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New Coordination Compounds of $Cd(AsF_6)_2$ with HF and XeF_2

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Two new coordination compounds of cadmium with HF and XeF_2 as ligands have been synthesized. Solid white $[Cd(HF)](AsF_6)_2$ is obtained from an anhydrous HF (aHF) solution of $Cd(AsF_6)_2$. It crystallizes in a monoclinic $P2_1/c$ space group with $a = 9.4687(14)$ Å, $b = 9.2724(11)$ Å, $c = 10.5503(18)$ Å, $\beta = 104.887(7)°$, and $Z = 4$. The coordination sphere of Cd consists of 7 + 2 fluorine atoms, which are in a capped trigonal-prismatic arrangement. The reaction between $Cd(AsF_6)_2$ and XeF_2 in aHF yields a solid white product at room temperature having the composition $[Cd(XeF_2)_4](AsF_6)_2$ after the excess XeF_2 and solvent have been removed under dynamic vacuum. $[Cd(XeF_2)_4](AsF_6)_2$ crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 8.6482(6)$ Å, $b = 13.5555(11)$ Å, $c = 16.6312(14)$ Å, and $Z = 4$. The coordination sphere of Cd consists of eight fluorine atoms, which are at the corners of a trigonal prism with two capped side faces.

Introduction

One of the interesting subjects of research in fluorine chemistry is the synthesis of coordination compounds of various metal cations with weakly coordinating anions (AsF_6^-, SbF_6^-, BiF_6^-,...) and different ligands. With the right choice of metal cation, anion, and solvent, coordination compounds can be obtained in which even weaker ligands and solvents are coordinated to the metal ion. The first coordination compound to be made with HF bonded to the metal ion was $[La(HF)_2](AsF_6)_3$.[1] Similar compounds with HF as the ligand are $[Pb(HF)](AsF_6)_2$,[2] $[Ca(HF)](AsF_6)_2$,[3] $[Ca(HF)_2](SbF_6)_2$,[4] $[Mg(HF)_2](SbF_6)_2$,[4] $([OsO_3F)(HF)_2]$-$(AsF_6))_2$,[5] $[(OsO_3F)(HF)](SbF_6)$,[5] and $[Au(HF)_2](SbF_6)_2\cdot 2HF$.[6]

Xenon difluoride bonded directly to a metal ion was first observed in $[Ag(XeF_2)_2]AsF_6$.[7] This compound is not stable under a dynamic vacuum at room temperature and slowly loses XeF_2, yielding $AgAsF_6$ as a final product. A whole series of new compounds of the type $[M^x(XeF_2)_n](AF_6)_x$ (M is a metal in the oxidation state $+x$, $x = 2, 3$; A = As, Sb, Bi), stable at room temperature, were isolated recently, and the majority of their crystal structures were determined: $[Ln(XeF_2)_3](AF_6)_3$ (Ln = La, Nd, Sm, Eu, Gd; A = As, Bi),[3] $[Nd(XeF_2)_{2.5}](AsF_6)_3$,[8] $[Pb(XeF_2)_3](AsF_6)_2$, $[Sr(XeF_2)_3](AsF_6)_2$,[9] $[Ca(XeF_2)_n](AsF_6)_2$ ($n = 2.5, 4$),[10] and $[Ba(XeF_2)_5](SbF_6)_2$.[11]

The syntheses, crystal structures, and vibrational spectra of $[Cd(XeF_2)_4](AsF_6)_2$ and $[Cd(HF)](AsF_6)_2$ are described in the present paper.

Experimental Section

General Experimental Procedures. A Teflon and nickel vacuum line and system were used as described previously.[12] 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 tetrafluoroethylene-hexafluoropropylene copolymer (FEP) and equipped with Teflon valves and Teflon-coated stirring bars

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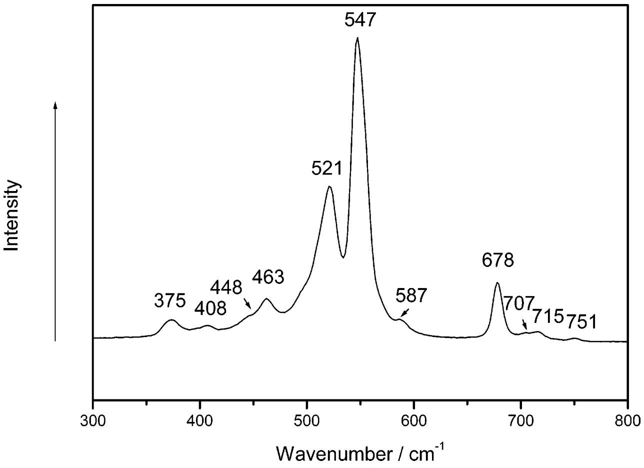

Figure 1. Raman spectrum of $[Cd(XeF_2)_4](AsF_6)_2$.

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 tube and a smaller 4 mm i.d. FEP 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 anhydrous HF (aHF) as a solvent at 298 K. Fluorine was partially condensed three times at a pressure of 700 kPa from a vessel of known volume into a reaction vessel cooled in liquid nitrogen. Cadmium difluoride was characterized by the X-ray powder diffraction pattern and by chemical analyses (Calcd: Cd, 74.7; F, 25.3. Found: Cd, 74.6; F, 25.2). aHF (Fluka, purum) was treated with K_2NiF_6 (Ozark-Mahoning, 99%) for several days prior to use. Arsenic pentafluoride was prepared by high-pressure fluorination of As_2O_3, using the procedure described for PF_5.[13] Xenon difluoride was prepared by the photochemical reaction between Xe and F_2 at room temperature.[14] (Caution: aHF and AsF_5 must be handled in a well-ventilated hood, and protective clothing must be worn at all times.)

Synthesis of $Cd(AsF_6)_2$. $Cd(AsF_6)_2$ was prepared from CdF_2 (0.518 g, 3.44 mmol) and AsF_5 (1.341 g, 7.89 mmol) in an aHF solvent as previously described.[15] The product was dried under dynamic vacuum for 3 days to remove all traces of aHF and characterized by the X-ray powder diffraction pattern and chemical analysis (Calcd for $Cd(AsF_6)_2$: Cd, 22.9; As, 30.6; F_{total}, 46.5; F_{free}^-, 0; AsF_6^-, 77.1. Found: Cd, 22.7; As, 31.4; F_{total}^-, 46.3; F_{free}^-, 0.5; AsF_6^-, 77.0).

Synthesis of $[Cd(HF)](AsF_6)_2$. All attempts to synthesize this compound in bulk were unsuccessful. $[Cd(HF)](AsF_6)_2$ is not stable under dynamic vacuum even at −20 °C, losing HF to get $Cd(AsF_6)_2$ as the final product.

Synthesis of $[Cd(XeF_2)_4](AsF_6)_2$. $Cd(AsF_6)_2$ (1.032 g, 2.11 mmol) was dissolved in aHF. Xenon difluoride (2.387 g, 14.10 mmol) was sublimated into the reaction vessel at −196 °C followed by warming of the reaction vessel to room temperature. The product of the reaction was not completely dissolved in aHF. The excess of XeF_2 and aHF were pumped off at room temperature for 6 h, yielding a white product (1.4131 g) with a mole ratio of 1:3.97 Cd/XeF_2. The compound was characterized by Raman spectroscopy (Figure 1), chemical analyses (Calcd for $[Cd(XeF_2)_4](AsF_6)_2$: Cd, 9.6; As, 12.8; AsF_6^-, 32.4; F_{total}, 32.6; F_{free}, 13.0. Found: Cd, 9.6; As, 13.0; AsF_6^-, 32.4; F_{total}, 32.0; F_{free}, 13.0), and X-ray powder diffraction pattern.

The reaction was subsequently repeated with all of the reagents added in stoichiometric amounts [$Cd(AsF_6)_2$ (0.340 g, 0.694 mmol); XeF_2 (0.471 g, 2.78 mmol); mole ratio of 1:4 Cd/Xe]. The Raman and IR spectra and X-ray powder diffraction pattern of the product were identical to those obtained in the experiment described above.

Preparation of Single Crystals of $[Cd(HF)](AsF_6)_2$. $Cd(AsF_6)_2$ (0.250 g) was placed in the wider tube of a crystallization vessel and dissolved in aHF. This solution was decanted into the narrower part of the T-shaped crystallization vessel. The crystals were grown with a temperature gradient of 28 °C, isolated from the mother liquid, and immersed in perfluorinated oil (ABCR, FO5960) in a drybox. A suitable crystal was selected under the microscope and transferred into the cold nitrogen stream of the X-ray diffractometer.

Preparation of Single Crystals of $[Cd(XeF_2)_4](AsF_6)_2$. Approximately 0.3 g of $[Cd(XeF_2)_4](AsF_6)_2$ was placed in the wider part of a crystallization vessel and dissolved in aHF. The remainder of the procedure was the same as that described above.

Elemental Analysis. The total fluoride content (F_{total}^-) was determined after complete decomposition of the sample by fusion with $KNaCO_3$.[16,17] The content of free fluoride (F_{free}^-) was determined in an aqueous solution of the sample after hydrolysis.[18] Both fluoride contents were determined by direct potentiometry using a fluoride ion selective electrode.[16] Total arsenic was determined potentiometrically by titration with $Na_2S_2O_3$[19] after prior fusion of the sample with $KNaCO_3$. The content of AsF_6^- was determined gravimetrically by precipitation with tetraphenylarsonium chloride,[20] and the cadmium content was determined by complexometric titration with EDTA.[21]

X-ray Powder Diffraction Patterns. Diffraction data of the samples were taken in sealed quartz capillaries on a 143 mm 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 −73 °C using a Mercury CCD area detector coupled with a Rigaku AFC7 diffractometer with graphite-monochromatized 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.[22] Structures were solved by direct methods[23] and expanded using Fourier techniques. Full-matrix least-squares refinement of F^2 against all reflections was performed using the SHELX97 program.[24] More details on the data collection and structure determination are given in Table 1.

Raman Spectroscopy. Raman spectra of the powdered samples in sealed quartz capillaries were recorded on a Renishaw Raman

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Table 1. Crystal Data and Structure Refinement for $[Cd(XeF_2)_4](AsF_6)_2$ and $[Cd(HF)](AsF_6)_2$[a]

	$[Cd(XeF_2)_4](AsF_6)_2$	$[Cd(HF)](AsF_6)_2$
a (Å)	8.6482(6)	9.4687(14)
b (Å)	13.5555(11)	9.2724(11)
c (Å)	16.6312(14)	10.5503(18)
β (deg)	90	104.887(7)
V (Å)	1949.7(3)	895.2(2)
Z	4	4
formula weight	1167.4	510.2
space group	$P2_12_12_1$	$P2_1/c$
T (°C)	−73(1)	−73(1)
λ (Å)	0.710 69	0.710 69
D_{calcd} (g/cm^3)	3.977	3.786
μ (mm^{-1})	11.491	9.960
R1	0.037	0.050
wR2	0.076	0.127

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

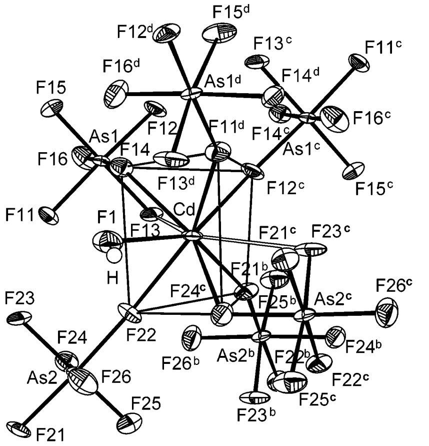

Figure 2. Coordination sphere of Cd in the structure of $[Cd(HF)](AsF_6)_2$.

Imaging Microscope System 1000 by use of the 632.8 nm exciting line of a He−Ne laser. The geometry for all of the Raman experiments was 180° backscattering with a laser power of 25 mW.

Results

Description of the Crystal Structure of $[Cd(HF)](AsF_6)_2$. The cadmium cation is surrounded by six bulky AsF_6 units and one HF molecule (Figure 2). The AsF_6 units interact with cadmium via six fluorine atoms arranged at the apexes of distorted trigonal prisms, with the Cd−F(As) distances in the range of 2.263−2.326 Å. The HF molecule caps a trigonal-prismatic face at a distance of 2.376(5) Å. Additionally, the AsF_6 units interact with cadmium at slightly longer distances, Cd−F23(As2) = 2.681(4) Å and Cd−F13(As1) = 2.921(4) Å. The sum of the respective van der Waals radii[25] is 3.05 Å. The cadmium cation is thus located in an environment of nine fluorine atoms, forming a distorted, tricapped trigonal prism. Two longer Cd−F contacts that bring the edges of the AsF_6 units into the coordination sphere of cadmium are considered as being mainly electrostatic.

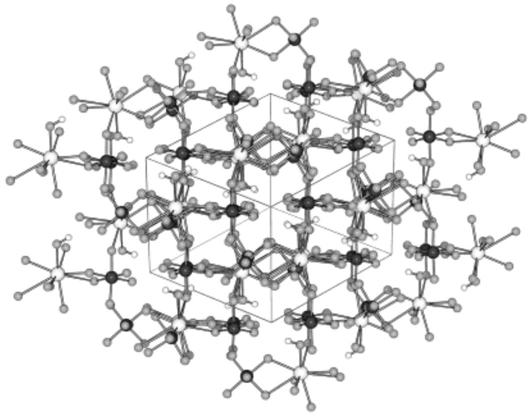

Figure 3. Connected ladders in the $[Cd(HF)](AsF_6)_2$ structure, viewed along the [1, 1, 1] direction.

Table 2. Selected Bond Lengths and Angles in $[Cd(HF)](AsF_6)_2$[a]

bond	distance (Å)	angle	degrees
Cd1−F1	2.376(5)	F11^b−Cd1−F12^c	74.3(1)
Cd1−F11^b	2.299(3)	F11^b−Cd1−F1	78.2(1)
Cd1−F12^c	2.326(3)	F12−Cd1−F1	145.3(1)
Cd1−F13	2.921(4)	F13−Cd1−F1	114.0(1)
Cd1−F14	2.263(3)	F14−Cd1−F1	74.7(1)
Cd1−F21^d	2.285(3)	F14−Cd1−F11^b	81.1(1)
Cd1−F22	2.309(3)	F14−Cd1−F12^c	80.4(1)
Cd1−F23^c	2.681(4)	F14−Cd1−F22	89.1(1)
Cd1−F24^c	2.287(4)	F21^d−Cd1−F1	142.9(1)
As1−F11	1.752(3)	F21^d−Cd1−F12^c	71.5(2)
As1−F12	1.742(3)	F21^d−Cd1−F22	72.9(1)
As1−F13	1.717(3)	F21^d−Cd1−F24^c	83.2(1)
As1−F14	1.760(3)	F22−Cd1−F1	74.9(1)
As1−F15	1.689(4)	F23^c−Cd1−F1	115.7(1)
As1−F16	1.681(4)	F24^c−Cd1−F1	73.8(1)
As2−F21	1.749(3)	F24^c−Cd1−F11^b	94.4(1)
As2−F22	1.755(3)	F24^c−Cd1−F22	80.8(1)
As2−F23	1.719(3)	As1^b−F11^b−Cd1	146.9(2)
As2−F24	1.764(4)	As1−F14−Cd1	124.8(2)
As2−F25	1.665(4)	As2−F22−Cd1	155.2(2)
As2−F26	1.689(4)	As2^c−F24^c−Cd1	117.0(2)

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

There are two crystallographically different AsF_6 units in the structure, but both bridge cadmium cations in a similar manner. The two Cd atoms are connected by *fac*-F ligands from two $As1F_6$/$As2F_6$ units, thus forming a square ring of 10 atoms. The square rings $[Cd_2(As1F_6)_2]^{2+}$/$[Cd_2(As2F_6)_2]^{2+}$ are alternately connected by *trans* bridges of $As1F_6$ and $As2F_6$ units, forming zigzag ladders running in the [1, 1, 1] direction (Figure 3). Each Cd atom from the [1, 1, 1] ladder is part of an identical ladder running in the [−1, −1, −1] direction. Cadmium atoms connect both types of ladders in a 3D network, where channels are formed along the a axis. Space in the channels is occupied by HF molecules coordinated through fluorine directly to Cd atoms. According to the position of the hydrogen atoms found in the Fourier difference map, the HF molecule alternately forms a hydrogen bond to the F26 atoms from the neighboring ladder running in the opposite direction and in addition joins the ladders.

Selected bond distances and angles are given in Table 2.

Description of the Crystal Structure of $[Cd(XeF_2)_4](AsF_6)_2$. The coordination sphere around cadmium consists of eight fluorine atoms forming a trigonal prism with two capped side faces. The fluorine atoms of one trigonal face are contributed by the monodentate $As2F_6$ unit, the nonbridging $Xe4F_2$ molecule, and the bridging $Xe1F_2$ molecule, while those of the other trigonal face are from the nonbridg-

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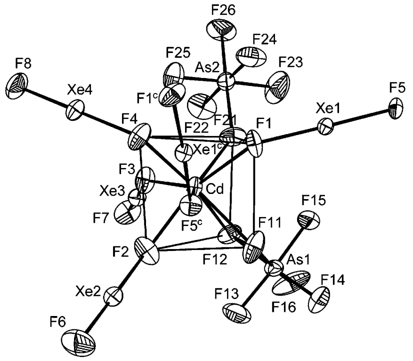

Figure 4. Coordination sphere of Cd in the structure of $[Cd(XeF_2)_4](AsF_6)_2$.

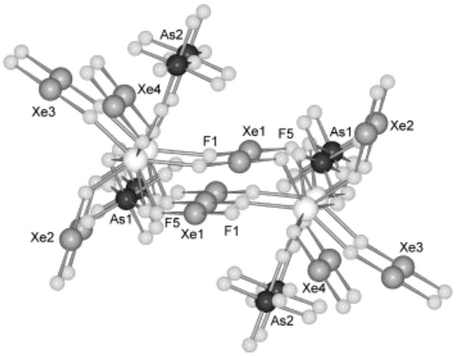

Figure 5. Chain of molecules in the structure of $[Cd(XeF_2)_4](AsF_6)_2$.

Table 3. Selected Bond Lengths and Angles in $[Cd(XeF_2)_4](AsF_6)_2$[a]

bond	distance (Å)	angle	degrees
Xe1−F1	2.017(5)	F5−Xe1−F1	177.3(2)
Xe1−F5	1.995(5)	F6−Xe2−F2	179.2(4)
Xe2−F2	2.045(6)	F7−Xe3−F3	177.7(3)
Xe2−F6	1.952(8)	F8−Xe4−F4	179.9(3)
Xe3−F3	2.043(6)	F1−Cd1−F11	75.4(2)
Xe3−F7	1.968(6)	F1−Cd1−F12	110.3(2)
Xe4−F4	2.079(6)	F2−Cd1−F1	140.3(2)
Xe4−F8	1.953(6)	F2−Cd1−F3	76.6(2)
Cd1−F1	2.328(6)	F2−Cd1−F5[b]	74.0(2)
Cd1−F2	2.220(6)	F2−Cd1−F11	80.4(3)
Cd1−F3	2.271(6)	F2−Cd1−F12	82.6(2)
Cd1−F4	2.211(6)	F2−Cd1−F21	148.5(2)
Cd1−F5[b]	2.426(5)	F3−Cd1−F1	141.9(2)
Cd1−F11	2.399(6)	F3−Cd1−F5[b]	138.1(2)
Cd1−F12	2.418(6)	F3−Cd1−F11	133.2(2)
Cd1−F21	2.309(6)	F3−Cd1−F12	77.4(2)
As1−F11	1.750(6)	F3−Cd1−F21	77.7(2)
As1−F12	1.762(6)	F4−Cd1−F1	87.9(2)
As1−F13	1.675(7)	F4−Cd1−F2	93.1(3)
As1−F14	1.711(6)	F4−Cd1−F3	79.0(2)
As1−F15	1.699(7)	F4−Cd1−F5[b]	73.5(2)
As1−F16	1.689(7)	F4−Cd1−F11	142.8(2)
As2−F21	1.774(6)	F4−Cd1−F12	156.4(2)
As2−F22	1.712(7)	F4−Cd1−F21	99.6(2)
As2−F23	1.685(8)	F11−Cd1−F12	59.5(2)
As2−F24	1.720(7)	F21−Cd1−F1	69.4(2)
As2−F25	1.690(7)	F21−Cd1−F11	104.9(2)
As2−F26	1.694(6)	F21−Cd1−F12	74.3(2)

[a] Symmetry operations used for the generation of equivalent atoms. [b] $x + ^1/_2, -y + ^1/_2, -z$.

ing $Xe2F_2$ molecule and the edge-sharing bidentate $As1F_6$ unit. The cadmium coordination prism is additionally capped by the nonbridging $Xe3F_2$ molecule and by the symmetry-generated bridging $Xe1F_2$ molecule, both placed at the square faces opposite to the edge shared by the $As1F_6$ unit (Figure 4). Thus, each Cd atom is only connected to the neighboring cadmium atoms via two bridging $Xe1F_2$, forming a spiral chain running along the *a* axis (Figure 5). There are long-range electrostatic interactions between positively charged Xe atoms and negatively charged F atoms from XeF_2 and AsF_6 units inside each chain and also between the chains. The latter are responsible for keeping the chains together. The consequences of these interactions and of the steric activity of the electron lone pairs at the XeF_2 molecules are the slightly deformed angles F7−Xe3−F3 = 177.7° and F1−Xe1−F5 = 177.3°. Sterically reasonable electrostatic contacts range from 3.143 to 3.639 Å (see the Supporting Information).

The Cd−F(Xe) distances range from 2.211 to 2.271 Å for nonbridging XeF_2 molecules, shorter than the Cd−F distance in the structure of CdF_2 (2.333 Å[26]) and in the bridging XeF_2 molecules (2.328(6) and 2.426(5) Å). The Cd−F(As) distances range from 2.309 to 2.418 Å.

Selected bond distances and angles are given in Table 3.

Discussion

Syntheses. Metal salts containing the large anions AF_6^-, where A is As, Sb, or Bi, have rather low lattice energies. These anions are also poor Lewis bases, so that even poor Lewis base solvents, such as aHF, can supply enough solvation energy to dissolve $M^x(AF_6)_x$ salts. $Cd(AsF_6)_2$ readily dissolves in aHF, forming $[Cd(HF)_y]^{2+}$ cations and AsF_6^- anions. During the process of crystallization from a saturated aHF solution, crystals of the compound $[Cd(HF)](AsF_6)_2$ were obtained. They could be separated from the solvent by rapid removal of the solvent under dynamic vacuum at 20 °C. The material in noncrystalline form is unstable under dynamic vacuum, even at −20 °C. The final product was always only pure $Cd(AsF_6)_2$, which was used for the reaction with XeF_2 (eq 1).

$$Cd(AsF_6)_2 + nXeF_2 \xrightarrow[\text{aHF}]{\text{298 K}} [Cd(XeF_2)_4](AsF_6)_2 + (n-4)XeF_2 \qquad n \geq 4 \quad (1)$$

Addition of XeF_2 to a solution of $Cd(AsF_6)_2$ in aHF replaces the latter with the stronger Lewis base, XeF_2, to yield $[Cd(XeF_2)_4](AsF_6)_2$. On the other hand, Cd^{2+} is not a sufficiently strong Lewis acid to withdraw F^- from XeF_2 to give CdF_2 and $Xe_2F_3^+AsF_6^-$.

The compound $[Cd(XeF_2)_4](AsF_6)_2$ is a white solid having a negligible vapor pressure at room temperature and does not release significant quantities of XeF_2 during prolonged pumping at room temperature.

Crystal Structures. Although the 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), the structures of their analogous coordination compounds are not always the same. $[Cd(HF)](AsF_6)_2$ and $[Ca(HF)](AsF_6)_2$[3] are isostructural, while the structures of $[Cd(XeF_2)_4](AsF_6)_2$ and $[Ca(XeF_2)_4](AsF_6)_2$[10] differ. This implies that the XeF_2 molecule, as a ligand

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coordinated to a metal cation, is more affected by the cation properties than the HF molecule.

The XeF_2 molecule can bridge two metal cations, thus effectively substituting the AsF_6 units in forming the crystal network. In the structure of $[Cd(XeF_2)_4](AsF_6)_2$, the Cd^{2+} ions are surrounded by one monodentate AsF_6 unit, one bidentate AsF_6 unit, three nonbridging XeF_2 molecules, and only two bridging XeF_2 molecules, to yield the chain-structure arrangement. In the structure of $[Ca(XeF_2)_4](AsF_6)_2$,[10] the Ca^{2+} ions are surrounded by two nonbridging XeF_2 molecules, two monodentate AsF_6 units, and four bridging XeF_2 molecules, resulting in a layer-structure arrangement. In accordance with the much higher electron affinity of Cd^{2+} (16.91 eV[27]) than that of Ca^{2+} (11.87 eV[27]), a higher charge transfer from the XeF_2 molecule to the metal ion, and therefore a higher degree of covalency in the M−F bond, is expected in the case of the Cd compound. This makes bridging interactions in the cadmium structure less favorable, resulting in the chain arrangement of the crystal packing. Although the bridging XeF_2 molecules in the cadmium and calcium compounds are not readily distinguishable, they lie in different electric fields, as is evident from their Raman stretching frequencies (Ca, 533 cm^{-1}; Cd, 521 cm^{-1}; Table 4). The difference can be attributed to the lower positive charge at the Cd^{2+} cations. The average M−F(Xe) distance for the calcium compound is 2.346(11) Å, and that for the cadmium compound is 2.377(6) Å.

$[Cd(XeF_2)_4](AsF_6)_2$ and $[Ca(XeF_2)_4](AsF_6)_2$ are the only known compounds in which metal cations are only bridged by XeF_2 molecules.

The HF molecule is a monodentate ligand and is therefore less effective in influencing crystal packing because of the charge transfer from the ligand to the metal ion as an XeF_2 molecule. Thus, $[Cd(HF)](AsF_6)_2$ and $[Ca(HF)](AsF_6)_2$ are isostructural. The structures are stabilized mostly by similar interactions between the metal cations, small HF molecules, and bulky AsF_6 units.

In the structure $[Cd(HF)](AsF_6)_2$, all of the Cd−F distances to the fluorines at the apexes of the coordination prism are shorter than those in the structure of CdF_2 (Cd−F = 2.333 Å[26]), indicating that the Cd^{2+} cations in $[Cd(HF)](AsF_6)_2$ bear a larger positive charge than those in the structure of CdF_2. This is a consequence of the weaker electron donor capabilities of fluorine atoms in the Cd−F−As bridges compared with those in the Cd−F−Cd bridges in the structure of CdF_2.

Because Cd has a higher electron affinity than Ca, the M−F bond is expected to be less ionic in the Cd compound. It should be mentioned that, in the $[Cd(HF)](AsF_6)_2$ compound, fluorine atoms from the AsF_6 units capping the side faces of the basic trigonal-prismatic polyhedra are at longer distances from the metal (Cd−F13 and Cd−F23 are 2.921(4) and 2.681(4) Å, respectively) than those in the Ca compound (2.773 and 2.679 Å[28]), although the other Cd−F(As) distances are shorter (average 2.295 Å) than those in Ca−F(As) (average 2.376 Å). This indicates that Cd^{2+} cations bear a lower positive charge than Ca^{2+} cations, which is probably a consequence of the higher covalency of the Cd−F bonds, which compensates for the lower Coulombic contribution to the lattice energy of the cadmium compound. Additionally, the narrower range of the M−F(As) distances in the calcium compound when compared with the cadmium compound shows a lower tendency toward multidentate and bridging AsF_6 moieties in the cadmium compound, as already discussed in the case of the compounds with XeF_2 as a ligand.

Table 4. Frequencies and Intensities of the $[Cd(XeF_2)_4](AsF_6)_2$ Raman Spectra

wavenumber (cm^{-1})	intensity		wavenumber (cm^{-1})	intensity	
751	0.1	ν(As−F)	521	5.1	$\nu(XeF_2)$
715	0.3	ν(As−F)	463	1.4	ν(Xe···F)
707	0.3	ν(As−F)	448	0.9	ν(Xe···F)
678	1.9	ν(As−F)	408	0.6	ν(As−F)
587	0.7	ν(As−F)	375	0.7	ν(As−F)
547	10	ν(Xe−F)			

Vibrational Spectra. The high polarizability of xenon usually results in intense Raman bands for the symmetric Xe−F stretching modes. Ordinarily, As−F and Cd−F vibrations are far less intense and are broad in their Raman spectra. The intense Raman band of the compound $[Cd(XeF_2)_4](AsF_6)_2$ at 521 and 547 cm^{-1} (Figure 1 and Table 4) can be confidently assigned to the symmetric XeF_2 stretching modes. The totally symmetric (ν_1) stretching mode for XeF_2 is close to 497 cm^{-1}.[29] By donating one of its F ligands, XeF_2 becomes distorted, and the band at 497 cm^{-1} is replaced by two bands. The band at the higher frequency is labeled as the shorter bond Xe−F stretch [ν(Xe−F)] and that at the lower frequency as the Xe−F stretch of the longer bond [ν(Xe···F)]. 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}.[30] In the case of the present compound, the peaks at 547 and 448 cm^{-1} can be assigned to the terminal XeF_2 molecules, while the peak at 521 cm^{-1} is assigned to the Xe−F stretching mode of the bridging XeF_2 molecules. The symmetric stretching mode of the bridging XeF_2 might have been expected at ~497 cm^{-1}. Because bridging XeF_2 molecules in the moiety Cd···F−Xe−F···Cd are anchored between two Cd^{2+} ions, a higher energy is required for the symmetric stretching mode, which results in an increase in the stretching frequency. The band at 463 cm^{-1} is most probably arisen from the vibrational coupling of the nonbridging XeF_2 vibrations. This band was also observed in other $[M^{x+}(XeF_2)_n](AsF_6)_x$ (M = Nd,[8] Ca[10]) coordination compounds.

The AsF_6^- octahedra in the compound are deformed. The ν_1 mode of AsF_6 is at 678 cm^{-1} (ν_1 of O_h AsF_6^- is at 689 cm^{-1}).[31] The O_h symmetry of AsF_6^- is reduced to the lower symmetry resulting in more Raman-active modes.[32−34]

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Supporting Information Available: An X-ray crystallographic file in CIF format, atomic coordinates and equivalent displacement parameters U_{eq} of $[Cd(XeF_2)_4](AsF_6)_2$ and $[Cd(HF)](AsF_6)_2$, a figure illustrating the $[Cd(HF)](AsF_6)_2$ basic building unit, a figure showing the $[Cd(XeF_2)_4](AsF_6)_2$ packing, and a table of the Xe−F interactions in the $[Cd(XeF_2)_4](AsF_6)_2$ structure. This information is available free of charge via the Internet at http://pubs.asc.org.

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