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Luminescent Mononuclear Gold(I) Phosphines

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Crystals of $Au(PPh_3)_2Cl$, $Au(PPh_3)_3BPh_4$, and other three-coordinate bis(phosphine)gold(I) compounds are luminescent. Solutions of $[Au(tht)_2]PF_6$ (tht = tetrahydrothiophene) with added PPh_3 in CH_3CN luminesce with $\lambda_{max} = 512$ nm and an excited-state lifetime of 10 μs. The emission intensity is sensitive to the phosphine concentration. The luminescent species is postulated to be the tris(phosphine)gold(I) cation, $Au(PPh_3)_3^+$, in equilibrium with $Au(PPh_3)_2^+$. Other PR_3 phosphine complexes (R = *n*-octyl, *n*-butyl, ethyl) also luminesce in solution when excess (>3:1 PR_3:Au) phosphine is present. The emission is attributed to a metal-centered $P_z \rightarrow (d_{x^2-y^2}, d_{xy})$ transition which can be dipole allowed under spin–orbit coupling or by Jahn–Teller splitting of the $^3E''$ excited state.

Introduction

A number of mononuclear,[1] binuclear,[2] and polynuclear[3] gold(I) compounds are luminescent. Gold excited-state luminescence and photochemistry with $(PPh_3)_2AuCl$ and other gold(I) compounds has led to their use as sensitizers in photographic emulsions.[4] However, mononuclear gold(I) compounds have only been reported to luminesce in the solid state. Here we report that some mononuclear gold(I)/phosphine compounds also phosphoresce both in the solid state and, like[5] the isoelectronic $Pt^0(PPh_3)_3$, in solution.

Experimental Section

The following compounds were made by literature methods: $Au(PPh_3)_2Cl$,[6] $Au(PPh_3)_3BPh_4$ (confirmed by unit cell X-ray measurements),[7] $Au(PPh_3)_2PF_6$,[8] Au(tht)Cl,[9] $AuN(CH_2CH_2PPh_2)_3[PF_6]$ and $Au_2(N(CH_2CH_2PPh_2)_3)_2[BPh_4]_2$.[10]

The compound $Au(tht)_2PF_6$ (tht = tetrahydrothiophene) was prepared in situ by adding 1 equiv of tht to[9] Au(tht)Cl in CH_3CN, followed by 1 equiv of $TlPF_6$. The TlCl precipitate was removed after 1 h. Although Tl(I) salts are known to luminesce,[11] its presence in these solutions is believed to be small. It is known to bind to Au(I) and Pt(II) anions such as $[Au(CN)_2]^-$ and $[Pt(CN)_4]^{2-}$. A solution of $TlPF_6$ with $NaAuCl_2$ in CH_3CN, after filtration to remove TlCl, shows no luminescence. The phosphines PPh_3, P(*n*-butyl)$_3$, P(*n*-octyl)$_3$, P(*o*-xylyl)$_3$, P(*m*-xylyl)$_3$, $P(OPh)_3$, and $P(OCH_2CH_3)_3$ were added to $[Au(tht)_2]PF_6$ solutions formed as above. The solutions were degassed with N_2 and then irradiated with a hand-held UV lamp to observe any emission.

Absorption spectra were obtained on a Perkin-Elmer 320 spectrophotometer connected to a Perkin-Elmer 3600 workstation. The path length of a KBr solution cell, usually used in the IR region, was found by counting interference fringes to be 0.0980 mm. This cell was used in the UV region. A 3.6-mg sample of $(PPh_3)_3AuBPh_4$ was dissolved in 1 mL of CH_3CN. The UV spectrum of this concentrated solution was obtained in the KBr solution cell. All of the solution was retrieved and diluted to 102 mL. The UV spectrum of this dilute solution was obtained in a 10.0-mm cell. The molar extinction coefficient for the solution based on the Au(I) concentration is estimated to be 22 700 at 270 nm.

Emission and excitation spectra, obtained with a Spex Fluorolog 2 fluorimeter, were uncorrected for instrumental response. Solutions were degassed with N_2. The excitation radiation for the solids was filtered through a Schott UG1 filter (325–380-nm band-pass) to reduce scattered light.

Lifetime measurements were made using about 0.8-ns excitation pulses from the 355-nm third harmonic of a Quantel YG481 Nd–YAG laser.[12]

No emission was observed from $[Au(tht)_2]PF_6$, even at 77 K, as a solid or in solution or after adding excess tht. No emission was observed from Au(tht)Cl. None was observed on adding 2 or 3 equiv of $P(OEt)_3$ to $[Au(tht)_2]PF_6$ in acetonitrile or on dissolving Au(tht)Cl in the neat phosphite. $P(OPh)_3$ has a strong blue emission of its own; no additional emission was observed on adding it to $[Au(tht)_2]PF_6$. No emission was observed from $K[Au(CN)_2]$ in water at room temperature, even after adding excess CN^-. No vibrational fine structure was observed in the emission spectra of any of the crystals or solutions at 20 °C or 77 K.

Results

Solid $(PPh_3)AuCl$ has only a slight bluish-white emission when pure;[2d] however, a bright yellow luminescence was observed on shining a hand-held UV lamp on a sloppily-prepared batch. This led to the observation that crystals of three-coordinate $(PPh_3)_2AuCl$ and $[(PPh_3)_3Au]BPh_4$ luminesce yellow and yellow-green, respectively (Figure 1). A similar luminescence was observed from crystals of the gold/tripod complexes;[10] crystals of the monomer $AuN(CH_2CH_2PPh_2)_3[PF_6]$ and dimer Au$_2$(N(CH$_2$-

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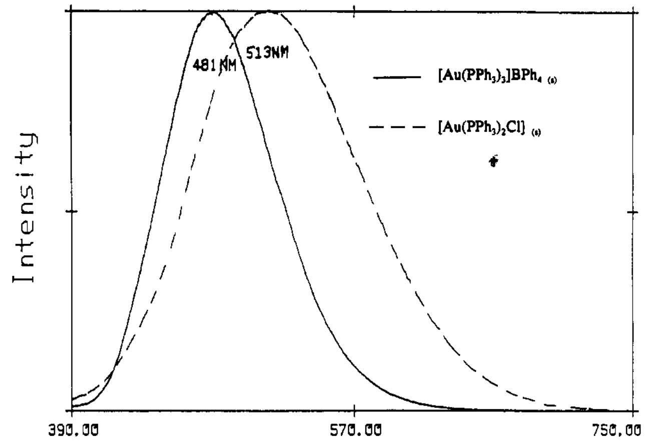

Figure 1. Room-temperature emission spectra of single crystals of Au$(PPh_3)_3BPh_4$ and $Au(PPh_3)_2Cl$ (330-nm excitation).

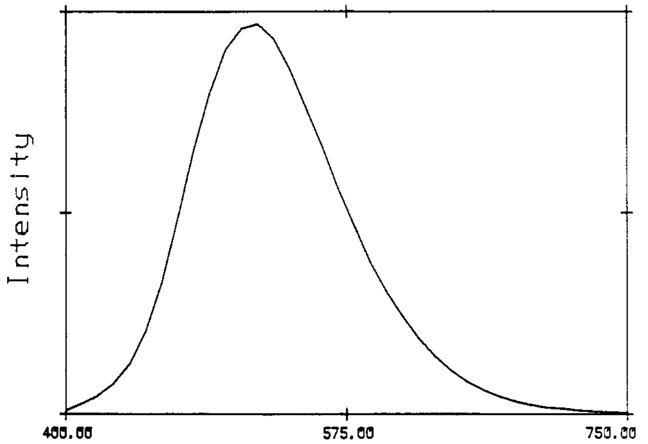

Figure 2. Room-temperature emission spectra of $Au(PPh_3)_3^+$ in acetonitrile.

$CH_2PPh_2)_3)_2[BPh_4]_2$ (Au- - -Au = 3.347 (5) Å) luminesce yellow and blue, respectively.

No emission was observed from $[Au(P(n\text{-}Bu)_3)_2]BPh_4$. Single crystals of $[Au(PPh_3)_2]PF_6$ are only weakly luminescent. However, when any one of the latter crystals was *very* finely pulverized with a spatula, a yellow-green luminescence appeared. The crystals were fairly pure; one had been used for an X-ray crystal structure determination.[8] Pulverization may lead to increased amounts of noncentrosymmetric gold(I) products such as $[Au(PPh_3)(H_2O)]PF_6$ and $Au(PPh_3)_3PF_6$.

The bis(phosphine) $[(PPh_3)_2Au]PF_6$ luminesced only weakly in solution, perhaps due to Tl(I) impurities, λ_{max} = 493 nm. However, a solution resulting from addition of excess PPh_3 to $[(PPh_3)_2Au]PF_6$ had an intense yellow luminescence (Figure 2). The same emission spectrum was also obtained upon adding excess PPh_3 to $Au(PPh_3)_2Cl$ or $Au(tht)_2PF_6$. The $[Au(tht)_2]^+$ cation was used because phosphines readily displace tht. An intense yellow luminescence was also obtained on addition of excess $P(ethyl)_3$, $P(n\text{-}butyl)_3$, or $P(n\text{-}octyl)_3$ to solutions of $[Au(tht)_2]PF_6$ or Au(tht)Cl. The excited-state lifetimes of the PPh_3 complexes in solution were about 8–10 μs (Table I), and the emission was quenched by oxygen. Luminescent solutions were obtained in acetonitrile, thf, and alcohols. Emission was almost unobservable from acetonitrile solutions that were 10–20% in either CH_2Cl_2 or 1,2-dichloroethane.

Solution luminescence was observed on adding excess $P(m\text{-}tolyl)_3$ to $[Au(tht)_2]PF_6$ but not upon adding excess $P(o\text{-}tolyl)_3$, which has a much larger Tolman cone angle[13] of 194° compared with 145° for the meta isomer and Ph_3P. Both the monomeric and dimeric gold/tripod complexes luminesce yellow-orange in solution without the addition of excess phosphine.

Table I. Emission Maxima and Lifetimes of $Au(I)/PPh_3$ Compounds

	λ_{max}, nm	t,[a] μs		λ_{max}, nm	t,[a] μs
$Au(PPh_3)_2PF_6$, solid	493	8	$Au(PPh_3)_2Cl$, solid	511	3.7
$Au(PPh_3)_3BPh_4$, solid	481	9.3	$Au(PPh_3)_3^+$, CH_3CN	512	10

[a] All were fit by first-order exponential decay.

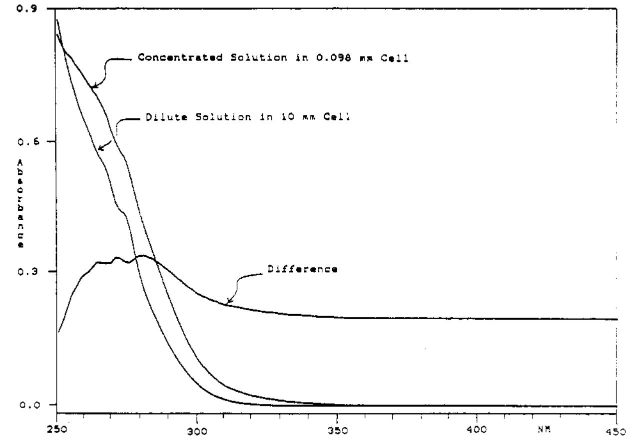

Figure 3. Absorption spectra of $(PPh_3)_3Au^+$: (a) concentrated solution of $(PPh_3)_3AuBPh_4$ in a 0.098-mm KBr cell; (b) diluted (1:102) solution in a 10-mm cell. The difference between (a) and (b) reveals an absorption attributable to $(PPh_3)_3Au^+$. This difference spectrum has been displaced 0.2 absorbance unit. The molar extinction coefficient of the complex is estimated to be 22 700 M^{-1} cm^{-1} at 270 nm.

Although concentrated solutions (≃1 mg/mL) of $(PPh_3)_2AuCl$ and $[(PPh_3)_3Au]BPh_4$ are luminescent, dilute solutions at room temperature are not. The dilute solutions will luminesce if cooled to 0 °C. A comparison of the UV absorption spectra of concentrated and dilute solutions was made by keeping the concentration to path length ratio constant (atom numbers in beam constant). In the concentrated solution (Figure 3), a reproducible absorbance appeared. The difference between concentrated and dilute solutions indicates that an increased absorption is present at about 280 nm in the concentrated solution. We were unable to obtain a standard (right-angle) excitation spectrum because the phenyl rings have intense absorptions in concentrated solution and PPh_3 luminesces in dilute solution. However, an excitation spectrum of the front face of the cuvette had a maximum at 290 nm. This corresponds well with the maximum in the absorption spectral differences for the concentrated and dilute solutions.

Discussion

The bis(phosphine) complexes $[Au(PR_3)_2]^+$ (R = Ph, Bu) do not have a characteristic luminescence. The weak emission from $[Au(PPh_3)_2]PF_6$ is attributed to a $\pi^* \rightarrow \pi$ transition on the phenyl ring, as assigned for $Cu(PPh_3)_2BH_4$.[14] The emission energy is within a few nanometers of that of PPh_3, which has λ_{max} = 500 nm and which is weakly fluorescent in solution.[15]

The compounds that give luminescent crystals all have at least three ligands coordinated to the gold with at least two of them being phosphines. All of the luminescent crystals have been crystallographically characterized; the emission in these compounds

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cannot be attributed to any intermolecular Au- - -Au interaction for the solids.

The luminescent species in solution is also postulated to be three-coordinate species such as tris(phosphine)gold(I). Three-coordinate [Au(PPh$_3$)$_3$]BPh$_4$ has been structurally characterized.[7] Emission is observed with tri-*m*-tolylphosphine but not with tri-*o*-tolylphosphine; presumably the bulkier phosphine with the larger cone angle does not form a tris(phosphine) complex. The luminescence of the PPh$_3$ complexes is not attributed to the tetrakis(phosphine) complex because, even as crystals,[16] [Au(PPh$_3$)$_4$]BPh$_4$ exhibits a trigonal geometry about Au^I with the Au^I 3.9 Å from the fourth phosphine. Dissolution clearly leads to complete dissociation.

Tris(phosphines) of Au^I dissociate somewhat in solution.[17] Dilute solutions of Au(PPh$_3$)$_3$BPh$_4$ are nonluminescent presumably because of phosphine dissociation with most of the gold being two-coordinate. Cooling a dilute solution entropically favors formation of the three-coordinate complex, and emission "turns on" at about 0 °C. Addition of excess PPh$_3$ also increases the concentration of the tris complex with a resulting increase in emission intensity. Concentrated solutions have an increased absorption relative to dilute solutions at around 280 nm that is attributable to formation of the tris(phosphine) complex.

The solution emission spectrum of Au(PPh$_3$)$_2$Cl is energetically the same as that of Au(PPh$_3$)$_3$BPh$_4$, an observation accounted for by the equilibrium

$$2\mathrm{Au(PPh_3)_2Cl} \rightleftarrows [\mathrm{Au(PPh_3)_3}]\mathrm{Cl(luminescent)} + \mathrm{AuPPh_3Cl}$$

Although phosphites are less bulky than phosphines, they are also poorer σ donors. No tris(phosphite)gold(I) complexes have been crystallographically characterized to date. Emission was not observed from gold(I) in the presence of excess phosphite. Either tris(phosphites) do not form, or if formed, they do not luminesce.

The long excited-state lifetimes and the large Stokes shifts between absorption (near 300 nm) and emission (near 510 nm) suggest that the emission is phosphorescence. Both P(*n*-Bu)$_3$ and PPh$_3$ tris(phosphine) complexes have similar emissions; therefore, the ***intense emission does not involve transitions to or from phenyl ring orbitals.*** As was suggested[5] for Pt^0(PPh$_3$)$_3$,[5] the emission may be interpreted as a metal-centered absorption–nonradiative transfer–phosphorescence; although these authors assumed any Jahn–Teller distortion to be small (from the (d$_{x^2-y^2}$, d$_{xy}$) degeneracy):

$$\text{singlet } (\mathrm{d}_{z2})^2(\mathrm{d}_{x2-y2})^2(\mathrm{p}_z)^0 \rightarrow \text{singlet } (\mathrm{d}_{z2})^1(\mathrm{d}_{x2-y2})^2(\mathrm{p}_z)^1 \rightarrow$$
$$\text{triplet } (\mathrm{d}_{z2})^2(\mathrm{d}_{x2-y2})^1(\mathrm{p}_z)^1 \rightarrow \text{singlet } (\mathrm{d}_{z2})^2(\mathrm{d}_{x2-y2})^2(\mathrm{p}_z)^0$$

The absorption is either a Laporte-allowed p$_z$ ← d$_{x^2}$ transition (*z* axis perpendicular to the AuP$_3$ plane) or a p$_z$ ← (d$_{x^2-y^2}$, d$_{xy}$) transition component allowed by spin–orbit coupling in D_{3h}. An intermediate nonradiative transition (d$_{xy}$, d$_{x^2-y^2}$) → d$_{z^2}$ is suggested, since the emission energy is much smaller than the absorption energy. A subsequent nuclear relaxation shortens the Au–P bonds. The (d$_{xy}$, d$_{x^2-y^2}$) degeneracy in this excited state would be removed by a Jahn–Teller distortion expected to be larger in these charged Au(I) complexes than in neutral Pt(0) species. Such geometry changes may contribute to the long lifetime of the excited state. Phosphorescence is assigned to the triplet to singlet transition p$_z$ → (d$_{x^2-y^2}$, d$_{xy}$).

That symmetric linear two-coordinate gold(I) complexes do not luminesce while three-coordinate species luminesce seems to be an inescapable conclusion from this work. Since dinuclear gold(I) complexes also generally show luminescence, it appears that loss of the centrosymmetric structure about the metal ion, through either metal–metal interaction or three-coordination, is important. We do not know at present if this reduction in symmetry increases more the allowed character of the absorbance from the ground state or promotes formation of the triplet excited state. Detailed spectroscopic studies will be required to unravel this point. However, we can speculate that the in-plane ligands (or in-plane metal–metal bond formation in dinuclear complexes) promote the stabilization of the triplet excited state with an electron on Au(I) in a p$_z$ orbital perpendicular to the metal–ligand or metal–metal–ligand plane. In the metal–metal dimers, this state is analogous to the triplet state formed from a combination of the two half-filled orthogonal (antisymmetric) metal p$_z$ orbitals.

The energy of the emission from Au(PPh$_3$)$_3^+$ is about 20% higher than that reported[5] from the isoelectronic platinum complex Pt^0(PPh$_3$)$_3$. A comparison of the energy separations between 5d^{10} and the 5d^{9}6p^1 configurations in the two gas-phase metal ions also shows a 65–85% larger energy separation for Au(I), further suggesting that the luminescence arises from a Au(I) state associated with the 5d^{9}6p^1 configuration. Further studies of the photophysical and photochemical properties of these and related gold(I) complexes look promising.

Note Added in Proof

McCleskey and Gray[19] report emission in solution from a three-coordinate Au(I) complex, with excitation at 370 nm, a much lower energy than we observe. Their phosphine ligand contains aliphatic cyclohexyl groups. With PPh$_3$ ligands, the π–π^* absorbance of the phenyl rings appears to dominate the excitation spectrum. Solvent quenching also may contribute to the lack of luminescence[1c] for [Au(PPh$_3$)$_2$]$^+$.

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