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Synthesis, Photophysical Properties and Crystal Structure of a Luminescent Binuclear Three-co-ordinated Gold(I) Complex without Metal–Metal Interaction

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The complex cation $[Au_2L_3]^{2+}$ [L = 2,6-bis(diphenylphosphino)pyridine] has an intramolecular $Au \cdots Au$ separation of 4.866 Å as determined by X-ray crystallography and displayed photoluminescence at 520 nm in fluid solutions at room temperature.

There has been a recent interest in polynuclear gold(I) complexes with bridging phosphine ligands, because of the intriguing photophysical and photochemical properties of this class of complexes.[1–3] Those polymetallic gold(I) phosphine complexes which exhibit room-temperature photoluminescence have been shown by X-ray crystallography to have intramolecular $Au \cdots Au$ separations around 2.9–3.2 Å, suggesting weak metal–metal interaction in these complexes. It has been suggested that the photoluminescence of polynuclear metal d^{10} complexes arises from metal-centred $nd^9(n + 1)s^1$ electronic excited states which are modified by metal–metal interaction.[4] Herein is described a binuclear three-co-ordinated gold(I) complex which exhibits room-temperature photoluminescence in the absence of a Au–Au interaction. Furthermore, this species can also be viewed as a luminescent inorganic host, an area of research recently investigated by Balch et al.[5]

The ligand 2,6-bis(diphenylphosphino)pyridine L was prepared by a literature method.[6] Reaction between $KAuCl_4$ (0.2 g) and 2,2'-thiodiethanol (1 cm³) in hot methanol (30 cm³) for 15 min gave a colourless solution of Au^I *in situ*, which rapidly reacted with excess L (0.3 g) to give the colourless perchlorate salt $[Au_2L_3]^{2+}$. Addition of $LiClO_4$ (1 g) to the solution gave $[Au_2L_3][ClO_4]_2$ (yield $\approx 70\%$). Recrystallization of the crude sample by diffusion of diethyl ether into acetonitrile solution gave colourless crystals from which the structure has been determined by X-ray crystallography.† Fig. 1 shows a per-

spective view of the complex cation with atom numbering. The structure resembles that of $[Au_2(Me_2PCH_2CH_2PMe_2)_3]^{2+}$ [7] and $[Au(PPh_3)_3]^+$ [8] in that the co-ordination around each gold atom is essentially trigonal planar with P–Au–P angles ranging from 115.8(1) to 122.1(1)°. The measured intramolecular $Au \cdots Au$ separation of 4.866 Å suggests no metal–metal interaction in this complex.

Unlike $[Au_2(dppm)_2]^{2+}$ [dppm = bis(diphenylphosphino)-methane] which shows an intense $d_{\sigma^*} \longrightarrow p_\sigma$ transition at 290 nm,[1a,2] the absorption spectrum of $[Au_2L_3]^{2+}$ in acetonitrile is dominated by a broad absorption band tailing from 250 to 360 nm ($\varepsilon_{max} = 8.03 \times 10^4$ dm³ mol⁻¹ cm⁻¹ at 260 nm, 3.12×10^4 dm³ mol⁻¹ cm⁻¹ at 300 nm). For a three-co-ordinated gold(I) phosphine complex, the highest occupied molecular orbital (HOMO) is $(5d_{xy}, 5d_{x^2-y^2})$ whereas the lowest unoccupied molecular orbital (LUMO) is $6p_z$ mixed with the π^* orbital of L.[9] Thus we assign tentatively the low-energy absorptions at 300–360 nm to arise from $(5d_{x^2-y^2}, 5d_{xy}) \longrightarrow (6p_z, \pi^*)$ transitions.[10] Similar spectral assignments have also been suggested by Fackler and co-workers[10a] and Gray and co-workers[10b] on related gold(I) phosphine complexes. Although no metal–metal interaction is anticipated in this complex, it does show photoluminescence both in the solid state and in degassed acetonitrile. Fig. 2 shows the excitation and emission spectra measured in degassed acetonitrile at room temperature. Upon excitation at 300–360 nm, two emissions centred at 415 and 520 nm with lifetime of 0.3 and 1.8 μs respectively are observed. The lower energy emission with a quantum yield of 0.0018 is much more intense than the higher energy one. We assign the 415 nm emission to arise from the intraligand excited state since the free ligand L also shows weak emission at similar energy. The low-energy emission is likely to arise from the spin-forbidden $(6p_z, \pi^*) \longrightarrow (5d_{x^2-y^2}, 5d_{xy})$ transition[10] or a metal-perturbed intraligand[3] $(\pi,\pi^*) \longrightarrow (\pi^2)$ transition. The fact that the present complex has similar emission energy as that for $[Au_2(dppm)_2]^{2+}$ (emission at 570 nm)[1a,2] argues against the $[d_{\sigma^*}p_\sigma]$ triplet excited state to be responsible for the photoluminescence of polymetallic gold(I) phosphine complexes.[10]

Similar to its $[Rh_2L_2(CO)_2Cl_2]$ analogue which has been found to bind to $SnCl_2$,[11] the $[Au_2L_3]^{2+}$ complex cation can also be viewed as an inorganic host having a cavity size of about 4.8–5.0 Å in diameter. The pyridyl functional group should facilitate binding reactions with metal ions and the photo-
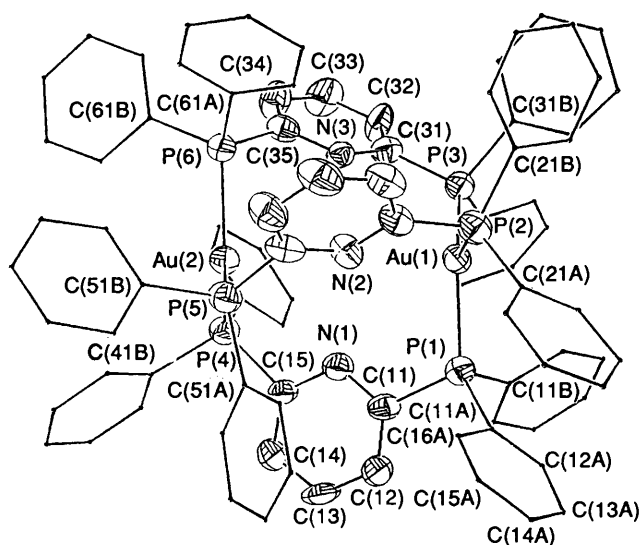
Fig. 1 A perspective view of the $[Au_2L_3]^{2+}$ cation with atom numbering. Selected bond distances (Å) and angles (°): Au(1)–P(1) 2.384(4), Au(1)–P(2) 2.362(4), Au(1)–P(3) 2.357(4), Au(2)–P(4) 2.338(4), Au(2)–P(5) 2.355(4), Au(2)–P(6) 2.366(4), P(1)–Au(1)–P(2) 118.6(1), P(1)–Au(1)–P(3) 118.1(1), P(2)–Au(1)–P(3) 122.0(1), P(4)–Au(2)–P(5) 122.1(1), P(4)–Au(2)–P(6) 122.1(1), P(5)–Au(2)–P(6) 115.8(1)
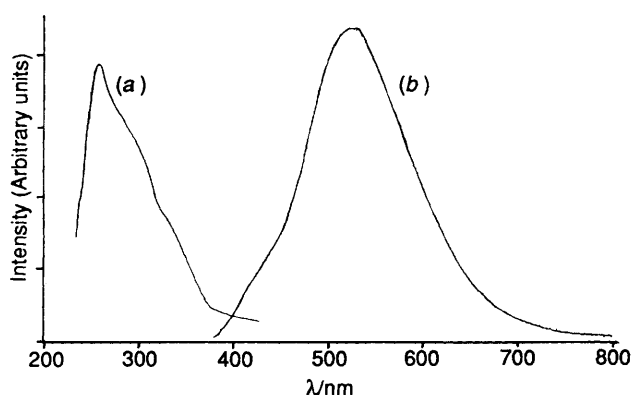

Fig. 2 Excitation (a) and emission (b) spectra of $[Au_2L_3]^{2+}$ ($\approx 10^{-5}$ mol dm^{-3}) measured in degassed acetonitrile at room temperature

luminescence can serve as a spectroscopic probe for such binding reactions. Preliminary studies revealed that the presence of Li$^+$ ion in acetonitrile does not affect the luminescence. However, in the presence of CF_3CO_2H, $AgCF_3SO_3$ or $[Cu(MeCN)_4]PF_6$, the emission spectrum is significantly perturbed, as illustrated in Fig. 3. Trifluoroacetic acid appears to quench the emission. The substantial enhancement of the emission intensity and the red-shift in its energy in the presence of Cu^I (see Fig. 3) suggests that $[Au_2L_3]^{2+}$ can be used as a sensor for this cation.
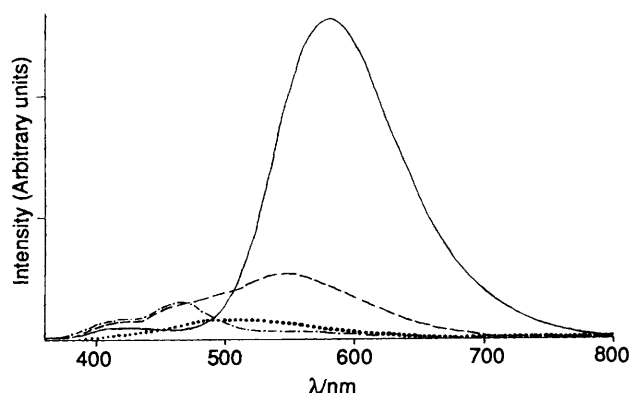

Fig. 3 Emission spectra of $[Au_2L_3]^{2+}$ (1×10^{-4} mol dm^{-3}) in degassed acetonitrile ($\cdots$) and in the presence of CF_3CO_2H (1×10^{-3} mol dm^{-3}, $-\cdot-\cdot-$), $AgCF_3SO_3$ (1×10^{-3} mol dm^{-3}, $----$) or $[Cu(MeCN)_4]PF_6$ (1×10^{-3} mol dm^{-3}, ——)

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