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$[Mg(XeF_2)_n](AsF_6)_2$ ($n = 4, 2$): First Compounds of Magnesium with XeF_2

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The reaction between $Mg(AsF_6)_2$ and XeF_2 in anhydrous HF (aHF) at room temperature yields two compounds with XeF_2 bonded directly to the Mg^{2+} cation: $[Mg(XeF_2)_4](AsF_6)_2$; $[Mg(XeF_2)_2](AsF_6)_2$. The 1:4 compound is obtained with excess XeF_2 while the 1:2 compound is prepared from stoichiometric amounts of $Mg(AsF_6)_2$ and XeF_2. $[Mg(XeF_2)_4](AsF_6)_2$ crystallizes in an orthorhombic crystal system, space group $P2_12_12_1$, with $a = 8.698(15)$ Å, $b = 14.517(15)$ Å, $c = 15.344(16)$ Å, $V = 1937(4)$ Å^3, and $Z = 4$. The octahedral coordination sphere of Mg consists of one fluorine atom from each of the four XeF_2 molecules and two fluorine atoms from the two AsF_6 units. $[Mg(XeF_2)_2](AsF_6)_2$ crystallizes in the orthorhombic crystal system, space group *Pbam*, with $a = 8.9767(10)$ Å, $b = 15.1687(18)$ Å, $c = 5.3202(6)$ Å, $V = 724.42(14)$ Å^3, and $Z = 2$. The octahedral coordination sphere consists of two fluorine atoms, one from each of the two XeF_2 molecules and four fluorine atoms from the four bridging AsF_6 units.

Introduction

$[Ag(XeF_2)_2]AsF_6$[1] is the first example of a compound in which XeF_2 acts as a ligand coordinated to a metal ion. Recently, an entire series of new compounds of the type $[M^x(XeF_2)_n](AF_6)_x$ (M = Ca, Sr, Ba, Pb, Ag, La, Nd, A = As, Sb, P) were synthesized and characterized structurally: $[Ln(XeF_2)_{2.5}](AsF_6)_3$ (Ln = La,[2] Nd[3]); $[Pb(XeF_2)_3](AsF_6)_2$;[4,5] $[Sr(XeF_2)_3](AsF_6)_2$;[4] $[Ba(XeF_2)_5](SbF_6)_2$;[6] $[Ca(XeF_2)_n](AsF_6)_2$, $n = 4$ and 2.5;[7] $[Ag(XeF_2)_2]PF_6$.[8]

In this paper the syntheses of the first two compounds in which XeF_2 is bonded directly to a magnesium ion are described. The structures of the compounds and their Raman spectra are also presented.

Experimental Section

General Experimental Procedure. Volatile materials (anhydrous HF (aHF), AsF_5) were manipulated in an all-Teflon vacuum line equipped with Teflon valves. Nonvolatile materials that were very sensitive to traces of moisture were handled in an argon atmosphere in a drybox, which limited the maximum water vapor content to 1 ppm (M Braun, Garching, Germany). PFA reaction vessels, equipped with a Teflon valve and a Teflon-covered mixing bar, were used for the syntheses. T-shaped PFA reaction vessels, constructed from large (16 mm i.d.) and smaller (4 mm i.d.) PFA tubes joined at right angles and equipped with a Teflon valve, were used for crystallization.

Reagents. MgF_2 (Aldrich, 99.9%) was used as purchased. Its purity was checked by elemental analysis (Anal. Calcd for MgF_2: Mg, 39.0; F, 61.0%. Found: Mg, 38.8; F, 59.7). Anhydrous HF (Fluka, purum) was treated with K_2NiF_6 (Ozark-Mahoning, 99%) for several days prior to use. AsF_5 was prepared by high-pressure fluorination of As_2O_3, as previously described for PF_5.[9] Its purity was checked by IR spectroscopy. XeF_2 was prepared by the photochemical reaction between Xe and F_2 at room temperature.[10] $Mg(AsF_6)_2$ was prepared as previously described[11] and characterized by X-ray powder diffraction data and chemical analysis (Anal. Calcd

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for $Mg(AsF_6)_2$: Mg, 6.0; As, 37.3; F_t^-, 56.7%. Found: Mg, 6.2; As, 38.0; F_t^-, 57.3).

Caution! *Anhydrous HF (aHF), AsF_5, and XeF_2 must be handled in a well-ventilated hood, and protective clothing must be worn at all times.*

Preparation of $[Mg(XeF_2)_n](AsF_6)_2$ ($n = 4, 2$). Synthesis of $[Mg(XeF_2)_4](AsF_6)_2$. $Mg(AsF_6)_2$ (1.056 g, 2.63 mmol) and excess XeF_2 (5.00 g, 29.5 mmol) were weighed into the reaction vessel inside the drybox. Anhydrous HF was added and the reaction allowed to proceed at room temperature for several days. The product was isolated by pumping off the solvent and excess XeF_2. The pumping was stopped when a 1:4 mole ratio between Mg and XeF_2 was reached (weight of the product: 2.833 g). The compound still released XeF_2 at room temperature in a dynamic vacuum (approximately 8 mg of XeF_2/(mmol of the product/h of pumping)). The product was characterized by chemical analysis (Anal. Calcd for $[Mg(XeF_2)_4](AsF_6)_2$: Mg, 2.2; As, 13.9; F_t^-, 35.2; F_f^-, 14.1; AsF_6^-, 35.0%. Found: Mg, 2.1; As, 13.6; F_t^-, 35.0; F_f^-, 14.6; AsF_6^-, 34.1), Raman spectroscopy, and the X-ray powder diffraction pattern.

Synthesis of $[Mg(XeF_2)_2](AsF_6)_2$. $Mg(AsF_6)_2$ (0.835 g, 2.08 mmol) and XeF_2 (0.705 g, 4.16 mmol) were weighed directly into the reaction vessel inside the drybox. The reaction was allowed to proceed for 24 h after the solvent (aHF) was added. A crystalline white solid (1.531 g, 2.07 mmol) was isolated by pumping off aHF at 0 °C for 4 h. The product was characterized by chemical analysis (Anal. Calcd for $[Mg(XeF_2)_2](AsF_6)_2$: Mg, 3.3; As, 20.2; F_t^-, 41.0; F_f^-, 10.3; AsF_6^-, 51.0%. Found: Mg, 3.5; As, 21.0; F_t^-, 40.8; F_f^-, 10.4; AsF_6^-, 50.9), Raman spectroscopy, and its X-ray powder diffraction pattern.

Preparation of Single Crystals. The product (approximately 200 mg) of the reaction between $Mg(AsF_6)_2$ and excess XeF_2 (estimated molar ratio between Mg and XeF_2 in this product was 1:3.5, calculated from the mass balance of the reaction) was transferred to the wider tube of the reaction vessel and dissolved in aHF. This solution was decanted into the narrower arm of the reaction vessel, which was left at room temperature while the wider arm was cooled with running water. In this way a small temperature gradient of 6 °C was achieved. Crystals were obtained in the narrower tube of the reaction vessel after several days. The mother liquor was poured from them into the wider tube of the vessel, and the aHF was pumped off from the reaction vessel. Crystals with compositions $[Mg(XeF_2)_4](AsF_6)_2$ and $[Mg(XeF_2)_2](AsF_6)_2$ were immersed in perfluorinated oil (ABCR, FO5960) in the drybox, selected under the microscope, and transferred into the cold nitrogen stream of the diffractometer. The quality of the data for crystals having the composition $[Mg(XeF_2)_2](AsF_6)_2$ was not good enough (see Crystal Structure Determination) so another crystallization process was adopted. $Mg(AsF_6)_2$ (0.144 g, 0.36 mmol) and XeF_2 (0.122 g, 0.72 mmol) were weighed at the exact 1:2 mole ratio (Mg:XeF_2) into the wider tube of the reaction vessel inside the drybox. Anhydrous HF was added, and crystallization was carried out as described above. Crystals were selected under the microscope inside the drybox and mounted in 0.3 mm thin-walled quartz capillaries.

Elemental Analysis. The total fluoride content (F_t^-) was determined after total decomposition of the sample by fusion with $KNaCO_3$.[12,13] The content of free fluoride (F_f^-) was determined in aqueous solution of the sample after it was hydrolyzed.[14] Both fluoride contents were determined by direct potentiometry using a fluoride ion selective electrode.[12] Magnesium was determined by complexometric titration.[15] AsF_6^- was determined gravimetrically by precipitation with tetraphenylarsonium chloride.[16] Arsenic was determined by the ICP-AES method.[17]

Table 1. Crystal Data and Structure Refinement for $[Mg(XeF_2)_n](AsF_6)_2$ ($n = 4, 2$)[a]

param	$MgXe_4As_2F_{20}$	$MgXe_2As_2F_{16}$
fw	1079.35	740.75
temp (°C)	−173(2)	20
a (Å)	8.698(15)	8.9767(10)
b (Å)	14.517(15)	15.1687(18)
c (Å)	15.344(16)	5.3202(6)
V (Å^3)	1937(4)	724.42(14)
Z	4	2
D_{calcd} (g/cm^3)	3.701	3.396
λ (Å)	0.71069	0.71069
μ (mm^{-1})	10.529	9.417
space group	$P2_12_12_1$ (No. 19)	*Pbam* (No. 55)
R1, wR2	0.0508, 0.1098	0.0390, 0.0753

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

Crystal Structure Determination. Both single-crystal data sets were collected using a Mercury CCD area detector coupled to a Rigaku AFC7 diffractometer with graphite-monochromated Mo Kα radiation. The data were corrected for Lorentz and polarization effects. A multiscan absorption correction was applied to both data sets. All calculations during the data processing were performed using the CrystalClear software suite.[18] Structures were solved using direct methods[19] and expanded using Fourier techniques. Full-matrix least-squares refinement of F^2 against all reflections was performed using the SHELX 97 program.[20] More details on the data collection and structure determinations are given in Table 1.

Diffraction data for $[Mg(XeF_2)_2](AsF_6)_2$, collected for single crystals at −73 °C, showed split reflections and systematic absence violations for glide planes under the *Pbam* space group. Peaks merged at higher temperature (about −15 °C). Systematic absences under the *Pbam* space group were obeyed for diffraction data for single crystals collected at room temperature. Data for the high-temperature form are presented here, while the low-temperature data will be analyzed in a further study.

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.

X-ray Powder Diffraction. X-ray powder diffraction patterns of samples in sealed quartz capillaries were obtained with a 114 mm diameter Debye−Scherrer camera with X-ray film, using Cu Kα radiation ($\lambda = 1.5418$ Å) with a Ni filter. Intensities were estimated visually.

Results

Description of the Crystal Structure of $[Mg(XeF_2)_4]$-$(AsF_6)_2$. Magnesium is octahedrally coordinated to six

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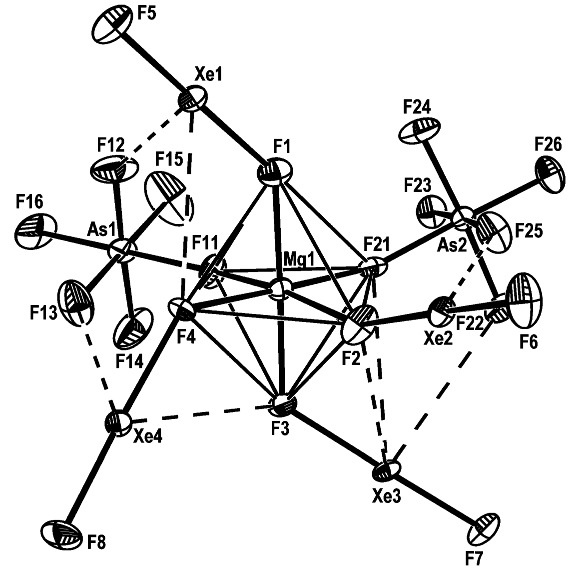

Figure 1. Coordination sphere of Mg in the structure of [Mg(XeF$_2$)$_4$]-(AsF$_6$)$_2$ (50% probability level).

Table 2. Selected Bond Lengths and Angles in [Mg(XeF$_2$)$_4$](AsF$_6$)$_2$

Distance (Å)		Angle (deg)	
Mg1−F1	1.966(10)	F1−Mg1−F2	95.9(5)
Mg1−F2	1.981(10)	F2−Mg1−F11	170.8(5)
Mg1−F3	2.003(10)	F3−Mg1−F1	178.4(5)
Mg1−F4	1.981(10)	F4−Mg1−F11	92.2(4)
Mg1−F11	1.984(10)	F11−Mg1−F21	87.5(4)
Mg1−F21	1.996(10)	F21−Mg1−F3	90.2(4)
Xe1−F1	2.059(9)	Mg1−F1−Xe1	133.9(5)
Xe1−F5	1.947(9)	F5−Xe1−F1	178.0(4)
Xe2−F2	2.079(9)	Mg1−F2−Xe2	156.3(6)
Xe2−F6	1.963(10)	F6−Xe2F2	177.9(4)
Xe3−F3	2.087(8)	Mg1−F3−Xe3	124.0(5)
Xe3−F7	1.940(8)	F7−Xe3−F3	178.9(4)
Xe4−F4	2.083(8)	Mg1−F4−Xe4	130.2(5)
Xe4−F8	1.945(10)	F8−Xe4−F4	178.0(4)
As1−F11	1.773(9)	As1−F11−Mg1	149.7(6)
As1−F12	1.707(12)	F12−As1−F16	91.1(6)
As1−F13	1.703(11)	F13−As1−F11	88.5(5)
As1−F14	1.701(12)	F14−As1−F12	177.5(6)
As1−F15	1.705(12)	F15−As1−F12	89.3(7)
As1−F16	1.726(10)	F16−As1−F11	178.2(5)
As2−F21	1.786(9)	As2−F21−Mg1	148.7(5)
As2−F22	1.720(10)	F22−As2−F21	87.8(4)
As2−F23	1.707(9)	F23−As2−F25	175.8(5)
As2−F24	1.702(9)	F24−As2−F22	176.6(5)
As2−F25	1.710(9)	F25−As2−F21	88.5(4)
As2−F26	1.713(10)	F26−As2−F21	178.5(5)

fluorine atoms. Four fluorine atoms originate from the four XeF$_2$ molecules, and two cis fluorine atoms, from the two monodentate AsF$_6$ units. Each of the four XeF$_2$ molecules and the two AsF$_6$ units are crystallographically different. The structure is illustrated in Figure 1, and bond lengths and angles are given in Table 2.

The Mg−F distances range from 1.966(10) to 2.003(10) Å. The octahedron of fluorine atoms around Mg is distorted, which is apparent from the cis and trans F−Mg−F angles. Xe−F bridging distances range from 2.059(9) to 2.087(8) Å while the Xe−F terminal distances range from 1.940(8) to 1.963(10) Å. The bridging As−F distances are 1.773(9) and 1.786(9) Å while terminal As−F distances range from 1.701(12) to 1.726(10) Å.

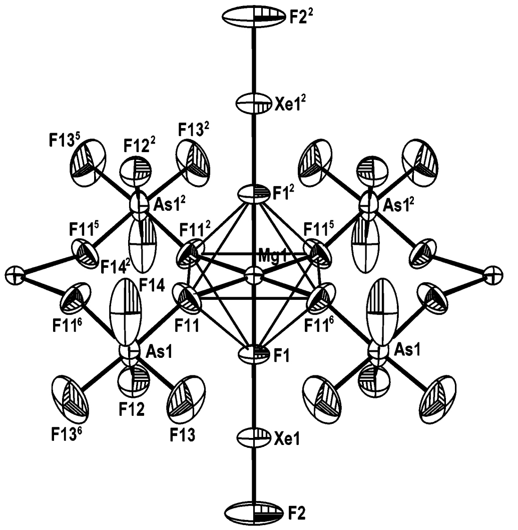

Figure 2. Coordination sphere of Mg in the structure of [Mg(XeF$_2$)$_2$]-(AsF$_6$)$_2$ and connection of Mg atoms via AsF$_6$ units (50% probability level).

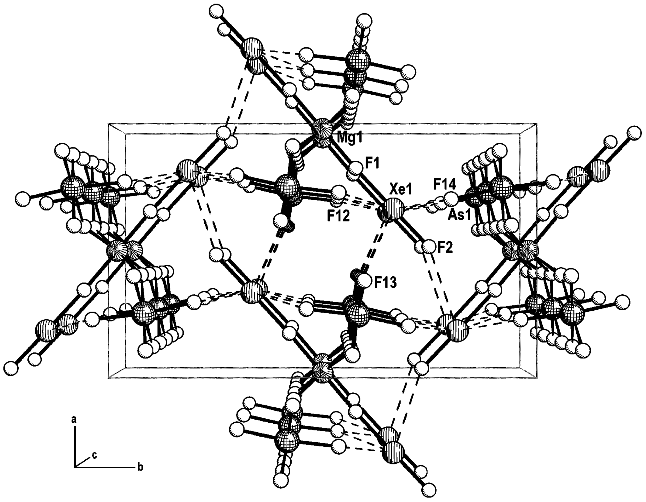

Figure 3. Arrangement of chains in the structure of [Mg(XeF$_2$)$_2$](AsF$_6$)$_2$ viewed down the *c* axis.

There are several close intra- and intermolecular electrostatic interactions between the positively charged Xe atoms and fluorine atoms of the XeF$_2$ and AsF$_6$ units (for the arrangement of [Mg(XeF$_2$)$_4$](AsF$_6$)$_2$ molecules, see Supporting Information). The [Mg(XeF$_2$)$_4$](AsF$_6$)$_2$ molecules in the crystal packing are connected by electrostatic forces only, with Xe···F distances ranging from 3.180 to 3.698 Å (the sum of the respective van der Waals radii is 3.63 Å [21]). As a consequence of these long-range interactions and of the steric activity of the electron lone pairs of Xe atoms, F−Xe−F angles deviate from the ideal linear arrangement and range from 177.9(4) to 178.9(4)°. Similarly, due to packing interactions and intramolecular contacts, the AsF$_6^-$ octahedra are deformed (see Table 2).

Description of the Crystal Structure of [Mg(XeF$_2$)$_2$]-(AsF$_6$)$_2$. Magnesium is octahedrally coordinated to six fluorine atoms. Two fluorine atoms originate from two XeF$_2$ molecules in the axial position and four fluorine atoms from four AsF$_6$ units in the equatorial plane. The two XeF$_2$

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

Distance (Å)		Angle (deg)	
Mg1−F1, Mg1−F1^2	1.917(4)	F1−Mg1−F1^2	180.0(2)
Mg1−F11, Mg1−F11^2		F11−Mg1−F11^5	180.0(2)
Mg1−F11^5, Mg1−F11^6	2.019(3)		
Xe1−F1	2.051(4)	Mg1−F1−Xe1	177.5(3)
Xe1−F2	1.913(5)	F2−Xe1−F1	179.5(3)
As1−F11, As1−F11^6	1.747(3)	As1−F11−Mg1	151.0(2)
As1−F12	1.708(7)	F12−As1−F11	87.9(2)
As1−F13	1.677(4)	F13−As1−F11	176.6(2)
As1−F14	1.669(8)	F14−As1−F12	174.2(4)

[a] Symmetry operations used for generating 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) $x + 1/2, -y + 1/2, z$.

molecules and all four AsF_6 units are crystallographically identical. The structure is illustrated in Figures 2 and 3, and selected bond lengths and angles are given in Table 3.

In the direction of the *c* axis, the Mg atoms are connected by two *cis*-AsF_6 units, with arsenic atoms in the mirror plane perpendicular to the *c* axis, forming eight-membered rings with the composition $[Mg_2(AsF_6)_2]^{2+}$. Because the Mg atoms are at inversion centers, these rings are further connected, forming infinite chains along the *c* axis (Figure 3). The Mg−F1 distance of 1.917(4) Å is shorter than the Mg−F11 distance of 2.019(3) Å, resulting in compression of the octahedron of fluorine atoms around the Mg atoms. The Xe−F terminal distance is 1.913(5) Å while the Xe−F bridging distance is 2.051(4) Å. The As−F bridging distance is 1.747(3) Å, and the As−F terminal distances range from 1.669(8) to 1.708(7) Å. Positively charged Xe atoms interact with negatively charged fluorine atoms arising from AsF_6 units and XeF_2 molecules of neighboring chains at distances ranging from 3.245 to 3.440 Å. These electrostatic forces apparently hold the neighboring chains together.

Raman Spectroscopy. Raman spectra of $[Mg(XeF_2)_n](AsF_6)_2$, $n = 4$ and 2, are shown in Figure 4.

Discussion

Synthesis. The lattice energy of $Mg(AsF_6)_2$ is rather low as a consequence of the relatively large volume of AsF_6^- (110 Å^3 [22]). The AsF_6^- anion is a weak Lewis base so even poor Lewis base solvents, such as aHF, can provide sufficient solvation energy to dissolve the $Mg(AsF_6)_2$ salt to form $[Mg(HF)_n]^{2+}$ cations and AsF_6^- anions. XeF_2 is a medium strong Lewis base, stronger than HF, and, on addition to such a solution, competes not only with HF but also with AsF_6^- in providing Coulomb energy, because the charge on the F ligands in free XeF_2 is about −0.5e.[23] The Mg^{2+} ion is, like other alkaline earth cations, a relatively weak Lewis acid and cannot withdraw F^- from XeF_2 to form an XeF^+ salt. The XeF_2 molecule acts as a fluoro ligand, coordinating to the magnesium ion as a consequence of the relatively high charge on the fluorine atoms, the polarizability of the XeF_2 molecule, and the partially covalent character of the Mg−F bonds.

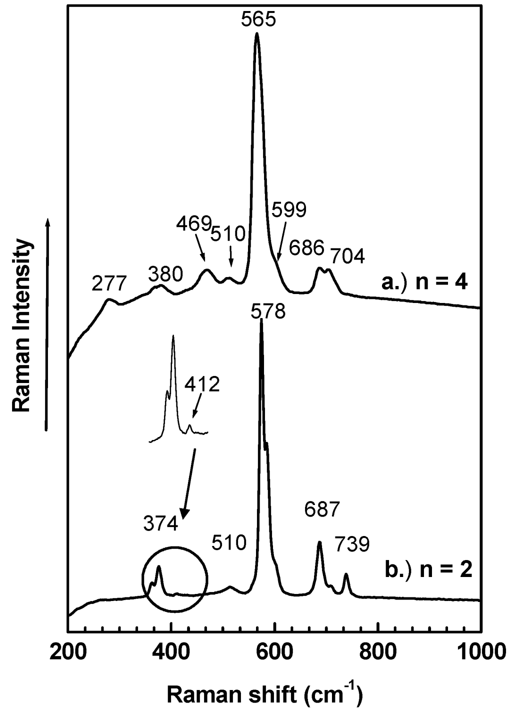

Figure 4. Raman spectra of $[Mg(XeF_2)_n](AsF_6)_2$ ($n = 4$, 2).

When $Mg(AsF_6)_2$ was reacted with excess XeF_2, using aHF as a solvent, and Raman spectra were recorded during isolation of the product, it was found that there was no free XeF_2 present when the mole ratio Mg:XeF_2 was ≤1:6. The compound $[Mg(XeF_2)_6](AsF_6)_2$ was not stable as a solid but kept losing XeF_2 in dynamic vacuum at room temperature until a composition 1:4 was reached. Characterization of this product by X-ray powder diffraction, Raman spectroscopy, chemical analysis, and a single-crystal X-ray structure determination established that the product is $[Mg(XeF_2)_4](AsF_6)_2$. This compound is not stable but slowly loses XeF_2 under dynamic vacuum at room temperature. The preparation of pure 1:2 compound was possible only by reacting stoichiometric amounts of $Mg(AsF_6)_2$ and XeF_2 in aHF and subsequently removing the solvent under dynamic vacuum at 0 °C. The 1:2 compound was also characterized by X-ray powder diffraction, Raman spectroscopy, chemical analysis and a single-crystal X-ray structure determination.

Crystal Structures. The crystal structure of $[Mg(XeF_2)_4](AsF_6)_2$ is the first molecular structure found in the system $M^x(AF_6)_x/XeF_2$/aHF (M = Mg, Ca, Sr, Ba, La, Nd, Pb, Ag; A = P, As, Sb). In all other known coordination compounds containing XeF_2 as a fluorine-donating ligand, the metal ions are connected, either by XeF_2 molecules and AF_6^- (A = As, Sb, P) anions[1−8] forming polymeric compounds (chains, layers, three-dimensional networks) or just by XeF_2 molecules, as in the case of $[Ca(XeF_2)_4](AsF_6)_2$.[7] The Mg−F(Xe) and Mg−F(As) distances in the 1:4 compound are practically the same. This implies that F ligands from monodentate AsF_6^- can, in terms of relative Lewis basicity, compete effectively with F ligands of XeF_2 molecules in coordinating to the Mg^{2+} ion. Significant elongation of the bridging As−F bonds of each monodentate AsF_6 unit (1.773(9) and 1.786-

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(9) Å) also indicates accumulation of negative charge at those F ligands relative to the terminal ones. A similar situation was observed in the Ca compounds [Ca(XeF$_2$)$_n$](AsF$_6$)$_2$, $n = 4$ and 2.5.[7] In the compounds [Mg(XeF$_2$)$_n$](AsF$_6$)$_2$, $n = 4$ and 2, all XeF$_2$ molecules are nonbridging (i.e. they do not connect two metal centers), which is again unique among the compounds of the type [M^x(XeF$_2$)$_n$](AF$_6$)$_x$ (M = Mg, Ca, Sr, Ba, Pb, Ag, La, Nd; A = As, Sb, P). This indicates that the electron charge of the XeF$_2$ molecule is delocalized toward the magnesium cation, which renders the XeF$_2$ molecule less capable of bridging two magnesium cations. In addition to bridging XeF$_2$ molecules, nonbridging molecules of XeF$_2$ were observed in [Ca(XeF$_2$)$_4$](AsF$_6$)$_2$ and in [Ln(XeF$_2$)$_{2.5}$](AsF$_6$)$_3$ (Ln = La,[2] Nd[3]) while crystal structures of [Ca(XeF$_2$)$_{2.5}$](AsF$_6$)$_2$, [M(XeF$_2$)$_3$](AsF$_6$)$_2$ (M = Pb, Sr[4,5]), [Ba(XeF$_2$)$_5$](SbF$_6$)$_2$,[6] and [Ag(XeF$_2$)$_2$]AF$_6$ (A = As,[1] P[8]) contain no nonbridging XeF$_2$ molecules. This is the consequence of the decreasing Lewis acidity of the cation and charge transfer from the XeF$_2$ molecule to the cation due the covalent character of the M−F bond. It appears that compounds with magnesium cations prefer to crystallize in molecular ([Mg(XeF$_2$)$_4$](AsF$_6$)$_2$) or chain ([Mg(XeF$_2$)$_2$](AsF$_6$)$_2$) arrangements, while [Ln(XeF$_2$)$_{2.5}$](AsF$_6$)$_3$ (Ln = La,[2] Nd[3]) contains double chains, [Ca(XeF$_2$)$_4$](AsF$_6$)$_2$[7] is a layer structure, [M(XeF$_2$)$_3$](AsF$_6$)$_2$ (M = Pb, Sr)[4] contains strongly interconnected double layers, and [Ca(XeF$_2$)$_{2.5}$](AsF$_6$)$_2$,[7] [Ba(XeF$_2$)$_5$](SbF$_6$)$_2$,[6] and [Ag(XeF$_2$)$_2$]AF$_6$ (A = As,[1] P[8]) form a 3D network.

[Mg(XeF$_2$)$_4$](AsF$_6$)$_2$ is not stable in a dynamic vacuum at room temperature, slowly losing XeF$_2$ to yield [Mg(XeF$_2$)$_2$](AsF$_6$)$_2$. The lost XeF$_2$ ligands around the Mg^{2+} cation are replaced by F ligands from AsF$_6^-$ units that transform from monodentate to cis bridging units (compare Figures 1 and 2). The Mg−F(Xe) distances are significantly shorter (1.917(4) Å) than the Mg−F(As) distances (2.019(3) Å), indicating that four cis-bridging AsF$_6^-$ units in the Mg coordination sphere are electrostatically and sterically less favorable than the two F ligands of the XeF$_2$ molecules for coordinating a magnesium cation (Figure 2). In addition, the Raman stretching frequency of the nonbridging XeF$_2$ molecule (ν(Xe−F)) in the compound [Mg(XeF$_2$)$_2$](AsF$_6$)$_2$ is higher (578 cm^{-1}) than that in [Mg(XeF$_2$)$_4$](AsF$_6$)$_2$ (565 cm^{-1}; see Raman spectroscopy), which can be attributed to a higher positive charge on the magnesium cation in [Mg(XeF$_2$)$_2$](AsF$_6$)$_2$. This shows that the four AsF$_6^-$ units accompanied by two XeF$_2$ molecules in the magnesium coordination sphere of [Mg(XeF$_2$)$_2$](AsF$_6$)$_2$ are weaker electron donors that the two AsF$_6^-$ units accompanied by four XeF$_2$ molecules in the magnesium coordination sphere of [Mg(XeF$_2$)$_4$](AsF$_6$)$_2$. [Mg(XeF$_2$)$_2$](AsF$_6$)$_2$ has a structure similar to that of [Mg(SO$_2$)$_2$](AsF$_6$)$_2$.[24] The Mg−O distances are 2.077(12) and 2.121(13) Å, showing that SO$_2$ is a weaker electron donor than the cis-bridged AsF$_6$ unit. The Mg−F(As) distances range from 1.953(11) to 1.987(10) Å.[24]

Raman Spectroscopy. The Raman spectra of [Mg(XeF$_2$)$_n$](AsF$_6$)$_2$ with $n = 4$ and 2 are shown in Figure 4. The high polarizability of xenon usually results in intense Raman bands for the symmetric Xe−F stretching modes. Modes involving Mg−F and As−F vibrations are usually far less intense and broader.

The totally symmetric (a$_{1g}$) stretching mode for XeF$_2$ occurs at 497 cm^{-1}.[25] When XeF$_2$ is distorted by bridging through one F atom to Mg^{2+} ion, the band at 497 cm^{-1} is replaced by two bands: that at higher frequency is labeled as the shorter bond Xe−F stretching (ν(Xe−F)), and the band at lower frequency is labeled as the longer bond Xe−F stretching (ν(Xe···F)). In the 1:4 compound ν(Xe−F) is 565 cm^{-1}, and in the 1:2 compound, it is 578 cm^{-1}. The higher frequency in the case of the latter is a consequence of a shorter and therefore stronger Xe−F(terminal) bond. The vibration of the longer Xe−F bond (ν(Xe···F)) in the 1:4 compound is probably hidden under the broad band at 469 cm^{-1}. In the case of the 1:2 compound, ν(Xe···F) is at 412 cm^{-1}. The origin of the band at 469 cm^{-1} is not clear but could be a consequence of the vibrational coupling of four nonbridging XeF$_2$ molecules. A similar band was found in the compounds with nonbridging XeF$_2$ molecules, e.g. [Ca(XeF$_2$)$_4$](AsF$_6$)$_2$ at 463 cm^{-1} and [Nd(XeF$_2$)$_{2.5}$](AsF$_6$)$_3$ at 461 cm^{-1}.[3,7]

In both compounds, the O_h symmetry of the AsF$_6^-$ octahedra is reduced, due to interactions with Mg^{2+} ions. Thus, instead of three Raman bands (ν_1 685, ν_2 576, and ν_5 372 cm^{-1}),[26] more bands appear. The bands at 686, 704, 599, and 380 cm^{-1} in the case of the 1:4 compound and 687, 739, and the 374 cm^{-1} in the 1:2 compound can be assigned to As−F vibrations. The symmetry reduction of AsF$_6^-$ octahedra in the XeF$^+$, XeF$_3^+$, and KrF$^+$ salts has been reported by several authors in the past.[27−29]

As reported,[30] the ν_1 vibrations of matrix-isolated MgF$_2$ were found at frequencies between 514 and 544 cm^{-1}, depending on the matrix used. The band at 510 cm^{-1} in the Raman spectra of [Mg(XeF$_2$)$_n$](AsF$_6$)$_2$ can tentatively be assigned to the Mg−F vibrations.

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Supporting Information Available: An X-ray crystallographic file in CIF format, a figure showing the arrangement of [Mg(XeF$_2$)$_4$](AsF$_6$)$_2$ molecules, and tables of X-ray powder diffraction data for [Mg(XeF$_2$)$_n$](AsF$_6$)$_2$ ($n = 4$, 2). This material is available free of charge via the Internet at http://pubs.asc.org.

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