The investigated solid-state reaction is highly unusual and remarkable in two ways: First, the conversion of the starting material proceeds quickly and second, its morphology is unmodified. Taking into account the massive weight loss during the reaction, it is remarkable that not only the length but also the diameter of the iron wire used as starting material remained unaltered. Considering the densities of iron and iron silicide, and taking into account the weight loss of the product, a 34.5 % loss of volume could be calculated for the product according to Equation (1). This is not reflected in the outer shape, diameter, or length of the product in any way. In this case, the loss of volume must be accounted for by the formation of pores in the inner core of the material. The black areas in the electron backscattering images (Figure 3) are indicative of such pores. In our opinion, the formation of hollows and channels in the center of the wire is necessary for the reaction to proceed quickly. Through these channels, transport of material is made possible from the gaseous to the solid phase and back. In this way, the formation of a completely coated surface of the starting material, which would hinder further reaction, is avoided.

The iron core present at the beginning of the reaction allows the formed iron silicide to remain on the surface of the wire at first, then intergrow, and after completion of the reaction, the iron is converted into iron silicide while maintaining its original shape.

In general, it should be possible to transform solids into other solids while maintaining the starting material's morphology by employing reactions such as that we have reported here. Our ongoing research shows that this reaction is not a particular case but widely applicable. We have repeated this experiment with nickel and found that it reacts in an analogous way to iron. At 1000 °C it reacts with silicon chloride under the conditions employed for the synthesis of FeSi to form the γ-phase ($Ni_{31}Si_{12}$) with retention of the morphology. Also, chromium reacts with silicon tetrachloride to give the compound Cr_3Si. However, molybdenum and tungsten do not form gaseous dichlorides under these conditions. Accordingly, no particular gain in entropy occurs during the strongly endothermic reaction; thus, the reaction equilibrium favors silicon tetrachloride and the reaction does not proceed. In the future, it will be interesting to direct research towards the synthesis of micro- and nanostructured materials. In this context, the major problems that arose during the preparation of wires from high-temperature superconducting materials should be remembered.

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[7] Microprobe analyzer Camebax, Microbeam, Cameca, Institut für Mineralogie der Universität Hannover.

Gold Pentafluoride: Structure and Fluoride Ion Affinity**

In-Chul Hwang and Konrad Seppelt*

Our knowledge about binary gold fluorides is still limited. AuF can be detected as a molecule,[1] and according to recent calculations has a dissociation energy of 73 kcal mol^{-1}.[2] All attempts to isolate it in the condensed phase have failed so far. $F_3As{-}Au\cdots F\cdots SbF_5$ is evidently the only fully characterized compound having a $Au^{I}{-}F$ interaction.[3]

AuF_2 has not been isolated at all, although calculations predict it should be a linear molecule.[4] An Au^{II} ion surrounded only by fluorine atoms is observed in $Au(SbF_6)_2$; however, attempts to convert this into AuF_2 have failed.[5]

AuF_3, however, has been known for a long time.[6] Its helix structure with *cis*-fluorine bridges between almost square AuF_4 units is remarkable and is observed for a second time only in AgF_3.[7, 8] Salts with the $[AuF_4]^-$ ion are possibly the most stable gold fluorides.[6, 9] Thus, mixed-valent Au_3F_8 should evidently be formulated as $Au(AuF_4)_2$.[10]

The existence of AuF_4, prepared by the reaction between Au and F_2 in a nickel reactor at 500 °C,[11] however, is highly questionable. Reproduction of this synthesis under similar conditions yields NiF_2[12] and $Ni(AuF_4)_2$,[13] as shown by X-ray powder measurements.[12]

Gold pentafluoride was obtained shortly after the first isolation of hexafluoroaurates(V) $[Xe_2F_{11}]^+[AuF_6]^-$,[11] $Cs^+[AuF_6]^-$,[14] $[O_2]^+[AuF_6]^-$,[14, 15] and $[KrF]^+[AuF_6]^-$.[16] It is prepared by thermal decomposition of $[O_2]^+[AuF_6]^-$ or $[KrF]^+[AuF_6]^-$ [Eq. (1) and Eq. (2), respectively].[16, 17]

$$2\,Au + 7\,KrF_2 \xrightarrow{20\,^\circ C,\ -5\,Kr} [KrF]^+[AuF_6]^- \xrightarrow{60-65\,^\circ C} AuF_5 + Kr + F_2 \qquad (1)$$

$$Au + O_2 + 3\,F_2 \xrightarrow{400\,^\circ C} [O_2]^+[AuF_6]^- \xrightarrow{150-180\,^\circ C} AuF_5 + O_2 + 1/2\,F_2 \qquad (2)$$

Finally, according to our ab initio and density functional theory (DFT) calculations, AuF_6 should not exist, either as an octahedral or as a nonoctahedral molecule.

AuF_5 is an extreme oxidant and fluorination agent which makes its manipulation difficult. In contrast, salts with $[AuF_6]^-$ ions are quite stable. $[O_2]^+[AuF_6]^-$ can be recrystallized from anhydrous HF, and it does not react with HF/SbF_5 solutions. This is a first indication of the high acidity of the HF/AuF_5 system. The single-crystal structure determination (Figure 1) shows ordered $[O_2]^+$ and octahedral $[AuF_6]^-$ ions in an almost regular rhombohedral unit cell.[18]

The high-temperature phase of $[O_2]^+[AuF_6]^-$ is regular rhombohedral, which results inevitably in a threefold disorder of the $[O_2]^+$ ions around their center of gravity, as has

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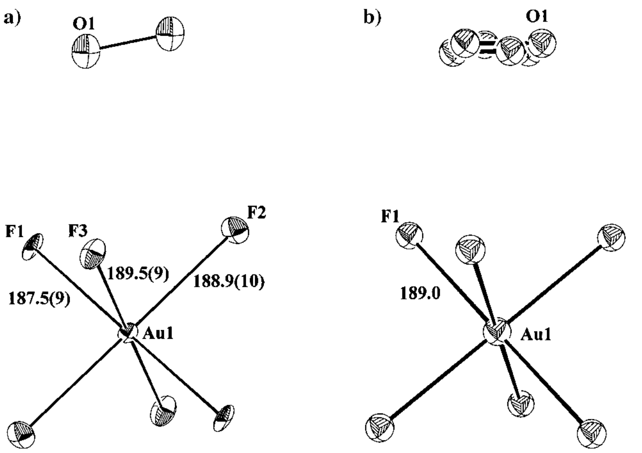

Figure 1. ORTEP representations of an $[O_2]^+[AuF_6]^-$ unit in the triclinic (a) and in the rhombohedrally disordered (b)[15] crystal structure (vibrational ellipsoids indicate 50% probability). One molecular unit is shown with the shortest interionic distance [pm]. Atoms without labels are generated by the center of symmetry.

been found earlier.[15] This rhombohedral–triclinic phase change is a very simple ordering process, since it affects only the cation. The determination of the O–O distance in $[O_2]^+$ salts is often difficult because of partial or complete disorder, and values between 95.0 and 121.6 pm are given in the literature.[15, 19–21] Here a value of 107.9(27) pm is obtained, which still has a large uncertainty but is at least fairly close to the value for the gaseous $[O_2]^+$ ion (112.3 pm).[22]

We have prepared AuF_5 according to route outlined in Equation (2) and have obtained single crystals by sublimation. The crystal structure determination reveals that AuF_5 exists as a dimer in the solid state (Figure 2).[23] AuF_5 is evidently the only pentafluoride that is dimeric. Other pentafluorides are monomeric (P,[24] As,[25] Cl,[26] Br,[27] I[27, 28]), tetrameric[29, 30] (Nb,[31] Ta,[31] Cr,[32] Mo,[33] W,[34] Tc,[35] Re,[36] Ru,[37] Os,[38] Rh,[39, 40] Ir,[41] Pt[42, 43]), or polymeric (Bi,[44] V,[36] α-UF_5,[45] β-UF_5[46]).

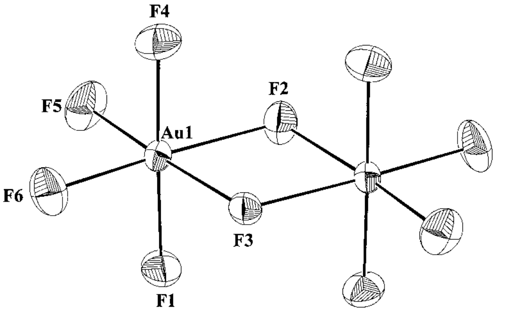

Figure 2. ORTEP representation of the dimer $(AuF_5)_2$ in the crystal (vibrational ellipsoids indicate 50% probability). Atoms without labels are generated by a mirror plane. Distances and angles, see Table 1.

In the gas phase AuF_5 is evidently also strongly associated.[47] A structure determination from electron diffraction data revealed a mixture of dimer and trimer in the ratio 82:18.[48] The structure data of the gaseous dimer agree well with our crystal structure data (Table 1). In this double fluorine-bridged structure the gold atoms get quite close to each other (313.5 pm). According to our calculations there is no gold···gold interaction that is frequently found among lower valent gold compounds. An earlier attempt to solve the crystal structure of AuF_5 from X-ray powder data gave a hexagonal cell with completely different metrics, and a spiral polymeric AuF_6 chain structure was suggested. Since the Au···Au distances of 424 pm are extremely large even for linear Au-F-Au bridges, this structure model appears questionable.[49] The surprisingly simple and temperature-independent Raman spectrum does not support the existence of several solid-state modifications (see Experimental Section and references [17, 49]).

Table 1. Distances [pm] and angles [°] in the $(AuF_5)_2$ molecule according to the crystal structure analysis, in comparison to the values for the gas structure (electron diffraction), and the results of ab initio calculations.

	Crystal structure	Electron diffraction[a]	Ab initio calculation
Au-F1, Au-F4	189.1(6), 190.1(5)	188.9(9)	196.5
Au-F2, Au-F3	201.3(5), 203.1(5)	203.0(7)	207.7
Au-F5, Au-F6	185.4(6), 187.5(6)	182.2(8)	192.5
F2-Au-F3	78.4(2)	80.1(5)	79.0
F1-Au-F4[b]	178.5(3)	181.0(11)	179.3
F5-Au-F6	87.0(3)	92.3(17)	96.2

[a] See ref. [48]. [b] Measured over center of ring.

The enthalpy of dimerization of two AuF_5 molecules, which are predicted to be square pyramidal, is calculated to be -70.1 kcal mol^{-1}.[50] This already indicates a very high fluoride ion affinity for AuF_5. Christe et al. have recently established a quantitative Lewis acid scale based on fluoride ion affinities which have been calculated by simplified ab initio methods.[51] Typical values are 83.1 (BF_3), 94.9 (PF_5), 105.9 (AsF_5), 114.6 ($AlCl_3$), 115.0 (AlF_3), 120.3 kcal mol^{-1} (SbF_5). The record of SbF_5 on this scale is broken by AuF_5 with 141.2 kcal mol^{-1} and $(AuF_5)_2$ with 128.8 kcal mol^{-1}. To describe the competition between AuF_5 and SbF_5 for an F^- ion we calculated the structure of the so far unknown dinuclar anion $[F_5Au\cdots F\cdots SbF_5]^-$ (Figure 3). It turns out that the bridging fluorine atom is closer to the gold than to the antimony atom, in spite of the larger ionic radius of gold. Thus, the structure is best described as $[AuF_6]^-\cdot SbF_5$.

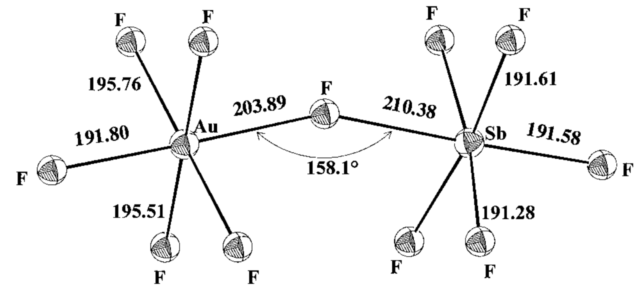

Figure 3. Calculated structure of the $[AuSbF_{11}]^-$ ion. Distances are given in pm.

It can therefore be assumed HF/AuF_5 solutions are stronger Brønstedt acids than the so far strongest acid HF/SbF_5.[52] But the extreme acidity of such a HF/AuF_5 solution is also the reason why AuF_5 dissolved in HF decomposes to AuF_3 and F_2. It is well known that the highest oxidation states are destabilized in acidic solutions.[5] Were it not such an unstable system, HF/AuF_5 could be used for protonation reactions that otherwise are not even possible with HF/SbF_5.

Experimental Section

$[O_2]^+[AuF_6]^-$ was prepared as described in reference [14, 15] After the autoclave had been cooled (0.05 K min^{-1}) from 400 °C to room temperature, and the pressure of excess O_2/F_2 had been relieved, $[O_2]^+[AuF_6]^-$ was obtained as cubic, light yellow crystals, which had formed by sublimation in the upper part of the monel autoclave. Single crystals of $[O_2]^+[AuF_6]^-$ were obtained by recrystallization from anhydrous HF on cooling from 50 to +20 °C, or from HF/SbF_5 on cooling from 20 to −18 °C. Raman spectra (1064 nm, 200 mW, RT, crystals): $\tilde{\nu} = 1833, 595, 228\ \mathrm{cm}^{-1}$. Crystal structure analysis:[18] With the help of a special device[53] a suitable crystal was mounted on a Bruker-SMART-CCD-1000-TM-diffractometer and measured. The SHELX programs were used for structure solution and refinement.[54, 55]

$(AuF_5)_2$: $[O_2]^+[AuF_6]^-$ (1 g) was placed into an 80 cm long perfluoroethylenepropylene (FEP) pyrolysis tube. This tube was connected to a metal vacuum line and cooled to −20 °C by external cooling. The solid was then pyrolyzed at 180 °C in high vacuum for 15 h. In the cooled zone at 60 °C a yellow solid, at +25 °C a red viscous liquid phase, and at 0 °C brown-red crystalline platelets were formed. After complete pyrolysis the tube was sealed. Raman spectra identified the yellow solid as $[O_2]^+[AuF_6]^-$, the red viscous liquid and the brown-red crystals were identified as AuF_5. AuF_5 is insoluble in anhydrous HF below 0 °C, above 0 °C it decomposes to AuF_3 and F_2. Raman spectrum (−100 °C, 1064 nm, 70 mW), (rel. intensities in parentheses): $\tilde{\nu} = 654(60), 596(100), 501(5), 279(3), 254(2), 239(7), 228(3), 220(7), 213(1), 178(1)\ \mathrm{cm}^{-1}$. Crystal structure analysis:[23] Measurement as described above.

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-411864 ($[O_2]^+[AuF_6]^-$) and CSD-411877 ($(AuF_5)_2$).

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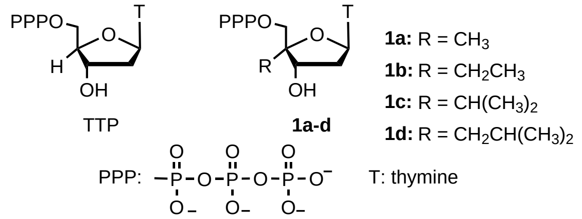
DNA Polymerase Selectivity: Sugar Interactions Monitored with High-Fidelity Nucleotides[**]

Daniel Summerer and Andreas Marx[*]

The essential prerequisite of any organism is to keep its genome intact and to accurately duplicate it before cell division. All DNA synthesis required for DNA repair, recombination, and replication depends on the ability of DNA polymerases to recognize the template and correctly insert the complementary nucleotide. In a current model, fidelity is achieved by the ability of DNA polymerases to edit nucleobase pair shape and size.[1] This model is supported by crystal structures of DNA polymerases that suggest the formation of nucleotide binding pockets, which exclusively accommodate Watson–Crick base pairs.[2] Nevertheless, structural data of DNA polymerases complexed with the DNA substrates and a noncanonical triphosphate, which would be very helpful for gaining insights into the causes of error-prone DNA synthesis, have at present not been reported. Thus, functional studies of DNA polymerases with nucleotide analogues have been shown to be extremely valuable.[1] Since most functional studies have focused on nucleobase recognition processes,[1] little is known about the impact of DNA polymerase interactions with the 2′-deoxyribose moiety and the participation of these interactions in processes which contribute to fidelity. Crystal structures of DNA polymerases together with enzyme mutation studies suggest that the sugar moiety of the incoming triphosphate is fully embedded in the nucleotide binding pocket and undergoes essential interactions with the enzyme.[1a, 2] Here we report a functional strategy to monitor steric constraints in DNA polymerases that act on the sugar moiety of an incoming nucleoside triphosphate within the nucleotide binding pocket. We found that novel modified nucleotide probes are substrates for a DNA polymerase with significantly increased selectivity compared to their natural counterpart. Through use of these high-fidelity nucleotides in functional investigations we could show that enzyme–sugar interactions are involved in DNA-polymerase fidelity mechanisms.

In order to sense interactions of DNA polymerases with the sugar moiety of incoming triphosphates we introduced alkyl labels at the 4′-position in the 2′-deoxyribose moiety in such a way that they do not interfere with hydrogen bonding, nucleobase pairing, and stacking. We designed steric probes **1a–d** by substituting the hydrogen atom at the 4′-position of thymidine triphosphate (TTP) with alkyl groups of different size (Scheme 1).



Scheme 1. Thymidine-5′-triphosphate (TTP) and the steric probes **1a–d**.

The synthesis of nucleosides **4a** and **4b** with different synthetic strategies (see Scheme 2) has been reported previously.[3, 4] However, these methods are not suitable for the synthesis of all the targeted compounds and the formation of undesired by-products was observed in the synthesis of **4a**.[3] Thus, we developed a more suitable access to the target compounds. Our synthesis started with the known alcohol **2**, which is easily accessible as described recently.[5] Compound **2** was converted into the methylated thymidine **4a** by functional-group interconversions (Scheme 2). Alkylated nucleosides **4b–d** were synthesized from known compounds[5] by employing Wittig reaction, desilylation, and subsequent reduction of the aliphatic double bond. Next, nucleosides **4a–d** were converted into the desired triphosphates **1a–d** following standard procedures.[6] In order to gain insights into potential effects of the modifications on the sugar conformation we performed conformation analysis based on coupling constants deduced from the ^1H NMR data by employing described methods.[7] We found only small differences in **1a–d** compared to natural TTP, which indicates that similar sugar conformations are present in solution (see Supporting Information).

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