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Synthesis and photophysics of dinuclear gold(I) thiolates of bis(diphenylphosphino)-alkyl- and -aryl-amines. Crystal structure of $[Au_2\{Ph_2PN(C_6H_{11})PPh_2\}(SC_6H_4F\text{-}p)_2]$

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A series of luminescent dinuclear gold(I) thiolates, $[Au_2\{Ph_2PN(R)PPh_2\}(SR')_2]$ ($R = C_6H_{11}$, $R' = C_6H_4F\text{-}p$, $C_6H_4Cl\text{-}p$, $C_6H_4Me\text{-}p$; R = Ph, $R' = C_6H_4Me\text{-}p$; $R = Pr^n$, $R' = C_6H_4Me\text{-}p$; $R = Pr^i$, $R' = C_6H_4Me\text{-}p$) have been synthesized and their photophysical properties studied. The crystal structure of $[Au_2\{Ph_2PN(C_6H_{11})PPh_2\}(SC_6H_4F\text{-}p)_2]$ has been determined. These complexes have been shown to exhibit low-energy emission at *ca.* 600 nm, attributed to a ligand-to-metal charge transfer (thiolate to Au^I) origin.

The rich luminescent properties of polynuclear d^{10} metal complexes have attracted much attention.[1–5] Recent work by a number of groups [5a,d–g] showed that gold(I) thiolates containing phosphine ligands are emissive in the solid state. Recently, Fackler and co-workers [5a] showed that the emission energies are a function of both gold–gold interactions and the nature of the thiolates. In view of our recent interest on the luminescent behaviour of polynuclear d^{10} and d^8 metal complexes containing chalcogen ligands,[3f,j,6] a series of luminescent dinuclear gold(I) thiolates have been synthesized employing bis(diphenylphosphino)-alkyl- and -aryl-amine ligands $Ph_2PN(R)PPh_2$, the electronic properties of which could readily be tuned through a variation of the R substituent on nitrogen. We believe that through a systematic variation of the diphosphinoamine ligands and the thiolate groups, further insights into the origin of the emission can be obtained. Herein we report the synthesis, characterization and photophysical properties of a series of $[Au_2\{Ph_2PN(R)PPh_2\}(SR')_2]$ ($R = C_6H_{11}$, $R' = C_6H_4F\text{-}p$ **1**, $C_6H_4Cl\text{-}p$ **2**, $C_6H_4Me\text{-}p$ **3**; R = Ph, $R' = C_6H_4Me\text{-}p$ **4**; $R = Pr^n$, $R' = C_6H_4Me\text{-}p$ **5**; $R = Pr^i$, $R' = C_6H_4Me\text{-}p$ **6**. The crystal structure of $[Au_2\{Ph_2PN(C_6H_{11})PPh_2\}(SC_6H_4F\text{-}p)_2]$ **1** has been determined.

Experimental

Potassium tetrachloroaurate(III) was obtained from Aldrich Chemical Co., *p*-methyl-, *p*-fluoro- and *p*-chloro-benzenethiol from Lancaster Synthesis Ltd. Bis(diphenylphosphino)-cyclohexylamine, -aniline, -*n*-propylamine and -isopropylamine were synthesized by published procedures.[7] The $[Au_2\{Ph_2PN(R)PPh_2\}Cl_2]$ complexes were prepared by modification of previous procedures.[3b,8] All solvents were purified and distilled by standard procedures before use. All other reagents were of analytical grade and were used as received.

Synthesis of gold(I) complexes

All reactions were carried out under anhydrous and anaerobic conditions using standard Schlenk techniques.

$[Au_2\{Ph_2PN(C_6H_{11})PPh_2\}(SC_6H_4F\text{-}p)_2]$ 1. To a solution of $[Au_2\{Ph_2PN(C_6H_{11})PPh_2\}Cl_2]$ (100 mg, 0.11 mmol) in dichloromethane (15 cm^3) was added an ethanolic solution (1 cm^3) containing *p*-fluorobenzenethiol (27 mg, 0.21 mmol) and triethylamine (33 μl, 0.24 mmol). The reaction mixture was stirred at room temperature for 30 min, after which the solvent was removed under reduced pressure. The yellow residue was then recrystallized from benzene–dichloromethane–hexanes to give yellow crystals of complex **1**. Yield: 103 mg, 86%. ^1H NMR (300 MHz, CD_2Cl_2, 298 K, relative to $SiMe_4$): δ 0.45–1.46 (m, 10 H, cyclohexyl), 3.34–3.43 (m, 1 H, NCH of cyclohexyl), 6.79 (dd, 8 H, SC_6H_4) and 7.27–7.73 (m, 20 H, PPh_2). Positive-ion FAB mass spectrum: *m/z* 988 ($[M - SC_6H_4F\text{-}p]^+$) (Found: C, 45.0; H, 3.50; N, 1.25. Calc. for $C_{42}H_{39}Au_2F_2NP_2S_2$: C, 45.2; H, 3.50; N, 1.25%).

$[Au_2\{Ph_2PN(C_6H_{11})PPh_2\}(SC_6H_4Cl\text{-}p)_2]$ 2. The procedures were similar to those for complex **1** except that *p*-chlorobenzenethiol (31 mg, 0.21 mmol) was used instead of *p*-fluorobenzenethiol to give yellow crystals of **2**. Yield: 108 mg, 87%. ^1H NMR (300 MHz, CD_2Cl_2, 298 K, relative to $SiMe_4$): δ 0.55–1.45 (m, 10 H, cyclohexyl), 3.42–3.51 (m, 1 H, NCH of cyclohexyl), 7.00 (dd, 8 H, SC_6H_4) and 7.50–7.88 (m, 20 H, PPh_2). Positive-ion FAB mass spectrum: *m/z* 1004 ($[M - SC_6H_4Cl\text{-}p]^+$) (Found: C, 44.05; H, 3.50; N, 1.30. Calc. for $C_{42}H_{39}Au_2Cl_2NP_2S_2$: C, 43.95; H, 3.40; N, 1.2%).

$[Au_2\{Ph_2PN(C_6H_{11})PPh_2\}(SC_6H_4Me\text{-}p)_2]$ 3. Similarly, *p*-methylbenzenethiol (26 mg, 0.21 mmol) was used instead of *p*-fluorobenzenethiol to give yellow crystals of complex **3**. Yield: 100 mg, 84%. ^1H NMR (300 MHz, CD_2Cl_2, 298 K, relative to $SiMe_4$): δ 0.68–2.00 (m, 10 H, cyclohexyl), 2.22 (s, 6 H, Me group of SC_6H_4Me), 3.40–3.55 (m, 1 H, NCH of cyclohexyl), 6.95 (dd, 8 H, SC_6H_4) and 7.50–7.81 (m, 20 H, PPh_2). Positive-ion FAB mass spectrum: *m/z* 984 ($[M - SC_6H_4Me\text{-}p]^+$) (Found: C, 49.1; H, 4.55; N, 1.35. Calc. for $C_{44}H_{45}Au_2NP_2S_2{\cdot}0.5C_6H_{14}$: C, 49.05; H, 4.50; N, 1.20%).

$[Au_2\{Ph_2PN(Ph)PPh_2\}(SC_6H_4Me\text{-}p)_2]$ 4. The procedures were similar to those for complex **3** except that $[Au_2\{Ph_2PN(Ph)PPh_2\}Cl_2]$ (102 mg, 0.11 mmol) was used instead of $[Au_2\{Ph_2PN(C_6H_{11})PPh_2\}Cl_2]$ to give yellow crystals of **4**. Yield: 97 mg, 81%. ^1H NMR (300 MHz, CD_2Cl_2, 298 K, relative to $SiMe_4$): δ 2.24 (s, 6 H, Me group of SC_6H_4Me), 6.30 (dd, 2 H, NPh), 6.74 (dd, 2 H, NPh), 6.78 (dd, 4 H, SC_6H_4), 6.95 (t, 1 H, Ph proton *para* to N of NPh), 7.22 (dd, 4 H, SC_6H_4) and 7.38–7.69 (m, 20 H, PPh_2). Positive-ion FAB mass spectrum: *m/z* 978 ($[M - SC_6H_4Me\text{-}p]^+$) (Found: C, 46.25; H, 3.70; N, 1.55. Calc. for $C_{44}H_{39}Au_2NP_2S_2{\cdot}0.5CH_2Cl_2$: C, 46.7; H, 3.50; N, 1.20%).

$[Au_2\{Ph_2PN(Pr^n)PPh_2\}(SC_6H_4Me\text{-}p)_2]$ 5. Similarly, $[Au_2\{Ph_2PN(Pr^n)PPh_2\}Cl_2]$ (98 mg, 0.11 mmol) was used instead of $[Au_2\{Ph_2PN(C_6H_{11})PPh_2\}Cl_2]$ to give yellow crystals of complex **5**. Yield: 96 mg, 80%. ^1H NMR (300 MHz, CD_2Cl_2, 298 K, relative to $SiMe_4$): δ 0.16 (t, 3 H, Me group of

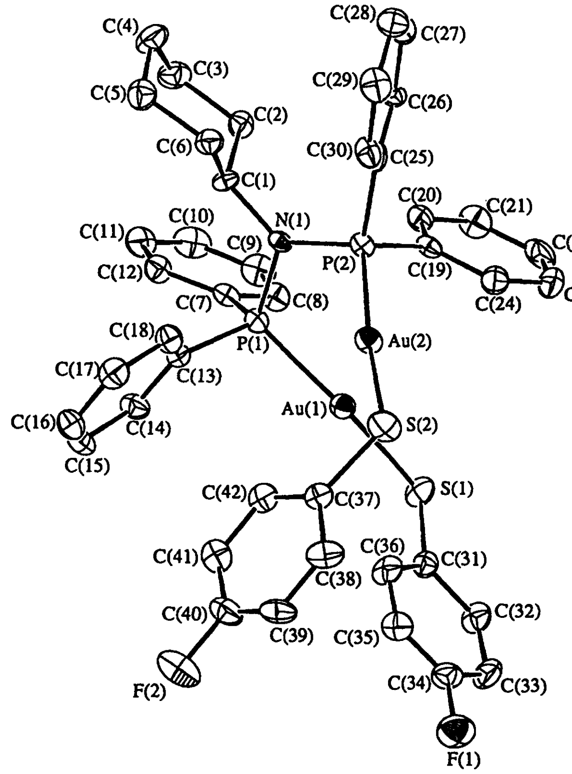

Fig. 1 Perspective view of complex **1** with the atomic numbering scheme. Thermal ellipsoids are shown at the 30% probability level

n-propyl), 0.76–0.87 (m, 2 H, CH_2 of *n*-propyl), 2.18 (s, 6 H, Me group of SC_6H_4Me), 2.70–2.83 (m, 2 H, NCH_2), 6.74 (dd, 8 H, SC_6H_4) and 7.49–7.80 (m, 20 H, PPh_2). Positive-ion FAB mass spectrum: *m/z* 945 ($[M - SC_6H_4Me\text{-}p]^+$) (Found: C, 46.2; H, 3.85; N, 1.30. Calc. for $C_{41}H_{41}Au_2NP_2S_2$: C, 46.15; H, 3.85; N, 1.30%).

$[Au_2\{Ph_2PN(Pr^i)PPh_2\}(SC_6H_4Me\text{-}p)_2]$ 6. Similarly, $[Au_2\{Ph_2PN(Pr^i)PPh_2\}Cl_2]$ (98 mg, 0.11 mmol) was used instead of $[Au_2\{Ph_2PN(C_6H_{11})PPh_2\}Cl_2]$ to give yellow crystals of complex **6**. Yield: 97 mg, 81%. ^1H NMR (300 MHz, CD_2Cl_2, 298 K, relative to $SiMe_4$): δ 1.00–1.05 (m, 6 H, Me groups of *i*-propyl), 2.20 (s, 6 H, Me group of SC_6H_4Me), 4.10–4.20 (m, 1 H, NCH), 6.98 (dd, 8 H, SC_6H_4) and 7.52–7.98 (m, 20 H, PPh_2). Positive-ion FAB mass spectrum: *m/z* 945 ($[M - SC_6H_4Me\text{-}p]^+$) (Found: C, 45.35; H, 3.80; N, 1.35. Calc. for $C_{41}H_{41}Au_2NP_2S_2\cdot0.5CH_2Cl_2$: C, 44.9; H, 3.80; N, 1.25%).

Physical measurements and instrumentation

The UV/VIS spectra were obtained on a Hewlett-Packard 8452A diode-array spectrophotometer, and steady-state excitation and emission spectra on a Spex Fluorolog 111 spectrofluorometer. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. Proton NMR spectra were obtained on a Bruker DPX-300 Fourier-transform spectrometer with chemical shifts reported relative to tetramethylsilane, positive-ion FAB mass spectra on a Finnigan MAT95 spectrometer. Elemental analyses of the new complexes were performed by Butterworth Laboratories Ltd.

Emission lifetime measurements were performed using a conventional laser system. The excitation source was the 355 nm output (third harmonic) of a Quanta-Ray Q-switched GCR-150-10 pulsed Nd-YAG laser. Luminescence decay signals were recorded on a Tektronix model TDS 620A digital oscilloscope and analysed using a program for exponential fits. All solutions for photophysical studies were prepared under vacuum in a round-bottomed flask (10 cm^3) equipped with a side-arm 1 cm fluorescence cuvette and sealed from the atmosphere with a Kontes quick-release Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze–pump–thaw cycles.

Crystallography

Crystals of complex **1** were obtained by slow evaporation of a solution of it in benzene–dichloromethane–hexanes.

Crystal data. $C_{42}H_{39}Au_2F_2NP_2S_2$, $M = 1115.77$, monoclinic, space group $P2_1/n$ (no. 15), $a = 10.005(5)$, $b = 20.973(6)$, $c = 19.240(7)$ Å, $\beta = 104.07(4)°$, $U = 3916(2)$ Å^3, $Z = 4$, $D_c = 1.892$ g cm^{-3}, μ(Mo-Kα) = 77.39 cm^{-1}, $F(000) = 2144$, $T = 301$ K.

A pale yellow crystal of dimensions 0.25 × 0.20 × 0.35 mm sealed inside a glass capillary was used for data collection at 28 °C on a Rigaku AFC7R diffractometer with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.710\ 73$ Å) using ω–2θ scans with ω-scan angle $(0.73 + 0.35 \tan\theta)°$ at a scan speed of 16.0° min^{-1} [up to six scans for $I < 15\sigma(I)$]. Intensity data ($2\theta_{max} = 45°$; *h* 0–10, *k* 0–22, *l* −20 to 20 and three standard reflections measured after every 300, decay 0.72%) were corrected for decay and for Lorentz-polarization effects, and empirical absorption corrections based on the ψ scans of four strong reflections (minimum and maximum transmission factors 0.583 and 1.000). Upon averaging the 5650 reflections, 5294 of which were uniquely measured ($R_{int} = 0.023$), 4180 with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. The space group was determined from systematic absences and the structure solved by Patterson methods and expanded by Fourier methods (PATTY[9]) and refined by full-matrix least squares using the software package TEXSAN[10] on a Silicon Graphics Indy computer. All 51 non-hydrogen atoms of the complex molecule were refined anisotropically; 39 hydrogen atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 460 variable parameters by least-squares refinement on *F* with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = \sigma^2(I) + 0.014(F_o^2)^2$ for 4180 reflections with $I > 3\sigma(I)$ was reached at $R = 0.025$ and $R' = 0.027$ with a goodness of fit of 1.57; $(\Delta/\sigma)_{max} = 0.01$. The final Fourier-difference map was featureless, with maximum positive and negative peaks of 0.76 and 0.85 e Å^{-3} respectively. The Au(1) ··· Au(2) non-bonded distance is 3.4379(4) Å. There is an intermolecular contact involving non-hydrogen atoms of 3.24(1) Å between C(11) and C(31) at $1 + x, y, z$. Selected bond distances and angles are summarized in Table 1.

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 186/215.

Results and Discussion

The dithiolatogold(I) phosphine complexes were prepared by reactions of the corresponding dichlorogold(I) phosphine complexes with arenethiolates generated *in situ* from the arenethiol and triethylamine as the base. Similar reactions were used for the preparation of analogous thiolatogold(I) phosphine complexes using bases such as KOH and ethanolamine.[5a,d] All the newly synthesized complexes gave satisfactory elemental analyses and have been characterized by positive-ion FAB mass spectrometry and ^1H NMR spectroscopy. Complex **1** has also been characterized by X-ray crystallography.

The perspective drawing of complex **1** with atomic numbering is depicted in Fig. 1. The molecular structure shows a highly unsymmetrical geometry. Each gold atom is two-co-

Table 1 Selected bond distances (Å) and angles (°) for complex **1** with estimated standard deviations in parentheses

Au(1) ··· Au(2)	3.4379(4)	Au(2)–P(2)	2.267(2)
Au(1)–S(1)	2.290(2)	S(1)–C(31)	1.757(7)
Au(2)–S(2)	2.290(2)	S(2)–C(37)	1.761(7)
Au(1)–P(1)	2.257(2)	N(1)–C(1)	1.517(8)
S(1)–Au(1)–P(1)	165.41(7)	Au(2)–P(2)–N(1)	111.4(2)
S(2)–Au(2)–P(2)	172.38(7)	P(1)–N(1)–P(2)	114.5(3)
Au(1)–S(1)–C(31)	110.3(2)	P(1)–N(1)–C(1)	115.3(4)
Au(2)–S(2)–C(37)	111.9(3)	P(2)–N(1)–C(1)	130.2(4)
Au(1)–P(1)–N(1)	115.7(2)		

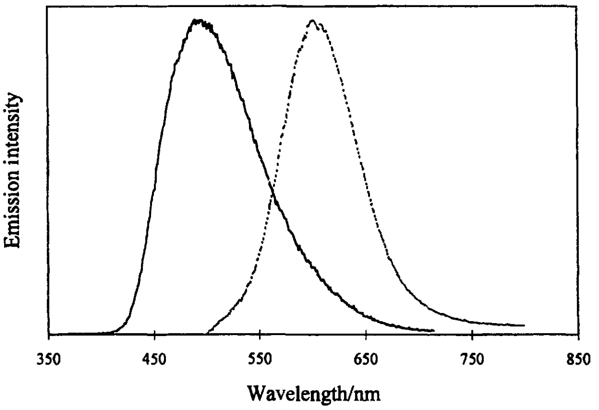

Fig. 2 Normalized emission spectra of complex **5** as a 77 K $CHCl_3$ glass excited at 300 (——) and 440 nm (– – –)

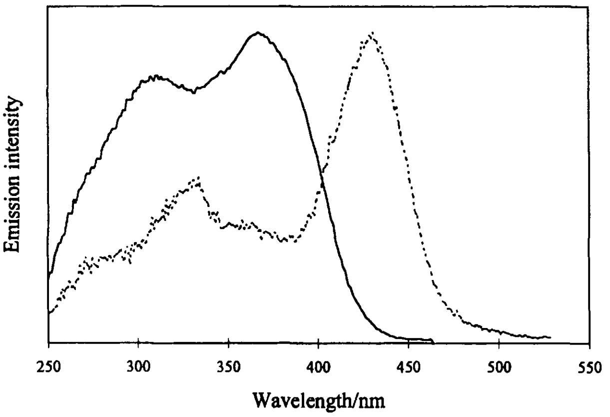

Fig. 3 Normalized excitation spectra of complex **5** as a 77 K $CHCl_3$ glass monitored at λ = 500 (——) and 650 nm (– – –)

Table 2 Photophysical data for complexes **1**–**6**

Complex	Absorption λ/nm (ε/dm^3 mol^{-1} cm^{-1})^a	Medium (T/K)	Emission λ/nm (τ_0/μs)
1	278 (sh) (23 310),	Solid (298)	519 (0.18, 0.77)^b
	304 (sh) (14 615),	Solid (77)	540
	372 (sh) (2475)	CH_2Cl_2 (298)	503
		$CHCl_3$ glass (77)	488, 567
2	280 (sh) (29 945),	Solid (298)	513 (0.64, 3.6)^b
	298 (sh) (24 450),	Solid (77)	528
	364 (sh) (3355)	CH_2Cl_2 (298)	499
		$CHCl_3$ glass (77)	485, 545
3	276 (sh) (28 265),	Solid (298)	519, 552 (0.19, 0.81)^b
	304 (sh) (15 125),		
	380 (sh) (1550)	Solid (77)	522, 590
		CH_2Cl_2 (298)	503
		$CHCl_3$ glass (77)	498, 607
4	276 (sh) (22 590),	Solid (298)	506 (0.28)
	298 (sh) (14 620),	Solid (77)	508, 578
	382 (sh) (1810)	CH_2Cl_2 (298)	518
		$CHCl_3$ glass (77)	495, 618
5	264 (sh) (29 915),	Solid (298)	530 (0.11, 0.45)^b
	298 (sh) (22 970),	Solid (77)	525, 602
	378 (sh) (4270)	CH_2Cl_2 (298)	557
		$CHCl_3$ glass (77)	495, 602
6	268 (sh) (26 875),	Solid (298)	517 (0.29, 1.4)^b
	300 (sh) (19 305),	Solid (77)	520, 609
	382 (sh) (3130)	CH_2Cl_2 (298)	540
		$CHCl_3$ glass (77)	493, 604

[a] All spectra were recorded in CH_2Cl_2. [b] All lifetimes measured were double exponential.

ordinate, bound to the sulfur atom of the thiolate group and the phosphorus atom of the diphosphine ligand, with P(1)–Au(1)–S(1) and P(2)–Au(2)–S(2) angles of 165.41(7) and 172.38(7)°, respectively. Interestingly, the latter angle only slightly deviates from ideal linearity which is typical of sp hybridization in Au^I, while the former is distorted to a larger extent. It is also interesting that the bis(diphenylphosphino)amine ligand has a bite distance within separations well suited for short Au ··· Au contacts [P(1) ··· P(2) 2.87 Å], and yet the Au ··· Au separation of 3.4379(4) Å is indicative of very weak to no gold–gold interactions. It is likely that the absence of short Au ··· Au and S ··· S contacts [S(1) ··· S(2) 5.75 Å] as well as the highly unsymmetrical structure in **1** are a consequence of the steric requirements of the ligands. The shorter non-bonded contact of Au(1) ··· P(2) of 3.449(2) Å than that of Au(2) ··· P(1) [3.657(2) Å] may be a result of the larger deviation of the P(1)–Au(1)–S(1) angle from linearity. The P(1)–N(1)–P(2) bond angle of 114.5(3)° and P–N bond distances of 1.708(5) and 1.705(5) Å are typical of those found in complexes containing this type of ligand in the bridging mode.[11] The dihedral angle between the planes of the two phenyl rings of the thiolate ligands is 81.09°. The arrangement of the two adjacent Au–P groups is neither *syn* nor *anti*, with a P(1)–Au(1)–Au(2)–P(2) torsion angle of 50.6°. The Au–S bond distances of 2.290(2) Å and Au–P distances of 2.257(2) and 2.267(2) Å are typical of two-co-ordinate gold(I) compounds.[5d,12] The cyclohexyl unit on the bis(diphenylphosphino)amine ligand adopts a typical chair conformation, while the co-ordination about the nitrogen atom is highly planar, with the atoms N(1), P(1), P(2) and C(1) all lying more or less on the same plane. Such a planar geometry is always found in compounds involving this class of ligand.[11,13]

The electronic absorption spectra of complexes **1**–**6** show low-energy absorption bands at *ca.* 365–385 nm, which are absent for the corresponding dichlorogold(I) precursors. It is likely that such bands originate from a thiolate to gold ligand-to-metal charge-transfer (l.m.c.t.) transition, given the better σ-donor ability of the thiolate ligand relative to the chloro group. Similar assignments have been made for analogous gold(I) thiolate systems.[5] The high-energy absorptions at *ca.* 265–305 nm, which are also present for the chloro analogues, are tentatively assigned as intraligand transitions characteristic of the diphosphine ligands. Excitation of solid samples of complexes **1**–**6** with visible light at room temperature and at 77 K results in intense luminescence. The photophysical data are summarized in Table 2. At room temperature, the solid-state and fluid-solution emission spectra are dominated by a broad intense blue-green emission, typical of metal-perturbed ligand-centred emission. However, upon excitation of the solid sample at 77 K, the shape of the emission band becomes highly unsymmetrical; sometimes this could be resolved into two broad bands, a higher-energy one in the blue-green region similar to that observed at room temperature and a lower-energy band in the orange. This becomes even more obvious for the 77 K emissions in $CHCl_3$ glass matrices (Fig. 2). Such dual emissive behaviour is suggestive of two closely lying emissive states of separate origins. The excitation spectra of the complexes monitored at the low-energy emission band at *ca.* 600 nm show excitation bands at *ca.* 440 nm, while those monitored at *ca.* 500 nm show bands at *ca.* 300 nm (Fig. 3). This is in agreement with the assignment that the 500 nm emission arises from states derived from the metal-perturbed intraligand (i.l.) transitions. The possibility of the involvement of a phenyl-localized $^3\pi\pi^*$ origin on the phosphine ligands is not unlikely since similar emission has also been reported in other related gold(I) systems.[14] It is likely that the low-energy emissions at *ca.* 600 nm, which are absent for the chlorogold(I) counterparts, originate from emissive states derived from thiolate-to-gold l.m.c.t. transitions. The large Stokes shifts together with the observed lifetimes in the microsecond range are suggestive of a triplet parentage. The 440 nm excitation band, which appears as a very weak tail and is possibly obscured by the more intense absorption bands in the electronic absorption spectrum of **5**, is tentatively assigned as derived from a ^{3}l.m.c.t. origin, in line with the phosphorescent nature of the 600 nm emission band. Further support for an l.m.c.t. origin comes from the observed trends in emission energies upon variation of the thiolate ligands. Complexes **1** and **2** emit at higher energies than that of **3** (567 nm for **1** and 545 nm for **2** *vs.* 607 nm for **3**), in line with an assignment involving states derived from a l.m.c.t. transition, where the σ-donor ability of the thiolate moiety containing a tolyl substituent is expected to be the best. On pure electronic grounds, the fluoro-substituted thiolate in **1** should be a poorer σ donor than its chloro counterpart in **2**. Thus the anomalously lower emission energy of **1** relative to **2** probably arises as a result of the stronger mesomeric effect of the fluoro substituent which increases the electron density on the sulfur atom through π donation into its empty 3d orbital. Similar observations have been reported in ^{31}P NMR spectroscopic studies of fluoro-substituted phosphines.[15] With complexes **3**–**6**, the low-energy emissions are relatively insensitive to the nature of the bis(diphenylphosphino)amine ligands. The slightly lower emission energy for **4** (618 nm) may be accounted by the presence of the less electron-rich $Ph_2PN(Ph)PPh_2$ ligand, which renders the gold(I) centres more electron deficient and hence lowers the metal acceptor-orbital energy. Although we cannot completely exclude the possibility of a thiolate to phosphine ligand-to-ligand charge-transfer (l.l.c.t.) transition as the origin of the emission, we favour the assignment of a l.m.c.t. origin on the following grounds. First, only a small dependence of emission energies on the nature of the diphosphine ligand is observed. An emission of l.l.c.t. origin should give rise to a much larger energy dependence. Secondly, spectroscopic studies on other similar gold(I) thiolate systems have also confirmed a l.m.c.t. origin for the emission.[5] A ligand to metal–metal-bonded charge-transfer (l.m.m.c.t.) origin which has been suggested to operate in the solid-state emission of some gold(I) thiolate complexes[5a] is unlikely in the present complexes since there is no evidence of gold–gold interactions of any kind, neither intra- nor inter-molecular.

Acknowledgements

V. W.-W. Y. acknowledges financial support from the Research Grants Council, the Croucher Foundation and The University of Hong Kong. C.-L. C. acknowledges the receipt of a Croucher Studentship, administered by the Croucher Foundation.

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Received 8th May 1996; *Paper* 6/03206K