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Article

$Ba(SbF_6)_2 \cdot 5XeF_2$: First Xenon(II) Compound with Barium. Synthesis, Vibrational Spectra, and Crystal Structure

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The reaction between $Ba(SbF_6)_2$ and excess XeF_2 in anhydrous HF at room temperature yields the white solid $Ba(SbF_6)_2 \cdot 5XeF_2$ after the excess XeF_2 and the solvent have been removed under vacuum. $Ba(SbF_6)_2 \cdot 5XeF_2$ crystallizes in the monoclinic space group $C2/m$, with $a = 13.599(6)$ Å, $b = 12.086(4)$ Å, $c = 9.732(5)$ Å, $\beta = 134.305(6)°$, $V = 1144.7$ (8) Å^3, and $Z = 2$. The coordination sphere of each barium atom consists of 12 fluorine atoms. The structure consists of alternating layers of $Ba(SbF_6)_2 \cdot XeF_2$ and 4 XeF_2 molecules. The Ba atoms in the $Ba(SbF_6)_2 \cdot XeF_2$ layer are in a nearly rhombic-net array and are linked with trans F-bridging ligands of SbF_6^-. A XeF_2 molecule is placed in the center of each rhombus of the Ba^{2+} array so that its symmetry axis is perpendicular to the plane of the $Ba(SbF_6)_2 \cdot XeF_2$ layer. This layer is linked to its neighbors by a layer of centrosymmetric XeF_2 molecules. Raman spectra are in accord with all XeF_2 molecules being symmetrical.

Introduction

Metal(II) fluorides of alkaline earths react with excesses of Lewis acids (e.g., AF_5 with A = As, Sb) in anhydrous HF (aHF), as a solvent, yielding compounds of the type $[M(HF)_m](AF_6)_2$. Almost "naked" metal centers surrounded with weakly interacting AF_6^- anions can coordinate even weak ligands of the solvent. Compounds such as $[M(HF)_m](AF_6)_2$ represent excellent starting materials for the preparation of new coordination compounds of the type$[M(L)_n](AF_6)_2$ with a variety of ligands (L). In this paper, we concentrate on the moderately strong F^- ligand donor XeF_2.

The first compound in which XeF_2 was observed to be bound directly to a metal ion was $[Ag(XeF_2)_2](AsF_6)$.[1] In the alkaline earth series, only two compounds with XeF_2 bound directly to a metal center have been isolated up to now: $[Ca(XeF_2)_4](AsF_6)_2$[2] and $[Sr(XeF_2)_3](AsF_6)_2$.[3] In this paper, the synthesis, Raman and infrared spectra, and crystal structure of the compound $Ba(SbF_6)_2 \cdot 5XeF_2$ are discussed. This compound represents the first xenon(II) compound of barium and the first xenon(II) compound in the hexafluoroantimonates(V) of the alkaline earth series. The compound $Ba(SbF_6)_2 \cdot 5XeF_2$ has been briefly mentioned in a review paper,[2] but details of its synthesis and crystal structure are given here for the first time.

Experimental Section

General Experimental Procedures. Volatile materials (SbF_5, aHF) were manipulated in an all-Teflon vacuum line equipped with Teflon valves. The manipulation of the nonvolatile materials sensitive to traces of moisture was done in a drybox (M Braun). The water vapor in the argon atmosphere of the drybox never exceeded 1 ppm. Reactions were carried out in FEP or PFA reaction vessels equipped with Teflon valves. The reaction vessels were passivated with fluorine before use.

Reagents. BaF_2 (Riedel-de Haen), SbF_5 (Merck, > 98%), and fluorine (Solvay, 99.98%) were used as supplied. BaF_2 and SbF_5 purity was checked by elemental analysis (Calcd for BaF_2: Ba, 78.3%; F, 21.7%. Found: Ba, 78.1%; F, 21.5%. Calcd for SbF_5: F_{total}, 43.8%. Found: F_{total}, 42.6%). Anhydrous HF (Fluka, purum) was treated with K_2NiF_6 for several days prior to use.

Preparation of $Ba(SbF_6)_2$. BaF_2 (0.481 g, 2.74 mmol) was loaded into a PFA trap. SbF_5 (2.014 g, 9.29 mmol) was sublimated into the cooled trap under dynamic vacuum, and then, aHF (8 mL) was condensed onto it. The reaction was completed in 5 min by forming a clear, colorless solution on warming the vessel to room temperature. A white solid was obtained after aHF and excess SbF_5 were pumped off. Anal. Calcd for $Ba(SbF_6)_2$: F_{total}, 37.5%. Found: F_{total}, 37.5%.

Synthesis of $Ba(SbF_6)_2 \cdot 5XeF_2$. aHF (7 mL) was condensed in the PFA trap containing $Ba(SbF_6)_2$ (1.451 g, 2.38 mmol) to form

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Table 1. Crystal Data and Structure Refinement for $Ba(SbF_6)_2{\cdot}5XeF_2$[a]

empirical formula	$BaXe_5Sb_2F_{22}$
fw	1455.29
temp (K)	200(2)
a (Å)	13.599(6)
b (Å)	12.086(4)
c (Å)	9.732(5)
β (deg)	134.305(6)
V (Å^3)	1144.7 (8)
Z	2
D_{calcd} (g/cm^3)	4.222
λ (Å)	0.71069
μ (cm^{-1})	114.8
space group	*C*2/*m* (No. 12)
GOF indicator	1.09
R1; wR2[b] ($I > 2.00\sigma(I)$)	0.0468; 0.144

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$, $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_p)]^{1/2}$, where N_o = no. of reflns and N_p = no. of refined params.

a clear, colorless solution. XeF_2 (4.889 g, 28.88 mmol) was sublimated into the cooled trap in a dynamic vacuum and gave a clear, colorless solution on warming to room temperature. Removal of aHF and excess XeF_2 in a dynamic vacuum over 24 h left a white solid.

Preparation of Single Crystals of $Ba(SbF_6)_2{\cdot}5XeF_2$. The white solid $Ba(SbF_6)_2{\cdot}5XeF_2$ (1.166 g, 0.80 mmol) was loaded into one leg of a two legged PFA reaction vessel, and aHF (2 mL) was condensed on it to bring it into solution. The solution was kept at room temperature (291 K), while the other leg was cooled by slowly running water to 283 K. Slow transfer of the aHF out of the solution led to deposition of single crystals. After a few colorless single crystals had formed, the mother liquor was poured from them into the second leg of the vessel, and the aHF was pumped off.

Elemental Analysis. The content of free and total fluoride ions was determined with a fluoride ion selective electrode.[4,5] Barium was determined by complexometric titration with EDTA,[6] and antimony, by redox titration.[7] The chemical analyses are given in mass percents.

X-ray powder diffraction photographs were taken of samples in sealed quartz capillaries on a 143 mm diameter Debye−Scherrer camera with X-ray film, using Mo Kα radiation ($\lambda = 7.107$ Å) with a Zr filter. Intensities were estimated visually.

X-ray Structure Determination of $Ba(SbF_6)_2{\cdot}5XeF_2$. Single-crystal data were collected at 200(2) K on a Mercury CCD area detector coupled with a Rigaku AFC7 diffractometer with graphite monochromated Mo Kα radiation. Data were corrected for Lorentz, polarization, and absorption effects and processed using CrystalClear (Rigaku).[8] The structure was solved by direct methods (SHELXS)[9] and expanded using Fourier techniques. Some details on the single-crystal data collection, data processing, and refinement are given in Table 1. Atomic coordinates are given in the Supporting Information.

Infrared and Raman Spectroscopy. The infrared spectrum was taken on a Perkin-Elmer FT-IR 1710 spectrometer, with powdered sample between AgCl windows in a leak-tight brass cell. A Raman spectrum of the solid in a PFA reaction vessel was taken on a Renishaw Raman Imaging Microscope System 1000, with the 632.8 nm exciting line of a He−Ne laser.

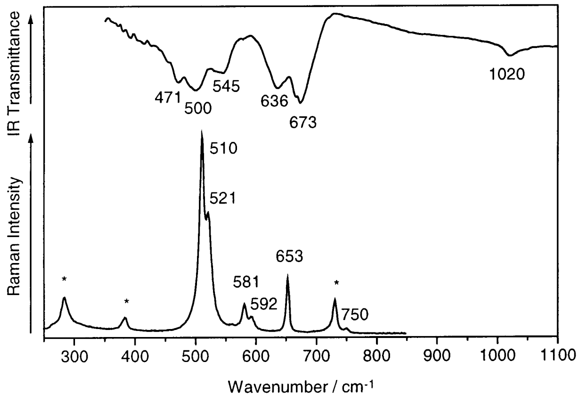

Figure 1. Infrared and Raman spectra of $Ba(SbF_6)_2{\cdot}5XeF_2$ (asterisk denotes PFA or FEP reaction vessel peak).

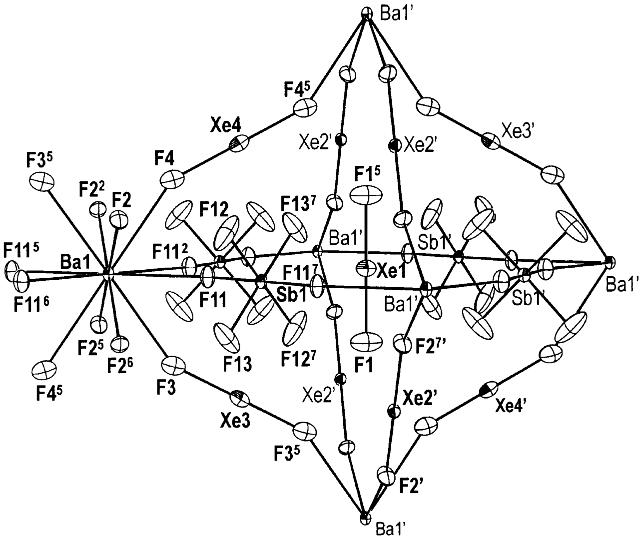

Figure 2. Coordination of barium atom and view of the fluorine environment of the Xe1 atom in the structure of $Ba(SbF_6)_2{\cdot}5XeF_2$ (thermal ellipsoids drawn at 30% probability level).

Results

Elemental Analysis. Calcd for $Ba(SbF_6)_2{\cdot}5XeF_2$: Ba, 9.4%; Sb, 16.7%; F_{total}, 28.7%; F_{free}, 18.3%.[10] Found: Ba, 9.3%; Sb, 16.7%; F_{total}, 28.7%; F_{free}, 18.2%.

Raman and IR spectra of bulk of $Ba(SbF_6)_2{\cdot}5XeF_2$ are shown in Figure 1.

An X-ray powder pattern of the bulk of $Ba(SbF_6)_2{\cdot}5XeF_2$ matches the powder pattern calculated from the single-crystal data (see Supporting Information).

Description of the Crystal Structure of $Ba(SbF_6)_2{\cdot}5XeF_2$. For each formula unit $Ba(SbF_6)_2{\cdot}5XeF_2$, this structure consists of alternating layers of composition $Ba(SbF_6)_2{\cdot}XeF_2$ and 4 XeF_2. The structure is illustrated in Figures 2 and 3, and bond lengths and angles are available in Table 2.

In each $Ba(SbF_6)_2{\cdot}XeF_2$ layer, each heavy atom is at a center of symmetry. The Ba^{2+} ions of the layer are in a nearly

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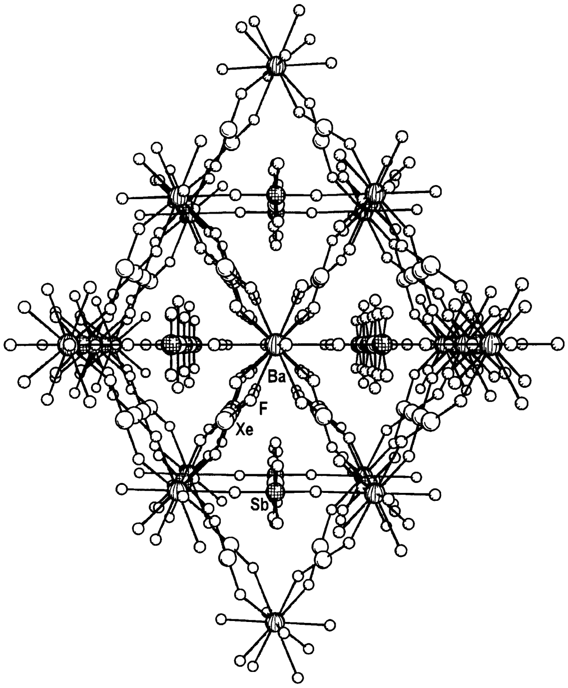

Figure 3. 3D network formed from interconnected $Ba(SbF_6)_2{\cdot}XeF_2$ layers and XeF_2 layers viewed down [110] direction.

Table 2. Selected Bond Lengths and Angles in $Ba(SbF_6)_2{\cdot}5XeF_2$[a]

Bond Distance (Å)		Bond Angle (deg)	
Ba1−F2; Ba1−F2^{2}		F2^{2}−Ba1−F2^{5}; F2−Ba1−F2^{6}	70.7(3)
Ba1−F2^{5}; Ba1−F2^{6}	2.730(6)	F2−Ba1−F2^{2}; F2^{5}−Ba1−F2^{6}	109.3(3)
Ba1−F3; Ba1−F3^{5}	2.99(1)	F3−Ba1−F4^{5}; F3^{5}−Ba1−F4	69.2(3)
Ba1−F4; Ba1−F4^{5}	3.00(1)	F3−Ba1−F4; F3^{5}−Ba1−F4^{5}	110.8(3)
Ba1−F11; Ba1−F11^{2}		F11−Ba1−F11^{2}; F11^{5}−Ba1−F11^{6}	64.2(2)
Ba1−F11^{5}; Ba1−F11^{6}	2.806(5)	F11^{6}−Ba1−F11; F11^{2}−Ba1−F11^{5}	115.8(2)
Xe1−F1; Xe1−F1^{5}	1.99(1)	F1−Xe1−F1^{5}; F2−Xe2−F2^{7}	
Xe2−F2; Xe2−F2^{7}	1.986(5)	F3−Xe3−F3^{5}; F4−Xe4−F4^{5}	180.0
Xe3−F3; Xe3−F3^{5}	2.01(1)	Xe2−F2−Ba1	148.9(3)
Xe4−F4; Xe4−F4^{5}	2.01(1)	Xe3−F3−Ba1	152.6(4)
		Xe4−F4−Ba1	151.8(4)
Sb1−F11; Sb1−F11^{7}	1.888(5)	Sb1−F11−Ba1	157.9(3)
Sb1−F12; Sb1−F12^{7}	1.824(7)		
Sb1−F13; Sb1−F13^{7}	1.823(7)	F11−Sb1−F11^{7}; F12−Sb1−F12^{7}	
		F13−Sb1−F13^{7}	180.0
		F12−Sb1−F11	90.6(3)
		F12^{7}−Sb1−F11	89.4(3)
		F13−Sb1−F11	90.5(3)
		F13^{7}−Sb1−F11	89.5(3)
		F13−Sb1−F12	91.2(5)
		F13−Sb1−F12^{7}	88.8(5)

[a] Symmetry operations used for generation of equivalent atoms: (2) $x, -y, z$; (3) $x + 1/2, y + 1/2, z$; (4) $x + 1/2, -y + 1/2, z$; (5) $-x, -y, -z$; (6) $-x, y, -z$; (7) $-x + 1/2, -y + 1/2, -z$; (8) $-x + 1/2, y + 1/2, -z$.

rhombic-net array. In that plane, each Ba^{2+} is at the center of a rectangle of four Fs of separate SbF_6^- species. The SbF_6^- are centered in the edges of each "rhombus" of the Ba^{2+} array, and each is linked to the two Ba^{2+} via trans F-bridging ligands. A XeF_2 molecule is placed at the center of each "rhombus", with its symmetry axis perpendicular to the plane of the layer. The xenon of this XeF_2 (Xe1) interacts with 12 other F ligands. Four of these, (each bound to a Xe2) two from two XeF_2 of the layer above and two from XeF_2 molecules in the layer below, are in a rectangular distribution, perpendicular to the $Ba(SbF_6)_2{\cdot}XeF_2$ layer, with the Xe1 at the center. On *each side* of the plane containing this rectangular set, the Xe1 is also coordinated to four F ligands of two SbF_6^- species, two F above the $Ba(SbF_6)_2{\cdot}XeF_2$ layer plane and two below.

Each $Ba(SbF_6)_2{\cdot}XeF_2$ layer is linked to its neighbors by a layer of centrosymmetric XeF_2 molecules, each coordinated via its F ligands to a Ba^{2+} in the layer above, and to a Ba^{2+} of the layer below. These interactions bring each Ba^{2+} of one sheet over the center of the "rhombus" of Ba^{2+} of its neighboring related sheet, and, therefore, over the XeF_2 of the $Ba(SbF_6)_2{\cdot}XeF_2$ layer.

The Ba^{2+} ions are each coordinated by 12 F ligands, in 3 4-fold planar sets mutually at right angles. The Ba−F interatomic distances for the F of the SbF_6^- species, at 2.806(5) Å, are slightly longer than for that 4-fold set of F ligands of XeF_2 (identified with Xe2) where Ba−F is 2.730(6) Å. These F ligands are also attracted to the Xe1 of the $Ba(SbF_6)_2{\cdot}XeF_2$ layer, as already described. The F ligands of the other XeF_2 molecules of the XeF_2 layer (identified with Xe3 and Xe4) are attracted to Xe(2) atoms in that layer but are screened from Xe(1). Their F^- ligands are therefore attracted only to the Ba^{2+} of the $Ba(SbF_6)_2{\cdot}XeF_2$ layer. The four Ba−F interatomic distances for these XeF_2 molecules are longer (3.00(1) Å).

Discussion

Synthesis. Salts containing hexafluorometalate anions have rather low lattice energies as a consequence of the anion volume (>100 Å^3).[11] Most of these anions are also poor Lewis bases, especially AF_6^-, where A is As, Sb, or Bi. So, even poor Lewis base solvents, such as aHF, can provide sufficient solvation energy to bring about dissolution of $M(AF_6)_x$ salts. The ready solubility of $Ba(SbF_6)_2$ in aHF and the isolation of compounds of the type $[M(HF)_m](AF_6)_2$ (M is an alkaline earth element)[2] indicate that the cations at least are solvated. Addition of XeF_2 to such a solution, however, introduces a stronger Lewis base than HF. XeF_2, by virtue of its semi-ionic (and quadrupolar) character and its relatively small formula volume of 65 Å^3,[12] competes effectively with SbF_6^- in providing Coulomb energy. This is because the charge on the XeF_2 F ligand is nearly −0.5e and that at the xenon +1. The latter was demonstrated by the excellent agreement between the enthalpy of sublimation calculated for such a charge distribution by Jortner et al.[13] and the experimental value obtained by Schreiner et al.[14]

As with other alkaline earth cations, Ba^{2+} is not a sufficiently strong Lewis acid to withdraw F^- from XeF_2 to generate $Xe_2F_3^+$ or XeF^+ salts. The composition of $Ba(SbF_6)_2{\cdot}5XeF_2$ was confirmed both by the chemical analysis and the structure determination.

Structure. The greater Lewis basicity of the XeF_2 F ligand, compared with the F ligands of SbF_6^- (which accounts for the existence of this compound), is illustrated

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in the Ba−F interatomic distances. That of the Xe2 XeF_2 molecule is 2.730(6) Å, whereas that involving the SbF_6^- ligands is 2.806(5) Å. Only two F ligands of the anion interact with the cation, but the Sb−F distance for those ligands, at 1.888(5) Å, is not significantly different from that in a simple salt, where Sb−F is 1.882(2) Å.[15] The other four F ligands of the anion are so arranged that they interact with a Xe1 atom, about which they are clustered (Xe1−F12 and Xe1−F13 are 3.578(4) and 3.588(7) Å, respectively), and also with Xe2, Xe3, and Xe4 atoms of the XeF_2 molecular layer (Xe2−F12 and Xe2−F13 are 3.321(9) and 3.318(5) Å, Xe3−F12 is 3.251(5) Å, and Xe4−F13 is 3.253(8) Å). These interactions must be weaker than with the Ba^{2+}, however, because the Sb−F distances for these ligands are 1.823(7) and 1.824(7) Å. Perhaps the greatest interest in this structure, however, centers on the three different types of XeF_2 seen here.

The XeF_2 molecule in the $Ba(SbF_6)_2{\cdot}XeF_2$ layer is not simply a space filler. It is so oriented that it presents the +1 charge of Xe1 not only to the previously mentioned F ligands of the anion but also to the F ligands of the Xe2 XeF_2 molecules of the XeF_2 layer (Xe1−F2 is 4.131(4) Å) while F ligands of the Xe3 and Xe4 XeF_2 molecules are screened from Xe1 positive charge by F ligands of the anion (Xe1−F3 is 5.808(2) Å and Xe1−F4 is 5.817(3) Å) (Figure 2). This coordination of the Xe1 XeF_2 molecule resembles the coordination of XeF_2 in the solid XeF_2, which has been described as “a semi-ionic solid”.[13] It is this interaction of the Xe2 XeF_2 molecule with Xe1, as well as with Ba^{2+}, which distinguishes those molecules from the others of the XeF_2 layer. Indeed, the F ligands of the Xe2 molecules are pulled down into the $Ba(SbF_6)_2{\cdot}XeF_2$ layer by the interaction with both Ba^{2+} and Xe1. These F ligands are clearly well anchored there in comparison with F ligands of the Xe3 and Xe4 molecules, as is evident from their small vibrational amplitudes. This 2-fold attraction, into the $Ba(SbF_6)_2{\cdot}XeF_2$ layer, gives these ligands primacy in the Ba^{2+} coordination. Although the F ligands of Xe3 and Xe4 XeF_2 molecules also interact with xenon centers as well as with the Ba^{2+}, those centers are Xe2 of XeF_2 molecules of the XeF_2 layer (Xe2−F3 is 3.594(1) Å, and Xe2−F4 is 3.588(1) Å). There is therefore no cooperative pull on those Xe3 and Xe4 XeF_2 ligands to bring them close to the Ba^{2+}. This accounts for the rather long Ba−F distances of 3.00(1) Å for these ligands.

Vibrational Spectra. Although the different XeF_2 molecules are not distinguished significantly from one another by interatomic distances and angles, the electric fields, in which the F ligands of the different types lie, are different. The F ligands of the Xe2 XeF_2 molecules are closest to the positive centers. It is these molecules therefore which may be responsible for the Raman band (Figure 1) at 521 cm^{-1}. This represents a small increase in frequency for the a_{1g} mode in the solid at 496 cm^{-1}.[16] The other close strong Raman band must be due to the same vibration in the other XeF_2 molecules. Strong peaks in the Raman at 653, 592, and 581 cm^{-1} can be attributed to vibrations derived from the ν_1 and ν_2 modes of the slightly distorted octahedral SbF_6^-, for which ν_1 is 668 cm^{-1} and ν_2 is 558 cm^{-1}.[17] The broad absorption in the infrared, peaked at 673 and 636 cm^{-1}, may derive from the ν_3 octahedral mode of SbF_6^- which for the octahedral species is at 669 cm^{-1}.[17] Those infrared bands at 545, 500, and 471 cm^{-1} could all be related to ν_3 vibrational modes of the XeF_2 molecules. In solid XeF_2, the ν_3 vibrational mode is at 547 cm^{-1}.[16]

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Supporting Information Available: X-ray crystallographic file in CIF format, table of atomic coordinates and equivalent displacement parameters U_{eq}, and table of X-ray powder diffraction data for $Ba(SbF_6)_2{\cdot}5XeF_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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