

Triphenylphosphine Complexes of Platinum(0); their Absorption and Emission Spectra and Luminescence Lifetimes

SILVANA SOSTERO, MAURIZIO LENARDA*, ORAZIO TRAVERSO**

Centro di Studio sulla Fotochimica e Reattività Degli Stati Eccitati dei Composti di Coordinazione and Istituto Chimico, Università di Ferrara, 44100 Ferrara, Italy

W. JOHN REED and TERENCE J. KEMP

Department of Chemistry and Molecular Sciences, University of Warwick, Coventry, CV4 7AL, U.K.

Received May 11, 1981

The spectroscopy and photophysics of a series of Pt⁰ complexes [L₂Pt·X] (L = PPh₃, AsPh₃; X = ethylene, tetracyanoethylene, fumaronitrile and tetracyanocyclopropane) have been examined from the following viewpoints:

- i) the dependence of the ground-state absorption peaks upon solvent,*
- ii) the vibronic progression of the observed structure of the emission band in a host of cellulose acetate film,*
- iii) the luminescence lifetimes.*

It is concluded that the luminescence is ligand-centred, but with a lifetime strongly affected by the heavy atom.

Complexes of type [L₂Pt·X] (L = PPh₃, AsPh₃; X = C₂H₄, TCNE, FMN and TCCP, where TCNE = tetracyanoethylene, FMN = fumaronitrile, TCCP = tetracyanocyclopropane) show luminescence in the 20000–28000 cm⁻¹ region following excitation in their low-energy absorption bands (260–315 nm). This emission is unusually energetic for transition metal complexes, most of these exhibiting *d*–*d* emission at λ > 500 nm [1]. This property makes the [L₂PtX] complexes potential candidates as sensitizers of electron- and energy-transfer processes in solution. We report here:

- i) The absorption maxima in a variety of solvents, which indicate ν_{max} to be rather dependent on the solvent;*

- ii) The highly structures luminescence and the luminescence lifetimes;*

- iii) The influence of spin-orbit coupling (SOC) caused by the heavy-metal centre on the lifetimes.*

Experimental

The compounds under consideration were prepared as previously described [2, 3]. Solvents were of spectroscopic grade and were dried with molecular sieves. Electronic absorption spectra were measured on Cary 219 and Perkin-Elmer 323 spectrophotometers. Emission spectra were obtained both at 77 and 298 K on a Perkin-Elmer MPF-3 spectrofluorimeter equipped with a Hamamatsu R955 photomultiplier tube. Lifetime determinations were performed at room temperature on a frequency-quadrupled (264.8 nm) neodymium laser, and at 77 and 300 K with an Ortec time-resolved spectrometer (output pulse duration 3 ns at half the maximum intensity).

Results and Discussion

Absorption Spectra

Table I summarises the salient absorption features of the compounds investigated in the present study. The bands in the 30000–37000 cm⁻¹ region arise from the complex formation, because C₂H₄ and the cyanide-substituted ligands (FMN, TCNE and TCCP) do not show strong absorptions below 37000 cm⁻¹. The dominant bands in the 37000–45500 cm⁻¹ are probably a composite of those of the various ligands (C₂H₄, cyanoalkenes, the cyanoalkane and aryl-containing phosphines [4]). The large solvent effect on the 30000–37000 cm⁻¹ bands in the spectra of Pt complexes (Table I) has been found to be of the same magnitude (*ca.* 1200 cm⁻¹) on going from ethanol to chloroform and in the same direction as those for a number of complexes of Pt(II), Mo, W and Fe [6]. A correlation [5, 6] between the values of ν_{max} and E_T (the Dimroth solvent parameter) [7] is clear from Table I. Since the solvent-dependent band in transition metal complexes can be assigned to metal to ligand charge transfer (MLCT) [5, 6], it seems likely that the solvent-dependent transitions observed in this series of Pt(0) complexes can be attributed to a MLCT process from the *d*-orbitals of Pt to the π*-orbitals of the alkene. On the other hand, successive substitution of the H atoms of the coordinated ethylene molecule by cyano-groups shifts the bands towards lower ener-

*Present address: Facoltà di Chimica Industriale, Università di Venezia, Venezia, Italy

**Author to whom all correspondence should be addressed.

TABLE I. Absorption Data (298 K) of Pt(0) Complexes in Various Solvents with the Respective Solvent E_T Values.

Solvent	$E_T/\text{kJ mol}^{-1}$	$\nu_{\text{max}}/\text{cm}^{-1}$					
		Compound: ^a	1	2	3	4	5
EtOH	217		35 086	33 989	33 333	34 483	32 787
i-PrOH	203		34 800	33 557	33 000	34 193	32 573
t-BuOH	184		34 350	33 223	32 467	33 784	32 150
CH ₂ Cl ₂	172		34 100	32 895	32 258	33 445	31 949
CHCl ₃	164		33 898	32 787	32 051	33 113	31 746
		$\Delta\nu (\text{EtOH}-\text{CHCl}_3)/\text{cm}^{-1} =$	1 188	1 111	1 282	1 370	1 041

^aCompound: 1 = [(PPh₃)₂Pt·C₂H₄]; 2 = [(PPh₃)₂Pt·FMN]; 3 = [(PPh₃)₂Pt·TCNE]; 4 = [(PPh₃)₂Pt·TCCP]; 5 = [(AsPh₃)₂Pt·FMN].

TABLE II. Spectroscopic and Kinetic Characteristics^a of Selected [(MPh₃)₂Pt·X] Complexes ($\lambda_{\text{ex}} = 300 \text{ nm}$).

M	X	Medium	Emission _{max} /nm	Vibronic Structure/cm ⁻¹	Lifetime ^b /ns
P	C ₂ H ₄	CA film	385	405	42 ± c ^c
		EPA-CHCl ₃ , 77 K	390		45 ± 5 ^d
		EtOH	400		
P	FMN	CA film	390	410	47.8 ± 0.4 ^c
		EtOH	410		45 ± 3 ^c
		MeOH	410		
P	TCNE	CA film	402	423	200 ± 2 ^c
		EtOH	410		190 ± 4 ^c
P	TCCP	CA film	394	410	52 ± 2 ^d
		EtOH	400		50 ± 2 ^d
As	FMN	CA film	400	410	41 ± 6 ^c
		MeOH	410		

^aRecorded in aerated solutions as no O₂ quenching effect was detected. ^b300 K. ^cDetermined with Nd-laser system. ^dDetermined with ORTEC apparatus.

gies, reflecting the change in the conventional π -back-donation in the metal-alkene bond.

Luminescence Spectra

The series of platinum phosphine complexes reported in Table II give what appears to be a highly structured luminescence which occurs between 360–500 nm in a cellulose acetate (CA) film medium. A typical luminescence spectrum is given for [(PPh₃)₂Pt·TCNE] in Fig. 1 for which the observed structure was analysed in terms of a vibronic progression. Similar results are given by the other complexes as shown in Table II. That the luminescence of Pt complexes reported in Table II is genuine is suggested by (a) the invariance in the position of emission spectrum with changes in excitation wavelength (260–313 nm), (b) the observation of excitation spectra, which agree well with the corresponding absorption spectra (Fig. 2), (c) the similarity with the

phosphorescence of the free ligand, PPh₃ (Fig. 3) and, (d) the spectral 'blank' of the CA film. The CA film was preferred to solvents with C–H or O–H bonds which gave interfering Raman bands as well as almost unresolved vibronic structure. In comparing PPh₃ and the platinum phosphine complexes (Fig. 3 and Table II), the following features emerge:

(i) An obvious overall similarity between the emission of all complexes investigated and also that of the phosphorescence spectrum of the free ligand PPh₃ which at 77 K closely resembles that of [(PPh₃)₂Pt·TCNE] at 298 K (Fig. 1), with an emission maximum at 390 nm, and similar bandwidth and structure;

(ii) The emission maxima of the Pt complexes in alkanol solvents are red-shifted (10–20 nm) from those observed in CA film.

Feature (i) would suggest that the Pt(PPh₃)₂ moiety is responsible for the luminescence, with

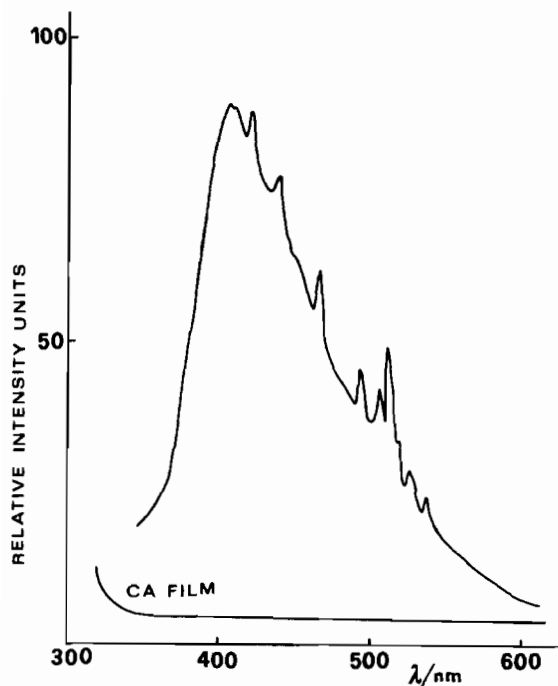


Fig. 1. Emission spectrum of $[(PPh_3)_2Pt \cdot TCNE]$ in CA film at 298 K ($\lambda_{ex} = 300$ nm). Base line: pure CA film.

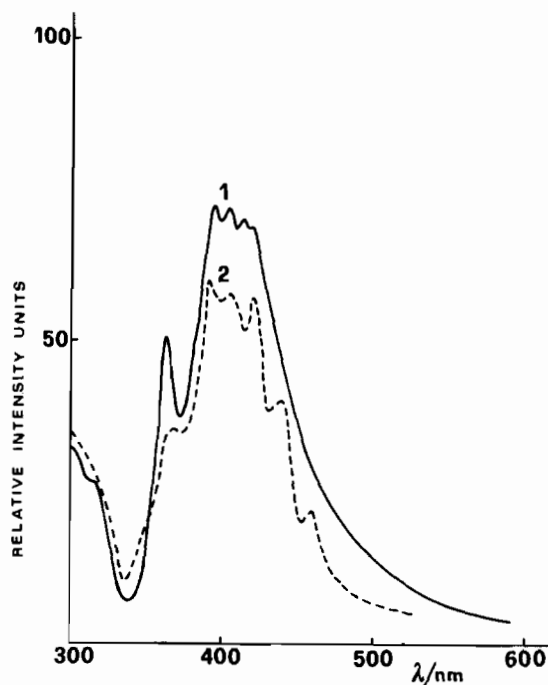


Fig. 3. Emission spectrum of PPh_3 in 12:1 EPA- $CHCl_3$ at 77 K. (1), (2) Emission spectrum of $[(PPh_3)_2Pt \cdot C_2H_4]$ in EPA- $CHCl_3$ at 77 K. $\lambda_{ex} = 300$ nm.

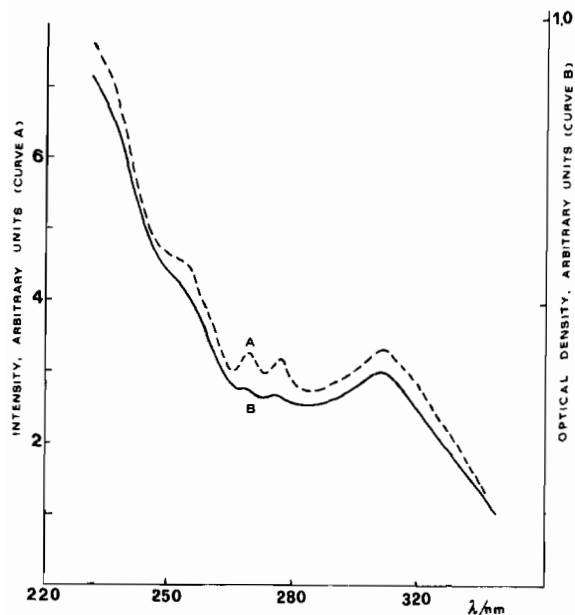


Fig. 2. Excitation (Curve A) and absorption (Curve B) spectra of $[(PPh_3)_2Pt \cdot TCNE]$ in ether-isopentane-ethanol-chloroform (EPA- $CHCl_3$) at 77 K and ethanol at 295 K respectively.

the third ligand acting merely as a perturbing influence. Feature (ii) indicates that the observed emission is a ligand-centred $\pi-\pi^*$ luminescence

although the possibility of phosphorescence from the free-ligand either as an impurity or resulting from the photodissociated complex have to be considered. Several lines of evidence militate against the occurrence of these possibilities. Firstly, ^{31}P NMR spectroscopy indicates the absence of free PPh_3 either as an impurity following irradiation. Secondly, the slight but definite changes in emission maxima for the different complexes suggests an impurity to be unlikely. Finally, the excitation maxima for the complexes reported in Table II varies from 280 to 313 nm, a region in which no strong absorption is observed for PPh_3 . This observation indicates that the luminescence follows an initial excitation of CTTL ($d-\pi^*$) type.

The luminescence of all the Pt complexes in both a CA film at 298 K and in glasses at 77 K appears highly structured. The observed structure was analysed in terms of a vibronic progression of 420 ± 30 cm^{-1} (Table II). The presence of this structure in the phosphorescence spectrum of PPh_3 itself implies a P-Ph vibration to be involved as a deactivation mode. The lifetimes of the luminescence, measured in CA film at 298 K, are orders of magnitude shorter than that of the free ligand (14.5 ms at 77 K [8]) despite the close similarity of the corresponding spectra. Coordination of PPh_3 to Pt has evidently altered one or more of the rate constants for population or depopulation of the emitting state. This effect is principally due to the increased

TABLE III. Emission and Lifetime Data of Some Metal Phosphine Complexes^a ($\lambda_{\text{ex}} = 300 \text{ nm}$).

Compound	λ_{max}	Lifetime/ns
$[(\text{PPh}_3)_2\text{Pd}\cdot\text{FMN}]$	405	130 ± 5
$[(\text{PPh}_3)_2\text{Pd}\cdot\text{TCNE}]$	410	245 ± 5
$[(\text{PPh}_3)_3\text{CuBr}]$	420	270 ± 5

^aMeasured in CA film medium at 298 K with ORTEC apparatus.

influence of SOC caused by the heavy-metal centre. A comparison of the data of Tables II and III reveals that the emission lifetimes appear to be sensitive to the metal atom, with smaller effects of temperature (77 to 298 K), and overall composition, on both the energy and the lifetime of the luminescence being apparent.

Acknowledgements

We thank the C.N.R. (Italy) for promoting the Ferrara-Warwick collaboration through a 'Progetto Bilaterale' and Prof. F. Wilkinson of the University of Loughborough for access to his Nd laser photolysis equipment.

References

- 1 P. D. Fleischauer and P. Fleischauer, *Chem. Revs.*, **70**, 199 (1970).
- 2 U. Belluco, 'Organometallic and Coordination Chemistry of Platinum', Academic Press, London (1973), Chap. 1.
- 3 S. Sostero, O. Traverso, M. Lenarda and M. Graziani, *J. Organometal. Chem.*, **134**, 259 (1977).
- 4 G. Shaw, J. K. Becconsall, R. M. Canadine and R. Murray, *J. Chem. Soc. Chem. Comm.*, 425 (1966).
- 5 C. Bartocci, S. Sostero, O. Traverso, A. Cox, T. J. Kemp and W. J. Read, *J. Chem. Soc., Faraday Trans. 1*, **76**, 797 (1980).
- 6 J. Burgess, *Spectrochim. Acta*, **26A**, 1364, 1957 (1970).
- 7 C. Reichardt, *Angew. Chem., Internat. Ed.*, **4**, 29 (1964).
- 8 R. F. Ziolo, S. Lipton and Z. Dori, *J. Chem. Soc., Chem. Commun.*, 1124 (1970).