

Synthesis and X-ray Structures of Dinuclear and Trinuclear Gold(I) and Dinuclear Gold(II) Amidinate Complexes†

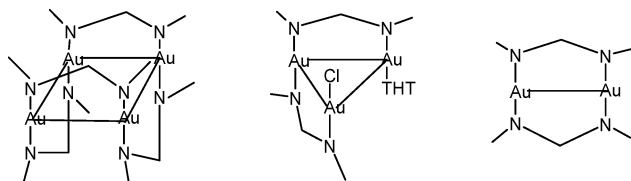
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The structures of the trinuclear gold(I), $[\text{Au}_3(2,6\text{-Me}_2\text{-form})_2\text{-(THT)Cl}]$, the dinuclear $[\text{Au}_2(2,6\text{-Me}_2\text{-form})_2]$, and the oxidative-addition product $[\text{Au}_2(2,6\text{-Me}_2\text{-form})_2\text{Cl}_2]$ formamidinate complexes are reported. The trinuclear complex is stable with gold–gold distances 3.01 and 3.55 Å. The gold–gold distance in the dinuclear complex decreases upon oxidative-addition with halogens from 2.7 to 2.5 Å, similar to observations made with the dithiolates and ylides.

Anionic, bridging, nitrogen bonded ligands display a rich chemistry with gold(I), not unlike the extensive chemistry developed with ylide ligands.¹ Furthermore, small molecular gold clusters which serve as catalyst precursors for CO and olefin oxidation have prompted additional interest in gold cluster syntheses, especially with cluster precursors not containing elements that are potential catalyst poisons.² The amidinates contain only C, H, N, and sometimes O and/or halogens. Gold(I) cluster compounds also have attracted much attention due to their intriguing structural diversity and short metal–metal aurophilic bonding interactions. This is the case for tetranuclear gold(I) amidinate complexes where short $\text{Au}\cdots\text{Au}$ contacts are often observed.^{3–7} Visible photoluminescence under UV excitation also is present.



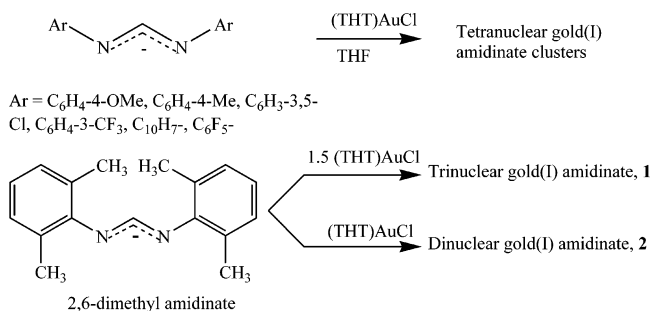
Formamidines, ArNHC(H)NAr , are capable of forming flexible coordination modes (see graphic with structures) with metal ions, which lead to various molecular arrangements.⁸

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† Dedicated to Professor F. A. Cotton on the occasion of his 75th birthday.

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Scheme 1



Among the best known examples are the “paddlewheels”⁹ Upon attempting to synthesize gold(I) complexes with the ligand Hpp, 1,3,4,6,7,8-hexahydro-pyrimido[1,2-a]pyrimidine, used successfully by Cotton⁹ to form $[\text{M}_2]^{4+}$ paddlewheel complexes, an oxidized, dinuclear Au(II) product was isolated.¹⁰ This compound formed spontaneously upon reacting the anionic ligand with the $(\text{THT})\text{AuCl}$ in CH_2Cl_2 . It has the shortest Au–Au (2.47 Å) distance recorded to date. By removing the halogenated solvent from the reaction, using THF, the same product was obtained in about 50% yield, along with Au metal. Thus, dinuclear amidinate complexes support the formation of metal–metal bonded Au(II)–Au(II) products.

The tetranuclear gold(I) clusters $[\text{Au}_4(\text{ArNC(H)NAr})_4]$, Ar = C₆H₄-4-OMe,³ C₆H₃-3,5-Cl,³ C₆H₄-4-Me,³ C₆H₄-2-CF₃,⁷ C₆F₅,⁷ and C₁₀H₇,⁷ were synthesized in ~55–80% yield by reaction of sodium or potassium amidinate with gold(I)

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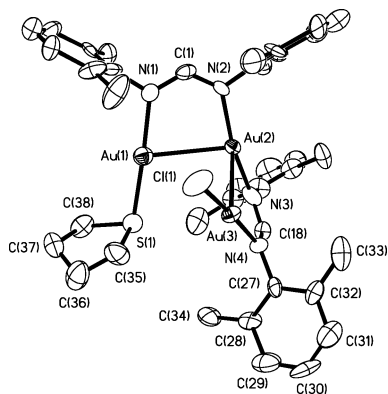


Figure 1. Thermal ellipsoid drawing of **1**. Selected distances (Å) and angles (deg): Au(3)–Cl(1) 2.258(6), Au(3)···Au(2) 3.0181(10), Au(1)–N(1) 2.044(16), Au(1)–S(1) 2.245(6), Au(1)···Au(2) 3.0132(12), N(3)–Au(2)–N(2) 167.5(7).

chloride in THF (Scheme 1). The base-stabilized tetranuclear gold(I) 3,5-diphenylpyrazolate cluster [(dppm)₂Au₄(Ph₂pz)₂](NO₃)₂ also has been reported.⁵ The four gold atoms are located at the corners of a rhomboid with the amidinate ligands bridging above and below the near plane of the four Au(I) atoms. The average Au···Au distance is ~3.0 Å, typical of Au(I)···Au(I) auriphilic interactions. Similar structural arrangements have been found in the tetrameric 1,3-diphenyltriazenidogold(I) complex, [Au₄(PhNNNPh)₄] (Au···Au = 2.85 Å),⁴ and the tetranuclear gold pyrazolate complex [Au₄(μ-4^{-t}Bu-pz)₄] (Au···Au = 3.1155(7)–3.1886(7) Å).⁶

A trinuclear species [Au₃(2,6-Me₂-form)₂(THT)Cl] is isolated when a sterically bulky formamidinate ligand is used such as the 2,6-dimethyl derivative (Supporting Information). By the reaction of the potassium salt of the formamidinate ligand and (THT)AuCl in a (1:1.5) stoichiometric ratio, the trinuclear species forms and is isolated as monoclinic (*P*₂₁/*n*), prismatic crystals.¹¹ Attempts to obtain a tetranuclear gold species with this ligand, using different stoichiometric ratios, were not successful, and instead, a dinuclear species is isolated (vide infra). ¹H NMR of the trinuclear species shows the characteristic resonances of the tetrahydrothiophene ligand. The complex is stable at room temperature and in light for months. The structure contains two short Au···Au distances of ~3.01 Å and a long Au···Au distance of 3.55 Å (Figure 1). The Au–S distance is 2.245(6) Å, and Au–Cl is 2.258(6) Å.

The chemistry of gold(I) pyrazolates includes various species such as trinuclear, tetranuclear, and hexanuclear compounds, with the trinuclear product being the most common. A tetranuclear gold(I) pyrazolate compound forms when a bulky group such as *tert*-butyl is used.⁶ In the amidinate

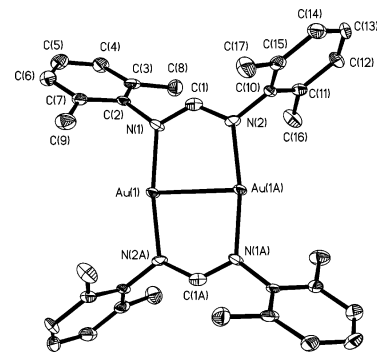


Figure 2. Thermal ellipsoid drawing of **2**. Selected distances (Å) and angles (deg): Au(1)–N(1) 2.035(7), Au(1)···Au(2) 2.711(3); N(1)–Au(1)–N(2) 170.2(3).

chemistry, a trinuclear species forms when methyl groups are in the ortho position. Similar results are obtained when ortho isopropyl groups are used.¹² In gold(I) carbenate and imidazolate chemistry, the trinuclear species are the only neutral complexes isolated to date.¹³

The dinuclear complex, **2**, [Au₂(2,6-Me₂-form)₂], is isolated in quantitative yield by the reaction of (THT)AuCl and the potassium salt of 2,6-Me₂-form in a 1:1 stoichiometric ratio (Supporting Information). The Au···Au distance is 2.711(3) Å, and the N–Au–N angle is 170.2(3)° (Figure 2). To our knowledge, there is only one other example of a symmetrically bridged dinuclear gold(I) nitrogen complex, {Au₂[(Me₃SiN)₂C(Ph)]₂} with Au···Au = 2.646 Å.¹⁴

Few nitrogen ligand complexes of gold(II) are known compared with the more common gold(I) and gold(III) species. The gold(II) complexes generally are synthesized by oxidative addition of halogens or pseudo-halogens to the dinuclear gold(I) species, often forming darkly colored products.^{15–17} The dihalide amidinate species (vide infra) release the halogen upon gentle heating.

When 1 mmol of Cl₂, Br₂, or I₂ is added to 1 mmol of [Au₂(2,6-Me₂-form)₂] in THF at room temperature, an immediate color change from colorless to a very dark green or brown occurs. Well-shaped dark orange or brown block crystals grow out of the solution by slow evaporation. Thermal gravimetric analysis and differential thermal analysis show the release of solvent of crystallization followed by the loss of the halogen. X-ray structures of the products (X = Cl, Br, I) show slight differences in the Au···Au distances, from 2.71 Å in **2** to 2.51–2.57 Å in the gold(II) species. The Au–X distances, Au–Cl = 2.36 Å, Au–Br = 2.47 Å, Au–I = 2.68 Å, are normal. The oxidized products also can

(11) Crystal data for **1**, C₃₈H₄₆Au₃ClN₄S: *M*_r = 1217.22, monoclinic, space group *P*₂₁/*n*, *a* = 10.8294(6) Å, *b* = 21.4450(13) Å, *c* = 16.7756(10) Å, β = 99.5270(10)°, *V* = 3842.2(4) Å³, *Z* = 4, *R*₁ = 0.0858, and *wR*₂ = 0.1671. Crystal data for **2**, C₃₄H₃₈Au₂N₄: *M*_r = 896.62, triclinic, space group *P*₁, *a* = 7.354(6) Å, *b* = 9.661(7) Å, *c* = 11.421(10) Å, α = 81.74(5)°, β = 99.5270(10)°, γ = 86.07(9)°, *V* = 760.1(4) Å³, *Z* = 1, *R*₁ = 0.0465, and *wR*₂ = 0.1243. Crystal data for **3**, C₃₄H₃₈Au₂Cl₂N₄·1.5C₆H₁₂: *M*_r = 1093.76, monoclinic, space group *P*₂₁/*c*, *a* = 11.012(2) Å, *b* = 18.464(4) Å, *c* = 19.467(4) Å, β = 94.86(3)°, *V* = 3943.7(14) Å³, *Z* = 4, *R*₁ = 0.0689, *wR*₂ = 0.1707.

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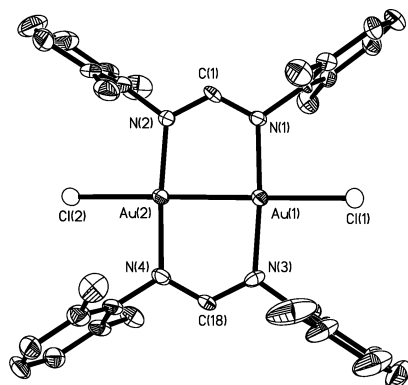


Figure 3. Thermal ellipsoid drawing of **3**. Selected bond distances (Å) and angles (deg): Au(1)–N(1) 2.020(8), Au(1)–Cl(1) 2.356(2), Au(1)···Au(2) 2.5176(7); N(1)–Au(1)–N(3) 174.9(3), N(1)–C(1)–N(2) 123.9(9).

be isolated by using various halogenating agents such CH_2X_2 , CX_4 , or $\text{XCH}_2\text{CH}_2\text{X}$. Aqua regia also chlorinates **2** (Figure 3). An unsymmetrical product is obtained when methyl iodide, CH_3I , is added to **2** at a low temperature, in the absence of light and oxygen.¹⁸ The dinuclear Au(II) complexes $[\text{Au}(\text{CH}_2)\text{PPh}_2\text{X}]_2$ and $[\text{Au}(\text{MTP})\text{X}]_2$ (MTP =

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$\text{CH}_2(\text{S})\text{PPh}_2$; X = Cl, Br, I) have short Au(II)–Au(II) bonds with distances around 2.6 Å. The Au(I) precursors have gold–gold distances close to 3.0 Å. This dramatic decrease in the Au–Au distance is a result of the formation of two Au–X bonds and a single Au–Au bond along the common axis, forming stable, tetracoordinated d^9 – d^9 Au(II) centers.¹⁷

While theoretical and experimental data exist relating the aurophilic distance to “softness” of the ligands,¹⁹ recent density functional theory calculations produce unexpected results with these N ligands.²⁰ The ground state for the dinuclear gold(I) species is calculated to be a HOMO with δ metal–metal antibonding, not σ metal–metal antibonding as had been observed with the ylides.²¹

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Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **1**, **2**, and **3**. Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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