Noble Gas Compounds

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XeF_4 as a Ligand for a Metal Ion**

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In memory of Neil Bartlett

Soon after the first noble-gas compound $XePtF_6$[1] was published, many laboratories around the world commenced research in the field of noble-gas chemistry. Soon the first binary fluoride of xenon, XeF_4,[2] was prepared. Xenon tetrafluoride is a weak Lewis base that reacts only with strong Lewis acids yielding $[XeF_3]^+$ salts with appropriate anions, such as $[SbF_6]^-$, $[Sb_2F_{11}]^-$[3] or $[BiF_6]^-$, and $[Bi_2F_{11}]^-$.[4] Some molecular adducts with XeF_4 were also described that resulted from the semi-ionic bonding in the molecule.[5] The first coordination compound with a noble-gas fluoride acting as a ligand to a metal ion was $[Ag(XeF_2)_2]AsF_6$.[6] A series of such coordination compounds has since been prepared,[7] but coordination compounds with XeF_4, (a poorer Lewis base or less thermally stable than XeF_2[8]) as a metal ion ligand, were not known.

The first attempt to coordinate XeF_4 to a metal center was made using $Mg(AsF_6)_2$ because of the strong interaction of Mg^{2+} with XeF_2.[9] Excess XeF_4 was used to favor the formation of a coordination compound. After the removal of excess XeF_4 under vacuum at room temperature, Raman spectroscopy of the product showed that XeF_4 was coordinated to the metal center. Crystallization of the product gave single crystals of composition $[Mg(XeF_2)(XeF_4)](AsF_6)_2$.[10] The synthesis of $[Mg(XeF_2)(XeF_4)](AsF_6)_2$ was repeated using the molar ratio $XeF_2{:}XeF_4 = 1{:}1$. The product obtained had the same Raman spectrum as the isolated crystal. Subsequently, preparations with higher amounts of XeF_2 ($XeF_2{:}Mg > 1$) were made and the intensity of the Raman band at $575\,cm^{-1}$ increased, indicating that this band is associated with coordinated XeF_2. At the molar ratio $XeF_2{:}Mg = 2{:}1$ or higher the only product was $[Mg(XeF_2)_2](AsF_6)_2$, which is in accord with the lower Lewis basicity of XeF_4.[8]

The magnesium ion is surrounded by six fluorine atoms, four from $[AsF_6]^-$ units, one from XeF_2, and one from XeF_4 (Figure 1). Both xenon fluorides are nonbridging ligands, whereas the surrounding $[AsF_6]^-$ units connect magnesium atoms forming layers along the *b* axis (Figure 2). The $[As1F_6]^-$ unit is *trans* bridging, whereas the $[As2F_6]^-$ unit is a *cis* bridging in the complex. In both cases, the bridging As–F distances are elongated. These elongations, therefore distort the $[AsF_6]^-$ octahedra and the As2 center is notably noncentric.

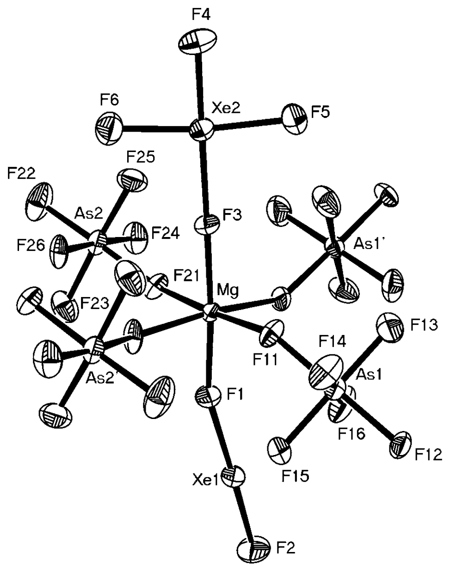

Figure 1. Coordination of Mg atom in the crystal structure of $[Mg(XeF_2)(XeF_4)](AsF_6)_2$. Interatomic distances [pm]: Xe1–F1 205.9(7), Xe1–F2 193.6(7), Xe2–F3 208.3(6), Xe2–F4 187.1(7), Xe2–F5 191.6(7), Xe2–F6 190.6(7), As1–F11 176.1(6), As1–F12 176.4(6), As1–F13 167.4(7), As1–F14 168.2(7), As1–F15 170.2(6), As1–F16 169.4(8), As2–F21 175.1(6), As2–F22 168.8(7), As2–F23 169.1(7), As2–F24 170.9(7), As2–F25 168.7(7), As2–F26 176.8(6), Mg–F1 193.5(7), Mg–F3 195.6(7), Mg–F11 199.6(7), Mg–F12 201.4(7), Mg–F21 201.9(7), Mg–F26 201.9(7).

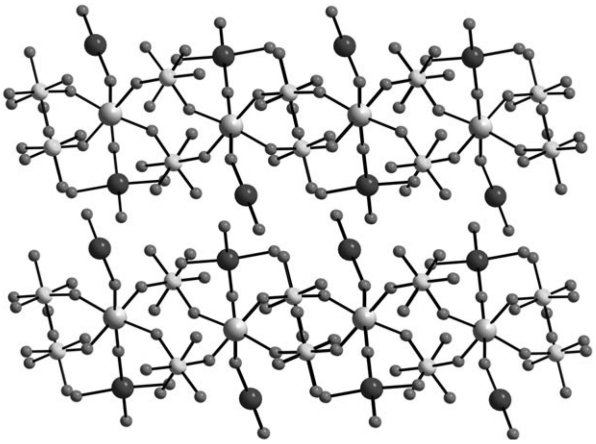

Figure 2. View of the structure of $[Mg(XeF_2)(XeF_4)](AsF_6)_2$ along the *b* axis.

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There are eight electrostatic interactions in the range 329.3(8)–380(3) pm between the positively charged xenon atom of XeF$_2$ and negatively charged F$^-$ ligands of the XeF$_4$ and [AsF$_6$]$^-$ units. In accordance with the higher positive charge at the Xe atom in XeF$_4$, this molecule forms six electrostatic interactions with F$^-$ ligands in the range of 310.3(8)–357.7(11) pm. The shorter XeF$_4$···XeF$_2$ interaction of 310.3(8) pm is especially important in connecting the layers (Figure 3). In the XeF$_2$·XeF$_4$ adduct,[5] this Xe–Fe distance is 335.9 pm. The bridge angle, F-Xe-F, between XeF$_4$ and XeF$_2$ is 134.2(4)°.

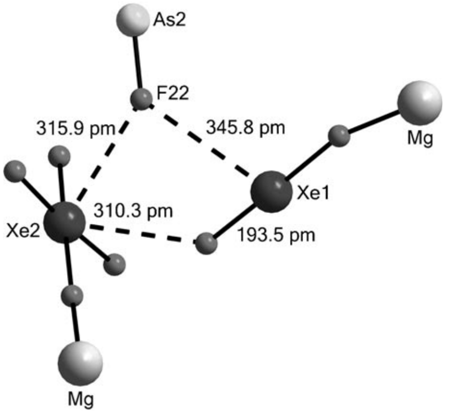

Figure 3. Interactions between XeF$_4$ and XeF$_2$ molecules in the crystal structure of [Mg(XeF$_2$)(XeF$_4$)](AsF$_6$)$_2$.

The most intense Raman bands of the single crystal of [Mg(XeF$_2$)(XeF$_4$)](AsF$_6$)$_2$ occurring at 605, 596 (sh), 575, and 552 cm^{-1} (see Figure 4) can be assigned to Xe–F vibrations. Solid molecular XeF$_4$ has D_{4h} symmetry with Raman bands at 551(ν_4), 543(ν_1), 506(ν_5), 503(ν_1), 238(ν_6), and 216(ν_3) cm^{-1}.[11] When the XeF$_4$ molecule donates one fluorine atom to a strong Lewis acid yielding the [XeF$_3$]$^+$ cation of C_{2v} symmetry, the Raman bands are found to be at higher frequencies.

In XeF$_3$SbF$_6$ the Raman bands assigned to [XeF$_3$]$^+$ are at 643(ν_1), 571(ν_2), 607(ν_4), 608(ν_4), and 316(ν_5) cm^{-1}.[12] In the magnesium compound, the XeF$_4$ species is not as far along the ionization pathway as in the [SbF$_6$]$^-$ salt and thus the lower Xe–F stretching frequencies are expected. The bands at 605, 596 (sh), and 552 cm^{-1} can be attributed to the XeF$_4$ ligand coordinated to the Mg^{2+} ion. The band at 575 cm^{-1} can be assigned to the vibration of the nonbridging XeF$_2$ ligand, as in the [Mg(XeF$_2$)$_2$](AsF$_6$)$_2$ compound.[9] The band at 460 cm^{-1} could be a consequence of a coupling between vibrations of XeF$_2$ and XeF$_4$. The bands at 728, 704, 687, 370, and 265 cm^{-1} probably arise from the two crystallographically distinct and distorted [AsF$_6$]$^-$ units.

The Raman spectrum of the product isolated from the experiment using a higher molar excess of XeF$_4$ shows the Xe–F modes at 622, 590, 575, and 549 cm^{-1} (see Figure 4). A weak band at 575 cm^{-1} probably arises from some of the coordinated XeF$_2$ and the bands at 622, 590, and 549 cm^{-1} are most likely the signature of coordinated XeF$_4$ molecules. These Raman bands are different from those of [Mg(XeF$_2$)(XeF$_4$)](AsF$_6$)$_2$ because two XeF$_4$ molecules are now coordinated to the same metal center (Figure 4). Efforts to prepare single crystals of this compound failed. Although large excess of XeF$_4$ was used, the only crystalline product obtained always had the composition [Mg(XeF$_2$)(XeF$_4$)](AsF$_6$)$_2$. Thorough prefluorination of the reaction vessel and very careful purification of XeF$_4$ did not help. The most probable reason for the formation of XeF$_2$ is the reduction of XeF$_4$ during the four weeks of crystallization in a FEP reaction vessel. The structure of the coordination compound with only XeF$_4$ ligands is still unknown.

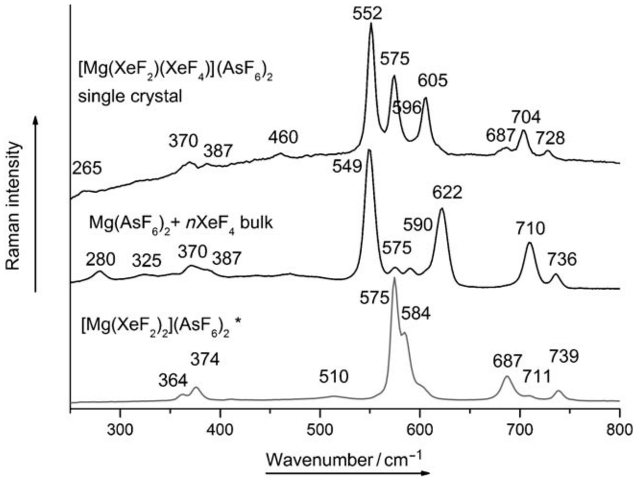

Figure 4. Comparison of the Raman spectra of different products in the system Mg(AsF$_6$)$_2$/XeF$_2$/XeF$_4$. * Spectrum of [Mg(XeF$_2$)$_2$](AsF$_6$)$_2$ from Reference [9].

Experimental Section

Mg(AsF$_6$)$_2$ was prepared by the reaction between MgF$_2$ and AsF$_5$ in anhydrous HF (aHF) as a solvent. XeF$_4$ was prepared by the fluorination of XeF$_2$ with elemental fluorine under UV light in aHF as a solvent at room temperature. The purity of XeF$_4$ was checked by gas-phase IR spectroscopy and Raman spectroscopy of the solids. Solid product showed only the vibrational bands associated with XeF$_4$. Reactants Mg(AsF$_6$)$_2$ (0.2116 g, 0.557 mmol), XeF$_2$ (0.1074 g, 0.634 mmol), and XeF$_4$ (0.1191 g, 0.575 mmol) were weighed out in a dry box. The solvent, aHF, was added on a vacuum line.

Caution: Anhydrous hydrogen fluoride, AsF$_5$, XeF$_2$, and XeF$_4$ must be handled in a well-ventilated hood and protective clothing must be worn at all times! XeF$_4$ and all of its products are susceptible to moisture and they react with it forming XeO$_3$, a compound which easily detonates.[13] The experimentalist must become familiar with these reagents and the hazards associated with them. For treatment of HF injuries see reference [14].

Crystals were grown in a crystallization vessel made from a T-shaped poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) reaction vessel, constructed using FEP tubing of inner diameter 16 mm. A 30 cm long FEP tube of inner diameter 4 mm connected by a teflon valve provided flexibility for decanting the aHF solution from one arm of the T-reactor to the other. Reagents were placed in the wider tube of a crystallization vessel in stoichiometric amounts 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 at least 28 °C and were isolated from the mother liquid at −20 °C and immersed in perfluorinated oil (ABCR, FO5960) in a dry-box. A suitable crystal was selected under the microscope and transferred into the cold nitrogen stream of the X-ray diffractometer.

Keywords: fluorine · Lewis acids · magnesium · structure elucidation · xenon

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[10] Crystal data for [Mg(XeF$_2$)(XeF$_4$)](AsF$_6$)$_2$: $M_r = 778.75$, monoclinic space group $P2_1/n$, $a = 1291.5(19)$, $b = 856.0(11)$, $c = 1325(3)$ pm, $\beta = 101.558(15)$, $V = 1.435(4)$ nm^3, $Z = 4$, $\rho_{calcd} = 3.604$ g cm^{-3}, $F(000) = 1392$, $T = 200(2)$ K, Final R indices $R1 = 0.0760$ and $wR = 0.1605$ (all). Of the 6575 measured reflections 3342 were independent. The final difference Fourier synthesis gave min/max residual electron density of −2328/2545 e$_0$ nm^{-3}. Single crystal data sets were collected using a Mercury CCD area detector coupled to a Rigaku AFC7 diffractometer using graphite monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Programs used: SIR-92,[15] TeXsan,[16] SHELXL-97[17] and DIAMOND 3.1 software.[18] Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the deposition numbers CSD-419632.

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