Photophysical properties, electronic and crystal structure of a luminescent pentanuclear gold(I) complex

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A novel pentanuclear gold(I) complex with five gold(I) centres held by weak metal–metal interactions has been prepared and its structure characterized by X-ray analysis; it shows interesting photochemistry and dual emissions in solution upon photoexcitation.

The design of new luminescent inorganic materials with novel electrooptical properties is of considerable interest. Our approach to this area is to take advantage of 'aurophilicity',[1] ligand–ligand interactions and the photoluminescence of gold(I) building blocks.[2] In this context, a gold(I) quinolinethiolate should be a good building block since: (*i*) visible photoluminescence arising from S→Au charge-transfer excitation is anticipated[3] and (*ii*) in addition to the gold(I)–gold(I) bonding interaction, it is possible to have a ligand–ligand interaction between the two quinolinethiolate units, thus providing an additional driving force for the formation of polynuclear gold(I) complexes with high nuclearity. Herein is described the preparation and crystal structure of a luminescent pentanuclear gold(I) complex. This is an unprecedented pentanuclear gold(I) complex, which has both gold(I)–gold(I) and ligand–ligand interactions.

The yellow complex $[Au_5L_3(dppm)_2][MeO][ClO_4]$ [HL = quinoline-2-thiol, dppm = bis(diphenylphosphino)methane] was prepared by the reaction of $[(AuCl)_2(dppm)]$[4] with NaL in MeOH.† Fig. 1 shows a perspective view of the $[Au_5L_3(dppm)_2]^{2+}$ cation.‡ The anions include ClO_4^- and MeO^-, and the latter is most probably due to the excess amount of NaOMe in the reaction. The structure features one of the few examples of pentanuclear gold(I) complexes and has the five gold(I) centres held by the bridging dppm and L ligands and perhaps weak metal–metal interactions. The arrangement of the five gold(I) centres is different from that of the $[\{Au(C_6H_2Me_3\text{-}2,4,6)\}_5]$ complex reported in the literature[6] which has a star-shaped structure and with $Au^I \cdots Au^I$ ranging from 2.692(4) to 2.710(3) Å. The $Au^I \cdots Au^I$ separations in the present complex lie between 2.936(3) and 3.351(3) Å. The Au(1), Au(2) and Au(3) atoms are roughly in a linear array with Au(1)–Au(2)–Au(3) 161.4(1)°, a slight deviation from linearity, with Au(1) having a weak bonding interaction with Au(5) [Au(1)–Au(5) 3.067(3) Å]. Both the Au(2)–Au(5) [3.351(3) Å] and Au(3)–Au(4) [3.333(4) Å] distances are very long, suggesting very weak metal–metal interaction. It is noted that the closest L ⋯ L separation is around 3.30 Å [C(7) ⋯ C(25) 3.31, C(6) ⋯ C(23) 3.35 Å; the average separation between the two least-squares quinoline planes is 3.80 Å] suggesting the existence of a weak π–π interaction between the quinoline ligands. These ligands bridge in a bidentate manner with Au–S(av.) 2.28(2) and Au–N(av.) 2.10(4) Å.

The pentanuclear gold(I) complex shows room-temperature photoluminescence upon excitation at 300–400 nm. The UV/VIS spectrum measured in acetonitrile at room temperature [Fig. 2 (insert)] displays intense absorption ranging from *ca.* 330 to 420 nm with absorption maxima at *ca.* 370 nm (ε = 21 900 dm^3 mol^{-1} cm^{-1}) and a shoulder at *ca.* 385 nm (ε = 18 250 dm^3 mol^{-1} cm^{-1}). Since the free thiol (HL) shows absorptions at similar energies, the 330–420 nm absorptions seem to be dominated by the intraligand transitions of the thiolate ligands. It is likely that the metal-centred 5d ⟶ 6s/6p transition arising from the weak Au(I) ⋯ Au(I) interactions, and the S→Au charge-transfer transition sit underneath the intraligand transition. Recently, Bruce and co-workers[3] reported a series of dinuclear gold(I) thiolate complexes with Au(I) ⋯ Au(I) interactions, which show absorption bands at 330–360 nm assignable to S→Au charge-transfer transitions. The complex $[Au_5L_3(dppm)_2][MeO][ClO_4]$ shows dual emissions with maxima at *ca.* 500 ($\tau \approx 1.9$) and 605 nm ($\tau \approx 1.6$ μs) in degassed acetonitrile solution. The emission spectrum is shown in Fig. 2. The high-energy emission most likely comes from the intraligand (L) or metal-to-ligand [Au ⟶ π*(dppm) or Au ⟶ π*(L)] excited state. Since the low-energy emission is comparable in energy to those emissions of $[Au_2(dppm)_2]^{2+}$ (575),[7] $[Au_3(dmmp)_2]^{3+}$ [580, dmmp = bis(dimethylphosphinomethyl)methylphosphine],[8] $[Au_3(dpmp)_2]^{3+}$ [600, dpmp = bis(diphenylphosphinomethyl)phenylphosphine][9] and [Au(SPh)(tpa)] (596 nm, tpa = 1,3,5-triaza-7-phosphaadamantane),[10] the emitting state could arise from the metal-centred 5d ⟶ 6s/6p transition, although the possibility of having the S→Au and/or the intraligand π ⟶ π* charge-transfer character in the excited state cannot be excluded.

This communication highlights the synthesis of luminescent polynuclear gold(I) complexes from [AuL]. The resulting pentanuclear gold(I) complex would be a good precursory candidate to study the effect of gold(I)–gold(I) and ligand–

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† The reaction of equimolar amounts of NaL (183 mg) [obtained from HL (161 mg) and NaOMe (60 mg) in MeOH (25 cm^3)] and $[(AuCl)_2(dppm)]$[4] (850 mg) in CH_2Cl_2–MeOH (1 : 1, 50 cm^3) for 4 h at room temperature gave a yellow solution. Upon addition of $LiClO_4$, the yellow complex $[Au_5L_3(dppm)_2][MeO][ClO_4]$ was obtained and could be recrystallized by diffusion of diethyl ether into a CH_2Cl_2–MeOH solution (Found: C, 39.55; H, 3.20; N, 1.40. Calc. for $C_{80}H_{75}Au_5ClN_3O_8P_4S_3$: C, 39.25; H, 3.05; N, 1.70%).

‡ Crystal data for $[Au_5L_3(dppm)_2][MeO][ClO_4]\cdot CH_2Cl_2\cdot EtOH\cdot 2H_2O$. $C_{81}H_{77}Au_5Cl_3N_3O_8P_4S_3$, *M* 2531.78, triclinic, space group $P\bar{1}$, a = 15.835(4), b = 17.115(4), c = 17.461(4) Å, α = 85.43(2), β = 83.70(2), γ = 67.68(2)°, U = 4347.8(17) Å^3, D_c = 1.921 g cm^{-3}, D_m = 1.915 g cm^{-3}, Z = 2, $F(000)$ = 2355, crystal dimensions 0.01 × 0.10 × 0.35 mm. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å), 11 187 unique reflections ($2\theta < 45°$) were measured and 4228 with $I > 2\sigma(I)$ were used in the refinement. The structure was solved and refined by full-matrix least squares using the NRCVAX program.[5] Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms (866 variables) converged to R = 0.067 and R' = 0.064 [$w^{-1} = \sigma^2(F)$]. The final Fourier-difference map showed residual extrema from 2.24 to −1.50 e Å^{-3}. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/10.

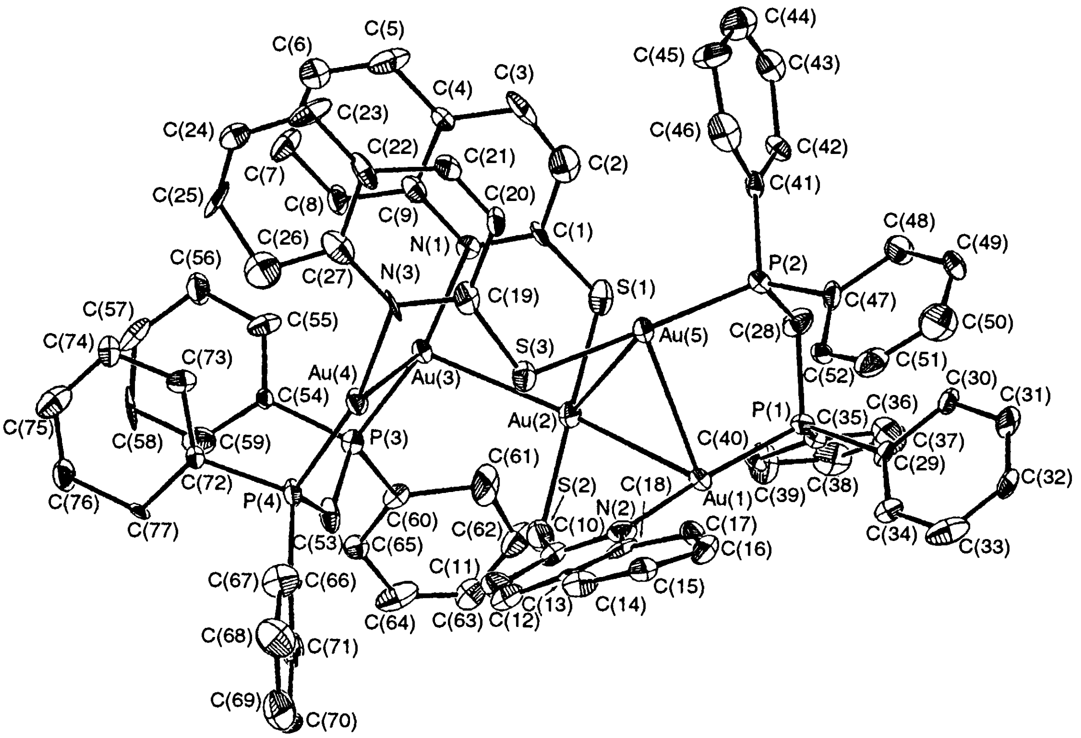

Fig. 1 A perspective view of the $[Au_5L_3(dppm)_2]^{2+}$ cation. Selected bond lengths (Å) and angles (°): Au(1)–Au(2) 3.038(3), Au(2)–Au(3) 2.936(3), Au(3)–Au(4) 3.333(4), Au(1)–Au(5) 3.067(3), Au(2)–Au(5) 3.351(3), Au(1)–P(1) 2.25(1), Au(1)–N(2) 2.09(4), Au(2)–S(1) 2.269(16), Au(2)–S(2) 2.242(15), Au(3)–P(3) 2.246(14), Au(3)–N(1) 2.10(4), Au(4)–P(4) 2.260(14), Au(4)–N(3) 2.12(4), Au(5)–S(3) 2.321(14), Au(5)–P(2) 2.266(14); Au(1)–Au(2)–Au(3) 161.4(1), Au(1)–Au(2)–Au(5) 57.13(7), Au(2)–Au(1)–Au(5) 66.57(8), Au(2)–Au(3)–Au(4) 90.26(9), Au(3)–Au(2)–Au(5) 110.7(1), P(1)–Au(1)–N(2) 167.0(12), S(1)–Au(2)–S(2) 171.3(6), P(3)–Au(3)–N(1) 165.9(10), P(4)–Au(4)–N(3) 167.3(10), S(3)–Au(5)–P(2) 178.8(5)

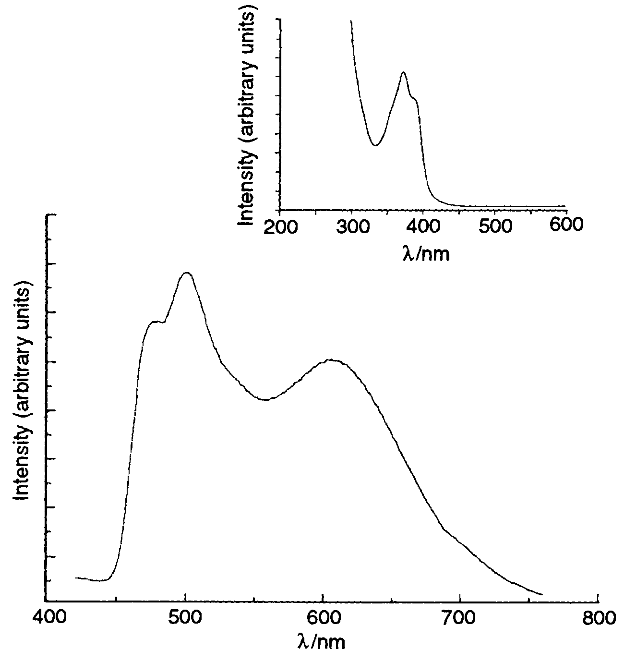

Fig. 2 The emission spectrum of $[Au_5L_3(dppm)_2][MeO][ClO_4]$ in degassed acetonitrile at room temperature (insert is the absorption spectrum in acetonitrile). Excitation at 325 nm

ligand interactions on the photophysical and photochemical properties of polyaurated gold(I) systems. Preliminary study reveals some interesting photochemistry. Photolysis of a degassed acetonitrile solution of $[Au_5L_3(dppm)_2][MeO][ClO_4]$ (10^{-4} mol dm^{-3}) and MV^{2+} [methyl viologen (1,1′-dimethyl-4,4′-bipyridinium), 10^{-4} mol dm^{-3}] for 10 min led to a net reaction of MV^+, which was identified by its visible-absorption spectrum at 500–700 nm.

Acknowledgements

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