6330 *Inorg. Chem.* **1995,** *34,* 6330−6336

Luminescence Studies of Gold(I) Thiolate Complexes

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Received May 5, 1995[⊗]

A series of monomeric gold(I) complexes containing phosphine and thiolate ligands have been synthesized. The two phosphines used were triphenylphosphine and the 1,3,5-triaza-7-phosphaadamantanetriylphosphine (TPA). Substituted benzenethiolate ligands were used with the substituent in either the ortho, meta or para position. All of the compounds synthesized luminesce at 77 K in the solid state, where the excitation is assigned to a ligand to metal charge transfer (LMCT) transition from the sulfur of the thiolate ligand to the gold center. The large Stokes shifts and long lifetimes measured imply that the emission is phosphorescence. The position of the emission maxima can be affected by both the substituents on the thiolate ligand and the presence of gold−gold interactions between neighboring molecules in the solid state. Four of these compounds have been structurally characterized. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with cell constants a = 8.641(2) Å, b = 11.423(2) Å, c = 12.118(2) Å, α = 103.36(3)°, β = 99.34(3)°, γ = 105.95(3)°, and Z = 2. Refinement of 2861 reflections and 253 parameters yields R = 0.0275 and R_w = 0.0669. Compound **4** crystallizes in the orthorhombic space group $P2_12_12_1$ (No. 18) with cell constants a = 6.3100(10) Å, b = 12.127(3) Å, c = 18.193(3) Å, and Z = 4. Refinement of 1231 reflections and 163 parameters yields R = 0.0292 and R_w = 0.0360. Compound **5** crystallizes in the monoclinic space group $P2_1/n$ (No. 13) with cell constants a = 12.252(3) Å, b = 17.002(6) Å, c = 22.845(4) Å, β = 91.25(2)°, and Z = 12. Refinement of 5534 reflections and 541 parameters yields R = 0.0698 and R_w = 0.0786. Compound **10** crystallizes in the monoclinic space group $C2/c$ (No. 15) with cell constants a = 17.542(5) Å, b = 18.831(6) Å, c = 11.647(4) Å, β = 119.52(2)°, and Z = 8. Refinement of 2207 reflections and 181 parameters yields R = 0.0327 and R_w = 0.0441.

Introduction

The photochemistry of d^{10} gold(I) complexes has attracted a great deal of attention over the last few years.[1] Of particular interest is the relationship between the observation of emission and the presence of weak bonding interactions between neighboring gold centers. These interactions, shown to be present in many binuclear complexes (e.g. $[Au_2(dppm)_2]^{2+}$, dppm = (diphenylphosphino)methane), are thought to be responsible for the observed luminescence. The assignment for the emission is as a metal-centered transition.[1b,c] Mononuclear gold(I) complexes have also been shown to exhibit an interesting luminescence. The (TPA)AuX (X = Cl, Br, I) complexes all show short gold contacts between neighboring molecules in the solid state, and they also luminesce at 77 K.[2] In solution, where it is assumed that these weak intermolecular interactions no longer exist, no luminescence is observed. For $[(TPA)AuCl]_2$, the emission is also assigned as being metal-centered, and it was found that the emission energy maxima can be correlated with the distance between the two gold atoms of neighboring molecules. In addition, it was found that the strength of the gold−gold interaction increases with an increase in the softness of the ligand X. This is in agreement with SCF calculations performed by Pyykko on the perpendicular dimers $[(H_3P)AuX]_2$ (X = CH_3, H, Cl, CN, Br, I).[3]

In order to investigate whether a correlation between the emission energy and the Au···Au distance is a general phenomenon, a series of gold(I) monomeric complexes were synthesized containing phosphine and thiolate ligands. These complexes are not only of interest due to their photochemistry; many theoretical and experimental studies have been carried out on the L−Au−SR linkage due to its presence in many antiarthritic and cancerostatic drugs. 1,3,5-Triaza-7-phosphaadamantanetriylphosphine (TPA) was chosen experimentally because it has a small cone angle (102°), which means that the close approach of two molecules should not be hindered by steric effects. It also has no π-system, so no low-energy intraligand transitions need to be considered (UV/vis of a water solution of TPA shows no absorption above 210 nm). For comparison, a short series of complexes containing triphenylphosphine was synthesized, **1**−**3**. These latter complexes are similar to a series of binuclear complexes studied by Elder, Bruce, Bruce, and co-workers which contained bridging bidentate ligands.[4,5] These authors concluded that the emission observed arises from a S−Au CT excited state that is perturbed by changes in both the phosphine and the thiolate ligands. EXAFS was used to determine the gold−gold distance in the solid state, but no correlation between this distance and the emission energy was found.

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[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1995.

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Table 1. NMR Data and Elemental Analyses for **1**–**11**

			elemental anal., %					
	$^{31}P\{^1H\}$ NMR	^1H NMR	calcd			found		
complex	δ, ppm	δ, ppm	C	H	N	C	H	N
$(Ph_3P)AuSPh$, **1**	38.6	6.8–7.5 (m, 20H)						
$(Ph_3P)AuSPh(o\text{-}OMe)$, **2**	38.1	3.79 (s, 3H), 6.9–7.8 (m, 19H)						
$(Ph_3P)AuSPh(o\text{-}Cl)$, **3**	38.1	6.8–7.8 (m, 19H)	47.80	3.15		47.77	3.23	
(TPA)AuSPh, **4**	−49.8	4.2 (s, 6H), 4.5 (d, 6H), 7.0–7.5 (m, 4H)	31.10	3.67	9.07	31.04	3.74	8.78
(TPA)AuSPh(*o*-OMe), **5**	−45.6	3.85 (s 3H), 4.3 (s, 6H), 4.5 (d, 6H), 6.8–7.6 (m, 4H)	31.64	3.85	8.52	31.92	3.94	8.24
(TPA)AuSPh(*m*-OMe), **6**	−49.9	3.75 (s, 3H), 4.3 (s, 6H), 4.5 (d, 6H), 7.1 (m, 4H)	31.64	3.85	8.52	31.83	3.97	8.17
(TPA)AuSPh(*o*-Cl), **7**	−45.3	4.3 (s, 6H), 4.5 (d, 6H), 7.0–7.7 (m, 4H)	28.94	3.22	8.44	29.12	3.27	8.21
(TPA)AuSPh(*m*-Cl), **8**	−50.1	4.3 (s, 6H), 4.5 (d, 6H), 7.0–7.5 (m, 4H)	28.94	3.22	8.44	28.76	3.25	8.13
(TPA)AuSPh(*p*-Cl), **9**	−50.2	4.3 (s, 6H), 4.5 (d, 6H), 7.1–7.4 (m, 4H)	28.94	3.22	8.44	28.74	3.22	7.90
$(TPA)AuSPh(3,5\text{-}Cl)_2$, **10**	−50.7	4.3 (s, 6H), 4.5 (d, 6H), 7.0–7.5 (m, 3H)	27.07	2.82	7.89	27.16	2.75	7.91

Table 2. Crystallographic Data for **3**, **4**, **5** and **10**

	$(Ph_3P)AuSPh(o\text{-}Cl)$, **3**	(TPA)AuSPH, **4**	(TPA)AuSPh(*o*-OMe), **5**	$(TPA)AuSPh(3,5\text{-}Cl_2)$, **10**
chem formula	$C_{24}H_{19}AuClPS$	$C_{12}H_{17}AuN_3PS$	$C_{13}H_{19}AuN_3OPS$	$C_{12}H_{15}AuCl_2N_3PS$
mol wt	602.8	463.3	493.3	532.2
crystal size, mm	4.0 × 2.4 × 2.0	0.25 × 0.2 × 0.1	0.24 × 0.8 × 0.8	0.4 × 0.3 × 0.3
crystal system	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$	$C2/c$
a, Å	8.641(2)	6.3100(10)	12.252(3)	17.542(5)
b, Å	11.423(2)	12.127(3)	17.002(6)	18.831(6)
c, Å	12.118(2)	18.193(3)	22.845(4)	11.647(4)
α, deg	103.36(3)			
β, deg	99.34(3)		91.25(2)	119.52(2)
γ, deg	105.95(3)			
V, Å^3	1085.9(4)	1392.2(5)	4758(2)	3348(2)
Z	2	4	12	8
μ, mm^{-1}	7.07	10.82	9.51	9.32
D_c, g cm^{-3}	1.844	2.21	2.072	2.112
temp, K	298	298	298	298
radiation (λ, Å)	graphite-monochromated Mo Kα (0.710 73)			
transm factors: max, min	0.970, 0.589	0.934, 0.753	0.796, 0.755	0.969, 0.609
R, R_w	0.0275, 0.0669	0.0292, 0.0556	0.0698, 0.0786	0.0327, 0.0668

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{[\sum w(|F_o| - |F_c|)]/\sum w|F_o|\}^{1/2}$.

Experimental Section

All experiments were routinely carried out under pure and dry nitrogen using standard Schlenk line apparatus. The organic solvents were rigorously dried before use. The mononuclear gold phosphine chloride complexes (TPA)AuCl[2] and $(Ph_3P)AuCl$[6] were prepared by published procedures. The thiolate ligands were purchased from Aldrich and used without further purification. Triphenylphosphine was also purchased from Aldrich, and TPA was synthesized as reported in the literature.[7]

X-ray structural analysis was performed on a Nicolet R3m/E diffractometer employing SHELXS and a micro-vax II computer. The $^{31}P\{^1H\}$ NMR were collected on a Varian XL-200E spectrometer operating at 81 MHz, in 10 mm tubes. Chemical shifts, in ppm, were referenced to an external standard of 80% H_3PO_4. ^1H NMR spectra were recorded on a Varian XL-200 spectrometer. Emission and excitation spectra were measured at 77 K with a SLM/AMINCO Model 8100 spectrofluorometer using a xenon lamp. Spectra were corrected for instrumental response. The lifetime measurements were obtained at 77 K using a Laser Photonics Model LN300C sealed nitrogen/dye laser and an SLM 8000 monochromator. The output was sent to a LeCroy 9130M 300 MHz oscilloscope coupled to a Gateway 2000 486 DX/33 computer for data analysis.

General Synthesis. The gold(I) thiolate complexes were prepared from the reaction of the gold phosphine chloride with 1 equiv of the deprotonated thiolate ligand. The synthesis described for compound **1** illustrates the general procedure used for the triphenylphosphine complexes, **1**–**3**, and the synthesis described for compound **4** illustrates the general procedure used for the TPA complexes, **4**–**14**.

$(Ph_3P)AuSPh$, 1. A solution of HSPh (0.022 g, 2.02 × 10^{-4} mol) and KOH (0.0113 g, 2.02 × 10^{-4} mol) in methanol was added to a solution of $(Ph_3P)AuCl$ (0.1 g, 2.02 × 10^{-4} mol) in 5 mL of acetone. After the reaction mixture was allowed to stir for 1 h, the solution was taken to dryness under reduced pressure. The white product was first washed with MeOH (2 × 5 mL) and then extracted with CH_2Cl_2 (3 × 5 mL). Reduction of the solvent volume and addition of ether gave a white crystalline solid.

(TPA)AuSPh, 4. A solution of HSPh (0.028 g, 2.57 × 10^{-4} mol) and KOH (0.014 g, 2.57 × 10^{-4} mol) in methanol was added to a suspension of (TPA)AuCl (0.1 g, 2.57 × 10^{-4} mol) in 10 mL of acetonitrile. After the reaction mixture was stirred for 1 h, the solution was taken to dryness under reduced pressure and the residue was washed with MeOH (3 × 5 mL). Extraction with CH_2Cl_2 followed by addition of ether gave a white crystalline solid.

Yields varied between 50% and 80%. Elemental analyses and ^1H and $^{31}P\{^1H\}$ NMR data are shown in Table 1.

X-ray Data Collection and Refinement of the Structures. Single crystals of **3**, **4**, **5**, **8**, and **10** were grown from CH_2Cl_2/benzene/hexane. The structure determination procedures (Nicolet R3m/E diffractometer, SHELXTL 5.1 software) are described in detail elsewhere.[8] Single crystals of each compound were mounted on glass fibers with epoxy resin, and data were collected. No decay was observed for the chosen standard reflections. Crystallographic data are contained in Table 2. The data were corrected for decay and for Lorentz and polarization effects. Heavy-atom positions were determined from direct methods and used as the initial phasing model for difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed to the carbon atoms in idealized positions at a distance of 0.96 Å.

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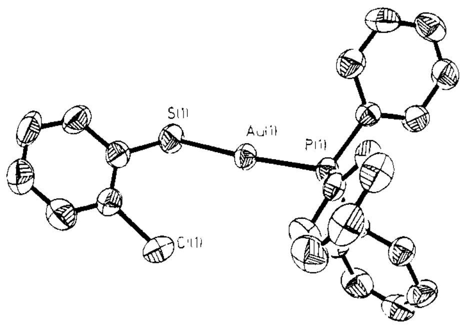

Figure 1. Thermal ellipsoid plot of (Ph$_3$P)AuSPh(*O*-Cl), **3**.

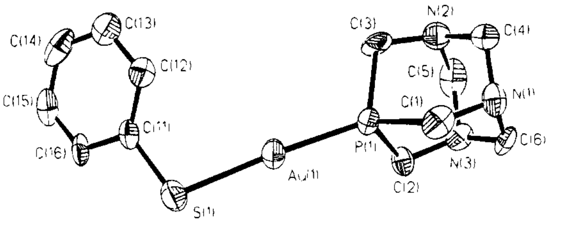

Figure 2. Thermal ellipsoid plot of (TPA)AuSPh, **4**.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for (PPh$_3$)AuSPh(*o*-OMe), **3**^{a}

	x	*y*	*z*	*U*(eq)
Au(1)	1451(1)	4052(1)	1954(1)	43(1)
P(1)	2814(2)	6083(1)	2068(1)	39(1)
S(1)	307(2)	1924(2)	1736(2)	56(1)
Cl(1)	−562(3)	3669(2)	4008(2)	76(1)
C(11)	4540(7)	6880(6)	3343(5)	41(1)
C(12)	5172(8)	8192(6)	3749(6)	52(2)
C(13)	6467(8)	8784(8)	4745(6)	63(2)
C(14)	7114(9)	8060(10)	5327(6)	72(2)
C(15)	6504(9)	6779(9)	4927(6)	70(2)
C(16)	5215(8)	6168(7)	3942(6)	56(2)
C(21)	1534(7)	7116(5)	2200(5)	40(1)
C(22)	818(9)	7215(7)	3153(6)	60(2)
C(23)	−102(10)	8011(8)	3320(7)	73(2)
C(24)	−332(8)	8721(7)	2580(7)	65(2)
C(25)	362(8)	8610(7)	1624(7)	61(2)
C(26)	1282(7)	7804(6)	1439(5)	47(2)
C(31)	3600(7)	6206(5)	797(5)	38(1)
C(32)	2533(8)	5570(7)	−307(6)	61(2)
C(33)	3076(9)	5696(8)	−1298(6)	66(2)
C(34)	4681(10)	6419(7)	−1209(6)	62(2)
C(35)	5721(9)	7008(7)	−160(6)	64(2)
C(36)	5221(8)	6917(6)	868(6)	54(2)
C(41)	−1651(8)	1634(6)	2065(5)	49(2)
C(42)	−2940(10)	558(7)	1329(6)	66(2)
C(43)	−4491(10)	206(8)	1536(8)	76(2)
C(44)	−4829(10)	939(8)	2495(7)	74(2)
C(45)	−3590(10)	1975(8)	3257(7)	70(2)
C(46)	−2037(9)	2323(6)	3034(6)	56(2)

^{a} *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for (Ph$_3$P)AuSPh(*m*-Cl), **3**

Au(1)−P(1)	2.255(2)	P(1)−Au(1)−S(1)	173.11(6)
Au(1)−S(1)	2.292(2)	C(41)−S(1)−Au(1)	109.5(2)
S(1)−C(41)	1.761(7)		

The structure of **3** is shown in Figure 1. Atomic coordinates are given in Table 3, and selected bond angles and distances are given in Table 4. There are no significant gold−gold interactions in the solid state, and the closest gold−gold distance is 6.105 Å.

The structure of **4** is shown in Figure 2. Atomic coordinates are given in Table 5, and selected bond angles and distances are given in Table 6. There are no significant gold−gold interactions in the solid state, and the closest gold−gold distance is 5.243 Å. The packing diagram for this compound is shown in Figure 3.

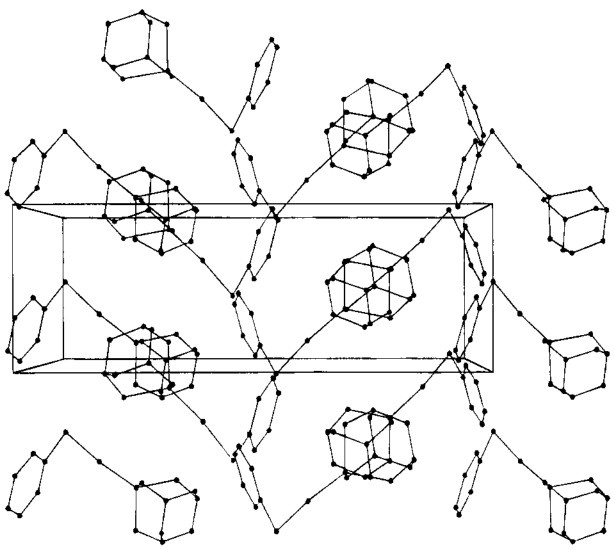

Figure 3. Packing diagram for (TPA)AuSPh, **4**, viewed along the *b* axis.

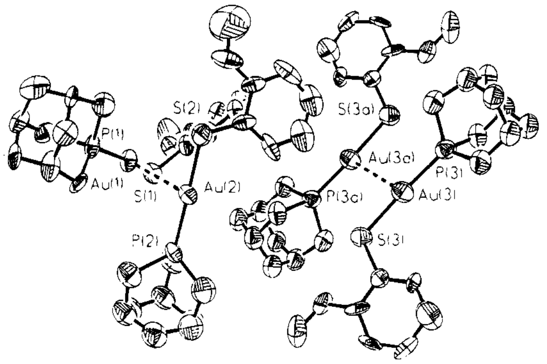

Figure 4. Thermal ellipsoid plot of (TPA)-AuSph(*o*-OMe), **5**.

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for (TPA)AuSPh, **4**^{a}

	x	*y*	*z*	*U*(eq)
Au(1)	8269(1)	2363(1)	8853(1)	36(1)
S(1)	10454(7)	1268(3)	9560(2)	47(1)
P(1)	6276(6)	3326(3)	8054(2)	32(1)
N(1)	4888(28)	5285(9)	7464(7)	37(3)
N(2)	2420(18)	3717(8)	7458(7)	44(3)
N(3)	5421(20)	3737(9)	6599(6)	39(3)
C(1)	6253(25)	4864(9)	8038(7)	42(4)
C(2)	6840(25)	3090(9)	7070(6)	35(3)
C(3)	3381(24)	3097(10)	8051(7)	43(4)
C(4)	2686(23)	4927(11)	7557(8)	44(4)
C(5)	3243(29)	3445(10)	6729(7)	54(4)
C(6)	5641(24)	4917(9)	6721(7)	38(4)
C(11)	8694(24)	281(12)	9943(6)	33(4)
C(12)	6620(30)	536(10)	10132(7)	37(4)
C(13)	5313(28)	−238(12)	10447(8)	48(4)
C(14)	6060(31)	−1313(14)	10576(8)	57(6)
C(15)	8163(33)	−1562(12)	10390(8)	51(4)
C(160	9436(26)	−791(11)	10074(6)	36(4)

^{a} *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The structure of **5** is shown in Figure 4. Atomic coordinates are given in Table 7, and selected bond angles and distances are given in Table 8. There are three molecules in the asymmetric unit. Two of the molecules are crossed approximately perpendicular to each other where the distance between the two gold atoms is 3.263 Å. The third molecule is related by symmetry to a fourth molecule where the two lie approximately parallel to each other with a gold−gold distance of 3.341(2) Å.

Table 6. Selected Interatomic Distances (Å) and Angles (deg) for (TPA)AuSPh, **4**

Au(1)−P(1)	2.239(3)	P(1)−Au(1)−S(1)	173.58(14)
Au(1)−S(1)	2.307(4)	C(11)−S(1)−Au(1)	103.5(5)
S(1)−C(11)	1.77(2)		

Table 7. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for (TPA)AuSPh(*o*-OMe), **5**[a]

	x	*y*	*z*	*U*(eq)
Au(1)	1322(1)	4782(1)	9429(1)	53(1)
Au(2)	3627(1)	4304(1)	10078(1)	51(1)
Au(3)	6243(1)	8(1)	10315(1)	65(1)
P(1)	2134(4)	5930(3)	9201(3)	47(2)
P(2)	2881(4)	4440(3)	10967(2)	47(2)
P(3)	7378(5)	−587(4)	9704(3)	56(2)
S(1)	162(5)	3756(3)	9633(2)	60(2)
S(2)	4476(5)	4223(3)	9191(2)	61(2)
S(3)	5199(5)	638(4)	10990(3)	70(2)
O(1)	−1331(12)	2636(8)	9143(6)	64(4)
O(2)	4758(14)	3581(11)	8061(8)	90(6)
O(3)	4554(12)	1481(9)	11998(6)	59(5)
N(1)	1792(14)	7423(9)	8757(8)	52(5)
N(2)	3536(16)	6795(10)	8511(8)	53(5)
N(3)	3259(15)	7271(10)	9508(9)	65(6)
N(4)	1212(15)	4117(12)	11707(9)	77(4)
N(5)	2057(16)	5407(10)	11839(9)	83(3)
N(6)	3073(16)	4231(14)	12156(9)	86(4)
N(7)	8521(15)	−589(10)	8680(8)	72(3)
N(8)	9525(14)	−1019(11)	9576(8)	72(3)
N(9)	8160(16)	−1888(10)	9130(9)	75(3)
C(1)	1199(15)	6694(11)	8919(8)	53(6)
C(2)	2642(20)	7295(14)	8306(10)	78(8)
C(3)	3171(17)	5969(13)	8619(9)	76(8)
C(4)	2835(17)	6540(12)	9775(8)	65(7)
C(5)	2331(19)	7740(11)	9304(10)	59(7)
C(6)	3992(17)	7139(13)	9058(11)	58(7)
C(11)	529(18)	2968(11)	9199(9)	54(4)
C(12)	1593(18)	2793(12)	9040(9)	57(4)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 8. Selected Interatomic Distances (Å) and Angles (deg) for (TPA)AuSPh(*o*-OMe), **5**

Au(1)−Au(2)	3.263(2)	P(1)−Au(1)−S(1)	168.0(2)
Au(3)−Au(3′)	3.341(2)	C(11)−S(1)−Au(1)	107.5(7)
Au(1)−P(1)	2.257(5)	P(1)−Au(1)−Au(2)	86.51(14)
Au(2)−P(2)	2.257(5)	S(1)−Au(1)−Au(2)	104.6(2)
Au(3)−P(3)	2.233(6)		
Au(1)−S(1)	2.304(5)		
Au(2)−S(2)	2.301(6)		
Au(3)−S(3)	2.291(6)		

The structure of **8** is complicated due to twinning and poor crystal quality.[9] The preliminary structure shows the same basic geometry as that of **10** with a gold−gold distance of 3.078(2) Å.

The structure of **10** is shown in Figure 5. Atomic coordinates are given in Table 9, and selected bond angles and distances are given in Table 10. There is only one molecule in the asymmetric unit, but it is symmetry-related to a second molecule. These two molecules lie approximately perpendicular to each other with a gold−gold distance of 3.05(1) Å.

Structural Results

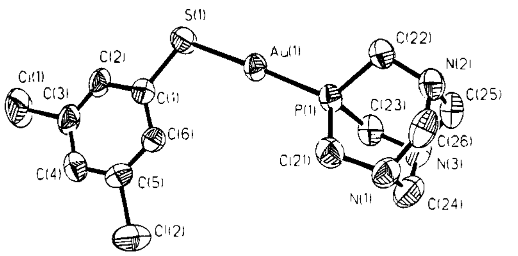

Figure 5. Thermal ellipsoid plot of (TPA)AuSPh(3,4-Cl_2), **10**.

Table 9. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for (TPA)AuSPh(3,5-Cl_2), **10**[a]

	x	*y*	*z*	*U*(eq)
Au(1)	530(1)	4592(1)	1785(1)	46(1)
S(1)	−402(2)	3812(1)	162(2)	60(1)
P(1)	1510(1)	5339(1)	3312(2)	45(1)
Cl(1)	−840(2)	1012(1)	−780(3)	110(1)
Cl(2)	1927(2)	1907(2)	3700(2)	84(1)
N(1)	2681(5)	5582(4)	5939(6)	58(2)
N(2)	1953(5)	6621(4)	4563(7)	56(2)
N(3)	3087(5)	6005(4)	4313(7)	59(2)
C(1)	−15(5)	2943(4)	723(7)	44(2)
C(2)	−500(6)	2385(5)	−96(8)	55(2)
C(3)	−239(6)	1705(5)	270(9)	59(2)
C(4)	498(6)	1527(5)	1453(9)	59(3)
C(5)	976(5)	2099(5)	2236(8)	52(2)
C(6)	739(5)	2793(4)	1905(7)	44(2)
C(21)	2038(6)	5056(5)	5042(8)	59(2)
C(22)	1209(5)	6247(4)	3516(8)	55(2)
C(23)	2502(6)	5548(4)	3233(9)	58(2)
C(24)	3359(6)	5667(5)	5588(10)	70(3)
C(25)	2670(6)	6677(5)	4286(10)	65(3)
C(26)	2286(6)	6276(5)	5837(8)	65(3)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 10. Selected Interatomic Distances (Å) and Angles (deg) for (TPA)AuSPh(3,5-Cl_2), **10**

Au(1)−Au(1′)	3.0468(10)	P(1)−Au(1)−S(1)	175.70(8)
Au(1)−P(1)	2.255(2)	P(1)−Au(1)−Au−(1′)	90.12(6)
Au(1)−S(1)	2.314(2)	S(1)−Au(1)−Au(1′)	94.07(7)
S(1)−C(1)	1.769(8)	C(1)−S(1)−Au(1)	107.3(3)

All the complexes that have been structurally characterized show the same linear geometry about the gold center, and all the bond distances and angles are normal. Compound **3**, containing the Ph_3P ligand, shows no significant gold−gold interaction between neighboring molecules, and the closest gold−gold distance is 6.105 Å. The structures of compounds **1** and **2** have been published elsewhere.[10,11] The unsubstituted gold(I) thiolate, **1**, is the only one of these three PPh_3 compounds that crystallizes with a gold−gold interaction in the solid state (Au−Au = 3.154 Å) where the two molecules are approximately perpendicular to each other. It is thought that the substituent in the ortho position and the relatively bulky phosphines for compounds **2** and **3** prevent the close approach of the two molecules. This steric hindrance is also observed in the series of substituted complexes (Ph_3P)Au(S-2,4,6-$C_6H_2R_3$) (R = H, Me, Et, *i*-Pr), studied by Schmidbaur.[12]

No gold−gold interactions are observed for compound **4**, and the closest gold−gold distance is 5.243 Å. However, it is unlikely that steric factors can be the reason for this lack of interaction, as there are no substituents on the phenyl ring and the TPA ligand has a small cone angle (102°). The packing diagram viewed along the *b* axis (Figure 3) shows a relatively close-packed arrangement of the molecules, and it may be that

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(9) The structure of (TPA)AuSPhCl-*m*, **8**, has been solved in the space group $Pca2_1$ with $R_1 = 0.0678$ and $wR_2 = 0.1624$ using SHELXTL-93 refinement of F^2. Large amounts of electron density exists which resides near atom positions. This suggests, as did the data collection, the presence of a twin component. We were unable to achieve a better refinement. Cell parameters: $a = 19.553(4)$ Å, $b = 6.276(2)$ Å, $c = 24.688(5)$ Å, $V = 3030(1)$ $Å^3$, $d = 2.182$ g cm^{-3}, $Z = 8$.

(10) Fackler, J. P., Jr.; Staples, R. J.; Elduque, A.; Grant, T. *Acta Crystallogr.* **1989**, *C45*, 520.

(11) Fackler, J. P., Jr.; Staples, R. J.; Raptis, R. *Acta Crystallogr.* **1989**, *C45*, 523.

(12) Nakamoto, M.; Hiller, W.; Schmidbaur, H. *Chem. Ber.* **1993**, *126*, 605.

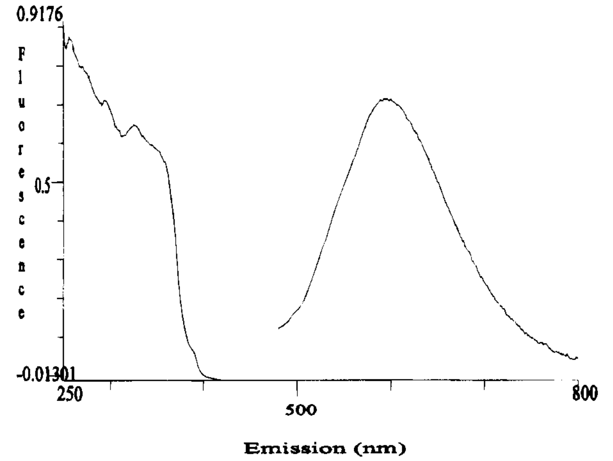

Figure 6. Solid state excitation and emission spectra for (TPA)AuSPh, **4**.

Table 11. Luminescence and Lifetime Data for **1**−**11**

complex	excitation max, nm	emission max, nm	lifetime, μs
$(Ph_3P)AuSPh$, **1**	360	413	17 + short component
$(Ph_3P)AuSPh$(*o*-OMe), **2**	350	429	75, 0.013
$(Ph_3P)AuSPh$(*o*-Cl), **3**	317	461	189 + short component
(TPA)AuSPh, **4**	358	596	8
(TPA)AuSPh(*o*-OMe), **5**	365	589	11
(TPA)AuSPh(m-OMe), **6**	368	685	15
(TPA)AuSPh(*o*-Cl), **7**	363	540	217
(TPA)AuSPh(m-Cl), **8**	365	702	15
(TPA)AuSPh(*p*-Cl), **9**	362	698	16
(TPA)AuSPh(3,5-Cl_2), **10**	366	485	6
(TPA)AuSCH$(CH_3)_2$, **11**	348	669	17

the energy gained from this arrangement is greater than the gold−gold interaction energy. Compound **5** does show gold−gold interactions, but the distances between the gold centers are relatively long. As in the Ph_3P complexes **2** and **3**, the ortho substituent on the phenyl ring prevents the close approach of the two molecules. This compound is unusual in that there are two different arrangements of the two molecules in the unit cell: two are arranged parallel to each other and two are arranged perpendicular to each other. The longer gold−gold distance for the parallel arrangement, 3.341(2) Å compared with 3.263(2) Å for the perpendicular arrangement, is also probably a steric effect. In the monomeric gold complexes that have previously been structurally characterized, the perpendicular arrangement is the most common. For example, the complexes (TPA)AuX (X = Cl, Br) show two molecules crossed at approximately 90° to one another.[2]

With the substituent in the meta postions, complexes **8** and **10** show relatively short gold−gold distances (3.078 and 3.047 Å, respectively). Both structures show the two molecules crossed at approximately 90° to one another.

Spectroscopic Results

All of the gold phosphine thiolate complexes that have been synthesized luminesce at 77 K in the solid state. Complexes **6**, **8**, and **9** luminesce at room temperature. Table 11 summarizes the excitation and emission data measured for these complexes as well as the lifetimes for the excited states.

The TPA complexes show a wide variation in the emission energy observed, from a blue emission for compound **10** (485 nm) to a red emission for compound **8** (702 nm). Figures 6 and 7 show the solid state excitation and emission spectra for (TPA)AuSPh, **4**, and (TPA)AuSPh(*m*-Cl), **8**, respectively, measured at 77 K. The excitation profiles are all very similar for compounds **4**−**10**, and all give maxima between 355 and 365 nm. The lifetimes that have been measured are all relatively long (6−217 μs).

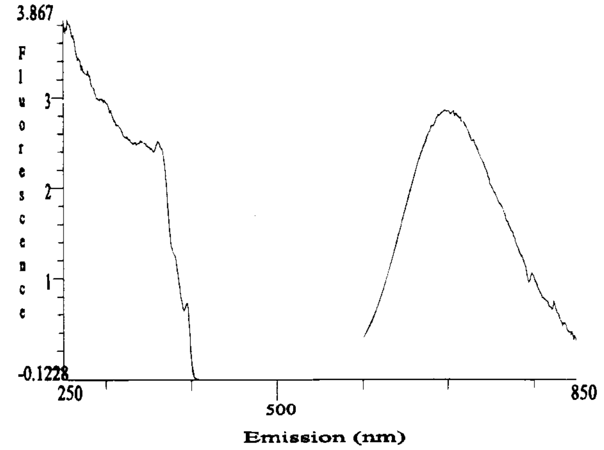

Figure 7. Solid state excitation and emission spectra for (TPA)AuSPh-(*m*-Cl), **8**.

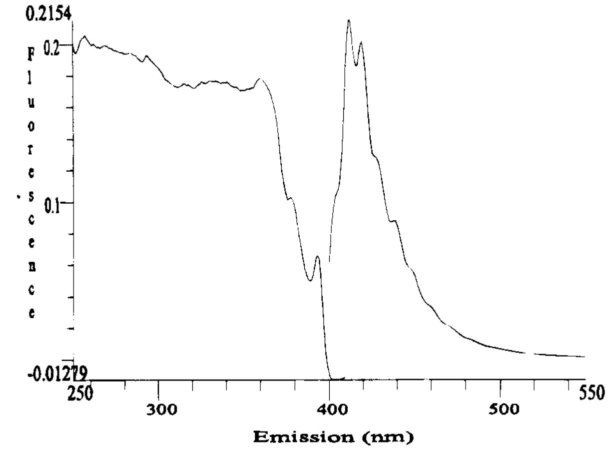

Figure 8. Solid state excitation and emission spectra for $(Ph_3P)AuSPh$, **1**.

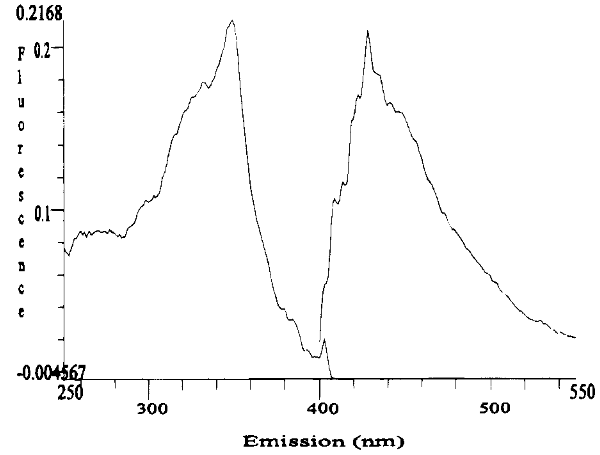

Figure 9. Solid state excitation and emission spectra for $(Ph_3P)AuSPh$-(*o*-OMe), **2**.

All three of the triphenylphosphine complexes show a blue emission at 77 K; Figures 8 and 9 show the excitation and emission spectra for $(Ph_3P)AuSPh$, **1**, and $(Ph_3P)AuSPh$(*o*-OMe), **2**, respectively. The excitation spectrum for **1** resembles closely those measured for the TPA complexes, but the emission spectrum is relatively narrow and shows some band structure. This can be compared to the emission spectra for the TPA complexes, which are all broad and featureless. The excitation and emission spectra for **2** are almost exact mirror images of

Table 12. Luminescence and X-ray Data for **4**, **5**, **8**, and **10**

complex	emission max, nm	Au − Au dist, Å
(TPA)AuSPh(3,5-Cl$_2$), **10**	485	3.047
(TPA)AuSPh(*o*-OMe), **5**	589	3.263, 3.341
(TPA)AuSPh, **4**	596	none
(TPA)AuSPh(*m*-Cl), **8**	702	3.078

one another, suggesting that the dominant emission in this complex is fluorescence.[13] Lifetime measurements show that all the triphenylphosphine complexes have two lifetime components, one that is long (17−189 μs) and one that is short. For compounds **1** and **3**, the percentage of the short-lifetime contribution is small and cannot be measured. For compound **2**, which exhibits fluorescence-type excitation and emission spectra, the short lifetime is the major component and was measured as 13 ns.

Discussion

For the TPA complexes, the large Stokes shift (>4000 cm^{-1}) observed implies that there is a large distortion in the excited state compared to the ground state. The long lifetimes (6−217 μs) indicate that the emission transition is forbidden and is phosphorescent. We assign the emission to a metal to ligand charge transfer (LMCT) with the excitation from an orbital primarily associated with the sulfur to the metal-based orbital of the excited state. The observation that the excitation profiles are similar for compounds **4**−**10** suggests that the excitation is from the sulfur orbital on the thiolate ligand and not from a π-orbital associated with the phenyl group, as the energy would be expected to change more significantly with substitution on the phenyl ring if a π-orbital is involved. This assignment has also been made by Bruce et al. from the UV and emission spectra for a related series of binuclear gold(I) thiolate complexes involving bridging bidentate phosphine ligands.[4,5] For these complexes these authors conclude that substitution of electron-withdrawing groups on the sulfur ligands causes a blue shift of the emission as expected for ligand to metal charge transfer (LMCT) transitions. In addition, they suggest that the presence of a gold−gold interaction in the solid state does not significantly perturb the emission energy maxima. SCF−MO calculations performed by Brown et al. on the hypothetical molecule {Au(PPh$_3$)[SCH$_2$CH(NH$_2$)CO$_2$H]} also confirm the assignment as a LMCT transition.[14]

The advantage in looking at a series of complexes containing the TPA ligand, compared with the phosphines used by others, is the absence of the π,π* orbitals associated with the aromatic phenyl rings on the triphenylphosphine ligand. As to be described later, the Ph$_3$P complexes show excitation and emission profiles different from those of the TPA complexes, where these differences are thought to be due to the involvement of intraligand transitions. The TPA ligand also has a small cone angle (102°), so steric factors should not affect the gold−gold interactions between neighboring molecules. However, as the crystal structure of (TPA)AuSPh, **4**, shows, packing forces may also dictate whether or not the molecules crystallize in the solid state with these intramolecular Au···Au interactions.

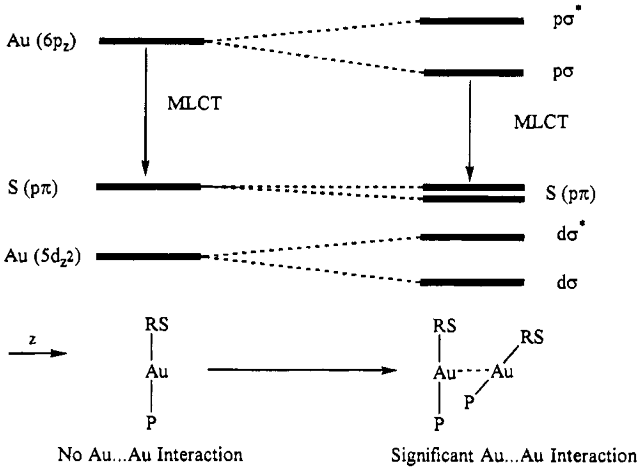

Figure 10. Schematic representation of the orbital splittings expected with Au···Au interactions in (phosphine)gold thiolates.

In Table 12, the gold−gold distances obtained from the X-ray studies are compared with the results from the fluorometry experiments. It is clear from this table that although no correlation exists between the gold−gold distance and the emission energy, the gold−gold interactions do affect the emission maxima. The results in this table can be understood by considering the factors that can affect the emission maxima for this series of complexes. There are two factors of importance: (1) the presence of electron-withdrawing groups on the thiolate ligand and (2) an interaction between two gold atoms of neighboring molecules. Electron-withdrawing groups on the thiolate ligand stabilize the sulfur orbital, making the ligand more difficult to oxidize. This blue-shifts the emission to higher energies.[15] Figure 10 illustrates the effect of a gold−gold interaction is expected to have on the filled sulfur and metal orbitals involved in the transition. The gold 5d$_{z^2}$ orbital (where the z axis is along the metal−metal interaction direction) is destabilized by bringing to two gold centers together while the empty 6p$_z$ orbital is stabilized. This would have the net effect of lowering the energy of the transition and red-shifting the emission energy. Thus, the two important factors that influence the position of the emission maxima can have opposing effects: with electron-withdrawing substituents on the thiol, a blue shift occurs in the emission, while metal−metal interactions red-shift the emission. To determine which of these factors is the most significant, the emission energies of the substituted compounds are compared to the emission energy observed for compound **4** (596 nm), which has no substituents on the thiolate ligand and no gold−gold interactions in the solid state.

The ortho-substituted compounds, **5** and **7**, only show weak gold−gold interactions in the solid state, probably due to steric interactions of the substituents on the thiol ligand. The transition energy is thus more affected by the electron-withdrawing groups, and the emission energy is blue-shifted compared to that of the unsubstituted compound, **4**. The meta- and para-substituted compounds, **6**, **8**, and **9**, all show an emission energy that is red-shifted compared to that of the unsubstituted compound, **4**. Of these, only compound **8** has been structurally characterized, and it shows a relatively short gold−gold interaction of 3.078 Å between neighboring molecules. The red shift of the emission demonstrates that the gold−gold interactions significantly perturb the orbital energies involved in the LMCT transition and consequently the emission maxima. It allows us to predict that the complexes **6** and **9** would also show short gold−gold

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(13) Parker, C. A. *Photoluminescence of Solutions*; Elsevier: Amsterdam, 1968; pp 11−28.

(14) Brown, D. H.; McKinlay, G.; Smith, W. E. *J. Chem. Soc., Dalton Trans.* **1977**, 1874.

(15) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*, Academic Press: New York 1979.

interactions in the solid state. The X-ray structure of compound **10** also shows a close gold−gold interaction between neighboring molecules in the solid state (3.047 Å), but the emission maximum is at 485 nm, significantly blue-shifted in comparison to that of the unsubstituted compound **4**. In this case, although the gold−gold interaction is short, the major influence on the emission maximum must be the enhanced stabilization of the sulfur orbital due to two strongly electron-withdrawing groups on the thiolate ligand.

This series of complexes illustrates that the emission maxima alone cannot be used to predict the presence of a gold−gold interaction. However, it does show that gold−gold interactions can, in some circumstances, shift the emission maxima to lower energies. This red shift is as much as 2500 cm^{-1} for compounds **8** and **9** compared to the unsubstituted compound **4**.

For the triphenylphosphine complexes, the excitation and emission spectra are very different, depending on the substituent on the thiolate ligand. Compound **1** shows an excitation profile very similar to these of the TPA compounds, indicating that the excitation in this case is probably from a sulfur orbital on the ligand. Compound **2**, however, shows a very different excitation spectrum, and the emission appears to be fluorescence. Each compound shows two different lifetimes, one of microsecond length and one of nanosecond length, which implies that two separate transitions are possible. It is thought that the longer lifetimes can be attributed to the LMCT transitions between an orbital based on the sulfur to a metal orbital similar to that seen for the TPA complexes. The short lifetimes are most likely intraligand transitions associated with the π and π^* orbitals of the triphenylphosphine ligand. It is clear from the different excitation and emission profiles found for the three compounds that these orbitals are all very close in energy and the electron-withdrawing substituents on the thiolate ligand can affect the relative ordering of these orbitals. The exact ordering and mixing of these orbitals have not been determined.

These results clearly show that mononuclear gold(I) complexes containing thiolate ligands can show luminescence at low temperatures. The energy of the emission can be changed either by changing the substituents on the ligand or by the presence of gold−gold interactions in the solid state. However, no direct correlation has been found in this study between the distance between two neighboring gold atoms and the emission energy as found for (HTPA)AuCl and (TPA)AuCl. Further elucidation of the parameters influencing luminescence of gold(I) thiolates cannot be made at this time.

Acknowledgment. The National Science Foundation (Grant CHE9300107) and the Robert A. Welch Foundation generously supported these studies. Lifetime measurements were run by D. J. Casadonte, Jr., at Texas Tech University, Lubbock, TX. We are grateful for his contribution to this study.

Supporting Information Available: Listings of crystal data and refinement parameters, thermal ellipsoid plots, packing diagram plots, and tables giving bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for $(Ph_3P)AuSPh(o\text{-}Cl)$ **3**, (TPA)AuSPh, **4**, (TPA)AuSPh(*o*-OMe), **5**, and $(TPA)AuSPh(3,5\text{-}Cl_2)$, **10** (27 pages). Ordering information is given on any current masthead page.

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