The first sandwich silver cluster of a trinuclear cyclic gold(I) complex

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A new type of metal sandwich structure $[Ag\{[Au(\mu\text{-}N^3,C^2\text{-}bzim)]_3\}_2]BF_4{\cdot}CH_2Cl_2$ 1, is formed by reacting the neutral, triangular cluster $[Au(\mu\text{-}N^3,C^2\text{-}bzim)]_3$ with Ag^+; these units stack with two short intermolecular Au···Au distances of *ca.* 3.2 Å.

In 1970 Vaughan[1] reported the synthesis of organogold derivatives of the 2-pyridyl ligands that were thought to be trinuclear cyclic gold(I) species, based upon the coordination requirements of the gold(I) atoms. In the following years analogous compounds were isolated and depending upon the types of 1,2 bridging ligands, N–Au–C[2] or N–Au–N[3] arrangements were described. Some of these were structurally characterized.[4] The structures all have nine-atom rings where the intramolecular Au···Au distances range between 3.224(1) and 3.368(1) Å. Only weak metal–metal interactions are present, hence these compounds are classified as polynuclear non-cluster species.

Reactivity investigations of these trimeric gold(I) complexes indicate that the bridging ligand plays an important role. While the carbeniato gold(I) derivatives undergo stepwise oxidative halogen addition to form three distinct complexes, $[AuC(OMe){=}NMe]_3X_n$ (n = 2,4, 6; X = Br, I),[5] the pyrazolato trimers $[Au(\mu\text{-}3.5\text{-}R_2pz)_3\}$ (R = alkyl, aryl) only oxidized at one center yielding mixed valence $Au^I{}_2Au^{III}$ complexes: $[Au(\mu\text{-}3,5\text{-}R_2pz)]_3I_2$;[6] $[Au(\mu\text{-}3,5\text{-}Ph_2\text{-}4\text{-}Cl\text{-}pz)]_3Cl_2$.[7] Additionally, $[Au(\mu\text{-}N^3,C^2\text{-}bzim)]_3$ (N^3,C^2-bzim = 1-benzylimidazolate) also undergoes oxidation by only 1 equiv. of I_2 yielding the mixed-valence complex $[Au(\mu\text{-}N^3,C^2\text{-}Bzim)]_3I_2$.[8] However, this complex can be oxidized completely to a Au^{III} derivative $[Au(\mu\text{-}N^3,C^2\text{-}bzim)]_3C1_6$[9] by $SOCl_2$.

While reactions of metal ions such as $AuPPh_3^+$, $Ag(PPh_3)_2^+$ or Ag^+ with transition metal clusters represent a well known method for cluster expansion synthesis,[10] few examples of the addition of metal ions to dinuclear gold(I) complexes have been reported.[11] An addition strategy has not been reported at all for cyclic trimer gold(I) compounds. Here we describe the results of the reaction of $[Au(\mu\text{-}N^3,C^2\text{-}bzim)]_3$ with Ag^+ to produce a novel[12] silver sandwich cluster $[Ag\{[Au(\mu\text{-}N^3,C^2\text{-}bzim)]_3\}_2]^+$. By layering a solution of $AgBF_4$ in MeCN over a CH_2Cl_2 solution of $[Au(\mu\text{-}N^3,C^2\text{-}bzim)]_3$, a yellow luminescent† precipitate was formed immediately in almost quantitative yield. After several months, the precipitate, standing in contact with the solvent was completely transformed into small yellow crystals of the cluster $[Ag\{[Au(\mu\text{-}N^3,C^2\text{-}bzim)]_3\}_2]BF_4{\cdot}CH_2Cl_2$ **1**. The compound is stable in the solid state‡ but dissolution in a coordinating solvent like Me_2SO yields the starting materials as determined by NMR spectroscopy.

The molecular structure§ of the cation **1** is shown in Fig. 1 while Fig. 2 presents the stacking arrangement observed. The naked silver ion center is bonded to six gold atoms to form a distorted, Ag^I centered trigonal prism of Au^I atoms with Ag–Au distances ranging from 2.731(2) to 2.922(2) Å, indicative of appreciable metal–metal bonding. These distances are close to distances observed in other gold–silver derivatives[11] wherein the silver atoms bridging two gold centers are always supported by other ancillary ligands.

The gold–silver bonds may be regarded as arising from a nucleophilic or Lewis base interaction of the gold atoms with the silver ion, which acts as a Lewis acid. The d^{10}–d^{10} closed shell Au^I–Ag^I bonds probably also relate to the weak Au···Au bonds, estimated to be 6–8 kcal mol^{-1} (1 cal = 4.184 J), which arise from correlation and relativistic effects.[13] The average Au···Au intramolecular distance in the cyclic trimer moiety

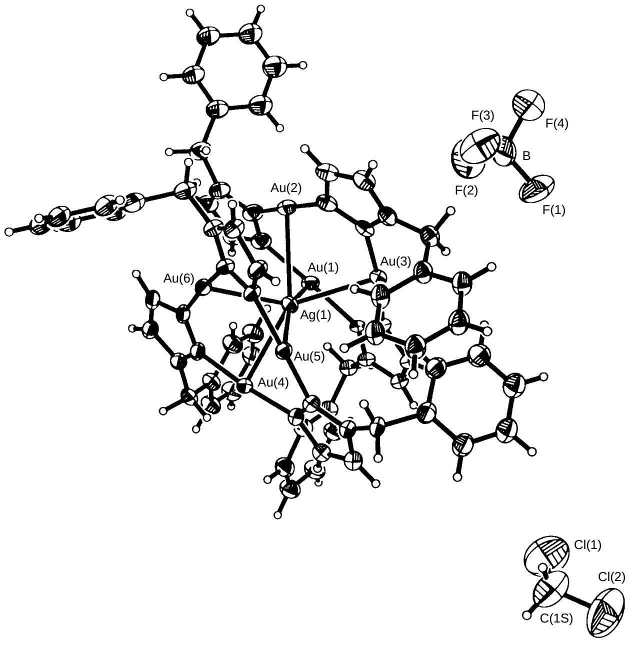

Fig. 1 Thermal ellipsoid drawing (50% probability) of the structure of $[Ag\{[Au(\mu\text{-}N^3,C^2\text{-}bzim)]_3\}_2]BF_4{\cdot}CH_2Cl_2$ **1**. The Ag–Au distances range from 2.731(2) to 2.922(2) Å.

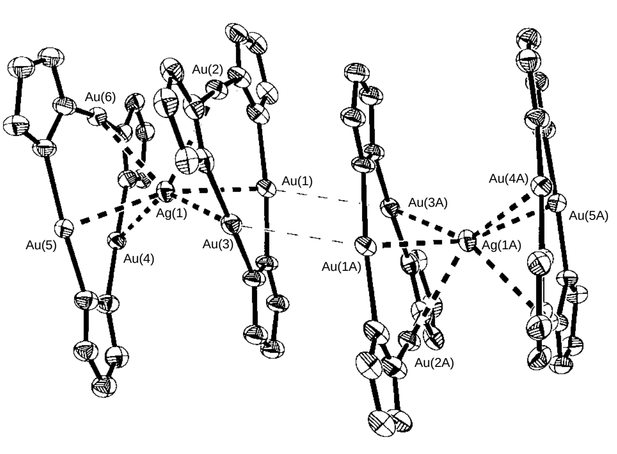

Fig. 2 Stacked sandwich structure of the cation of $[Ag\{[Au(\mu\text{-}N^3,C^2\text{-}bzim)]_3\}_2]BF_4{\cdot}CH_2Cl_2$ **1**. The intermolecular Au(1)···Au(3A) distance is 3.268(2) Å.

forming the sandwich unit is 3.19 Å. This is shorter than the distance observed for $Au^I\cdots Au^I$ in $[Au(\mu\text{-}N^3,C^2\text{-Bzim})]_3I_2$.[8]

In Fig. 2, the interactions between two close sandwich units can be seen. The short distances Au(3)···Au(1A) 3.268 Å and Au(4)···Au(5A) 3.116 Å, are indicative of weak intermolecular bonds between gold atoms. Considering also the atoms Au(2) and Au(2A) which are widely separated, a characteristic Au_6 cycle is formed in a chair conformation. This arrangement also was observed in the carbeniato trimer $[AuC(OEt){=}NC_6H_4Me]_3$ structure.[4] The inter- and intra-molecular interactions present in **1** result in the formation of an infinite chain of gold–silver atoms which are expected to show interesting properties as observed for molecular chain compounds such as $[Rh_6(MeCN)_4]^{9+}$.[14]

In cluster **1** the bridging imidazole rings show C–Au and N–Au distances of *ca.* 2.0 Å, similar to distances found in $[Au(\mu\text{-}N^3,C^2\text{-bzim})]_3I_2$.[8] Three of the N–Au–C angles show significant distortions from linearity, namely N(1)–Au(1)–C(9) [173.9(8)], N(3)–Au(3)–C(5) [172.9(7)] and N(6)–Au(6)–C(17) [172.9(7)]. This distortion could be a result of the interaction of the silver atom with the gold atoms. Further investigations into the reactivity of other trinuclear cyclic gold(I) complex with electrophilic metal ions are underway.

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Footnotes and References

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† Luminescence studies will be reported elsewhere.

‡ Anal. Found; C, 30.83; H.2.61; N, 6.65. Calc. for $C_{61}H_{56}AgAu_6BC1_2F_4N_{12}$; C, 30.47; H, 2.35; N, 6.99%.

§ *Crystal data* for 1; $C_{61}H_{56}AgAu_6BC1_2F_4N_{12}$, $M = 2404.57$; triclinic, space group $P\bar{1}$, $a = 14.4505(1)$, $b = 15{,}098(2)$, $c = 15.9571(1)$ Å, $\alpha = 106.189(3)$, $\beta = 103.551(5)$, $\gamma = 101.310(5)°$, $U = 3120.3(5)$ Å^3, $Z = 2$, $D_c = 2.547$ g cm^{-3}, $F(000)$ 2192, $\lambda = 0.710\,73$ Å , $T = 213(2)$ K, crystal size = 0.15 × 0.10 × 0.05 mm.

Data were collected using a Siemens SMART CCD (charge coupled device) based diffractometer equipped with an LT-2 low temperature apparatus operating at 213 K. A total of 13 371 reflections were collected using ω scans with $1.40 < 2\theta < 22.50°$. Of these 8077 were unique ($R_{int} = 0.0503$ after absorption correction applied, based on ψ scans, $T_{min,max}$ 0.9361, 0.6366). The structure was solved by the direct method using the SHELXS-97 program and refined by least squares methods on F^2. SHELXL-97[16] incorporated in SHELXTL-PC V 5.03.[17] All non-hydrogen atoms were refined anisotropically. Hydrogens were calculated by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection. The refinement converged at $R_1 = 0.0583$ [$I > 2\sigma(I)$] and $wR_2 = 0.1217$ (all data). The final difference map showed no peak greater than + 0.639 e Å^{-3} and no hole larger than −0.454 e Å^{-3}. CCDC 182/688.

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