoms belonging to Xe2 is not pulled towards Xe2 atom but it mostly remains on F2 atoms. This explains why their interaction with the Ba atom is strong.

The interactions between Xe3 atoms and F12 terminal atoms of the anion in the range from 3.229(10) Å for Nb to 3.296(4) Å for As are very strong. As they are the only interactions of Xe3 with neighbouring fluorine atoms, there is still enough positive charge on Xe3 to withdraw some negative charge from F3 atoms, thus making their interaction with Ba weaker, in the range from 2.973(6) Å for As to 3.025(13) Å for Nb.

It is known[5] that the influence of the anion on the structure diversity of the coordination compounds with XeF_2 as a ligand is small. It was proven that also the effect of the strength of different Lewis bases in the series of the salts $[Ba(XeF_2)_5](AF_6)_2$, A = As, Sb, Ru and Nb on the structures of these compounds is not significant.

Raman Spectroscopy

The Raman spectrum of compound $[Ba(XeF_2)_5](RuF_6)_2$ is shown in Fig. 3, and the Raman spectrum of the compound $[Ba(XeF_2)_5](NbF_6)_2$ in Fig. 4. Although the different XeF_2 molecules do not significantly differ in inter-atomic distances and angles, the electric fields in which the F atoms of different types lie are different. The F atoms of $Xe(2)F_2$ molecules are closest to the positive centres. We believe that these molecules are responsible for the Raman band at 525 cm^{-1} for Ru compound. The band shows a small

increase in frequency for the a$_{1g}$ mode in the solid at 496 cm^{-1} (ref.[6]). The other close strong Raman band at 512 cm^{-1} for Ru compound must be due to the same vibrations in the other XeF$_2$ molecules. In the Nb case, the vibrations of all XeF$_2$ molecules are represented by the band at 510 cm^{-1}. The other peaks are due to the anion which is slightly distorted compared with the octahedral symmetry. The peaks at 656, 571 and 589 cm^{-1}, and peak at 269 cm^{-1} can be attributed to vibrations derived from ν_1, ν_2 and ν_5 modes

Fig. 3
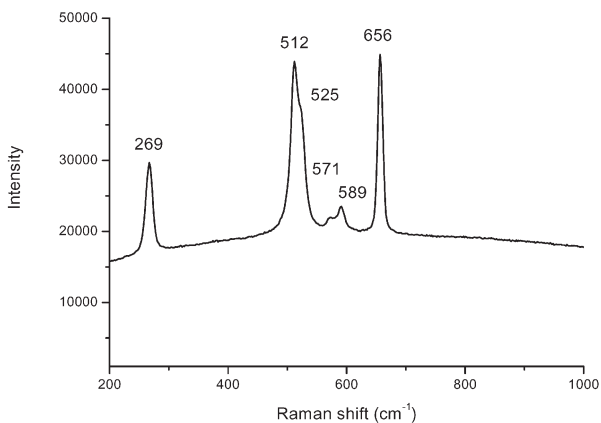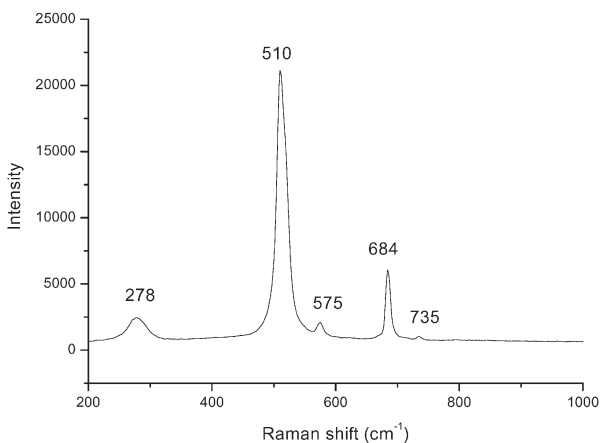Raman spectrum of [Ba(XeF$_2$)$_5$](RuF$_6$)$_2$

Fig. 4
Raman spectrum of [Ba(XeF$_2$)$_5$](NbF$_6$)$_2$

of slightly distorted octahedral RuF_6^-, for which $\nu_1 = 670$, $\nu_2 = 579$ and $\nu_5 = 279$ cm^{-1} (ref.[7]), while the corresponding peaks at 684, 575 and 278 cm^{-1} can be attributed to vibrations derived from ν_1, ν_2 and ν_5 modes of slightly distorted octahedral NbF_6^-, for which $\nu_1 = 683$, $\nu_2 = 562$ and $\nu_5 = 280$ cm^{-1} (ref.[8]).

EXPERIMENTAL

General Experimental Procedures

Volatile materials (aHF, F_2) were handled in an all-Teflon vacuum line equipped with Teflon valves. The manipulation of the non-volatile materials sensitive to traces of moisture was performed in a dry box (Braun). The content of water in the argon atmosphere of the dry box never exceeded 1 ppm. Reactions were carried out in FEP reaction vessels equipped with Teflon valves and passivated before use with elemental fluorine.

Reagents

BaF_2 (Riedel-de-Haen), Ru metal (Johnson Matthey & Co.), Nb metal (Aldrich, 99.8%) and fluorine (Solvay, 99.98%) were used as supplied. The purity of BaF_2 was checked by chemical analysis (for BaF_2 calculated: 78.3% Ba, 21.7% F; found: 78.1% Ba, 21.5% F). XeF_2 was prepared by the photochemical reaction of xenon and fluorine at room temperature[9]. Anhydrous HF (Fluka, purum) was treated with K_2NiF_6 (Ozark-Mahoning, 99%) for several days prior to use.

Synthesis of $[Ba(XeF_2)_5](NbF_6)_2$

BaF_2 and Nb were weighed into the reaction vessel inside the dry box. After argon was pumped off, the vessel was cooled with liquid nitrogen and aHF was added at –196 °C. The reaction vessel was slowly warmed up and kept at room temperature for at least 24 h. The reaction mixture was stirred continuously. Then the reaction vessel was cooled to –196 °C and H_2 was pumped off. This procedure was repeated as long as H_2 formed in the reaction vessel. Then F_2 was added and the reaction proceeded at room temperature for several days. After the reaction was complete and a colorless solution was obtained, aHF and excess F_2 were pumped off at room temperature. The reaction vessel was weighed to check completion of the reaction and that the amount of the obtained $Ba(NbF_6)_2$ corresponds to the starting amount of BaF_2. After a small portion of the product was put into another reaction vessel and excess XeF_2 and aHF were added at –196 °C. The reaction vessel was warmed up to room temperature and kept at this temperature for at least one day. After clear colorless solution was obtained, aHF and excess of XeF_2 were pumped off. The obtained product was $[Ba(XeF_2)_5](NbF_6)_2$. Details of the synthesis were as follows: BaF_2 (0.213 g, 1.21 mmol), Nb (0.226 g, 2.43 mmol), F_2 (0.257 g, 6.77 mmol), $Ba(NbF_6)_2$ (0.678 g, 1.23 mmol), starting $Ba(NbF_6)_2$ (0.134 g, 0.24 mmol), XeF_2 (0.248 g, 1.47 mmol), product $[Ba(XeF_2)_5](NbF_6)_2$ (0.415 g, 0.297 mmol).

Synthesis of [Ba(XeF$_2$)$_5$](RuF$_6$)$_2$

Ru metal was put into the reaction vessel in a dry box. Then XeF$_2$ was added at –196 °C followed by aHF and the reaction vessel was slowly warmed up. The reaction proceeded already below room temperature yielding a light green solution of the XeF$_2$·Xe$_2$F$_3$RuF$_6$ product. Xenon and aHF were pumped away at 0 °C and BaF$_2$ was added in a dry box. Anhydrous HF was again added at –196 °C. The reaction vessel was warmed up and the reaction proceeded yielding a colorless solution and white precipitate. Anhydrous HF and excess of XeF$_2$ were pumped off. The details of the synthesis were as follows: metal Ru (0.199 g, 1.97 mmol), XeF$_2$ (3.170 g, 18.72 mmol), product XeF$_2$·Xe$_2$F$_3$RuF$_6$ and excessive XeF$_2$ (2.534 g), BaF$_2$ (0.181g, 1.03 mmol), product (1.414 g, 1.00 mmol).

Growth of Single Crystals

A small amount of [Ba(XeF$_2$)$_5$](AF$_6$)$_2$, A = Ru, Nb was transferred in the dry box into a T-shaped crystallization vessel. Anhydrous HF was added and a saturated solution was prepared. This solution was decanted into the narrower part of the reaction vessel and left standing at room temperature while the wider part was slightly cooled to generate a small temperature gradient. The crystallization proceeded for several days. Crystals were isolated by pumping off the aHF, put inside the dry box in perfluorinated oil (ABCR, F05960), selected under microscope and transferred into cold nitrogen stream in the X-ray diffractometer.

Raman Spectroscopy

Raman spectra of powdered samples in sealed quartz capillaries were taken on a Renishaw imaging microscope System 1000 with the 632.8 nm exciting line of a He-Ne laser. The laser power was 25 mW and the recording technique was 180° backscattering.

Determination of the Crystal Structures

Data were collected on a Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector using graphite-monochromatized MoKα radiation at 200 K. The data were corrected for Lorentz and polarization effects. A multiscan absorption correction was applied to all data sets. Structure was solved by direct methods using SIR-92 [10] program implemented in program package TeXsan [11] and refined with SHELX97 [12] software (program packages TeXsan and WinGX[13]). The figures were prepared using DIAMOND 3.1 software[14]. Further details of the crystal structure investigation(s) can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (49) 7247-808-666, e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD-418900 for [Ba(XeF$_2$)$_5$](RuF$_6$)$_2$ and CSD-419480 for [Ba(XeF$_2$)$_5$](NbF$_6$)$_2$.

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