Communications

Coordination of Noble-Gas Atoms

Gold(I) and Mercury(II) Xenon Complexes**

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During detailed investigation of the reaction which produced the first gold xenon compound $[AuXe_4]^{2+}[Sb_2F_{11}]_2^{[1]}$ a number of further gold(II) xenon compounds were discovered.^[2] In only one instance could a gold(III) xenon compound be detected.^[2] However, gold occurs most frequently in its complexes as gold(i). At a first glance a gold(i) xenon bond may not appear particularly favored as gold(i) has a fully occupied 5d shell, but this consideration totally overlooks the relativistic effect, which, in the periodic system, reaches a first maximum for gold.^[3] The [AuXe]⁺ ion has already been detected by mass spectrometry.^[4] According to experimentation and calculation this cation has a bond energy of 30 ± 3 kcal mol^{-1,[4]} a gold–xenon bond length of 276.1 pm was predicted. A linear [AuXe_2]⁺ ion could also exist.^[5]

The fundamental difficulty in the preparation of a gold(i) xenon compound is that gold(i) always exists in the form of complexes whose ligands, predictably, bind more effectively than xenon. Therefore a displacement reaction appears to be impossible. On the other hand, a highly promising educt would be a compound of an (almost) naked Au⁺ ion and a weakly coordinating anion. The compound $[(F_3As)Au]^+[SbF_6]^-$, which according to structural analysis contains a gold(i) center that is only complexed on one side,^[6] appears to be a suitable model for the desired educt. Complexation with xenon could be achieved by exchange of the only weakly basic $[SbF_6]^-$ ion for a still weaker basic anion. Thus the reaction of $[(F_3As)Au]^+[SbF_6]^-$ with xenon in SbF_5 -rich HF/SbF₅ solution leads to the xenon complex $[(F_3As)AuXe]^+[Sb_2F_{11}]^-$ (1).

Complex 1 crystallizes as colorless needles which are stable at room temperature. Crystal-structure analysis shows that the $[(F_3As)AuXe]^+$ and $[Sb_2F_{11}]^-$ ions in 1 interact only weakly with each other (Figure 1 and Table 1). The smallest Au···F separation is 284.8 pm. The As-Au-Xe unit is almost linear (173.26(2)^D); at 260.72(6) pm the gold(i)–xenon bond in 1 is as short as the gold(III)–xenon bond in $[AuXe_2F]^{2+}$ $[SbF_6]^-[Sb_2F_{11}]^-$ and significantly shorter than gold(II)–xenon bonds. With the help of a basis set for gold specially optimized for the MP2 approximation, calculation of the structure of the $[(F_3As)AuXe]^+$ ion is achieved with astonishing accuracy (Table 1). The calculated bond energy of 32.7 kcalmol⁻¹ between $[(F_3As)Au]^+$ and Xe agrees well

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Figure 1. Crystal structure of 1 (ORTEP representation, thermal ellipsoids set at 50% probability). For numerical values see Table 1.

Table 1: Selected structural data for $[(F_3As)AuXe]^+[Sb_2F_{11}]^-$ (1) and $[HgXe]^{2+}[SbF_6]^-[Sb_2F_{11}]^-$ (2).

Separations r [pm] and angles [°]	Crystal structure analysis 1	MP2 calculation [(F ₃ As)AuXe] ^{+[a]}	
rAu-Xe	260.72(6)	260.5	
<i>r</i> Au-As	231.52(8)	230.6	
<i>r</i> As-F	165.9(5), 166.4(4),	169.7	
	166.7(5)		
rAu…F(Sb)	284.8-325.8	-	
∢As-Au-Xe	173.26(2)	180	
∢F-As-F	97.1(3), 98.5(3),	101.3	
	99.3(3)		
	2	[HgXe] ^{2+[b]}	$[HgXe]^{2+} \cdot 6 HF^{[c]}$
rHg-Xe	276.9(4)	261.3	267.2
rHg…F	259.4(2), 249.9(2),		256.8
	246,1(2)		
	245.4(2), 237.3(2),		236.2
	227.9(2)		
∢Xe-Hg…F	75.24(6), 80.49(6), 83.73(7)		86.7
	131.06(6), 137.57(6), 140.18(6)		134.4

[a] Total energy, with zero-point energy correction: -455.812215 a.u. [b] Total energy, with zero-point energy correction: -167.697137 a.u. [c] Total energy, uncorrected: -769.5592037 a.u.

with the bond energy in the [AuXe]⁺ ion.^[4] Ab initio calculation also allows the prediction of the frequency of the gold-xenon vibration v(AuXe) (147.5 cm⁻¹). The Raman spectrum shows a band at $\tilde{\nu} = 138.3 \text{ cm}^{-1}$ which doubtlessly overlaps with the δ (SbFSb) band of the anion (Figure 2 and Table 2).^[7] If **1** is labeled with ¹³⁶Xe (c.f. natural xenon isotope mixture: $M_r = 131.3$) this band appears displaced at $\tilde{\nu} =$ 136.7 cm⁻¹. The band at $\tilde{\nu} = 190.7$ cm⁻¹ shows the only other isotope effect (displacement to 189.5 cm⁻¹, at the limit of measurement accuracy). This band is assigned to the goldarsenic vibration which, because of the linearity of the As-Au-Xe framework, is strongly coupled with the gold-xenon vibration. It is noticeable that the intensity of the v(AuXe)band is significantly lower than that of the $v(AuXe_4, A_{1g})$ band in the $[AuXe_4]^{2+}$ ion. The latter band is extraordinarily strong and dominates the Raman spectrum of $[AuXe_4]^{2+}[Sb_2F_{11}]^{-2}$. Here too calculation gives an answer: the calculated Raman



Figure 2. Raman spectrum of **1**. For numerical values see the Experimental Section, assignment see Table 2.

 $\mbox{\it Table 2:} Experimental and calculated (MP2) vibrational frequencies <math display="inline">[cm^{-1}]$ of the $[(F_3As)AuXe]^+$ ion in 1.

Raman ^[a]	MP2 ^[a]	Assignment ^[b]
764.4(25)	747.6(25)	$v_s AsF_3$
752.6(10)	764.2(8)	$v_e AsF_3$
354.9(4)	349.3 (1.5)	$\delta_s AsF_3$
260.0(sh) ^[c]	261.9(0.9)	$\delta_{e} AsF_{3}$
190.7(2)	207.9 (0.6)	ν AuAs
138.3 (50 ^[d])	147.5 (2.3)	ν AuXe
117.2(3 ^[d])	138.0 (0.4)	$\delta_{e} AuAsF_{3}$
	40.2 (0.1)	δ_{e} XeAuAs

[a] Values in parenthesis are relative intensities. [b] Strongest components. [c] $sh\!=\!shoulder.$ [d] Superimposed with $\delta(SbFSb)$ of $[Sb_2F_{11}]^-$ ions.

intensity of the v(AuXe₄, A_{1g}) band is greater than that of the v(AuXe) band in the [(F₃As)AuXe]⁺ ion by a factor of 25. In the ¹²⁹Xe NMR spectrum (¹²⁹Xe: $I = \frac{1}{2}$, natural

In the ¹²⁹Xe NMR spectrum (¹²⁹Xe: $I = \frac{1}{2}$, natural abundance 26.4%), because of the xenon excess necessary in the solution, a signal for the [(Fe₃As)AuXe]⁺ ion and one for atomic xenon are expected. However, at room temperature only one signal at $\delta = -5180.7$ ppm is observed; clearly rapid exchange is taking place. On cooling the sample to $-30 \text{ }^{\circ}\text{C}$ this signal shifts and splits (Figure 3). The complicated appearance of the signal can be explained by ¹⁹⁷Au-¹²⁹Xe (¹⁹⁷Au: $I = \frac{3}{2}$, 100%) and ⁷⁵As-¹²⁹Xe coupling (⁷⁵As: $I = \frac{3}{2}$, 100%). The large quadrupole moment of one or both $I = \frac{3}{2}$ nuclei leads to extensive broadening of the signals; the ¹²⁹Xe NMR signal of the [XeCI]⁺ ion (³⁵CI/³⁷CI, $I = \frac{3}{2}$) has a similar shape.^[8] In addition in the spectrum at -30° C the anticipated sharp signal for free xenon is also observed.

AsF₃ is clearly such a poor ligand that xenon can compete with it, even when AsF₃ is present in excess. In contrast the $[(F_3P)_2Au]^+$ ion is formed immediately and irreversibly with the homologue of AsF₃, PF₃, under identical conditions.^[6] Apart from the $[(F_3As)Au]^+$ and $[(F_3As)AuXe]^+$ ions we are unaware of any arsenic-bonded AsF₃ complexes, whereas a large number of PF₃ complexes are known.^[9]) In HF/AsF₅ the AsF₃ unit binds as a ligand to trivalent lanthanide cations, but in these species coordination takes place through a fluorine atom.^[10] In contrast to PF₃, however, AsF₃ is not protonated



Figure 3. ¹²⁹Xe NMR signal of a solution of 1 in HF/SbF₅ at -30 °C in the presence of xenon. In addition to the sharp signal of elemental xenon (right) the highly broadened signal for the [(F₃As)AuXe]⁺ ion arising from quadrupole interactions can be seen.

by HF/SbF₅.^[11] In agreement with this observation the first ionization energy of AsF₃ (13.0 eV) is higher by 0.72 eV than that of PF₃ (12.28 eV).^[12] These particularities of AsF₃ are usually explained by inadequate shielding by the fully occupied 3d shell (transition-metal contraction).

The Hg²⁺ ion is isoelectronic with the Au⁺ ion. However, compounds that contain uncomplexed Au⁺ ions have not been reported, whereas compounds such as HgF₂ which contain uncomplexed Hg²⁺ ions are known. If HgF₂ reacts with an excess of SbF₅ in the presence of xenon above room temperature highly refractive crystals are formed which decompose at room temperature in moist air with the release of gas. In dry air the compound is stable at room temperature, and under xenon pressure up to 60 °C. This compound was identified as $[HgXe]^{2+}[SbF_6]^{-}[Sb_2F_{11}]^{-}$ (**2**, see Figure 4) by



Figure 4. Crystal structure **2** (ORTEP representation, thermal ellipsoids set at 50% probability). The immediate environment of an $[HgXe]^{2+}$ ion is shown. The coordination sphere of the Hg^{2+} ion has a highly distorted, capped octahedral configuration.

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crystal-structure analysis. At 276.93(4) pm the mercuryxenon bond is about as long as the gold(II)-xenon bond in the [AuXe₄]²⁺ ion. The coordination sphere of the mercury center is completed by six fluorine atoms at distances between 227.9(2) and 259.4(2) pm. Compound **2** has a highly distorted capped structure in which the xenon atom assumes the capping position. For calculation on **2** with ab initio methods we replaced the fluoroantimonate anions with HF molecules and assumed a regular, capped octahedral structure. The calculation gave a mercury-xenon separation of 267.2 pm and mercury-fluorine separations of 236.2 and 256.8 pm (see Table 1). In view of the simplifications the agreement with experiment is satisfactory in our view. The calculated mercury-xenon bond energy for [HgXe]^{2+.6}HF is 24.5 kcal mol⁻¹.

Neither ¹²⁹Xe nor ¹⁹⁹Hg NMR spectra could be obtained for **2** because the compound decomposed in HF solution. The Raman spectrum shows a relatively intense band at 139.8 cm⁻¹ (138.7 cm⁻¹ for [Hg¹³⁶Xe]²⁺) which can be assigned to the mercury–xenon vibration and again is superimposed with the δ (SbFSb) band of the [Sb₂F₁₁]⁻ ion. Only the anion combination [SbF₆]⁻/[Sb₂F₁₁]⁻ was detected following reactions under a number of conditions. The Raman spectrum of a sample of crystals, several of which were studied crystallographically, is identical to the spectrum of the bulk product. Consequently the reaction yields quantitatively a uniform product.

Finally, reference is made to a peculiarity of this mercuryxenon compound. All noble-gas compounds, including the novel gold-xenon compounds, require elemental fluorine in at least one step of their synthesis (e.g. for the synthesis AuF₃). Compound **2** is the first noble-gas compound whose synthesis occurs without the use of elemental fluorine: SbF₅ and HgF₂ are obtainable by metathesis reactions. Our results show that a number of xenon-metal complexes could be prepared if it is possible to obtain educts with sufficiently weakly coordinated metals ions.

Experimental Section

1: Under the exclusion of moisture, AuF_3 (210 mg, 0.8 mmol) and SbF_5 (2.29 g, 10.6 mmol) were placed into a polyperfluorovinyl ether/ tetrafluoroethylene copolymer (PFA) reaction tube. Anhydrous HF (800 mg, 40 mmol) and AsF_3 (350 mg, 2.6 mmol) were condensed into the tube with a stainless steel vacuum apparatus at -196 °C. Warming to room temperature led to gas evolution (AsF_3) and the formation of a small amount of black precipitate, probably gold. When the gas evolution ceased xenon (800 mg, 6 mmol) was condensed into the mixture at -196 °C. The reaction tube was sealed and the reaction mixture cooled from room temperature to -50 °C. Compound 1 crystallized out as colorless needles which immediately turned black on exposure to air. Yield: 750 mg, m.p. 62 °C (decomp.). Removal of the adhering HF/SbF₅ in vacuum leads to decomposition of the compound.

¹²⁹Xe NMR (HF/SbF₅, 110.45 MHz, XeOF₄, 25 °C): $\delta = -5180.7 \text{ ppm}$ (s), ¹²⁹Xe NMR (HF/SbF₅, 110.45 MHz, XeOF₄, -30 °C): 5149.9–5150.3 ppm (m); Raman (1064 nm, 25 °C): $\tilde{\nu}(I_{rel}) = 764.4(25)$, 752.6(10), 676.5(sh), 666.3(60), 657.7(sh), 646.0(100), 591.0(10), 354.9(4), 316.9(6), 293.3(15), 282.9(sh), 260.0(sh), 226.5(15), 190.7(2), 151.8(3), 138.3(50), 117.2(2) cm⁻¹.

Crystal structure analysis: a suitable crystal was mounted onto a specially constructed apparatus^[13] with cooling in an inert atmosphere on a Bruker SMART CCD 1000 TM diffractometer and analyzed.^[14] After semi-empirical absorption correction by equalization of like-symmetry reflections (SADABS), structure solution and refinement was carried out with the SHELX programs.^[15,16]

Ab initio calculations: Gaussian 98 program.^[17] 2nd-order Møller–Plesset approximation (MP2) for electron correlation as implemented in Gaussian. Basis set: 6-311G(d,p) for F and H as implemented in Gaussian. Au and Hg, relativistically corrected basis set for MP2, optimized by P. Schwerdtfeger and R. Wesendrup, in each case 9s 9p 6d 4f with pseudopotentials for 60 core electrons. Xe 6s, 6p, 3d, 1f with relativistically corrected pseudopotentials for 46 core electrons. As: 3s, 3p, 1d with pseudopotentials for 28 core electrons.^[18]

2: HgF₂ (130 mg, 0.54 mmol) and SbF₅ (4.06 g, 18.73 mmol) were placed into a PFA reaction tube under exclusion of moisture. HF (280 mg, 14.0 mmol) was condensed onto this mixture with a stainless steel apparatus at -196°C. On warming to room temperature a colorless solid formed which remained partly in solution. The mixture was then evaporated to dryness in vacuum at room temperature. 10 mg of the colorless residue was placed into a thick-walled glass ampoule of 3-mm inner diameter and treated with SbF₅ (660 mg, 3.0 mmol). Liquid xenon (220 µL) was condensed into the mixture and the tube was sealed by melting. On warming to room temperature the SbF₅ and xenon mixed. The reaction mixture was homogenized in an ultrasound bath and then heated at 80 °C for 6 h. Slow cooling to room temperature (0.05 °Cmin⁻¹) afforded colorless platelet crystals of 2. The pure, colorless product was obtained by decantation of the xenon/SbF₅ excess at low temperature (-100 °C); m.p. ≈ 30 °C (decomp.). The reaction is quantitative. Raman (1064 nm, 25 °C): $\tilde{\nu}(I_{\text{rel}}) = 714(75), 703(20), 687(10), 673(18), 652(100), 640(35), 594(3),$ 572(5), 553(15), 525(10), 385(3), 341(5), 329(9), 306(8), 289(35), 264(20), 227(30), 209(7), 194(3), 181(2), 140(40), 136(30), 119(10) cm⁻¹. Crystal structure analysis was carried out as described above.[19]

Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344, Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-412994 (1) and CSD-412993 (2)

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