Dramatic solvent effect on the luminescence of a dinuclear gold(i) complex of quinoline-8-thiolate

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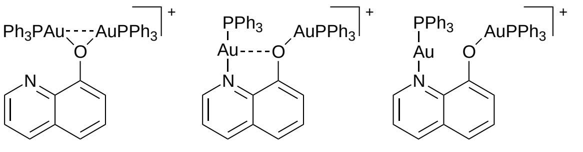
The complex [{Au(PPh$_3$)}$_2$(8-qnS)]BF$_4$ (8-qnS = quinoline-8-thiolate) with intramolecular gold(i)···gold(i) distances of 2.991(2) and 3.081(2) Å in two independent asymmetric units, shows a long-lived emission at 640 nm which is quenched by polar solvents such as acetonitrile and alcohol.

Study on the solvent and/or medium effect on the occurrence of gold(i)···gold(i) interactions could shed new insight into the molecular self-assembly of gold(i) atoms, which was found to give polynuclear gold(i) compounds with novel structural and electro-optical properties.[1] This is particularly important in understanding the chemistry of gold(i) drugs,[2] where such interaction might occur under biological conditions. Schmidbaur and co-workers had reported an interesting study indicating scrambling of the [Au(PPh$_3$)]$^+$ units in a solution of the complex (8-quinolinyl)bis[(triphenylphosphine)gold(i)]-oxonium tetrafluoroborate[3] (Scheme 1). Spectroscopic evidence in support of the equilibrium reactions depicted in Scheme 1 only came from ^{31}P NMR spectral data of **B**, which revealed two ^{31}P signals at low temperature. Herein is described the molecular structures and photophysical properties of [Au(PPh$_3$)(8-qnS)] (8-qnS = quinoline-8-thiolate) and [{Au(PPh$_3$)}$_2$(8-qnS)]BF$_4$ indicating an interesting case, whereby a solvent effect on the association of the [Au(PPh$_3$)]$^+$ units through a bridging sulfur atom could be reflected by a distinct change in emissive properties.

Complexes **1** and **2**BF$_4$† were prepared by modified literature procedures[3,4] and perspective views of their structures‡ are shown in Figs. 1 and 2, respectively. In **1**, the Au(1) atom is two-coordinate, but the measured P(1)–Au(1)–S(1) angle of 163.7(3)° and Au(1)–N(1) distance of 2.627(9) Å suggest a weak Au(1)···N(1) interaction. This is different from the related [Au(PPh$_3$)(2-pyS)] (2-pyS = pyridine-2-thiolate) complex,[4] where an approximate linear geometry about the Au atom has been found [P–Au–S 177.9(1)°]. In **2**, there are two independent asymmetric units, and the 8-qnS is bonded to 2 nearly equivalent [Au(PPh$_3$)]$^+$ units through the sulfur atom. The intramolecular gold(i)···gold(i) contacts of 2.991(2) and 3.081(2) Å are longer than those in [{Au(PPh$_3$)}$_4$S]$^{2+}$ [Au···Au$_{av}$ 2.910(2) Å],[5] but shorter than those values of 3.110(3) Å in [{Au(PPh$_3$)}$_2$SR]$^{+}$[6] and 3.299(3) Å in [{Au(PPh$_3$)}$_3$S]$^+$.[7] It is noted that the mean Au–S–Au angle of 80.6(1)° lies in the range of values found in related complexes[6] which show intramolecular gold(i)···gold(i) interactions.

The absorption spectra of **1** and **2**BF$_4$ measured in dichloromethane and in acetonitrile are shown in Fig. 3. Irrespective of the solvents, complex **1** shows an intense absorption at 386 nm,



Scheme 1

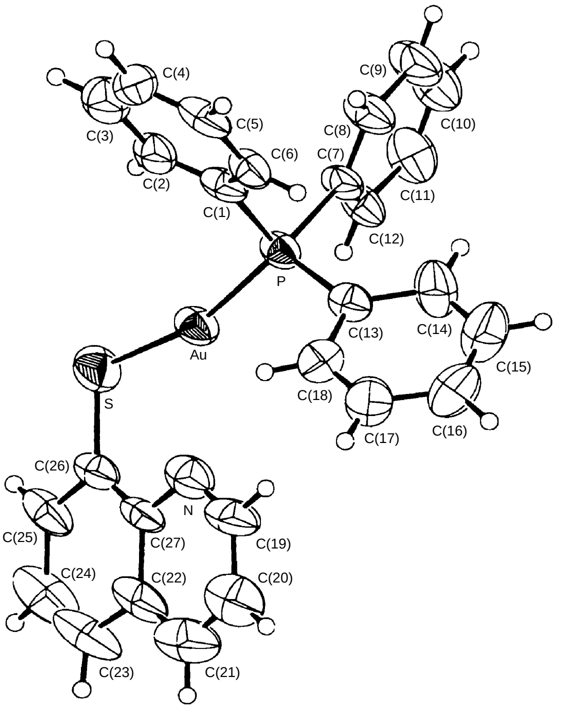


Fig. 1 A perspective view of [Au(PPh$_3$)(8-qnS)] (bond lengths in Å, angles in °): Au(1)–S(1) 2.296(8), Au(1)–P(1) 2.248(7); S(1)–Au(1)–P(1) 163.7(3)

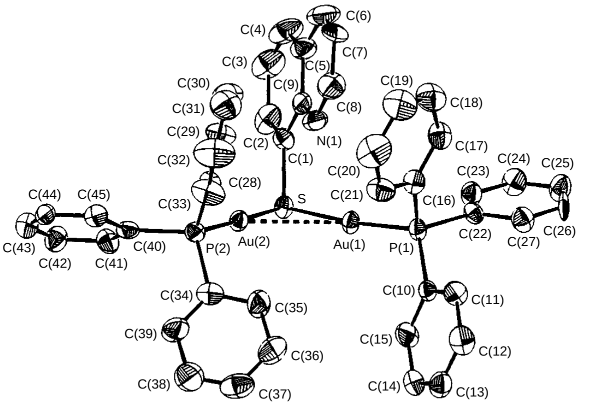


Fig. 2 A perspective view of [{Au(PPh$_3$)}$_2$(8-qnS)]$^+$ (bond lengths in Å, angles in °): Au(1A)···Au(2A) 3.081(2), Au(1B)···Au(2B) 2.991(2), Au(1A)–S(1A) 2.343(3), Au(2A)–S(1A) 2.342(3), Au(1A)–P(1A) 2.256(3), Au(2A)–P(2A) 2.268(3), Au(1B)–S(1B) 2.357(3), Au(2B)–S(1B) 2.351(3), Au(1B)–P(1B) 2.253(3), Au(2B)–P(2B) 2.254(3); S(1A)–Au(1A)–P(1A) 174.6(1), S(1A)–Au(2A)–P(2A) 178.6(1), S(1B)–Au(1B)–P(1B) 172.6(1), S(1B)–Au(2B)–P(2B) 169.6(1) (A and B represent two independent asymmetric units)

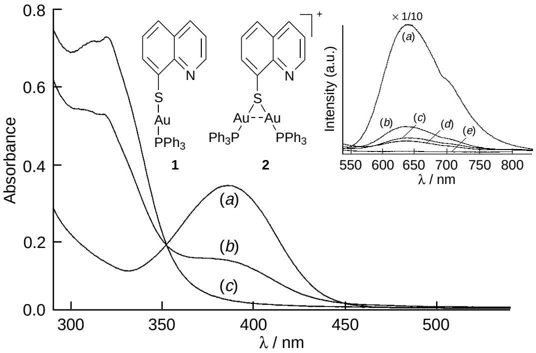
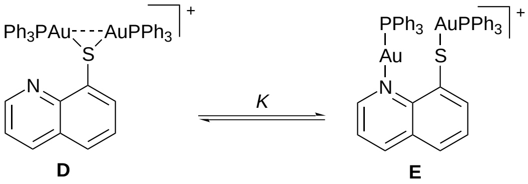


Fig. 3 The absorption spectra of **1** in CH_2Cl_2 (*a*), **2**BF_4 in MeCN (*b*) and **2**BF_4 in CH_2Cl_2 (*c*); complex concentration = 9 × 10^{-5} m. [Insert is the emission spectra of **2**BF_4 (1 × 10^{-4} m) in (*a*) CH_2Cl_2, (*b*) thf, (*c*) EtOH, (*d*) MeOH and (*e*) MeCN; excitation at 320 nm].

which is assigned to $S \rightarrow Au^I$ charge transfer (LMCT) transition. For **2**BF_4 there is a distinct difference in the spectra measured in dichloromethane and in acetonitrile. In dichloromethane, the complex shows an intense absorption band at *ca.* 320 nm, which is assigned to the $5d(d_{\sigma^*}) \rightarrow 6p(p_\sigma)$ transition modified by gold(i)···gold(i) interation. We suggest that coordinating the electrophilic $[Au(PPh_3)]^+$ unit on the sulfur atom of the [Au(8-qnS)] moiety would blue shift the $S \rightarrow Au^I$ transition and hence explain the apparent blue shift of the spectrum of **2**BF_4 from that of **1**. Notably, addition of acetonitrile to a dichloromethane solution of **2**BF_4 increases the absorption at *ca.* 386 nm with a concomitant decrease in the absorption at *ca.* 320 nm; the spectral changes with an isosbestic point at 352 nm. Other solvents such as MeOH and EtOH also give similar spectral changes. We rationalize this finding by the following equilibrium reaction (Scheme 2).



Scheme 2

Form **E** would be isostructural to form **B** in Scheme 1 and would show no intramolecular gold(i)···gold(i) interaction. Its absorption spectrum, therefore, is anticipated to be similar to that of **1**. Thus the spectral changes shown in Fig. 3 could be rationalized by a decrease in the equilibrium constant *K* (*K* = [**E**]/[**D**]) from acetonitrile to dichloromethane. The scrambling of the $[Au(PPh_3)]^+$ units is very fast on the NMR timescale, since the ^{31}P NMR spectrum of an acetonitrile solution of **2**BF_4 shows only a single peak (δ 34.12) at room temperature and even at −35 °C (δ 32.97).

The reaction in Scheme 2 could also be shown by emission spectroscopy. In solution, complex **1** shows a very weak emission at 477 nm. Excitation of a dichloromethane solution of **2**BF_4 gives a very weak emission at 460 nm and an intense low-energy one with a lifetime of 26 μs at 640 nm (Fig. 3, insert). The low energy emission is absent in **1** and a gold(i)···gold(i) interaction is most probably responsible for it. The excitation spectrum of the 640 nm emission matches with the absorption spectra. The excited state is tentatively assigned to come from the metal-centred $5d(d_{\sigma^*}) \rightarrow 6p(p_\sigma)$ excitation, although mixing with some $S \rightarrow Au$ charge-transfer character in the excited state could not be precluded. Notably, the emission depends on solvent polarity. Polar solvents such as MeCN, MeOH, EtOH and thf were found to quench it with quenching rate constants in the order MeCN > MeOH > EtOH > thf (k_q = 1.25 × 10^5, 0.50 × 10^5, 0.32 × 10^5 and 0.24 × 10^5 m^{-1} s^{-1} respectively). In acetonitrile, the 640 nm emission virtually disappears, whereas it has the highest quantum yield and longest lifetime in dichloromethane. Importantly, addition of dichloromethane to a methanol solution revives the emission. Thus, the decrease in the 640 nm emission in polar solvents is consistent with the UV–VIS absorption data. Because the low-energy emission at 640 nm is associated with a gold(i)···gold(i) interaction, the reaction of Scheme 2 may well explain the apparent solvent-induced quenching of the emission of **2**BF_4.

We acknowledge support from the University of Hong Kong, the Hong Kong Research Grants Council, and the Croucher Foundation.

Footnotes

† *Syntheses*: $[Au(PPh_3)(8\text{-qnS})]$ **1**: NEt_3 was added dropwise to a methanol solution (15 ml) of quinoline-8-thiol (8-HqnS, 99 mg). A dichloromethane solution of $[AuCl(PPh_3)]$ (250 mg) was then added and stirred for 30 min. Then $Ag(CF_3SO_3)$ (130 mg) was added and the insoluble AgCl was filtered. The pale yellow filtrate was reduced to *ca.* 2 ml to give the product (yield = 50%).

$[Au_2(8\text{-qnS})(PPh_3)_2]$ **2**BF_4: A solution of Na(8-qnS) was prepared by adding 8-HqnS (99 mg) and NaOMe (30 mg) in CH_2Cl_2–MeOH (1 : 1, 25 ml). $[AuCl(PPh_3)]$ (500 mg, 25 ml in dichloromethane) was added to the solution, which was stirred for 4 h at room temp. After addition of $NaBF_4$ (60 mg) the pale yellow solution was evaporated to dryness. The resulting solid was extracted with thf (yield = 45%).

‡ *Crystal data*: $[Au(PPh_3)(8\text{-qnS})]$ **1**: $C_{27}H_{21}AuNPS$, *M* = 619.47, monoclinic, space group $P2_1/n$, *a* = 14.632(3), *b* = 10.424(1), *c* = 16.360(3) Å, β = 110.08(1)°, *U* = 2344(1) $Å^3$, *Z* = 4, D_c = 1.756 g cm^{-3}, crystal dimensions 0.2 × 0.15 × 0.25 mm, μ(Mo-Kα) = 64.24 cm^{-1}, *F*(000) = 1200. Intensity data were collected on Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å) using ω–2θ scan mode with $2\theta_{max}$ = 45°. 3489 unique reflections were measured and 1965 reflections with $I > 3\sigma(I)$ were used in the refinement. Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms (281 variables) converged to *R* = 0.074 and R_w = 0.090. The final Fourier difference map showed residual extrema in the range of 1.89 to −2.54 e $Å^{-3}$.

$[\{Au(PPh_3)\}_2(8\text{-qnS})]BF_4 \cdot 0.5thf$ **2**$BF_4 \cdot 0.5thf$: $C_{47}H_{40}Au_2BF_4NP_2SO_{0.5}$, *M* = 1201.58, triclinic, space group $P\bar{1}$, *a* = 14.049(5), *b* = 17.319(6), *c* = 19.623(8) Å, α = 90.09(3), β = 108.72(3), γ = 101.20(3)°, *U* = 4425(3) $Å^3$, *Z* = 4, D_c = 1.805 g cm^{-3}, crystal dimensions 0.20 × 0.30 × 0.50 mm, μ(Mo-Kα) = 67.28 cm^{-1}, *F*(000) = 2300. Intensity data were collected on Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å), 11585 unique reflection (2θ < 45°) were measured and 7758 with $I > 2\sigma(I)$ were used in the refinement. Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms (1046 variables) converged to *R* = 0.035 and R_w = 0.037. The final Fourier difference map showed residual extrema in the range of 1.34 to −2.34 e $Å^{-3}$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/310.

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Received, 20th September 1996; Com. 6/06494I