Diphosphine Platinum(II) Photo-oxidants. Synthesis and Photochemistry of Luminescent Diphosphine Platinum(II) Complexes of 5,6-Dimethyl-1,10-phenanthroline

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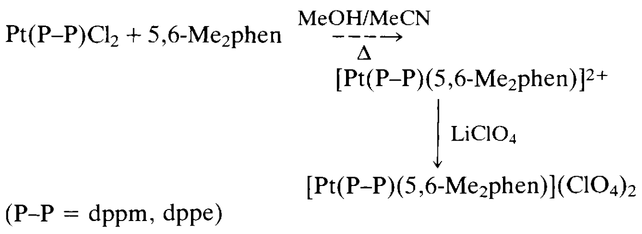
The $[Pt(P–P)(5,6\text{-}Me_2phen)]^{2+}$ complexes (P–P = chelating diphosphine, $5,6\text{-}Me_2phen$ = 5,6-dimethyl-1,10-phenanthroline) exhibit photoluminescence at 490—495 nm: the excited state lifetimes and excited oxidation potentials are 22—25 μs and ~2.1 V *vs.* normal hydrogen electrode (NHE), respectively.

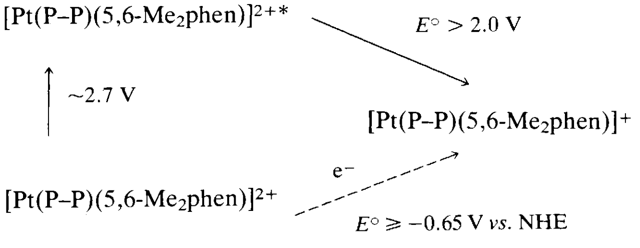
There has been considerable interest in the photochemistry of transition metal polypyridine complexes, which have been found to have useful applications in photo-induced electron transfer reactions, photo-catalysts, and studies of DNA recognition.[1,2] The $Ru(bpy)_3^{2+}$ (bpy = 2, 2′-bipyridine) and its related complexes are commonly employed in these studies. This class of compounds, however, are co-ordinatively saturated, and hence their interactions with substrates are usually restricted to ionic/hydrophobic binding. In the search for luminescent metal complexes which may covalently attach to biomolecules and undergo inner-sphere atom-transfer reactions, we are interested in those complexes which are co-ordinatively unsaturated and have long-lived and high-energy excited states in fluid solutions. In previous work, we have found that the monomeric dicyanoplatinum(II) complexes of π-aromatic diimines are sensitizers for photo-redox reactions.[3] However, the $Pt(L–L)(CN)_2$ (L–L = aromatic diimine) complexes suffer from the disadvantages that the excitation energies for this class of compounds are in the high UV region and they are virtually insoluble in protic solvents, thus limiting their applications in photo-redox studies in aqueous solutions. We describe here the excited-state properties of two dicationic $[Pt(P–P)(5,6\text{-}Me_2phen)]^{2+}$ {P–P = dppm, [bis(diphenylphosphino)methane] or dppe, [bis(diphenylphosphino)ethane]; $5,6\text{-}Me_2phen$ = 5,6-dimethyl-1,10-phenanthroline} complexes, which fulfil all the extreme features required in probing inorganic as well as bio-inorganic photochemistry.

The synthesis of the platinum complexes $[Pt(P–P)(5,6\text{-}Me_2phen)]^{2+}$ [P–P = (**1**), dppm; (**2**), dppe] are outlined in Scheme 1. They are yellow crystalline solids, which are very stable in the solid state and in fluid solutions. Table 1 summarizes their UV-VIS and emission spectral data. Like $[Pt(phen)_2]^{2+}$ (phen = 1,10-phenanthroline), both (**1**) and (**2**) have an intense absorption band at 367 nm with $\lambda_{max.} > 10^3$ $mol^{-1}\ dm^3\ cm^{-1}$, which is probably due to the spin-allowed metal (Pt) to ligand ($5,6\text{-}Me_2phen$) charge transfer transition (MLCT). Figure 1 shows the optical spectrum of (**1**). The presence of a low energy and intense absorption band is essential to the $Pt^{II}\text{-}5,6\text{-}Me_2phen$ complexes for applications in photochemistry and photobiology.

Unlike $[Pt(bpy)_2]^{2+}$ or $[Pt(phen)_2]^{2+}$ which have vanishingly weak emission at room temperature,[4] excitation of (**1**) or (**2**) in degassed acetonitrile at 367 nm leads to an intense photoluminescence centred at 490—495 nm (Figure 2); the emission spectral data are summarized in Table 1. The large Stoke shift between the excitation and emission energies and the long lifetimes of the emission suggest that the emitting



Scheme 1



Scheme 2

Table 1. UV-VIS absorption and emission spectral data of (**1**) and (**2**).

Complex	$\lambda_{max.}$/nm	(ε/mol^{-1} dm^3 cm^{-1})^a	$\lambda_{max.}^{emission}$ /nm	τ_0/μs	k_{self}/mol^{-1} dm^3 s^{-1}
(**1**)	382(sh)	(1.39×10^3)	490	25	4.7×10^7
	367	(1.53×10^3)			
	320(sh)	(5.84×10^3)			
	291	(2.43×10^4)			
	282	(2.39×10^4)			
(**2**)	381(sh)	(9.46×10^2)	495	22	1.7×10^8
	367	(1.05×10^3)			
	318(sh)	(5.02×10^3)			
	290	(1.77×10^4)			
	281	(1.83×10^4)			

[a] sh = shoulder.

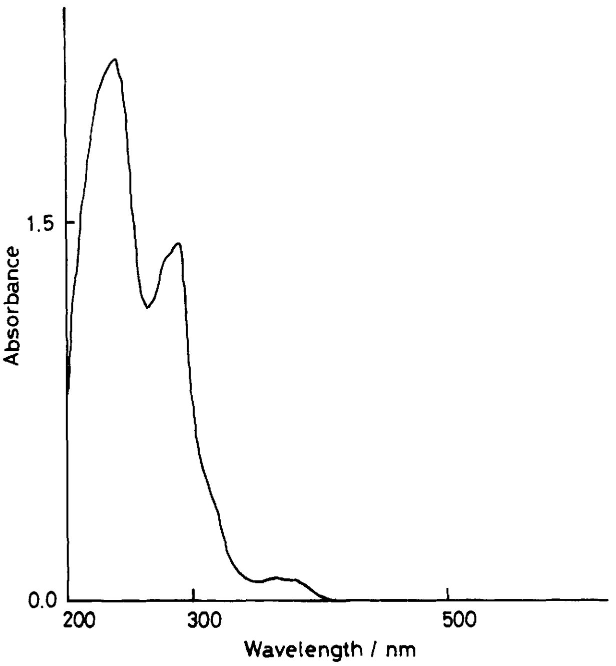


Figure 1. UV-VIS spectrum of (**1**) in acetonitrile.

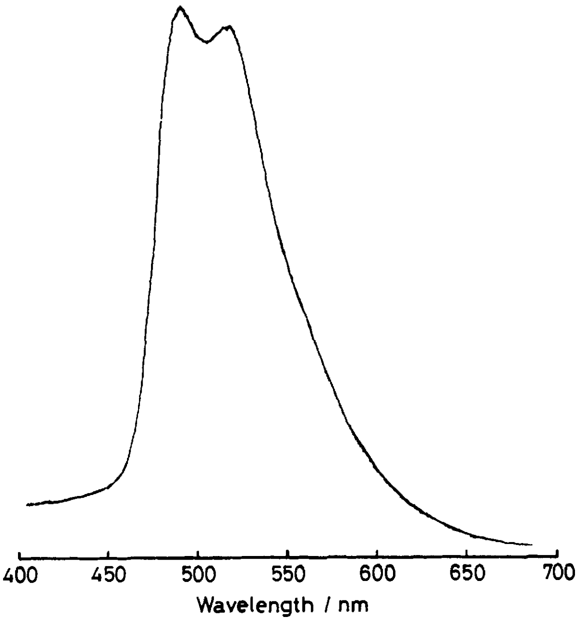


Figure 2. Room temperature emission spectrum of (**1**) in degassed acetonitrile (excitation: 367 nm).

state is an excited triplet. As in the case of [Pt(5,5'-Me_2bpy)$(CN)_2$] (5,5'-Me_2bpy = 5,5'-dimethyl-2,2'-bipyridine),[3] the emission lifetime (τ) shows dependence on the concentration of the platinum complex. Linear plots between $1/\tau$ and [Pt] have been obtained, from which the τ_0 (lifetime at infinite dilution) and k_{self} (self quenching rate constant) values were determined (Table 1). The much lower k_{self} values of (**1**) and (**2**) compared to [Pt(5,5'-Me_2bpy)$(CN)_2$] can readily be explained by the dicationic nature of the former system, which prohibits the approach of two platinum complexes through electrostatic repulsive interaction. Complexes (**1**) and (**2**) have very long excited state lifetimes, making them very desirable for photochemical studies. In fact, luminescent metal complexes with excited state lifetimes greater than 20 μs in fluid solutions at room temperature are rare; the reported examples are $[Mo_6Cl_{12}]^{2-}$ (ref. 5) and $[Au_2(dppm)_2]^{2+}$.[6]

Taking the spectroscopic and electrochemical data together, the excited redox potentials of (**1**) and (**2**) can be estimated. Complex (**1**) [or (**2**)] undergoes irreversible electrochemical reduction at potential −0.61 (−0.65) V *vs.* normal hydrogen electrode (NHE). From the emission spectrum, the 0–0 energy for (**1**) or (**2**) is about 2.7 eV. Thus, the excited triplet state of $[Pt(P–P)(5,6\text{-}Me_2phen)]^{2+}$ is a very powerful oxidant, with $E^\circ\{[Pt(P–P)(5,6\text{-}Me_2phen)]^{2+*}/[Pt(P–P)(5,6\text{-}Me_2phen)]^{+}\}$ estimated to be greater than 2.0 V *vs.* NHE (Scheme 2). To our knowledge, this is the first example of a co-ordinated unsaturated metal complex with excited state potential greater than 2 V and a long lifetime in fluid solutions. Although the excited states of dioxo-osmium(VI) and nitrido-osmium(VI) amine complexes are also powerful oxidants,[7] the reported osmium complexes are co-ordinatively saturated.

Given the high energies and long emission lifetimes of complexes (**1**) and (**2**), it is not difficult to envisage that these two platinum complexes should possess rich photochemistry. Preliminary studies established that the excited $[Pt(P–P)(5,6\text{-}Me_2phen)]^{2+}$ species rapidly undergoes reductive quenching with organic hydrocarbons. For complex (**1**) in acetonitrile, the quenching rate constants determined by the equation $\tau_0/\tau = 1 + k_q \tau_0$ [organic substrate] are 6.0×10^9 and 1.9×10^9 mol^{-1} dm^3 s^{-1} at 25 °C for hexamethylbenzene and pentamethylbenzene, respectively. The high quenching rate constants are in accordance with a redox quenching pathway.

The present mixed phosphine and aromatic diimine complexes of platinum(II) should allow the tuning in geometry, size, hydrophobicity, and chirality through variation in the structure of chelating diphosphine. The platinum(II) ion is also well known for its affinity towards binding to biomolecules. Preliminary studies indicate that the UV-VIS absorption spectra of [Pt(P–P)(5,6-Me$_2$phen)]$^{2+}$ are perturbed by the addition of nitrogen bases such as imidazole. Thus, one could envisage that this class of compounds could be useful for studies of DNA recognition by transition metal complexes.[2]

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