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Article

Coordination of XeF_2 to Calcium and Cadmium Hexafluorophosphates(V)

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$[M(XeF_2)_5](PF_6)_2$ (M = Ca, Cd) complexes were prepared by the reaction of MF_2 and XeF_2 under pressure of gaseous PF_5 in anhydrous HF as solvent. The coordination sphere of the Ca atom consists of nine fluorine atoms: three from two PF_6^- units (one bidentate and one monodentate) and one from each of six XeF_2 molecules. The coordination sphere of the Cd atom consists of eight fluorine atoms: one from each of two PF_6^- units and one from each of six XeF_2 molecules. Two of the XeF_2 ligands about M in each compound are bridging ligands and are each linked to two M, generating infinite (–M–F–Xe–F-M–F–Xe–F–) chains along the *b*-axis in the Ca salt and along the *c*-axis in the Cd compound. The Cd^{2+} cation is smaller and more electronegative than the Ca^{2+} cation. These differences account for the higher F ligand coordination in the Ca^{2+} salt and for other structural features that distinguish them. The different stoichiometry of the PF_6^- salts when compared with their AsF_6^- analogues, which have the composition $[M(XeF_2)_4](AsF_6)_2$ (M = Ca, Cd), is in accord with the lower F ligand charge in the AsF_6^- when compared with that in the PF_6^- compound. Indeed, the AsF_6^- ligand charges appear to be similar to those in the XeF_2-bridged species.

Introduction

$[Ag(XeF_2)_2]AsF_6$ was discovered when cationic Ag^{II} (with AsF_6^- as the counteranion) was shown to oxidize xenon in liquid anhydrous HF (aHF) at room temperature. It was the first example of a compound in which XeF_2 acts as a ligand coordinated to a metal ion.[1] Attempts, at that time, to make alkali metal analogues of the silver salt failed. In recent years, however, a series of compounds of the type $[M(XeF_2)_n](AF_6)_2$ have been synthesized and structurally characterized [2] including calcium[3,4] and cadmium[5] compounds with the AsF_6^- anion. Until this study, the only related PF_6^- salt was $[Ag(XeF_2)_2]PF_6$.[6] $[Ca(XeF_2)_5](PF_6)_2$ has been briefly mentioned in our review paper,[7] but preparative details, crystallographic data, and Raman spectra of the compounds $[M(XeF_2)_5](PF_6)_2$ (M = Ca, Cd) are given here for the first time.

Experimental Section

General Experimental Procedures. A Teflon and nickel vacuum line was used as described previously.[8] Moisture-sensitive materials were handled in the dry argon atmosphere of a glovebox 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 FEP reaction vessel, constructed from one 16-mm i.d. FEP tubing. An ~30 cm length of 4-mm i.d. FEP tube connected by a Teflon valve provided the flexibility for decanting the aHF solution from one leg of the T-reactor to the other.

Reagents. CaF_2 (Merck, Suprapur) and fluorine (Solvay, 99.98%) were used as purchased. The purity of CaF_2 was checked by

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elemental analysis. (Anal. Calcd for CaF$_2$: Ca, 51.3; F, 48.7. Found: Ca, 51.2; F, 48.6.) Cadmium difluoride was prepared by direct fluorination of CdCl$_2$·H$_2$O (2.805 g) (Zorka Šabac, 99%) with F$_2$ in aHF as solvent at 25 °C. Fluorine was added in three portions by condensation from a reaction vessel of known volume and pressure of fluorine (700 kPa) into a reaction vessel cooled with liquid nitrogen. Cadmium difluoride was characterized by its X-ray powder diffraction pattern and by chemical analyses. (Calcd: Cd, 74.7; F, 25.3. Found: Cd, 74.6; F, 25.2.) PF$_5$ was prepared by fluorination of P$_2$O$_5$ powder under high pressure as previously described.[9] Its purity was checked by IR spectroscopy. XeF$_2$ was prepared by the photochemical reaction between xenon and F$_2$ at room temperature.[10] Anhydrous HF (Fluka, purum) was treated with K$_2$NiF$_6$ (Ozark-Mahoning, 99%) for several days prior to use.

Caution: Anhydrous hydrogen fluoride, PF$_5$, and XeF$_2$ must be handled in a well-ventilated hood, and protective clothing must be worn at all times! The experimentalist must become familiar with these reagents and the hazards associated with them. Fresh tubes of calcium gluconate gel should always be on hand for the fast treatment of skin exposed to these reagents. For treatment of HF injuries, see ref 11.

Synthesis of [M(XeF$_2$)$_5$](PF$_6$)$_2$. CaF$_2$ (0.229 g, 2.92 mmol) and XeF$_2$ (2.493 g, 14.73 mmol) were weighed into the reaction vessel inside the glove box. The reaction vessel was cooled with liquid nitrogen, and HF was added by condensation at − 196 °C. The reaction vessel was then warmed to room temperature and weighed. PF$_5$ in excess of that required to convert all CaF$_2$ to Ca(PF$_6$)$_2$ (1.573 g, 12.48 mmol) was added to the reaction vessel, again with liquid-nitrogen cooling. The reaction proceeded at room temperature for 24 h. The product was isolated from the clear and colorless solution by pumping off the solvent and excess PF$_5$ at −40 °C. The reaction vessel was warmed to room temperature and weighed; the mass of the product was 3.454 g (2.93 mmol, as calculated for [Ca(XeF$_2$)$_5$](PF$_6$)$_2$).

The preparation of the cadmium compound was similar: CdF$_2$ (0.195 g, 1.30 mmol), XeF$_2$ (1.132 g, 6.68 mmol), and PF$_5$ (1.118 g, 8.88 mmol). The product was isolated under dynamic vacuum from a clear, colorless solution at −40 °C. The mass of the product was 1.653 g (1.32 mmol of [Cd(XeF$_2$)$_5$](PF$_6$)$_2$). In both cases, the products were characterized by Raman spectroscopy. Both compounds, [M(XeF$_2$)$_5$](PF$_6$)$_2$ (M = Ca, Cd), decompose under dynamic vacuum at room temperature releasing PF$_5$ and XeF$_2$.

Preparation of Single Crystals of [M(XeF$_2$)$_5$](PF$_6$)$_2$. [M(XeF$_2$)$_5$](PF$_6$)$_2$ (M = Ca, Cd) complexes were placed in the 16-mm tube of a crystallization vessel and dissolved in aHF. This solution was decanted into the 4-mm tube of the T-shaped crystallization vessel. The crystals were grown by static distillation into the 16-mm tube using a temperature gradient of 30 °C. The crystals were isolated by decantation of the mother liquid, dried under dynamic vacuum at − 10 °C, transferred into the glovebox, and then immersed in perfluorinated oil (ABCR, FO5960). A suitable crystal was selected under the microscope and transferred into the cold nitrogen stream of the X-ray diffractometer.

Crystal Structure Determination. Single-crystal data sets were collected using a Mercury CCD area detector coupled to a Rigaku AFC7 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). The data were corrected for Lorentz and polarization effects. A multiscan absorption correction was applied to data sets. All calculations during the data processing were performed using the CrystalClear software suite.[12] Structures were solved using direct methods[13] and expanded Fourier techniques. Full-matrix least-squares refinement of F^2 against all reflections was performed using the SHELX 97 program.[14]

Table 1. Crystal and Structure Refinement Data for [M(XeF$_2$)$_5$](PF$_6$)$_2$ (M = Ca, Cd)[a]

param	CaXe$_5$P$_2$F$_{22}$	CdXe$_5$P$_2$F$_{22}$
fw	1176.52	1248.84
space group	*Pna*2$_1$	*Pna*2$_1$
temp (K)	100(2)	100(2)
a (Å)	14.339(13)	14.082(2)
b (Å)	8.366(8)	17.177(12)
c (Å)	17.215(16)	8.4700(15)
V (Å^3)	2065(3)	2048.8(15)
Z	4	4
D_{calcd} (g/cm^3)	3.784	4.049
μ (mm^{-1})	8.705	9.534
R1, wR2	0.0413, 0.0801	0.0367, 0.0728

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

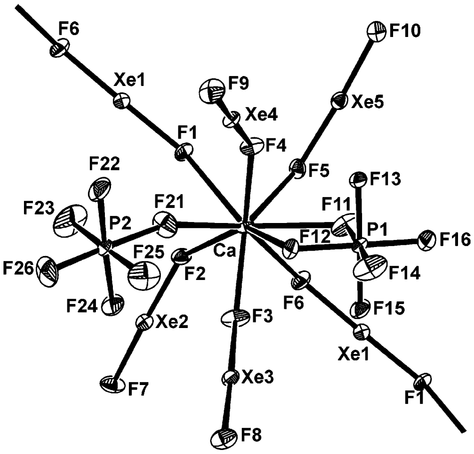

Figure 1. Coordination sphere of calcium in [Ca(XeF$_2$)$_5$](PF$_6$)$_2$.

Crystal structure data for [Ca(XeF$_2$)$_5$](PF$_6$)$_2$ and [Cd(XeF$_2$)$_5$](PF$_6$)$_2$ were collected at −73 °C, and the structures were initially refined in the space group *Pccn*. In this space group, the single PF$_6$ unit was disordered, with two possible orientations. The symmetry was lowered to the acentric space group *Pna*2$_1$, which resulted in two different PF$_6$ units. To decrease the possible rotation of the PF$_6$ units the crystals were cooled to −173 °C and the data were recollected. Each crystal structure was refined in space group *Pna*2$_1$. Each crystal was a racemic twin with the enantiomorphs in an approximately 50:50 ratio. Details of the data collection and structure refinement 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 with the 632.8 nm exciting line of a He−Ne laser. The geometry for all the Raman experiments was 180° backscattering with a laser power of 25 mW.

Description of the Crystal Structure of [Ca(XeF$_2$)$_5$](PF$_6$)$_2$. The coordination sphere around the Ca atom consists of nine fluorine atoms of two PF$_6$ units and six XeF$_2$ molecules (Figure 1). Both PF$_6$ units are nonbridging; the octahedral P(1)F$_6$ unit is coordinated

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Table 2. Selected Bond Distances in $[M(XeF_2)_5](PF_6)_2$ (M = Ca, Cd)

$[Ca(XeF_2)_5](PF_6)_2$		$[Cd(XeF_2)_5](PF_6)_2$	
bond	dist (Å)	bond	dist (Å)
Ca1−F1	2.548(6)	Cd1−F1	2.590(7)
Ca1−F2	2.270(8)	Cd1−F2	2.220(6)
Ca1−F3	2.334(8)	Cd1−F3	2.254(6)
Ca1−F4	2.332(7)	Cd1−F4	2.262(6)
Ca1−F5	2.316(8)	Cd1−F5	2.216(5)
Ca1−F6	2.403(7)	Cd1−F6	2.473(8)
Ca1−F11	2.570(8)	Cd1−F11	2.412(7)
Ca1−F12	2.759(8)	Cd1−F12	3.144
Ca1−F21	2.363(7)	Cd1−F21	2.375(6)
Xe1−F1	1.999(6)	Xe1−F1	1.990(7)
Xe1−F6	2.016(6)	Xe1−F6	2.010(8)
Xe2−F2	2.037(8)	Xe2−F2	2.048(6)
Xe2−F7	1.965(8)	Xe2−F7	1.955(7)
Xe3−F3	2.026(7)	Xe3−F3	2.047(6)
Xe3−F8	1.963(7)	Xe3−F8	1.956(6)
Xe4−F4	2.059(6)	Xe4−F4	2.048(6)
Xe4−F9	1.961(7)	Xe4−F9	1.948(6)
Xe5−F5	2.037(8)	Xe5−F5	2.049(5)
Xe5−F10	1.945(9)	Xe5−F10	1.966(6)
P1−F11	1.627(7)	P1−F11	1.641(7)
P1−F12	1.618(8)	P1−F12	1.595(7)
P1−F13	1.585(8)	P1−F13	1.591(8)
P1−F14	1.564(7)	P1−F14	1.565(7)
P1−F15	1.604(7)	P1−F15	1.590(8)
P1−F16	1.581(8)	P1−F16	1.589(7)
P2−F21	1.640(9)	P2−F21	1.642(7)
P2−F22	1.589(8)	P2−F22	1.599(7)
P2−F23	1.556(8)	P2−F23	1.606(6)
P2−F24	1.593(9)	P2−F24	1.594(8)
P2−F25	1.612(8)	P2−F25	1.567(6)
P2−F26	1.588(9)	P2−F26	1.599(7)

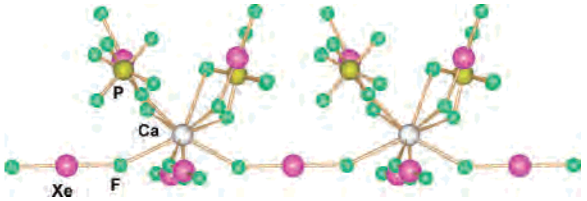

Figure 2. Chain along the *b*-axis in the structure of $[Ca(XeF_2)_5](PF_6)_2$.

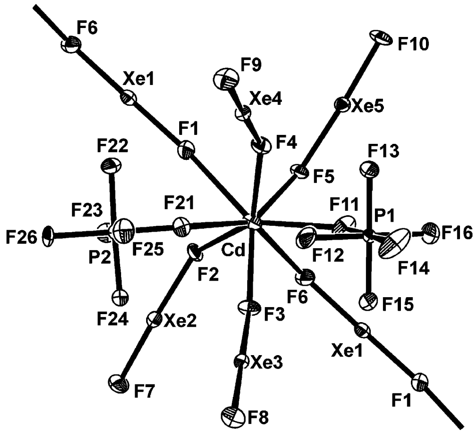

Figure 3. Coordination sphere of cadmium in $[Cd(XeF_2)_5](PF_6)_2$.

nearly edge on to Ca through two F atoms, while $P(2)F_6$ coordinates through only one F ligand. Selected bond distances are given in Table 2. The Ca−F21 interatomic distance for the $P(2)F_6$ unit is 2.363(7) Å. This is shorter than both bidentate $P(1)F_6$ distances: Ca−F11, 2.570(8) Å; Ca−F12, 2.759(8) Å. There are four nonbridging XeF_2 molecules, each linked to one Ca atom through one F ligand, with Ca−F(Xe) distances in the range 2.270(8)−2.334(8) Å. The two bridging XeF_2 molecules give rise to longer Ca−F(Xe) distances of 2.403(7) and 2.548(6) Å. Each Ca atom is connected to neighboring calcium atoms only through the two bridging $Xe(1)F_2$ molecules, forming infinite chains running parallel to the [010] axis (Figure 2). The extended structure consists of $[Ca(XeF_2)_5](PF_6)_2$ chains in which the orientation alternates along the [100] axis (Figure S1, Supporting Information). There are long-range electrostatic interactions between the positively charged Xe atoms and negatively charged F atoms from XeF_2 molecules and PF_6 units inside each chain and also between adjacent chains. The latter are responsible for keeping the chains together. As a result of these interactions and the steric activity of the electron lone pairs on xenon, the XeF_2 molecules have slightly deformed F−Xe−F angles (F1−Xe1−F6, 178.7(4)°; F7−Xe2−F2, 177.2(3)°; F8−Xe3−F3, 179.0(3)°; F9−Xe4−F4, 178.8(3)°; F10−Xe5−F5, 175.9(3)°). Inter- and intrachain electrostatic interactions, involving F interaction with Xe, range from 3.131 to 3.632 Å, while the sum of F and Xe van der Waals radii is 3.63 Å.[15]

Description of the Crystal Structure of $[Cd(XeF_2)_5](PF_6)_2$. The coordination sphere around the Cd atom consists of eight fluorine atoms of two PF_6 units and six XeF_2 molecules (Figure 3). Each of the crystallographically inequivalent PF_6 units is linked to Cd through one F ligand, with distances of Cd−F11, 2.412(7) Å, and Cd−F21, 2.375(6) Å. The four nonbridging XeF_2 molecules have Cd−F(Xe) distances in range 2.216(5)−2.262(6) Å, while the two bridging Cd−F(Xe) distances are 2.473(8) and 2.590(7) Å. Selected bond distances are given in Table 2. Each Cd atom is exclusively connected to neighboring Cd atoms by two bridging $Xe(1)F_2$ molecules, forming chains that run parallel to the [001] axis (Figure S2, Supporting Information). The chain, but not the M^{2+} coordination, has similarities to that of the calcium compound. The extended structure consists of $[Cd(XeF_2)_5](PF_6)_2$ infinite chains in which the orientation alternates along the [010] axis.

There are long-range electrostatic interactions between positively charged Xe atoms and negatively charged F atoms from XeF_2 molecules and PF_6 units within each chain and also between the chains. The latter are responsible for keeping the chains together. As a result of these interactions and the steric activity of the electron lone pairs on xenon, the XeF_2 molecules have slightly deformed F−Xe−F angles (F1−Xe1−F6, 178.8(3)°; F7−Xe2−F2, 177.0(3)°; F8−Xe3−F3, 179.0(3)°; F9−Xe4−F4, 178.5(3)°; F10−Xe5−F5, 176.1(3)°). Sterically reasonable electrostatic interactions range from 3.165 to 3.611 Å.

Results and Discussion

Synthesis. The best synthetic route for the preparation of the coordination compounds of the type $[M(XeF_2)_5](PF_6)_2$ (M = Ca, Cd) is by direct reaction between the corresponding binary fluoride, XeF_2, and gaseous PF_5 in aHF solvent. Because the solubility of PF_5 in aHF is poor,[16] a high pressure of PF_5 must be employed. $M(PF_6)_2$ is formed in situ and interacts with XeF_2, yielding $[M(XeF_2)_5](PF_6)_2$ on removal of the aHF. PF_5 is not a strong enough F^- acceptor to form stable $XeF^+PF_6^-$ salt at room temperature, as is the case for AsF_5.[17,18] The white solids, $[M(XeF_2)_5](PF_6)_2$ (M = Ca, Cd), slowly lose XeF_2 and PF_5 under dynamic vacuum at room

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temperature ultimately yielding only the corresponding binary metal fluoride. Therefore, to obtain the appropriate stoichiometry it is necessary to remove HF at −40 °C and to maintain the solids at low temperature. In the cases of the related metal hexafluoroarsenates or hexafluoroantimonates with the metal-coordinated XeF_2, this synthetic approach could not be used because formation of the rather stable and aHF soluble compounds $Xe_2F_3AF_6$ or $XeFAF_6$ (A = As, Sb)[19,20] resulted.

Crystal Structures. The unit cell volumes of these stoichiometrically and structurally related salts indicate that the effective volume of the Ca^{2+} ion must be about 4 $Å^3$ larger than that of the Cd^{2+} ion. This is in accord with the greater effective nuclear charge of the Cd^{2+} ion, as illustrated by the second ionization potentials of the atoms: Cd^{2+}, 16.91 eV; Ca^{2+}, 11.87 eV.[21] Thus, the greater F-ligand coordination of Cd^{2+} is readily understood.

Initial considerations lead to the expectations that if these F ligands all bore the same charge (the impact of their pendant groups is ignored), the F ligands would all be on a spherical surface, centered on the cation with the coordination sphere of the Ca^{2+} ion being larger than that of the Cd^{2+} ion. But if the charges on the F ligands are not equal, a ion distortion of the coordination shell is anticipated. Clearly, the most negatively charged F ligands will approach the cation more closely, and F⋯F interactions with the other, less charged F ligands will repel the latter so that they are further from the cation. From the data in Table 2, taken together with Figures 1 and 3, we note first that the closest F ligands to the M^{2+} are the four-rod shaped XeF_2 molecules that are linked through only one F ligand to one M^{2+}. In accord with the higher effective nuclear charge on the Cd^{2+} ion, the F 2−5 ligands are closer to Cd^{2+} than to Ca^{2+}, indeed on average 0.07 Å closer. The F ligands of these nonbridging XeF_2 molecules are being pulled away form their Xe atoms. Each of these XeF_2 molecules is on the ionization pathway: $F{-}Xe{-}F \rightarrow F{-}Xe^+ + F^-$.[22] The other F ligand approaches the Xe atom more closely (becoming more XeF^+ like) as the F atom approaching the M^{2+} cation moves away from the Xe atom. It should also be noted that the roughly tetrahedral positioning of the four nonbridging XeF_2 ligands tends to maximize the separation of the more positive XeF ends of the partially ionized molecules. Clearly, the F ligand approaching the M^{2+} must be more negatively charged than in the more symmetrical, bridging XeF_2 molecules. This has the effect of crowding out the bridging XeF_2 ligands. In molecular XeF_2, the effective F ligand negative charge has been reported to be approximately at −0.5 e.[23,24] Because the bridging XeF_2 F ligands are farther from the M^{2+} ion in both salts than any other ligands, it seems likely that the charges on other F ligands close to M^{2+}, provided both by the partially ionized nonbridging XeF_2 and the PF_6^-, exceed −0.5 e.

The close approach of the PF_6^- anions to the M^{2+} is a necessity of good lattice energy, but any loss of that energy caused by the slight displacement by the partially ionized nonbridging XeF_2 must be compensated for by the Coulomb energy derived from the higher charge of the more ionized F ligands of the nonbridging XeF_2.

In isostructural salts (e.g., those of smaller alkali metal cations[25]) the PF_6^- anion is smaller than the AsF_6^- anion. This could be a factor in causing the change in stoichiometry to $[M(XeF_2)_4](AsF_6)_2$ (M = Ca^{2+}, Cd^{2+}),[3,5] when the latter anion is substituted for the former. However, the fluoroarsenate anion is a significantly weaker F^- donor than the fluorophosphate anion,[26] the gaseous ionization energies for the processes $EF_6^- \rightarrow EF_5 + F^-$ being 4.08 (E = P) and 4.42 eV (E = As). This must be a consequence of greater effective nuclear charge at the As center than at the P atom. It is therefore to be expected that the F ligands of the AsF_6^- will bear less charge than those in the PF_6^- anion. The structural details of the AsF_6^- salts,[3,5] when compared with those of the PF_6^- salts from this study, support this view. The calcium salts provide two AsF_6^- complexes for the comparison, one with 4 XeF_2 molecules/Ca^{2+} and the other with 2.5 XeF_2 molecules/Ca^{2+}.

In the $[Ca(XeF_2)_{2.5}](AsF_6)_2$ salt, the Ca^{2+} coordination by F ligands is rather like that in the $[Ca(XeF_2)_5](PF_6)_2$ salt, with eight F ligands at less than 2.6 Å from the Ca^{2+} ion and an additional F at about 2.8 Å. The Ca^{2+} F-ligand coordination in the $[Ca(XeF_2)_4](AsF_6)_2$ salt is eight with all Ca−F distances being less than or equal to 2.4 Å. In all of these structures there are bridging XeF_2 molecules coordinated to two Ca^{2+}, and two EF_6^- anions each coordinated to one Ca^{2+}. The closely packed 8-fold Ca⋯F coordination sphere is somewhat more regular in the AsF_6^- salt than in the PF_6^- salt (see ref 27). The striking difference, when compared with the $[Ca(XeF_2)_5](PF_6)_2$ structure, concerns the Ca−F distances of the bridging XeF_2 molecules (see ref 28). Overall, there is a closer approach of the bridging XeF_2 to the Ca^{2+} in the AsF_6^- salt than in the PF_6^- salt. This is consistent with the AsF_6^- ligands being less strongly attracted to Ca^{2+}, relative to XeF_2. This contrasts with the situation

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(27) In $[Ca(XeF_2)_4](AsF_6)_2$, Ca−F distances range from 2.27 to 2.40 Å, and in $[Ca(XeF_2)_{2.5}](AsF_6)_2$, they range from 2.33 to 2.44 Å. In the phosphorus salt the eight close Ca−F distances are 2.27, 2.32, 2.33 twice, 2.36, 2.40, 2.55, and 2.57 Å.

(28) In $[Ca(XeF_2)_5](PF_6)_2$ (Figure 1, Table 2), CaF6 = 2.40 and CaF1 = 2.55 Å, whereas, in $[Ca(XeF_2)_4](AsF_6)_2$, the Ca−F distances for the four bridging XeF_2 ligands are 2.27, 2.36 twice, and 2.39 Å. In $[Ca(XeF_2)_{2.5}](AsF_6)_2$ (in which all XeF_2 groups are each bridging two Ca^{2+}) the bridging XeF_2 Ca−F distances are 2.36, 2.42 twice, 2.44, and 2.46 Å.

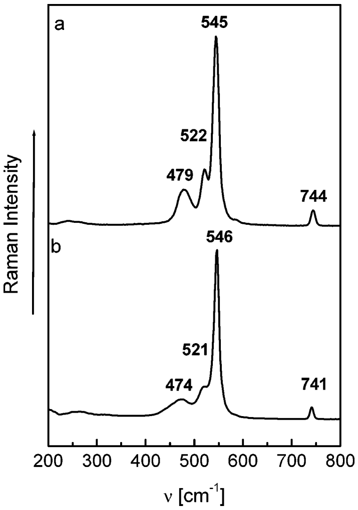

Figure 4. Raman spectra of $[M(XeF_2)_5](PF_6)_2$: (a) M = Ca; (b) M = Cd.

in the PF_6^- salts where the anion, as well as the nonbridging XeF_2, are tending to push (by F···F repulsion) the bridging XeF_2 ligands out of the Ca^{2+} coordination sphere.

Because even bridging XeF_2 F ligands can compete in charge with the F ligands of the AsF_6^- anion and are associated with a less bulky species, the Ca^{2+} ion in the AsF_6^- salt can have more bridging XeF_2 ligands than in the PF_6^- salt. (In the latter, as we have seen, it is only the partially ionized, nonbridging XeF_2 ligands that more closely approach Ca^{2+} than the F ligands of the PF_6^-.) Thus, a lower XeF_2 content can satisfy the cation coordination requirements in the arsenic salt, as observed.

In the case of the arsenic Cd^{2+} salt, the smaller cation size diminishes the coordination number, as we have already seen in the case of the PF_6^- salt. The lower charge on the AsF_6^- anion F ligands means that the bridging XeF_2 can crowd in as close or, in the case of the nonbridging XeF_2, even closer to the Cd^{2+} than in the PF_6^- case. Again, this can result in a diminished XeF_2 content, as observed. That the $[Ca(XeF_2)_4](AsF_6)_2$ salt is a two-dimensional XeF_2-bridged system (with four bridging XeF_2 about each cation) whereas the $[Cd(XeF_2)_4](AsF_6)_2$ salt is a chain polymer with two bridging XeF_2/Cd^{2+} is in accord with these considerations.

Raman Spectroscopy. The Raman spectra (Figure 4) for the calcium and cadmium salts are in accord with the structures. The high polarizability of xenon usually results in intense Raman bands for the symmetric Xe−F stretching modes. Raman P−F vibrations are usually far less intense because of the lower polarizabilities of these small atoms. The symmetric (ν_1) stretching mode for solid XeF_2 is close to 497 cm^{-1}.[29] In partially ionized XeF_2 the band at 497 cm^{-1} is replaced by two bands: ν(Xe−F) at the higher frequency and ν(Xe···F) at the lower frequency. In the case of the present compounds, the peaks at 545 (Ca) and 546 cm^{-1} (Cd) can be assigned to ν(Xe−F) of the nonbridging XeF_2 molecules, while the peaks at 522 (Ca) and 521 cm^{-1} (Cd) are assigned to the ν(Xe−F) of the bridging XeF_2 molecules. These values are in accord with findings for the XeF_2 complexes with XeF_5^+ salts.[22,30] The somewhat broader bands at 479 (Ca) and 474 cm^{-1} (Cd) can be confidently assigned to ν(Xe····F) of the XeF_2, all of which exhibit some distortion. Because ν_1 of O_h PF_6^- occurs at 756 cm^{-1},[31] the bands at 744 (Ca) and 741 cm^{-1} (Cd) can be confidently assigned to the symmetric stretching mode of the anion. The symmetry of PF_6^- is no longer O_h, and more Raman bands are expected. Symmetric stretching vibration of PF_6^- (ν_1) is very weak in comparison to Xe−F stretching vibrations; therefore, the other bands of PF_6^- were not observed.

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Supporting Information Available: An X-ray crystallographic file in CIF format, tables of Xe−F interactions in the structures of $[M(XeF_2)_5](PF_6)_2$ (M = Ca, Cd), and figures of packing in the structure of $[Ca(XeF_2)_5](PF_6)_2$ (Figure S1) and the chain in the structure of $[Cd(XeF_2)_5](PF_6)_2$ (Figure S2). This material is available free of charge via the Internet at http://pubs.asc.org.

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