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Article

XeF_2 as a Ligand in a Coordination Compound with the BF_4^- Anion

Gašper Tavčar* and Boris Žemva*

Department of Inorganic Chemistry and Technology, Jožef Stefan Institute,
Jamova 39, SI-1000 Ljubljana, Slovenia

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The first tetrafluoroborate compound with XeF_2 coordinated to a metal center, $[Cd(XeF_2)](BF_4)_2$, has been synthesized. It crystallizes in monoclinic space group $P2_1/a$ with $a = 8.785(11)$ Å, $b = 9.079(2)$ Å, $c = 10.718(6)$ Å, $\beta = 110.824(6)$, and $Z = 4$. Its crystal structure and that of $Cd(BF_4)_2$ have been solved. The latter crystallizes in orthorhombic space group *Pbca*. Both syntheses were performed in aHF as solvent, at room temperature, yielding colorless solids. The Raman spectra of the solids are in harmony with the crystallographic findings. $[Cd(XeF_2)](BF_4)_2$ has been shown to be in equilibrium with XeF_2 and $Cd(BF_4)_2$ in aHF.

Introduction

The first known compound with xenon difluoride coordinated to metal cations with weakly coordinated anions was $[Ag(XeF_2)_2]AsF_6$.[1] Many similar coordination compounds with the AsF_6^- anion have been synthesized recently.[2] Only two other weakly coordinated anions forming coordination compounds with XeF_2 are known: $[Ag(XeF_2)_2]PF_6$[3] was the first compound with the PF_6^- anion and $[Ba(XeF_2)_5](SbF_6)_2$[4] was the first compound with SbF_6^-. All of the octahedral anions AF_6^- (A = P, As, Sb) have similar chemistry. The tetrahedral BF_4^- group is of much smaller volume (volume PF_6^-: volume BF_4^- 1.57:1)[5] and the charge on each fluorine ligand in the BF_4^- anion is bigger than that in any AF_6^-. This causes the F ligands of BF_4^- to be stronger Lewis bases than the F of AF_6^-, and more competitive with the F ligands of XeF_2 in donation to a Lewis acid center such as a metal cation.

Experimental Section

General Experimental Procedures. A Teflon and nickel vacuum line and system were used as described previously.[6] Moisture-sensitive materials were handled in a dry argon atmosphere in a drybox having a maximum water content of 0.1 ppm of water vapor (M. Braun, Garching, Germany). Reaction vessels made of PFA and equipped with Teflon valves and Teflon-coated stirring bars were used for the syntheses. Crystals were grown in a crystallization vessel made from a T-shaped PFA reaction vessel, constructed from one 16 mm i.d. PFA tube and a smaller 4 mm i.d. PFA tube connected by a Teflon valve.

Reagents. Cadmium difluoride was prepared by direct fluorination of $CdCl_2 \cdot H_2O$ (2.805 g) (Zorka Šabac, 99%) with F_2 in aHF as a solvent at 298 K. Fluorine was added three times at a pressure of 700 kPa from a vessel of known volume into the reaction vessel cooled in liquid nitrogen. Cadmium difluoride was characterized by X-ray powder diffraction pattern and by chemical analysis (calculated: Cd, 74.7%; F, 25.3%; found: Cd, 74.6%; F, 25.2%;). Anhydrous HF (aHF) (Fluka, purum) was treated with K_2NiF_6 (Ozark-Mahoning, 99%) for several days prior to use. Boron trifluoride (Union Carbide, 99.5%) was used as supplied. Xenon difluoride was prepared by photochemical reaction between Xe and F_2 at room temperature.[7] **Caution:** Anhydrous HF must be handled in a well-ventilated hood and protective clothing must be worn at all times.

Synthesis of $Cd(BF_4)_2$. It was prepared from CdF_2 (0.8519 g, 5.66 mmol) and BF_3 (0.9685 g, 14.28 mmol) in aHF. Because of the low solubility of BF_3 in aHF, the reaction was left to proceed for a week with continuous stirring. Anhydrous HF and excess of BF_3 were pumped off on a vacuum line. The product was characterized by its X-ray powder diffraction pattern and chemical analysis. (Calculated for $Cd(BF_4)_2$: Cd, 39.9%; F_t, 53.1%; Found: Cd, 39.3%; F_t^-, 53.6%;).

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* Correspondence may be addressed to either author. E-mail: gasper.tavcar@ijs.si (G. Tavčar); boris.zemva@ijs.si (B. Žemva). Phone: +386 1 477 35 40. Fax: +386 1 423 21 25.

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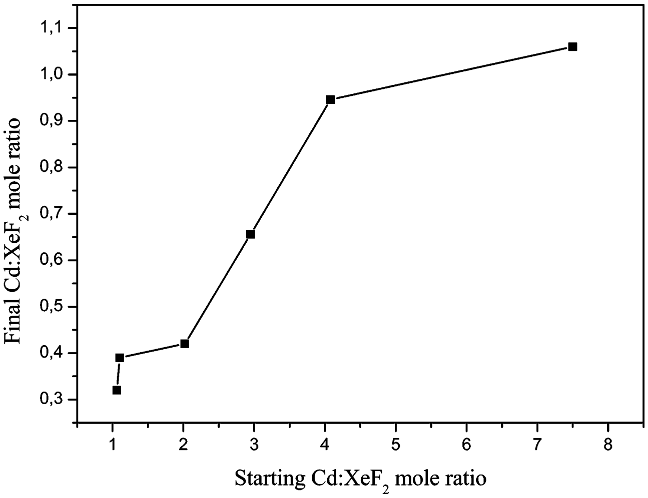

Figure 1. Equilibrium of $Cd(BF_4)_2$ and XeF_2 in aHF solution.

Synthesis of $[Cd(XeF_2)](BF_4)_2$. $[Cd(XeF_2)](BF_4)_2$ was synthesized from $Cd(BF_4)_2$ (0.3265 g, 1.14 mmol) and excess of XeF_2 (1.4575 g; 8.61 mmol) in aHF. $Cd(BF_4)_2$ and XeF_2 were weighed in the reaction vessel in a drybox. After the reaction excessive xenon difluoride and aHF were pumped off on a vacuum line at room temperature. The final mole ratio Cd:Xe gained by following mass balance through the experiment was 1:1.06. The reaction was later repeated with all the reagents added in stoichiometric amounts: $Cd(BF_4)_2$ (0.250 g, 0.875 mmol); XeF_2 (0.154 g, 0.910 mmol). The isolated product was a mixture of $Cd(BF_4)_2$ and $[Cd(XeF_2)](BF_4)_2$ according to its Raman spectrum and X-ray powder diffraction pattern. The mole ratio Cd:Xe calculated from a weight difference was only about 1:0.4. The influence of the mole ratio of the reactants was studied and is illustrated in Figure 1.

Preparation of Single Crystals of $Cd(BF_4)_2$. $Cd(BF_4)_2$ (0.105 g) in a wide-bore tube was dissolved in aHF. This solution was decanted into a narrower long tube of the T-shaped crystallization vessel and aHF was back-distilled into the cooled wide-bore tube. The crystals were grown with a temperature gradient of 28 K, were separated by decantation from the mother liquor, and were sealed in quartz capillaries.

Preparation of Single Crystals of $[Cd(XeF_2)](BF_4)_2$. Crystals of $[Cd(XeF_2)](BF_4)_2$ were obtained from previously synthesized $Cd(BF_4)_2$ (0.072 g, 0.251 mmol) and XeF_2 (0.508 g, 3.00 mmol) in the mole ratio Cd:Xe 1:12.0. Both reagents were weighed in the drybox and put into the wider part of the crystallization vessel. Anhydrous HF was added and a solution with some precipitate was obtained. Only the precipitate-free solution was decanted into the narrower part of the T-shaped crystallization vessel. The crystals were grown with a temperature gradient of 28 K and were isolated by decantation of the mother liquor. The crystals were immersed in perfluorinated oil (ABCR, FO5960) in a drybox. A suitable crystal was selected under the microscope and was transferred into a cold nitrogen stream of the X-ray diffractometer.

Elemental Analysis. The total fluoride content was determined after complete decomposition of the sample by alkali fusion using $KNaCO_3$. The melt was dissolved by using concentrated HCl to prevent complexation of free fluoride by boron and then neutralized to pH not lower than 7. The fluoride content was determined by fluoride ion selective electrode.[8]

Table 1. Crystal Data and Structure Refinement for $[Cd(XeF_2)](BF_4)_2$ and $Cd(BF_4)_2$[a]

	$Cd(BF_4)_2$	$[Cd(XeF_2)](BF_4)_2$
a (Å)	9.127(2)	8.785(11)
b (Å)	8.746(2)	9.0793(18)
c (Å)	13.23(1)	10.718(6)
β (deg)	90	110.824(6)
V (Å)	1055.7(9)	799.0(11)
Z	8	4
fw	286.02	455.32
space group	$Pbca$	$P2_1/a$
T (°C)	25(2)	−73(2)
λ (Å)	0.71069	0.71069
$D_{\text{calculated}}$ (g/cm^3)	3.599	3.785
μ (mm^{-1})	4.248	7.033
R1	0.0363	0.0279
wR2	0.0720	0.0587

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$.

Content of cadmium was determined by complexometric titration.[9]

X-ray Powder Diffraction Patterns. Diffraction data of the samples were taken in sealed quartz capillaries on a 143 mm diameter Debye-Scherer camera with X-ray film, using Cu Kα radiation. Intensities were estimated visually.

X-ray Structure Determination. Both single-crystal data sets were collected at 200 K using a Mercury CCD area detector coupled with a Rigaku AFC7 diffractometer with graphite monochromated Mo Kα radiation. The data were corrected for Lorentz and polarization effects. Multiscan absorption corrections were applied to each data set. All calculations during the data processing were performed using the CrystalClear software suite.[10] Structures were solved by direct methods[11] and expanded using Fourier techniques. Full-matrix least-squares refinement of F^2 against all reflections was performed using the SHELX97 program.[12] More details on the data collection and structure determination are given in Table 1.

Raman Spectroscopy. Raman spectra of powdered samples in sealed quartz capillaries were recorded on a Renishaw Raman Imaging Microscope System 1000 by use of the 632.8 nm exciting line of a He−Ne laser. Geometry for all the Raman experiments was 180° backscattering with laser power 25 mW.

Results

Description of the Crystal Structure of $Cd(BF_4)_2$. $Cd(BF_4)_2$ is isostructural with previously described $Ca(BF_4)_2$.[13] The coordination sphere around Cd consists of eight fluorine atoms from eight separate BF_4 groups (Figure 2). Cd−F(B) distances are in the range from 2.296(2) to 2.381(3) Å. The basic building block consists of two Cd atoms connected through four BF_4 units. The extended structure consists of columns of BF_4 units and columns of alternating Cd and BF_4 units all parallel to [010]. There are twice as many $[Cd^{2+}, BF_4^-]$ columns as $[BF_4^-, BF_4^-]$ columns. The columns are linked together through Cd···F interactions. Since each

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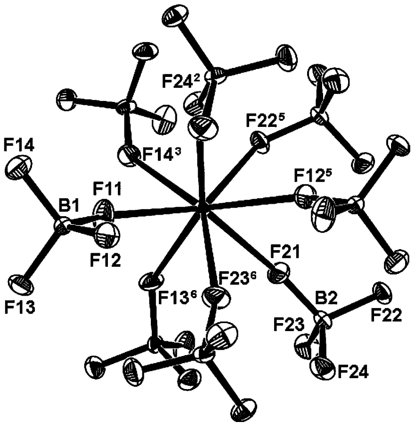

Figure 2. Coordination sphere of Cd in the structure of $Cd(BF_4)_2$.

Table 2. Selected Bond Lengths and Angles in $Cd(BF_4)_2$[a]

bond	distance (Å)	angle	degrees
Cd1−F11	2.334(2)	F11−Cd1−F12^{d}	116.29(9)
Cd1−F12^{d}	2.381(3)	F11−Cd1−F13^{e}	82.48(9)
Cd1−F13^{e}	2.308(3)	F11−Cd1−F14^{c}	76.77(9)
Cd1−F14^{c}	2.306(3)	F11−Cd1−F21	140.57(9)
Cd1−F21	2.351(2)	F11−Cd1−F22^{d}	143.66(9)
Cd1−F22^{d}	2.296(2)	F11−Cd1−F23^{e}	72.61(9)
Cd1−F23^{e}	2.300(3)	F11−Cd1−F24^{b}	77.02(10)
Cd1−F24^{b}	2.336(3)	F11−B1−F12	110.2(3)
B1−F11	1.388(5)	F11−B1−F13	109.6(4)
B1−F12	1.386(5)	F11−B1−F14	109.6(3)
B1−F13	1.398(5)	F12−B1−F13	109.1(3)
B1−F14	1.393(5)	F13−B1−F14	110.2(4)
B2−F21	1.387(5)	F21−B1−F22	109.3(3)
B2−F22	1.389(5)	F21−B1−F23	108.6(3)
B2−F23	1.398(5)	F21−B1−F24	111.0(3)
B2−F24	1.383(5)	F22−B1−F23	109.4(3)

[a] Symmetry operations used for generation of equivalent atoms: [b] $x + 1/2, -y + 1/2, -z$. [c] $-x, y + 1/2, -z + 1/2$. [d] $-x, -y, -z$. [e] $-x + 1/2, y + 1/2, z$.

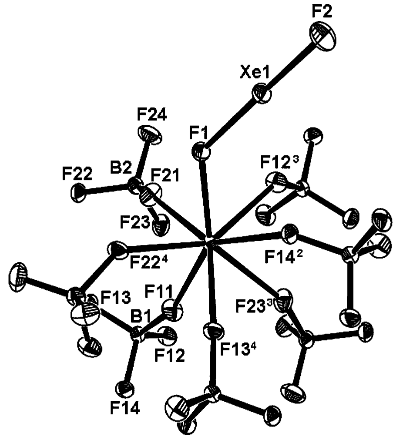

Figure 3. Coordination sphere of Cd in the structure of $[Cd(XeF_2)](BF_4)_2$.

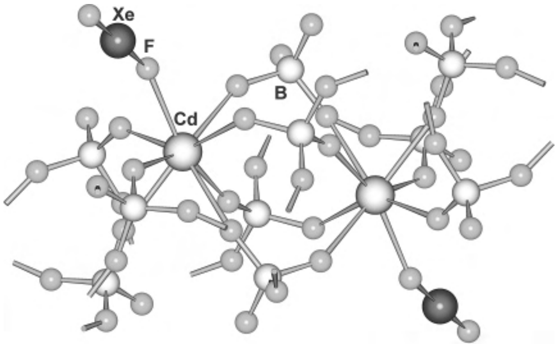

Figure 4. Basic building block of the layer structure of $[Cd(XeF_2)](BF_4)_2$.

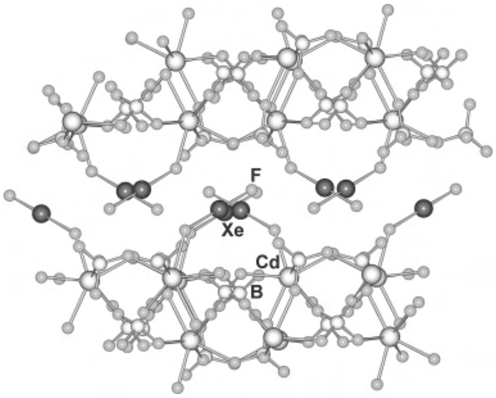

Figure 5. Packing of the layers in the structure of $[Cd(XeF_2)](BF_4)_2$.

fluorine atom is coordinated to only one Cd atom, both BF_4 units are essentially undistorted from tetrahedral geometry with B−F interatomic distances in the range 1.383(5)−1.398(5) Å. Selected distances and angles are given in Table 2.

Description of the Crystal Structure of $[Cd(XeF_2)](BF_4)_2$. The coordination sphere around the Cd atom consists of eight F ligands, seven from BF_4 groups and one from the XeF_2 molecule, in an Archimedean antiprism arrangement (Figure 3). Cd−F(B) distances are in the range from 2.287(3) to 2.370(3) Å, while the Cd−F(Xe) distance of 2.250(3) Å is the shortest Cd−F interaction in this structure.

There are two different BF_4 units. The $B(1)F_4$ tetrahedron is essentially undistorted and is similar to that in the structure of $Cd(BF_4)_2$. It is coordinated to four different Cd atoms. The other unit ($B(2)F_4$) is coordinated only to three different Cd atoms and is thereby deformed from the tetrahedral shape. The noncoordinating F ligand (B2−F24) with interatomic distance 1.350(6) Å is the shortest B−F bond in either of the present structures or that of $Ca(BF_4)_2$.[13]

Each Cd atom is eight-coordinated by F ligands, one from each of seven BF_4 units and one from a XeF_2 molecule forming a layered structure. The XeF_2 ligands are in layers which sandwich sheets of Cd coordinated to BF_4 units. Each of the four $B(1)F_4$ units is linked to four Cd and each of the three $B(2)F_4$ units has three such connections (Figure 4).

Layers are connected by electrostatic interactions between Xe of the XeF_2 molecules and F ligands from XeF_2 molecules and BF_4 units. The Xe···F interactions between layers are in the range from 3.202 to 3.564 Å. These interactions involve each Xe atom in interaction with four F ligands: one from each of two XeF_2 molecules and one from each of two BF_4 units in a neighboring layer. Four other Xe···F interactions in the range from 3.125 to 3.610 Å are within the same layer (Figure 5). The consequences of these interactions and of the steric activity of the electron lone pairs at the XeF_2 molecule have little impact on the angle F(1)−Xe(1)−F(2) = 179.1°. Selected interatomic distances and angles are given in Table 3. Sterically reasonable electrostatic contacts range from 3.125 to 3.610 Å (see Supporting Information).

Table 3. Selected Bond Lengths and Angles in $[Cd(XeF_2)](BF_4)_2$[a]

bond	distance (Å)	angle	degrees
Xe1−F1	2.065(2)	F1−Xe1−F2	179.1(1)
Xe1−F2	1.943(3)	F1−Cd1−F11	148.2(1)
Cd1−F1	2.250(3)	F1−Cd1−F12[c]	73.2(1)
Cd1−F11	2.287(3)	F1−Cd1−F13[d]	121.1(1)
Cd1−F12[c]	2.370(3)	F1−Cd1−F14[b]	72.9(1)
Cd1−F13[d]	2.334(3)	F1−Cd1−F21	77.4(1)
Cd1−F14[b]	2.337(3)	F1−Cd1−F22[d]	77.7(1)
Cd1−F21	2.342(4)	F1−Cd1−F23[c]	137.8(1)
Cd1−F22[d]	2.310(3)	F11−B1−F12	108.3(4)
Cd1−F23[c]	2.364(3)	F11−B1−F13	110.0(4)
B1−F11	1.388(5)	F11−B1−F14	109.2(3)
B1−F12	1.399(5)	F12−B1−F13	111.0(3)
B1−F13	1.383(5)	F21−B1−F22	110.1(4)
B1−F14	1.398(5)	F21−B1−F23	108.1(4)
B2−F21	1.420(6)	F21−B1−F24	110.1(4)
B2−F22	1.414(5)	F22−B1−F23	107.7(4)
B2−F23	1.405(6)	F22−B1−F24	110.4(4)
B2−F24	1.350(6)	F23−B1−F24	112.0(4)

[a] Symmetry operations used for generation of equivalent atoms: [b] $-x + 1/2, y + 1/2, -z$. [c] $-x, -y, -z$. [d] $x + 1/2, -y + 1/2, z$.

Table 4. Raman Spectra of $Cd(BF_4)_2$ and $[Cd(XeF_2)](BF_4)_2$

$Cd(BF_4)_2$ frequency (cm^{-1})	intensity	$[Cd(XeF_2)](BF_4)_2$ frequency (cm^{-1})	intensity	tentative assignment
1016	0.7			ν_3(B−F)
1003	0.9			ν_3(B−F)
800	10	798	0.5	ν_1(B−F)
787	0.5			ν_1(B−F)
		770	0.3	ν_1(B−F)
		568	7.1	ν(Xe−F)
		550	10	ν(Xe−F)
545	0.4			ν_4(B−F)
		535	0.2	ν_4(B−F)
531	1.8			ν_4(B−F)
520	1.3			ν_4(B−F)
		495	0.4	$\nu(XeF_2)$
		449	2.2	ν(Xe···F)
375	0.5	365	0.1	ν_2(B−F)
364	0.7			ν_2(B−F)
354	1.1			ν_2(B−F)

Discussion

Syntheses. The reaction between $Cd(BF_4)_2$ and XeF_2 was performed at room temperature in aHF and later repeated under different Cd:Xe starting molar ratios (Figure 1). It was shown that in order to obtain a pure product, $[Cd(XeF_2)](BF_4)_2$, in this solvent at room temperature the mole ratio $Cd(BF_4)_2$:XeF_2 needed to be at least 1:5 or higher, in accord with the equilibrium [eq 1].

$$Cd(BF_4)_2 + nXeF_2 \underset{RT}{\overset{aHF}{\rightleftharpoons}} [Cd(XeF_2)](BF_4)_2 + (n-1)XeF_2 \quad (1)$$

Solutions of $Cd(BF_4)_2$ in aHF like those of $Mn(BF_4)_2$[14] must contain solvated cations $[Cd(HF)_n]^{2+}$ and BF_4^- anions. Although XeF_2 provides very few fluoride ions when dissolved in aHF,[15] the molecule is semi-ionic. The F ligand of XeF_2 is therefore able to compete effectively, as a Lewis base, with the F ligand of BF_4^-. The relative weakness of the Lewis basicity of the F ligands of the AF_6^-(A = P, As, Sb) species[16] accounts for the relative ease of syntheses of XeF_2 complexes with those anions.

During the removal of the aHF, the concentration of XeF_2 and BF_4^- gradually becomes significant and both species slowly substitute the HF molecules around the Cd^{2+} cation. Despite the good Lewis basicity of the XeF_2 F ligands, it is essential that the concentration of XeF_2 be high enough, to prevent the formation of $Cd(BF_4)_2$. In those circumstances when the last molecules of HF are removed, the layered structure of $[Cd(XeF_2)](BF_4)_2$ crystallizes.

Crystal Structures. In each of $[Cd(XeF_2)](BF_4)_2$ and $Cd(BF_4)_2$ the coordination sphere of the Cd^{2+} consists of eight fluorine ligands, which form an Archimedean antiprism about it. This is in harmony with the eight coordination of Cd^{2+} in CdF_2, although in that instance the fluorite structure requires cubic symmetry.[17] The main difference between the two fluoroborate structures (Figure 4) is that one BF_4 unit is exchanged with a XeF_2 molecule, thus transforming a 3D structure into a layer structure.

Cd^{2+} and Ca^{2+} cations have very similar ionic radii (Cd^{2+}, CN = 8, r = 1.24 Å; Ca^{2+}, CN = 8, r = 1.26 Å)[18] and $Cx(BF_4)_2$ (Cx = Ca, Cd) are isostructural.

That we were not able to synthesize the XeF_2 complex of calcium tetrafluoroborate requires comment. Lattice tends to favor retention of the BF_4^- anion, but molecular XeF_2 can be lost. The higher first electron affinity of Cd^{2+} (16.91 eV[19]) than that of Ca^{2+} (11.87 eV[19]) indicates that the Cd^{2+} will be the stronger Lewis acid. So the XeF_2 molecule is likely to be more strongly attracted to that metal ion. This is probably the main cause of the $[Cd(XeF_2)](BF_4)_2$ stability.

The Cd−F(Xe) interatomic distance of 2.250(3) Å is similar to analogous distances in the structure of $[Cd(XeF_2)_4](AsF_6)_2$[2] (2.220(6) Å to 2.271(6) Å), indicating that the influence of the anion is less pronounced than previously thought.[20] Evidently, the Cd−F(Xe) distance is dependent primarily upon the effective charge at the Cd^{2+}, and the Lewis basicity of the F ligand of the XeF_2 closest to the cation, and these factors do not change much from one Cd^{2+} complex to another.

Vibrational Spectra. Raman spectra of $[Cd(XeF_2)](BF_4)_2$ and $Cd(BF_4)_2$ are shown in Table 4 and Figure 6. The most intense bands are usually the Xe−F stretching modes because of the high polarizability of xenon. B−F vibrations are far less intense. The intense Raman bands at 550 and 568 cm^{-1} can be confidently assigned to XeF_2 stretching modes. The totally symmetric (ν_1) stretching (Raman) mode for solid XeF_2 is close to 497 cm^{-1} [21] and the asymmetric stretching (IR) mode (ν_3) is at 547 cm^{-1} (solid). But when XeF_2 is coordinated asymmetrically to a Lewis acid (as in $XeF_2 \cdot XeF_5^+AsF_6^-$), the 497 cm^{-1} Raman band is replaced by one at higher frequency (559 cm^{-1}) and a second

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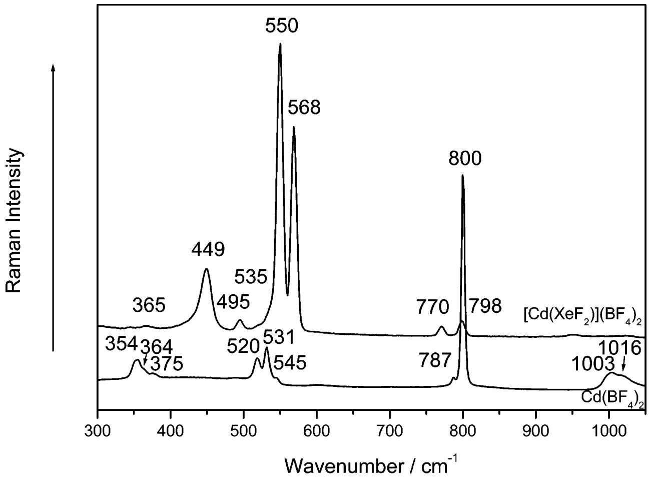

Figure 6. Raman spectra of $[Cd(XeF_2)](BF_4)_2$ and $Cd(BF_4)_2$.

at lower (433 cm^{-1}). In the instance of XeF_2 coordinated symmetrically to two Lewis acid centers, as in $XeF_2 \cdot 2(XeF_5^+AsF_6^-)$, there is only one Raman band at 497 cm^{-1}.[22] In $(Xe-F)^+$ salts, one F ligand is pulled away from the XeF_2 molecule. The $(Xe-F)^+$ stretching frequency is normally higher than 600 cm^{-1}.[23] In $[Cd(XeF_2)](BF_4)_2$ (Figure 6) the peaks at 550, 568, and 449 cm^{-1} can be confidently assigned to stretching modes of the noncentric XeF_2 molecule that is coordinated to the Cd^{2+}. The peak splitting of $\nu(Xe-F)$ is probably a consequence of the weak vibrational coupling between interacting XeF_2 molecules. The weak band at 495 cm^{-1} may be due to free XeF_2 created by decomposition of $[Cd(XeF_2)](BF_4)_2$ in the laser beam.

The other bands can be attributed to the vibrations of the two crystallographically distinct BF_4^- anions. Tetrahedral BF_4^- has Raman bands at 1070(ν_3), 777(ν_1), 533(ν_4), and 360(ν_2) cm^{-1}.[24] Lowering of the anion site symmetry as is in the case of $NaBF_4$ (orthorhombic space group *Cmcm*) splits these modes as follows: 1115, 1055(ν_3 related), 785(ν_1 related), 554, 534, 532(ν_4 related), and 369, 344(ν_2 related) cm^{-1},[25] and there is a similar complexity seen in the Cd(BF4)$_2$ Raman spectra: 1016,1003 (ν_3 related), 800, 787 (ν_1 related), 545, 531, 520 (ν_4 related), 375, 364, 354(ν_2 related) cm^{-1}. Clearly, even greater complexity should be anticipated for the BF_4^- anion spectra of $[Cd(XeF_2)](BF_4)_2$, especially since the BF_4 species is so markedly distorted from T_d symmetry.

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Supporting Information Available: An X-ray crystallographic file in CIF format, atomic coordinates, and equivalent displacement parameters U_{eq} of $[Cd(XeF_2)](BF_4)_2$ and $Cd(BF_4)_2$ and a table of Xe···F interactions in the $[Cd(XeF_2)](BF_4)_2$ structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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