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Synthesis and X-ray structures of silver and gold guanidinate-like complexes. A Au(II) complex with a 2.47 Å Au–Au distance

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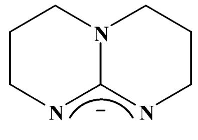
The structures of the tetranuclear silver(I), [$Ag_4(hpp)_4$], and the dinuclear gold(II), [$Au_2(hpp)_2Cl_2$], (hpp = 1,3,4,6,7,8-hexahydro-pyrimido[1,2-*a*]pyrimidinate) guanidinate-like bases are reported and show a silver–silver distance of 2.8614(6) Å and a gold–gold distance of 2.4752(9) Å, the shortest Au–Au bond heretofore reported.

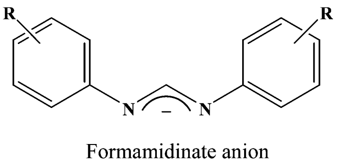
Previous work in our laboratory involving gold-nitrogen chemistry has led to the structural characterization of the homogenous group (11) pyrazolates, [M(μ-3,5-Ph_2pz)]$_3$, M = Cu^I, Ag^I, Au^I which includes the hexanuclear product [Au_6(μ-3,5-Ph_2pz)$_6$].[1,2] During recent studies of the chemistry of these metal pyrazolates as materials for the synthesis and study of polynuclear Ag(I) complexes, the silver μ-3,5-diphenylpyrazolate [Ag_3(μ-3,5-Ph_2pz)$_3$]$_2$ has been synthesized.[3] The base-stabilized tetranuclear gold(I) 3,5-diphenylpyrazolate cluster [(dppm)$_2Au_4(Ph_2pz)_2$]NO_3 also has been synthesized.[4] Recently we reported the structures and characterization of the tetranuclear gold(I) formamidinate clusters, [Au(ArNC(H-)NAr)]$_4$, by the reaction of Au(THT)Cl (THT = tetrahydrothiophene) with sodium formamidinates.[5] These formamidinate clusters show that the four gold atoms are located at the corners of a rhombus with the formamidinate ligands bridged above and below the near plane of the four Au^I atoms.

The remarkable ability of the anion of the guanidinate-type molecule Hhpp (1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine) to form complexes with extra short M–M bonding distances has been described by Cotton *et al.*[6] Complexes with extremely low ionisation enthalpies (3.51 eV), even lower than that of the caesium atom, have been characterized.[7] Cotton reported that the $Mo_2(hpp)_4$ molecule is so easily oxidized that a chlorinated solvent such as CH_2Cl_2 oxidizes it essentially quantitatively to $Mo_2(hpp)_4Cl_2$ and $Mo_2(hpp)_4Cl$.[8] A special characteristic of the hpp anion is its ability to stabilize metals in a high oxidation state. We report here the dinuclear gold(II) complex, [$Au_2(hpp)_2Cl_2$], **1**, which has the shortest Au–Au bond distance reported to date. Earlier work with ylides[1d] and sulfur bonded ligands (*vida infra*) has led to the formation of many Au(II)–Au(II) bonded materials but none previously with nitrogen ligands.

The tetranuclear silver(I) complex, [$Ag_4(hpp)_4$], **2**, forms in remarkable contrast to the copper(I) complex previously reported, [$Cu_2(hpp)_2$] (Cu–Cu = 2.453(1) Å),[6] and the gold(II) complex reported here. The relative roles of ligand bite distances and electronic properties in dictating the structures formed and the distances between metal atoms are still vague.



Hpp anion



Formamidinate anion

Complexes **1**[†] and **2**[‡] are synthesized by the reaction of Au(THT)Cl and $AgNO_3$ with sodium hpp in CH_2Cl_2 and MeCN, respectively. Crystallization of a product from the dark green solution of **1** in CH_2Cl_2/hexanes gave a black semi-crystalline material that is quite hygroscopic and has a tar-like appearance when exposed to moist air. From this tar, crystals were grown using CH_2Cl_2 or THF layered with hexanes as orange blocks in about 50% yield. The mass spectrum of **1** shows that the dichloride species **1**, easily loses a chlorine atom (m/z = 705) and one Hhpp ligand (m/z = 559). The orange product dissolves in CH_2Cl_2 to form a yellow solution when very dilute.

The X-ray structure of **1** [§] reveals a gold–gold distance of 2.4752(9) Å, which is significantly shorter than the distance observed in metallic gold (2.884 Å) (Fig. 1).[9] The dinuclear Au^{II} complexes [Au(CH_2)PPh_2X]$_2$ and [Au(MTP)X]$_2$ (MTP = CH_2(S)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 distance results from the formation of two Au–X bonds and a single Au–Au bond along a common axis, forming stable d^9–d^9 systems.[10] In 1988, we reported the short Au^{II}–Au^{II} distance of 2.55 Å found in [Ph_4As]$_2$[Au_2(*i*-MNT)$_2Cl_2$], MNT = $S_2C_2(CN)_2^{2-}$, a product formed by chlorine oxidation of the corresponding digold(I) dithiolate.[11] The oxidation of Au^I in the hpp complex occurs spontaneously in the synthesis. When the complex is synthesized in THF, a product of unknown structure is initially formed which appears to undergo a self-redox reaction to form the Au^{II} product and Au^0. A gold mirror forms on the reaction flask walls after standing. Since the maximum yield is only 50% in this solvent, the solvent was replaced by CH_2Cl_2 which can act as the oxidant. This approach to the redox reaction was reported by Cotton.[8]

Accumulated data regarding the reactivity of dinuclear and polynuclear metal complexes is consistent with the ability of neighbouring metal atoms and coordinated ligands to influence

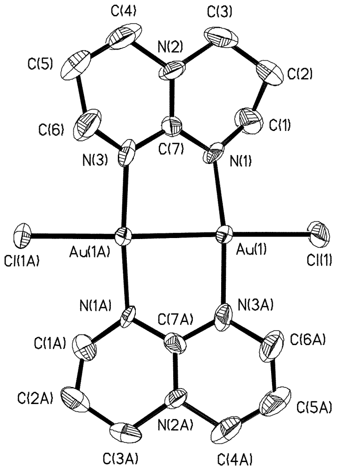


Fig. 1 A thermal ellipsoid drawing of **1**. The nonplanarity of the ligands is clearly shown. Selected distances (Å) and angles (°): Au(1)–Au(1A) 2.4752(9), Au(1)–N(3A) 2.010(11), Au(1)–N(1) 2.062(9), Au(1)–Cl(1) 2.408(3); N(3A)–Au(1)–N(1) 169.4(6), N(3A)–Au(1)–Cl(1) 91.9(3), N(1)–Au(1)–Cl(1) 94.2(3), N(3A)–Au(1)–Au(1A) 87.2(3), N(1)–Au(1)–Au(1A) 86.1(3), Cl(1)–Au(1)–Au(1A) 176.0(6), N(1)-C(7)-N(3) 122.5(10).

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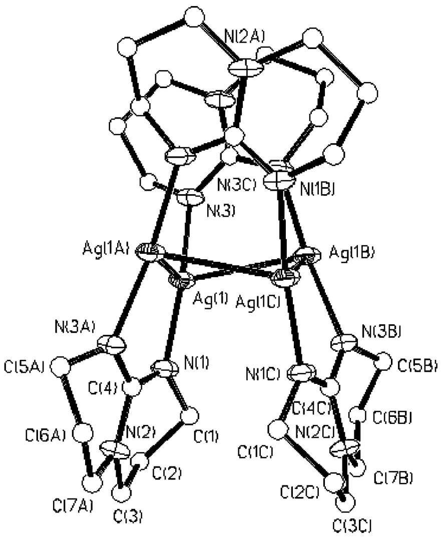

Fig. 2 A thermal ellipsoid drawing of **2**. The nonplanarity of the ligands is clearly shown. Selected distances (Å) and angles (°): Ag(1)–Ag(1A) 2.8614(6), Ag(1)–N(1) 2.076(4), Ag(1)–N(3) 2.076(4); N(1)–Ag(1)–N(3) 172.1(2), Ag(1A)–Ag1-Ag(1B) 88.058(5).

the oxidative addition process generally, both positively and negatively.[12] Cationic metal centers or electron withdrawing ligands near the oxidation center can be expected to stabilize the HOMO or "closed-shell" ground state. This increases the HOMO–LUMO separation, thereby making oxidative addition less favourable. Electron-rich anionic complexes or complexes with strongly donating ligands will decrease the HOMO–LUMO separation rendering oxidative addition process more feasible.

The reaction of $AgNO_3$ with Nahpp forms a tetranuclear product $[Ag_4(hpp)_4]$, **2**. ¶ The four silver atoms are located at the corners of a rhomboid with the hpp ligands bridged above and below the near plane of the four Ag^I atoms (Fig. 2). The Ag···Ag distance is 2.8614(6) Å, typical of $Ag^I\cdots Ag^I$ interactions. The angle at Ag···Ag···Ag is 88.058(5)°. The four silver atoms in **2** lie in a near plane with a torsion angle of 20.9° at Ag(1)Ag(1A)Ag(1C)Ag(1B). The rhomboidal geometry of the Ag_4 complex seems to be attributable to steric factors. The deviation from the mean plane is 1.61 Å. The silver(I) centers in the *C*-alkyl functionalized formamidinate tetranuclear clusters have a planar rhombic arrangement with bridging amidinate ligands above and below the Ag_4 plane, typical of the structure of **2**. The Ag···Ag distances range from 2.87–2.98 Å.[13]

Attempts to isolate the parent gold compound, $[Au_2(hpp)_2]$ in crystalline form continue, using reducing agents such as $NaHBEt_3$ and potassium metal.

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Notes and references

† Preparation of $Au_2(hpp)_2Cl_2$, **1**. A reaction flask was charged with 0.321 g (1.0 mmol) of Au(tht)Cl and 0.161 g (1.0 mmol) of Na(hpp) in 10 mL DCM and cooled to −78 °C. After 1 h, a black solid, namely $Au_2(hpp)_2Cl_2$, was separated with hexane. $Au_2(hpp)_2Cl_2$ was washed with 5 mL of hexane and dried under vacuum (200 mg, 54%). Orange crystals of $Au_2(hpp)_2Cl_2$ are grown from a THF solution carefully layered with hexanes. ^1H NMR ($CDCl_3$, ppm): δ = 1.95 (quin, CH_2), 3.40 (t, CH_2), 3.51 (t, CH_2).

‡ Preparation of $Ag_4(hpp)_4$, **2**. The same preparation as for $Au_2(hpp)_2Cl_2$ was used except $AgNO_3$ was added to MeCN to form an orange solution after work-up. Yellow crystals of $Ag_4(hpp)_4$ grow from a THF solution carefully layered with hexanes.

§ Crystal data for **1**, $C_{14}H_{24}Au_2Cl_2N_6$: M_r = 741.22, orthorhombic, space group *Iba*2, a = 10.866(5), b = 20.745(5), c = 8.164(5) Å, $\alpha = \beta = \gamma$ = 90° , V = 1840.3(15) Å^3, T = 110(2) K, Z = 4, μ(Mo–Kα) = 16.226 mm^{-1}, 4576 reflections measured, d_{calc} = 2.675 g cm^{-3}, $R1$ = 0.0365, and $wR2$ = 0.0903 (for $I > 2\sigma(I)$). CCDC 217313. See http://www.rsc.org/suppdata/cc/b3/b309724m/ for crystallographic data in .cif or other electronic format.

¶ Crystal data for **2**, $C_{28}H_{48}Ag_4N_{12}$: Mr = 982.25, tetragonal, space group $I\bar{4}$, a = 16.2031(9), b = 16.2031(9), c = 12.7823(14) Å, $\alpha = \beta = \gamma$ = 90°, V = 3355.9(5) Å^3, T = 110(2) K, Z = 4, μ(Mo–K$_\alpha$) = 2.339 mm^{-1}, 11033 reflections measured, d_{calc} = 1.948 g cm^{-3}, $R1$ = 0.0441, $wR2$ = 0.1063 (for $I > 2\sigma(I)$). Data were collected using a Siemens (Bruker) SMART CCD (charge coupled device) based diffractometer equipped with a LT-2 low-temperature apparatus operating at 110 K. A suitable crystal was chosen and mounted on a glass fiber using cryogenic grease. Data were measured using omega scans of 0.3° per frame for 60 seconds, such that a hemisphere was collected. The structure was solved and refined as described in ref. 4. Hydrogen atom positions were calculated by geometrical methods and refined as a riding model. CCDC 217314.

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