Syntheses, Crystal Structures and Photophysics of Organogold(III) Diimine Complexes

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A series of luminescent organogold(III) diimine complexes have been synthesised and the crystal structures of [Au(bipy)(mes)$_2$]ClO$_4$ (bipy = 2,2′-bipyridine, mes = mesityl) and [Au(phen)(CH$_2$SiMe$_3$)$_2$]-ClO$_2$ (phen = 1,10-phenanthroline) have been determined.

Recently the search for luminescent inorganic materials which are co-ordinatively unsaturated has attracted much attention in view of their high potential as excited-state atom-transfer reagents. Although a number of luminescent d^8 complexes of platinum(II) have been studied,[1–4] relatively little is known about the luminescence of the isoelectronic d^8 gold(III) species. A probable reason for the absence of luminescent properties in gold(III) species is the presence of low-energy d–d states. Mononuclear d^8 metal complexes of diimine ligands, if they are luminescent, emit from either intraligand (i.l.) π–π* or metal-to-ligand charge-transfer (m.l.c.t.) states. We believe that the introduction of good σ-donor ligands would render the metal centre more electron-rich, with the additional advantage of raising the energy of the d–d states which would improve the chance of obtaining luminescent complexes. In this contribution we report on the syntheses and photophysics of a new class of organogold(III) diimine complexes, two of which namely, [Au(bipy)(mes)$_2$]ClO$_4$ **1** (bipy = 2,2′-bipyridine, mes = mesityl) and [Au(phen)(CH$_2$SiMe$_3$)$_2$]ClO$_4$ **2** (phen = 1,10-phenanthroline) have been characterised by X-ray crystallography.

The [Au(L–L)R$_2$]ClO$_4$ complexes were prepared by the reaction of [Au(L–L)Cl$_2$]ClO$_4$ (200 mg in 30 cm^3 thf) with MgR(X) (2 equivalents) in tetrahydrofuran (thf) under nitrogen at −78 °C [L–L = bipy, phen or dpphen(4,7-diphenylphenanthroline); R = CH$_2$SiMe$_3$ or mes]. The mixture was stirred for 3–4 h at room temperature, the solvent removed *in vacuo*, and the residue extracted with MeCN. The complexes were recrystallised from MeCN–Et$_2$O as air-stable colourless to pale yellow crystals (yield *ca.* 60–70%), all of which gave satisfactory elemental analyses and have been characterised by ^{1}H NMR spectroscopy. The structures of the cations of **1** and **2** are depicted in Figs. 1 and 2, respectively.† The co-ordination geometry of the gold atom in both complexes is distorted slightly from square planar. The Au–N bond distances are comparable to those found in [Au(terpy)Cl]$^{2+}$ (terpy = 2,2′:6′,2″-terpyridine),[6] [Au(dien)Cl]$^{2+}$ (dien = diethylenetriamine)[7] and [Au(en)(SO$_3$)$_2$]$^-$ (en = ethane-1,2-diamine).[8] The Au–N and Au–C distances are also similar to those found for [AuMe$_2${HB(pz)$_3$}][9] (pz = pyrazolyl) and [AuMe$_2$(dpk·H$_2$O)]NO$_3$ (dpk = di-2-pyridyl ketone).[10] The N(1)–Au–N(2) angles of 78.6(2) and 78.2(2)° in **1** and **2**, which deviate from the square-planar geometry, are a result of the steric requirements of the diimine ligands. A stereoview of the unit-cell packing of **2** shows the phenanthroline ligands are oriented with their planes roughly parallel to each other.

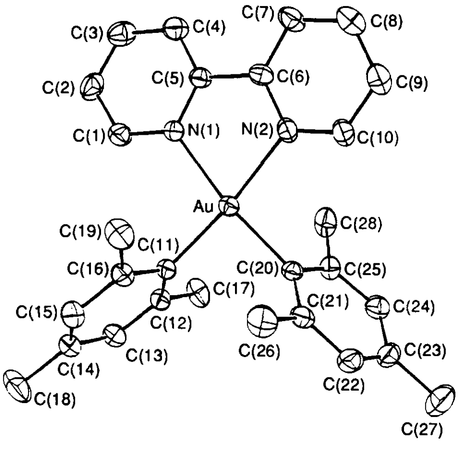

Fig. 1 Structure of [Au(bipy)(mes)$_2$]$^+$ showing atomic numbering. Selected bond distances (Å) and angles (°); Au–N(1) 2.120(4), Au–N(2) 2.131(5), Au–C(11) 2.029(6), Au–C(20) 2.020(5); N(1)–Au–N(2) 78.6(2), C(11)–Au–C(20) 91.9(2), N(1)–Au–C(11) 95.0(2), N(2)–Au–C(20) 95.4(2), Au–C(11)–C(12) 123.0(5), Au–C(11)–C(16) 115.9(6), Au–C(20)–C(21) 124.2(4), Au–C(20)–C(25) 116.6(4), Au–N(1)–C(5) 113.7(3), Au–N(2)–C(6) 113.5(4)

The electronic absorption spectra of all the complexes studied are dominated by intense bands at *ca.* 300 nm (ε > 10^4 dm^3 mol^{-1} cm^{-1}), with some weaker ones at 330–380 nm in acetonitrile. The intense bands are assigned as diimine intraligand [$\pi(a_2) \longrightarrow \pi^*(b_2)$] (^{1}i.l.) transitions assuming C_{2v} symmetry. The less-intense ^{1}m.l.c.t. absorption [$d_{z^2}(a_1) \longrightarrow \pi^*(b_2)$] in C_{2v} symmetry occurs in the same region and is often partially or wholly obscured. Excitation of organogold(III) diimine complexes in the solid state and in fluid solutions at λ > 30 nm at room temperature gave rise to photoluminescence. The low-temperature solid-state emission spectra of [Au(L–L)R$_2$]$^+$ show well resolved vibronically structured bands with vibrational spacings of *ca.* 1300–1400 cm^{-1}, corresponding to the C=N and C=C stretches of the aromatic diimine ligands. The emission spectra of [Au(bipy)(CH$_2$SiMe$_3$)$_2$]$^+$ (Fig. 3) and [Au(phen)(CH$_2$SiMe$_3$)$_2$]$^+$ in degassed acetonitrile also exhibit vibronically structured emission. The photophysical data are summarized in Table 1. The observation of vibronic structures to a diimine effective frequency indicates diimine participation in the excited state. The emissions are probably ^{3}i.l. [$\pi(a_2) \longrightarrow \pi^*(b_2)$] or ^{3}m.l.c.t. [$d_{z^2}(a_1) \longrightarrow \pi^*(b_2)$] in origin assuming C_{2v} symmetry. Although the relatively lower emission energies of

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† *Crystal data.* 1, C$_{28}$H$_{30}$AuClN$_2$O$_4$, M_r = 690.98, monoclinic, space group $P2_1/c$, crystal dimensions 0.05 × 0.12 × 0.46 mm, a = 17.725(3), b = 11.236(1), c = 14.727(4) Å, β = 113.54(2)°, U = 2689(2), Å^3, Z = 4, D_c = 1.707 g cm^{-3}, μ(Mo-Kα) = 55.95 cm^{-1}, F(000) = 1360, 325 parameters, R = 0.034, R' = 0.038 for 3712 observed data with $I > 1.5\sigma(I)$ with $w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$. 2, C$_{20}H_{30}$AuClN$_2O_4Si_2$, M_r = 651.07, monoclinic, space group $P2_1/c$, dimensions 0.12 × 0.39 × 0.42 mm, a = 17.928(3), b = 11.005(2), c = 13.400(2) Å, β = 101.36(1)°, U = 2592(1) Å^3, Z = 4, D_c = 1.668 g cm^{-3}, μ(Mo-Kα) = 58.85 cm^{-1}, F(000) = 1280, 251 parameters, R = 0.050, R' = 0.067 for 3902 observed reflections with $I > 1.5\sigma(I)$ with $w = 4F_o^2/[\sigma^2(F_o^2) + (0.07F_o^2)^2]$. Diffraction data were collected on an Enraf-Nonius diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Both structures were solved by heavy-atom methods and refined by full-matrix least squares. All calculations were performed on a MicroVax II computer using the SDP package.[5] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Photophysical data for gold(III) diimine complexes

Complex	Absorption [a] λ/nm(ε_{max}/dm^3 mol^{-1} cm^{-1})	Emission λ/nm (τ_o/μs)
$[Au(bipy)(mes)_2]^+$	307 (15 070), 319 (15 680)	480 (1.2 ± 0.1),[b] 478,[c] 506 (0.60 ± 0.06)[d]
$[Au(phen)(mes)_2]^+$	278 (32 055), 301 (10 210), 333 (1665), 350 (1125)	531 (0.34 ± 0.03),[b] 508,[c] 541 (0.40 ± 0.04)[d]
$[Au(bipy)(CH_2SiMe_3)_2]^+$	306 (12 540), 318 (13 830)	495 (0.35 ± 0.03),[b] 490,[c] 503 (0.28 ± 0.03)[d]
$[Au(phen)(CH_2SiMe_3)_2]^+$	277 (22 935), 300 (5890), 310 (2900), 332 (810), 348 (545)	540 (0.32 ± 0.03),[b] 517,[c] 485,515 (4.0 ± 0.5)[d]
$[Au(dpphen)(mes)_2]^+$	294 (41 150), 325 (11 695), 351 (4835), 365 (3395)	466 (0.30 ± 0.03),[b] 512–540,[c] 505 (0.23 ± 0.02)[d]
$[Au(bipy)Cl_2]^+$	282 (12 275), 308 (5085), 324 (4590)	457 (0.30 ± 0.03),[b] 444,640[c]
$[Au(phen)Cl_2]^+$	264 (43 355), 275(sh) (28 970)	487 (0.32 ± 0.03),[b] 466[c]
$[Au(dpphen)Cl_2]^+$	274 (40 980), 299(sh) (21 265)	522 (0.32 ± 0.03),[b] 491[c]

[a] In MeCN at 298 K. [b] Solid at 298 K. [c] Solid at 77 K. [d] In MeCN at 298 K.

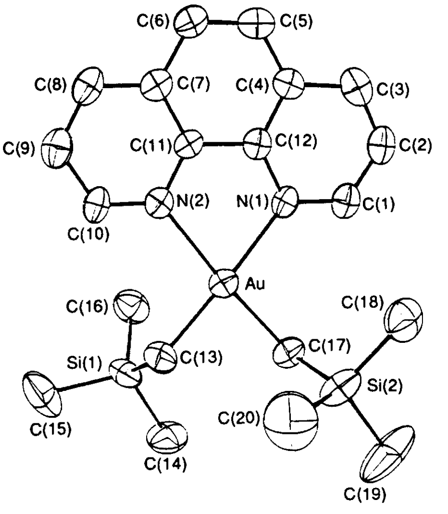

Fig. 2 Structure of $[Au(phen)(CH_2SiMe_3)_2]^+$ showing atomic numbering. Selected bond distances (Å) and angles (°): Au–N(1) 2.128(6), Au–N(2) 2.169(6), Au–C(13) 2.031(9), Au–C(17) 2.039(9), N(1)–Au–N(2) 78.2(2), C(13)–Au–C(17) 86.5(4), N(1)–Au–C(17) 97.4(3), N(2)–Au–C(13) 97.9(3), Au–C(13)–Si(1) 116.5(5), Au–C(17)–Si(2) 115.7(4), Au–N(1)–C(12) 113.6(5), Au–N(2)–C(11) 112.3(5)

$[Au(bipy)R_2]^+$ and $[Au(phen)R_2]^+$ compared to their dichloro precursors might suggest a ^{3}m.l.c.t. origin for these organogold(III) emissions, the similar emission energies and band shapes observed for $[Au(bipy)R_2]^+$ and $[Pt(bipy)(en)]^{2+}$[2c] would favour the assignment of an ^{3}i.l. origin. Moreover, this is further complicated by the observation that the excitation maxima for the $[Au(bipy)R_2]^+$ and $[Au(phen)R_2]^+$ complexes occur at much lower energy than that of the dichloro counterparts and are centred at *ca.* 340–450 nm, suggestive of a ^{3}m.l.c.t. origin. Therefore it is too early unambiguously to assign the observed emissions as either i.l. or m.l.c.t. or a mixture of both. On the other hand, the similarity in emission energies of $[Au(dpphen)(mes)_2]^+$ and $[Au(dpphen)Cl_2]^+$ is probably suggestive of a common origin for the emission, which is likely to be ^{3}i.l. An interesting point concerning the emissive properties of $[Au(bipy)Cl_2]^+$ is that its spectrum at 77 K shows an additional band at 640 nm which is absent at 298 K. This is likely to result from stacking Au ··· Au interactions or ligand–ligand excimeric interactions at low temperature where a contraction of the solid-state lattice is anticipated. Similar observations have been reported on the platinum(II) diimine system.[2c,d] Also of interest is that, with the introduction of organic functionalities on the gold(III) diimine complexes, the relative luminescence quantum yields have improved significantly over those of their dichloro counterparts, probably as a result of raising the ligand-field d–d excited-state energies. It is envisaged that the gold(III) diimine system would exhibit rich and interesting photophysical and photochemical properties. Further work to elucidate the origin of these emissions and other related systems is now in progress.

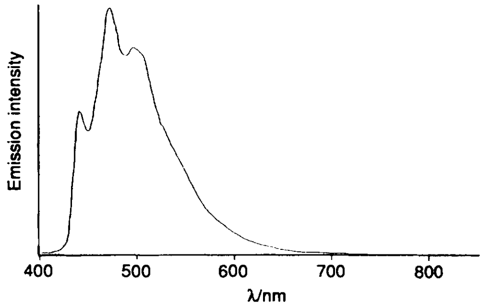

Fig. 3 Emission spectrum of $[Au(bipy)(CH_2SiMe_3)_2]ClO_4$ in degassed MeCN at 298 K

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