Luminescent Gold Complexes

Luminescent Gold(III) Alkynyl Complexes: Synthesis, Structural Characterization, and Luminescence Properties**

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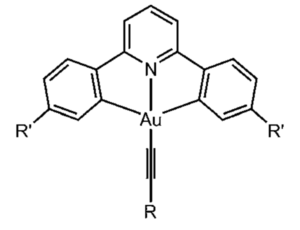
In contrast to the related gold(I)[1–3] and the isoelectronic platinum(II) compounds,[4,5] which are known to show rich luminescence properties, luminescent gold(III) compounds are rare, with very few exceptions that emit at room temperature in solution.[6] The reasons for the lack of luminescence in gold(III) species are probably the presence of low-energy d–d ligand field (LF) states and the electrophilicity of the gold(III) center. The presence of a nonemissive low-lying d–d state would quench the luminescence excited state by thermal equilibration or energy transfer.[7] Coupling of strong σ-donating alkynyl ligands to gold(III) should render the metal center more electron rich, with the additional advantage of raising the energy of the d–d states, which would result in enhanced luminescence by increasing the chances of populating the emissive state for the construction of luminescent organometallic materials. Despite the fact that alkynyl complexes of gold(I)[3] and the isoelectronic platinum(II)[5] are known and have been shown to display rich photoluminescence properties, to our surprise, alkynyl complexes of gold(III) are extremely rare.[8] Although there is increasing interest in the use of gold(III) compounds for catalysis of organic synthetic reactions of alkynes,[9] the chemistry of gold(III) alkynyls is essentially unexplored and underdeveloped, and their luminescence properties are virtually unknown.

Herein we describe the synthesis of a novel series of bis-cyclometalated gold(III) alkynyl complexes [Au(C^N^C)-(C≡CR)] [HC^N^CH = 2,6-diphenylpyridine, R = C_6H_5 (**1**), C_6H_4-Cl-*p* (**2**), C_6H_4-OCH_3-*p* (**3**), C_6H_4-NH_2-*p* (**4**); HC^N^CH = 2,6-bis(4-*tert*-butylphenyl)pyridine, R = C_6H_5 (**5**)], which are the first of their kind (Scheme 1). The molecular structure of **1** was determined by X-ray crystallography. The photophysical properties of **1**–**5** were also studied.



R' = H; R = C_6H_5 (**1**)
C_6H_4-Cl-*p* (**2**)
C_6H_4-OCH_3-*p* (**3**)
C_6H_4-NH_2-*p* (**4**)
R' = *t*Bu; R = C_6H_5 (**5**)

Scheme 1.

Unlike most other gold(III) compounds, which exhibit luminescence only at low temperature or are nonemissive, complexes **1**–**5** display luminescence in various media at both low and ambient temperature.

Figure 1 shows the crystal structure of **1**, in which the gold(III) center adopts a distorted square-planar coordination geometry with C(9)-Au(1)-C(25) and N(1)-Au(1)-C(1) angles of 162.0(3) and 178.5(3)°, respectively, as is characteristic of d^8 metal complexes. The C^N^C ligand and the gold(III) center are essentially coplanar, with the plane lying at a dihedral angle of 64.97° with respect to the ethynylbenzene moiety. The bond lengths about the gold(III) center and the C^N^C

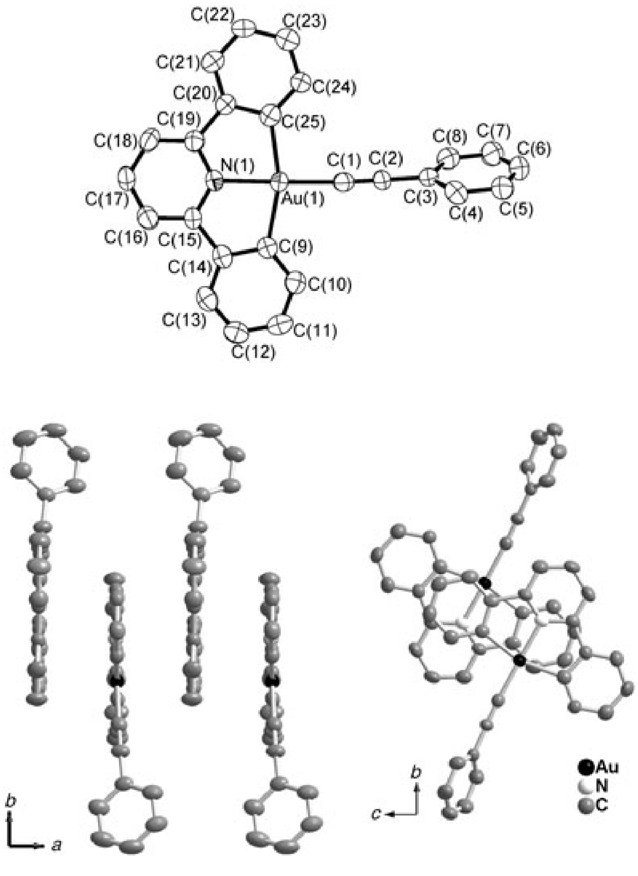


Figure 1. Top: Crystal structure of **1** with atomic numbering scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths [Å] and angles [°]: Au(1)–C(1) 1.979(7), Au(1)–C(9) 2.073(7), Au(1)–C(25) 2.071(7), Au(1)–N(1) 1.999(5), C(1)–C(2) 1.185(9); C(9)-Au(1)-C(25) 162.0(3), N(1)-Au(1)-C(1) 178.5(3), Au(1)-C(1)-C(2) 176.6(7), C(1)-C(2)-C(3) 177.6(9). Bottom: Crystal packing showing the π···π stacking arrangement in different views.

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ligand [Au(1)–C(9) 2.073(7), Au(1)–C(25) 2.071(7), Au(1)–N(1) 1.999(5) Å] are similar to the Au–C and Au–N distances in related gold(III) bis-cyclometalated complexes[10] and are also comparable to the Pt–C and Pt–N distances in analogous platinum(II) complexes.[5c–f] The Au–C(1) and C(1)–C(2) bond lengths of 1.979(7) and 1.185(9) Å, respectively, as well as the Au(1)-C(1)-C(2) bond angle of 176.6(7)° are comparable to those found in gold(I) alkynyl[3] and analogous platinum(II) alkynyl complexes.[5c–f] The shortest Au···Au distance of 5.003(1) Å indicates the absence of significant Au···Au interaction. However, the crystal packing of **1** (Figure 1) reveals the presence of partially staggered [Au$^{\text{III}}$-C^N^C] units with interplanar distances of 3.384 Å between the adjacent C^N^C ligands, suggestive of the presence of aromatic π···π stacking interactions.

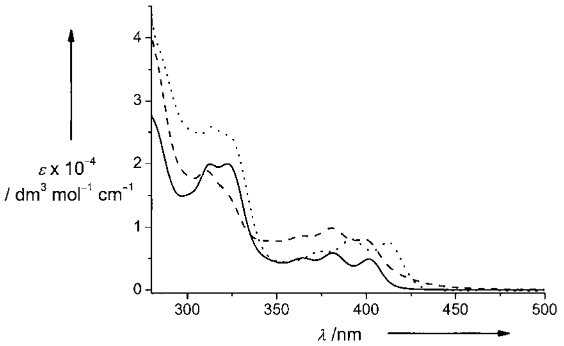

Figure 2. Electronic absorption spectra of **1** (——), **4** (-----), and **5** (•••••) in dichloromethane solution at room temperature.

All complexes exhibit an intense absorption band at 312–323 nm and a moderately intense vibronic-structured absorption band at 362–412 nm in dichloromethane. The photophysical data of **1**–**5** are collected in Table 1, and the electronic absorption spectra of **1**, **4**, and **5** are shown in Figure 2. The vibrational progressional spacings of 1310–1380 cm^{-1} in the lower energy absorption band correspond to the skeletal vibrational frequency of the C^N^C ligand. The absorption energy was found to be rather insensitive to the nature of the alkynyl ligand. In addition, the observation of similar absorption bands for the chloro counterpart [Au(C^N^C)Cl] is suggestive of the lack of involvement of the alkynyl ligands in this transition. In view of this, and the nonreducing nature of gold(III), such low-energy absorptions are assigned as metal-perturbed intraligand (IL) π–π* transition of the C^N^C ligand, involving some charge transfer from the phenyl moiety to the pyridyl unit. This is further supported by the lower absorption energy of **5** compared to **1** with the same alkynyl ligand. The observation of a lower energy metal-perturbed IL π–π* transition in **5** is ascribed to the better electron-donating properties of the *tert*-butyl group on the phenyl rings, which raises the energy of the HOMO localized on the phenyl ring and thus narrows the gap between the HOMO and the pyridine-localized LUMO. Similar assignments were also suggested for other related gold(III) complexes.[10] Interestingly, an additional shoulder was observed in the electronic absorption spectrum of **4** at about 415 nm (Figure 2). Since the alkynyl ligand with an electron-rich amino substituent has better electron-donating ability, the presence of a low-lying alkynyl-to-diarylpyridine

Table 1: Photophysical data for **1**–**5**.

Complex	Absorption λ_{max} [nm] (ε_{max} [dm^3 mol^{-1} cm^{-1}])[a]	Medium (T [K])	Emission λ_{max} [nm] (τ_0 [μs])	Φ_{em}[b]
1	312 (19890), 322 (19980), 364 (5050), 381 (5870), 402 (4870)	CH_2Cl_2 (298)[c]	476, 506, 541, 582 (<0.05)	1.0×10^{-3}
		solid (298)	588	
		thin film (298)[d]	568	
		solid (77)	496 (28.3, 310.4)[f]	
		glass (77)[c,e]	470, 503, 537, 585 (194)	
2	312 (19400), 322 (19640), 365(4640), 382 (5170), 402 (4305)	CH_2Cl_2 (298)[c]	476, 506, 539, 584 (<0.05)	0.2×10^{-3}
		solid (298)	550 (<0.05)	
		solid (77)	500 (25.3, 256.6)[f]	
		glass (77)[c,e]	470, 504, 534, 590 (151)	
3	312 (13820), 322 (13455), 362 (6400), 380 (6245), 400 (4190)	CH_2Cl_2 (298)[c]	474, 505, 539, 584 (<0.05)	0.5×10^{-3}
		solid (298)	555 (<0.05)	
		solid (77)	485 (28.4, 268.2)[f]	
		glass (77)[c,e]	470, 503, 536, 585 (137)	
4	310 (19195), 322 sh (15680), 365 (8855), 381 (10100), 399 (8300), 415 sh (3410)	CH_2Cl_2 (298)	611 (0.3)	2.0×10^{-3}
		solid (298)	585 (0.2)	
		solid (77)	548 (0.3, 1.7)[f]	
		glass (77)[c,e]	470, 503, 535, 587 (107)	
5	313 (26190), 323 (24460), 374 (6130), 392 (8035), 412 (7465)	CH_2Cl_2 (298)[c]	484, 514, 548, 593 (0.1)	6.0×10^{-3}
		solid (298)	550 (<0.05)	
		solid (77)	503 (18.2, 171.9)[f]	
		glass (77)[c,e]	478, 512, 548, 600 (200)	

[a] In dichloromethane at 298 K. [b] Luminescence quantum yield, measured at room temperature with $[Ru(bpy)_3]^{2+}$ as standard. [c] Vibronic-structured emission band. [d] Prepared by vacuum deposition. [e] In CH_2Cl_2/EtOH/MeOH (1:40:10). [f] Double-exponential decay.

ligand-to-ligand charge-transfer (LLCT) transition is possible. Thus, the low-energy absorptions in **4** are assigned as an admixture of intraligand (IL) π–π*(C^N^C)/LLCT π(C≡C-C_6H_4-NH_2-*p*)→π*(C^N^C) transitions.

Unlike most other gold(III) compounds, which are non-emissive or only show luminescence at low temperature, **1**–**5** display intense luminescence at 468–611 nm in solution on excitation at $\lambda \geq 360$ nm at room temperature (Table 1). This supports the idea that introduction of strong σ-donating alkynyl ligands into gold(III) compounds would enhance the luminescence properties by increasing the d–d splitting, as opposed to the observation of emission only in low-temperature glasses of the chloro analogue [Au(C^N^C)Cl].[10] The long-lived emission with lifetimes in the microsecond range is suggestive of a triplet parentage. In general, the emission energies of the compounds were found to be rather insensitive to the nature of the alkynyl ligands. A vibronic-structured emission band with band maximum at around 480 nm was observed for **1**–**3** and **5** in dichloromethane at room temperature (Figure 3). The vibrational progressional spacings of about 1300 cm^{-1} are in line with the C=C and C=N stretching frequencies of the tridentate ligand, indicative of the involvement of the tridentate ligand in the excited state origin. The luminescence is assigned as originating from a metal-perturbed IL ^{3}[π-π*] state of the tridentate C^N^C ligand. Similar to the low-energy absorption band in the electronic absorption studies, **5** emits at lower energy than **1**, since the electron-rich *tert*-butyl groups on the phenyl rings of the C^N^C ligand in **5** lead to a higher energy phenyl-localized HOMO and hence a lower energy ^{3}[π-π*] excited state. In contrast to **1**–**3** and **5**, which show a vibronic-structured emission band in dichloromethane, **4** exhibits a structureless emission band at 611 nm even in dilute solution (5×10^{-6} mol dm^{-3}; Figure 3). On the basis of the energetically higher lying π(C≡C-C_6H_4-NH_2-*p*) orbital, the lower energy emission band in **4** is tentatively assigned as derived from an LLCT ^{3}[π(C≡C-C_6H_4-NH_2-*p*)→π*(C^N^C)] excited state. It is noteworthy that the emission spectra of **1**–**5** in the solid state show a low-energy structureless band at 550–585 nm (Figure 3). The red shift of the solid-state emission relative to that in solution is attributed to dimeric or excimeric emission arising from the π···π stacking of the C^N^C ligand, probably due to the ordered packing of the molecules in the solid state, as supported by the observation of such π···π stacking in the crystal packing of **1** (Figure 1).

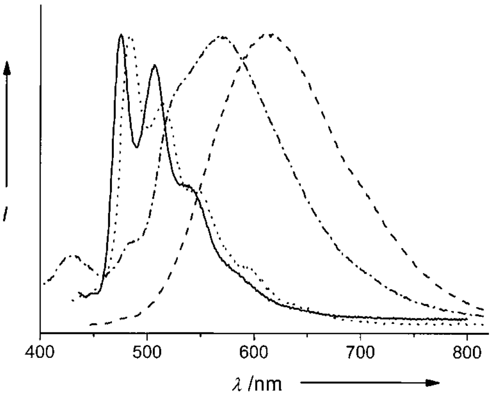

Figure 3. Normalized emission spectra of **1** (——), **4** (-----), **5** (•••••) in degassed CH_2Cl_2 and **1** in the solid state (thin film, –•–•) at 298 K.

Experimental Section

Complexes **1**–**5** were synthesized by reaction of [Au(C^N^C)Cl] with various terminal alkynes in the presence of a catalytic amount of copper(I) iodide in triethylamine and dichloromethane. Pale yellow crystals were obtained by slow diffusion of diethyl ether vapor into a dichloromethane solution of the complexes after column chromatography on silica gel with dichloromethane as eluent. **1**: Yield: 88%. ^{1}H NMR (300 MHz, CH_2Cl_2, 298 K, relative to Me_4Si): $\delta = 8.04$ (dd, $J = 7.4$, 1.0 Hz, 2H, C^N^C), 7.92 (t, $J = 8.0$ Hz, 1H, C^N^C), 7.62 (m, 4H, C^N^C and C_6H_5), 7.54 (d, $J = 8.0$ Hz, 2H, C^N^C), 7.26–7.44 ppm (m, 7H, C^N^C and C_6H_5); positive EI-MS: *m*/*z*: 527 $[M]^+$; IR (KBr): $\tilde{\nu} = 2147$ cm^{-1} ν(C≡C); elemental analysis (%) calcd for $C_{25}H_{16}NAu$ (found): C 56.93 (56.57), H 3.04 (3.05), N 2.66 (2.66). **2**: Yield: 85%. ^{1}H NMR (300 MHz, CH_2Cl_2, 298 K, Me_4Si): $\delta = 8.00$ (dd, $J = 7.2$, 1.0 Hz, 2H, C^N^C), 7.90 (t, $J = 8.0$ Hz, 1H, C^N^C), 7.50–7.60 (m, 6H, C^N^C and C_6H_4), 7.25–7.42 ppm (m, 6H, C^N^C and C_6H_4); positive EI-MS: *m*/*z*: 562 $[M]^+$; IR (KBr): $\tilde{\nu} = 2157$ cm^{-1} ν(C≡C); elemental analysis (%) calcd for $C_{25}H_{15}NClAu \cdot 0.5H_2O$ (found): C 52.59 (52.85), H 2.80 (2.66), N 2.45 (2.40). **3**: Yield: 86%. ^{1}H NMR (400 MHz, CH_2Cl_2, 298 K, Me_4Si): $\delta = 8.02$ (dd, $J = 7.6$, 1.0 Hz, 2H, C^N^C), 7.90 (t, $J = 8.0$ Hz, 1H, C^N^C), 7.60 (dd, $J = 7.6$, 1.0 Hz, 2H, C^N^C), 7.50–7.56 (m, 4H, C^N^C and C_6H_4), 7.40 (dt, $J = 7.3$, 1.3 Hz, 2H, C^N^C), 7.27 (dt, $J = 7.3$, 1.3 Hz, 2H, C^N^C), 6.91 (d, $J = 8.9$ Hz, 2H, C_6H_4), 3.88 ppm (s, 3H, OCH_3); positive EI-MS: *m*/*z*: 557 $[M]^+$; IR (KBr): $\tilde{\nu} = 2157$ cm^{-1} *ν*(C≡C); elemental analysis (%) calcd for $C_{26}H_{18}NOAu \cdot 0.5H_2O$ (found): C 55.12 (55.15), H 3.36 (3.28), N 2.47 (2.48). **4**: Yield: 80%. ^{1}H NMR (300 MHz, CH_2Cl_2, 298 K, Me_4Si): $\delta = 8.07$ (dd, $J = 7.4$, 1.0 Hz, 2H, C^N^C), 7.92 (t, $J = 8.0$ Hz, 1H, C^N^C), 7.65 (dd, $J = 7.4$, 1.0 Hz, 2H, C^N^C), 7.56 (d, $J = 8.0$ Hz, 2H, C^N^C), 7.39–7.45 (m, 4H, C^N^C and C_6H_4), 7.30 (dt, $J = 7.5$, 1.3 Hz, 2H, C^N^C), 6.67 (d, $J = 8.6$ Hz, 2H, C_6H_4), 3.84 ppm (s, 2H, NH_2); positive EI-MS: *m*/*z*: 542 $[M]^+$; IR (KBr): $\tilde{\nu} = 2143$ cm^{-1} ν(C≡C); elemental analysis (%) calcd for $C_{25}H_{17}N_2Au \cdot 0.5H_2O$ (found): C 54.45 (54.59), H 3.27 (3.13), N 5.08 (5.04). **5**: Yield: 85%. ^{1}H NMR (400 MHz, CH_2Cl_2, 298 K, Me_4Si): $\delta = 8.18$ (d, $J = 2.0$ Hz, 2H, C^N^C), 7.86 (t, $J = 8.0$ Hz, 1H, C^N^C), 7.60 (d, $J = 7.6$ Hz, 2H, C_6H_5), 7.56 (d, $J = 8.0$ Hz, 2H, C^N^C), 7.46 (d, $J = 8$ Hz, 2H, C^N^C), 7.35 (m, 5H, C^N^C and C_6H_5), 1.39 (s, 9H, *t*Bu), 1.53 ppm (s, 18H, *t*Bu); positive EI-MS: *m*/*z*: 640 $[M]^+$; IR (KBr): $\tilde{\nu} = 2149$ cm^{-1} ν(C≡C); elemental analysis calcd for $C_{33}H_{32}NAu \cdot 0.5H_2O$ (found): C 61.11 (61.02), H 5.09 (5.08), N 2.16 (2.17).

Crystal data for **1**: $C_{25}H_{16}AuN$, $M_r = 527.35$, crystal dimensions $0.4 \times 0.2 \times 0.2$ mm, orthorhombic, space group $P2_12_12_1$, $a = 6.735(1)$, $b = 14.265(3)$, $c = 19.583(4)$ Å, $V = 1881.4(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.862$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 7.827$ mm^{-1}, $F(000) = 1008$, $T = 253$ K. Final $R = 0.0262$, $wR = 0.0555$ with $I > 2\sigma(I)$; $R = 0.0339$, $wR = 0.0569$ for all data; GOF = 0.925 for 244 parameters and a total of 10500 reflections, of which 3283 were independent ($R_{int} = 0.0377$). MAR diffractometer, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); collection range $2\theta_{max} = 50.62°$ with 3° oscillation step of ϕ, 300 s exposure time, and scanner distance of 120 mm. 54 images were collected. CCDC-260767 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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