Novel metallamacrocyclic gold(I) thiolate cluster complex: structure and luminescence of $[Au_9(\mu\text{-dppm})_4(\mu\text{-}p\text{-tc})_6](PF_6)_3$

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The structure of a novel metallamacrocyclic phosphine gold(I) thiolate cluster, $[Au_9(\mu\text{-dppm})_4(\mu\text{-}p\text{-tc})_6](PF_6)_3$, where dppm = bis(diphenylphosphine)methane and *p*-tc = *p*-thiocresolate, is reported and shows Au···Au attractions of ~3.0 Å and gold(I) atoms linked to thiolate and phosphine ligands in distorted trigonal and nearly linear geometries.

There has been a growing interest in the synthesis and characterization of polynuclear gold(I) thiolates and sulfides. These complexes are known to form aggregates and clusters, which have wide applications in nano- and semiconducting materials.[1] The photophysics of d^{10} gold(I) complexes has attracted considerable attention over the past few years, particularly the relationship between the observation of emission and the presence of weak intermolecular bonding interactions between neighboring gold centers.[2] These weak intermolecular aurophilic Au–Au interactions are estimated to have energies on the order of hydrogen bonds (5–15 kcal mol^{-1}).[3] The presence of such weak intermolecular metal–metal interactions has been implicated in the design of electronic and sensor devices.[4]

Accumulated data from our laboratory (AEB and MRMB) regarding the oxidation of neutral mononuclear and dinuclear phosphine gold(I) thiolate complexes established that these complexes undergo sulfur-based oxidation at *ca.* +0.7 to +0.9 V producing disulfide and multinuclear, cationic gold(I) clusters.[5] The isolated clusters show tetranuclear gold(I) atoms arranged in a square with pairs of gold atoms bridged by thiolate ligands. We now report the synthesis, structure, and luminescence properties of an unusual phosphine gold(I) thiolate cluster of nine gold atoms. The cluster is obtained by the chemical oxidation of the dinuclear complex, $dppm(Au\text{–}p\text{-tc})_2$ using the one electron oxidizing agent, the ferrocenium cation. To our knowledge this is the first report on a phosphine gold(I) thiolate complex of high nuclearity that incorporates a range of intramolecular Au–Au interactions.[6] The reaction of $(Cp_2Fe)PF_6$ with $dppm(Au\text{–}p\text{-tc})_2$ (1 : 1 molar equivalents) in dichloromethane occurs readily to form **1** (43% yield based on moles of Au), ferrocene, and the disulfide, $(p\text{-tc})_2$.† The formation of **1** was confirmed by elemental analysis, ^1H NMR, $^{31}P\{^1H\}$ NMR, and X-ray diffraction. The formation of disulfide and ferrocene were confirmed by ^1H NMR. The $^{31}P\{^1H\}$ NMR of **1** shows a singlet at 37 ppm characteristic of dppm coordinated to gold(I) and a septet at −143 ppm assigned to PF_6^-. The cluster is highly soluble in organic solvents such as CH_2Cl_2, CH_3CN, and $CHCl_3$. A small amount of white solid was also isolated during workup and a solution $^{31}P\{^1H\}$ NMR showed a broad singlet at 72 ppm. Further investigation of this complex was hampered by its low solubility.[7]

The observations of broad peaks in the ^1H NMR, a single, slightly broadened peak for the dppm ligands in the ^{31}P NMR, and an unsymmetrical solid state structure suggest that **1** is fluxional in solution. The fluxional nature of **1** is supported by UV–vis studies in CH_2Cl_2 solution that show non-linear absorbance *vs.* concentration behavior with a red-shift in the low energy absorption bands as concentration increases. While the identities of the complexes in solution are unknown at this time, the UV–vis studies of **1** rule out the presence of a significant percentage of $dppm(Au\text{–}p\text{-tc})_2$ (>1%) on the basis of the previously reported extinction coefficient of $dppm(Au\text{–}p\text{-tc})_2$.[3b] In comparison, concentration-dependent UV–vis studies of the tetranuclear gold(I) cluster, $[(PPh_3Au)_4(SC_6H_4CH_3)_2][PF_6]_2$, in CH_2Cl_2 solution show linear behavior.[8]

Cluster **1** crystallizes from CH_2Cl_2/ether to form small yellow plates. The molecular structure of the cation of **1** (see Fig. 1) consists of nine gold atoms arranged in an irregular cluster. Four

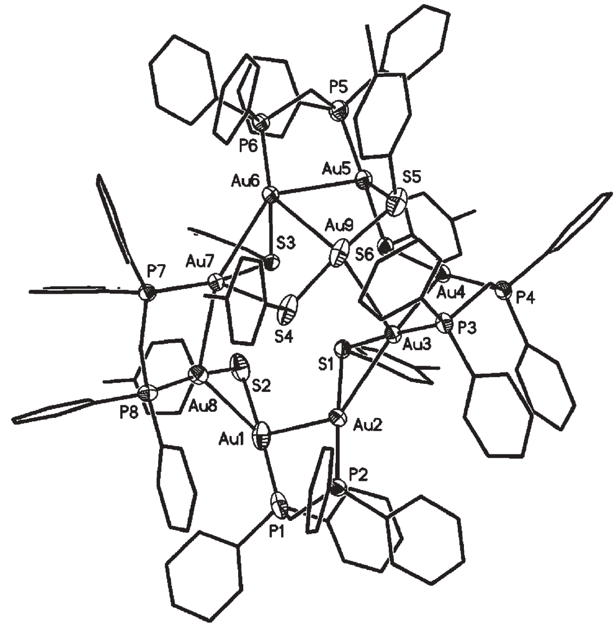

Fig. 1 Diagram of the tricationic structure of 1; ORTEP, 50% probability thermal ellipsoids for Au, P, and S atoms. Hydrogen atoms and PF_6^- anions are omitted for clarity.

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distinct environments are observed for the gold atoms: (a) Au–Au phosphine bridged single bonds (3.0084(6)–3.1439(6) Å); (b) Au–Au sulfur bridged single bonds (2.9950(7)–3.1632(6) Å); (c) Au–Au non-bridged single bonds (3.0135(7)–3.1825(7) Å); and (d) sulfur bridged non-bonded Au–Au interactions (3.7155(8)–3.9571(7) Å). Two gold atoms [Au(5) and Au(7)] are in distorted trigonal ($PAuS_2$) geometries (excluding the Au–Au interactions). The remaining gold atoms exhibit nearly linear coordination (PAuS and SAuS). Each thiolate is bridging between two gold atoms and each Au_2S unit is bridged by dppm, except the central AuS_2. An exceptionally long Au–S distance of ~2.7 Å exists in Au(7)–S(4) and Au(5)–S(5). No intermolecular Au···Au attractions exist in the solid state lattice of complex **1**. The P–Au–S linkages are not "parallel" but exhibit a "crossed" orientation or twist.‡

The excitation of **1** at room temperature results in a weak emission, which is enhanced, but not shifted by lowering the temperature to 77 K. The cluster shows a brillant yellow luminescence at 77 K under black light. Excitation at ~450 nm in the solid state and a 77 K results in an unsymmetrical emission centered at 540 nm (Fig. 2). The long radiative lifetime of **1** (13.5 μs) at 77 K indicates a triplet involvement in the emission. The absorption spectrum of **1** in CH_2Cl_2 shows a broad absorption band (λ_{max} = 280 nm) that tails into the near visible.

High nuclearity Au(I) sulfide complexes with bridging dppm and dppa ligands [dppa = bis(diphenylphosphine)amine] were reported.[9] The complex $[Au_{12}(\mu\text{-dppm})_6(\mu_3\text{-S})_4][PF_6]_4$ emits at room temperature in the solid state at ~648 nm and has a lifetime of 2.7 μs. The emission was assigned as LMCT in character (S → Au CT) with contributions from metal-centered states.[9a] Earlier spectroscopic studies on neutral phosphine gold(I) thiolate complexes assigned absorption and emission bands as originating from S → Au CT in which band maxima were influenced in some cases by the presence of Au–Au interactions.[3b,10] The origin of the emission at ~540 nm for **1** (Fig. 2) is assigned tentatively as sulfur-to-gold charge transfer (LMCT) with possible contributions from metal-centered states influenced by Au–Au interactions.

Mild oxidation of mononuclear [*e.g.* $Ph_3PAu(p\text{-tc})_2$] and dinuclear [*e.g.* $(dppe)Au_2(p\text{-tc})_2$] gold(I) complexes produces tetranuclear gold(I) complexes.[5a] In contrast, ferrocenium oxidation of $(dppm)Au_2(p\text{-tc})_2$ produces the nine-gold(I) cluster described here. In previous studies we observed unique physical, spectroscopic, and reactivity properties for $(dppm)Au_2(p\text{-tc})_2$ compared to the mononuclear and dinuclear complexes mentioned above. For example, $(dppm)Au_2(p\text{-tc})_2$ is bright yellow, has a Au–Au bond in solution as evidenced by VT NMR experiments,[3b] and reacts readily with disulfide to facilitate thiolate-disulfide exchange.[5c] The ability of dppm to promote formation of higher nuclearity clusters with silver and gold has also been noted.[2a] We are continuing to investigate the mechanism of oxidation of $dppm(Au\text{–}p\text{-tc})_2$ and the reactivity of **1**.

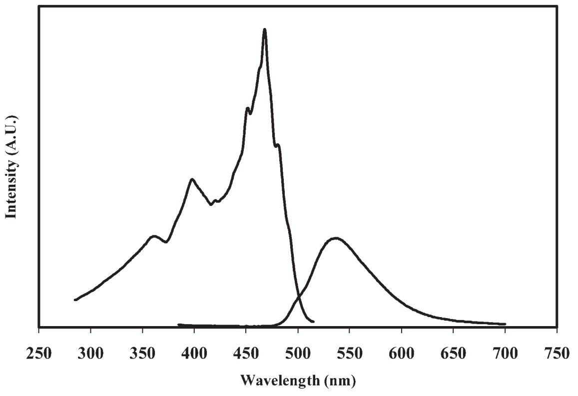

Fig. 2 Excitation (left) and emission (right) spectrum of **1** at 77 K.

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Notes and references

† To 500 mg (0.73 mmol) of $dppm(Au\text{–}p\text{-tc})_2$ dissolved in 100 mL of CH_2Cl_2 under N_2 was added 241 mg (0.73 mmol) of $(Cp_2Fe)PF_6$ (1 : 1). Stirring continued for 24 h until the reaction mixture changed from blue (ferrocenium) to yellow (ferrocene). The solvent was evaporated *in vacuo*, and the residue was washed with ether (3 × 10 mL) to remove Cp_2Fe and disulfide. The yellow solid was recrystallized by dissolving in 3 mL of CH_2Cl_2, followed by addition of ether or hexane. Yield 210 mg, 43% (based on moles of Au). Anal. Calc for $[Au_9(dppm)_4(p\text{-tc})_6](PF_6)_3$ ($C_{142}H_{130}P_{11}S_6F_{18}Au_9$): C 38.03; H 2.92. Found, C 38.28; H 2.85. ^1H NMR (300 MHz; $CDCl_3$). 2.4 (s, CH_3), 3.8 (br, CH_2), 7.0–7.7 (m, C_6H_4). ^{31}P NMR (300 MHz; $CDCl_3$) 37 (dppm) and −143 (PF_6^-).

‡ Empirical formula $[C_{142}H_{130}P_8S_6Au_9][PF_6]_3$, formula weight 4484.19, temperature 150(2) K, crystal system: monoclinic, space group $P2_1/n$, a = 21.5548(8) Å, b = 29.0974(11) Å, c = 23.1299(10) Å, β = 91.295(1)°, V = 14503.1(10) $Å^3$, and Z = 4. Intensity data were collected at 150 K on a standard Bruker SMART 1 K CCD diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å). An absorption correction based on the multi-scan technique and beam corrections was applied using SADABS. The structure was solved by a combination of the Patterson method using SHELXTL and the difference Fourier technique and refined by full matrix least squares on F^2. It should be noted that several phenyl rings exhibit disorder as indicated by the large anisotropic displacement parameters for the carbon atoms. Crystallographic agreement factors for the refinement are as follows: R_1 = 5.15%, wR_2 = 11.72% for 18990 reflections with $I > 2\sigma(I)$ (R_1 = 9.75%, wR_2 = 14.47% and S = 1.039 for all data) and 1561 variable parameters. CCDC 250901. See http://www.rsc.org/suppdata/cc/b4/b415488f/ for crystallographic data in .cif or other electronic format.

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