

Optical and Conformational Studies on (*o*-Tolyl)₃PAuCl

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Mono- and multi-nuclear phosphinegold(I) complexes show characteristic luminescence in the visible region. Solid Ph₃PAuX produce two emission bands with a broad low-energy shoulder,^{1,2} and some bis(phosphine)gold(I) complexes produce one band.³ The observed luminescence in these complexes have been discussed in terms of metal-centered transitions^{1,3} or ligand-to-gold charge-transfer transitions.^{4,5} Furthermore, Au...Au (*i.e.* aurophilic) interactions, sometimes observed in the solid-state structures of phosphinegold(I) complexes, have been proposed to influence the luminescence characteristics.⁶⁻⁸ Against this background, it is not surprising that extensive studies of the photophysical properties of Au(I) complexes have been performed, but despite this, the optical processes have yet to be characterized in detail. The present study was undertaken to investigate optical properties of (*o*-tolyl)₃PAuCl in which the Au(I) center is linearly coordinated by P and Cl atoms as revealed by X-ray crystallographic studies on the two polymorphs found for this complex; aurophilic interactions are precluded owing to steric hindrance afforded by the *o*-methyl groups.⁹

In this study, the CIS post-HF calculations on the molecular orbitals and excited states of (*o*-tolyl)₃PAuCl are undertaken to determine the nature of the orbitals and the transition probabilities involved in the optical processes. The electronic structures of (*o*-tolyl)₃PAuCl are clearly established and a model for the absorbing and emitting levels presented. This work has importance in delineating the luminescent properties of related mononuclear Au(I) complexes where there is some debate as to the optical processes and their relationship to different structural conformations.

Experimental Section

The (*o*-tolyl)₃PAuCl complex was prepared in accord with a literature procedure.⁹ For PL and excitation spectra measurements, samples in microcrystalline or powder states were placed on the cold finger of an Oxford CF-1104 cryostat using silicon grease. Excited light from a He-Cd 325-nm laser line or an Oriel 1000-W Xe arc lamp, passed through an Oriel MS257 monochromator, was focused on the sample. The spectra were measured at a 90° angle with an ARC 0.5 m Czerny-Turner monochromator equipped with a cooled Hamamatsu R-933-14 photomultiplier tube.

Results and Discussion

Figure 1(a) shows the solid-state reflectance spectrum of (*o*-tolyl)₃PAuCl measured at room temperature. There are three characteristic bands in the visible-UV region, referred to as the A-, B- and C-bands, in order of increasing energy. The A-band, appearing in the 370-420 nm region, is very weak, the B-band, appearing in the 300-370 nm region, has a moderate intensity, and the C-band, peaking at 280 nm, is strong. The PL spectrum of (*o*-tolyl)₃PAuCl was measured at 10 K. Unlikely, its luminescence is weak when compared to

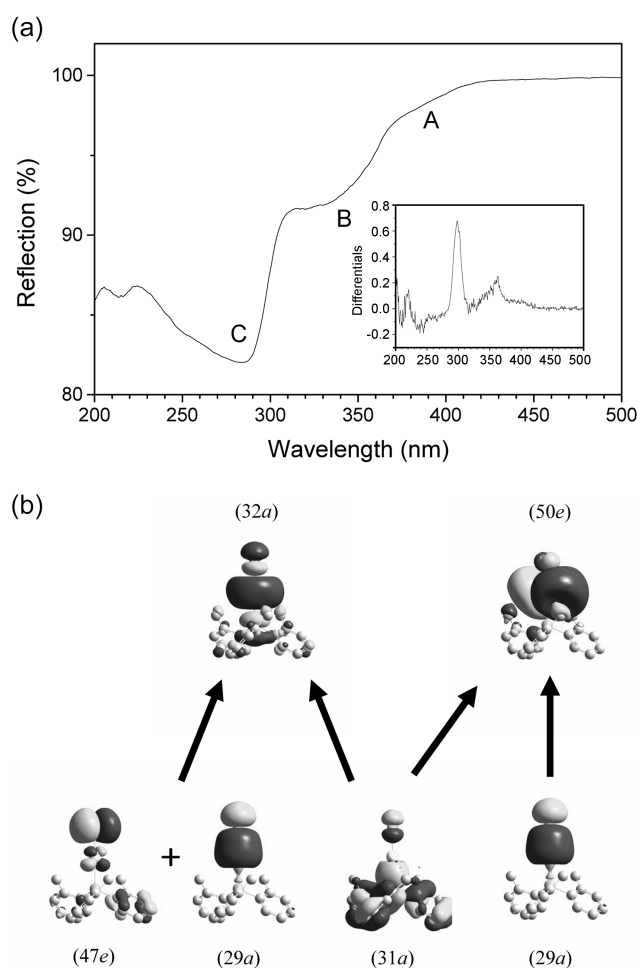


Figure 1. (a) Reflectance (solid state) spectra of (*o*-tolyl)₃PAuCl and (b) predominant orbital-transitions involved in the A, B and C-absorption bands. The differential reflection spectrum is inserted in (a).

that exhibited by (*o*-tolyl)₃P, as inserted in Figure 2(a). The PL spectrum of (*o*-tolyl)₃PAuCl is resolved into at least five components, with peaks at 412, 438, 458, 483 and 507 nm, and with a weak shoulder at the low-energy side (550 nm). The peak position in the PL spectrum is close to that found in (*o*-tolyl)₃P (437 nm), suggesting that the observed luminescence of (*o*-tolyl)₃PAuCl might be emission from (*o*-tolyl)₃P. To conform this hypothesis, the excitation spectra of the emissions from (*o*-tolyl)₃PAuCl and (*o*-tolyl)₃P were measured. As shown in Figures 2(b), the two spectra are quite different. For (*o*-tolyl)₃PAuCl, the excitation spectrum of the 458-nm emission shows three bands, peaking at 305, 325, and 375 nm. It is very comparable with only one band being observed for (*o*-tolyl)₃P. In the complex, the 305-nm band is very strong and narrow, while the others are weak and broad. The shape of this excitation spectrum is almost identical to that of the differential reflection spectrum. The strong 305 nm excitation corresponds to the C-absorption band and the weak bands, appearing in the 350-450 and 315-350 nm regions, can be attributed to the A- and B-absorptions, respectively. The relative intensities of the 305 and 375 nm excitation bands indicate that the high-energy emission is produced more efficiently via the high-energy excitation and vice versa.

The theoretical calculations for complexed molecules¹⁰ provide useful information about the electronic and optical properties. The CIS post-HF calculations were performed so as to interpret the absorption and emission spectra of (*o*-tolyl)₃P and (*o*-tolyl)₃PAuCl. Prior to the calculations, the geometry of (*o*-tolyl)₃PAuCl was optimized using Gaussian03 at the level of HF/lan2mz.¹¹ The optimized geometry of (*o*-tolyl)₃PAuCl conforms to C₃ symmetry. The results of the molecular orbital (MO) calculation are listed in Table 1;

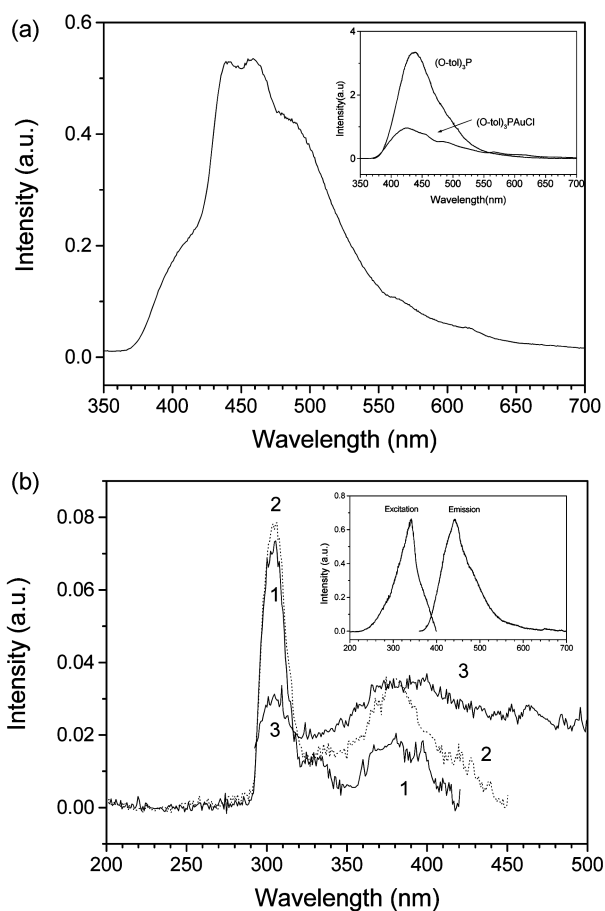


Figure 2. (a) PL and (b) excitation ($\lambda_{\text{ems}} = 1: 458 \text{ nm}, 2: 490 \text{ nm}, \text{ and } 3: 565 \text{ nm}$) spectra of (*o*-tolyl)₃PAuCl at 10 K. PL, and emission (1, $\lambda_{\text{exc}} = 348 \text{ nm}$) and excitation (2, $\lambda_{\text{ems}} = 438 \text{ nm}$) spectra of (*o*-tolyl)₃P at 78 K are inserted in (a) and (b), respectively.

Table 1. Some HF molecular orbitals calculated for (*o*-tolyl)₃PAuCl

No.	hartree	% contribution from each part of the complex																
		Cl				Au						P				<i>o</i> -tolyl		
		<i>s</i>	<i>p_x</i>	<i>p_y</i>	<i>p_z</i>	<i>s</i>	<i>p_x</i>	<i>p_y</i>	<i>p_z</i>	<i>d_{z2}</i>	(<i>d_{yz}</i> , <i>d_{xz}</i>)	(<i>d_{x2-y2}</i> , <i>d_{xy}</i>)	<i>s</i>	<i>p_x</i>	<i>p_y</i>		<i>p_z</i>	
34a	0.24																	100
33a	0.23	1	1			2	2							5				89
51e	0.21							2	1						3	6		88
51e	0.21							1	2						6	3		88
32a	0.16	5	3			50				2		6	9	10				
50e	0.12			2	4			25	54									14
50e	0.12			4	2			54	24									14
31a	-0.29		6			2							1	13				79
49e	-0.31																	100
49e	-0.31																	100
30a	-0.31													1				99
48e	-0.32			7	1							1						92
48e	-0.32			1	7							1						92
47e	-0.32			20	65		1					5	1					8
47e	-0.32			65	20		1					1	5					8
29a	-0.34	2	63				19	1		1		9	1					
28a	-0.38				3		6			14			1				31	45

Table 2. CI excited states and predominant transitions of (*o*-tolyl)₃PAuCl

excited state	eV	oscillator strength, <i>f</i>	main transitions
1E	6.51	0.007	47e → 32a
1A	7.00	0.008	29a → 32a
2,3A	7.38	0.003	47e → 50e
4A	7.40	0	47e → 50e
2E	7.47	0.072	31a → 50e
5A	7.48	0.065	31a → 32a
3E	7.56	0.009	31a → 50e
6A	7.59	0.152	31a → 32a, 34a; 48, 49e → 51e
4E	7.88	0.396	29a → 50e
5E	8.05	0.122	29a → 50e; 31a → 50e, 51e

here, the C₃ axis is taken as *x*-axis. The π -bonding orbitals of the three *o*-tolyl groups become the highest-occupied-molecular-orbital high-energy-molecular-orbitals. The highest-occupied-molecular-orbital (HOMO), 31a, is comprised, in the main, of the π -orbital character of the *o*-tolyl groups with minor contributions from the two σ -orbitals, of opposite parity, formed between Au and coordinated Cl and P atoms. The contributions of the π -electron systems of the *o*-tolyl groups to the next four HOMOs, *i.e.* 48e-49e, are each 92%. The next pair doubly-degenerate HOMOs, 47e, effectively correspond to the two *p_y* and *p_z* orbitals of the Cl atom, each occupied by a lone-pair electrons; their energies are almost the same to those of 48e. The next two low-energy MOs are non-degenerate 29a and 28a. The linear combination of *s* and *d_{xy}* of Au with *p_x* of Cl results in 29a, and *s* and *p_z* of Au with *p_z* of P and π system of *o*-tolyl produce 28a. The Cl atom *p_x* orbital contributes as much as 63% of its character to 29a. The lowest-unoccupied-molecular-orbital (LUMO) is the doubly-degenerate 50e, which arises from the linear combination of the *p_y* and *p_z* orbitals of Au. The next LUMO is the σ^* -type 32a, formed between the *s* and *d_{xy}* orbitals of the central Au atom and the *s* and *p_x* orbitals of the Cl and P atoms. The *s* orbital of Au atom contributes as much as 50% of its character to 32a.

On the basis of the calculated CI results, the three absorption bands of (*o*-tolyl)₃PAuCl were assigned. As listed in Table 2, the lowest excited state is 1E, arising from the transitions mostly from 47e to 32a and additionally from 48e to 32a. However, the transition probability from the ground state, X, to the first excited state, 1E, is only 0.007. The next lowest excited state is 1A, arising from the electron transition mostly from 29a to 32a. The probability of this transition is also very small with oscillator strength *f* = 0.008. Accordingly, the X → 1E and 1A transitions may give rise to the first weak A-absorption. According to the atomic charges determined from the Mulliken population analysis, for the X → 1E transition, the atomic charges of Au and Cl change from 0.20 to -0.11 and from -0.53 to -0.11, respectively, while the change of the atomic charge of P is

almost negligible. For the X → 1A transition, the changes of the electron atomic charges of Au and Cl are 0.23 and -0.27, respectively. These changes quite clearly indicate that these transitions are associated with the charge transfer from Cl to Au. The next excited states can be grouped from 2E, 5A, 3E and 6A and comprise the B-absorption band. These transitions are associated with the electronic transitions from the π -system of the aromatic rings to the *s*, *p_y* and *p_z* orbitals of Au. Accordingly, the B-absorption band can be attributed to charge transfer from the phenyl groups to Au. As listed in Table 2, the X → 4E and 5E transitions have large probabilities with *f* = 0.396 and *f* = 0.122, respectively. The 4E and 5E excited states predominantly arise from transitions from 29a to 50e and can be attributed to the strong C-absorption band. The charge densities of Au and Cl vary by 0.23 and -0.17, respectively, for the X → 4E, indicating that the C-absorption band is associated with the charge transfer from Cl to Au. The predominant orbital-transitions involved in the A, B and C-absorption bands are represented in Figure 1(b).

The observed luminescence of (*o*-tolyl)₃PAuCl is strongly associated with the charge transfer from Cl to Au. As seen in the excitation spectrum, the strong C-band excitation produce strong luminescence with the main components in the 375-550 nm region, while the weak A-band excitation produce the weak luminescence in the low-energy side. Although the intensity of the B-band is stronger than that of the A-band, the B-band excitation produce luminescence as a trace. This indicates that the charge transfer from the π -system of phenyl groups to Au may be ineffective in producing the emission from Au. Clearly, the characteristic optical-properties of the (*o*-tolyl)₃PAuCl complex are attributed to the Cl-to-Au charge transfer for the absorption and *vice versa* for the emission.

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