Gold – Xenon Complexes[**]

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The recent isolation of the metal – xenon compound $[AuXe_4]^{2+}$-$([Sb_2F_{11}]^-)_2$ (**1**)[1] raises a number of questions. The salt **1** is formed from Au^{2+}, dissolved in HF/SbF_5, in the presence of xenon. If the concentration of SbF_5 is fairly high (ca. 0.5 mol SbF_5 in 1 mol HF) **1** forms as the sole product in two crystallographically different modifications: a triclinic modification,[1] and a tetragonal modification, which has been seldomly observed. Both modifications differ only with respect to the cation – anion interactions. The triclinic modification has one particularly short $Au \cdots F$ contact

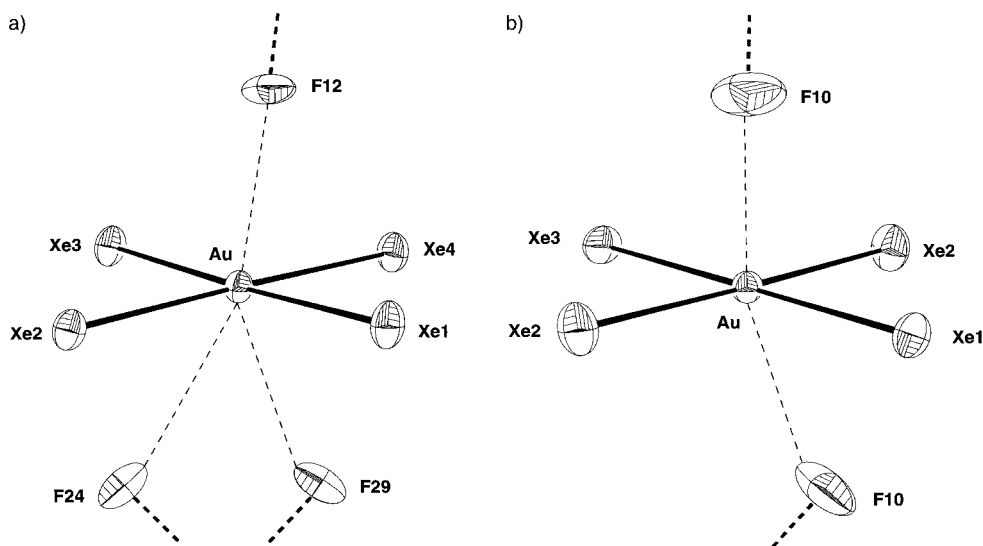Figure 1. The $[AuXe_4]^{2+}$ ion and its closer fluoride environment in the two crystallographically different modifications (ORTEP representation with 50% probability ellipsoids). a) Triclinic modification; bond lengths [pm]: Au-Xe1 273.30(6), Au-Xe2 274.98(5), Au-Xe3 277.79(6), Au-Xe4 274.56(5), Au-F12 267.1(4), Au-F24 315.3(4), Au-F29 295.0(4). b) Tetragonal modification; bond lengths [pm]: Au-Xe1 273.7(1), Au-Xe2 275.9(1), Au-Xe3 267.0(1), Au-F10 292.8(7).

(Au-F12 267.1(4) pm; Figure 1 a), which supplements the square $[AuXe_4]^{2+}$ unit resulting in a square pyramid. In the tetragonal modification the contacts are weaker (Au-F10 292.8(7) pm; see Figure 1 b. The ESR spectra of such reaction mixtures are quite complex and dependent on the xenon pressure and on the temperature—this is a first indication that in solution mixtures of products are present.

The first question is then whether only $[AuXe_4]^{2+}$ exists, or if, during the ligand substitution on Au^{2+} with xenon, intermediates of the kind $[AuXe_n]^{2+}$ ($n < 4$) can also be isolated. Of the many parameters that can be varied in these experiments the xenon pressure and the acid strength of the HF/SbF_5 play a dominant role. The importance of the Xe pressure is clear, that of the acid strength of the HF/SbF_5 arises since upon reduced acidity HF^- or $[SbF_6]^-$ could replace xenon as a ligand. We succeeded in isolating cis-$[AuXe_2]^{2+}([Sb_2F_{11}]^-)_2$ (**2**) in the form of violet-black crystals from solutions of $HF/SbF_5 \approx 2:1$ after removal of excess xenon under vacuum at $-78\,°C$. The crystals of **2**, like those of **1**, are strongly dichroitic. The crystal structure of **2** is shown in Figure 2. The gold atom resides in a square-planar environment, surrounded by the two Xe atoms and two F atoms of the $[Sb_2F_{11}]^-$ ion. The Au-Xe distances of 265.8(1) and 267.1(1) pm are slightly shorter than those in the $[AuXe_4]^{2+}$ ion. Also the $Au \cdots F$ contacts are quite short: 218.1(4) and 223.8(4) pm. Salt **2** is thermally slightly more stable than **1** with respect to loss of Xe.

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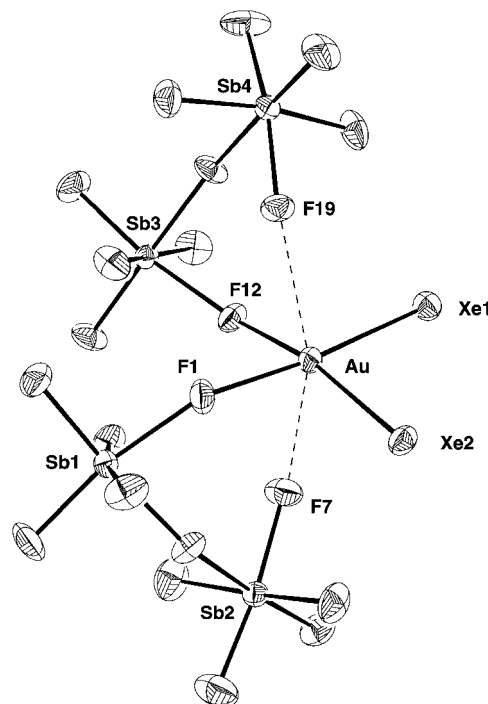Fax: (+49) 30-838-4289
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Figure 2. Structure of **2** (ORTEP representation with 50% probability ellipsoids); selected bond lengths [pm]: Au-Xe1 265.8(1), Au-Xe2 267.1(1), Au-F1 218.1(4), Au-F12 223.8(4).

We have also isolated the trans-$[AuXe_2]^{2+}$ ion but in this case as the $[SbF_6]^-$ salt, trans-$[AuXe_2]^{2+}([SbF_6]^-)_2$ (**3**). Unlike **1** and **2**, however, **3** was not prepared by reaction of AuF_3 and Xe in HF/SbF_5, but rather by oxidation of finally divided gold in HF/SbF_5 with XeF_2 under pressure of xenon. Salt **3** forms ochre-colored, thermally very unstable crystals; the crystal structure is depicted in Figure 3. The Au-Xe distance of 270.9(1) pm is slightly longer than that in the cis compound **2**.
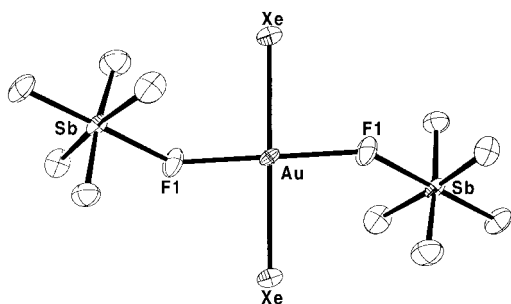
Figure 3. Structure of **3** (ORTEP representation with 50% probability ellipsoids); selected bond lengths [pm]: Au-Xe 270.9(1), Au-F1 215.9(6), Sb-F1 198.6(6).

The Au atom in **3** resides in a square-planar environment, with the Au atom coordinated to two Xe atoms and to two fluorine atoms of the $[SbF_6]^-$ ions. The Au···F distances of 215.9(6) pm are markedly shorter than in the *cis* isomer **2**, due to the higher basicity of $[SbF_6]^-$ in comparison to $[Sb_2F_{11}]^-$. That **3** is thermally less stable than **2** is possibly attributed to the anion: $[Sb_2F_{11}]^-$ salts of weak bases are generally more stable than the corresponding $[SbF_6]^-$ salts. The intense Raman band at 121 cm^{-1} is assigned to the symmetric AuXe$_2$ stretch. Obviously xenon has a larger *trans* effect for F$^-$ since replacement of two xenon ligands in AuXe$_4$$^{2+}$ should result in *cis*-AuXe$_2$$^{2+}$, while introduction of two xenon ligands into Au^{2+}·(HF)$_x$ should give the *trans*-product.

If in the syntheses a lower Xe pressure is applied, green crystals are isolated, which are remarkably stable and decompose only slightly below room temperature if moisture is excluded. The single-crystal structure determination reveals a binuclear Au–Xe complex containing a Z-shaped [Xe-Au-F-Au-Xe]$^{3+}$ ion (Figure 4). Again the Au atom resides in a

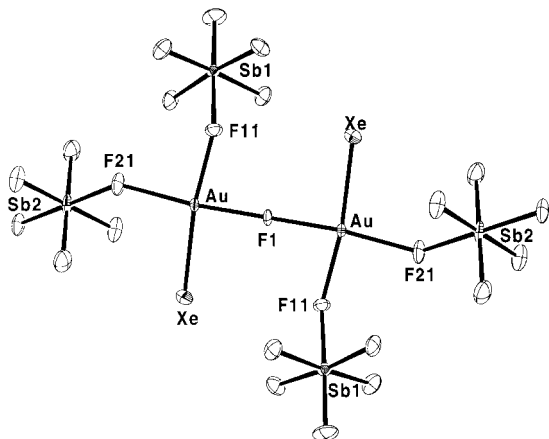Figure 4. Structure of the [Xe-Au-F-Au-Xe]$^{3+}$ ion and its closer anion environment in [Au$_2$Xe$_2$F$_2$$^+$]([SbF$_6$]$^-$)$_3$ (**4**; (ORTEP representation with 50% probability ellipsoids); selected bond lengths [pm]: AuXe 264.7(1), Au-F1 204.5(2), Au-F11 216.6(4), Au-F21 218.9(4), Sb1-F11 194.0(4), Sb2-F21 193.7(4).

square-planar environment, with the Au center coordinated to one Xe atom and three fluorine atoms. The bridging fluorine atom (F1) diplays very short distances to gold (204.5213) pm. According to MP2 ab initio calculations this binuclear gold complex should be diamagnetic.[2] The intense

Raman bonds at 153 and 101 cm^{-1} are assigned to the AuXe stretching modes. In the series [AuXe$_n$]$^{2+}$ ($n = 1-4$) only the example for $n = 3$ is missing.

Another question is why is the Au^{2+} ion (a rather rare oxidation state in gold chemistry) so willing to form complexes with xenon, whereas the Au$^+$, Au^{3+}, and Au^{5+} ions are not. Although [AuXe]$^+$ has been detected in the mass spectrometer as a stable particle,[3] our attempts to reduce the Au^{2+}–Xe complexes have proved unsuccessful to date. On the other hand we have succeeded in isolating an Au^{3+}–Xe complex from a less acidic solution (HF/SbF$_5$ ≈ 5:1). The ochre-colored crystals are surprisingly stable, and the crystal structure is shown in Figure 5. The gold center again resides in

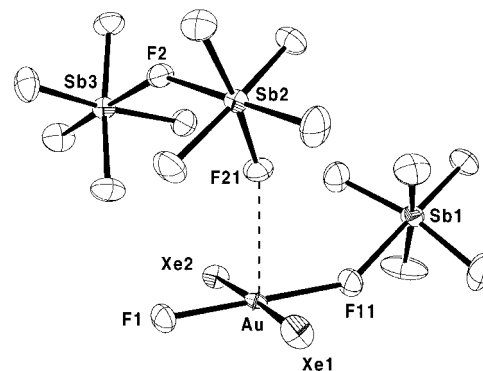Figure 5. Structure of *trans*-[AuXe$_2$F]$^{2+}$ [SbF$_6$]$^-$[Sb$_2$F$_{11}$]$^-$ (**5**) (ORTEP representation with 50% probability ellipsoids); selected bond lengths [pm]: Au-Xe1 259.3(1), Au-Xe2 261.9(1), Au-F1 187.8(3), Au-F11 198.1(3), Sb1-F11 206.6(4), Sb2-F21 205.1(4), Au···F21 264.46(5).

a square-planar environment, with the Au atom surrounded by two *trans* Xe atoms and and two fluorine atoms. The oxidation state of +3 for Au is not only derived from the stoichiometry (in the single-crystal structure determination undetected H atoms could falsify this result), but also from the bond lengths: The Au^{3+}–Xe distances of 259.3(1) and 261.9(1) pm are markedly shorter than the Au–Xe distances in the Au^{2+}–Xe complexes, the F–Au distances (187.8(3) and 198.1(3) pm) are typical values for Au^{3+}, such as in AuF$_3$.[4]

The synthesis of Au–Kr complexes has so far not been achieved. Calculations for the reaction [AuXe$_2$]$^{2+}$ + 2Kr →[AuKr$_2$]$^{2+}$ + 2Xe with relativistically corrected basis sets at the MP2 level gave positive reaction enthalpies of about 40 kcal mol^{-1}. Since the Au–Xe complexes seem to be at the limit of thermodynamic stability, the outlook for the successful synthesis fof Au–Kr complexes is not good.

Further unanswered questions are: Why is it of all the metals that gold is able to act as central atom for these Xe complexes; and is it possible to isolate Xe complexes in solvent systems other than HF/SbF$_5$, for example in alkanes. The advantage of the HF/SbF$_5$ system is that the concentrations of F$^-$ and HF$_2$$^-$ are suppressed to such an extent by acidification that these cannot compete any longer with Xe as ligands.

Experimental Section

1: A poly(perfluoroethylene)–perfluorovinylether copolymerisate (PFA) reaction tube with an internal diameter of 12 mm was filled with AuF$_3$

(250 mg, 0.98 mmol) and SbF$_5$ (6.8 g, 31 mmol) under exclusion of moisture (dry box, < 0.1 ppm H$_2$O), and connected to a steel vacuum line whereupon anhydrous HF (1.4 g, (70 mmol) was condensed in. The tube was allowed to warm to room temperature and the components were well mixed (note the AuF$_3$ dissolved only slightly in HF/SbF$_5$). The tube was then cooled to $-196\,°C$ and Xe (1.2 g, 9 mmol) was condensed in, and the tube was sealed. After the tube had been allowed to warm to room temperature (*caution*: pressure!) a dark red solution formed, from which black-red or light brown dichroitic single crystals were obtained on slow cooling to $-40\,°C$. Raman spectrum (1064 nm, $-120\,°C$, solid, cm^{-1}): $\tilde{v} = 710$ (4), 697 (5), 681 (shoulder), 673 (41), 658 (14), 646 (8), 627 (4), 614 (9), 603 (6), 384 (6), 307 (8), 293 (8), 229 (9), 129 (100).

Crystal structure determination of the tetragonal modification of **1** (for the triclinic modification see reference [1]): With the help of a special device a suitable crystal was mounted on a Bruker-Smart-CCD-1000-TM diffractometer and measured (Mo$_{K\alpha}$ radiation, graphite monochromator). Space group $P4_32_12$ (no. 96), $a = 944.1(1)$, $c = 2763.1(5)$ pm, $V = 2463.1 \times 10^6$ pm^3, $T = -100\,°C$, $Z = 8$, 1800 frames were measured at ω distances of $0.3°$ with 10 s/frame, 9616 measured, 2531 independent reflections, 143 parameters, $R(F \geq 4\sigma(F)) = 0.031$, $wR_2 = 0.060$. Absorption correction by equilibration of symmetry-related reflections (SADABS). Structure solution and refinement: SHELX programs.[5]

2: A sample of **1** was cooled to $-78\,°C$, and the excess xenon was pumped off with the vacuum system. The sample was sealed and warmed to $5\,°C$; gas evolution was observed. After slow cooling of the solution to $-30\,°C$, black, needle-shaped single crystals were formed. Crystal structure determination as described for **1**; space group $Pna2_1$ (no. 23), $a = 1451.9$, $b = 780.9(1)$, $c = 1857.2(3)$ pm, $V = 2105.8 \times 10^6$ pm^3, $T = -100\,°C$, $Z = 4$, 26556 measured, 6445 independent reflections, 263 parameters, $R(F \geq 4\sigma(F)) = 0,027$, $wR_2 = 0.054$.

3: Finely divided gold powder (140 mg, 0.71 mmol), prepared by reducing a HAuCl$_4$ solution with SO$_2$, was placed with HF (383 mg, 1.92 mmol), SbF$_5$ (1.04 g, 4.8 mmol), and XeF$_2$ (120 mg, 0.71 mmol) in a PFA reaction tube. Then Xe was condensed into the tube until a pressure of about 10 bar was reached at room temperature. The solution was initially orange, the gold dissolved very slowly and not completely. Cooling to $0\,°C$ for 12 h resulted in a violet solution from which ochre-colored crystals were obtained at $-35\,°C$. Raman spectrum (1064 nm, $-120\,°C$, solid, cm^{-1}): $\tilde{v} = 749$ (10), 732 (50), 717 (10), 694 (4), 675 (55), 646 (40), 589 (10), 577 (10), 483 (15), 380 (10), 272 (10), 204 (10), 121 (100). Crystal structure determination as described for **1**; space group $P\bar{1}$, (no. 2), $a = 560.5(3)$, $b = 730.6(4)$, $c = 807.6(3)$ pm, $\alpha = 90.99(2)$, $\beta = 91.24(2)$, $\gamma = 97.86(1)°$, $V = 327.42 \times 10^6$ pm^3, $T = -100\,°C$, $Z = 1$, 5067 measured, 1942 independent reflections, 80 parameters, $R(F \geq 4\sigma(F)) = 0.050$, $wR_2 = 0.133$.

4: Finely divided gold (160 mg, 0.8 mmol), XeF$_2$ (137.3 mg, 0.81 mmol), HF (200.4 mg, 10.2 mmol), and SbF$_5$ (1.48 g, 6.8 mmol) were placed into a PFA

reaction tube, and subsequently Xe was condensed in. The initial dark green (Xe$_2^+$) solution soon changed to red-brown at room temperature. The mixture was diluted with more HF to give a ratio of HF/SbF$_5$ of about 5:1, whereby gas evolution was observed and the color changed to orange. After the mixture had been cooled to $5\,°C$ for 12 h, a violet solution resulted from which green crystals of **4** were obtained at $-35\,°C$; in addition, small amounts of Xe-free gold products were formed. Raman spectrum (1064 nm, $-120\,°C$, solid, cm^{-1}): $\tilde{v} = 750$ (3), 687 (5), 671 (100), 659 (20), 525 (5), 499 (3), 300 (10), 281 (4), 228 (4), 153 (30), 101 (30). Crystal structure determination as described for **1**; space group $P\bar{1}$ (no. 2), $a = 661.6(1)$, $b = 852.8(1)$, $c = 925.1(1)$ pm, $\alpha = 72.44(1)$, $\beta = 79.27(1)$, $\gamma = 67.93(1)°$, $V = 459.6 \times 10^6$ pm^3, $T = -100\,°C$, $Z = 2$, 5695 measured, 2768 independent reflections, 122 parameters, $R(F \geq 4\sigma(F)) = 0.030$, $wR_2 = 0.066$.

5: Au (140 mg, 0.71 mmol), XeF$_2$ (120 mg, 0.71 mmol), SbF$_5$ (1.0 g, 4.6 mmol), and HF (500 mg, 25 mmol) were allowed to react with Xe (ca. 12 bar) as described for **3**; however, the mixture was only warmed to $-10\,°C$. A violet solution resulted from which black **1** and ochre-colored **5** crystallized at $-35\,°C$. Crystal structure determination as described for **1**; space group $P2_1/c$, $a = 795.2(1)$, $b = 995.9(2)$, $c = 2206.8(4)$ pm, $\beta = 97.11(1)°$, $V = 1734.3 \times 10^6$ pm^3, $T = -100\,°C$, $Z = 4$, 21402 measured, 5292 independent reflections, $R(F \geq 4\sigma(F)) = 0.030$, $wR_2 = 0.055$.

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[4] F. U. B. Einstein, P. R. Rao, J. Trotter, N. Bartlett, *J. Chem. Soc. A* **1967**, 478–482.
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