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Luminescent Metal−Metal-Bonded Exciplexes Involving Tetrakis(μ-diphosphito)diplatinate(II) and Thallium(I)

Sarah A. Clodfelter, Tina M. Doede, Bridget A. Brennan, Jeffrey K. Nagle,* David P. Bender, Warren A. Turner, and Paul M. LaPunzina

Contribution from the Department of Chemistry, Bowdoin College, Brunswick, Maine 04011

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Abstract: Spectroscopic and kinetic evidence is presented and used to identify and characterize three luminescent, metal−metal-bonded exciplexes. Two long-lived, strongly phosphorescent triplet exciplexes involving the lowest energy triplet excited state of $Pt_2(P_2O_5H_2)_4^{4-}$ ($^*Pt_2, \bar{\nu}_{max} = 1.95\ \mu m^{-1}$, $\Phi_{lum} = 0.5$, $\tau = 10\ \mu s$) and Tl^I in aqueous solution at room temperature ($^*Pt_2Tl, \bar{\nu}_{max} = 1.79\ \mu m^{-1}$, $\Phi_{lum} = 0.5$, $\tau = 10\ \mu s$; $^*Pt_2Tl_2, \bar{\nu}_{max} = 1.70\ \mu m^{-1}$, $\Phi_{lum} = 0.5$, $\tau = 10\ \mu s$) and one weakly fluorescent singlet exciplex ($\nu_{max} = 2.32\ \mu m^{-1}$, $\Phi_{lum} < 1 \times 10^{-3}$) are formed as a result of direct Pt−Tl bonding. An inner-sphere mechanism for the formation of the two triplet exciplexes is proposed in which a diffusional approach of the ionic reactants results in relativistically influenced Pt−Tl bonding and is accompanied by substantial desolvation effects. Free energies (−30 and −20 kJ/mol), enthalpies (−19 and −10 kJ/mol), and entropies (36 and 31 J/(mol K)) for the formation of $^*Pt_2Tl$ and $^*Pt_2Tl_2$, respectively, are derived through a novel procedure and, along with the corresponding kinetic values, are consistent with the proposed mechanism. These three exciplexes are the only examples known which form as a result of metal−metal bonding between the reactants.

Introduction

Exciplex formation is a well-established phenomenon of electronically excited organic compounds.[1] In contrast it is only now becoming recognized as an important reaction pathway for excited states of coordination compounds. Claims of outer-sphere exciplex formation involving coordinatively saturated compounds include those between Re(4,7-dimethyl-1,10-phenanthroline)$(CO)_3Cl$ and an aromatic amine,[2] Ru^{II}−polypyridine compounds and Ag^I,[3−5] $Ir(phen)_3^{3+}$ or $Ir(terpy)_2^{3+}$ and $HgCl_2$,[6] Ir(C^3,N'-bpy)$(bpy)_2^{2+}$ and Br^-,[7] and the uranyl ion and aqueous metal ions.[8] Coordinatively unsaturated compounds thought to form inner-sphere exciplexes include metalloporphyrins with electron acceptors,[9] Tl^I with chloride ions,[10] Cu(2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline)$_2$ with Lewis bases,[11] and $Cu(CN)_2^-$ with halide ions.[12] In addition some examples of luminescent eximers of square planar Pt^{II} compounds have also been reported,[13−16] and the relative ease with which coordinatively unsaturated planar compounds undergo both eximer and exciplex formation has been discussed.[15]

Among metal−metal-bonded compounds only $Pt_2(P_2O_5H_2)_4^{4-}$ (abbreviated Pt_2)[17] with Tl^I,[18−20] and $Cu_4I_4(py)_4$ with Lewis bases[21] have been reported to form exciplexes. The former example is especially noteworthy, not only in providing the first example of exciplex formation involving metal−metal bonding,[22] but also in that the resulting luminescence is, as for the lowest triplet excited state of Pt_2 (designated here as $^*Pt_2$),[23] intense and long-lived. Unfortunately only preliminary results have been obtained to date, precluding a thorough understanding of the phenomenon.

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Spectroscopic and kinetic evidence is presented here for the formation of two strongly phosphorescent triplet exciplexes resulting from diffusional encounters involving $^*Pt_2$ and Tl^I in aqueous solution. As described below we attribute this to relativistically influenced Pt–Pt–Tl and Tl–Pt–Pt–Tl bonding interactions. To our knowledge these are the only known examples of exciplex formation resulting from metal–metal bonding between the reactants. A novel approach is used to derive thermodynamic and kinetic parameters characterizing the formation of these two species. Spectroscopic evidence is presented also for the existence of a weakly fluorescent singlet exciplex involving Pt_2 and Tl^I.

Experimental Section

Potassium Tetrakis(μ-diphosphito-*P,P'*)diplatinate(II) Dihydrate. Samples were prepared according to established procedures[24] and were stored in the dark under nitrogen to prevent decomposition.

Other Materials. Aldrich Gold Label 99.9+% thallium sulfate, Burdick and Jackson HPLC grade water, and Aldrich Gold Label 1,2-ethanediol were used as received.

Physical Measurements. An NSG Type 71 FL-H quartz luminescence cell designed for convenient degassing was used to purge aqueous solutions of oxygen with a stream of high-purity nitrogen gas passed through an Alltech Associates oxygen trap and connected to the cell via a Teflon tube inserted directly into its glass arm. The concentration of Pt_2 in aqueous solution was determined by absorbance measurements at 2.72 μm^{-1} ($\epsilon = 3.45 \times 10^4$ L mol^{-1} cm^{-1}). Glassware was carefully cleaned with aqua regia or concentrated nitric acid followed by thorough rinsing with water to remove traces of metal ions and other impurities. All spectroscopic measurements were made within 3 h after preparation of the solutions to minimize problems due to sample decomposition.

Absorption spectra at room temperature (~293 K) were recorded with a Shimadzu UV-240 spectrophotometer (1 nm slit widths) interfaced to an IBM-PC computer and controlled with Shimadzu PC-265 Spectroscopy Interface software. Luminescence and luminescence excitation spectra at room temperature were recorded with a Spex 1680 0.22 m double monochromator luminescence spectrophotometer interfaced to an IBM-PC computer. A 450 W xenon lamp, slit widths of 1 or 2 nm, and an integration time of 1 s were used in all cases. Both luminescence and luminescence excitation spectra were corrected for instrument response variations.

Temperature dependent uncorrected luminescence spectra of an air-saturated 2:1 1,2-ethanediol/water solution of Pt_2 and Tl^I were obtained with an experimental apparatus described previously.[25] The solution was placed in a copper sample holder with a plastic wrap liner and sealed under glass with a silicon O-ring. A layer of Dow-Corning silicone high-vacuum grease between the holder and liner was used to maintain thermal contact. The sample holder was mounted on a copper plate inside a Janis Research 6RD dewar, and the temperature of the sample block was controlled from 1.7 to 300 K with a calibrated Lake Shore Cryotronics DT-500K silicon diode thermometer, resistance heater, and Lake Shore Cryotronics DTC 500-SP proportional temperature controller. The maximum error in the sample temperature reported here was ±0.3%. The sample was excited with a mercury vapor lamp filtered by an Oriel 5181 UV band-pass filter (2.50–3.25 μm^{-1}). The excitation light was transmitted to the sample through an American Optical UV-transmitting clad rod light guide with an effective upper transmission cutoff at approximately 2.86 μm^{-1}, thus selecting the mercury spectral line at 2.74 μm^{-1}. The luminescent light signal was transmitted from the dewar through an identical light guide, selected with a McKee Pederson MP-1018B scanning monochromator and detected with an RCA 931A photomultiplier tube connected to a Princeton Applied Research HR-8 lock-in detector.

Luminescence lifetime measurements were made with an LSI VSL-337LRF pulsed nitrogen laser (2.97 μm^{-1} excitation), a Hammamatsu 1P21 photomultiplier tube, and a LeCroy 9410 dual 150 MHz digital storage oscilloscope and represent the average of several hundred signal pulses.

Data Analysis. Spectral files were imported into the Spectra Calc (Galactic Industries) computer program, and the data were converted from wavelengths to wavenumbers for analysis. The observed spectra could be reproduced as the sums of individual Gaussian–Lorentzian bands located at different wavenumbers. They were resolved into their component bands (the additive Lorentzian contribution to each band was found to be less than 25% in all cases) by least-squares data fits with either the Data Fit 1.10 (part of the Square Tools 2.0 data package for Spectra Calc available from Spectrum Square Associates) or Curve Fit routines in Spectra Calc.

The three parameters characterizing the phosphorescence band position (wavenumber of maximum phosphorescence intensity) and shape (width and relative amounts of Lorentzian and Gaussian character) for $^*Pt_2$ were easily determined in the absence of Tl^I, and established the reliability of the fitting procedure. The parameters for $^*Pt_2Tl$ and $^*Pt_2Tl_2$ were more difficult to determine owing to the presence of overlapping bands and were determined by an iterative procedure whereby the results of the fitting at Tl^I concentrations yielding predominately one species were given the most weight. After an internally consistent set of parameters for each of the three species was established, some or all of these values could be fixed in the data analysis used to determine relative integrated intensities. This was particularly useful when a component band represented only a small fraction of the overall intensity. The individual band intensities were assumed to be proportional to the relative concentrations of the three species since their phosphorescence quantum yields were found to be identical within experimental uncertainty.

Results

The absorption spectrum of Pt_2 in aqueous solution at room temperature is only slightly affected by the addition of up to 10^{-3} mol/L Tl^I (from Tl_2SO_4), in accord with previous findings for $Tl(NO_3)$[18] and TlBr.[20] A small but noticeable shift of the spin-allowed 2.72 μm^{-1} band of Pt_2[17] to lower wavenumber occurs at higher concentrations of Tl^I. A least-squares Gaussian–Lorentzian resolution of the observed spectra at these higher concentrations revealed the presence of a second band at 2.56 μm^{-1}. No evidence for the formation of a third band at still lower wavenumber was obtained, even at Tl^I concentrations as high as 0.1 mol/L. The luminescence excitation spectra of $^*Pt_2$ yielded similar results and no noticeable excitation band shifts were observed when monitoring the luminescence over the range from 1.70 to 1.95 μm^{-1}.

Figure 1 shows the effects on the luminescence spectrum of $^*Pt_2$ at room temperature of adding up to 2.5×10^{-5} mol/L Tl^I to deoxygenated aqueous solutions of 1.0×10^{-5} mol/L Pt_2 irradiated at 2.72 μm^{-1}.[26] The 1.95 μm^{-1} phosphorescence band of $^*Pt_2$ is diminished in intensity, and is accompanied by the appearance of a lower wavenumber band. The observed spectra have, within experimental uncertainty, identical integrated intensities and were resolved by computer analysis into two Gaussian–Lorentzian component bands located at 1.95 and 1.79

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[22] We (Hinkle, R. J.; Doede, T. M.; Nagle, J. K., unpublished results) and others (Crosby, G., personal communication) have observed similar effects with Ag^I. In that case there are much greater effects on the absorption spectrum of Pt_2 than for Tl^I, indicative of a substantially larger ground state interaction.

[23] The 5×10^5 ratio of 1.95 to 2.49 μm^{-1} lifetimes for the two excited states of Pt_2,[17] the 3×10^3 ratio of 2.72 to 2.21 μm^{-1} molar absorption coefficients of Pt_2, and the relative energies of the two absorption and luminescence bands[17] all support the use of singlet–triplet designations in this case. The same reasoning applies also to the two triplet exciplexes and one singlet exciplex of Pt_2 with Tl^I reported here. For a detailed consideration of the fluorescence of Pt_2, see: Milder, S. J.; Brunschwig, B. S. *J. Phys. Chem.* **1992**, *96*, 2189–2196.

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[26] Irradiation at 2.21 μm^{-1} (the spin-forbidden absorption band maximum) yields similar, though much less sensitive, results.

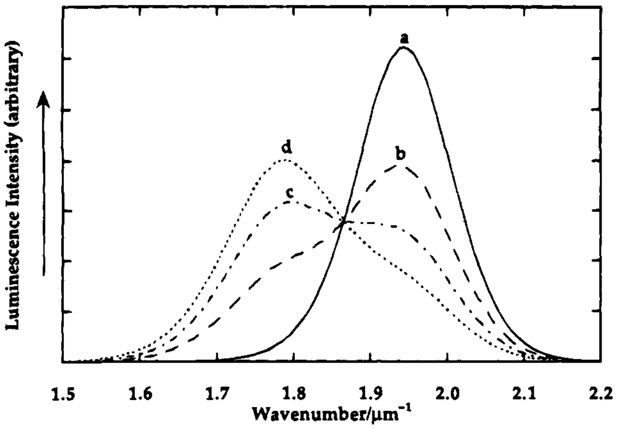

Figure 1. Luminescence spectra at room temperature of deoxygenated aqueous solutions of 1.0 × 10^{-5} mol/L Pt_2 with (a) 0, (b) 4.5 × 10^{-6}, (c) 1.1 × 10^{-5}, and (d) 2.5 × 10^{-5} mol/L Tl^I.

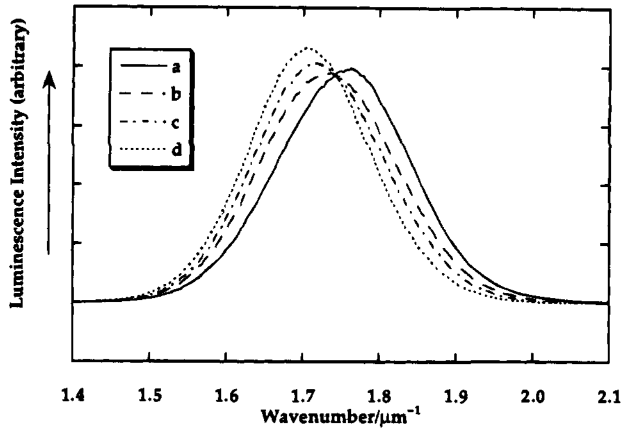

Figure 3. Luminescence spectra at room temperature of deoxygenated aqueous solutions of 1.0 × 10^{-5} mol/L Pt_2 with (a) 2.5 × 10^{-4}, (b) 4.9 × 10^{-4}, (c) 1.1 × 10^{-3}, and (d) 1.2 × 10^{-2} mol/L Tl^I.

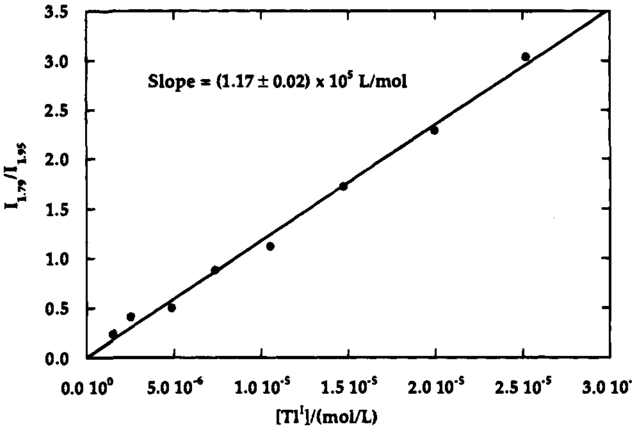

Figure 2. Ratio of 1.79 μm^{-1} luminescence intensity ($I_{1.79}$) versus 1.95 μm^{-1} luminescence intensity ($I_{1.95}$) for deoxygenated aqueous solutions of 1.0 × 10^{-5} mol/L Pt_2 with varying amounts of Tl^I.

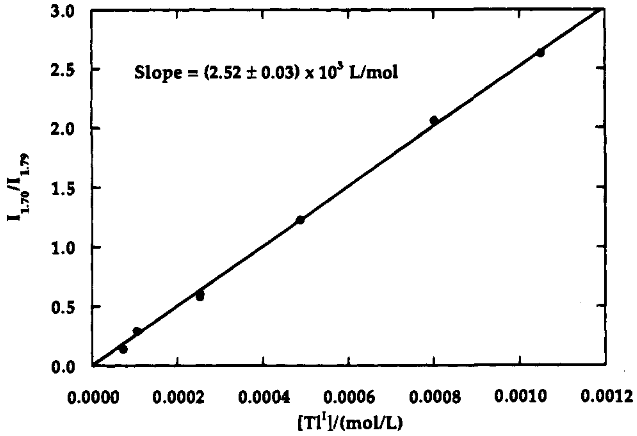

Figure 4. Ratio of 1.70 μm^{-1} luminescence intensity ($I_{1.70}$) versus 1.79 μm^{-1} luminescence intensity ($I_{1.79}$) for deoxygenated aqueous solutions of 1.0 × 10^{-5} mol/L Pt_2 with varying amounts of Tl^I.

μm^{-1}. A plot of the ratio of the integrated intensities of these two bands versus Tl^I concentration (approximated as its formal concentration) is shown in Figure 2. A linear relationship is revealed with a linear least-squares slope (assuming the y-intercept to pass through the origin) equal to (1.17 ± 0.02) × 10^5 L/mol. The width (full width at half-maximum) of the 1.79 μm^{-1} band was found to be 0.21 ± 0.01 μm^{-1}, slightly broader than the 0.18 ± 0.01 μm^{-1} width of the 1.95 μm^{-1} band of $^*Pt_2$. An isoluminescent point is seen at 1.866 ± 0.002 μm^{-1}, virtually identical to the 1.867 ± 0.002 μm^{-1} average of the wavenumbers of the maximum intensities of the two bands.

Figure 3 shows the effects on the luminescence spectrum of $^*Pt_2$ at room temperature (~293 K) of adding up to 1.2 × 10^{-2} mol/L Tl^I to deoxygenated aqueous solutions of 1.0 × 10^{-5} mol/L Pt_2 irradiated at 2.72 μm^{-1}. The 1.79 μm^{-1} band appears to shift to near 1.70 μm^{-1}. Once again the observed spectra have, within experimental uncertainty, identical integrated intensities. Attempts to fit the observed spectra in this concentration range to a single Gaussian–Lorentzian band were unsuccessful, and a minimum of two bands were required to achieve satisfactory fits. The two component bands were located by this procedure at 1.79 and 1.70 μm^{-1}. A plot of the ratio of the integrated intensities of these two bands versus Tl^I concentration is shown in Figure 4. A linear relationship is revealed with a linear least-squares slope (assuming the y-intercept to pass through the origin) equal to (2.52 ± 0.03) × 10^3 L/mol. The widths (full width at half-maximum) of the two bands were both found to be 0.21 ± 0.01 μm^{-1}. This result, along with the 0.18 ± 0.01 μm^{-1} width determined in the absence of Tl^I, demonstrates that the shapes of all three component bands are nearly the same.[27] An isoluminescent point is seen at 1.742 ± 0.005 μm^{-1}, virtually identical to the 1.743 ± 0.002 μm^{-1} average of the maximum intensities of the two bands.

Lifetime measurements of the phosphorescence as a function of Tl^I concentration at room temperature, taken beginning 10 ns following laser pulse excitation, revealed monoexponential decays over 2 orders of magnitude. Lifetimes were found to be identical within experimental uncertainty (9.2 ± 1.0 μs) up to Tl^I concentrations of 0.05 mol/L, in accord with published results.[28,29] Quantum yields were also found to be the same as for $^*Pt_2$ (0.55).[17] This was established by the fact that the integrated intensities of the observed spectra at each of the concentrations shown in Figures 1 and 3 are the same within experimental uncertainty.

Figure 5 shows the effect of temperature on the uncorrected luminescence spectrum (excitation at 2.74 μm^{-1}) of an air-saturated 2:1 1,2-ethanediol/water solution of 2 × 10^{-6} mol/L Pt_2 with 3 × 10^{-2} mol/L Tl^I (from $TlNO_3$). As the temperature is lowered from 300 to 190 K to give a frozen solution, luminescence thermochromism is revealed as the yellow-orange luminescence in the 1.7–1.8 μm^{-1} region decreases in intensity while the green luminescence at 1.95 μm^{-1} reappears. At temperatures as low as 5 K, a small shoulder at 1.7–1.8 μm^{-1}

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[27] The minor amount of Lorentzian character in the nearly Gaussian bands was also found to be about the same for all three bands.

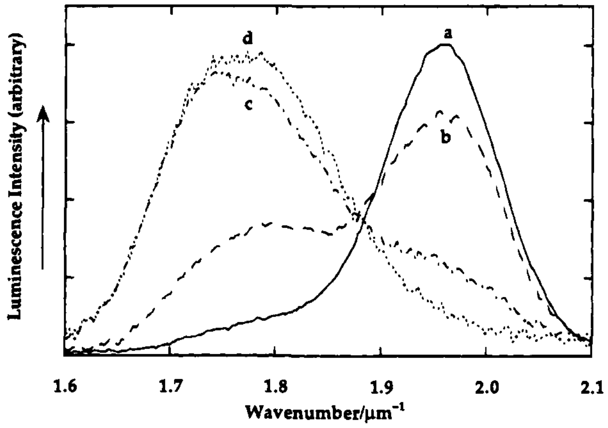

Figure 5. Uncorrected luminescence spectra of an air-saturated 2:1 1,2-ethanediol/water solution of Pt_2 with 10^{-3} mol/L Tl^I at (a) 190 , (b) 210 , (c) 230, and (d) 250 K.

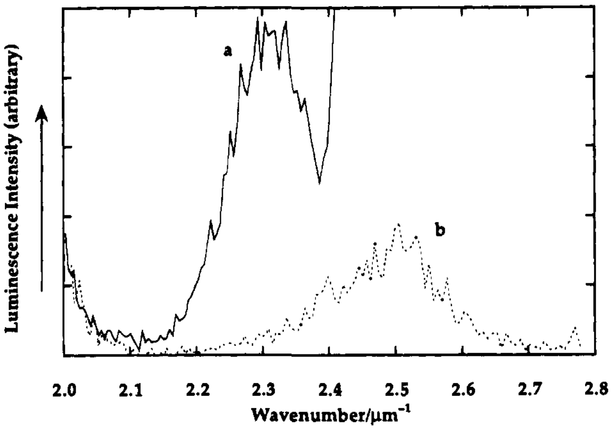

Figure 6. Luminescence spectra at room temperature of a deoxygenated aqueous solution containing 1.0×10^{-5} mol/L Pt_2 and 0.050 mol/L Tl^I produced by excitation at (a) 2.44 μm^{-1} and (b) 2.86 μm^{-1}.

Scheme 1

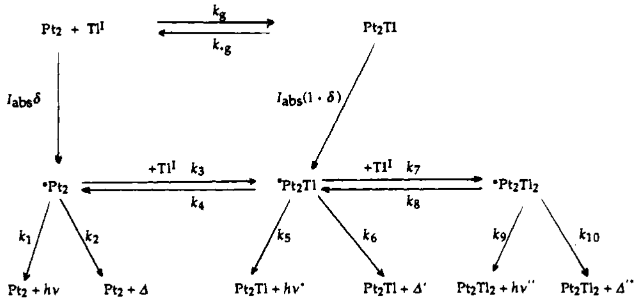

Table 1. Summary of Spectroscopic Assignments for Aqueous Solutions of Pt_2 with Tl_2SO_4[a]

species	absorption bands $\bar{\nu}_{max}$ (μm^{-1})[b]	luminescence bands $\bar{\nu}_{max}$ (μm^{-1})
Pt_2, $*Pt_2$	2.208 ± 0.016	1.947 ± 0.002
	2.717 ± 0.008	2.494 ± 0.013
Pt_2Tl, $*Pt_2Tl$	2.558 ± 0.018	1.786 ± 0.004
		2.320 ± 0.013
Pt_2Tl_2, $*Pt_2Tl_2$	c	1.700 ± 0.002

[a] The two absorption bands given for Pt_2 correspond to spin-forbidden (lower wavenumber) and spin-allowed (higher wavenumber) transitions in each case. The two luminescence bands given for $*Pt_2$ and $*Pt_2Tl$ correspond to phosphorescence (lower wavenumber) and fluorescence (higher wavenumber). [b] Luminescence excitation spectra give similar results. [c] No absorption bands observed.

still remains, but otherwise the luminescence behavior of the solution is identical to that of $*Pt_2$ without added Tl^I. The luminescence lifetime variation of this solution over the temperature range 1.7–300 K is also identical within experimental uncertainty to the phosophorescence lifetime behavior of $*Pt_2$ without added Tl^I.

The 2.49 μm^{-1} fluorescence of $*Pt_2$[17] (not shown in Figures 1 and 3) intensity and band maximum resulting from excitation at 2.72 μm^{-1} are virtually unaffected by Tl^I at concentrations as high as 0.05 mol/L. However, as shown in Figure 6a, excitation at 2.44 μm^{-1} (the 2.72 μm^{-1} band shows negligible absorbance here) of a solution containing 1.0×10^{-5} mol/L Pt_2 and 0.050 mol/L Tl^I results in the appearance of a new, weak ($\Phi_{lum} < 1 \times 10^{-3}$) luminescence band at 2.32 μm^{-1}, presumably fluorescence. Excitation at 2.86 μm^{-1} (the 2.56 μm^{-1} band shows negligible absorbance here) is shown also (Figure 6b) and, as for excitation at 2.72 μm^{-1}, results only in the appearance of the 2.49 μm^{-1} fluorescence band. In contrast, identical phosphorescence bands (the tails of which are just discernable below 2.1 μm^{-1} in Figure 6) are obtained with either 2.44 or 2.86 μm^{-1} excitation.

Discussion

Mechanism. A mechanism which accounts for these observations is presented in Scheme 1 where I_{abs} represents the intensity of the light absorbed by Pt_2 and δ is the fraction of the ground state of Pt_2 that does not interact with Tl^I to form the weakly bound Pt_2Tl ion pair. Two luminescent triplet exciplexes, $*Pt_2Tl$ and $*Pt_2Tl_2$, are proposed to form[30] with radiative decays designated $h\nu'$ and $h\nu''$ and nonradiative decays Δ' and Δ'', respectively.

While preliminary reports of $*Pt_2Tl$ have appeared,[18-20] the effects of forming $*Pt_2Tl_2$ at higher Tl^I concentrations were not taken into account in those studies and led to misinterpretations of some of the results. The singlet exciplex $*Pt_2Tl$ postulated to be responsible for the weak luminescence band at 2.32 μm^{-1} (Figure 6a) has not been previously reported and represents the first documented example of a singlet exciplex of a metal–metal-bonded compound in solution. It is formed only upon excitation at the 2.56 μm^{-1} band of Pt_2Tl and not the 2.72 μm^{-1} band of Pt_2 (Figure 6b), presumably because the lifetime of the singlet excited state of $*Pt_2$ (~24 ps)[17,23] is too short to allow for diffusional formation of the singlet exciplex.

The spectroscopic assignments are summarized in Table 1. Two absorption band maxima are given for Pt_2 which correspond to spin-forbidden (lower wavenumber band) and spin-allowed (higher wavenumber band) transitions.[17,23] In addition two luminescence bands each for $*Pt_2$ and $*Pt_2Tl$ are given which correspond to phosphorescence (lower wavenumber band) and fluorescence (higher wavenumber band).[17,23] The values of the fluorescence Stokes shifts for $*Pt_2$ (0.223 ± 0.015 μm^{-1}) and $*Pt_2Tl$ (0.238 ± 0.022 μm^{-1}) are the same within experimental uncertainty, and nearly the same as the phospho-

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(28) The most reliable reported lifetimes of $*Pt_2$ in deoxygenated aqueous solution lie in the range 9.3 ± 0.7 μs. See, for example: Yamaguchi, T.; Sasaki, Y. *Inorg. Chem.* **1990**, *29*, 493–495 ($\tau = 8.7$ μs). Fetterolf, M.; Friedman, A. E.; Yang, Y.-Y.; Offen, H.; Ford, P. C. *J. Phys. Chem.* **1988**, *92*, 3760–3763 ($t = 8.8 \pm 0.1$ μs). Che, C.-M.; Butler, L. G.; Gray, H. B. *J. Am. Chem. Soc.* **1981**, *103*, 7796–7797 ($t = 9.8 \pm 0.2$ μs). Small amounts of impurities, including molecular oxygen, reduce the measured lifetime and thereby account in large part for the discrepancies among the various reported values.[17] This suggests also that the actual lifetimes are probably closer to the highest measured values of 10 μs than to 8 or 9 μs.

(29) The lifetime has been reported to be unchanged in the presence of either 1×10^{-3} mol/L $Tl(NO_3)$[18] or TlBr[20] also.

(30) Tl^I luminesces in aqueous solutions, but at substantially higher energies than seen here (Sheperd, T. M. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 644–650).

rescence Stokes shift for *$\mathrm{Pt_2}$ (0.261 ± 0.016 μm^{-1}).[31] The results for *$\mathrm{Pt_2}$ are consistent with previously reported values, and the close correspondence between the Stokes shifts for *$\mathrm{Pt_2}$ and *$\mathrm{Pt_2Tl}$ lends support to the proposed assignments for the 2.56 μm^{-1} absorption of $\mathrm{Pt_2Tl}$ and the 2.32 μm^{-1} luminescence of *$\mathrm{Pt_2Tl}$ as being due to spin-allowed processes.

Attempts to determine a value for the ground state equilibrium constant corresponding to the ion-pairing process $\mathrm{Pt_2 + Tl^I \rightleftarrows Pt_2Tl}$ were only partially successful owing to the small observed changes in the absorption spectrum, even at $\mathrm{Tl^I}$ concentrations as high as 0.1 mol/L.[32] A preliminary value of 6 ± 4 L/mol (assuming equal molar absorption coefficients for $\mathrm{Pt_2}$ and $\mathrm{Pt_2Tl}$[33]) was derived.[34]

The temperature dependence of the luminescence spectrum (Figure 5) and lifetime lends support to the proposal that diffusional encounters between *$\mathrm{Pt_2}$ and $\mathrm{Tl^I}$ (as opposed to static encounters resulting from ground state $\mathrm{Pt_2Tl}$ ion-pairing) are largely responsible for the formation of *$\mathrm{Pt_2Tl}$ (the same remarks apply to the formation of *$\mathrm{Pt_2Tl_2}$ from *$\mathrm{Pt_2Tl}$ and $\mathrm{Tl^I}$). Additional evidence to support this argument comes from the observations that molecular oxygen, acids, and salts such as $\mathrm{K_2SO_4}$ all diminish the effects of $\mathrm{Tl^I}$ on the *$\mathrm{Pt_2}$ phosphorescence, $\mathrm{O_2}$ presumably by competitive quenching of *$\mathrm{Pt_2}$[17] and the latter two by ion-pairing effects which are known to interfere with the diffusional approach of oppositely charged ions. Furthermore, static quenching would be expected to cause the 2.49 μm^{-1} fluorescence to be affected to a similar extent, and this is not observed (Figure 6b).

Why should $\mathrm{Tl^I}$ form exciplexes with *$\mathrm{Pt_2}$ instead of becoming oxidized or reduced by excited state electron transfer quenching, or promoted to an electronically excited state by energy transfer quenching? The answer is found in the energetics of formation of aqueous $\mathrm{Tl^{II}}$, $\mathrm{Tl^0}$, and *$\mathrm{Tl^I}$, respectively, from $\mathrm{Tl^I}$. The standard reduction potentials (vs NHE) for the redox couples $\mathrm{Tl^{II}/Tl^I}$ and $\mathrm{Tl^I/Tl^0}$ are known to be 2.22 V[35] and −1.94 V,[36] respectively, both too large in magnitude to allow for efficient electron transfer.[17] Likewise, the 0–0 energy for the formation of the s–p excited state of $\mathrm{Tl^I}$ (>325 kJ/mol)[30] is much too large to allow for efficient energy transfer quenching.

Kinetic Parameters. A steady state kinetic analysis based on the mechanism given in Scheme 1[37] yields eqs 1–3 which account for the observed linear relationships between the luminescence intensity ratios and $\mathrm{Tl^I}$ concentration shown in Figures 2 and 4 and provides an interpretation of the observed slopes in terms of the various rate constants.[38,39]

$$I_{1.79}/I_{1.95} = k_5/k_1\{k_7/k_3[1 - k_8/(k_8 + k_9 + k_{10})] + (k_4 + k_5 + k_6)/k_3[\mathrm{Tl^I}]\}^{-1} \quad (1)$$

$$\approx k_5k_3[\mathrm{Tl^I}]/[k_1(k_4 + k_5 + k_6)] \quad (2)$$

$$I_{1.70}/I_{1.79} = k_9k_7[\mathrm{Tl^I}]/[k_5(k_8 + k_9 + k_{10})] \quad (3)$$

Although the observed slopes represent a combination of several different rate constants, these rate constants can all be either independently measured or reliably estimated. For example, from the known phosphorescence quantum yield (0.55)[17] and lifetime (10 μs)[17,28] of *$\mathrm{Pt_2}$, values of 5.5 × 10^4 and 4.5 × 10^4 s^{-1} for k_1 and k_2, respectively, are readily calculated. Furthermore, since the phosphorescence quantum yields and measured lifetimes for *$\mathrm{Pt_2Tl}$ and *$\mathrm{Pt_2Tl_2}$ are, within experimental uncertainty, the same as those for *$\mathrm{Pt_2}$, it holds that $k_9 \approx k_5 \approx k_1$ and $k_{10} \approx k_6 \approx k_2$.[3,37] On the basis of this result and eqs 2 and 3, the slopes in Figures 2 and 4 are predicted to be approximately equal to $k_3/(k_4 + k_5 + k_6)$ and $k_7/(k_8 + k_9 + k_{10})$, respectively. Since the reactions leading to the formation of *$\mathrm{Pt_2Tl}$ and *$\mathrm{Pt_2Tl_2}$ are assumed to be diffusional processes, values for k_3 of 3 × 10^{10} L mol^{-1} s^{-1} and k_7 of 1.5 × 10^{10} L mol^{-1} s^{-1} can be estimated.[40] These values, along with the experimental slopes[41] and the approximate values derived above for k_5, k_6, k_9, and k_{10}, yield k_4 = 1.6 × 10^5 s^{-1} and k_8 = 5.9 × 10^6 s^{-1}.

Thermodynamic Parameters. Since the values of k_4 and k_8 are tied to those assumed for k_3 and k_7, respectively, the equilibrium constants for the formation of *$\mathrm{Pt_2Tl}$ from *$\mathrm{Pt_2}$ and $\mathrm{Tl^I}$ ($K_1 = k_3/k_4$) and *$\mathrm{Pt_2Tl_2}$ from *$\mathrm{Pt_2Tl}$ and $\mathrm{Tl^I}$ ($K_2 = k_7/k_8$) can be established with somewhat more certainty. Within the framework of the proposed mechanism, the observed slope of 1.17 × 10^5 mol/L given in Figure 2 requires that k_3 must be greater than 1.17 × 10^{10} if k_4 is to be greater than 0. If 1.9 × 10^{10} L mol^{-1} s^{-1} is taken as a lower limit and 1 × 10^{13} L mol^{-1}

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(31) This is not surprising since it has been demonstrated that the $\mathrm{Pt_2}$ singlet and triplet $A_{2u}(d\sigma^* \rightarrow d\sigma)$ potential surfaces are virtually the same (Stiegman, A. E.; Rice, S. F.; Gray, H. B. Miskowski, V. M. *Inorg. Chem.* **1987**, *26*, 1112–1116).

(32) For example, the absorption band at 2.72 μm^{-1} shifts only to 2.71 μm^{-1}, even in 0.01 mol/L $\mathrm{Tl^I}$. This makes the quantitative resolution of the observed spectrum into its component bands centered at 2.72 and 2.56 μm^{-1} quite difficult.

(33) The molar absorption coefficient for $\mathrm{Pt_2Tl}$ at 2.56 μm^{-1} is likely to be greater than that for $\mathrm{Pt_2}$ at 2.72 μm^{-1} in accord with observations for linear $\mathrm{Rh^I}$ dimers (Balch, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 8049–8054) and trimers (Balch, A. L.; Fossett, L. A.; Nagle, J. K.; Olmstead, M. M. *J. Am. Chem. Soc.* **1988**, *110*, 6732–6738). Therefore, the estimated value is possibly somewhat high.

(34) Peters, D. G.; Hayes, J. M.; Hieftje, G. M. *Chemical Separations and Measurements: Theory and Practice of Analytical Chemistry*; Saunders: New York, 1974; pp 614–619.

(35) Stanbury, D, M. *Adv. Inorg. Chem.* **1989**, *33*, 69–138.

(36) Schwarz, H. A.; Dodson, R. W. *J. Phys. Chem.* **1989**, *93*, 409–414.

(37) Ware, W. R. *NATO Adv. Sci. Inst., Ser. A* **1983**, *69*, 299–317, 341–362. Hui, M.-H.; Ware, W. R. *J. Am. Chem. Soc.* **1976**, *98*, 4718–4727. Ware, W. R. *Pure Appl. Chem.* **1975**, *41*, 635–660. Similar kinetic schemes have been employed in studies of the effects of hydrogen bonding on the luminescence spectra of organic compounds (Mataga, N.; Kubota, T. *Molecular Interactions and Electronic Spectra*; Marcel Dekker: New York, 1970; pp 342–351).

(38) The approximation leading from eq 1 to eq 2 that $k_7/k_3[1 - k_8/(k_8 + k_9 + k_{10})] \ll (k_4 + k_5 + k_6)/k_3[\mathrm{Tl^I}]$ can be shown, under the conditions of Figure 2 and with values of the rate constants derived below, to be valid within 3% at even the highest $\mathrm{Tl^I}$ concentration used.

(39) Under the conditions of the experiments shown in Figures 1 and 2 the fraction of $\mathrm{Pt_2}$ existing in the form $\mathrm{Pt_2Tl}$ is estimated to be less than 1% (based on $k_g/k_{-g} \approx 6$ L/mol). Furthermore, since the amount of light absorbed by $\mathrm{Pt_2Tl}$ (absorption maximum 2.56 μm^{-1}) at 2.72 μm^{-1} is small, the effects of the formation of $\mathrm{Pt_2Tl}$ on the observed luminescence can be ignored.

(40) Diffusion-limited rate constants for reactions between ions of opposite charge in aqueous solution are generally about 10^{11} L mol^{-1} s^{-1} (Connors, K. A. *Chemical Kinetics: The Study of Reaction Rates in Solution*; VCH: New York, 1990; pp 134–136). The lower estimates used here are based on experimental results for diffusion-controlled quenching of *$\mathrm{Pt_2}$ by doubly and triply charged cations in aqueous solution which lie in the range (4–5) × 10^{10} L mol^{-1} s^{-1} for ionic strengths comparable to those used here (Peterson, J, R.; Kalyanasundaram, K. *J. Phys. Chem.* **1985**, *89*, 2486–2492.). Since the diffusion-limited rate constant should be somewhat lower for the singly charged $\mathrm{Tl^I}$ ion, a value of 3 × 10^{10} L mol^{-1} s^{-1} for k_3 has been adopted. The value for k_7 should be somewhat smaller than that for k_3 due to the reduced ionic charge of *$\mathrm{Pt_2Tl}$ (−3) versus *$\mathrm{Pt_2}$ (−4) and for statistical reasons (one less available site for interaction). A decrease by a factor of 2 has been adopted in the present case to account only for the likely possiblilty that the interactions between *$\mathrm{Pt_2}$ and $\mathrm{Tl^I}$ occur at the axial sites of *$\mathrm{Pt_2}$.

(41) In Figure 1 the fraction of *$\mathrm{Pt_2}$ existing in the form of *$\mathrm{Pt_2Tl_2}$ is estimated from the equilibrium constants derived below to be less than 5%, a result supported by the results of resolving the spectra into three components. In Figure 3 the amount of free *$\mathrm{Pt_2}$ is similarly estimated to be less than 3% at all $\mathrm{Tl^I}$ concentrations.

s^{-1} as an upper limit to k_3, K_1 is calculated to be 1.92×10^5 L/mol, the range of values being $(1.17-3.05) \times 10^5$ L/mol (the slope of 1.17×10^5 L/mol imposes a strict lower limit to K_1).[42] Similarly, the value for K_2 can be established as 2.59×10^3 L/mol, the calculated range being $(2.52-2.63) \times 10^3$ L/mol for any reasonable value of k_7. With these values for K_1 and K_2 in hand, the corresponding free energies of formation at 25 °C for $*Pt_2Tl$ and $*Pt_2Tl_2$, ΔG_1 and ΔG_2, are calculated to be -30.1 ± 1.3 and -19.5 ± 0.1 kJ/mol, respectively. The difference between these values is also sensitive to the value assumed for k_3 and lies within the range 10.6 ± 1.1 kJ/mol for any value of k_3 greater than 1.9×10^{10} L mol^{-1} s^{-1}.

Since the absorption band shapes for Pt_2 and Pt_2Tl are nearly identical, as well as the luminescence band shapes for $*Pt_2$, $*Pt_2Tl$, and $*Pt_2Tl_2$, and since the fluorescence Stokes shifts for $*Pt_2$ and $*Pt_2Tl$ are nearly identical, the 0–0 energies for the three species can be used to provide estimates for ΔH_1 and ΔH_2.[43] It has been shown for $*Pt_2$ that the overlap of its phosphorescence and phosphorescence excitation spectra at 77 K is in excellent agreement with its spectroscopically determined origin and so provides a reliable estimate of its 0–0 transition energy.[44] Under the conditions employed here this overlap occurs at 2.056 ± 0.003 μm^{-1} (246.0 ± 0.4 kJ/mol).[45]

Since spin-forbidden absorption bands for Pt_2Tl and Pt_2Tl_2 have not been observed, the 0–0 transition energies for these species can not be determined by this procedure. However, an estimate of their values can be made by assuming that the difference between the phosphorescence band maximum and the 0–0 energy of these species is the same as that for $*Pt_2$, namely, 0.109 ± 0.004 μm^{-1}. This procedure yields 0–0 values of 1.895 ± 0.005 μm^{-1} (226.7 ± 0.6 kJ/mol) and 1.809 ± 0.004 μm^{-1} (216.4 ± 0.5 kJ/mol) for $*Pt_2Tl$ and $*Pt_2Tl_2$, respectively.[45]

It is now possible to calculate ΔH_1 and ΔH_2 for the formation of $*Pt_2Tl$ and $*Pt_2Tl_2$ from $*Pt_2$ and $*Pt_2Tl$, respectively, if it is assumed that the enthalpies of formation for the corresponding ground state species Pt_2Tl and Pt_2Tl_2 are negligible.[46] This assumption leads to values of $\Delta H_1 = -19.3 \pm 0.5$ kJ/mol and $\Delta H_2 = -10.3 \pm 0.5$ kJ/mol. The difference between these values is 9.0 ± 0.8 kJ/mol, identical within experimental uncertainty to the difference between the corresponding free energy values. This requires the entropies of formation for $*Pt_2Tl$ and $*Pt_2Tl_2$, calculated from the free energies and enthalpies to be $\Delta S_1 = 36 \pm 5$ J mol^{-1} K^{-1} and $\Delta S_2 = 31 \pm 2$ J mol^{-1} K^{-1}, to also be nearly equal. This appears to be a reasonable result given the proposed mechanism. A summary of the thermodynamic quantities for the formation of the two exciplexes is given in Table 2. To our knowledge the determination of thermodynamic parameters from luminescence data in this way is unprecedented.

Table 2. Summary of Estimated Values of Thermodynamic Parameters for the Formation of $*Pt_2Tl$ and $*Pt_2Tl_2$ from the Reactions between $*Pt_2$ and $*Pt_2Tl$, Respectively, with Tl^I in Aqueous Solution at 25 °C[a]

excited state	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
$*Pt_2Tl$	-30.1 ± 1.3	-19.3 ± 0.5	36 ± 5
$*Pt_2Tl_2$	-19.5 ± 0.1	-10.3 ± 0.5	31 ± 2

[a] The uncertainties given are estimates of random errors only and do not include systematic contributions resulting from the approximations and assumptions used to derive these values (see text).

The enthalpies shown in Table 2 are consistent with, and receive independent comfirmation from, the results of a recent photoacoustic calorimetry study of an aqueous solution of $*Pt_2$ with 0.01–0.02 mol/L $Tl(NO_3)$.[19] Under those conditions nearly all of the $*Pt_2$ is expected to be converted to $*Pt_2Tl_2$, and so the predominant excited state species can be identified as $*Pt_2Tl_2$, and not $*Pt_2Tl$ as previously assumed.[19] The difference between the enthalpies of formation for $*Pt_2$ and for the excited state species formed in the presence of Tl^I was reported to be -36 ± 21 kJ/mol,[19] in good agreement with the value of -29.6 ± 0.7 kJ/mol calculated here as the sum of the enthalpies of formation for $*Pt_2Tl$ and $*Pt_2Tl_2$.

The positive values for the entropies of formation of $*Pt_2Tl$ and $*Pt_2Tl_2$[47] deserve some comment since the formation of organic exciplexes is generally characterized by negative entropies lying in the range of -40 to -100 J mol^{-1} K^{-1}.[19] As pointed out elsewhere[19] the solvation of Tl^I by water molecules is accompanied by a large and negative absolute entropy of -72 J mol^{-1} K^{-1}.[48] Therefore, the desolvation of both Tl^I and, to a lesser extent, $*Pt_2$ upon the formation of $*Pt_2Tl$ and $*Pt_2Tl_2$ could account for the positive entropies of formation determined here.

Qualitatively, the positive entropies are consistent with the temperature dependent spectra shown in Figure 5 in that an increase in temperature leads to an increase in the intensity of exciplex luminescence relative to that of $*Pt_2$. The data shown in Figure 5 cannot provide reliable quantitative values for ΔH and ΔS however since, among other things, the solvent undergoes a phase transition in this region, the solution is air-saturated, and the spectra are uncorrected. Analysis of temperature dependent data of the type shown in Figures 1 and 3 should enable reliable thermodynamic parameters to be obtained.

The positive entropies obtained for what is presumably an associative process highlight the importance of obtaining reaction volumes for exciplexes when additional insight into the dynamics of their formation is needed. Thus, the negative reaction volume of -11 ± 1 cm^3/mol determined by photoacoustic calorimetry[19] (presumably for the formation of $*Pt_2Tl_2$ from $*Pt_2$ and $2Tl^I$) is, as expected, indicative of bond formation between the reactants. In contrast the positive entropy of 67 ± 5 J mol^{-1} K^{-1} (the sum of the entropies of formation

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(42) The discrepancy between this value and that reported previously[18] is due to the more effective deoxygenation procedure used here as well as a more reliable procedure for resolving the phosphorescence spectra into their component bands.

(43) Discussions of the relationship between exciplex spectroscopic and thermodynamic properties can be found: Stevens, B. *Adv. Photochem.* **1971**, *8*, 161–226. Beens, H.; Weller, A. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: New York, 1975; Vol. 2, Chapter 4. See also refs 1 and 37. As usual, it is assumed here that the differences between internal energies and enthalpies are negligible.

(44) Fordyce, W. A.; Brummer, J. G.; Crosby, G. A. *J. Am. Chem. Soc.* **1981**, *103*, 7061–7064. The 0–0 energy was determined to be 2.033 μm^{-1} under the conditions reported in that study.

(45) The error given is a measure only of the uncertainty in determining the wavenumber of the overlap of the phosophorescence and phosphorescence excitation spectra. It does not account for any systematic error resulting from the assumptions behind this procedure. In any case, judging from the results reported elsewhere[44] any such systematic error is expected to be small (~0.001 μm^{-1}).

(46) This is reasonable since the value of the ground state equilibrium constant for the formation of Pt_2Tl from Pt_2 and Tl^I as estimated from absorbance data is somewhat less than 6 ± 4 L/mol, and the corresponding entropy is probably small and positive.

(47) The uncertainties given for ΔS_1 and ΔS_2 are estimates of the random errors only. The two key assumptions made in the derivation of the thermodynamic quantities that k_3 is greater than or equal to 1.9×10^{10} L mol^{-1} s^{-1} and that the ground state enthalpies of formation for both Pt_2Tl and Pt_2Tl_2 are negligible may lead to systematic errors in the derived values. However, if k_3 is less than 1.9×10^{10} L mol^{-1} s^{-1} and if the enthalpies of formation for Pt_2Tl and Pt_2Tl_2 are less than 0, both effects would make the calculated entropies more positive than those given. Furthermore, a positive entropy for the sum of ΔS_1 and ΔS_2 of 46 ± 71 J mol^{-1} K^{-1} is calculated from the free energies determined here and the enthalpy (presumably corresponding to the sum of ΔH_1 and ΔH_2) of -36 ± 21 kJ/mol derived from photoacoustic calorimetry measurements.[19]

(48) Marcus, Y. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 233–242.

for $*Pt_2Tl$ and $*Pt_2Tl_2$) determined here is generally attributed (in the absence of a consideration of desolvation energies) to ligand loss and represents an exception to the empirical observation that negative reaction volumes are accompanied by negative reaction entropies.[19] It is unclear why in the present case desolvation effects appear to manifest themselves so clearly in entropy but not volume changes.

In trying to assess the strengths of the Pt–Tl bonds in $*Pt_2Tl$ and $*Pt_2Tl_2$, the enthalpies of formation reported in Table 2 should be viewed only as approximations of the actual bond energies between Tl^I and $*Pt_2$. This is because the same desolvation effects which appear to influence the entropies will undoubtedly influence the enthalpies of these reactions as well. The absolute enthalpy of formation of aqueous Tl^I from gaseous Tl^0 is known to be −329 kJ/mol,[48,49] and provides an indication of the importance of such desolvation effects. In fact, the situation is further complicated by the fact that Tl^I may displace K^I (the thermodynamics of hydration of the two ions are nearly identical[48,49]) upon interacting at the axial sites of $*Pt_2$.

Structural and Electronic Properties. An attempt has been made to estimate the Pt–Tl bond distance in $*Pt_2Tl$ by molecular mechanics calculations.[19] It was based on the known Pt–Pt bond lengths for Pt_2 and $*Pt_2$ of 2.92 and 2.71 Å, respectively,[17] and an assumed Pt–Pt bond length in $*Pt_2Tl$ of 2.71 Å, along with the experimentally determined volume of formation of −11 cm^3/mol for the interaction of $*Pt_2$ with Tl^I ions.[19] Since the predominant excited state species under the conditions of the photoacoustic calorimetry experiments was presumably $*Pt_2Tl_2$, and not $*Pt_2Tl$ as assumed, the derived Pt–Tl bond length of 2.6 Å is therefore most likely too short, and a value in the range 2.7–3.0 would seem more realistic.

The ability of Tl^I to form inner-sphere exciplexes with $*Pt_2$ can be understood in terms of the structural and electronic properties of $*Pt_2$ and Tl^I. $*Pt_2$ possesses two axial coordination sites which, on steric grounds alone,[50] appear to be more susceptible to coordination by Tl^I than are the corresponding sites in Pt_2. But more importantly the electronic structure of $*Pt_2$ also favors axial interactions with Tl^I ions compared to Pt_2, for which the ground state species Pt_2Tl and Pt_2Tl_2 should experience only relatively weak van der Waals interactions due to filled $5d_{z^2}$ (Pt) and 6s (Tl) orbital mixing with empty $6p_z$ orbitals and where the resultant metal–metal bond orders are predicted to be 0.[51,52] Light absorption by diamagnetic Pt_2 results in the promotion of an electron from a σ^* ($5d_{z^2}$) antibonding orbital to a bonding σ ($6p_z$) orbital and a concomitant increase in the Pt–Pt bond order from 0 to 1.[17] These half-filled σ^* ($5d_{z^2}$) and σ ($6p_z$) frontier orbitals of $*Pt_2$ lying along the axial sites of the molecule can interact with the nearly isoenergetic filled 6s and empty $6p_z$ orbitals of Tl^I ions, respectively.

To the extent that these frontier orbitals are isolobal, the resultant relativistically influenced[51] metal–metal bonding in $*Pt_2Tl$ can be interpreted analogously to that in the lowest triplet excited state of $Tl_2Pt(CN)_4$[51] and other species involving linear arrays of three such heavy metal ions. Any Pt–Tl bonding formed in $*Pt_2Tl$ can be viewed as coming at the expense of the Pt–Pt bond in $*Pt_2$. In fact, if the three metal atoms were the same, and had identical coordination environments, then the resultant molecular orbital diagram would lead to the prediction of a total Pt–Pt–Tl formal bond order of 1 in which each metal–metal bond would have a bond order of 1/2.[52] The interaction between $*Pt_2Tl$ and a second Tl^I ion should lead to further delocalization of electrons in the proposed Tl–Pt–Pt–Tl bonding unit and can be expected to provide some additional stability, although the total metal–metal bond order is still predicted to be only 1.

This simple molecular orbital model[52] predicts that the direct metal–metal bonding between $*Pt_2$ and Tl^I should, as observed, lower the energies of the luminescence bands in $*Pt_2Tl$ and $*Pt_2Tl_2$ compared to $*Pt_2$. Furthermore, this bonding must be weak to produce such a small energy lowering (<20 kJ/mol in each case). In spite of these small shifts in luminescence energies, it is still remarkable that neither the luminescence quantum yield nor lifetime of $*Pt_2$ is substantially altered upon formation of $*Pt_2Tl$ and $*Pt_2Tl_2$, which suggests that the dynamics of the excited state deactivation processes are largely determined by the diphosphito ligand framework (which presumably is little affected by the Pt–Tl interactions). Such behavior appears to be unique among inorganic exciplexes and provides an interesting contrast to the claim for exciplex formation between $*Ir(phen)_3^{3+}$ or $*Ir(trpy)_2^{3+}$ and $HgCl_2$.[6] In those cases just the opposite effect occurs; only the luminescence quantum yields and lifetimes, not the energies, of the excited states are observed to change.

The question of what really constitutes an exciplex has been raised, and it was suggested that, rather than the more restrictive criterion that the corresponding ground state interaction be dissociative ("true" [6] or "ideal" [12] exciplexes), any situation in which the excited state equilibrium constant is larger than the corresponding ground state value provides a more useful definition of exciplex formation.[12,18] For example, it would make little sense to refer to $*Pt_2Tl_2$, but not $*Pt_2Tl$, as an exciplex simply because the equilibrium constant for Pt_2Tl might be greater than 1 whereas that for Pt_2Tl_2 might be less than 1. Furthermore, it even seems reasonable to refer to the singlet excited state of Pt_2Tl as an exciplex, even though it is observed to form only as a result of light absorption by the ground state Pt_2Tl ion pair.

Conclusions

$*Pt_2Tl$ and $*Pt_2Tl_2$ are the only reported examples of exciplexes formed as a result of metal–metal bonding between the reactants, and further illustrate the tendency of Tl^I cations to coordinate to 5d-metal ions.[51,53] Their intense luminescence and long lifetimes are unparalleled among inorganic exciplexes and allow for the novel type of luminescence data analysis described here. This analysis has enabled estimates of excited state kinetic and thermodynamic values to be made, making these perhaps the most thoroughly characterized inorganic exciplexes to date. These results add to the growing body of evidence that highlights the relative ease with which coordina-

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(49) Marcus, Y. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2995–2999.

(50) The more extensive contraction of the P atom planes (0.52 ± 0.13 Å; Thiel, D. J.; Livins, P.; Stern, E. A. *Nature (London)* **1993**, *362*, 40–43; **1993**, *363*, 565) surrounding each Pt atom compared to the contraction of the two Pt atoms (~0.20 Å[17]) in the lowest triplet excited state relative to the singlet ground state results in a greater exposure of the Pt atoms to incoming Tl^I ions in $*Pt_2$ compared to Pt_2.

(51) Accounts of the Pt–Tl bonding in $Tl_2Pt(CN)_4$ (Nagle, J. K.; Balch, A. L.; Olmstead, M. M. *J. Am. Chem. Soc.* **1988**, *110*, 319–321. Ziegler, T.; Nagle, J. K.; Snijders, J. G.; Baerends, E. J.; Ravenek, W. *J. Am. Chem. Soc.* **1989**, *111*, 5631–5635) and a detailed study of its luminescence (Weissbart, B.; Balch, A. L.; Tinti, D. S. *Inorg. Chem.* **1993**, *32*, 2096–2103) have been reported.

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tively unsaturated metal compounds in triplet excited states can undergo exciplex or eximer formation.$^{9-22}$

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