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Three-coordinate, luminescent, water-soluble gold(I) phosphine complexes: structural characterization and photoluminescence properties in aqueous solution

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Dedicated to the successful career of Martin A. Bennett, a pioneer in the chemistry of metal phosphine complexes including some beautiful work involving gold

Abstract

The trigonal planar Au(I) complex $Cs_8[Au(TPPTS)_3] \cdot 5.25H_2O$, TPPTS = tris-sulfonatophenyl phosphine, has been structurally characterized. The X-ray data for the triclinic crystal, $P\bar{1}$, are a = 13.7003(4) Å, b = 18.0001(6) Å, c = 18.2817(2) Å, $\alpha = 100.249(2)^\circ$, $\beta = 99.593(2)^\circ$, $\gamma = 109.818(2)^\circ$, V = 4046.3(2) Å³, Z = 2. The complex has Au–P distances of 2.374(6), 2.394(5), and 2.417(5) Å. A network of bonding has been found involving the Cs⁺ ions, the sulfonate groups of the ligands, and the H₂O solvent molecules. Luminescence studies of $[Au(TPPTS)_3]^{8-}$ and $(TPA)_3AuCl$, TPA = 1,3,5-triaza-7-phosphaadamantane, in the solid state and in solution are discussed and quenching studies of the luminescence of $[Au(TPPTS)_3]^{8-}$ are reported with alkyl halides and oxygen. (C) 2003 Elsevier B.V. All rights reserved.

Keywords: Trigonal planar Au(I) complexes; Luminescence; Emission intensity

1. Introduction

The photoluminescent properties of several types of three-coordinate gold(I) complexes in organic solvents and in the solid state have been reported [1-4]. In general, the gold center is three-coordinate. A variety of anions have been used to balance the charge of cationic complexes.

The first report of luminescence by a gold(I) complex was presented in 1971 by Dori [1]. He reported the synthesis of $[Au(PPh_3)_3]Cl$ which exhibits luminescence. The solid-state crystal structure shows that Cl^- is weakly coordinated to the gold, forming a distorted pyramidal structure about the gold(I) center. An indepth study of the luminescent properties of this complex with various non-coordinating anions was performed by our group [2]. These studies showed that mononuclear Au(I) complexes can luminesce under UV excitation in solution as well as in the solid state. It was demonstrated that the addition of excess PPh₃ to [Au(PPh₃)₂]PF₆ produces an intense yellow luminescence for the solution in acetonitrile. The same emission was observed from similar complexes with a Cl⁻ ion and with other phosphines such as PEt₃, P(*n*-butyl)₃, or P(*n*-octyl)₃. The luminescence using saturated phosphine ligands demonstrated that it was not associated with π - π * transitions on the phenyl rings of PPh₃.

The synthesis and structure of another three-coordinate Au(I) complex was reported using tris(2-diphenylphosphino)ethyl amine (NP₃) as the ligand [3]. A monomeric cationic complex with the formula $[Au(NP_3)]^+$ was formed. The Au(I) center is trigonal planar with the three phosphorous donor atoms co-

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ordinated to the metal and no interaction between Au(I) and the amine nitrogen. Au(I)–N bond distances are typically of the order of 2 Å while in the reported complex the Au–N distance is 2.683(6) Å, a distance which is too long to be considered as bonding. This complex was synthesized with a variety of non-coordinating anions and exhibits luminescence in the solid state. No luminescence was observed in solution due to dissociation of the phosphines from Au(I).

We reported that the photoluminescent properties of gold can be studied in aqueous solution with the use of water-soluble phosphines such as 1,3,5-triaza-7-phosphaadamantane (TPA) and the tris-sulfonatophenyl phosphine (TPPTS) sodium salt [4]. Here we describe the structural characterization of the three-coordinate Au(I) complex $Cs_8[Au(TPPTS)_3] \cdot 5.25H_2O$, where the gold center is trigonal planar, and details of its luminescent properties. There are no coordinating anions in the crystal lattice with several water molecules coordinated to the Cs cation and H-bonded to the sulfonate groups. This complex exhibits luminescence in the solid state and in aqueous solution. We report also luminescence studies of the cation $[(TPA)_3Au]^+$.

2. Experimental

2.1. Materials and methods

The starting material Au(THT)Cl was prepared by published methods [5]. The sodium salt of TPPTS, TPPTS = tris(*m*-sulfophenyl)phosphine, was obtained from Celanese and the cesium salt of TPPTS was obtained at VPI. The TPA ligand, TPA = 1,3,5-triaza-7-phosphaadamantane, was prepared according to the literature methods [6]. All other chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The solution NMR spectra were recorded on a Varian 200 broadband spectrometer or on a Varian Unity Plus 300 spectrometer. H₃PO₄ (85%) was used as an external reference for ³¹P spectra. UV–Vis absorption spectra were obtained on a Cary 17 spectrometer.

2.1.1. Synthesis of sodium [tris(tris(msulfonatophenyl)phosphine)gold(I)], Na₈[Au(TPPTS)₃] (1)

To a stirred solution of Au(THT)Cl (0.100 g, 3.1×10^{-4} mol) in 10 ml CH₂Cl₂ was added TPPTS sodium salt (0.53 g, 9.4×10^{-4} mol) along with 10 ml H₂O. After stirring for 5 h, the biphasic mixture was removed under vacuum. To this solid, 10 ml H₂O was added and the solution was filtered to remove any suspension. A white product in a quantitative yield was obtained by removal of the solvent under vacuum. ³¹P{¹H} NMR (D₂O, 85% H₃PO₄) 43.5 ppm (br).

2.1.2. Synthesis of cesium [tris(tris(msulfophenyl)phosphine)gold(I)], Cs₈[Au(TPPTS)₃]. 5.25H₂O (2)

The cesium salt was prepared using a procedure analogous to that used for 1. Au(THT)Cl (0.010 g, 3.1×10^{-5} mol) and the cesium salt of the TPPTS ligand (0.053 g, 9.4×10^{-5} mol) were used. Yield was quantitative. ³¹P{¹H} NMR (D₂O, 85% H₃PO₄) 43.5 ppm (br). Single crystals were obtained from H₂O at room temperature.

2.1.3. Synthesis of bis(1,3,5-triaza-7-

phosphaadamantane)gold(I) chloride, $(TPA)_2AuCl(3)$ To Au(THT)Cl (45 mg, 0.14 mmol) suspended in 3 ml CH₃CN was added the TPA ligand (22 mg, 0.14 mmol) at once. After stirring for about 10 min, a white precipitate emerged. The solution was stirred for two more hours and an additional 22 mg of the TPA ligand was added. The solution was stirred for 2 h and 10 ml Et₂O was added to precipitate out a bulk of white product. After filtering and washing with cold EtOH (2 × 1 ml) and Et₂O, the product was dried in air. ³¹P{¹H} NMR (CD₃CN, 85% H₃PO₄) - 36.1 ppm (s).

2.1.4. Synthesis of tris(1,3,5-triaza-7-

phosphaadamantane)gold(I) chloride, $(TPA)_3AuCl(4)$

To a stirred suspension of Au(THT)Cl (100 mg, 0.31 mmol) in 10 ml MeOH:CH₃CN (2:1) was added TPA ligand (49 mg, 0.31 mmol). After stirring for 2 h, an additional 49 mg of the ligand was added. The white suspension was stirred for 3 h after which the third portion of the TPA ligand was added. In 10 min a clear solution formed and stirring continued for 3 h followed by filtration to remove any suspension. A white product was precipitated out by the addition of Et₂O. ³¹P{¹H} NMR (MeOD, 85% H₃PO₄) - 56.3 ppm (br).

2.2. Photoluminescence studies

Emission and excitation spectra were recorded on an SLM AMINCO, Model 8100 spectrofluorometer using a xenon lamp. Spectra were corrected for instrumental response. The emitted radiation was filtered through a 0.1 M KNO₂ solution, which was used as a short wavelength cut-off filter. Solution experiments were carried out in aqueous solution with doubly distilled water. Unless specified otherwise, ionic strength was held constant by the addition of 0.5 M NaCl solutions. Deoxygenating was accomplished by bubbling N_2 (g) through the analyte solution for a minimum of 15 min. The Supracil quartz cuvettes used were of 1 cm path length. A fitted septum was used to seal the cuvette. All solutions were freshly prepared approximately 2 h prior to the measurements. Solid-state room- and low-temperature measurements were made with a cryogenic

2.3. Spectroscopic studies

The absolute luminescence quantum yield was measured against quinine sulfate of 10^{-4} mol dm⁻³ in 0.05 mol dm⁻³ sulfuric acid ($\varphi = 0.56$) [7]. The result was checked against [Ru(bpy)₃]²⁺ ($\varphi = 0.042$), which was used as an additional standard. The integrated areas of the emission bands of the standard and sample were used in the comparison. Absorbance of both the standard and sample solutions was measured at the respective excitation wavelengths prior to the luminescence measurements and the data were used for correction purposes. The quantum yield was calculated using Eq. (1) [7a]

$$\varphi_{\rm sp} = \varphi_{\rm st} \left(\frac{I_{\rm sp}}{I_{\rm st}} \right) \left(\frac{A_{\rm st}}{A_{\rm sp}} \right) \tag{1}$$

where φ is the quantum yield, *I* the integrated area of the corrected emission band, *A* the absorbance at the excitation wavelength, and subscripts sp and st correspond to sample and standard solutions, respectively. Dilute solutions (10⁻⁴ M) were used to minimize inner filter effects.

Stern-Volmer quenching experiments were carried out in aqueous solution with doubly distilled deionized water. Deoxygenation was accomplished by bubbling N_2 gas vigorously through the analyte solution for a minimum of 10 min. Unless specified otherwise, ionic strength was held constant by the addition of 0.5 M NaCl. The Supracil quartz cuvettes were of 1 cm path length. A fitted Teflon stopper was lightly coated with glycerol to seal the cuvette and the emission intensity of deoxygenated solutions was stable under UV radiation for at least 0.5 h. All solutions were freshly prepared approximately 2 h prior to the measurements. Variable pH studies were carried out on a series of unbuffered deoxygenated 1 µM solutions of (TPA)₃AuCl. The pH adjustment was performed by using either 0.1 M HCl or 0.1 M KOH solutions.

For complexation studies, stock solutions of 2.5 mM of the ligand and $(TPA)_2AuCl$ were prepared. Various concentrations of the ligand were then prepared by dilution. To 5 ml of 2.5 mM $(TPA)_2AuCl$ solution were added equal volumes of the TPA solutions. The mixture was stirred for approximately 20 min to attain equilibrium and deaerated for an additional 10 min before the luminescence measurements were conducted. Effect of excess L on the emission intensity was further investigated by adding 5 ml of L (various concentrations) to a 5 ml of a 5.1 μ M solution of $(TPA)_3AuCl$. The luminescence measurements were performed with and without maintaining the ionic strength constant. A 0.5

M KCl solution was used to maintain the ionic strength. The pH of the solution remained in 6-6.5 range and, thus, no effort was made to adjust it. Solution Raman measurements were conducted on Spectra Physics 2020 instrument using the 488 nm argon ion laser line as the excitation source.

2.4. MO calculations

Extended Hückel (EH) calculations were performed on Macintosh IIfx computer using the molecular modeling CAChe software package [8]. Energy minimization was conducted using the MM2 program, which is included in the CAChe software, prior to running the EH calculations. The orbital energy and exponent parameters used in the EH calculations were obtained from Pyykko's [9] work and correspond to relativistic values.

For p- and d-orbitals, the weighted average of the low and high angular momentum values were used to satisfy the CAChe criteria. For the $(TPA)_2Au^+$ species in $D \infty_h$ symmetry the z-axis is taken as the molecular axis. For the three-coordinate $(TPA)_3Au^+$ in a planar geometry the z-axis is perpendicular to the xy-molecular plane. The Au-P distances correspond to those found in the crystal structure of the $(TPA)_2AuCl$ compound [10]. All other bond distances were used as found in the energyminimized CAChe structure.

2.5. Stern–Volmer quenching experiments

Quenching experiments were performed in deoxygenated water solutions of Na₈[Au(TPPTS)₃] (10⁻³ M) in the presence of a quencher (Q). In each case, the bimolecular quenching rate constant (k_q) was determined from Stern–Volmer plots of I_0/I vs. [Q], where I_0 and I refer to the integrated emission intensity in the absence and presence of quencher, respectively.

2.6. X-ray diffraction analysis

Data were collected using a Siemens (Bruker) SMART CCD (charge-coupled device)-based diffractometer equipped with an LT-2 low-temperature apparatus operating at 213 K. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were measured using omega scans of 0.3° per frame for 60 s, such that a hemisphere was collected. A total of 1271 frames were collected with a final resolution of 0.75 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART software [11] and refined using SAINT on all observed reflections. Data reduction was performed using the SAINT software [12], which corrects for Lp and decay. Absorption corrections were applied using SADABS [13] supplied by George Sheldrick. The structure was solved by the direct method using the SHELXS-97 program [14] and refined by least-squares method on F^2 , SHELXL-97 [15], incorporated in SHELXTL-PC, V 5.03 [16]. The structure was solved in the space group $P\bar{1}$ by analysis of systematic absences. All non-hydrogen atoms are refined anisotropically other than C, S, and O atoms. Hydrogen atoms were placed into calculated positions by geometrical methods and refined as a riding model. The crystal used for the diffraction study showed no decomposition during data collection.

3. Results and discussion

The three-coordinate $[Au(TPPTS)_3]^{8-}$ complex is readily soluble in aqueous solution and is air-stable at room temperature. It is synthesized by the addition of 3 equiv. of TPPTS ligand to 1 equiv. of Au(I) starting material with a labile ligand such as THT or Me₂S. The complex exhibits a green emission in the solid state and in aqueous solution.

3.1. Structural results for the $Cs_8[Au(TPPTS)_3]$ complex

Crystals of 2 were obtained from a water solution of the complex. Compound 2 crystallizes in the triclinic space group $P\bar{1}$ with two formula units in the unit cell (Fig. 1). The lattice contains discrete $[Au(TPPTS)_3]^{8-1}$ units that are interconnected through a complex network of bonds between the sulfonate groups and the cesium cations. Disregarding the phenyl rings, the AuP₃ moiety closely obeys D_{3h} symmetry. 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. The sum of the P-Au-P angles is equal to 360° which indicates that the geometry about the gold center is trigonal planar. The diameter of a single complex is in the order of 15 Å. Eight Cs⁺ ions are present in the crystal lattice associated with the nine sulfonate groups. 1 equiv. of CsCl does not crystallize in the lattice. The carbon and oxygen atoms were refined isotropically with some disorder among the oxygen atoms of the sulfonate groups. There are 5.25 molecules of water present in the lattice and they are bonded to the Cs⁺ ions. The crystallographic details are given in Table 1, and the atomic coordinates and isotropic thermal parameters are listed in Table 2. Selected bond distances and angles are presented in Table 3.

The X-ray crystal structure of 2 is the first structure of a three-coordinate, trigonal planar Au(I) complex that exhibits luminescence in the solid state and in aqueous solution. The TPPTS ligand itself plays an important role in the formation of this trigonal planar species.



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

Since the ligand is ionic, it has allowed the formation of a chloride-free, charge-balanced complex.

Although gold(I) is typically a two-coordinate linear species, there are some structural reports of threecoordinated Au(I) complexes in the literature. The topic has recently been reviewed by Gimeno and Laguna [17]. Two crystal structures of three-coordinate Au(I) watersoluble complexes have been reported utilizing the small water-soluble phosphine 1,3,5-triaza-7-phosphaadamantane [18,19]. However, single crystals of $[Au(TPA)_3]^+$ have not been successfully obtained without a counterion present. An iodide is loosely coordinated at 2.9 Å perpendicular to the Au-P₃ plane in both structures. Another water-soluble, three-coordinate complex utilizes diphenylhydroxymethylphosphane as the ligand [20]. The structure contains an Au(I) centercoordinated by three phosphorous atoms and is very near planarity. The anion in this system is Cl⁻ but the Au-Cl distance is not reported.

The crystal structure of 2 is significant because it is the first structurally characterized homoleptic, ionic metal complex with three TPPTS ligands coordinated to a metal center. There are only a few other structures of metal complexes with TPPTS [21,22]. These complexes and others with sulfonated phosphine ligands [23] crystallize in layers consisting of hydrophilic planes of

Table 1 Crystal data and structure refinement for $\rm Cs_8[Au(TPPTS)_3]\cdot 5.25H_2O$

Formula weight 2850.59 Temperature (K) $213(2)$ Wavelength (Å) 0.71073 Crystal systemtriclinicSpace group $P\hat{1}$ Unit cell dimensions a (Å) a (Å) $13.7003(4)$ b (Å) $18.0001(6)$ c (Å) $18.2817(2)$ r (°) $100.240(2)$	
Temperature (K) $213(2)$ Wavelength (Å) 0.71073 Crystal systemtriclinicSpace group $P\hat{1}$ Unit cell dimensions a (Å) a (Å) $13.7003(4)$ b (Å) $18.0001(6)$ c (Å) $18.2817(2)$ x (°) $100.240(2)$	
Wavelength (Å) 0.71073 Crystal systemtriclinicSpace group $P\hat{1}$ Unit cell dimensions a (Å) a (Å) $13.7003(4)$ b (Å) $18.0001(6)$ c (Å) $18.2817(2)$ r (°) $100.240(2)$	
Crystal systemtriclinicSpace group $P\hat{1}$ Unit cell dimensions a a (\hat{A}) 13.7003(4) b (\hat{A}) 18.0001(6) c (\hat{A}) 18.2817(2) r (\circ) 100.249(2)	
Space group $P\hat{1}$ Unit cell dimensions 13.7003(4) a (Å) 13.0001(6) c (Å) 18.2817(2) x (°) 100.249(2)	
Unit cell dimensions a (Å) 13.7003(4) b (Å) 18.0001(6) c (Å) 18.2817(2) x (°) 100.249(2)	
a (Å) 13.7003(4) b (Å) 18.0001(6) c (Å) 18.2817(2) x (°) 100.249(2)	
b (Å) 18.0001(6) c (Å) 18.2817(2) r (°) 100.240(2)	
c (Å) 18.2817(2) r (°) 100.249(2)	
~ (°) 100 249(2)	
α () 100.249(2)	
β (°) 99.593(2)	
γ (°) 109.818(2)	
Volume (Å ³), Z 4046.3(2), 2	
Density (calculated) $(mg m^{-3})$ 2.340	
Absorption coefficient (mm^{-1}) 5.736	
<i>F</i> (0 0 0) 2668	
Crystal size (mm) $0.05 \times 0.15 \times 0.15$	
Theta range for data collection $1.47-22.50$ (°)	
Limiting indices $-14 \le h \le 12, -19 \le k \le 16,$	
$-19 \le t \le 19$ Reflections collected 1/18/	
Independent reflections $10164 [R_{-} - 0.0701]$	
Absorption correction semi-empirical from psi scans	
Max and min transmission 0.9054 and 0.6857	
Refinement method full-matrix least-squares on \vec{F}	:
Data/restraints/parameters 10164/54/543	
Goodness-of-fit on F^2 0.946	
Final <i>R</i> indices $[I > 2\sigma(I)]$ $R_1 = 0.0659, wR_2 = 0.0986$	
<i>R</i> indices (all data) $R_1 = 0.1723, wR_2 = 0.1121$	
Largest difference peak and hole 2.735 and -1.300 (e Å ⁻³)	

 $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|; \ wR_2 = \{ \Sigma [w(F_0^2 - F_c^2)^2] / \Sigma [wF_0^4] \}^{1/2}.$

sulfate groups, cations, and solvent and hydrophobic planes containing the metal complex and ligands themselves. Single crystals of 2 were obtained due to the presence of the large Cs⁺ ions. Attempts to crystal-lize complexes using the sodium salt of TPPTS were unsuccessful.

The $[Au(TPPTS)_3]^{8-}$ structure is also significant as a model for water-soluble catalysts that utilize TPPTS ligands. It is a d¹⁰, trigonal planar system that is isoelectronic and isostructural to Pd catalysts that have been utilized for carbonylation of aryl halides [24]. The structure also suggests that a metal species such as $[Rh(TPPTS)_4]^{z-}$ is a very unlikely candidate for hydroformylation catalysis [25].

3.2. Photoluminescence studies of $[Au(TPPTS)_3]^{8-1}$

At room temperature, a broad emission band with a maximum at 494 nm is observed. By lowering the temperature to 77 K, an increase in the emission intensity is observed along with a blue shift of the band with a maximum occurring at 480 nm. The solid-

	X	У	Ζ	$U_{ m eq}$ a
Au(1)	7874(1)	-508(1)	7080(1)	26(1)
$C_{s}(1)$	11842(2)	5336(1)	9044(1)	73(1)
$C_{s}(2)$	7095(1)	5248(1)	8418(1)	54(1)
$C_{s}(2)$	5361(1)	-376(1)	11773(1)	38(1)
$C_{s}(4)$	3668(1)	-2038(1)	8938(1)	41(1)
$C_{3}(4)$	5000(1)	-2038(1)	746(1)	41(1)
$C_{s}(5)$	7025(1)	-2322(1)	740(1)	44(1)
$C_{s}(0)$	7923(1)	-3732(1)	5331(1)	4/(1)
$C_{S}(7)$	7931(2)	4/20(1)	$\frac{012}{(1)}$	104(1) 57(1)
Cs(0)	5056(1)	5091(1) 1106(2)	7080(1) 5720(2)	$\frac{37(1)}{27(2)}$
P(1) P(2)	7209(3) 9199(4)	-1190(3)	3730(3) 7478(2)	$\frac{27(2)}{22(2)}$
P(2)	8188(4) 8017(4)	900(3)	7860(2)	23(2)
$\mathbf{r}(3)$ $\mathbf{s}(1)$	3017(4)	-1420(3)	(707(5)	10(2)
S(1) = S(2)	5050(7) 7040(5)	-1804(3)	$\frac{0}{9}(3)$	90(3)
S(2) S(3)	6865(8)	-994(4)	2813(3)	30(2)
S(3) S(4)	5811(6)	-4324(4)	7067(5)	86(3)
S(4) S(5)	3811(0) 0078(7)	2813(3) 2850(4)	(3) 6840(4)	80(3) 70(2)
S(5) S(6)	11565(5)	3330(4)	0640(4)	70(2)
S(0) S(7)	10182(5)	3232(4)	7712(4)	$\frac{31(2)}{40(2)}$
S(7)	6270(5)	-3333(4)	10080(2)	40(2)
S(0)	4742(5)	-232(4)	8550(3)	29(2) 20(2)
O(3)	4743(3) 2665(17)	-3823(4)	6055(12)	50(2)
O(3)	3003(17)	-1134(14)	6353(12)	72(11)
O(1)	2440(3)	-2200(2)	7114(0)	/2(11) 80(6)
O(2)	3380(13)	-2436(11)	7114(9)	80(0)
O(3A)	4/60(3)	-12/0(2)	7575(19) 2758(7)	80(12) 20(4)
O(4)	7140(10)	-1801(8)	2736(7)	39(4) 28(4)
O(3)	7149(10)	-676(8)	2234(7)	30(4) 20(4)
O(0)	7006(11)	-314(8)	2642(7)	55(5)
O(7)	7161(16)	-4200(9)	3092(8) 4766(11)	115(8)
O(0)	5016(17)	-4011(13) 2038(13)	7385(12)	113(8)
O(10)	5010(17)	2930(13) 2455(11)	8220(0)	133(8)
O(11)	5426(14)	2557(11)	8589(10)	90(0) 85(6)
O(12)	9074(13)	2057(11) 3952(10)	7160(0)	78(6)
O(13)	11021(12)	4270(0)	7422(8)	55(5)
O(15)	0050(13)	4270(9)	6135(10)	90(6)
O(15)	12230(11)	3131(8)	10277(8)	48(5)
O(10)	112230(11) 11348(10)	4001(8)	9967(7)	$\frac{1}{38(4)}$
O(18)	11940(10) 11954(10)	3296(8)	9001(7)	43(4)
O(10)	11934(10) 11191(12)	-3398(9)	8189(8)	57(5)
O(20)	10008(12)	-3883(10)	6912(10)	72(5)
O(20)	9283(12)	-3952(9)	7995(8)	68(5)
O(22)	5633(17)	-4407(12)	4473(11)	121(8)
O(22)	5700(10)	-987(8)	10232(7)	35(4)
O(24)	5908(11)	-54(9)	9407(8)	52(5)
O(25)	5075(11)	-4484(9)	8729(8)	49(5)
O(26)	5016(10)	-3155(8)	9191(7)	36(4)
O(27)	3659(12)	-4140(9)	8145(8)	47(4)
O(1S)	10897(13)	6083(10)	10259(9)	86(6)
O(2S)	9287(13)	4772(10)	8581(9)	89(6)
O(3S)	5832(14)	4258(11)	6743(10)	111(7)
O(4S)	6849(10)	453(8)	10755(7)	34(4)
O(5S)	2888(14)	-2797(11)	10215(10)	104(7)
O(6S)	5050(3)	-4350(2)	390(2)	106(14)
O(7S)	8870(3)	-6320(2)	4654(19)	91(12)
O(8S)	10000	5000	5000	71(15)
C(1)	7465(14)	-655(11)	4981(10)	16(4)
C(2)	7615(13)	-1027(12)	4269(10)	19(4)
C(3)	7744(14)	-618(12)	3743(10)	24(4)
C(4)	7720(14)	191(12)	3877(11)	28(4)
C(5)	7574(14)	558(12)	4557(10)	27(4)

Table 2

Atomic coordinates (\times 10⁴) and equivalent isotropic displacement parameters (\times 10³ Å²) for Cs_8[Au(TPPTS)_3] \cdot 5.25H₂O

Tabla 2

P(3) - Au(1) - P(1)

Table 2 (Continued)

	X	У	Ζ	$U_{ m eq}$ $^{ m a}$
C(6)	7449(13)	121(11)	5099(10)	17(4)
C(7)	7848(17)	-1967(13)	5535(11)	28(4)
C(8)	7270(16)	-2738(13)	5121(11)	29(4)
C(9)	7642(17)	-3308(13)	5011(11)	33(4)
C(10)	8680(16)	-3168(13)	5377(11)	40(4)
càn	9324(18)	-2338(13)	5759(11)	42(4)
C(12)	8903(17)	-1723(13)	5845(11)	36(4)
C(13)	5812(16)	-1711(13)	5520(12)	38(4)
C(14)	5323(17)	-1691(12)	6155(12)	39(4)
C(15)	4228(18)	-2006(13)	6014(12)	40(4)
C(16)	3649(18)	-2366(13)	5303(12)	43(4)
C(17)	4028(17)	-2425(12)	4636(12)	42(4)
C(18)	5151(17)	-2096(12)	4756(12)	41(4)
C(19)	8800(15)	1442(12)	8444(10)	23(4)
C(20)	9862(15)	2049(11)	8653(10)	24(4)
C(21)	10303(15)	2475(12)	9430(11)	28(4)
C(22)	9700(15)	2271(12)	10012(11)	28(4)
C(23)	8725(15)	1688(11)	9797(11)	28(4)
C(24)	8248(15)	1260(11)	9046(10)	26(4)
C(25)	9031(16)	1523(13)	6941(11)	34(4)
C(26)	9105(16)	2343(13)	7040(11)	36(4)
C(27)	9752(17)	2793(13)	6664(12)	37(4)
C(28)	10180(16)	2459(13)	6186(12)	39(4)
C(29)	10097(16)	1704(13)	6064(11)	40(4)
C(30)	9477(15)	1200(13)	6455(11)	38(4)
C(31)	6990(17)	1093(13)	7260(12)	36(4)
C(32)	6826(16)	1772(12)	7658(11)	34(4)
C(33)	5930(18)	1936(13)	7407(12)	39(4)
C(34)	5090(17)	1396(13)	6800(12)	44(4)
C(35)	5175(17)	702(14)	6437(12)	47(4)
C(36)	6104(17)	519(13)	6681(11)	44(4)
C(37)	9191(14)	-1657(12)	7831(10)	16(4)
C(38)	9257(15)	-2386(11)	7821(9)	17(4)
C(39)	10124(15)	-2566(12)	7768(10)	21(4)
C(40)	11040(15)	-1933(12)	7714(10)	26(4)
C(41)	11040(16)	-1158(12)	7737(10)	28(4)
C(42)	10128(15)	-1011(12)	7779(9)	23(4)
C(43)	6972(15)	-2419(12)	7603(10)	20(4)
C(44)	6324(14)	-2687(11)	8146(10)	18(4)
C(45)	5490(14)	-3475(11)	7885(10)	16(4)
C(45)	5239(14)	-3951(12)	7163(10)	20(4)
C(47)	5857(14)	-3657(12)	6637(10)	23(1) 22(4)
C(48)	6649(15)	-2897(11)	6888(10)	23(4)
C(49)	8180(14)	-1037(11)	8867(10)	16(4)
C(50)	7446(14)	-728(11)	9063(10)	18(4)
C(51)	7431(15)	-475(11)	9820(11)	23(4)
C(52)	8225(14)	-526(11)	10391(11)	20(4)
C(52)	9021(15)	-772(10)	10197(10)	20(7) 21(4)
C(54)	8940(14)	-1075(10)	9423(9)	$\frac{21(7)}{15(4)}$
(17)	0740(14)	-10/3(10)	7425(7)	13(4)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

state emission and excitation spectra of $[Au(TPPTS)_3]^{8-1}$ recorded at 77 K are shown in Fig. 2.

The excitation and emission spectrum of $[Au(TPPTS)_3]^{8-}$ in H₂O solution, shown in Fig. 3, exhibits a broad unsymmetrical band centering at approximately 513 nm. The excitation spectrum has a band that maximizes at approximately 293 nm. The solution absorption spectrum exhibits two maxima at 270 and 280 nm. In aqueous solution the emission band

Selected bond distances (Å) $5.25H_2O$	and angles (°) for $Cs_8[Au(TPPTS)_3]\cdot$
Bond distances	
Au(1) - P(2)	2.374(6)
Au(1) - P(3)	2.394(5)
Au(1)–P(1)	2.417(5)
Bond angles	
P(2) - Au(1) - P(3)	128.4(2)
P(2)-Au(1)-P(1)	119.8(2)

111.8(2)



Fig. 2. The solid-state emission and excitation spectra of $[Au(TPPTS)_3]^{8-}$ recorded at 77 K.



Fig. 3. The excitation and emission spectra of $[Au(TPPTS)_3]^{8-}$ in aqueous solution. Ionic strength maintained with 0.5 M NaCl.

is red-shifted when compared to that of the solid. The aqueous emission of $[Au(TPPTS)_3]^{8-}$ does not exhibit a dependence on the pH of the solution. At low pH values, no shift is observed in the maximum. At high pH, the luminescence is quenched due to the formation of TPPTS oxide, ³¹P NMR = 34.5 ppm (D₂O). However, the $[Au(TPPTS)_3]^{8-}$ emission does show a depen-

dence on the dielectric constant of the solution. The emission intensity decreases with increasing percentages of a solvent with a lower dielectric constant than H_2O , such as MeOH or acetone [26].

The large Stokes shift between the excitation spectrum and the emission spectrum suggests that the emission arises from a triplet excited state. The emission lifetime, 8 µs, also supports this assignment. The overall similarity between the solution and solid excitation, and emission spectra indicate that the emitting species is intact in solution. The red shift in the solution band, when compared to the solid, suggests that a strong interaction exists between the emitting species and the solvent. However, in the solid state, the highest unoccupied molecular orbitals (HOMOs) must be more stabilized or the lowest occupied molecular orbitals must be more destabilized to account for the shift of the emission to higher energy. This could be due to the formation of a stronger Au-P bond in the solid state as opposed to the solution phase where some dissociation occurs.

The emission dependence on the dielectric constant of the solution is attributed to the fact that the threecoordinate species is stabilized in solutions with a high dielectric constant such as water. The quenching effect that is observed with the addition of solvents with lower dielectric constants appears to be due to the dissociation of the three-coordinate species into the two-coordinate species and the free ligand as shown in Eq. (2).

$$[Au(TPPTS)_{3}]^{8-} = [Au(TPPTS)_{2}]^{5-} + [TPPTS]^{3-}$$
(2)

As observed in the X-ray crystal structure, complex 2 is stabilized in aqueous solution by an extensive hydrogenbonding network involving the water molecules and the $[RSO_3]^-$ groups. Decreasing the dielectric constant of the aqueous solution by adding less-polar solvents reduces the stability of the three-coordinate species. A solution of $[Au(TPPTS)_3]^{8-}$ in pure MeOH shows emission primarily corresponding to the TPPTS ligand. The emission spectrum of TPPTS in H₂O exhibits the $\pi-\pi^*$ transitions of the phenyl rings.

The emission observed from $[Au(TPPTS)_3]^{8-}$ exhibits a dependence on the ionic strength of the water solution. Upon the addition of NaCl (0.5 M), and other salts such as KCl, Na(acetate), Na₂SO₄, and NaPF₆, the emission intensity increases. Since no shift in the emission band is observed, the anions of these salts do not interact with the gold(I) center. By increasing the ionic strength, the three-coordinate species in solution is stabilized and the intensity is therefore greater. This is in agreement with studies by Hanson and coworkers [27] in which they suggest that high ionic strength stabilizes the hydration sphere and that electrostatic repulsions between sulfonate groups of the TPPTS ligand are minimized. Dissociation of TPPTS becomes unfavorable due to the significant reorganization of the solvation sphere. It

Table 4 Photophysical properties of Na₈[Au(TPPTS)₃]

$\lambda_{\rm em}$ (nm), (aq), 298 K	513
$\lambda_{\rm em}$ (nm), (s), 298 K	494
$\lambda_{\rm em}$ (nm), (s), 77 K	486
τ (μs), (s), 77 K	1.9, 8.0
φ	0.046

is important to note that although the chloride concentration is 0.5 M, the Cl⁻ does not appear to coordinate to the gold center.

The luminescence properties of [Au(TPPTS)₂]Cl have been followed by monitoring the emission intensity in aqueous solution as a function of added ligand (L), L =TPPTS. An initial rise in the emission intensity is followed by leveling of the intensity as L is added to the solution. With no ligand added, the two-coordinate [Au(TPPTS)₂]Cl complex exhibits a weak luminescence. In the solid state, this complex is not luminescent. However, with addition of L, the emission intensity increases and reaches a maximum at approximately 1:1 mole ratio of $[Au(TPPTS)_2]^{5-}$:L. The initial rise in the emission intensity is indicative of the formation of a luminescent 1:1 complex where the gold center is threecoordinate. After the addition of L beyond the 1:1 molar ratio, the emission intensity does not significantly decrease which indicates that a four-coordinate complex, $[Au(TPPTS)_4]^{11-}$, does not form due to the bulkiness of the ligand. This is consistent with the structural results for the three-coordinate species, which shows little room for the addition of a fourth bulky ligand. Four-coordinate Au(I) complexes in general do not exhibit visible emission. Table 4 contains a summary of the emission properties of $[Au(TPPTS)_3]^{8-}$.

3.3. Photoluminescence studies of (TPA)₃AuCl

The solid emission and excitation spectra of $(TPA)_3AuCl$ compound recorded at various temperatures are compared in Fig. 4. At room temperature an unsymmetrical broad emission band maximizes at 517 nm (Fig. 4(c)). While lowering the temperature to 77 K increases the emission intensity, an atypical red shift of the band is evident (Fig. 4(a)). The emission band at 77 K is observed at 533 nm. The excitation spectrum of the solid shows a slight blue shift with a temperature decrease. At room temperature, excitation bands are observed at 295 and 321 nm that blue shift to 279 and 308 nm, respectively, at 77 K (Fig. 4(d) and (e)).

The emission spectrum of $(TPA)_3AuCl$ in CH₃CN/ MeOH solution (Fig. 5) exhibits a broad unsymmetrical band centering at approximately 520 nm. The excitation spectrum in solution has a sharp band that maximizes at approximately 317 nm. The band is observed at the tail of the solution absorption spectrum ($\lambda_{abs}^{max} = 268$ nm). In



Fig. 4. The solid-state emission and excitation spectra of (TPA)₃AuCl compound recorded at various temperatures: (a, d) 77 K; (c, e) 298 K; and (b) near 250 K.



Fig. 5. Aqueous excitation and emission spectrum of (TPA)₃AuCl.

aqueous solution, the emission band is observed at a significantly red-shifted position (by approximately 1000 cm^{-1}) when compared to that of the solid and the CH₃CN/MeOH solution spectra. At a neutral pH, the emission band in aqueous solution is observed at 547 nm. As shown in Fig. 6, the aqueous luminescence has an interesting pH-dependent behavior. At pH < 3 the emission is totally quenched. The solution emission "switches on" at a pH of approximately 3.5 and increases in intensity as the pH increases and reaches a maximum at approximately 6.5. Nearly a twofold increase in the emission intensity has been observed on going from pH 3.5 to 6.5. A slight red shift in the band position is also evident with a pH increase. The yellow broad emission (wfh = 4600 cm^{-1}) centering at 539 nm at pH approximately 4 shifts to 547 nm at pH 6.5. The intensity remains almost unchanged in the pH range 6.5-10. However, excitation for a prolonged period of time (>1 h) at high pH (>10) causes decomposition of the compound leaving a brown suspension of Au metal. The oxidation product of this process has been confirmed to be phosphine (TPA) oxide by ${}^{31}P{}^{1}H$ NMR



Fig. 6. Emission spectra of (TPA)₃AuCl in aqueous solution at different pH values: (a) pH 6.5, (b) pH 4.2, (c) pH 3.9, (d) pH 3.4, and (e) pH 2.7. The pH was adjusted with dilute HCl.

experiment ($\delta = -1.36$ ppm). Several anionic species including SCN⁻ and [Fe(CN)₆]⁴⁻ quench the emission at a neutral pH. In addition, the luminescence is quenched by known phosphorescence quenchers such as O₂ and NO₃⁻.

Information regarding complexation of gold with TPA in aqueous solution has been obtained using luminescence, ³¹P{¹H} NMR, and Raman spectroscopies. The luminescence of (TPA)2AuCl has been followed by monitoring the emission intensity as a function of added L (TPA). In Fig. 7, the integrated area of the emission band is plotted against the mole fraction of L. An initial rise is followed by a sharp drop in the emission intensity as L is added to a solution of (TPA)₂AuCl. With no ligand added, the two-coordinate (TPA)₂Au⁺ species is not luminescent. However, with the addition of L the emission intensity increases and reaches a maximum at approximately 1:1 molar ratio of $(TPA)_2Au^+$:L. The initial rise in the emission intensity is indicative of the formation of a luminescent 1:1 complex. Addition of L beyond the 1:1 mole ratio quenches the emission and suggests that further coordination of the ligand produces the four-coordinate $(TPA)_4Au^+$ species. Thus, two equilibria have been established from these studies. A typical plot of the emission intensity vs. [L] (at pH 6.5) shows two straight lines in the 0-0.5 and >0.5 mole fraction regions (Fig. 7). The quenching effect of excess L on the emission intensity of (TPA)₃AuCl was studied independently with and without maintaining a constant ionic strength. While the absolute emission intensity decreases significantly at a high ionic strength, the Stern-Volmer plot $\log((I_0/I) - 1)$ vs. $\log[L]$ (Fig. 8) remains unchanged. The formation constants (Eq. (3)) $pK_3 = -3.1$ and (Eq. (4)) $pK_4 = -2.6$ have been extracted from these plots.

$$L_2Au^+ + L = L_3Au^+$$
(3)

$$L_3Au^+ + L = L_4Au^+ \tag{4}$$



Fig. 7. Plot of the emission intensity vs. [L], L = TPA (at pH 6.5).

The three-coordinate (TPA)₃AuCl compound luminesces strongly both in solid and in solution. The solid emission spectrum ($\lambda_{ex} = 320$ nm) shown in Fig. 4(c) depicts a broad unsymmetrical band centering at 517 nm at 298 K. The solid emission band red shifts 580 cm⁻¹ upon cooling the sample to 77 K (Fig. 4(a)). The large Stokes shift between the excitation spectrum and emission band indicates that the emission arises from a spin forbidden excited state. This assignment is supported by the long lifetime measured at room temperature (approximately 3.2 µs).

In aqueous solution, (TPA)₃AuCl is fairly strongly emissive with a quantum efficiency, φ , 65% greater than that of $[Ru(bpy)_3]^{2+}$, where bpy is 2,2'-bipyridine [7b]. The measured quantum yield at a neutral pH is 0.069. To the best of our knowledge (TPA)_3AuCl was the first example of a gold(I) phosphine complex that shows luminescence in aqueous solution even though other complexes have been discovered [28]. When compared to the solid spectra nearly a onefold reduction in the lifetime of the aqueous solution has been observed. The measured lifetime at a neutral pH is 0.53 µs. The calculated radiative lifetime ($\tau_r = \tau_m/\varphi$) in aqueous solution is approximately 7.7 µs, which corresponds to a radiative rate constant ($k_r = \varphi/\tau$) of $1.3 \times 10^5 \text{ s}^{-1}$. The relatively large radiative rate constant suggests that the



Fig. 8. Stern–Volmer plot of $log((I_0/I)-1)$ vs. log[L], L = TPA.

transition is likely to be an orbitally allowed transition [29].

The overall similarity between the solution and solid excitation, and emission spectra indicate that the emitting species is intact in solution. The red shift in the solution emission band, when compared to the solid, suggests that some interaction between the emitting species and the solvent or solvent components exists. Excimer emission has been discounted because of the lack of concentration dependence. The emission in lesspolar organic solvents (CH₃CN and MeOH) is observed at a blue-shifted position when compared to that of the aqueous solution. It is likely that the long lifetime in aqueous solution allows rearrangement of the solvent dipoles and stabilizes the excited state. Comparison of the excitation spectra in solid and solution supports the idea of excited-state stabilization through solvent rearrangement. While the emission spectra clearly show a solvent-dependent shift, the excitation spectra closely resemble that of the solid.

While TPA is potentially a quadridentate ligand, complexation of the ligand with metal ions has so far been observed only through the P atom [30]. However, protonation and alkylation at one of the nitrogen sites have been demonstrated [29,31]. It is, thus, reasonable to expect a pH-dependent property with Au(I) complexes of this ligand. As shown in Fig. 6, the emission is totally switched-off at low pH (<3) and is observed only at a higher pH. The possibility of sample decomposition at low pH has been discounted, as the emission dependence on pH is reversible for a number of cycles. It is likely that a complete dissociation of the luminescent three-coordinate species to the non-luminescent twocoordinate quenches the emission. This postulate was tested by Raman spectroscopic measurements that were carried out on the complexes at various pH values. A large enhancement in the v_{Au-P} symmetric vibrational mode might be expected if dissociation of the threecoordinate species at low pH leads to a more polarizable two-coordinate species. However, no significant change either in the band position or in the relative intensity of the v_{Au-P} symmetric stretching (396 cm⁻¹) has been observed. The only difference between the neutral and low pH Raman spectra of the (TPA)₃AuCl solution has been observed in the region covering the ligand vibrational modes.

While several explanations potentially exist to explain these results, it is likely that dissociation of the H-TPA⁺ ligand occurs at low pH with the formation of [(H-TPA)AuCl]⁺, a polar two-coordinate species that itself is not expected to be luminescent.

3.4. Singlet-to-triplet $(S_0 \rightarrow T_1)$ absorption

The forbidden electronic absorption between the singlet ground state and the triplet excited state in

 $[Au(TPPTS)_3]^{8-}$ has been obtained in aqueous solution at room temperature. The absorption has a maximum near 600 nm ($\varepsilon = 1$) and a width at half-height equal to approximately 3300 cm^{-1} . The extinction coefficient clearly indicates that this is a forbidden transition. Pt(II) complexes have displayed long-wavelength absorptions with extinction coefficients = 90. These transitions have been assigned as absorptions to the triplet state and the large intensities come about due to strong spin-orbit coupling for Pt(II) [30]. Spin-orbit coupling effects split the electronic states of atoms and mix states of different symmetries. This facilitates the observation of singlet-totriplet transitions which are normally forbidden [32]. These effects are more significant in molecules containing heavy atoms. However, in the present Au(I) system, the extinction coefficient is extremely low because the ${}^{1}S \rightarrow {}^{3}D_{3}$ transition is spin and orbitally forbidden.

3.5. Luminescence quenching

Complex 1 exhibits luminescence in the solid state and in aqueous solution. In this work, the excited-state properties of $[Au(TPPTS)_3]^{8-}$ have been investigated specifically to study their ability to interact with various molecules. Energy transfer and electron transfer quenching have been demonstrated for other photoluminescent metal complexes including Au(I) complexes in organic solvents. We have found that gold(I) complexes can undergo photochemical reactions in aqueous solution as well. Molecules such as O₂, NO, and SO₂ quench the luminescence of $[Au(TPPTS)_3]^{8-}$ (aq). Dioxygen has been shown to quench luminescent Au(I) complexes in the solid state in thin films of gold containing polymer. This quenching process can also occur in aqueous solution and is reversible.

Luminescence quenching of dinuclear Au(I) complexes by dioxygen has been reported previously [33]. The mechanism of this quenching process was assigned to energy transfer and this pathway seems possible due to the low triplet energy of O_2 (7752 cm⁻¹). The energy transfer mechanism is represented as shown in Eq. (5), where $Q = O_2$.

$$[Au(TPPTS)_3]^{8-*} + Q = [Au(TPPTS)_3]^{8-} + Q^*$$
(5)

In the present case, the donor would be 3 [Au(TPPTS)₃]^{8-*} and the acceptor would be ground-state 3 O₂.

Another possible mechanism for the luminescence quenching of $[Au(TPPTS)_3]^{8-*}$ with O₂ is through electron transfer as represented in Eq. (6).

$$[Au(TPPTS)_3]^{8^{-*}} + Q = [Au(TPPTS)_3]^{7^{-}} + Q^{-}$$
(6)

Excited-state molecules typically are better electron donors or acceptors [34]. When an excited state is formed an electron is typically promoted from HOMO to the lowest lying unoccupied molecular orbital (LUMO). The electron that has been excited can be more easily transferred than it could in the ground state and the electron hole that was left in HOMO can more easily accept an electron than the complex could in the ground state. Overall, the electron ionization potential of the complex is reduced in the excited state and the electron affinity is increased [35]. The data obtained in the present work concerning $[Au(TPPTS)_3]^{8-}$ (aq) luminescence quenching with dioxygen, although they do not rule out the energy transfer quenching mechanism proposed by Che, do provide evidence that an electron transfer mechanism could occur, forming superoxide ion, O_2^{-} .

Superoxide, O_2^{-} , is capable of oxidizing TPPTS in H₂O. However, it may not be the actual species that performs the oxidation. It is known that O_2^{-} in H₂O immediately undergoes hydrolysis as shown in Eq. (7) [36].

$$O_2^- + H_2O = HOOH + O_2 \tag{7}$$

HOOH does oxidize TPPTS to TPPTS oxide. No matter which species is the actual one that performs the alkyl halides have been calculated using the Stern-Volmer relationship (Table 5).

Che and coworkers [37] have demonstrated that the dinuclear gold(I) complex, $[Au_2(\mu-dppm)_2]^{2+}$, can undergo photoreaction with alkyl halides in degassed acetonitrile solutions. The quenching rate constants that they obtained through Stern–Volmer plots and the results of flash photolysis experiments suggested that the likely mechanism for luminescence quenching of the dinuclear complex was through atom transfer. They have also determined that this binuclear gold(I) complex is a powerful photoreductant having $E^0(Au_2^{3+} - Au_2^{2+*}) = -1.6$ V vs. SSCE in acetonitrile and have demonstrated that it can undergo photo-induced redox reactions with electron donors and acceptors [37].

The rate constants obtained in the quenching experiments of $[Au(TPPTS)_3]^{8-}$ with alkyl halides in water do not alone provide enough evidence to distinguish between an atom transfer mechanism (Eq. (8)) or an electron transfer mechanism (Eq. (9)).

Alkyl halides with high reduction potentials would be

atom transfer:
$$[Au(TPPTS)_3]^{8^{-*}} + RX \rightarrow [Au(TPPTS)_3X]^{8^{-}} + R^{\bullet}$$
 (8)

electron transfer:
$$[Au(TPPTS)_3]^{8^{-*}} + RX \rightarrow [Au(TPPTS)_3]^{7^-} + RX^- RX^- \rightarrow R^{\bullet} + X^- [Au(TPPTS)_3]^{7^-} + X^- \rightarrow [Au(TPPTS)_3X]^{8^-}$$
(9)

oxidation of the phosphine, the initial formation of superoxide ion by electron transfer reduction of dioxygen from $[Au(TPPTS)_3]^{8-}$ is a plausible mechanism. Further studies are being carried out to explore the interaction of dioxygen with this complex in the excited state and will be reported elsewhere.

3.6. Quenching with alkyl halides

 $[Au(TPPTS)_3]^{8-}$ has also been found to undergo photoreaction with alkyl halides in aqueous solution. The bimolecular quenching rate constants for several

Table 5 Rate constants for the quenching of $[Au(TPPTS)_3]^{8-}$ by alkyl halides in H₂O at room temperature

Quencher	E^{0} , [RX-RX ^{-•}] [34]	$k_{\rm q} ({\rm M}^{-1}, {\rm s}^{-1})$
CHCl ₃	-1.67	9.1×10^{8}
CCl ₄	-0.78	1.5×10^{8}
CH_2Cl_2	-2.33	5.6×10^{6}
MeI	-1.63	$8.4 imes 10^8$
EtI	-1.67	$7.5 imes 10^{8}$
allylBr	-1.21	1.0×10^{9}

expected to produce quenching rate constants that approach the diffusion-controlled limit in water, approximately 10^9 . However, nearly diffusion-controlled quenching rate constants were obtained for alkyl halides having low reduction potentials, as well. Since both atom transfer and electron transfer pathways involve charge transfer from the excited complex $[Au(TPPTS)_3]^{8-*}$ to the alkyl halide, the similarity between the rate constants obtained is not a complete surprise [37].

3.7. Complex stoichiometries

While gold(I) has a strong tendency [38] for a linear two-coordination, this property, however, is not exclusive particularly in solution. Previous solution studies [39] have shown evidence of a rich coordination of gold(I) with tertiary phosphines. In several phosphine complexes of gold(I) it has been demonstrated that more species are capable of existence in solution than can be crystallized from solution. For $L = PEt_3$, for example, all the complexes of $[AuL_n]^+$ (n = 2-4) have been identified spectroscopically, even though only the

 $[Au(PEt_3)_2]^+$ species has been crystallized out in the presence of excess ligand [39]. In addition, a recent ${}^{31}P{}^{1}H{}$ NMR study [39e] on $[AuBr_2]^-$ with added PBu₃ has shown the existence of species with 1–4 coordinated ligands that exchange with one another in solution. The exchange process is known to have negative entropy and, thus, an associative mechanism is deduced.

Moreover, ligand scrambling is another phenomenon known [40] to alter the solution chemistry of gold(I) complexes of the type LAuCN compounds (L = PEt₃, PPh₃). Vibrational studies on (PEt₃)AuCN have shown that ligand-scrambling reactions favor formation of the symmetrically substituted complexes (PEt₃)₂Au⁺ and [Au(CN)₂]⁻ according to the equilibrium shown in Eq. (10). A similar equilibrium has been established for the anionic cyano(thiolato)gold(I) complex, RSAuCN [41].

$$2PEt_{3}AuCN = (PEt_{3})_{2}Au^{+} + Au(CN)_{2}^{-}$$
(10)

The emission studies of $(TPA)_2AuCl$ as a function of added ligand have been informative about the stoichiometries of the species present in solution. As shown in Fig. 7, the initial slow rise of the emission intensity indicates the formation of a 1:1 ($L_2Au^+:L$) complex. No shift in the position of the emission band has been observed and the spectral profile remained unchanged during the entire titration. All evidences, thus, suggest that (TPA)_3Au^+ species is the only luminescent species present in solution. Previous studies by Fackler and coworkers [42] and McClesky and Gray [43] have shown that mononuclear three-coordinate gold(I) phosphines luminesce in solution due to a metal-centered (MC) $\sigma(d_{z^2}) \rightarrow \sigma(p_z)$ transition. Gold(I) complexes of the tripod NP₃ ligand are also luminescent in solution [27].

In addition, the fact that the emission intensity decreases past the 1 equiv. of L most likely reflects a reduced concentration of the L_3Au^+ species that is present in solution. Dynamic quenching via energy transfer is unlikely, as TPA does not have a low-lying excited state that is capable of accepting the excited energy. Conditions that favor formation of the nonluminescent four-coordinate L4Au⁺ species are expected to reduce the concentration of the (TPA)₃Au⁺ species and by inference the emission intensity. It is interesting to note that four-coordinate gold(I) phosphines are not known to luminesce either in the solid or in solution. The lack of an MC emission (in the absence of Au-Au interaction) in the linear and tetrahedral Au(I) complexes indicates that the symmetry requirement is rigorous in these systems.

3.8. ${}^{31}P{}^{1}H$ NMR studies

 $[Au(TPPTS)_2]^{5-}$ and $[Au(TPPTS)_3]^{8-}$ complexes exhibit ${}^{31}P{}^{1}H{}$ signals at 45.5 and 43.5 ppm in D₂O, respectively. Both signals are broad indicating that the

compounds are fluxional at room temperature. Variable temperature studies were performed with a CD₃OD solution of $[Au(TPPTS)_3]^8^-$. When the temperature is decreased to -60 °C, the broad peak centered at 43.5 ppm is split into two peaks, which appear at 45.8 and 43.5 ppm. These signals correspond to the two- and three-coordinated complexes, respectively. The peak at -5.2 ppm corresponding to the free TPPTS ligand is also present. Rates faster than 8×10^{-7} s are expected to produce line broadening in this spectrum.

 ${}^{31}P{}^{1}H{}$ MAS solid-state NMR spectra of Na₈[Au(TPPTS)₃] and the sodium salt of the TPPTS ligand were obtained. The spectrum of TPPTS shows a broad signal centered at -1.5 ppm and the spectrum of the three-coordinate Au(I) complex shows a broad signal centered at 41.2 ppm. These values are only slightly shifted from the values obtained in D₂O solution. The signals in the solid-state spectra are broad for both the ligand and the Au(I) complex. This is most likely because there are approximately 2⁹ possible conformations of the phenyl rings since there are nine rings with two *meta*-positions per ring [26].

 $(TPA)_2AuCl in D_2O$ solution shows a sharp ${}^{31}P{}^{1}H{}$ NMR resonance at -38.3 ppm. In the pH range 3-10, the ${}^{31}P{}^{1}H$ NMR resonance is only slightly affected and shows a downfield shift by approximately 0.3 ppm. On the other hand, $(TPA)_3AuCl$ has a broad ${}^{31}P{}^{1}H{}$ NMR resonance at -56.3 ppm in CD₃CN/CD₃OD (and approximately -63 ppm in D₂O/H₂O) and indicates that fast exchange among the equilibrium species occurs at room temperature as an averaged chemical shift. When the temperature is decreased to $0 \,^{\circ}C$ the ³¹P NMR signal splits into two broad bands and are observed at approximately -45 and -70 ppm. At -50 °C the two bands appear at -43.7 and -74.6 ppm in a 2:3 ratio, respectively. Both signals are broad indicating that the compound is fluxional even at this temperature.

3.9. MO calculation

The electronic structures of the two- and threecoordinate $(TPA)_2Au^+$ and $(TPA)_3Au^+$ species obtained from the EH calculations are correlated in Fig. 9. The calculations were conducted on structures optimized using the MM2 program on the CAChe system. All the ligand atoms were included in the calculation. In the two-coordinate $(TPA)_2Au^+$, HOMO consists of a 22% contribution from the metal 5 d_{z²}, 6 s and 75% from the ligand p_{σ} orbitals. The LUMO has a 20% π contribution from the metal 6 p and 70% from the P, 3 p, orbitals.

On going from the two- to the three-coordinate complexes a significant change takes place in the composition of HOMO. The Au, 5 d_{π_g} , orbitals are destabilized significantly and contribute more in the



Fig. 9. Electronic structures of the two- and three-coordinate $[(TPA)_2Au]^+$ and $[(TPA)_3Au]^+$ species obtained from the EH calculations.

HOMO orbital. Compared to the two-coordinate species the metal 5 d_{z²} orbital is stabilized and its contribution in HOMO is negligible. In the planar threecoordinate geometry, HOMO consists of 20% Au, 5 $d_{x^2-y^2}$, 5 d_{xy} , and 70% P, 3 p_z , contributions. LUMO has a σ -symmetry (as opposed to the π -symmetry in the linear geometry) with a 26% Au, 6 p_z , and 70% P, 3 p_z , contributions. The HOMO–LUMO gap is significantly reduced mainly due to the destabilization of HOMO.

The EH calculations performed on the linear L_2Au^+ species, by approximating the phosphine as PH₃, provide HOMO with a large 5 d_{z²} and 6 s, and an LUMO with a large P, p_π, contributions. With this model the lowest transition is assignable as an MLCT band. However, when the calculations are performed with the inclusion of the whole TPA ligand the metal 5 d_{z²} and 6 s contributions in HOMO decrease and the ligand p_σ contribution dominates (75%). The metal 6 p_{π*} contribution in LUMO also increases.

In a planar three-coordinate geometry, the EH calculations performed on the $(TPA)_3Au^+$ complex indicate a large contribution of the metal 5 d_{π_g} orbital in HOMO. HOMO in $(TPA)_3Au^+$ consists of a 5 $d_{x^2-y^2}$ (20%) contribution from the gold atom and (70%) from

the P atom. The calculated HOMO-LUMO gap for L_3Au^+ (4.66 eV) is smaller by approximately 1.2 eV from the linear L_2Au^+ system (5.85 eV). The theoretical result is consistent at least qualitatively with the solution absorption data. On going from the linear two-coordinate to the three-coordinate, $(TPA)_3Au^+$, a red shift in the lowest absorption band has been observed (242 nm vs. 268 nm, respectively). A similar red shift has been observed in previous studies as well [24]. For example, in $(PPh_3)_3Au^+$ the lowest absorption band at 281 nm is red-shifted by more than 2700 cm^{-1} when compared to that of the two-coordinate $(PPh_3)_2Au^+$ species. Bending of the P-Au-P angle in linear L_2Au^+ to form threecoordination has been found to cause destabilization of the metal 5 d_{π} orbitals that activate the metal center for a better interaction with nucleophiles [44]. The red shift that has been observed in the lowest absorption band of the (TPA)₃AuCl complex is thus due to the expected destabilization of the HOMO orbital on going from two-coordination to three-coordination. Based on the EH calculations the lowest transition is best described as a σ -bonding to ligand charge transfer transition (SBLCT) rather than purely an MC transition. As shown in Fig. 9, the transition is assignable to the Laporte allowed ${}^{1}E_{1} \rightarrow {}^{1}A_{1}$ transition (assuming a C_{3v} symmetry and *z*-axis taken as perpendicular to the molecular plane). The emission however originates from the triplet ${}^{3}A_{1}$ state.

4. Conclusions

In conclusion, the structural characterization of $Cs_8[Au(TPPTS)_3] \cdot 5.25H_2O$ is important because it is the first clear example of a three-coordinated Au(I) complex that exhibits similar luminescence properties in the solid salt and in solution. TPPTS cesium salt has promoted the formation of single crystals. The ligand ionic properties have allowed the complex to crystallize without Cl⁻ being present in the Au(I) coordination sphere making this complex a true three-coordinated complex. Therefore, it can serve as a structural model for some of the water-soluble catalysts that are being investigated and whose crystal structures have not been determined so far 25.

The complex $[Au(TPPTS)_3]^{8-}$ exhibits luminescence in aqueous solution and in the solid state. Stokes shift and lifetime measurements suggest that the emission is phosphorescence from a triplet excited state. The photoluminescent properties of this complex in aqueous solution and the mechanisms by which it can interact with molecules in the excited state are being investigated. Reversible quenching experiments and photolysis studies in the presence of dioxygen have shown that the excited state of gold(I) can accelerate the oxidation of TPPTS. The mechanism for this process may be through electron transfer to O_2 to form singlet oxygen, $O_2^{-\bullet}$. Luminescence quenching of $[Au(TPPTS)_3]^{8-}$ by alkyl halides has also been observed. The bimolecular quenching rate constants obtained do not alone distinguish whether the mechanism for quenching is via atom transfer or electron transfer.

The solid emission and excitation spectra of the $(TPA)_3AuCl$ compound recorded at various temperatures are compared. While a luminescent three-coordinate species forms in solution and in the solid state, the ligands readily exchange in solution and up to four TPA ligands can associate with the metal ion at low pH. Luminescence quenching occurs when protonation of the TPA ligands changes the equilibrium distribution of the various Au(I) species present in water removing the three-coordinate species from concentration dominance.

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