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Photoluminescence of Gold(I) Phosphine Complexes in Aqueous Solution

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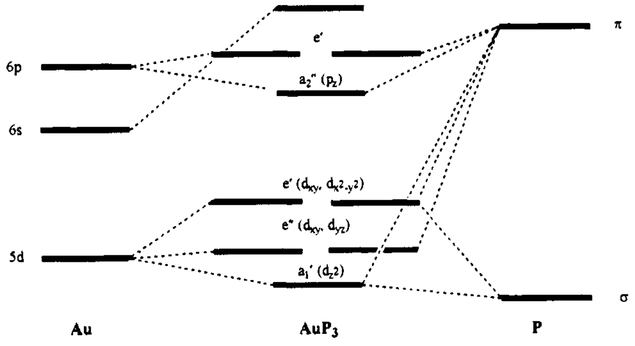
It is well known that the complexes $Au(PR_3)X$, (R = aryl or alkyl, X = halide), can react with excess phosphine to give $Au(PR_3)_2X$, $Au(PR_3)_3X$, and $Au(PR_3)_4X$.[1] More recently, it has been established that the three-coordinate species $Au(PR_3)_3X$, which contains gold(I) in a trigonal planar geometry, can show luminescence both in the solid state and in nonaqueous solvents.[2] Several other published examples have demonstrated that luminescence from a three-coordinate gold(I) center is a general phenomenon where the origin of the emission has been assigned to a metal-centered transition $a_2''(p_z) \rightarrow e'(d_{x^2-y^2}, d_{xy})$ (Scheme 1).[3-5] The two complexes described in this Communication are the first examples of gold(I) complexes which show luminescence in aqueous solution. The possibility that interesting photochemistry can take place in water is currently under investigation. Achieving luminescence in aqueous solution, with an aim toward understanding the electronic structure of gold(I) species in a biologically relevent media, motivated this study, since Corey and Khan had postulated singlet $^1\Delta_g$ O_2 quenching to be relevant to the mechanism of action of gold drugs used in crysotherapy.[6]

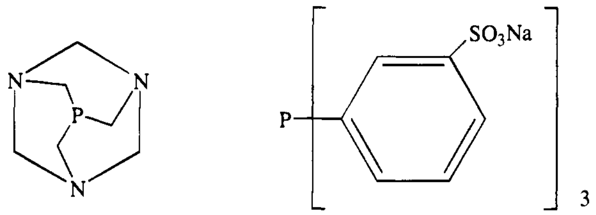
The water-soluble ligands TPA and TPPTS (Scheme 2) were used to synthesize a series of complexes AuLX,[7] AuL_2X, AuL_3X, and AuL_4X,[8] (L = TPA, TPPTS; X = Cl). The $[Au(TPPTS)_4]^{11-}$ complex is the only one in this series of complexes that does not form, presumably due to the relatively large steric bulk of the ligand (cone angle = 170°).[9] In this series of water-soluble complexes, only the three-coordinate species $[Au(TPA)_3]^+$ (**1**) and $[Au(TPPTS)_3]^{8-}$ (**2**) show a strong luminescence both in the solid state and in solution. The spectroscopic data for these complexes are summarized in Table 1. The geometry about the gold center in solution is believed to be trigonal planar AuP_3, similar to that found for $[Au(MeI.TPA)_3]I$,[10] which has been characterized by X-ray structural analysis. The long lifetimes and large Stokes shifts (~2000−3000 cm^{-1}) observed for the two luminescent complexes $[Au(TPA)_3]^+$ and $[Au(TPPTS)_3]^{8-}$ imply that the emission is a phosphorescence from a triplet excited state.[11] By comparison to related three-coordinate gold(I) systems[3,4] and d^{10} Pt(0) complexes,[12] the emission has been assigned to an essentially metal-centered transition.

Scheme 1. Orbital Scheme from Extended Hückel-Relativistically Corrected MO Calculations Performed on the CAChe[5] System for AuP_3[a]



[a] The z-axis is perpendicular to the AuP_3 plane.

Scheme 2



Tris-(1,3,5-triaza-7-phosphaadamantane)

TPA

Tris-(3,3',3''-phosphinidynetris-(benzenesulfonic acid) trisodium salt

Na_3(TPPTS)

Table 1. Spectroscopic Data for $[Au(TPA)_3]Cl$ and $Na_8[Au(TPPTS)_3]$ in the Solid State and in Aqueous Solution at Room Temperature

	λ_{em} (nm) solid state			
	solid state			
complex	77 K	298 K	aqueous soln	lifetime,[a] τ (μs)
$[Au(TPA)_3]Cl$	517	533	547	3.2 (solid) 0.53 (soln)
$Na_8[Au(TPPTS)_3]$	492	494	513	1.9, 8.0 (solid)

[a] Lifetime measurements for solids where done at 77 K.

In both the $[Au(TPA)_3]^+$ and the $[Au(TPPTS)_3]^{8-}$ systems, addition of stoichiometric amounts of ligand to the nonluminescent two-coordinate AuL_2X complex causes the appearance of an emission band corresponding to the formation of the three-coordinate species. Addition of further equivalents of ligand in the TPA system quenches the luminescence as the four-coordinate, nonluminescent[4] $[Au(TPA)_4]^+$ is formed. However, addition of 1 or more equiv of the TPPTS ligand to $[Au(TPPTS)_3]^{8-}$ gave no significant change in the emission intensity, providing further evidence that four-coordination of the gold(I) center is not achieved for this ligand.

The aqueous luminescence of $[Au(TPA)_3]^+$ shows an interesting pH dependence (Figure 1). The emission is completely quenched below pH = 3, but increases in intensity as the pH is increased, reaching a maximum at pH = 10. The pH dependence is reversible, but in strongly alkaline solutions (pH > 10), decomposition to gold metal and the TPA phosphine oxide ($^{31}P\{^1H\}$ NMR = −1.36 ppm) is observed. It is well known that, in acidic solutions, the TPA ligand is protonated at one of

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[8] Forward, J. M.; Assefa, Z.; Staples, R. J.; Fackler, J. P., Jr. Manuscript submitted to *Inorg. Chem.* Two structurally characterized three-coordinate complexes have been obtained with an alkylated (Me, Et) TPA ligand. These materials are luminescent, as we believe would be the case with the protonated, three-coordinate species in aqueous solution. Unfortunately, we have been unable to isolate such a protonated complex. Protonation does not quench the metal-centered luminescence of $[(TPA)AuCl]_2$.[7]

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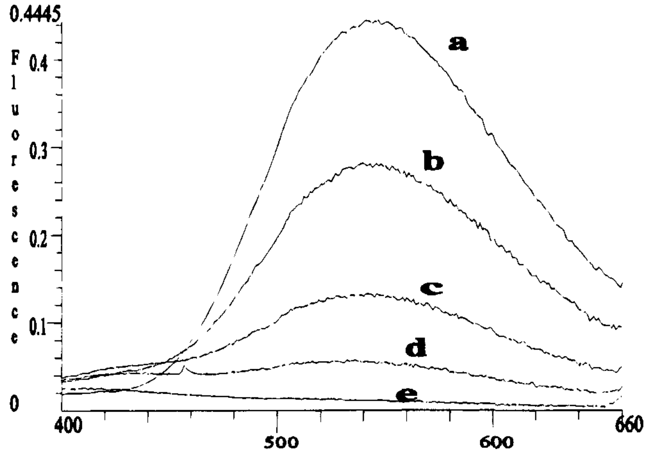
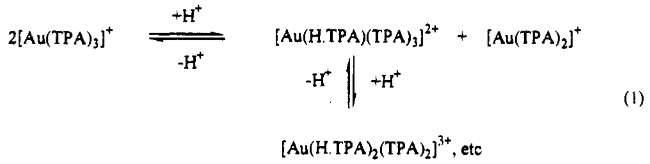


Figure 1. pH-dependent emission spectra with excitation at 320 nm at room temperature of $[Au(TPA)_3]Cl$ in aqueous solution. pH values: (a) 6.4, (b) 4.2, (c) 3.9, (d) 3.4, and (e) 2.7. The pH was adjusted with 0.1 M HCl or NaOH.

the nitrogen sites,[13,14] and recent work has shown that protonation of the ligand favors the formation of the four-coordinate species.[4,7] Several of the protonated four-coordinate complexes have been crystallographically characterized, and they each show an almost regular tetrahedral geometry that participates in a highly ordered hydrogen bonding network with the water. It is thought that this stabilization of the four-coordinate species in acidic solution promotes the disproportionation of the luminescent three-coordinate complex to the nonluminescent two- and four-coordinate species as the pH decreases (eq 1).



$$2[Au(TPA)_3]^+ \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} [Au(H.TPA)(TPA)_3]^{2+} + [Au(TPA)_2]^+ \quad \text{-H}^+ \Big\Updownarrow \text{+H}^+ \quad [Au(H.TPA)_2(TPA)_2]^{3+}, \text{etc} \qquad (1)$$

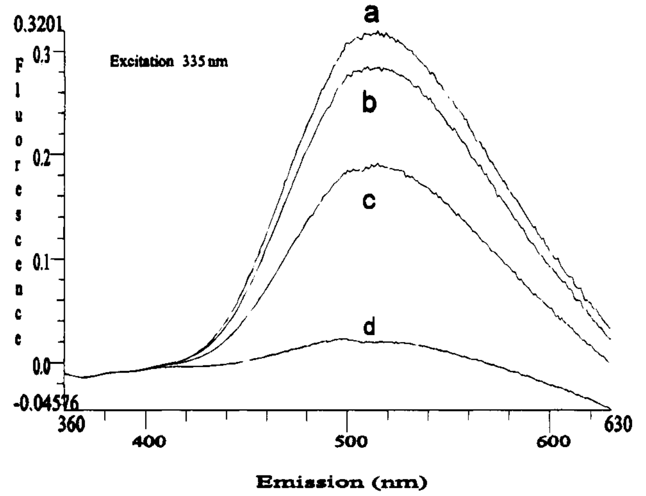


Figure 2. Effect of cosolvent addition (MeOH) on the aqueous emission intensity of the $[Au(TPPTS)_3]^{8-}$ complex. (a) $[Au(TPPTS)_3]^{8-}$ in water; (b) +10% MeOH; (c) +20% MeOH; (d) +30% MeOH.

The intensity of the luminescence of $[Au(TPPTS)_3]^{8-}$ does not show any pH dependence, but it does show an interesting solvent dependence. Addition of acetone, ethanol, and methanol to an aqueous solution of $[Au(TPPTS)_3]^{8-}$ causes a decrease in the intensity of the emission that cannot be explained as a simple dilution effect (Figure 2). A correlation is observed, however, between the decrease in intensity and the dielectric constant of the solvent added, i.e., the less polar the solvent, the more effectively the emission is quenched. The origin of this quenching effect appears to be the dissociation of the three-coordinate $[Au(TPPTS)_3]^{8-}$ complex to the nonluminescent two-coordinate $[Au(TPPTS)_2]^{5-}$ complex and the free ligand (eq 2).

$$[Au(TPPTS)_3]^{8-} \rightleftharpoons [Au(TPPTS)_2]^{5-} + [TPPTS]^{3-} \quad (2)$$

The three-coordinate complex is thought to be stabilized in aqueous solution by an extensive hydrogen bonding network involving the water molecules and the RSO_3^- groups, as suggested for related metal complexes containing this ligand.[8,15] Decreasing the dielectric constant of the aqueous solution by adding less polar solvents reduces this stabilizing effect, and the three-coordinate complex dissociates. Additional evidence for this mechanism comes from the $^{31}P\{^1H\}$ NMR. A small amount of acetone added to an aqueous solution of $[Au(TPPTS)_3]^{8-}$ causes the peak at 42.0 ppm to broaden considerably, implying the dynamical behavior expected with dissociation and exchange of the phosphines. Two phosphine resonances are observed at −60 °C in MeOH.

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