Synthesis and Structure of a Dinuclear Gold(II) Complex with Terminal Fluoride Ligands

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Ⓢ *Supporting Information*

ABSTRACT: The potential for reductive elimination of fluorine from dinuclear gold(II) for catalysis has prompted our efforts to synthesize a dinuclear gold(II) fluoride complex. This has been achieved with bis(2,6-dimethylphenyl)formamidinate bridging ligands. In order to obtain this product, it was necessary first to synthesize the corresponding dinuclear gold(II) nitrate, which reacts readily with KF in a metathesis reaction. The nitrate complex and fluoride complexes have been structurally characterized. The Au—Au distance in the dinuclear fluoride, 2.595 Å, is longer than the distance found in the analogous chloride complex, 2.567 Å. This result is consistent with the presence of a fluoride "π electron effect" on the filled Au 5d orbitals. The Raman spectrum shows an Au—Au stretch at 206 cm^{-1}, which agrees with Woodruff's rules and the density functional theory computational model used for modeling the complex.

As Mankad and Toste recently described,[1] the catalytic reactions of gold have exploited the gold(I)/gold(III) redox cycle. Dinuclear gold(II) complexes also are well-known to undergo redox reactions but, to date, have not been involved in discussions of gold catalysis.[2] A dinuclear gold complex in combination with fluoride offers a potential system for delivering fluorine to carbon moieties, although this has yet to be found. Given the importance of organofluorine in medicine and industry,[3] we have explored the synthesis of a dinuclear gold(II) fluoride.

As a result of the special bonding characteristics of fluorine and its small size, electronegativity, and polarizing ability, Au—F bonding has been a rarity. There are numerous anionic $[AuF_x]^{n-}$ moieties[4−7] but only one example of a gold(I) fluoride complex.[8] Dinuclear gold(II) complexes with Au—F bonds were not known prior to this work. Bennett et al.[9] treated the dinuclear complex $[Au_2Cl_2(\mu\text{-}C_6H_4PPh_2)_2]$ with AgF and isolated a material with singlet ^{31}P and ^{19}F NMR resonances. However, this material was not characterized. The use of XeF by Leary and Bartlett[6] to induce the oxidative addition of $[Au_2(\mu_2\text{-}MeC_6H_3PPh_2)_2]$ did not give consistent spectroscopic results. Here we report the first example of a well-characterized Au—Au-bonded complex with terminal fluoride ligands, **2**, and its precursor, **1**, with labile, terminal nitrate ligands (Figures 1 and 2).

With heavy-metal ions, there are a few reported dinuclear complexes with terminal fluoride. A neutral lantern type of Pt_2^{6+} complex containing cyclometalated tertiary arsine ligands is produced by metathesis with AgF.[9] Two others with Re_2^{6+} or Re_2^{7+} cores[10] and hpp (hpp = 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2a]pyrimidine) ligands contain terminal fluorines, formed using a fluorinating agent or from decomposition of the PF_6^- anion or from an oxidizing silver reagent.

Our approach to the elusive F—Au^{II} bond was through substitution of a labile gold(II) nitrate, **1**. The nitrate as a ligand attached to the dinuclear gold(II) is more labile than halides. By disproportionation under nitrogen of the dinuclear gold(I) formamidinate[2] in the presence of nitrate, the dinuclear gold(II) nitrate was formed. Metathesis of this complex with KF leads to the dinuclear fluoride, **2**, which was crystallized (see the Supporting Information). The nitrate complex also readily reacts with other halides to form previously characterized products.[2]

Both **1** and the dinuclear gold(II) fluoride complex **2** have been characterized structurally. The Au^{II}—F distance in **2** of 2.287(11) Å is shorter (ca. 0.07) than that found in the related[2] chloride [2.366(3) Å] but longer than the Au^{II}—F distances in discrete AuF_4^{2-} units [2.076(9)−2.190(9) Å].[11−13] This reflects the strong trans influence of the Au^{II}—Au^{II} bond, a result similar to that found in the lantern-type dinuclear complex of platinum(III).[9] The Au^{I}—F bond distance in the carbene monomer[8] is notably shorter [2.0281(17) Å]. The carbene ligand efficiently removes the electronic density from the Au^{I}—F bond into its π system. In the dicationic complexes[1] of N-heterocyclic carbene (NHC) gold(III) fluorides, the bridging Au^{III}—F bonds [2.034(3) Å] are in the expected range of other bridging bonds [2.03(4)−2.10(5) Å] and longer than terminal Au^{III}—F bonds [1.77(5)−1.84(5) Å].

The F—Au^{II} bond produces a lengthening of the Au—Au distance, 2.595(2) Å, in **2** compared to the nitrate **1** and also to the analogous chloride, 2.567(2) Å.[2] This is good evidence for the fluoride π-electron effect (filled 2p orbitals on F at a short Au—F distance) upon filled 5d orbitals in the Au^{II}—Au^{II} bond. A similar observation has been noted with Re_2^{6+} and hpp ligands,[10] yet the metal—metal distance in the dinuclear lantern complex of Pt_2^{6+} is shorter [2.6530(4) Å] with terminal fluorides than with chlorides or bromides.[9] The marked deviation from linearity of the Au—Au—F angle, 167.39(4)° [which in the chloride is 177.8°(3)], also was noted in the Pt_2^{6+} (d^7) lantern complex [166.78°(5)] but

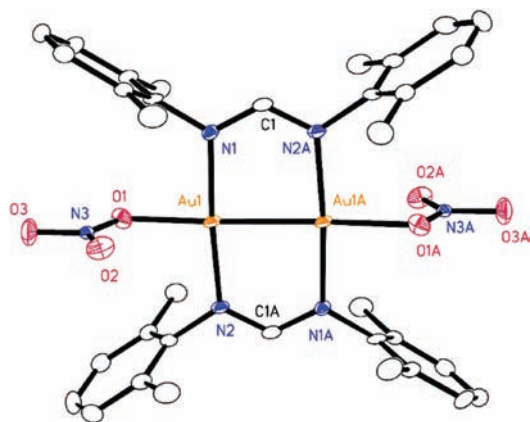**Figure 1.** Representation of [Au$_2$(2,6-dimethylformyl)$_2$(NO$_3$)$_2$] (**1**) with 50% probability ellipsoids. Hydrogen atoms and the solvent are omitted.
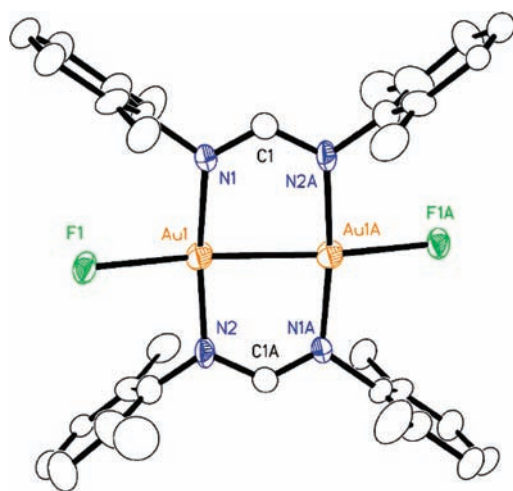

Figure 2. Thermal ellipsoid representation (50% probability) of **2**. Hydrogen atoms are omitted.

not in the Re$_2^{6+}$(d^4) analogue. Although this bent angle brings the fluoride close to two methyl hydrogen atoms on the ligand, the distance of 3.22(5) Å is larger than the sum of the C−H···F van der Waals radii (2.673 Å).

The negatively charged anions (nitrate or fluoride) connect laterally to the gold atoms. Crystallization of **1** in three solvents (toluene, THF, and acetone) renders triclinic crystals in the $P\bar{1}$ space group with each solvent molecule; even so, the *a*, *b*, and *c* parameters and the α, β, and γ angles are nearly the same from each solvent. The ^{1}H NMR spectrum in benzene shows 2,6-dimethylformamidinate methyl signals at 2.34 ppm for **1** and 2.65 ppm for **2**. In the aromatic region, the ^{1}H signals of the ring protons appear around 7.1 ppm, close to the N−CH−N proton signal at 7.46 ppm for the fluoride and at 7.4 ppm for the nitrate. In the UV−vis spectra (see the SI),[2] the shift to higher energy, I$^-$ < Br$^-$ < Cl$^-$ < F$^-$ (343 nm for the fluoride), correlates with a decrease in the Au−X distance. This tendency to a hypsochromic shift as the Au−OX distance shortens is seen with the nitrate **1** (359 nm) and benzoate analogues.[2]

In **1**, the strong anionic nature of the nitrate is reflected by the long Au−O distance of 2.118(5) Å, which in a benzoate analogue is 2.045(8) Å,[2] consistent with the lability of the gold−nitrate

bond. The short Au−Au distance of 2.4857(6) Å, similar to the distance found [2.489(10) Å] with terminal benzoates, is a result of the weak electron donation of oxo ligands. As is expected from this short distance, the associated Raman vibration ν is found to be the one with the highest frequency for a Au^{II}−Au^{II} bond. This observation is based on a computational model, 200.2 cm^{-1}, Woodruff's rules, 198.7 cm^{-1}, and the actual Raman measurement, 206 cm^{-1} (see the SI).

In **2**, the Au^{II}−F distance of 2.287(11) Å is shorter (ca. 0.07) than that in the related chloride[2] [2.366(3) Å] but longer[3] than Au^{II}−F bonds in discrete AuF$_4^{2-}$ units [2.076(9)−2.190(9) Å], reflecting the trans influence (vida infra) of the opposite Au^{II}−Au^{II} bond. The ^{19}F NMR spectrum shows a single peak at 2.314 ppm in C$_6$D$_6$. The analogous lantern-type complex[9] of platinum(III) also shows an enlargement of the terminal Pt−F bond compared to [PtF$_6$]$^{2-}$ units. In comparison, the Au^I−F bond in the Sadighi[8] monomer is notably shorter [2.0281(17) Å]. The carbene (NHC) ligand efficiently withdraws the electronic density into its π system. In the dicationic complex[1] of a NHC gold(III) fluoride, the bridging Au^{III}−F bonds [2.034(3) Å] are in the expected range of other bridging Au^{III}−F bonds [2.03(4)−2.10(5) Å] and longer than nonbridging ones [1.77(5)−1.84(5) Å].[14]

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Details of the syntheses, analytical results, Raman (experimental and computational), NMR, and UV−vis spectra, structural data, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

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