
Characterization of the Luminescent, Homoleptic, Three-Coordinate, Water Soluble Au(I) Complex of Trisulfonated Triphenylphosphine (TPPTS) as the Cesium Salt, $\text{Cs}_8[\text{Au}(\text{TPPTS})_3] \cdot 5.25 \text{H}_2\text{O}$

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The homoleptic metal-TPPTS complex $\text{Cs}_8[\text{Au}(\text{TPPTS})_3] \cdot 5.25 \text{H}_2\text{O}$ has been characterized structurally. The x-ray data for the triclinic crystal, P-1, with cell constants $a = 13.7003(4)$, $b = 18.0001(6)$, $c = 18.2817(2)$, $\alpha = 100.249(2)$, $\beta = 99.593(2)$, $\gamma = 109.818(2)$ shows trigonal planar Au(I) centers coordinated by three TPPTS ligands having Au-P distances equal to 2.374(6), 2.394(5), and 2.417(5)Å. The structure shows a complex network of bonding involving the Cs^+ ions, the sulfate groups of the ligand, and H_2O solvent molecules. The $[\text{Au}(\text{TPPTS})_3]^\ominus$ luminesces in the solid state and in aqueous solution with a broad emission at *ca* 520 nm which is quenched by O_2 and other small molecules. The forbidden singlet to triplet absorption at *ca* 552 nm with $\epsilon \sim 0.8 \text{Lmol}^{-1}\text{cm}^{-1}$ is also observed.

Phosphine complexes of transition metals are important in homogeneous catalysis (1, 2). During the past few years 'green-chemistry' has dictated that new solvents and catalysts be found that minimize the use of toxic chemicals. Processes that function under less hazardous reaction conditions (3) and with benign solvents have been sought. The use of water soluble phosphine catalysts is part of this green chemistry trend. A 1994 NATO workshop brought focus to this effort (4). The successful use of water-soluble sulfonated phosphine catalysts in hydroformylation, hydrogenation, and coupling reactions (5) has been especially important. These systems have provided a

simple means of separating the catalyst from the product soluble in the non-aqueous layer. The trisulfonated triphenylphosphine, TPPTS, tris(m-sulfophenyl)phosphine, is one of the more commonly employed phosphines in biphasic catalyst systems (6).

Luminescence studies of Au(I) compounds have produced some interesting results recently (7, 8). Photoluminescence (9) is observed in several classes of Au(I) compounds, including three-coordinate complexes (10, 11). Trigonal coordination about the gold center leads to an excited state which produces a long-lived (μs) metal-centered phosphorescence (12). With the use of water soluble phosphines such as

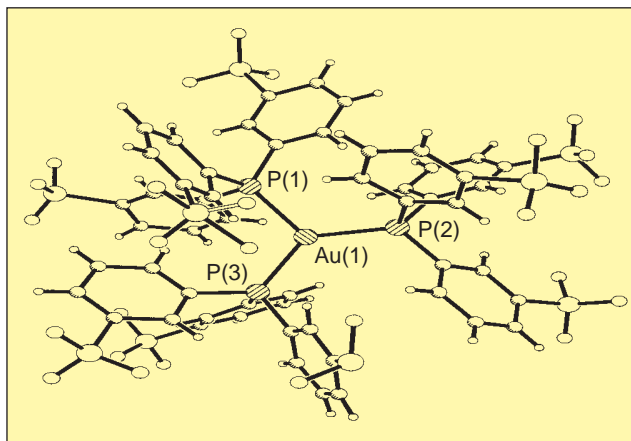


Figure 1 Molecular structure of the anion $[\text{Au}(\text{TPPTS})_3]^{8-}$. The Cs^+ ions and water molecules are omitted for clarity

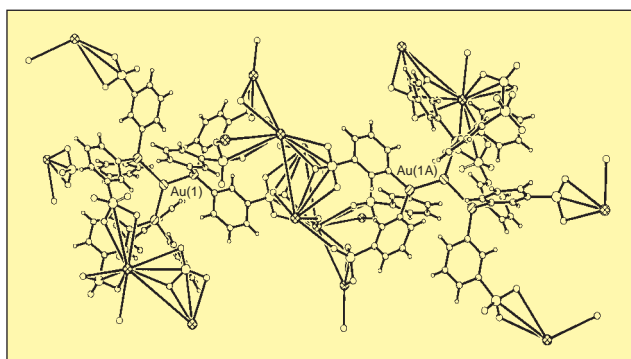


Figure 2 Molecular structure of $\text{Cs}_8[\text{Au}(\text{TPPTS})_3] \cdot 5.25\text{H}_2\text{O}$

1,3,5-triaza-7-phosphaadamantane (TPA) and TPPTS (13) aqueous solution phosphorescence is observed and has been suggested to be associated with a 3-coordinate, tris-phosphine species. However, prior to this work no strictly 3-coordinate, luminescent, water soluble tris-phosphine complex of Au(I) had been structurally characterized. Furthermore, no homoleptic metal complexes of the important TPPTS ligand have been characterized structurally and there are few examples of structurally characterized metal complexes containing this ligand (14 - 16).

The compound $\text{Cs}_8[\text{Au}(\text{TPPTS})_3] \cdot 5.25\text{H}_2\text{O}$ (**1**) which exhibits luminescence in the solid state and in aqueous solution, was synthesized by the addition of three equivalents of the cesium salt of TPPTS to one equivalent of $\text{Au}(\text{THT})\text{Cl}$ in a $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ (1:1) solution. Crystals of **1** were obtained from a water solution of the complex (17). The complex crystallizes in the triclinic space group P-1 with two formula units in the unit cell. The lattice contains discrete

$[\text{Au}(\text{TPPTS})_3]^{8-}$ units, Figure 1, that are interconnected through a complex network of bonds between the sulfonate groups and the cesium cations, Figure 2.

The coordination about Au(I) approximates D_{3h} symmetry, excluding the phenyl rings. The Au-P bond lengths are 2.374(6), 2.394(5), and 2.417(5) Å and are similar to those found in other gold-phosphine complexes. This same general ligand geometry (presumably ligand dictated) has been suggested (18) for the important hydroformylation catalyst $[\text{RhH}(\text{CO})\text{TPPTS}]$ used by Ruhrchemie AG. The sum of the P-Au-P angles is equal to 360° . The diameter of a molecule is on the order of 15 Å with 8 Cs^+ ions associated with the nine sulfate groups. The carbon and oxygen atoms were refined isotropically with some disorder the oxygen atoms of the sulfate groups and water molecules.

The cesium salt of TPPTS was used (19) to obtain single crystals of **1**. The large size of Cs^+ and its polarizability compared to the more common sodium salt of the ligand appear to be important factors in the crystallization in which CsCl is eliminated (Equation 1). Crystallization using the sodium salt of TPPTS was unsuccessful.



Although gold(I) is commonly two-coordinate there are a few structural reports of three-coordinate Au(I) complex (20), few of these compounds have been investigated for photoluminescence. Two crystal structures of water soluble, 3-coordinate Au(I) complexes of alkylated (at N) 1,3,5 triaza-7-phosphaadamantane (21, 22) have been described but these materials contain iodide weakly interacting with the Au(I) centers at ~ 2.9 Å. Another water soluble, nearly planar AuP_3 complex, uses the ligand diphenylhydroxymethylphosphane (23).

Compound **1** is the first metal complex structurally characterized which has a homoleptic arrangement of the commercially important TPPTS ligands. TPPTS complexes and others (24) with sulfonated phosphine ligands tend to crystallize in layers consisting of hydrophilic planes of sulfonate groups, cations, and solvent with hydrophobic planes containing the metal complex and the ligands. A similar arrangement is found here with the trigonally planar Au(I) TPPTS complex. It is isoelectronic and presumably structurally like the Pd(0) catalysts that have been used for carbonylation of aryl halides (25), as well as the Rh(I) catalysts mentioned above (2). The

$^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Au}(\text{TPPTS})_3]^{8-}$ shows a dynamic behavior similar to the behavior reported for the Pd(0) system. With $[\text{Au}(\text{TPPTS})_3]^{8-}$, a broad signal at 43.5 ppm is observed at room temperature which is the weighted average signal for $[\text{Au}(\text{TPPTS})_3]^{8-}$, $[\text{Au}(\text{TPPTS})_2]^{5-}$ and free TPPTS (at - 5ppm), seen as sharp peaks at low temperature (in CD_3OD), with the $[\text{Au}(\text{TPPTS})_3]^{8-}$ dominating. As further equivalents of the TPPTS ligand are added to a solution of the complex, this latter signal shifts upfield, as observed in the Pd(0) system, indicating chemical exchange.

The luminescence (26) exhibited by **1** in the solid state and in aqueous solution is illustrated in Figure 3. The solid state complex emits at 494 nm and is blue-shifted from the emission observed in aqueous solution at 513 nm. This 750 cm^{-1} difference in the peak maximum presumably is related to small differences in the strength of the Au-P bonds in the two phases. The overall similarity of the spectra confirms that the same 3-coordinate species is the luminescent species in both phases.

The forbidden electronic absorption between the singlet ground-state and the triplet excited state in $[\text{Au}(\text{TPPTS})_3]^{8-}$ can be observed in aqueous solution at room temperature. The absorption has a maximum at 552 nm ($\epsilon_{\text{max}} \sim 0.8\text{ ML}^{-1}\text{cm}^{-1}$, $f \sim 1.5 \times 10^{-5}$) and a width at half-height of about 4015 cm^{-1} . The oscillator strength is in a range expected (27) for spin forbidden transitions. The shift of $\sim 1800\text{ cm}^{-1}$ to higher energy for the emission maximum from the triplet excited state, compared with the absorption from the singlet ground state presumably reflects the presence of stronger Au-P bonds in the excited state. As reported previously (13) the HOMO for 3-coordinate AuP_3 complexes in D_{3h} symmetry is largely an antibonding $e'(d_{xy}, d_{x^2-y^2})$ orbital while the LUMO is a non-bonding $a''(p_z)$ orbital. The μs lifetime of the excited state allows for a relaxation and strengthening of the Au-P bonds to accommodate the removal of electron density from the antibonding HOMO (28).

Energy transfer and electron transfer quenching has been demonstrated for some photoluminescent metal complexes of Au(I) (29, 30). Excited state quenching reactions also occur with photoluminescent $[\text{Au}(\text{TPPTS})_3]^{8-}$ in aqueous solution. Dioxygen reversibly quenches luminescent Au(I) complexes in the solid state in thin films of gold containing polymers (31, 32). A reversible quenching process also occurs in aqueous solutions of $[\text{Au}(\text{TPPTS})_3]^{8-}$. Figure 4 shows the emission spectrum of $[\text{Au}(\text{TPPTS})_3]^{8-}$ in a de-oxygenated aqueous solution and in an aqueous solution saturated with O_2 ; before and after bubbling $\text{N}_2(\text{g})$ through the solution for

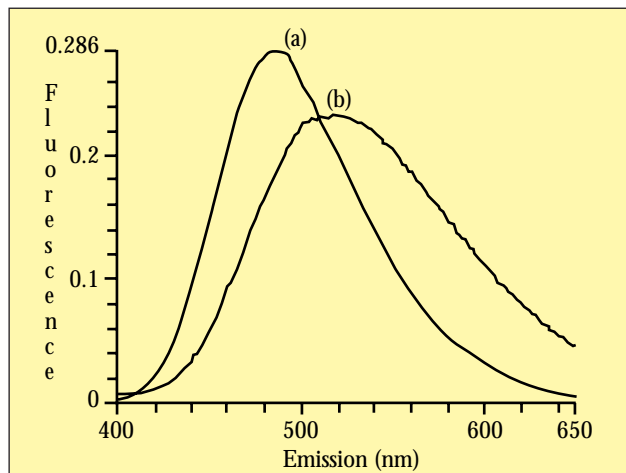


Figure 3 The emission spectra of $\text{Na}_8[\text{Au}(\text{TPPTS})_3]$ (a) as a solid at room temperature and (b) in aqueous solution, excited at 335 nm. The ionic strength is held constant in solution with 0.5 M NaCl

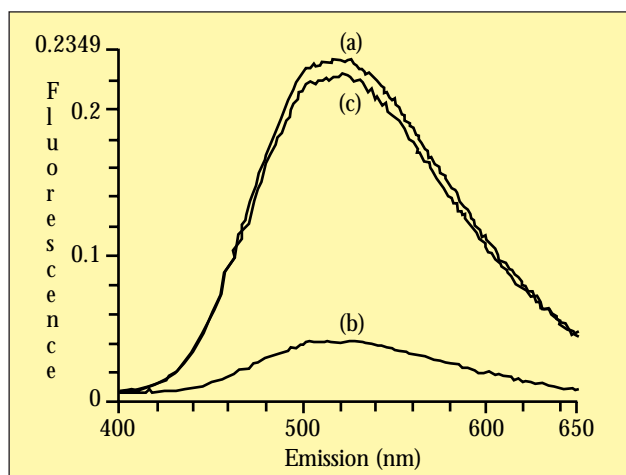


Figure 4 The reversible emission quenching of $\text{Na}_8[\text{Au}(\text{TPPTS})_3]$ by $\text{O}_2(\text{g})$ in aqueous solution: (a) 100% $\text{N}_2(\text{g})$ purge; (b) 100% $\text{O}_2(\text{g})$ purge; (c) 100% $\text{N}_2(\text{g})$ purge after oxygenation. Spectra were excited at 335 nm

15 minutes. This reversibility may be important for potential application of these systems as photoluminescent sensors. Small molecules such as nitric oxide, sulfur dioxide, and alkyl halides, and some metal ions such as Cu^{2+} also quench the emission in aqueous solution. These results will be reported in detail elsewhere.

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John P Fackler, Jr is Distinguished Professor of Chemistry at Texas A&M University and amongst his more than 280 publications there are over 100 papers relating to gold chemistry. Tiffany A Grant studied for her PhD with Fackler on the luminescent properties of gold(I) complexes and developed the crystallization of the water soluble phosphine complex reported here. Brian E Hanson is Professor of Chemistry at Virginia Polytechnic Institute and State University and is an expert in the use of biphasic systems for hydroformylation which involve sulfonated phosphine complexes of metal ions. Richard J Staples is staff crystallographer for the Chemistry Department at Harvard University and has structurally characterized over 50 gold compounds.

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