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Structural and Electronic Properties of Phosphino(oligothiophene) Gold(I) Complexes

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A series of gold(I) complexes containing phosphino(oligothiophene) ligands of varying conjugation length has been prepared. Solid state crystal structures of (PT_3)AuCl (PT_3 = 5-diphenylphosphino-2,2′:5′,2′′-terthiophene) and AuCl(PTP)AuCl (PTP = 2,5-diphenylphosphinothiophene) have been obtained. The complex AuCl(PTP)AuCl crystallizes as a dimer with two intermolecular Au–Au contacts. Variable temperature NMR spectroscopy is used to demonstrate the presence of aurophilic interactions in solution for AuI(PTP)AuI. Dual emission is observed for AuCl(PTP)AuCl in solution and is attributed to emission from both monomer and dimer. In the solid state, dimer emission is dominant. The iodo analogue, AuI(PTP)AuI, shows only low energy dimer emission in both solution and the solid state. Compounds in which the ligands contain longer bridges (either bithienyl or terthienyl) show absorption and emission bands due to the π–π* transition only, both in solution and the solid state.

Introduction

Conjugated oligomers and polymers are an important class of materials that have generated much research interest in recent years. Some possible applications of these materials include energy and memory storage, sensors, and nanoelectronics.[1−3] Crystalline oligomers, whose structure may be readily determined, have been used to better understand structure−property relationships.[4] Pendant metal groups attached to conjugated oligomers may be used both to control the structural interaction between oligomers and to modify the electronic and optical properties of the oligomer.[5] Metal groups have been attached to conjugated oligomers using a number of different coordinating groups.[6] Our research group has investigated the use of phosphine substituents as ligating groups, as they allow coordination of a wide range of transition metal complexes.[7−11]

Interest in the coordination chemistry of gold has grown in recent years with the discovery of novel electronic and structural properties of gold complexes.[12] Gold compounds can exhibit “aurophilicity”, where the formation of weak Au−Au interactions occurs,[13−15] resulting in a variety of structures, including dimeric[16−18] and polymeric[19−23] forms.

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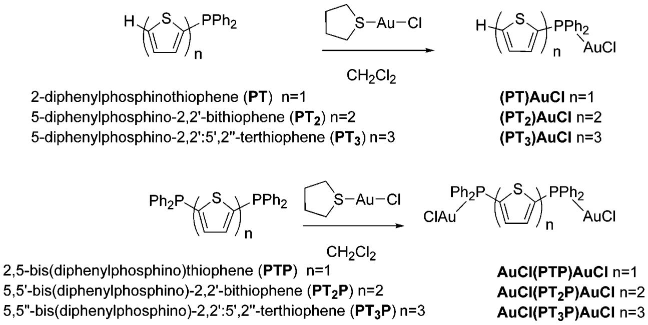
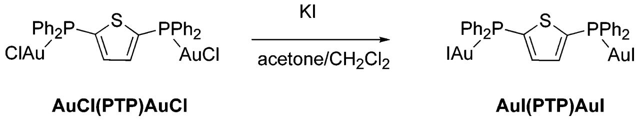
Scheme 1



Scheme 2



Many gold complexes have been shown to exhibit luminescence in solution and in the solid state,[17,24–26] and this has resulted in the testing of some gold compounds as potential light emitting materials[27,28] and sensors.[29] Our group has recently prepared some Au(I) phosphine complexes that exhibited intramolecular Au−Au interactions.[10] Here we report the preparation of a series of thiophene oligomers coordinated to Au(I) via a terminal or α-phosphine substituent, and the systematic study of their absorption and emission properties, both in solution and in the solid state, as a function of conjugation length of the oligomer.

Results and Discussion

Syntheses. Gold complexes were prepared according to the reactions shown in Scheme 1 and readily isolated by precipitation from hexanes to yield analytically pure samples. The iodo complex AuI(PTP)AuI was synthesized by halogen exchange (Scheme 2), and purified by washing with water. All of the gold complexes are stable in the solid state and in solution.

Solid State Crystal Structures. Single crystals of (PT)AuCl were grown by slow diffusion of hexanes into a dichloromethane solution of the complex. The molecular structure could not be completely refined, although it was established that no gold−gold contacts exist in the solid state. Single crystals of $(PT_3)AuCl$ were also grown by slow diffusion of hexanes into a dichloromethane solution. The molecular structure of $(PT_3)AuCl$ is shown in Figure 1, and selected interatomic distances and angles are presented in Table 1. Table 2 contains crystallographic data for this structure. The complex crystallizes as a monomer, with no gold−gold interactions present. No Au−S interactions are observed, with the shortest Au−S distance in the structure being 3.707 Å. The Au−Cl and Au−P bond lengths are very similar to those in $(PPh_3)AuCl$ (Au−Cl 2.279 Å and Au−P 2.235 Å).[30] The P−Au−Cl bond is somewhat less linear than that in $(PPh_3)AuCl$ (179.63°). The P−C bond lengths to the phenyl groups are slightly longer than the corresponding bond to the terthienyl group and are similar to the P−C bond lengths of $(PPh_3)AuCl$. The first two rings of the terthienyl moiety are essentially coplanar, with an interannular torsion angle (∠S−C−C−S) of 176°, whereas the ring furthest from the phosphine substituent is twisted slightly more with an interannular torsion angle between the second and third rings of −162°.

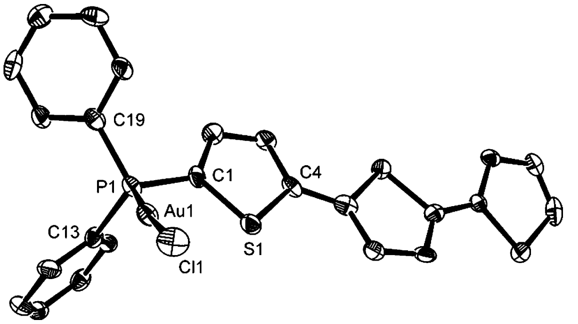


Figure 1. ORTEP view of $(PT_3)AuCl$. The hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at 50% probability.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for $(PT_3)AuCl$

Au(1)−Cl(1)	2.2899(19)	P(1)−Au(1)−Cl(1)	175.28(8)
Au(1)−P(1)	2.2345(19)	Au(1)−P(1)−C(19)	114.6(2)
P(1)−C(19)	1.824(8)	Au(1)−P(1)−C(13)	114.6(3)
P(1)−C(13)	1.830(8)	Au(1)−P(1)−C(1)	109.6(3)
P(1)−C(1)	1.776(7)	P(1)−C(1)−S(1)	120.7(4)
C(1)−S(1)	1.725(7)	C(1)−S(1)−C(4)	93.0(4)
C(4)−S(1)	1.725(7)		

Table 2. Selected Crystallographic Data for $(PT_3)AuCl$ and AuCl(PTP)AuCl

	$(PT_3)AuCl$	AuCl(PTP)AuCl
formula	$C_{24}H_{17}PS_3ClAu$	$C_{69}H_{74}P_4S_2Cl_6Au_4$
habit	prism	tablet
dimension/mm^3	0.30 × 0.20 × 0.20	0.50 × 0.40 × 0.15
T/K	173	173
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a/Å	9.6606(6)	11.339(1)
b/Å	18.844(1)	13.439(2)
c/Å	13.0096(8)	13.935(2)
α/deg	90	67.17(1)
β/deg	103.84(1)	69.44(1)
γ/deg	90	78.08(1)
V/Å^3	2299.6(2)	1826.4(4)
Z	4	1
D_{calc}/g cm^{-3}	1.921	1.902
unique data	4683	8476
μ(Mo Kα)/cm^{-1}	68.66	84.11
$R(F)^a$ ($I > 2\sigma(I)$)	0.044	0.034
$R_w(F^2)^b$ (all data)	0.103	0.073

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

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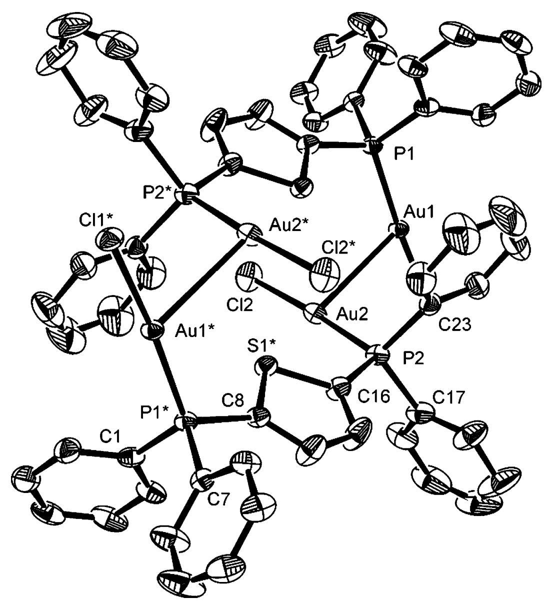


Figure 2. ORTEP view of AuCl(PTP)AuCl. The hydrogen atoms are omitted for clarity, and thermal ellipsoids are drawn at 50% probability.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for AuCl(PTP)AuCl

Au(1)−Au(2)	3.0966(5)	P(1)−Au(1)−Cl(1)	173.07(4)
Au(1)−Cl(1)	2.3041(10)	P(2)−Au(2)−Cl(2)	175.75(4)
Au(2)−Cl(2)	2.2997(12)	P(1)−Au(1)−Au(2)	103.45(3)
Au(1)−P(1)	2.2346(10)	P(2)−Au(2)−Au(1)	96.54(3)
Au(2)−P(2)	2.2404(11)	Cl(1)−Au(1)−Au(2)	83.00(3)
P(1)−C(1)	1.813(4)	Cl(2)−Au(2)−Au(1)	87.67(4)
P(1)−C(7)	1.813(4)	C(7)−P(1)−Au(1)	109.70(13)
P(1)−C(13)	1.803(4)	C(13)−P(1)−Au(1)	115.68(13)
P(2)−C(16)	1.802(4)	C(17)−P(2)−Au(2)	116.07(17)
P(2)−C(17)	1.812(5)	C(23)−P(2)−Au(2)	114.16(14)

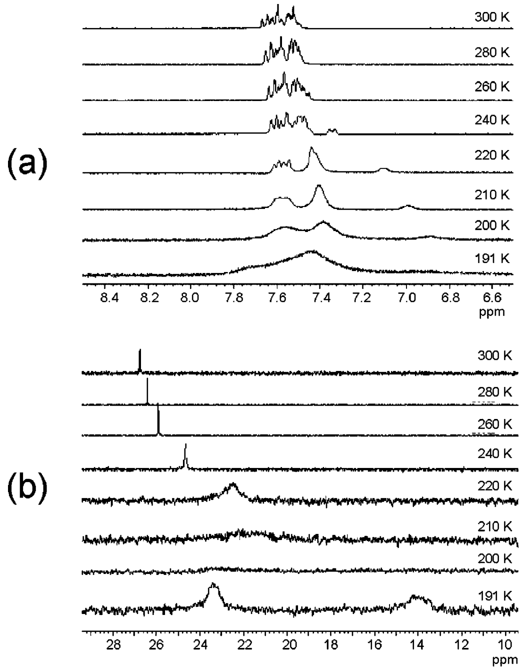
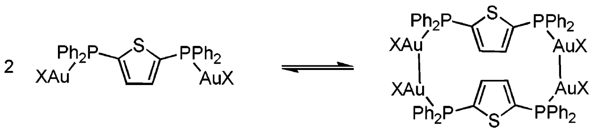


Figure 3. Variable temperature (a) ^1H NMR and (b) $^{31}P\{^1H\}$ NMR spectra of AuI(PTP)AuI in CD_2Cl_2.

Scheme 3



X = Cl, I

The X-ray crystal structure of AuCl(PTP)AuCl is shown in Figure 2, along with a table of selected interatomic distances and angles (Table 3). This complex, in contrast to $(PT_3)AuCl$, crystallizes as a dimer with inversion symmetry, which has two gold−gold interactions (3.0966(5) Å). Related structures have been previously observed,[18,31,32] with comparable Au−Au distances. The Au−P and Au−Cl bond lengths and the P−Au−Cl bond angles are similar to those in $(PT_3)AuCl$. The shortest Au−S distance in the structure, 3.504 Å for Au(2)−S(1), is beyond the sum of the van der Waals radii of these elements. A structural determination of AuI(PTP)AuI was attempted; however, the crystallographic data was only of sufficient quality to determine that the connectivity is the same as in AuCl(PTP)AuCl and that the Au−Au distance is 3.0210(9) Å. Anisotropic refinements of the structure were unsatisfactory. As predicted,[16,33,34] the gold−gold contacts are shorter than in AuCl(PTP)AuCl.

VT-NMR Spectroscopy. Variable temperature (VT) ^1H and ^{31}P NMR experiments were performed on (PT)AuCl, AuCl(PTP)AuCl, and AuI(PTP)AuI. The ^{31}P resonance for (PT)AuCl shifts slightly with temperature, and there is some broadening in the ^1H spectrum. These minor changes, similar to those seen in other complexes,[35−37] suggest that aurophilic interactions, as in the solid state, are absent in this temperature range. Some changes were observed in the NMR spectra of AuCl(PTP)AuCl as the temperature was decreased from 300 to 191 K.[38] In the ^1H NMR spectrum, the peaks broaden and separate. The ^{31}P NMR spectrum consists of a singlet at room temperature that begins to broaden below 210 K. It is very broad at the lowest accessible temperature (191 K) but does not split into two peaks. This may indicate that an equilibrium between monomer and dimer exists (Scheme 3), but it is still too rapid to allow observation of separate resonances on the NMR time scale.

The same experiment on the iodo analogue (AuI(PTP)-AuI) was carried out to determine if the shorter gold−gold distance in this complex results in the observation of separate resonances for monomer and dimer at a higher temperature. The spectra, shown in Figure 3, indicate that this does occur. Broadening is observed in the ^1H NMR spectrum with decreasing temperature, and some peaks begin to separate out at low temperature. In the ^{31}P NMR spectrum, coalescence occurs at 200 K, and two peaks are observed at 191 K, with a separation of 1150 Hz ($k_c = 2500$). $\Delta G^‡$ was

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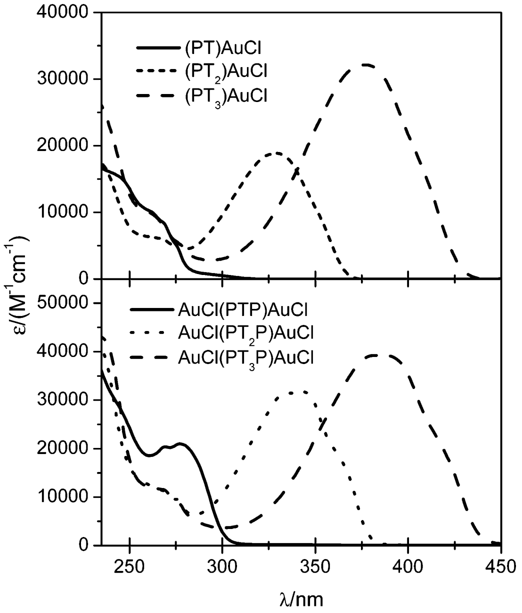

Figure 4. UV−vis spectra of gold complexes.

Table 4. Solution Absorption Data for Gold Complexes

complex	λ_{max}/nm (ϵ_{max}/M^{-1} cm^{-1})
(PT)AuCl	245 (sh) (1.7 × 10^4), 263(sh) (9.9 × 10^3), 269 (sh) (7.9 × 10^3), 275 (sh) (4.4 × 10^3)
(PT_2)AuCl	268 (sh) (5.9 × 10^3), 276 (4.8 × 10^3), 329 (1.9 × 10^4)
(PT_3)AuCl	263 (sh) (1.1 × 10^4), 279 (sh) (7.1 × 10^3), 377 (3.2 × 10^4)
AuCl(PTP)AuCl	269 (2.0 × 10^4), 277 (2.1 × 10^4)
AuCl(PT_2P)AuCl	263 (sh) (1.2 × 10^4), 267 (sh) (1.1 × 10^4), 275 (sh) (9.2 × 10^4), 334 (sh) (3.2 × 10^4), 342 (sh) (3.12 × 10^4)
AuCl(PT_3P)AuCl	263 (sh) (1.2 × 10^4), 267 (sh) (1.2 × 10^4), 276 (sh) (9.2 × 10^3), 386 (3.9 × 10^4)
AuI(PTP)AuI	251(sh) (2.8 × 10^4), 269 (sh) (2.0 × 10^4), 276 (sh) (1.8 × 10^4), 285 (sh) (1.7 × 10^4).

calculated to be 9 kJ/mol.[39] This is close to previously reported energies for gold−gold interactions;[22,40−42] accordingly, the dynamic process is assigned to the monomer−dimer equilibrium in solution. The presence of a monomer−dimer equilibrium is also supported by molecular weight values determined by vapor pressure osmometry, which were found to be higher in both cases than would be expected for a pure monomer (1228 for AuCl(PTP)AuCl and 1415 for AuI(PTP)AuI in CH_2Cl_2).

Solution Absorption Spectra. The solution electronic absorption spectra for the gold complexes in CH_2Cl_2 are shown in Figure 4 and the data summarized in Table 4, including the molar absorptivities (ϵ). The spectra are dominated by the thiophene $\pi-\pi^*$ transitions, which show the expected bathochromic shift with increasing conjugation length. Upon coordination of the gold centers, the $\pi-\pi^*$ transitions undergo a hypsochromic shift relative to the corresponding ligands,[43] and the n−π^* transitions disappear in the spectra. The hypsochromic shifts decrease with increasing chain length. The $\pi-\pi^*$ transitions in the complexes are of lower energy than in the corresponding unsubstituted oligomers (thiophene (231 nm), 2,2′-bithiophene (303 nm), 2,2′:5′,2″-terthiophene (354 nm)).[44] It is possible that the red shifts observed in the complexes relative to the unsubstituted oligomers are due to stabilization of the bridge-centered π^* LUMO by interaction with an unoccupied orbital on the phosphorus.[43] Several bands appear in the region between 260 and 280 nm that are assigned as vibrational structure of the phenyl group.[45] The spectra of (PT_3)AuCl, AuCl(PT_3P)AuCl, and (PT_2)AuCl all exhibit shoulders, and the bands are broad, likely due to the presence of multiple conformations in solution.[46,47] The molar absorptivities increase with increasing conjugation length.

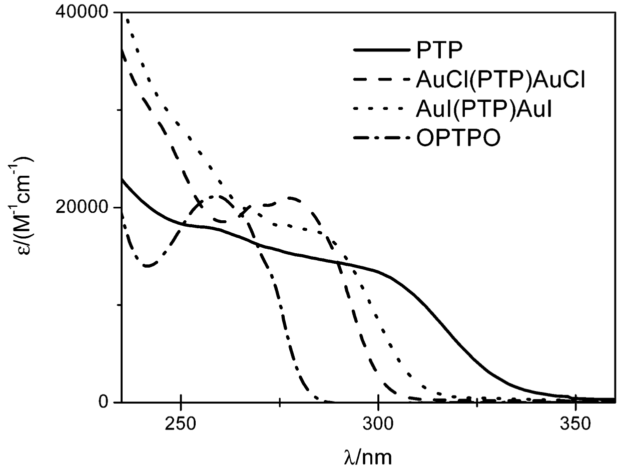

Figure 5. Comparison of UV−vis spectra of PTP, OPTPO, and complexes.

A comparison of the absorbance spectra of PTP, its complexes, and the diphosphine oxide OPTPO[43] is shown in Figure 5. OPTPO is more hypsochromically shifted relative to PTP than either of the gold complexes, possibly due to the greater electronegativity of O versus Au. The spectra of the two complexes show similar spectral features to those described above, that is, a blue shift relative to the ligand and the appearance of phenyl vibrational bands. However, the spectrum of the iodo complex is less blue shifted than that of the chloro complex. This effect has been previously explained for related complexes as a change in the HOMO from mainly Au 5d character in the chloro complex to a combination of Au 5d and I filled π orbital character in the iodo complex.[16,34,48] Though other groups have reported seeing new absorption bands at high concentrations for complexes exhibiting gold−gold interactions in

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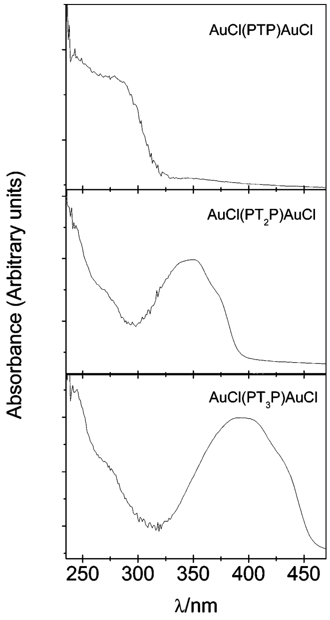

Figure 6. Solid state UV−vis spectra of selected gold complexes.

Table 5. Solid State Electronic Absorption Data for Gold Complexes

complex	λ_{max}/nm
(PT)AuCl	no clear peak
(PT$_2$)AuCl	270 (sh), 335, 360 (sh)
(PT$_3$)AuCl	270, 382, 420 (sh), 420 (sh)
AuCl(PTP)AuCl	no clear peak
AuCl(PT$_2$P)AuCl	275 (sh), 345, 375 (sh)
AuCl(PT$_3$P)AuCl	275 (sh), 395, 431 (sh)
AuI(PTP)AuI	no clear peak

the solid state and in VT-NMR,[16,22,49] new bands were not observed for either AuCl(PTP)AuCl or AuI(PTP)AuI.

Solid State Absorption Spectra. Solid state UV−vis spectra of selected complexes are shown in Figure 6, and the results for all the compounds are summarized in Table 5. The data generally show the same trends observed in the solution spectra; for example, a red shift in the $\pi-\pi^*$ transition occurs with increasing chain length, and decreases in magnitude as the chain length is increased. The wavelength of maximum absorption is slightly red-shifted relative to solution, which may be due to increased planarity in the solid state. Somewhat suprisingly, as AuCl(PTP)AuCl has gold−gold contacts in the solid state, no new absorption bands were observed in the spectrum of this compound.

Solution Emission Spectra. The gold complex (PT)AuCl is very weakly emissive in solution, while both AuCl(PTP)AuCl and AuI(PTP)AuI emit more strongly. AuCl(PTP)AuCl shows two emission bands, a high energy (HE) band at 345 nm and a low energy (LE) band at 485 nm (Figure 7). Both bands show similar excitation spectra, which match the absorbance spectrum of the complex. The iodo complex AuI(PTP)AuI shows only a single emission band at 490 nm, also with an excitation spectrum matching the absorbance spectrum.

The HE band in the spectrum of AuCl(PTP)AuCl is assigned to ligand-based (PTP) monomer emission. The LE band is due either to emission from a metal-based state of dimer present in solution or to an excimer. The large Stokes shift of this emission is typical of metal-based states in similar compounds.[12] Metal−metal bonded exciplexes have been previously observed, including examples resulting from Au−Au interactions, and typically show enhanced emission at higher concentrations relative to monomer.[50] Here only a small range of concentrations could be studied due to the weak emission; however, in dilute solutions the LE band is present, suggesting that this is due to ground state dimerization rather than excimer. In AuI(PTP)AuI, only LE emission is observed. Both VT-NMR and vapor pressure osmometry support the conclusion that both monomer and dimer are present in solution so the absence of the HE band in the spectrum of this complex is best attributed to quenching of this emission due to the iodo ligands.

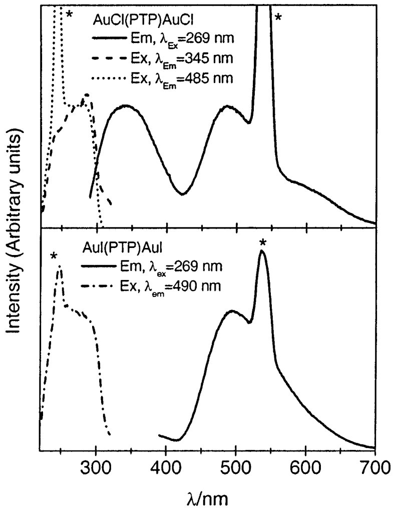

Figure 7. Solution excitation and emission spectra of AuCl(PTP)AuCl and AuI(PTP)AuI.

The complexes (PT$_2$)AuCl and AuCl(PT$_2$P)AuCl (Figure 8) do not exhibit dual emission. The spectra for these complexes consist of a single band at 392 and 400 nm, respectively. The emission is assigned as the $\pi-\pi^*$ transition of the bithienyl moiety and is bathochromically shifted relative to unsubstituted bithiophene (362 nm).[44] The emission spectra of the terthienyl complexes (PT$_3$)AuCl and AuCl(PT$_3$)AuCl (Figure 8) have maxima at 459 and 465 nm, respectively. Similar to the absorption spectra, these bands are blue-shifted relative to the free ligand[43] but occur at lower energy than the emission of unsubstituted 2,2′:5′,2′′-terthiophene (426 nm).[44]

Solid State Emission Spectroscopy. Emission from (PT)AuCl, which is very weak in solution, occurs at 390 nm in the solid state (Figure 9, Table 6). The excitation spectrum, with a peak at 350 nm, differs from the absorption spectrum of this compound. AuCl(PTP)AuCl has a similar emission band at 402 nm, with excitation at 360 nm, which also does not match the absorption spectrum. Several explanations for this phenomenon are possible, on the basis of literature observations of similar results. One is phenyl triplet emission,

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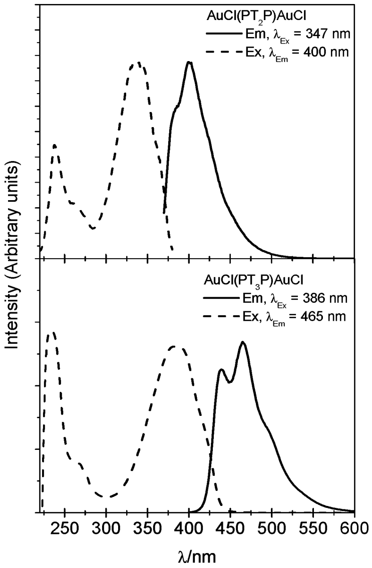

Figure 8. Solution excitation and emission spectra of AuCl(PT_2P)AuCl and AuCl(PT_3P)AuCl.

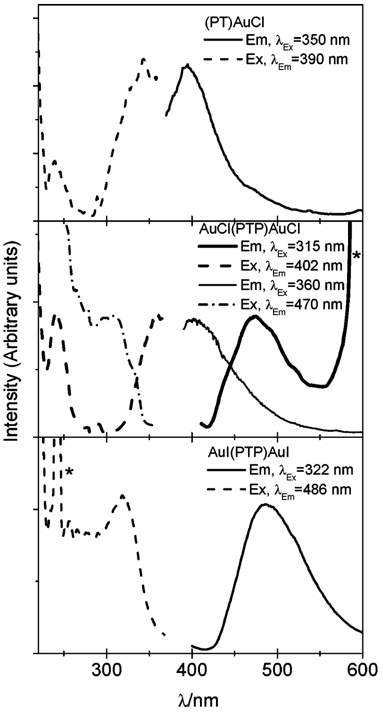

Figure 9. Solid state excitation and emission spectra of (PT)AuCl, AuCl-(PTP)AuCl, and AuI(PTP)AuI.

Table 6. Emission Data for Gold Complexes

complex	solution emission λ/nm	solid emission λ/nm
(PT)AuCl	no emission	403
(PT_2)AuCl	392	406
(PT_3) AuCl	442 (sh), 459	488
AuCl(PTP)AuCl	345, 485	402, 470
AuCl(PT_2P)AuCl	388 (sh), 400	408
AuCl(PT_3P)AuCl	439, 465	515
AuI(PTP)AuI	490	486

as others have noted a weak ($\epsilon = 2\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$) absorption band for Ph_3PAuCl between 300 and 365 nm, which also appears in the excitation spectrum of the emission band that originates from the phenyl $\pi-\pi^*$ triplet state at about 360 nm.[51] A second is a ligand-to-metal charge transfer (LMCT), similar to that reported by Fackler and co-workers.[52] A third explanation is that the band is due to an emissive impurity, although the emission and excitation spectra do not correspond to ligand[43] and it is not clear what this impurity might otherwise be. The analogous emission in (PT)AuCl is presumably also from a similar source. AuCl(PTP)AuCl also has a band at 470 nm, very similar to the solution spectrum, with an excitation spectrum that corresponds to the absorption spectrum. This band is assigned as arising from a Au−Au state, on the basis of the lack of a corresponding band in (PT)AuCl, and the large Stokes shift. AuI(PTP)AuI has a similar band at 486 nm, which is similar to that in solution, again pointing to emission from a Au−Au state.

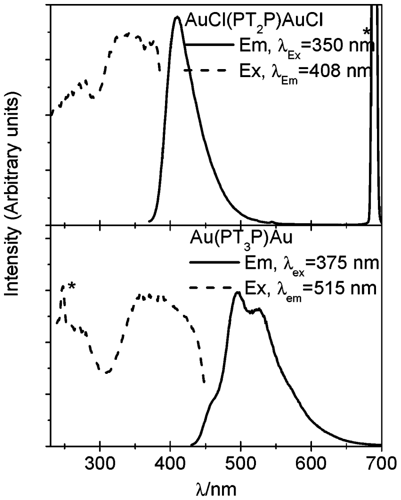

Figure 10. Solid state excitation and emission spectra of AuCl(PT_2P)-AuCl and AuCl(PT_3P)AuCl.

(PT_2)AuCl and AuCl(PT_2P)AuCl exhibit solid state emission spectra that are red shifted relative to solution by about 10 nm, and blue shifted relative to the free ligands[43] by 65 nm (Figure 10). The terthienyl complexes exhibit a small bathochromic shift (8 nm) upon coordination. The large bathochromic shift compared to the solution data for these complexes (29 nm for (PT_3)AuCl and 50 nm for AuCl(PT_3P)-AuCl) and the bithienyl complexes may be attributed to increased planarity in the solid state. No lower energy, gold-based emission was observed in these complexes.

Conclusions

The structural data and absorption and emission spectra of the series of Au compounds described here demonstrate interesting trends that shed light on the behavior of this class of metal-containing thiophene oligomers. Both AuCl(PTP)-AuCl and AuI(PTP)AuI crystallize as dimers with intermolecular Au−Au interactions. Although VT NMR experiments on AuCl(PTP)AuCl do not show the emergence of separate resonances due to monomer and dimer, the spectra broaden significantly at low temperature, consistent with a dynamic

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process. The VT NMR spectra of AuI(PTP)AuI also show dynamic behavior with a higher coalescence temperature than for AuCl(PTP)AuCl. This is indicative of a stronger Au−Au interaction in the iodo complex and is consistent with the observed shorter Au−Au contact in the solid state of this complex.

The solution absorption and emission spectra of AuCl(PTP)AuCl and AuI(PTP)AuI may then be interpreted in terms of a monomer−dimer equilibrium. Emission from the Au−Au dimer occurs in both compounds at low energy; however, AuCl(PTP)AuCl also has a higher energy emission assigned to ligand-based emission from the monomer. In the solid state only the low energy (dimer) emission occurs, with a higher energy emission also present in the spectrum of AuCl(PTP)AuCl, which cannot be definitively assigned. This unassigned band also occurs in (PT)AuCl in the solid state. Both solution and solid state absorption and emission spectra of the compounds containing either bithienyl or terthienyl groups are dominated primarily by the $\pi-\pi^*$ transition of the thienyl moiety. These compounds do not show any evidence for low energy emission from a Au−Au state.

Experimental

General. The following compounds were made by literature methods: 2,2′-bithiophene,[53] 2,2′:5′,2″-terthiophene,[53] PT,[43] PTP,[43] OPTPO,[43] PT_2,[54] PT_2P,[55] PT_3,[9,54] PT_3P,[54] and Au(tht)Cl (tht = tetrahydrothiophene).[56] ^1H and $^{31}P\{^1H\}$ NMR experiments were performed on either a Bruker AV-300 or a Bruker AV-400 spectrometer. Spectra were referenced to residual solvent (^1H) or external 85% H_3PO_4 (^{31}P). Electronic spectra were obtained on a Cary 5000 in HPLC grade CH_2Cl_2. Emission spectra were obtained on a Cary Eclipse, also in HPLC grade CH_2Cl_2. Solid state absorption and emission spectra were obtained by drop casting the compound from a CH_2Cl_2 solution onto a quartz slide. Some spectra contain peaks from overtones; these are indicated with an asterisk. Microanalyses were performed at UBC. Vapor pressure osmometry measurements were performed by Galbraith Laboratories, Tennessee.

General Synthesis of Au(I) Complexes. Au(tht)Cl and the appropriate ligand were stirred together for 1 h in CH_2Cl_2. The solvent was removed, and the resulting powder was dissolved in a minimum amount of CH_2Cl_2, and precipitated in 100 mL of hexanes. The precipitate was collected by filtration, washed with hexanes, and dried under vacuum, yielding analytically pure samples.

AuCl(PTP)AuCl. Yield: 78%. Anal. $C_{28}H_{22}Au_2Cl_2P_2S$ requires: C, 36.66; H, 2.42. Found: C, 36.99; H, 2.41. ^1H NMR ($CDCl_3$): δ 7.60−7.45 (m). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 19.9 (s).

AuCl(PT_2P)AuCl. Yield: 62%. Anal. $C_{32}H_{24}Au_2Cl_2P_2S_2$ requires: C, 38.46; H, 2.42. Found: C, 38.85; H, 2.36. ^1H NMR ($CDCl_3$): δ 7.62−7.44 (m, 10H), δ 7.39 (dd, J = 8.9, 3.9 Hz, 1H), δ 7.28 (dd, J = 3.8, 1 Hz, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 20.8 (s).

AuCl(PT_3P)AuCl. Yield: 57%. Anal. $C_{36}H_{26}Au_2Cl_2P_2S_3$ requires: C, 39.98; H, 2.42. Found: C, 40.28; H, 2.34. ^1H NMR ($CDCl_3$): δ 7.61−7.42 (m, 10H), δ 7.36 (dd, J = 8.9, 3.9 Hz, 1H), δ 7.23 (dd, J = 3.9, 1.2 Hz, 1H), δ 7.09 (s, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 20.6 (s).

(PT)AuCl. Yield: 67%. Anal. $C_{16}H_{13}AuClPS$ requires: C, 38.38; H, 2.62. Found: C, 38.74; H, 2.60. ^1H NMR ($CDCl_3$): δ 7.79 (ddd, J = 4.6, 1.2, 3.1 Hz, 1H), δ 7.62−7.40 (m, 11H), δ 7.22 (ddd, 5.0, 3.9, 1.5 Hz, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 20.5 (s).

(PT_2)AuCl. Yield: 75%. Anal. $C_{20}H_{15}AuClPS_2$ requires: C, 41.21; H, 2.59. Found: C, 41.20; H, 2.57. ^1H NMR ($CDCl_3$): δ 7.61−7.44 (m, 10H), δ 7.41 (dd, J = 9.1, 3.7 Hz, 1H), δ 7.28 (dd, J = 4.9, 0.91 Hz, 1H), δ 7.24 (m, incl CD_3Cl, 2H), δ 7.20 (dd, J = 3.7, 0.91 Hz, 1H), δ 7.01 (dd, J = 4.9, 3.7 Hz, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 19.9 (s).

(PT_3)AuCl. Yield: 93%. Anal. $C_{24}H_{17}AuClPS_3$ requires: C, 43.35; H, 2.58. Found: C, 43.61; H, 2.50. ^1H NMR ($CDCl_3$): δ 7.64−7.44 (m, 10H), δ 7.41 (dd, J = 8.9, 3.9 Hz, 1H), δ 7.23 (dd, J = 3.9, 1.2 Hz, 1H), δ 7.09 (s, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 20.0 (s).

AuI(PTP)AuI. This complex was synthesized by a modification of the literature method.[34] A mixture of AuCl(PTP)AuCl (0.05 mmol) and KI (1 mmol) was heated to reflux for 1 h in a 1:1 (vol/vol) degassed mixture of acetone and CH_2Cl_2 under N_2. The solution was then stirred for 24 h. The solvent was removed by rotary evaporation, and the resulting solid was washed with H_2O. Yield: 75%. Anal. $C_{28}H_{22}Au_2I_2P_2S$ requires: C, 30.57; H, 2.02. Found: C, 30.17; H, 2.14. ^1H NMR ($CDCl_3$): δ 7.62−7.45 (m). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 26.8 (s).

X-ray Crystallographic Analyses. Suitable crystals of (PT_3)AuCl and AuCl(PTP)AuCl were each mounted in oil on a glass fiber with data collected at 173(1) K. Their structures were solved using a direct methods structure solution[57] and refined using Shelxl-97.[58]

Data for (PT_3)AuCl were collected to a maximum 2θ of 55.8° on a Rigaku/ADSC CCD diffractometer in a series of two scan sets. Scans were carried out using 0.50° oscillations with 35.0 s exposures. Data were collected using the d*TREK program[59] and processed (integrated and corrected for absorption) using the TwinSolve function of CrystalClear.[60]

The structure of (PT_3)AuCl was determined by first indexing the unit cell as a two-component "split crystal" wherein the major and minor components are related by a rotation of 8.5° about an axis normal to an imaginary (−1.74, −9.14, 1.00) plane. Data for both components were then integrated, and the solution and subsequent refinements were carried out using an HKLF4 format data set containing only non-overlapped reflections. All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were included in calculated positions.

Data for AuCl(PTP)AuCl were collected to a maximum 2θ of 56.4° on a Bruker X8 APEX diffractometer in a series of 10 scan sets. Scans were carried out using 0.50° oscillations with 7.0 s exposures. Data were collected and integrated using the SAINT suite of software[61] and corrected for absorption using SADABS.[62] The material crystallizes with one-half-molecule residing on an

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(59) *d*TREK: Area Detector Software*, Version 7.1; Molecular Structure Corporation: The Woodlands, TX, 2001.

(60) *CrystalClear:* Version 1.2.5b20; Molecular Structure Corporation: The Woodlands, TX, 2002.

(61) *SAINT*: Version 6.0.2; Bruker AXS Inc.: Madison, WI, 1999.

(62) *SADABS:* Version 2.0.5; Bruker AXS Inc.: Madison, WI, 2001.

inversion center. In addition, one-half-molecule of methylene chloride, disordered about an inversion center, and one whole molecule of hexane solvent are found in the asymmetric unit. All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were included in calculated positions.

Data for AuI(PTP)AuI were collected to a maximum 2θ value of 50.0°. Data were collected in a series of scans in 0.50° oscillations with 30.0 s exposures. Data were integrated using the SAINT suite of software,[61] corrected for absorption using SADABS,[62] and corrected for Lorentz and polarization effects. The material crystallizes as a two-component twin, with the second component related to the first by a 180° rotation about the reciprocal 1,0,0 axis. The material crystallizes with one-half-molecule of hexane and one-half-molecule of methylene chloride in the asymmetric unit. While the final residuals (R1 ($I \geq 2\sigma(I)$)= 0.040, wR2 (all data) = 0.126) are acceptable, the final anisotropic displacement parameters (ADPs) for the phenyl and thiophene carbons are unacceptably distorted in a manner inconsistent with disordered fragments. The acceptable residuals are likely a result of reasonable modeling of the positions and ADPs of the majority of the electron density contained in the Au and I atoms. The distorted carbon atoms may arise from an incomplete description of the twinning, or an inadequate absorption correction.

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Supporting Information Available: CIF files for (PT_3)AuCl and AuCl(PTP)AuCl. Absorption and emission spectra for all compounds, ^1H and ^{31}P NMR VT spectra for AuCl(PTP)AuCl, crystallographic data for AuI(PTP)AuI. This material is available free of charge via the Internet at http://pubs.acs.org.

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