Synthesis, photoluminescent and electroluminescent behaviour of four-coordinate tetrahedral gold(I) complexes. X-Ray crystal structure of $[Au(dppn)_2]Cl$†

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Two tetrahedral four-coordinate Au(I) complexes, $[Au(4\text{-}R\text{-}dppn)_2]PF_6$ (R = H or Me), have been synthesized and the crystal structure of $[Au(dppn)_2]Cl$ has been determined by X-ray crystallography; the complexes have been found to exhibit both photoluminescent and electroluminescent behaviour.

Unlike d^{10} Cu(I) and Ag(I) species in which complexes with coordination number greater than two are commonly observed, most Au(I) complexes adopt a two-coordinate linear geometry.[1] Studies on four-coordinate Au(I) systems[2,3] have mainly been confined to those of structural characterization, with a few examples on cytotoxic[4a] and antitumor activities.[4b] Despite the recent growing interest in the study of luminescent two-[5] and three-coordinate[6] Au(I) systems, there have been no reports on the luminescence behaviour of four-coordinate Au(I) complexes. Besides, with the growing interest in the design and construction of light-emitting diodes (LEDs)[7] and the employment of metal complexes[8] as the emissive layer in electroluminescence (EL) devices, the use of Au(I) complexes in such studies is rare[8f,g] despite the rich luminescence behaviour associated with a number of Au(I) systems.[5,6,9]

Here, we report the synthesis of two four-coordinate Au(I) complexes, $[Au(4\text{-}R\text{-}dppn)_2]X$ [dppn = 1,8-bis(diphenylphosphino)naphthalene; R = H, X = PF_6 **1a**, Cl **1b**; R = Me, X = PF_6 **2**], and the X-ray crystal structure of **1b**. The first report on the photoluminescent and electroluminescent properties of this tetrahedral four-coordinate Au(I) system is also described.

To the freshly reduced solution of Au(I), prepared *in situ* by treatment of $K[AuCl_4]$ (0.1 mmol) with an excess of 2,2′-thiodiethanol in methanol (20 ml), was added the diphosphine ligand, 4-R-dppn (0.2 mmol). The chloride salt of the product was isolated by slow evaporation of the solvent. Diffraction quality crystals of **1b** were obtained by recrystallization from acetonitrile. Orange solids of **1a** and **2** were collected after the metathesis reaction with NH_4PF_6 in methanol. Recrystallization from dichloromethane–diethyl ether afforded **1a** and **2** as orange crystals. The identities of both have been confirmed by ^1H NMR spectroscopy, IR, positive FAB-MS, and elemental analyses.† The X-ray crystal structure of **1b** has also been determined.‡

Fig. 1 depicts the perspective view of the complex cation of **1b**. The structure shows a Au(I) centre in a highly distorted tetrahedral coordination geometry, as required by the steric demand of the dppn ligand. The P–Au–P angle of 86.9(2)–133.3(2)° are comparable to other four-coordinate Au(I) diphosphine complexes such as $[Au(dppe)_2]^+$ [P–Au–P 85.4(1)–129.6(1)°][3c] and $[Au(pdma)_2]^+$ [pdma = *o*-phenylenebis(dimethylarsine), P–Au–P 86.7–121.8°].[3a] The Au–P bonds of 2.379(6)–2.388(6) Å are slightly shorter than those of $[Au(dppe)_2]^+$ [2.389(3)–2.416(3) Å],[3c] but are longer than those of two-coordinate Au(I) phosphine complexes.[5e,f,9]

The electronic absorption spectra of **1a** and **2** are very similar, and are dominated by an intense high energy absorption band at *ca.* 300 nm with a weak low energy band at *ca.* 400 nm with tails extending to *ca.* 500 nm. The photophysical data of **1a** and **2** are collected in Table 1. With reference to previous spectroscopic work,[9,10] the intense absorption at *ca.* 300 nm which closely resembles that found in the free ligand, is assigned as an intraligand $\pi\rightarrow\pi^*$(naphthalene) transition while the lowest energy absorption band is a $\sigma\rightarrow\pi^*$(naphthalene) transition. An assignment of these low-energy absorption bands as d→p transitions, similar to those suggested for three-coordinate d^{10} complexes of Au(I)[6b,c] and Pt(0)[5a,11] is unlikely, given the approximately tetrahedral AuP_4 structure in which the valence p orbitals are strongly σ antibonding. Such d→p transitions are expected to occur at fairly high energy, for example, at 240 nm for $[Au(dcpe)_2]^+$ [dcpe = 1,2-bis(dicyclohexylphosphino)ethane].[6b] Excitation of solid samples of **1a** and **2** gave intense orange emission both at room temperature and 77 K. Room temperature luminescence in degassed dichloromethane solution has also been observed. The observation of the emission lifetime in the microsecond range is suggestive of an emission origin associated with a spin-forbidden transition. No such emission was observed in the related $[Au(dcpe)_2]^+$ complex, which was reported to be non-emissive both in the solid state and in solution.[6b] However, similar emission bands were observed in a related two-coordinate $[Au_2(dppn)(C{\equiv}CR)_2]$,[9d] in which an assignment of the emission origin as derived from states of $\sigma\rightarrow\pi^*$(naphthalene) transition is suggested. It is likely that the photoluminescent properties of **1a** and **2** are characteristic of the dppn unit. The observation that the emission of **2** in

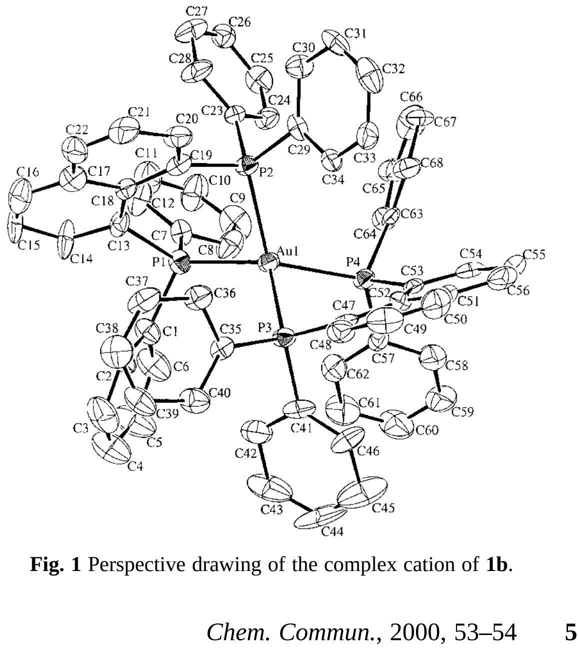

Fig. 1 Perspective drawing of the complex cation of **1b**.

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† Electronic supplementary information (ESI) available: characterisation data and crystal structure refinement and data for **1b**, experimental details for EL measurements. See http://www.rsc.org./suppdata/cc/a9/a908521a/

Table 1 Photophysical data for **1a** and **2**.

Complex	Medium (T/K)	λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})	λ_{em}/nm (τ_o/μs)
$[Au(dppn)_2]PF_6$ **1a**	Solid (298)		640 (3.2)
	Solid (77)		653
	CH_2Cl_2 (298)	294 (35 870), 398(sh) (5000)	693 (0.7)
$[Au(4\text{-}Me\text{-}dppn)_2]PF_6$ **2**	Solid (298)		642 (1.3)
	Solid (77)		647
	CH_2Cl_2 (298)	300 (33 720), 400(sh) (5330)	666 (1.5)

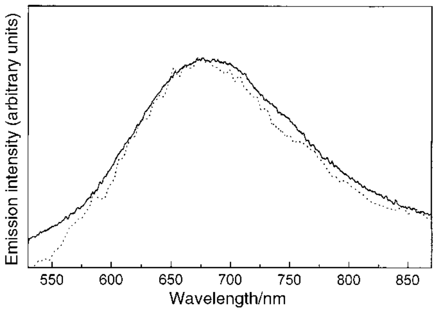

Fig. 2 EL (———) and PL (······) spectra **2** in thin films.

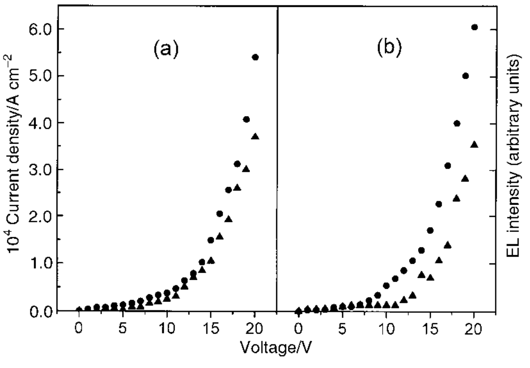

Fig. 3 Current density–voltage (●) and EL intensity–voltage (▲) curves for EL devices of ITO|**1a**–PC|Al (a) and ITO|**2**–PC|Al (b).

dichloromethane is at higher energy than **1a** is in agreement with an assignment of emissive states derived from the σ→π*(naphthalene) transition, since introduction of the methyl group would enhance the hyperconjugation effect, leading to an increase in the σ→π*(naphthalene) transition energy.

Besides exhibiting photoluminescence (PL) behaviour, both **1a** and **2** are also found to show electroluminescence (EL) when doped in polycarbonate (PC) as the emissive layer in a single-layered EL device (ITO|Au–PC|Al).† Upon being forward biased with the ITO electrode at positive polarity, the EL devices exhibit intense orange emission. The EL and PL spectra of **2** in thin films are shown in Fig. 2. The close resemblance of the EL and PL spectra suggests that the EL of these four-coordinate Au(I) complexes probably involves the same excited state as PL, *i.e.* triplet state of σ→π*(naphthalene) transition. The current density–voltage and EL intensity–voltage characteristics of the two single-layered EL devices, (ITO|**1a**–PC|Al) and (ITO|**2**–PC|Al), are shown in Fig. 3. The EL intensity exhibits an approximately linear relationship with current density and has a turn-on voltage of *ca.* 7 V. The EL intensities of the devices of **1a** and **2** at 13 V were 82 and 73 cd m^{-2} with an estimated external quantum efficiency of 0.02 and 0.01% respectively.

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Notes and references

‡ *Crystal data* for $[Au(dppn)_2]Cl$: M = 1225.47, monoclinic, space group $P2_1/n$ (no. 14), a = 16.981(4), b = 13.527(4), c = 26.399(4) Å, β = 98.75(2)°, V = 5993(2) Å^3, Z = 4, D_c = 1.358 g cm^{-3}, μ(Mo-Kα) = 26.53 cm^{-1}, $F(000)$ = 2464, T = 298 K. Convergence for 666 variable parameters by least-squares refinement of F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.036F_o^2)^2]$ for 4753 reflections with $I > 3\sigma(I)$ was reached at R = 0.060 and wR = 0.088 with a goodness-of-fit of 2.79. CCDC 182/1487. See http://www/rsc.org/suppdata/cc/a9/a908521a/ for crystallographic files in .cif format.

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