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Spectroscopic and Electrochemical Properties of Some Mixed-Ligand Cyclometalated Platinum(II) Complexes Derived from 2-Phenylpyridine

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The spectroscopic and electrochemical properties of some new cyclometalated Pt(II) complexes, [Pt(ppy)(N-N)]X, are reported. The 2-phenylpyridinate anion, ppy, acts as the cyclometalating ligand while (N-N) represents α,α′-diimines such as 2,2-bipyridine (bpy) and 1,10-phenanthroline (phen) or a saturated chelating ligand, 1,2-diaminoethane (en). The anion X^- is Cl^-, ClO_4^- or CH_3COO^-. The complexes show luminescence in fluid solutions.

The photophysical and electrochemical behaviour of the complexes is found to be related to the presence of vacant π* orbitals on the nitrogen chelating ligands. On the basis of the electrochemical and spectroscopic data the low-energy absorption and emission spectra of $[Pt(ppy)en]^+$ are essentially due to the ^{3}MLCT (d_{Pt}-π^*_{ppy}) transition while for the diimine complexes these spectra correspond to the ^{3}MLCT (d_{Pt}-$\pi^*_{diimine}$) transition. Contrary to $[Pt(ppy)en]ClO_4$ the emission spectra of [Pt(ppy)en]Cl and especially of [Pt(ppy)(α,α′-diimine)]X show solid state effects.

Transition-metal complexes having long-lived excited states have been suggested to have most interesting practical applications.[1–3] With appropriate photochemical and redox properties these compounds may have considerable potential as devices for interconversion between light and chemical energy.[3,4] Furthermore, with suitable luminescence, this class of complex may be used as labels for specific sites in polymeric arrays,[5] in biological systems [6] and also in microenvironmental research.[7] Owing to the remarkable photochemistry of the $[Ru(bpy)_3]^{2+}$ complex ion, d^6 metal complexes have frequently been employed in this kind of study. Coordinatively unsaturated four-coordinated d^8 metal complexes, however, as for example Pt(II) complexes, may be more promising candidates, since they are able to attach to substrates through inner-sphere interactions and atom transfer reactions.

In spite of the large number of d^6 transition-metal complexes known to exhibit room-temperature luminescence,[1,8–10] only a few d^8 metal complexes are reported to be emissive in fluid solution at room temperature. As far as mononuclear platinum(II) complexes are concerned, emission may originate from triplet metal-to-ligand charge transfer excited states (^{3}MLCT) or from triplet ligand-centered excited states (^{3}LC).[11–21] Most recent studies on relevant compounds in a polycrystalline matrix, the Shpol′skii technique,[22] seem to indicate that an increase in the ^{3}MLCT character is connected with decreasing nuclear shifts and that the simple picture of a transfer of one electron charge from the metal to the ligand may not be an adequate description.[23] In most of these systems a key role is undoubtedly played by the presence of a sufficiently high energy gap between the lowest emitting excited state and the upper-lying metal-centered (MC) excited states, states that are populated by thermal activation and will deactivate the excited state by fast radiationless processes and/or photoreactions.

Cyclometalated Pt(II) complexes derived from 2-aryl-substituted pyridines are promising candidates for the design of new luminescent complexes.[1] The strong ligand-field influence of the aromatic carbon donor combined with the possibility of π-back-donation into the chelate ring generally yields high-lying MC excited states. The bis(cyclometalated)Pt(II) complexes have been studied extensively in recent years.[11,12,20,23] These compounds, however, suffer from the disadvantage of being uncharged, and their insolubility in most protic solvents seriously limits their applications.

We report here some spectroscopic and electrochemical properties of salts of three cationic mixed-ligand Pt(II)

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complexes with the general formula [Pt(ppy)(N-N)]X; ppy representing the cyclometalated 2-phenylpyridinate ligand and (N-N) an α,α′-diimine, 2,2′-bipyridine, bpy, 1,10-phenanthroline, phen, or a saturated diamine, 1,2-diaminoethane, en. As counterions, X^-, were chosen ions which secured some solubility in several solvents. All compounds were found to be luminescent in solution at room temperature.

Experimental

Materials. The preparation and characterization of the complexes has been published.[24]

Instrumentation. The absorption spectra were recorded on a Varian Cary 1 UV–visible spectrophotometer. Diffuse reflectance spectra were measured on a SF-18 spectrophotometer with a MgO integrated sphere attachment. Emission spectra (not corrected) were recorded on a KSVU-1 spectrofluorimeter equipped with a FEU-100 photomultiplier and were corrected for instrument response by the method of Parker and Rees.[25] Emission lifetimes were measured with a pulse nitrogen laser, LGI-21, as light source with λ_{exc} = 337 nm and a pulse half-width of 10 ns. The emission was detected through nonfluorescing UV cutoff filters by a FEU-100 photomultiplier and an S1-70 oscilloscope with estimated errors of less than 10%. Emission quantum yields, estimated with the optically dilution method [26] using $[Ru(bpy)_3]^{2+}$ (Φ_{em} = 0.028) [27] and fluorescein (Φ_{em} = 0.85) [28] as standards, were corrected for the different refractive index of the solvents. The total error was estimated to be less than 30%. For measurements at low temperatures an optical quartz Dewar tube containing a quartz tube (thickness 2–3 mm) was used. The equipment was maintained at constant temperature with liquid nitrogen.

Electrochemical measurements were carried out in DMF solutions under an argon atmosphere with tetrabutylammonium perchlorate as supporting electrolyte using standard SVA-1B and N307/1-XY recorders. Cyclic voltammograms were measured using a three-compartment three electrode cell. A Pt wire was used as the counter-electrode, and a Ag/Ag^+ electrode functioned as the quasi-reference electrode. The working electrodes were a Hg (Au-amalgam), a platinum wire and a glassy carbon. The redox potentials of the ferrocenium/ferrocene couple under the same experimental conditions were used as reference redox system for the electrochemical measurements.[29] The reported potential values are relative to SCE.

Results and discussion

Discussions of spectroscopic and electrochemical properties of transition metal complexes are usually based on localized molecular-orbital configurations of the ground state and of the excited and redox states in the intramolecular photoinduced electron-transfer or electrochemically induced outer-sphere processes.[30] According to this simplified picture three types of electronic excited states can be considered as potential candidates being responsible for the absorption and emission spectra of cyclometalated platinum(II) complexes; metal centered, MC, ligand-field (d-d*), ligand centered, LC, (π-π*), and metal to ligand charge transfer, MLCT, (d-π*). Electrochemical oxidation and reduction processes are classified as being metal-centered or ligand-centered.[31] It should be emphasized that for cyclometalated Pt(II) complexes with a high degree of covalency in the metal–ligand bonds, the localized molecular-orbital approach can only be used as a first approximation. It has been shown for Pt(II) and Pd(II) complexes with two cyclometalated aromatic C,N ligands, $[M{<}N\text{-}C{>}_2]$,[32] that the LUMOs of the monomer complexes are stabilized ligand hybrid MOs, π^*_L, whereas the HOMOs in both Pt(II) and Pd(II) compounds are a mixture of destabilized metal d_{xy} and ligand π_L states. Thus, the character of the lowest excited states, predominantly LC for Pd(II) complexes[33] and with an admixture of MLCT for Pt(II) complexes,[23] differs only in the extent of mixing of the d_{xy} and π_L orbitals.

Electrochemistry. The nature of the HOMO and LUMO of the $[Pt(ppy)Cl_2]^-$ and $[Pt(ppy)(N\text{-}N)]^+$ complexes was examined using cyclic voltammetry in DMF solutions. From the cyclic voltammograms; cf. Fig. 1, $E_{1/2}$-values were determined for reversible and quasi-reversible reductions while E_P-values were measured for irreversible oxidation and reduction waves; cf. Table 1. For comparison, the data for $[Pt(ppy)_2]$ and $[Pt(bpy)_2]^{2+}$ are also listed.

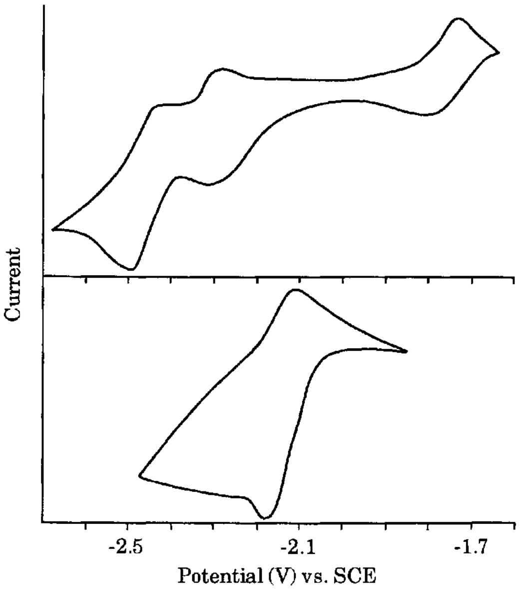


Fig. 1. Cyclic voltammograms of $[Pt(ppy)bpy]ClO_4$ (upper) and $[Pt(ppy)en]ClO_4$ (lower) in DMF solution.

Table 1. Cyclic voltammetry data in DMF solution (in 0.1 M TBAP).

	Potential/V vs. SCE				
	Reduction				
Complex	$E_{1/2}$	ΔE_P	Assignment	Oxidation E_P[a]	Ref.
$[Pt(bpy)_2]^{2+}$	−0.97[a]	–	MC		35
	−1.51	0.07	LC (bpy)		
	−2.53	0.06	LC (bpy)		
$[Pt(ppy)_2]$[b]	−1.94	0.07	LC (ppy)	0.26	38
	−2.19	0.07	LC (ppy)	0.54	35
$[Pt(ppy)Cl_2]^-$	−2.10[a]	–	MC	0.47	
	−2.29	0.07	LC (ppy)		
$[Pt(ppy)en]^+$	−2.15	0.07	LC (ppy)	0.96	
$[Pt(ppy)bpy]^+$	−1.78	0.06	LC (bpy)	0.89	
	−2.28	0.07	LC (ppy)		
	−2.49	0.09	LC (bpy)		
$[Pt(ppy)phen]^+$	−1.91	–	LC (phen)?	0.75	
	−2.14	0.07	LC (ppy)		
	−2.41	–	LC (phen)?		

[a] Irreversible wave, scan rate 50 mV s^{-1}. [b] In CH_3CN.

Since Pt(I) and Pt(III) complexes are unstable species,[34] metal-centered oxidation and reduction processes of Pt(II) complexes are expected to exhibit an irreversible behaviour. For the cyclometalated aromatic C,N ligand, ppy, as well as for the α,α′-diimine ligands bpy and phen, reduction is expected to be reversible or quasi-reversible, since delocalized π*-orbitals are involved.[1] Moreover, ligand-centered reduction processes of complexes containing C,N aromatic ligands or α,α′-diimine ligands lead to electron transfer to the pyridine rings. The observed $E_{1/2}$-values for the successive one-electron reductions for each of the pyridine rings of the α,α′-diimine ligands are separated by from 0.7 to 1.0 V. The first wave in Pt(II),[17,35–38] Rh(III)[39] and Ir(III)[40] complexes is observed at an $E_{1/2}$-range from − 1.4 to − 1.8 V. The electron transfer process to the partially reduced ppy ligand is observed at more negative values, $E_{1/2}$ being less than − 1.8 V. Consequently, one may expect one ligand-centered reduction wave due to electron transfer to ppy in the case of $[Pt(ppy)Cl_2]^-$ and $[Pt(ppy)en]^+$ and three reversible or quasi-reversible waves for $[Pt(ppy)bpy]^+$ and $[Pt(ppy)phen]^+$ owing to successive one-electron reductions of the two pyridine rings of the α,α′-diimine and the one pyridine ring of ppy. A weaker field complex such as $[Pt(ppy)Cl_2]^-$ may also be the subject of a metal-centered reduction process due to the presence of low energy metal-centered orbitals.

The results obtained for the mixed-ligand cyclometalated Pt(II) complexes (Table 1) are in agreement with the localized molecular orbital approach. Like the homoleptic complex $[Pt(ppy)_2]$[35] the examined mixed-ligand complexes show a ligand-centered reduction wave at $E_{1/2}$ from − 2.1 to − 2.3 V which can be assigned to electron transfer to the π*-orbital localized on the ppy ligand. The shift of this wave towards more negative potentials when changing the ligand in the series, phen, en, Cl^- and finally bpy, displays the change in electron density at the metal centre by varying the σ- and π-donor and the π-acceptor strength of the substituted ligands. It has been shown that the electron-withdrawing ability of the Pt-atom stabilizes the orbitals of ppy by operating more efficiently on the more polarizable π*-orbital.[41] As expected for a complex with a weak ligand field, $[Pt(ppy)Cl_2]^-$ shows one irreversible reduction wave at − 2.10 V which can be attributed to a metal-centered reduction process.

In addition to the ppy centered reduction wave at − 2.28 V, $[Pt(ppy)bpy]^+$ also shows two partially reversible waves at − 1.78 and − 2.49 V (Fig. 1). The position and separation of these two waves allow one to assign them to successive one-electron reduction of the two pyridine rings of the coordinated bpy; i.e. the wave at the least negative potential is attributed to a bpy-centered uptake of one electron. It should be emphasized that this assignment is in possible contrast to what has been suggested for species like $[Rh(ppy)_2bpy]^+$,[42,43] $[Ir(ppy)_2bpy]^+$ [44] and for related species derived from 2-(2′-thienyl)pyridine, tpy. The localization of the lowest unoccupied orbital in mixed-ligand coordination compounds is currently of great interest.[38,44–46] Part of the existing controversy may have its origin in the fact that octahedral and square planar complexes have not been considered separately.[47] The electrochemical behaviour of $[Pt(ppy)phen]^+$ is even more complicated. Similar to $[Pt(ppy)bpy]^+$, $[Pt(ppy)phen]^+$ shows two additional reduction waves, at − 1.91 and − 2.41 V. These waves, however, are broad and poorly resolved, and no corresponding anodic waves could be detected. This may be due to lower stability of the reduction product [Pt(ppy)phen] at room temperature as compared to [Pt(ppy)bpy].

The $[Pt(ppy)Cl_2]^-$ and $[Pt(ppy)(N\text{-}N)]^+$ complexes show a completely irreversible wave in the 0.5–1.0 V region which can be assigned to a metal-centered Pt(II) → Pt(III) oxidation followed by a fast chemical reaction.

Apparently, the mixed-ligand complexes are more difficult to oxidize than is [Pt(ppy)$_2$]; cf. Table 1. Owing to the irreversibility of the processes, however, it is not possible to draw any conclusions with regard to a possible correlation between the oxidation potential and the energy position of the HOMO of the complexes.

The electrochemical data (Table 1) show that replacement of the saturated diamine, en, with an unsaturated α,α′-diimine ligand, bpy or phen, in [Pt(ppy)(N-N)]$^+$ leads to a change in the nature of the redox LUMO of the complex from π*(ppy) to π*(α,α′-diimine). One may therefore conclude that a corresponding change in the nature of the lowest excited state and the luminescence properties of the complexes will take place.

Absorption and emission data. Absorption and emission spectra of [Pt(ppy)Cl$_2$]$^-$ and [Pt(ppy)(N-N)]$^+$ in solution are shown in Figs. 2 and 3. Table 2 contains a list of absorption features. The emission data are listed in Table 3.

The absorption and emission spectra of [Pt(ppy)en]$^+$ are in principle quite similar to the previously reported spectra of [Pt(ppy)Cl$_2$]$^-$.[13] The same electronic assignments are therefore suggested. Replacement of en by two Cl$^-$ ligands leads to a pronounced red shift of the structured absorption and emission spectra (Fig. 2), and is most likely due to the electron-donating effect of the Cl$^-$ ligands. In addition to the vibrational satellite structured singlet–singlet LC (π-π*) transition of 2-phenylpyridine with absorption bands around 320 nm, both complexes show a broad, intense solvatochromic absorption band at ca. 380 nm. This band can be assigned to an unresolved spin-allowed ^{1}MLCT (d_{Pt}–π^*_{ppy}) transition. The excitation spectrum of [Pt(ppy)Cl$_2$]$^-$ (Fig. 2) is better resolved and confirms a vibrational satellite structure of this broad band.

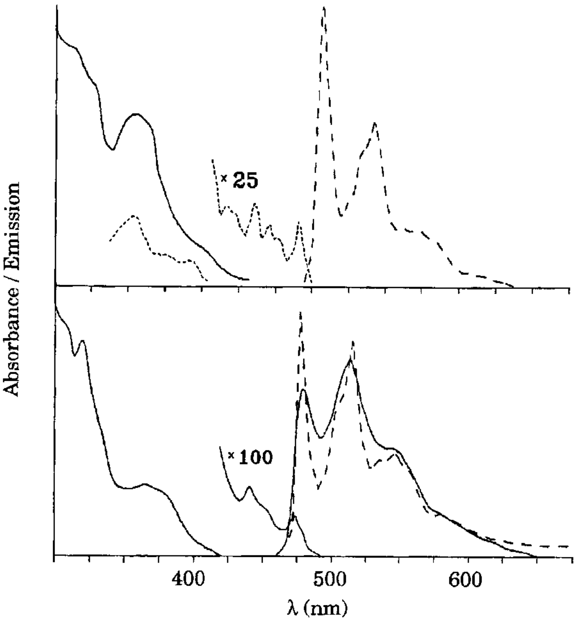


Fig. 2. Absorption, emission and excitation spectra of Bu$_4$N[Pt(ppy)Cl$_2$] (upper) and [Pt(ppy)en]ClO$_4$ (lower) in DMF solution: (——) room temperature; (- - - -) 77 K.

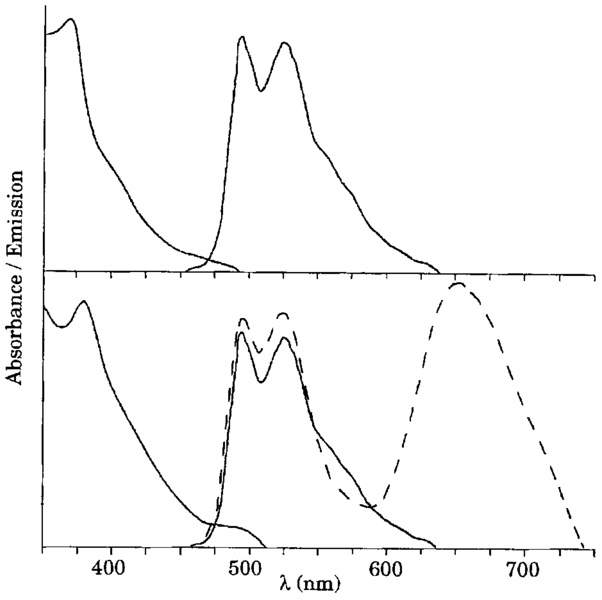


Fig. 3. Absorption and emission spectra of [Pt(ppy)bpy]Cl (upper) and [Pt(ppy)phen]Cl (lower) in DMF solution: (——) room temperature, (- - - -) 77 K.

A much weaker, structured solvatochromic absorption is detectable in the visible region (Table 2). The absorption at ca. 1500 cm^{-1} is characteristic of an excited-state distortion of the 2-phenylpyridine ligand.[42,48] The vibrational satellite structure (1450, 1120 and 730 cm^{-1}) observed for the long-lived emission, whose electronic origin overlaps with the absorption origin (Fig. 2), can be attributed to high-energy vibrations of the cyclometalated ligand. Like the corresponding absorption bands, the emission spectra of [Pt(ppy)Cl$_2$]$^-$ and [Pt(ppy)en]$^+$ show a solvatochromic effect. The low extinction coefficients at the electronic origin (Table 2) and the radiative rate constants, k_r, calculated from the measured emission lifetime, τ, and quantum yield, Φ, (Table 3) are consistent with dipole-allowed spin-forbidden transitions and display that the lowest excited states are mainly of triplet character with a singlet ground state.

The vibrational satellite structure exhibited by the examined complexes clearly indicates that the lowest excited states of the complexes can only be assigned to ^{3}MLCT or to ^{3}LC states. The following data allow one to assign the lowest excited states of [Pt(ppy)en]$^+$ and of [Pt(ppy)Cl$_2$]$^-$ to be predominantly ^{3}MLCT: (i) The emission spectra are strongly red-shifted (ca. 1600 cm^{-1}) as compared with the emission of Pt(ppy)$_2$(CH$_2$Cl)Cl, for which the lowest excited state is certainly a ^{3}LC state localized on the ppy ligand.[49] (ii) The energy of the lowest excited states is in agreement with the expected splitting, ca. 5000 cm^{-1}, for spin-allowed and spin-forbidden MLCT transitions of cyclometalated Pt(II) complexes.[37]

Table 2. Positions of MLCT absorption bands in solvents of different polarity.

		λ_{max}/nm ($\varepsilon \times 10^{-3}$)		
Complex	Solvent	$^3(d_{Pt}–\pi^*_{ppy})$		$^1(d_{Pt}–\pi^*_{ppy})$
$[Pt(ppy)Cl_2]^-$	CH_3OH			365(3.7)
	DMF	490(0.058)		380sh(4.0), 371(4.3)
	CH_2Cl_2	488(0.061)		
$[Pt(ppy)en]^+$	CH_3OH	474(0.015), 441(0.045)		368(1.7)
	CH_3CN	472(0.009), 440(0.040)		368(1.8)
	DMF	477(0.022), 445(0.041)		395sh(1.3), 375(1.8)
		$^3(d_{Pt}–\pi^*_{(N–N)})$	$^1(d_{Pt}–\pi^*_{(N–N)})$	$^3(d_{Pt}–\pi^*_{ppy})$
$[Pt(ppy)bpy]^+$	CH_3OH		408sh(2.8)	368(5.5)
	CH_3CN		408sh(2.0)	367(5.1)
	DMF		410sh(1.9)	368(4.4)
$[Pt(ppy)phen]^+$	CH_3OH		410sh(2.0)	379(5.5)
	CH_3CN		410sh(1.8)	377(4.4)
	DMF	482sh(0.06)	410sh(1.9)	379(5.0)

Table 3. Emission properties of the complex ions.

		293 K				77 K			
Complex	Solvent	λ_{max} /nm[a]	τ /μs[b]	$\Phi \times 10^2$ [b]	$k_r \times 10^{-4}$ /s^{-1}	λ_{max} /nm[a]	τ /μs[b]	$\Phi \times 10^2$ [b]	$k_r \times 10^{-4}$ /s^{-1}
$[Pt(ppy)Cl_2]^-$	MeOH:H_2O (1:1)	–	–	–	–	480	15.2	90	5.9
	EtOH	–	–	–	–	484	11.5	77	6.7
	i-PrOH	–	–	–	–	485	10.5	74	7.0
	DMF	–	–	–	–	491	7.9	65	8.2
$[Pt(ppy)en]^+$	H_2O	480	7.2	15	2.1	479	19.1	51	2.7
	MeOH	485	10.0	35	3.5	480	18.0	49	2.7
	DMF	487	1.7	5.8	3.4	481	15.0	72	4.8
$[Pt(ppy)bpy]^+$	DMF	495	4.0	1.7	0.4	496	[c]	–	–
	DMF:H_2O (1:1)	486	5.2	2.7	0.5	482	[c]	–	–
$[Pt(ppy)phen]^+$	DMF	494	3.5	1.3	0.4	496	[c]	–	–
	DMF:H_2O (1:1)	486	6.6	2.1	0.3	481	[c]	–	–

[a] Highest energy feature of the luminescence emission maxima. [b] Deareated solution. [c] Non-exponential decay of luminenscence.

(iii) The radiative rate constants, $(3–8) \times 10^4$ s^{-1}, are typical of spin-forbidden MLCT excited states [12] and are much larger than the radiative rate constants of spin-forbidden LC excited states of Pt complexes, ca. 10^3 s^{-1}.[49] (iv) The solvatochromic effect observed for emission and absorption is typical for charge-transfer transitions.[46] Unlike for $[Pt(ppy)en]^+$, the solutions of $[Pt(ppy)Cl_2]^-$ show strong emission only at low temperature in rigid media. The emission lifetime and the quantum yield decrease with increasing temperature and no luminescence can be detected at room temperature.

The quenching of luminescence as the temperature increases is generally explained by considering additional contributions to the radiationless decay process of the emitting excited state.[50] In agreement with the electrochemical data one may assign the strong temperature quenching of the luminescence in $[Pt(ppy)Cl_2]^-$, a weak ligand field complex, to a small energy gap, $\Delta E \approx 1700$ cm^{-1},[51] between the lowest emitting MLCT excited state and the upper lying MC excited states, the thermally activated population of which leads to fast radiationless processes. The increase in the energy gap between MLCT- and MC-excited states in $[Pt(ppy)en]^+$, a strong ligand field complex, leads to structured long-lived emission both at 77 K and at room temperature in fluid solutions; cf. Table 3.

The emission of the $[Pt(ppy)en]^+$ complex is most efficiently quenched by oxygen; the quenching constant being of the order of 10^9 M^{-1} s^{-1}. When taking into account the oxygen concentration in air-saturated solutions[42] the rate constant may be estimated to be $(2–3) \times 10^9$ M^{-1} s^{-1}. Moreover, the complex shows self-quenching processes. While the absorption and the emission spectra are practically unaffected by changing the complex concentration in the range $(1–50) \times 10^{-5}$ M^{-1}, the lifetime and the emission quantum yield decrease as the concentration increases. An inherent lifetime of 7.2 μs and a self-quenching rate constant of 6.7×10^8 M^{-1} s^{-1} could be evaluated from the linear Stern–Volmer plot (Fig. 4). In general, self-quenching processes in octahedral transition-metal complexes are explained by electron transfer reactions.[3] When using both spectroscopic and

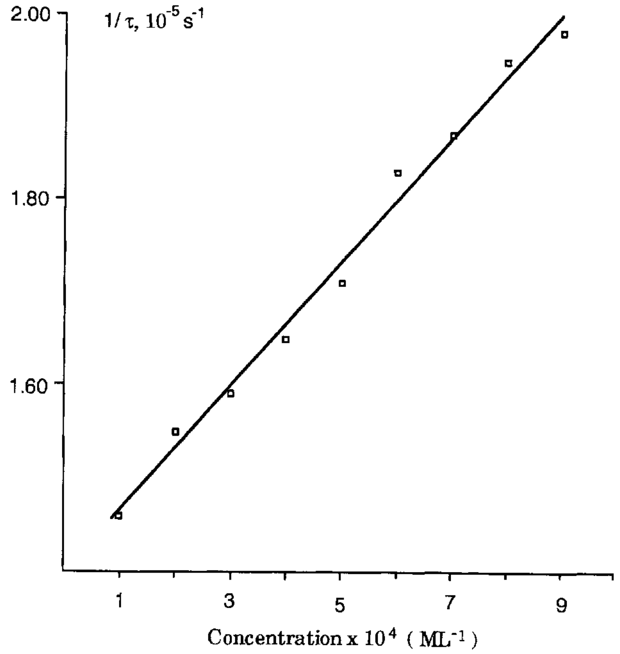
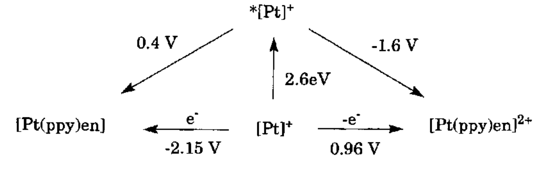


Fig. 4. Reciprocal of the emission lifetime vs. the consentration of [Pt(ppy)en]Cl in aqueous solution.

electrochemical data the excited state redox potentials of [Pt(ppy)en]$^+$ may be estimated as illustrated in Scheme 1.



Scheme 1.

The estimated redox potentials show that the fast ground-state quenching processes observed cannot be attributed to an electron transfer reaction such as

$$^*[Pt(ppy)en]^+ + [Pt(ppy)en]^+ \rightarrow [Pt(ppy)en]^{2+} + [Pt(ppy)en]$$

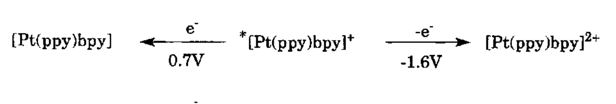
since they are endoergonic. An energy transfer process should therefore not be observable owing to recycling of the quenched excited state. We therefore suggest that the self-quenching process may be due to some other kind of interaction.

In contrast to octahedral transition metal complexes the planar structure of Pt(II) complexes allows for interactions along the free axis, leading to formation of oligomeric species.[52] The planar structure of the [Pt(ppy)en]$^+$ complex [53] and the rather long ^{3}MLCT excited-state lifetime suggest the relatively fast self-quenching process to be due to a bimolecular reaction between two complexes, one in the ground state and the other in the excited state via the formation of an excited dimer, an excimer. This suggestion is supported by the solid state effects on the emission of Pt(II) complexes.[54] Formation of excimer species from cyclometalated Pt(II) complexes has recently been suggested.[55]

The absorption and emission spectra of the [Pt(ppy)-(α,α′-diimine)]$^+$ complexes (Fig. 3) are strongly perturbed from those of [Pt(ppy)en]$^+$. The most remarkable feature in the absorption spectra is the appearance of a new intense absorption band at a longer wavelength. This band is observed as a shoulder at ca. 410 nm due to overlap with a higher-energy broad band at 370–380 nm. Based on the electrochemical data this low-energy absorption may be assigned to a ^{1}MLCT (d_{Pt}–$\pi^*_{\alpha,\alpha'\text{-diimine}}$) transition. The absorption spectrum of [Pt(ppy)phen]$^+$ in DMF also shows a much weaker absorption at 482 nm which most probably can be attributed to the corresponding spin-forbidden ^{3}MLCT (d_{Pt}–$\pi^*_{\alpha,\alpha'\text{-diimine}}$) transition. The band at 370–380 nm is also observed in the absorption spectra of [Pt(ppy)Cl$_2$]$^-$ and [Pt(ppy)en]$^+$, and the same electronic assignment to a ^{1}MLCT (d_{Pt}–π^*_{ppy}) transition is suggested.

The luminescence parameters of [Pt(ppy)bpy]$^+$ and [Pt(ppy)phen]$^+$ at room temperature (Table 3) are quite similar. Compared to the corresponding parameters of [Pt(ppy)en]$^+$, however, there are some remarkable differences; (i) the emission spectra are red shifted by ca. 300 cm^{-1}; (ii) the energy separation between emission bands is only 1200 cm^{-1}, (ca. 1400 cm^{-1} for [Pt(ppy)-en]$^+$); (iii) the radiative rate constants calculated from the measured emission lifetime and quantum yield are one order of magnitude smaller. These differences may, together with the electrochemical data concerning the different nature of the LUMOs of [Pt(ppy)(α,α′-diimine)]$^+$ and [Pt(ppy)en]$^+$, indicate that there is a different electronic structure for the lowest emitting excited state of [Pt(ppy)(α,α′-diimine)]$^+$ complexes as compared to [Pt(ppy)en]$^+$. Normally, low-temperature emission spectra show better resolution than room-temperature spectra and are therefore preferred when assigning an observed emission to the corresponding electronic transition. Unfortunately, owing to formation of crystals as the temperature was lowered, a true low-temperature glassy solution of these complexes could not be obtained. The formation of solid species in the solution at low temperatures led generally to the appearance of a broad structureless band at ca. 650 nm (Fig. 3), which was found to be characteristic for solid-state emission of the [Pt(ppy)(α,α′-diimine)]X complexes; cf. Fig. 7. The presence of this band complicated a correct calculation of the main luminescence parameters. It should be noted, however, that in contrast to [Pt(ppy)en]$^+$ and [Pt(ppy)Cl$_2$]$^-$, which showed a blue-shift as the temperature of the solution was lowered, the green low-temperature emission at 77 K of [Pt(ppy)(α,α′-diimine)]$^+$ was slightly red-shifted as compared to room temperature, Table 3. Based on the spectroscopic and electrochemical data, one may suggest that the most probable assignment for the room temperature emission of the $[Pt(ppy)(\alpha,\alpha'\text{-diimine})]^+$ complexes may be the spin-forbidden ^{3}MLCT $(d_{Pt}-\pi^*_{\alpha,\alpha'\text{-diimine}})$ electronic transition.

Like $[Pt(ppy)en]^+$, the emission of the $[Pt(ppy)(\alpha,\alpha'\text{-diimine})]^+$ complexes in solution is very efficiently quenched by oxygen with quenching constants also being of the order of $10^9\ M^{-1}\ s^{-1}$. However, owing to the very low solubility of these complexes, it was not possible to study the self-quenching processes. Based on the spectroscopic and electrochemical data the excited state redox potentials for the $[Pt(ppy)(\alpha,\alpha'\text{-diimine})]^+$ complexes can be estimated (Scheme 2).



Scheme 2.

The obtained data show that the lowest long-lived excited states of $[Pt(ppy)en]^+$ and the $[Pt(ppy)(\alpha,\alpha'\text{-diimine})]^+$ complexes are good reductants and oxidants. Based upon the high luminescence quantum yields and the long lifetimes of these Pt-complexes in fluid solutions at room temperature, it is not difficult to envisage that these complexes might possess rich photochemistry. Studies concerning photochemical behaviour are in progress in our laboratories. Owing to the strong temperature quenching a weak ligand-field complex such as $[Pt(ppy)Cl_2]^-$ does not show luminescence in fluid solution. The products from the substitution reactions of the Cl^- ions by the strong field ligands en, bpy and phen possess good emission properties.

Solid state effects. The electronic structures of square-planar Pt(II) complexes are often quite sensitive to solid-state effects owing to electronic interaction between nearest neighbours.[52] An electronic interaction between monomers may have a significant effect upon the absorption and emission properties of this kind of complexes in the solid state and may lead to some kind of cooperative excited structure. In general, there are three types of solid state structures in crystalline Pt(II) complexes dependent upon the nearest Pt–Pt distance, Δd, in the lattice.[54] (i) When $\Delta d \geq 4.5$ Å, a complex can be defined as "monomeric" and the electronic interaction between nearest neighbours is small. The solid-state emission and absorption spectra will not be significantly different from what is observed in solution or in glass. (ii) When Pt(II) complexes are stacked equidistantly, Δd being from 3.2 to 3.4 Å, the complex has a "linear chain" structure. (iii) Structures consisting of pairs of complexes with Δd from 3.5 to 3.7 Å, much shorter than the distance to the next pair, are generally considered as "dimers". In contrast to the "monomeric" structure, the "linear chain" and "dimer" structures cause marked changes in the electronic structure from what is observed in the isolated monomer. As has been demonstrated,[54,56–61] the electronic Pt(II)–Pt(II) interaction and/or ligand–ligand interaction leads to significant perturbation of the solid state emission and absorption spectra from what is observed in solution or glass.

The solid state diffuse reflectance and emission spectra of $Bu_4N[Pt(ppy)Cl_2]$ (Fig. 5), and $[Pt(ppy)en]ClO_4$ (Fig. 6) do not differ significantly from those in solution or in a low-temperature glass. The electronic origin of the emission at 510 nm for $Bu_4N[Pt(ppy)Cl_2]$ and at 495 nm for $[Pt(ppy)en]ClO_4$ overlap well with the corresponding diffuse reflectance origins at 502 and 488 nm. The vibrational satellite structure of the emission spectra, ca. 1450, 1100 and 700 cm^{-1}, is attributed to high-energy vibrations of the 2-phenylpyridine ligand. Like the emission spectra of the complexes in solution at 77 K, solid-state emission spectra are slightly blue-shifted and are better structured. These data indicate that there is small to negligible perturbation of the monomer electronic structure by crystalline packing and the complexes may be assumed to have a "monomeric" solid state structure.

Replacement of ClO_4^- by Cl^- as the counterion in $[Pt(ppy)en]X$ leads to remarkable changes in the solid state emission spectra; cf. Fig. 6. At room temperature the emission spectrum of $[Pt(ppy)en]Cl$ shows a broad and only slightly structured band at ca. 550 nm. In contrast to the "monomeric" complexes, the vibrational satellite structure is poorly resolved and a decrease in temperature leads to a red shift of the emission spectrum. This indicates that there is some kind of electronic interaction between the nearest molecules in the crystalline lattice which increases as the temperature decreases. However, the diffuse reflectance spectrum of [Pt(ppy)-

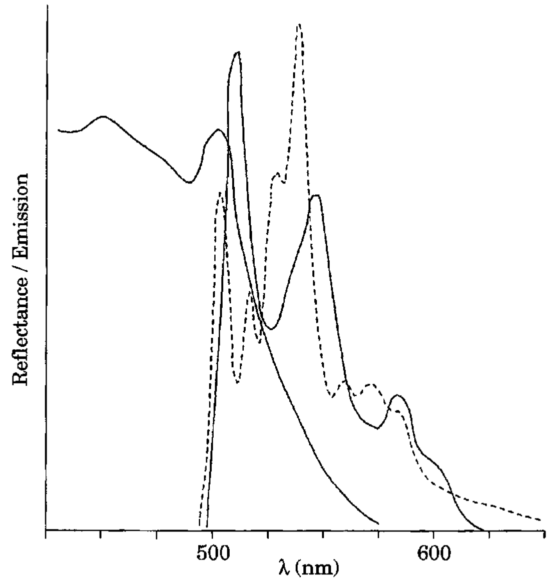


Fig. 5. Solid-state diffuse reflectance and emission spectra of $Bu_4N[Pt(ppy)Cl_2]$: (——) room temperature, (----) 77 K.

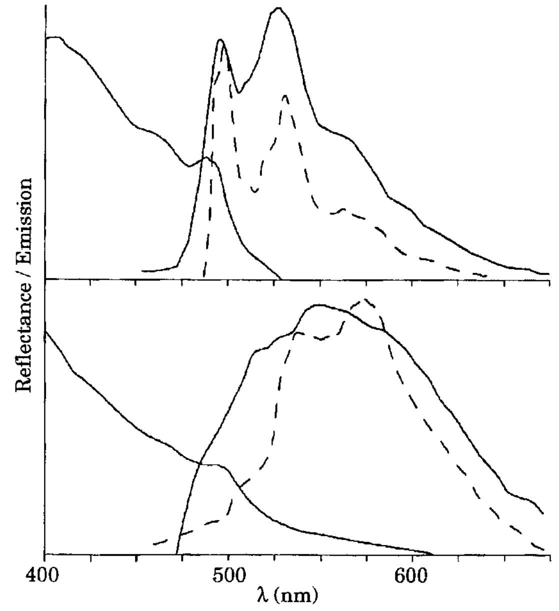


Fig. 6. Solid-state diffuse reflectance and emission spectra of $[Pt(ppy)en]ClO_4$ (upper) and [Pt(ppy)en]Cl (lower): (——) room temperature, (----) 77 K.

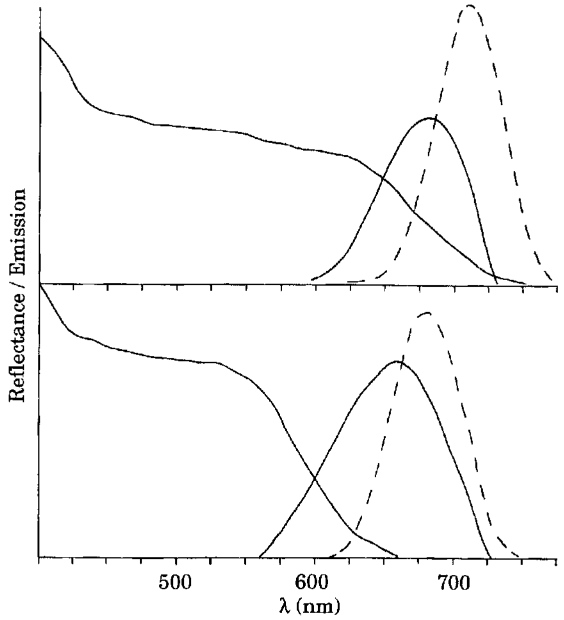


Fig. 7. Solid-state diffuse reflectance and emission spectra of [Pt(ppy)phen]Cl (upper) and [Pt(ppy)bpy]Cl (lower) in the solid state: (——) room temperature, (----) 77 K.

en]Cl is only slightly perturbed from that in solution. The lowest-energy spin-forbidden MLCT band has its origin at 496 nm. This suggests that the electronic interaction between the molecules in the solid state is weak. As has been shown for $[Pt(bpy)_2](ClO_4)_2$ and $[Pt(phen)_2]Cl_2$, the "dimer" solid-state structure of the complexes with a Pt–Pt distance of 3.71 Å leads to excimer-like emission.[57] This distance may be too long for significant Pt–Pt interaction but is sufficiently close to allow overlap of the α,α′-diimine π*-orbitals. We believe that the broad, red-shifted solid-state emission spectrum of [Pt(ppy)en]Cl is similarly due to interaction between the 2-phenylpyridine ligands of the nearest neighbours. The X-ray data for [Pt(ppy)en]Cl are in fair agreement with a "dimer" solid-state structure.[53]

All the [Pt(ppy)(α,α′-diimine)]X salts, X^- being Cl^-, ClO_4^- and CH_3COO^-, are strongly coloured in the solid state, from orange to purple. The solid state emission spectra (Fig. 7) are significantly red-shifted from what is observed in solution; at room temperature there is only a broad structureless band, FWHM being 2100 cm^{-1}. At 77 K the emission band is slightly narrower, FWHM being only 1400 cm^{-1}, and red-shifted, ca. 500 cm^{-1}. This is a typical behaviour of strong metal–metal interacting compounds with "dimer" or "linear chain" structures and is attributed to metal–metal bond shortening as a result of thermal lattice contraction.[56] The homoleptic $[Pt(ppy)_2]$ complex shows a similar solid-state effect, a green, highly structured MLCT emission in glass but a red structureless emission in the solid state.[61] The crystal structure of this complex shows a plane-parallel dimer packing with a Pt–Pt distance of 3.53 Å. We believe that the strong solid state effect observed for the [Pt(ppy)(α,α′-diimine)]$^+$ compounds also can be attributed to a dimer structure of the complexes in the solid state.

Conclusions

The replacement of the chloro ligands in a weak ligand field complex as $[Pt(ppy)Cl_2]^-$ by en, bpy or phen leads to the formation of $[Pt(ppy)(N\text{-}N)]^+$ complexes with a significantly higher energy gap between the lowest ^{3}MLCT and ^{3}MC excited states. As a result, these complexes are strongly emitting and are long-lived luminescent compounds in fluid solution at room temperature. They undergo a reversible one-electron reduction which is consistent with a ligand-localized nature of the lowest unoccupied orbitals; the π*(ppy) orbital for $[Pt(ppy)en]^+$ and the π*(α,α′-diimine) orbital for [Pt(ppy)(α,α′-diimine)]$^+$. The estimates of the redox potentials for the $[Pt(ppy)(N\text{-}N)]^+$ complexes in the long-lived excited state allow us to consider these compounds as promising candidates for photoinduced energy- and electron-transfer processes, as well as being useful excited state products for chemiluminescent and electro-chemiluminescent reactions.

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