Luminescent gold(I) supermolecules with trithiocyanuric acid. Crystal structure, spectroscopic and photophysical properties

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The first example of an ordered array of Au_6 clusters with trithiocyanuric acid, $[(LAu)(AuPPhMe_2)_2]_2$ (H_3L = trithiocyanuric acid), is prepared and characterized by X-ray crystallography; it has a two-dimensional structure *via* intermolecular $Au^I\cdots Au^I$ interactions and possesses photoluminescence properties; the ability of trithiocyanuric acid to act as a bridging ligand for molecular assembly of two-dimensional polymeric solids is demonstrated.

Molecular materials composed of discrete metal clusters arranged in extended structures are useful model systems for understanding surface chemistry and catalysis, but the synthesis of such materials is usually serendipitous. Herein we show that $Au^I\cdots Au^I$ interactions can provide a driving force for self-assembly of such molecular solids,[1–6] as well as the first example of an ordered array of Au_6 clusters arranged in a two-dimensional structure *via* intermolecular $Au^I\cdots Au^I$ interactions. While examples of one-dimensional gold(I) chains are not uncommon in the literature,[1a,2b,4–6] gold(I) solids with two-dimensional structures are rare.[1b]

Complexes $L(AuPPh_3)_3$ **1** and $L(AuPPhMe_2)_3$ **2** were prepared by treating $AuCl(PPh_3)$ and $AuCl(PPhMe_2)$ respectively with a methanolic solution of H_3L (H_3L = trithiocyanuric acid) and NaOMe. Slow diffusion of diethyl ether into a CH_2Cl_2–MeOH solution of complex **2** gave $[(LAu)(AuPPhMe_2)_2]_2$ **3** with low solubility.†

Complexes **1** and **3** have been characterized by X-ray crystallography. The structure of complex **1** features a triazine with three bent S–Au–PPh_3 appendages pointing away from each other. This is similar to that of the reported $[\{CSAu(PPh_3)\}_6]$ supermolecule,[2c] whereas there is no intermolecular close contact of the gold(I) atoms in both complexes. Presumably, this is due to the steric hindrance provided by the $AuPPh_3^+$ units.

A perspective view of complex **3** and its extended two-dimensional structure are shown in Figs. 1 and 2, respectively. Complex **3** is a hexanuclear gold(I) supermolecule with a crystallographic centre of inversion at the centre of the 12-membered ring metallocycle. Four gold(I) centres are arranged in the form of a parallelogram with $Au^I\cdots Au^I$ distances of 2.964(2) and 2.987(2) Å, and a long transannular $Au^I\cdots Au^I$ separation of 3.347(3) Å. A similar arrangement of Au_4 has been found in $[\{Au_2(C_6H_4S_2\text{-}1,2)(PEt_3)\}_2]$[2d] and $[Au_4(\mu\text{-}S_2C_6H_3Me)_2(PEt_3)_2]$.[7] Notably, there is an intermolecular $Au^I\cdots Au^I$ close contact of 3.130(2) Å resulting in a novel two-dimensional structure with the Au_6 supermolecule as the repeating unit. One recent novel example is $[L'(AuCl)_4]_\infty$ [L′ = 1,4,8,11-tetrakis(diphenylphosphinomethyl)-1,4,8,11-tetraazacyclotetradecane].[1b] The intermolecular $Au^I\cdots Au^I$ separation in complex **3** is comparable to related values in one- and two-dimensional gold(I) solids such as 3.104(1) Å in $[L'(AuCl)_4]_\infty$,[1b] 3.174(1) Å in $[Au_2(C{\equiv}CPh)_2(\mu\text{-}C{\equiv}NBu^t{}_2C_6H_2N{\equiv}C]_\infty$[5a] and 3.200(1) Å in $[Au_2(p\text{-}tc)_2(dpppn)]_\infty$ [*p*-tc = *p*-thiocresol; dpppn = 1,5-bis(diphenylphosphino)pentane].[6b] Another important structural feature is coordination of $Au(PPhMe_2)^+$ units to one of the nitrogen atoms in each of the triazine rings, which is isolobal to a proton. A reaction scheme which rationalizes the formation of the Au_6 supermolecule is shown in Scheme 1.

Recently, the gold(I) complexes of two tridentate bridging ligands, 1,3,5-tris(diphenylphosphino)benzene[4b] and

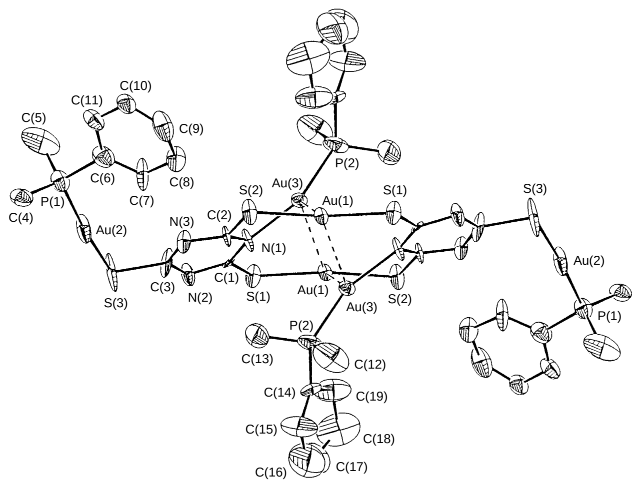


Fig. 1 A perspective view of complex **3** (bond lengths in Å, angles in °): Au(1)···Au(3) 2.987(2), Au(1)···Au(3′) 2.964(2), Au(3)···Au(3′) 3.347(3), Au(1)–S(1) 2.279(9), Au(1)–S(2) 2.280(9), Au(2)–P(1) 2.234(10), Au(2)–S(3) 2.310(10), Au(3)–P(2) 2.210(11), Au(3)–N(1) 2.094(22); S(1)–Au(1)–S(2) 168.1(3), S(3)–Au(2)–P(1) 174.7(5), P(2)–Au(3)–N(1) 160.4(7)

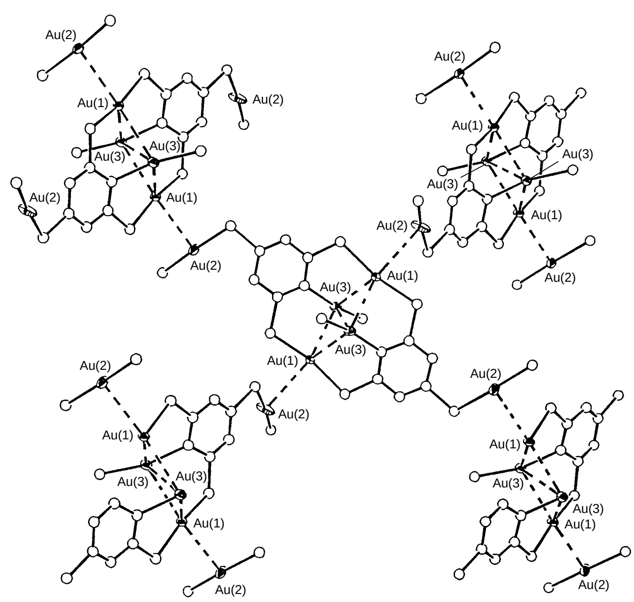
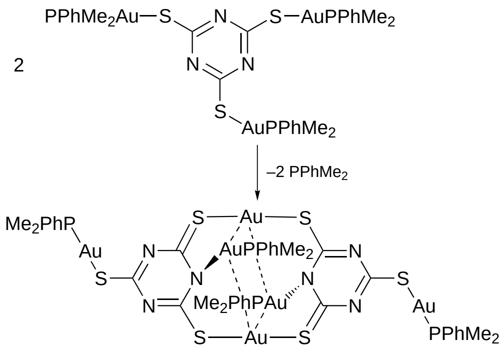


Fig. 2 An extended two-dimensional structure of complex **3** with intermolecular Au···Au distances of 3.130(2) Å (the phenyl and methyl groups are omitted for clarity)



Scheme 1

$[C_6H_3(C{\equiv}C)_3]^{3-}$[5b] are shown to form interesting one-dimensional polymeric solids *via* Au^I···Au^I interactions. Here, the trithiocyanuric acid demonstrates its ability to act as a bridging ligand for molecular assembly of two-dimensional polymeric solids.

The absorption spectra of complexes **1** and **2** measured in CH_2Cl_2 are very similar. As shown in Fig. 3 (insert), both complexes exhibit an intense absorption band at *ca*. 295 nm (ε_{max} = 51 320 and 45 650 dm^3 mol^{-1} cm^{-1} for complexes **1** and **2**, respectively). However, complex **3** shows intense absorption at 320 nm (ε_{max} = 44 870). This red shift in transition energy is not uncommon in d^{10}–d^{10} systems and hence the 320 nm band in complex **3** is assigned to the $5d(d_{\sigma*}) \rightarrow 6p(_{\sigma})$ tansition modified by Au^I···Au^I interactions.[8] As with most gold(I) complexes, complexes **1–3** are emissive both in solution and in the solid state, showing a broad emission at *ca*. 520–530 nm with long lifetimes (0.37, 0.34, 0.34 μs in degassed CH_2Cl_2; 3.7, 10.4, 11.6 μs in the solid state for complexes **1**, **2**, and **3**, respectively) upon photoexcitation at 300–400 nm (shown in Fig. 3), and these emissions are assigned to the S $\rightarrow$ Au excitation.[9]

This work highlights the application of Au^I···Au^I interactions as well as the judicious choice for bridging ligands in the formation of a two-dimensional array of luminescent metal clusters.

We acknowledge support from The University of Hong Kong, the Hong Kong Research Grants Council, and the Croucher Foundation.

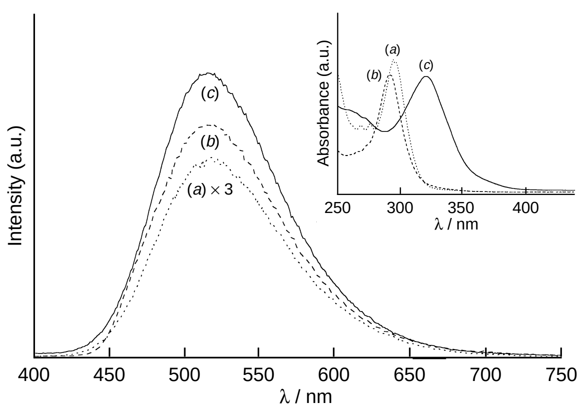


Fig. 3 The emission spectra of complexes **1–3** measured in degassed CH_2Cl_2 at room temp. (insert is the absorption spectra of complexes **1–3** (3.5×10^{-5} M) in CH_2Cl_2); (*a*) **1** (*b*) **2**, (*c*) **3**

Footnotes and References

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† $[L(AuPPh_3)_3]$ **1**: the reaction of Na_3L [61 mg, obtained from H_3L (44 mg) and NaOMe (41 mg) in MeOH (25 ml)] with $Au(PPh_3)Cl$ (148 mg) in CH_2Cl_2–MeOH (1 : 1, 50 ml) at room temp. for 4 h gave a pale-yellow solid which was recrystallized by diffusion of diethyl ether into CH_2Cl_2–dmf. Pale yellow crystals of $[L(AuPPh_3)_3]$ were obtained in *ca*. 80% yield. Its ^{31}P NMR spectrum recorded in $CDCl_3$ shows a singlet at δ 37.01. Anal. Calc.: C, 44.07; H, 2.90; N, 2.71. Found: C, 44.28; H, 2.74; N, 2.57%. FAB: {$[L(AuPPh_3)_3]$}, *m/z* = 1552, 40%.

$[L(AuPPhMe_2)_3]$ **2**: It was similarly prepared to give a pale-yellow solid in *ca*. 75% yield, and its ^{31}P NMR spectrum recorded in $CDCl_3$ shows a singlet at δ 10.78. Anal. Calc.: C, 27.48; H, 2.80: N, 3.56. Found: C, 27.25; H, 2.64; N, 3.27% FAB: {$[L(AuPPhMe_2)_3]$}, *m/z* = 1180, 80%.

$[(LAu)(AuPPhMe_2)_2]_2$ **3**: slow diffusion of diethyl ether into a CH_2Cl_2–dmf solution of complex **2** gave yellow crystals in *ca*. 40% yield. Anal. Calc.: C, 21.88; H, 2.11; N, 4.03. Found: C, 22.13; H, 2.34; N, 3.77% FAB: {$[(LAu)(AuPPhMe_2)_2]_2$}, *m/z* = 2082, 15%.

Crystal data: **1**·$2C_3H_7NO$: $Au_3C_{63}H_{59}Au_3N_5O_2P_3S_3$, M = 1698.18, monoclinic, space group $P2_1/n$, a = 13.993(4), b = 23.289(6), c = 19.245(6) Å, β = 92.07(3)°, U = 6267(3) Å^3, Z = 4, D_c = 1.800 g cm^{-3}, μ(Mo-Kα) = 71.90 cm^{-1}, $F(000)$ = 3249. Intensity data were collected on Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å), 8173 unique reflection ($2\theta < 45°$) were measured 4828 with $I > 2\sigma(I)$ were used in the refinement. Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms (713 variables) converged to R = 0.047 and R_w = 0.043. The final Fourier difference map showed residual extrema in the range of 1.57 to −2.07 e Å^{-3}.

3·2MeOH: $C_{40}H_{52}Au_6N_6O_2P_4S_6$, M = 2146.93, monoclinic, space group $P2_1/c$, a = 10.951(3), b = 18.827(3), c = 15.193(2) Å, β = 105.90(2)°, U = 3013(1) Å^3, Z = 2, D_c = 2.367 g cm^{-3}, μ(Mo-Kα) = 149.15 cm^{-1}, $F(000)$ = 1936. Intensity data were collected on Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å), 3926 unique reflection ($2\theta < 45°$) were measured and 2206 with $I > 2\sigma(I)$ were used in the refinement. Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms (290 variables) converged to R = 0.061 and R_w = 0.054. The final Fourier difference map showed residual extrema in the range of 1.80 to −2.05 e Å^{-3}. CCDC 182/541.

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Received in Cambridge, UK, 4th June 1997; Com. 7/03891G