Novel Luminescent Platinum(II) Complexes. Photophysics and Photochemistry of $Pt(5,5'\text{-}Me_2bpy)(CN)_2$ ($5,5'\text{-}Me_2bpy$ = 5,5'-Dimethyl-2,2'-bipyridine)

Chi-Ming Che,* Kam-To Wan, Li-Yan He, Chung-Kwong Poon, and Vivian Wing-Wah Yam
Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong

The $Pt(5,5'\text{-}Me_2bpy)(CN)_2$ complex ($5,5'\text{-}Me_2bpy$ = 5,5'-dimethyl-2,2'-bipyridine) displays intense photoluminescence in fluid solution (emission maximum, 502 nm; τ_0, 6.3 μs) at room temperature; the excited $\pi\pi^*$ triplet of $Pt(5,5'\text{-}Me_2bpy)(CN)_2$ is a powerful one-electron oxidant ($E°$, ~1.0 V) and reductant ($E° \leqslant -1.5$ V *vs.* $AgNO_3/Ag$) which undergoes oxidative and reductive quenching with inorganic and organic substrates.

Transition metal complexes which are strong oxidants and reductants in excited states have important applications in photo-chemical energy storage reactions[1] and in the study of Marcus electron transfer theory.[2] Despite recent advances in inorganic photochemistry, there are few examples of highly emissive metal complexes which are co-ordinatively unsaturated and have high energy and long-lived excited states in fluid solutions. In designing new photo-catalysts, we are interested in the $16e^-$ four-co-ordinated platinum(II) complexes because of recent works on $[Pt_2(P_2O_5H_2)_4]^{4-}$.[3] We describe here the photophysics and photochemistry of $Pt(5,5'\text{-}Me_2bpy)(CN)_2$ ($5,5'\text{-}Me_2bpy$ = 5,5'-dimethyl-2,2'-bipyridine). The result illustrates that a new class of relatively simple luminophores, $Pt(L\text{–}L)(CN)_2$ (L–L = aromatic di-imines) are good sensitizers for photoredox reactions.[4]

The $Pt(5,5'\text{-}Me_2bpy)(CN)_2$ complex was prepared by the reaction of $Pt(CN)_2{\cdot}xH_2O$ and $5,5\text{-}Me_2bpy$ in refluxing dimethylformamide (DMF). The complex is an orange-yellow solid which gave satisfactory elemental analyses and shows two $\nu(C{\equiv}N)$ stretches at 2150 and 2140 cm^{-1}. In DMF, electrochemical reduction of the platinum complex is reversible. Two reversible one-electron couples ($\Delta E_p \sim 60$—80 mV, $i_{pa}/I_{po} \simeq 1$ for scan rates of 50—200 mVs^{-1}) occur at potentials of −1.59 and −2.23 V *vs.* $Ag/AgNO_3$ (0.1 M). With reference to previous electrochemical works[4] on other metal-2,2'-bipyridine (bpy) complexes; the electrode reactions are ligand-centred, irreversible oxidation of the Pt^{II} complex occurs at ~1.1 V.

$$Pt(5,5'\text{-}Me_2bpy)(CN)_2 + e^- \rightarrow Pt(5,5'\text{-}Me_2bpy^-)(CN)_2, E° = -1.59\text{ V}$$

$$Pt(5,5'\text{-}Me_2bpy^-)(CN)_2 + e^- \rightarrow Pt(5,5'\text{-}Me_2bpy^{2-})(CN)_2, E° = -2.23\text{ V}$$

The absorption spectrum of $Pt(5,5'\text{-}Me_2bpy)(CN)_2$ in acetonitrile (Figure 1) is featured by an intense vibronic structured band centred at 320 nm (ε = 1.6 × 10^4 $mol^{-1}\,dm^3\,cm^{-1}$), which is the internal ligand $\pi \rightarrow \pi^*$ transition. There are also some weak absorptions at 350—400 nm. At room temperature, excitation of $Pt(5,5'\text{-}Me_2bpy)(CN)_2$ at 320—360 nm in acetontrile leads to an emission at 502 nm with resolved vibronic bands at 470 and 535 nm (Figure 2). The quantum yield of the emission in acetonitrile is $\sim 10^{-3}$ ([Pt] ~ 10^{-4} M). The spacings between the vibrational levels are 1300—1400 cm^{-1}, which correspond to the C=N and C=C stretches of the aromatic di-imine ligand in the excited state. The lifetime (τ) of the emission depends on the concentration of the Pt^{II} complex. A linear Stern–Volmer plot of $1/\tau$ *vs.* $[Pt^{II}]$ was found with τ_0 (lifetime at infinite dilution) and k_q (self-quenching rate constant) being 6.3 μs and 4.8 × 10^9 $mol^{-1}\,dm^3\,s^{-1}$. We assign the emission to

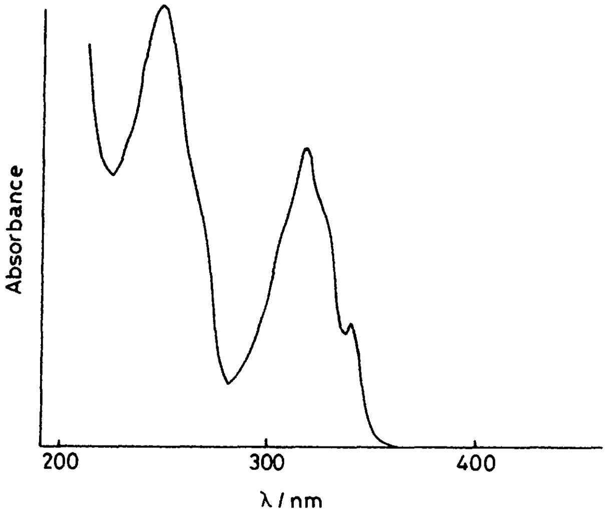


Figure 1. Absorption spectrum.

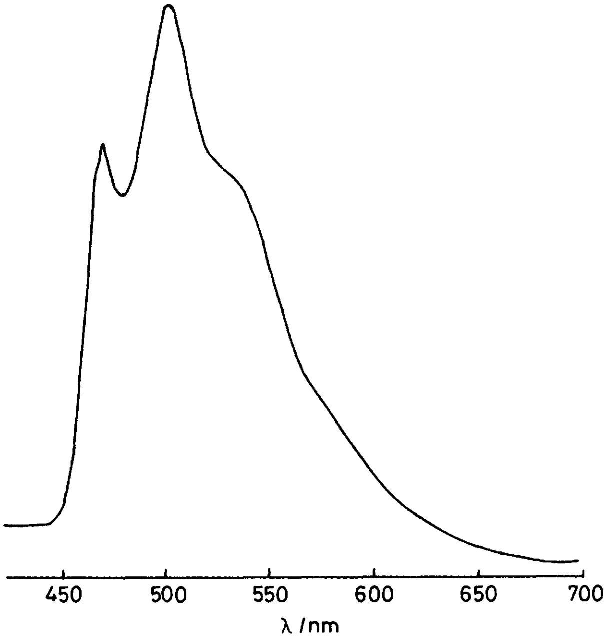
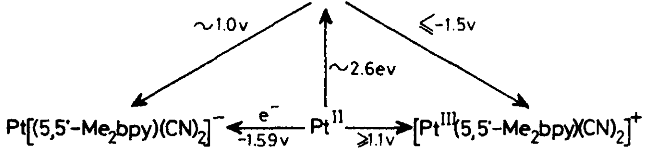


Figure 2. Emission spectrum.



Scheme 1

be due to the excited ππ* triplet state, with its lifetime and emission intensity being perturbed by the Pt^{II} ion.

Taking the spectroscopic and electrochemical data, the excited state redox potentials [V *vs.* $Ag/AgNO_3$ (0.1 M)] can be estimated, as illustrated in Scheme 1.

Thus the ππ* triplet is a good reductant and an extremely powerful oxidant having E° of ~1.0 V *vs.* $Ag/AgNO_3$ [~1.6 V *vs.* Normal hydrogen electrode (N.H.E.)]. In fact, there are few inorganic photo-oxidants which are long-lived and with excited potentials greater than 1.6 V *vs.* N.H.E.[6]

Experimentally, we have demonstrated both oxidative and reductive quenching of the ππ* excited state by methyl viologen (MV^{2+}) and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) respectively, with the respective quenching rate constants of 1.78×10^8 and $2.90 \times 10^{10}\,M^{-1}\,s^{-1}$ in acetonitrile. Flash-photolysis experiments provided spectroscopic evidence for the MV^+ ($\lambda_{max.}$ ~ 395,605 nm) and $TMPD^+$ ($\lambda_{max.}$ ~ 605 nm) intermediates, suggesting that the quenching reactions are electron-transfer in nature, as represented by equations (1) and (2). The nature of the photogenerated $[Pt(5,5\text{-}Me_2bpy)(CN)_2]^+$ is uncertain; however, we tentatively assign it to be a Pt^{III} species. The MV^+ and $[Pt(5,5'\text{-}Me_2bpy)(CN)_2]^+$ undergo rapid back reaction [equation (3)] with diffusion controlled rate (k_3 ~ $10^9\,M^{-1}\,s^{-1}$).

$$Pt^* + MV^{2+} \xrightarrow{k_1} MV^+ + [Pt(5,5'\text{-}Me_2bpy)(CN)_2]^+ \quad (1)$$

$$Pt^* + TMPD \xrightarrow{k_2} TMPD^+ + [Pt(5,5'\text{-}Me_2bpy^-)(CN)_2]^- \quad (2)$$

$$MV^+ + [Pt(5,5'\text{-}Me_2bpy)(CN)_2]^+ \xrightarrow{k_3} MV^{2+} + Pt(5,5'\text{-}Me_2bpy)(CN)_2 \quad (3)$$

Quenching of the ππ* excited triplet of $Pt^{II}(5,5'\text{-}Me_2bpy)(CN)_2$ by organic halides has also been observed. The respective quenching rate constants for CH_3I, C_2H_5I, and $(CH_3)_2CHI$ are 1.6×10^7, 1.5×10^7, and $2.2 \times 10^7\,M^{-1}\,s^{-1}$ respectively. The relatively small difference in quenching rates between primary and tertiary alkyl iodides suggests an electron transfer mechanism for the quenching reactions.

$$Pt^* + RI \rightarrow [Pt(5,5'\text{-}Me_2bpy)(CN)_2]^+ + RI^-$$

From these and related experiments, it is apparent that $[Pt(5,5'\text{-}Me_2bpy)(CN)_2]$ exhibits rich photoredox chemistry. An extensive study on the photoredox properties of this class of compounds should allow suitable design of new photocatalysts and further experiments on the reactivity of the excited state are in progress.

K. T. W. acknowledges the receipt of a Croucher Studentship, administered by the Croucher Foundation. Financial support from the University of Hong Kong and Croucher Foundation are gratefully acknowledged.

Received, 6th January 1989; Com. 9/00113A

References

1 For examples, see G. J. Kavarnos and N. J. Turro, *Chem. Rev.*, 1986, **86**, 401; V. Balzani and N. Sabbatini, *ibid.*, 1986, **86**, 219; M. Gratzel, in 'Energy Resources through Photochemistry and Catalysis,' Academic Press, 1983; A. W. Maverick and H. B. Gray, *Pure Appl. Chem.*, 1980, **52**, 2339.

2 R. Ballardini, G. Varani, M. T. Indelli, F. Scandola, and V. Balzani, *J. Am. Chem. Soc.*, 1978, **100**, 7219; C. Creutz, A. D. Keller, N. Sutin, and A. P. Zipp, *ibid.*, 1981, **104**, 3618; A. M. English, V. R. Lum, P. J. Delaive, and H. B. Gray, *ibid.*, 1982, **104**, 870; K. C. Cho, C. M. Che, F. C. Cheng, and C. L. Choy, *ibid.*, 1984, **106**, 6843.

3 A. P. Zipp, *Coord. Chem. Rev.*, 1988, **84**, 47; D. M. Roundhill, H. B. Gray, and C. M. Che, *Acc. Chem. Res.*, 1989, **22**, 55.

4 Related works on the photochemistry of platinum(II) complexes include, A. Vogler and H. Kunkely, *J. Am. Chem. Soc.*, 1981, **103**, 1559; R. H. Hill and R. J. Puddephatt, *ibid.*, 1985, **107**, 1218; L. Chassot, A. von Zelewsky, D. Sandrini, M. Maestri, and V. Balzani, *ibid.*, 1986, **108**, 6084; D. Sandrini, M. Maestri, V. Balzani, L. Chassot, and A. von Zelewsky, *ibid.*, 1987, **109**, 7720.

5 T. Saiji and S. Aoyagui, *J. Electroanal. Chem. Interfacial Electrochem.*, 1980, **110**, 329; A. A. Vlcek, *Coord. Chem. Rev.*, 1982, **43**, 39.

6 For examples, see C. M. Che, V. W. W. Yam, K. C. Cho, and H. B. Gray, *J. Chem. Soc., Chem. Commun.*, 1987, 948 and references cited therein; C. M. Che, T. C. Lau, H. W. Lam, and C. K. Poon, *ibid.*, 1989, 114.