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Photophysics, photochemistry and electrochemistry of mixed-ligand platinum(II) complexes with 2-phenylpyridine and 2-(2′-thienyl)pyridine as cyclometalating ligands

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Abstract

The spectroscopic and electrochemical properties of two series of some $[Pt(C^N)XY]^z$ complexes are studied where (C^N) is cyclometalated 2-phenyl-pyridinate, Ppy^-, and 2-(2-thienyl)pyridinate, Tpy^-; X and Y represent various monodentate and bidentate ligands: Cl^-, CN^-, CO, $(Mor)_3P$ = trismorpholinophosphine, Bpy = 2,2-bipyridine, Phen = 1,10-phenanthroline, En = ethylenediamine, Edp = 1,2-bis(diphenylphosphino)ethane, Etdp = 1,2-bis(diphenylphosphino)ethene, Edt = 1,2-bis(phenylthio)ethane, Mnt^{2-} = 1,2-dicyano-1,2-ethylenedithiolate. The lowest excited state in the $[Pt(Ppy)XY]^+$ complexes with an unsaturated ligand, (N–N) being Bipy and Phen, is assigned to a ^{3}MLCT $\{d(Pt)–\pi^*(N–N)\}$ transition, while for the Tpy^- complexes it corresponds to a $^3\{d(Pt)–\pi^*(C^N)\}$ transition. The lowest excited state of the $[Pt(C^N)Mnt]^-$ complexes is assigned to a $^3\{p(S)/d(Pt)–\pi^*(Mnt)\}$ transition. In the related complexes, in which a saturated chelating ligand replaces the unsaturated one, (N–N) = En, (S–S) = Edt, (P–P) = Edp, and in $Pt(C^N)(P(Mor)_3)Cl$, $Pt(C^N)COCl$, $[Pt(C^N)(CN)_2]^-$, $[Pt(C^N)Cl_2]^-$ the lowest excited

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state is assigned to a ^{3}(d(Pt)–π*(C^N)} transition. When replacing the cyclometalating ligand Ppy^- with Tpy^- the ^{3}MLCT {d(Pt)–π*(C^N)} absorption and emission bands are red shifted by ca. 3000 cm^{-1}. The redox potentials, however, are very similar and depend only on the additional ligands X and Y showing the linear relationship relative to Lever's electrochemical parameters. The values of the calculated radiative rate constants are sensitive both to the identity of the X,Y ligands ($Edp < Edt < (CN^-,CN^-) < En < ((Mor)_3P,Cl^-) < (CO,Cl^-) < (Cl^-,Cl^-)$) and the (C^N) ligands ($Tpy^- < Ppy^-$). This effect is suggested to be due to a reduction in the amount of charge transfer to the (C^N) ligand induced by an increase in π-back-bonding to the X,Y-ligands. The photochemical activity of this class of complexes in electron transfer reactions as well as in ground state quenching has been demonstrated. © 1997 Elsevier Science S.A.

1. Introduction

The design and study of luminescent transition metal complexes having long-lived excited states is currently of great interest. On the one hand, from a fundamental viewpoint such species are playing important roles in the development of several branches of the chemistry, such as 'the excited state dimension' of coordination chemistry, photochemistry, chemiluminescence, electrochemiluminescence, and electron-transfer chemistry [1]. On the other hand, the practical applications of luminescent transition metal complexes range from photochemical devices for interconversion of light and chemical energy [2] to environmental messengers [3] and luminescence sensors [4,5]. The $[Ru(bpy)_3]^{2+}$ and related octahedral d^6 transition metal complexes are commonly employed in these studies. These complexes, however, are coordinatively saturated, and hence their interactions and photochemical reactions with substrates are usually restricted to outer-sphere. The observation in the early 1980s that mononuclear square planar d^8 metal complexes could also be obtained as luminescent species, even in solution at room temperature, has gradually changed the focus of interest toward this class of species [6–39]. In most of these systems, a key role is surely 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, which are populated by thermal activation and deactivate the excited state by fast radiationless processes or photoreactions [11].

When square planar platinum(II) complexes are the subject of a metal to ligand charge transfer (MLCT) excitation, highly reactive and chemically most interesting 17e MC radicals are formed [34]. Since an increase in the MLCT character of the excited states seems to be connected with increasing covalency of the metal–ligand bonds [33], various homoleptic and heteroleptic bis-cyclometalated Pt(II) complexes derived from 2-aryl-substituted pyridines have been studied extensively in recent years [6,7,10–12,16,23,26,33]. The strong ligand-field influence of the aromatic carbon donor combined with the possibility of π-back-donation into metallocycle yields generally high-lying MC excited states. The bis-cyclometalated Pt(II) compounds, however, suffer from the disadvantage of being uncharged, and their insolubility in most protic solvents seriously limits their applications.

In comparison with bis-cyclometalated Pt(II) complexes, the mixed-ligand $[Pt(C^N)XY]^z$ complexes (where (C^N) is the *ortho*-C-deprotonated form of 2-phenylpyridine, Ppy^-, and 2-(2-thienyl)pyridine, Tpy^-) offer some additional and important advantages [15,35–40]: (i) a tuning of the necessary energy gap between the emitting MLCT and non-emitting MC excited states is possible also by altering non-cyclometalating X,Y-ligands, the charge of the complex, the counter ion and solvent: (ii) unlike bis-cyclometalated Pt(II) complexes, which can be prepared by using lithiated organic ligands [41], the $[Pt(C^N)XY]^z$ complexes, where X and Y represent monodentate and bidentate ligands with different donor and acceptor properties, are readily formed by the substitution of the chloride ligands in the parent $[Pt(C^N)Cl_2]^-$ complexes with various X and Y reagents [40].

In search of new complexes which might possess interesting excited state chemistry we want to discuss here some spectroscopic, electrochemical and photochemical properties of a series of $[Pt(Ppy)XY]^z$ and $[Pt(Tpy)XY]^z$ complexes. The first step would be to elucidate the nature of their excited states through photophysical and electrochemical methods. It seems essential to try to make changes in the nature of the lowest excited state of the compounds by a systematic variation of X,Y-ligands with different donor and acceptor properties: Cl^-, CN^-, CO, $(Mor)_3P$ = trismorpholinophoshine, En = ethylenediamine, Bpy = 2,2 – bipyridine, Phen = 1,10 – phenanthroline, Edp = 1,2-bis-(diphenylphosphino)ethane, Etdp = 1,2-bis(diphenylphosphino)ethene, Edt = 1,2-bis(phenylthio)ethane, Mnt^{2-} = 1,2-dicyano-1,2-ethylenedithiolate.

The mixed-ligand Pt(II) complexes to be discussed here are listed in Table 1 along with pertinent electrochemical data. Readers are referred to Refs. [36–40] for a detailed description of synthetic and experimental procedures.

Table 1
Reduction and oxidation potentials of $[Pt(C^N)XY]^z$ complexes in DMF vs. Fc^+/Fc (0.1 M TBAP)

No	Compound	Reduction $-E_{1/2}$ (V)		Oxidation[a] E_p (V)		CIS[b] (ppm)		$E_L(X,Y)$[c]
		Ppy	Tpy	Ppy	Tpy	Ppy	Tpy	
1	$[Pt(C^N)Cl_2]^-$	2.47	2.49	0.36	0.39	−0.2	0.4	−0.48
2	$Pt(C^N)COCl$	1.77	1.81	>1.1	>1.1	−1.9	−5.6	0.75
3	$Pt(C^N)(PMor_3)Cl$	2.24	2.23	0.9	0.89	−2.0	−2.2	0.11
4	$[Pt(C^N)En]^+$	2.22	2.25	0.84	0.86	1.5	1.8	0.12
5	$[Pt(C^N)(CN)_2]^-$	2.36	2.36	0.65	0.66	3.2	3.4	0.04
6	$[Pt(C^N)Edt]^-$	1.77	1.82	1.21	1.11	2.5	2.9	0.72
7	$[Pt(C^N)Edp]^+$	1.83		0.70		3.7		0.72
8	$[Pt(C^N)Etdp]^+$	1.79	1.76	0.70	0.48	4.0	3.6	0.98
9	$[Pt(C^N)Mnt]^-$	2.40	2.37	0.35[d]	0.41[d]	0.2	0.7	−0.66
10	$[Pt(C^N)Bpy]^+$	1.87	1.89	0.74	0.74	−0.2		0.52
11	$[Pt(C^N)Phen]^+$	1.98	1.95	0.70	0.76	3.4		0.52

[a] Irreversible wave, scan rate 50 mV s^{-1}. [b] Coordination-induced ^{13}C shift of C(6) carbon atom of the cyclometalated ligand from Refs. [36,40]. [c] Ligand electrochemical parameters from Ref. [42]. [d] Quasi-reversible wave, $E_{1/2}$.

2. Results and discussion

2.1. Electrochemistry

The nature of the HOMO and the LUMO of the $[Pt(C^N)XY]^z$ complexes were examined using cyclic voltammetry in DMF. From the cyclic voltammograms, Fig. 1, $E_{1/2}$ values were determined for reversible and quasi-reversible processes while the E_p values were determined for irreversible processes, see Table 1.

Electrochemical data obtained for the $[Pt(C^N)XY]^z$ complexes, Table 1, are found to depend on whether or not the X,Y ligands are unsaturated (contain a vacant π^*-orbital). All of the mixed-ligand complexes with saturated X,Y-ligands examined show a ligand-centered reduction wave, $E_{1/2}$, ranging from -1.8 to -2.5 V vs. Fc^+/Fc that can be assigned to electron transfer to the π^*-orbital localized on the cyclometalated ligand. The shift of the reduction wave to more negative potentials when changing the ligands in the series Etdp, Edp, Edt, En, and Cl^- is therefore in agreement with the NMR data [37,41] with regard to the shielding of the C(6) carbon atom of the pyridine ring, Fig. 2. The deviation in this plot for the two dicyano complexes can be attributed to additional deshielding of the C(6) carbon atom due to anisotropic effects by the cyano ligands.

The electron-withdrawing ability of the 'PtXY' moiety can also be considered in terms of the so-called Lever's 'ligand electrochemical parameter', E_L [42]. According to this approach, a correlation between the ligand-centered reduction potentials of the $[Pt(C^N)XY]^z$ and the sum of the E_L parameters of the X and Y ligands is to be expected [43]; see Fig. 2. It is notable that two dicyano complexes do not deviate in this plot.

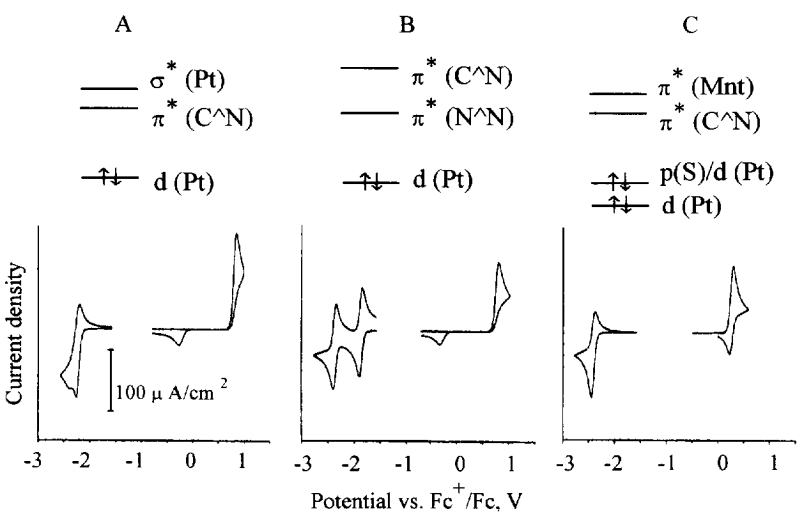

Fig. 1. Cyclic voltammograms and energy level ordering (not to scale) of the redox orbitals for $[Pt(C^N)En]^+$ (A), $[Pt(C^N)Bpy]^+$ (B), and $[Pt(C^N)Mnt]^-$ (C).

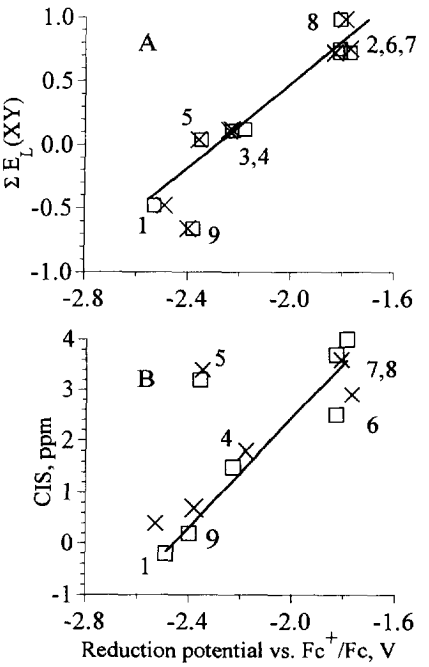

Fig. 2. Plot of CIS values, $\Delta = \delta$(complex) $- \delta$(free ligand), for the C(6) atom of the cyclometalated ligands (A) and the sum of the electrochemical parameters, E_L, of the X and Y ligands vs. the values of the reduction potentials of [Pt(C^N)XY]^z: Ppy complexes, □; Tpy complexes ×.

The electrochemical data, Fig. 1, show that replacement of the saturated diamine En with an unsaturated α,α′-diimine ligand, Bpy or Phen, in $[Pt(C^N)(N–N)]^+$ leads to a change in the nature of the redox LUMO of the complex from π*(C^N) to π*(α,α′-diimine).

The observed oxidation waves are completely irreversible, Fig. 1, and can be assigned to an MC Pt(II)→Pt(III) oxidation followed by a fast chemical reaction [36,37]. Owing to the irreversibility of the oxidation processes the experimental oxidation potentials cannot provide reliable information about the energy position of the HOMO in the complexes. The electrochemical data in Table 1, however, show that the reduction and oxidation potentials of [Pt(Ppy)XY]^z and [Pt(Tpy)XY]^z are quite similar. This observation suggest that the energies of the HOMO and the LUMO remain relatively fixed in the two types of complex.

Unlike the irreversible MC oxidation waves observed for $[Pt(C^N)(N–N)]^+$ and related cyclometalated species, the $[Pt(C^N)Mnt]^-$ complexes exhibit a one-electron quasi-reversible oxidation wave, Fig. 1, which can be assigned to a dithiolate ligand-centered process. It should be emphasized, however, that in the case of Pt(II) complexes with a high degree of covalency in the metal–ligand bonds this classification of the redox MO as well as of the excited states, as based on the localized molecular-orbital approach, can only be used as a first approximation. It has been shown for several Pt(α,α′-diimine)Mnt complexes that the HOMO is predominantly

sulfur-p orbitals but with an admixture, ca. 27%, of the metal d-state, giving a partial metal character of the HOMO, p(S)/d(Pt) [27]. A partial metal character of the HOMO for $[Pt(C^N)Mnt]^-$ is therefore to be expected.

The electrochemical data obtained show that when the En ligand is replaced by an unsaturated ligand, Bpy, Phen or Mnt, the nature of the redox orbitals of the $[Pt(C^N)XY]^z$ complexes is changed. One may therefore conclude that a corresponding change in the nature of the low-energy excited states and the absorption and emission properties of the complexes will take place.

2.2. Electronic spectroscopy

The absorption and emission spectra for each member in the two series of $[Pt(Ppy)XY]^z$ and $[Pt(Tpy)XY]^z$ complexes with saturated X,Y-ligands, Fig. 3, are in principle quite similar to the spectra obtained for the bis-cyclometalated complexes, $Pt(C^N)_2$, and the same electronic assignments are suggested [11]. In agreement with the redox orbitals nature, the lowest energy spin-allowed and spin-forbidden electronic transitions are assigned to MLCT (d(Pt)–π^*(C^N)). The vibrational satellite structure observed in the electronic spectra of $[Pt(C^N)XY]^z$ at 710, 1130 and 1450 cm^{-1} (Ppy) and at 660, 1040, 1400 cm^{-1} (Tpy) can be attributed to high-energy vibrations of the cyclometalated ligands. The radiative lifetimes τ_r range from 10 to 240 ms and are calculated from the measured emission lifetime τ and the quantum yield Φ, Table 2. These values are consistent with dipole-allowed spin-forbidden transitions.

The electronic spectroscopy data, Table 2, suggest that the character of the lowest excited state of $[Pt(C^N)XY]^z$ complexes is due to both the cyclometalated (C^N) ligand and the X and Y ligands. In agreement with NMR data, the increase in π-back-bonding from the electron rich metal to the X and Y ligands, $Edp > (CN^-)_2 > Edt > En > (PMor_3, Cl^-) > (CO, Cl^-) > (Cl^-)_2$, leads to a number of remarkable features in the absorption and emission data: (i) there is a blue shift of the spin-forbidden MLCT absorption and emission bands; (ii) the solvatochromic effect is decreased; (iii) the radiative lifetimes are increased and the extinction coefficients are decreased. These trends can be attributed to an increasing admixture of the cyclometalated ligand states, π(C^N), to the HOMOs leading to a corresponding increase in the contribution of the ligand-centered character of the lowest excited state of the complexes.

When replacing Ppy with Tpy a red shift of about 3000 cm^{-1} of the MLCT structured absorption and emission bands is observed. However, the redox potentials for the two series of the cyclometalated complexes are very similar, see Table 1. The highest energy emission and the lowest energy absorption maxima are very similar for the two series and depend only slightly on the donor and acceptor properties of the X and Y ligands. The extinction coefficients of $[Pt(Tpy)XY]^z$ are smaller and the radiative lifetimes are longer compared with the values for $[Pt(Ppy)XY]^z$; on average $\epsilon(Ppy)/\epsilon(Tpy) = (1.7 \pm 1)$ and $\tau_r(Tpy)/\tau_r(Ppy) = (2.6 \pm 1)$. Apparently, the lowest excited state of the Tpy complexes contributes more of the π-character of the cyclometalated ligand compared with the corresponding Ppy complexes.

The quenching of the luminescence of $[Pt(Ppy)Cl_2]^-$ by an increase in temperature

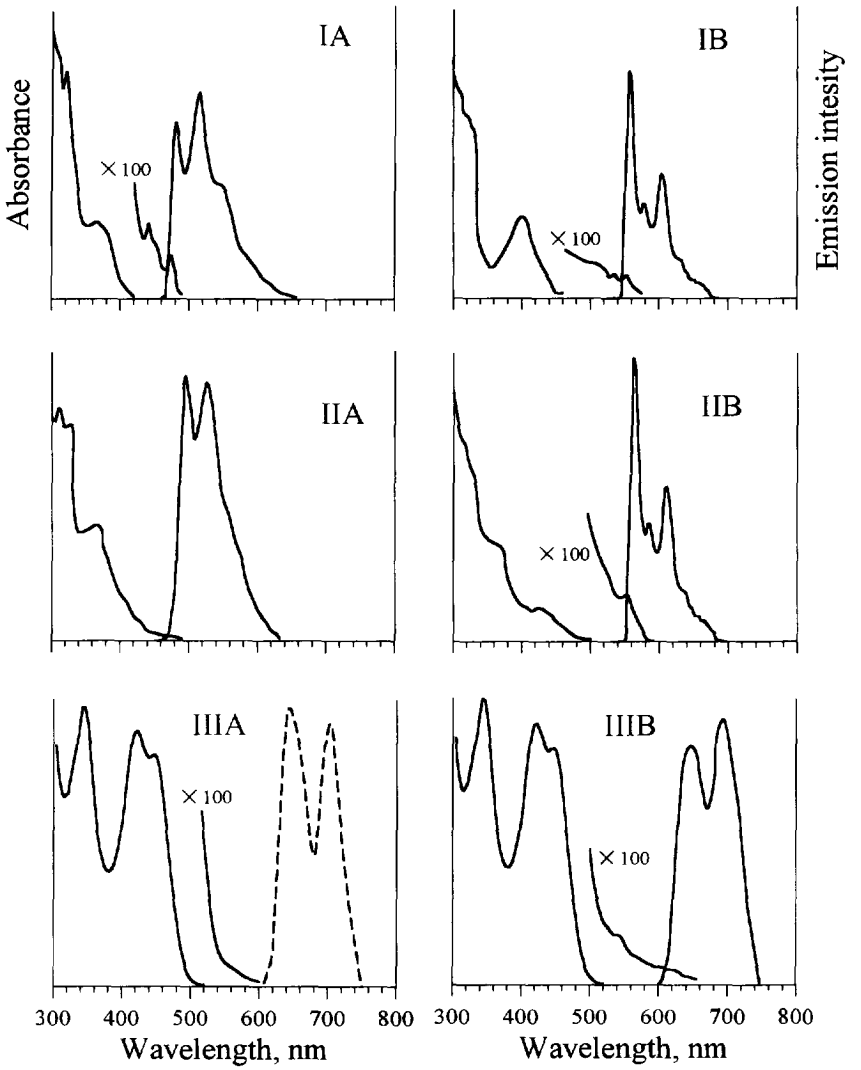

Fig. 3. Absorption and emission spectra of $[Pt(Ppy)En]^+$ (IA), $[Pt(Tpy)En]^+$ (IB), $[Pt(Ppy)Bpy]^+$ (IIA), $[Pt(Tpy)Bpy]^+$ (IIB), $[Pt(Ppy)Mnt]^-$ (IIIA), $[Pt(Tpy)Mnt]^-$ (IIIB) in DMF solution: (———) room temperature; (– – –) 77 K.

has been assigned to the thermally activated population of the upper lying MC excited states followed by fast radiationless processes [36]. This leads to a dependence of the parameters of the luminescence of the $[Pt(Ppy)XY]^z$ complexes in fluid solutions at room temperature on the ligand field strength of the X and Y ligands, Table 2. Contrary to most $[Pt(Ppy)XY]^z$ complexes, the $[Pt(Tpy)XY]^z$ complexes show strong emission both at 77 K and at room temperature. This indicates that when replacing Ppy with Tpy, the energy of the lowest emitting excited state (ca.

Table 2
Properties of the lowest excited state of $[Pt(C^N)XY]^z$ in DMF

Complex	$T=77$ K		$T=293$ K						Assignment
	λ^a (nm)	τ (μs)	λ^a (nm)	τ^b (μs)	$\Phi \times 10^b$	τ_r (μs)	$E_{red}{}^c$ (V)	$-E_{ox}{}^c$ (V)	
$[Pt(Ppy)Cl_2]^-$	491	8	—[d]	—	—	—	0.1	2.2	d(Pt)–π*(C^N)
Pt(Ppy)ClCO	484	—[e]	—[d]	—	—	—	0.8	>1.1	d(Pt)–π*(C^N)
$Pt(Ppy)ClPMor_3$	476	23	—[d]	—	—	—	0.4	1.7	d(Pt)–π*(C^N)
$[Pt(Ppy)En]^+$	481	15	487	1.7	0.6	30	0.4	1.7	d(Pt)–π*(C^N)
$[Pt(Ppy)(CN)_2]^-$	475	22	484	—[f]	—	—	0.3	1.9	d(Pt)–π*(C^N)
$[Pt(Ppy)Edt]^+$	476	29	493	—[f]	—	—	0.8	1.3	d(Pt)–π*(C^N)
$[Pt(Ppy)Edp]^+$	477	50	—[d]	—	—	—	0.8	1.9	d(Pt)–π*(C^N)
$[Pt(Ppy)Etdp]^+$	478	56	—[d]	—	—	—	0.8	1.9	d(Pt)–π*(C^N)
$[Pt(Ppy)Mnt]^-$	646	—[e]	—[d]	—	—	—	−0.5	1.5	p(S)/d(Pt)–π(Mnt)
$[Pt(Ppy)Bpy]^+$	496	—[e]	495	4.0	0.17	200	0.6	1.8	d(Pt)–π*(N–N)
$[Pt(Ppy)Phen]^+$	496	—[e]	494	3.5	0.13	300	0.5	1.8	d(Pt)–π*(N–N)
$[Pt(Tpy)Cl_2]^-$	560	16	565	9.1	1.5	60	−0.3	1.8	d(Pt)–π*(C^N)
Pt(Tpy)ClCO	559	17	565	12	3.1	40	0.4	>1.1	d(Pt)–π*(C^N)
$Pt(Tpy)ClPMor_3$	550	42	556	2.4	0.12	200	0.9	1.3	d(Pt)–π*(C^N)
$[Pt(Tpy)En]^+$	556	20	561	8.8	1.0	100	0.0	1.4	d(Pt)–π*(C^N)
$[Pt(Tpy)(CN)_2]^-$	555	29	558	19	3.1	60	−0.1	1.4	d(Pt)–π*(C^N)
$[Pt(Tpy)Edt]^+$	559	29	556	12	2.0	60	0.4	1.1	d(Pt)–π*(C^N)
$[Pt(Tpy)Mnt]^-$	647	16	668	0.7	0.04	200	−0.5	1.5	p(S)/d(Pt)–π(Mnt)
$[Pt(Tpy)Bpy]^+$	565	15	567	13	0.44	300	0.2	1.4	d(Pt)–π*(C^N)

[a] Highest energy feature of the luminescence emission maxima. [b] Deareated solution. [c] Excited state redox potentials vs. Fc^+/Fc. [d] Emission too weak. [e] Non-exponential decay. [f] Photochemically unstable.

3000 cm^{-1}) is lowered and will cause an increase in the energy gap between the emitting and upper lying MC excited state.

The absorption spectra of $[Pt(C^N)(\alpha,\alpha'\text{-diimine})]^+$ complexes, Fig. 3, are strongly perturbed from those of $[Pt(C^N)En]^+$. The most remarkable feature in the absorption spectra is the appearance of a new intense low-energy absorption band at 410–440 nm which can be assigned to a spin-allowed MLCT (d(Pt)–π*(α,α′-diimine)) transition. Thus, the electrochemical data and the order of the spin-allowed electronic transitions in the $[Pt(C^N)(\alpha,\alpha'\text{-diimine})]^+$ complexes suggest the energy of the π*-orbitals of the cyclometalated ligand to be higher than that of the π*-orbitals of the α,α′-diimine ligand. This leads to the following order for the lowest singlet excited states of $[Pt(C^N)(\alpha,\alpha'\text{-diimine})]^+$ complexes: ^{1}MLCT (d(Pt)–π*(α,α′-diimine)) < ^{1}MLCT (d(Pt)–π*(C^N)). The order for the triplet excited states, however, which determines the emission properties of the complexes, may be different. The important factor when attempting to order the triplet excited states is the singlet triplet energy splitting. The luminescence parameters of $[Pt(Ppy)Bipy]^+$ and $[Pt(Ppy)Phen]^+$, Table 2, are quite similar and differ from those of $[Pt(Ppy)En]^+$. In agreement with the character of the redox orbitals, the lowest energy emitting excited state of $[Pt(Ppy)(\alpha,\alpha'\text{-diimine})]^+$ complexes can be assigned to ^{3}MLCT (d(Pt)–π*(α,α′-diimine)). However, when replacing Ppy with Tpy the

energy of the ^{3}MLCT (d(Pt)–π^*(C^N)) excited state is lowered (ca. 3000 cm^{-1}). This leads to different ordering for the singlet and triplet excited states of [Pt(Tpy)(α,α'-diimine)]$^+$ complexes; for the singlet excited state ^{1}MLCT (d(Pt)–π^*(α,α'-diimine)) < ^{1}MLCT (d(Pt)–π^*(C^N)) and for the triplet excited state ^{3}MLCT (d(Pt)–π^*(C^N)) < ^{3}MLCT (d(Pt)–π^*(α,α'-diimine)).

The absorption and emission spectra of two [Pt(C^N)Mnt]$^-$ complexes are similar, Fig. 3. As expected from the electrochemical data, the absorption bands differ markedly from those of the [Pt(C^N)XY]^z complexes with saturated X,Y-ligands, the most remarkable feature being the appearance of two new intense bands in the visible region with a significant solvent dependence. Based on the electrochemical data and the solvatochromic effect, one may assign the lower energy absorption band to a spin-allowed (p(S)/d(Pt))→π^*(C^N) transition which can be classified as being predominantly of the ligand to ligand charge transfer (LLCT) type, while the second low-energy absorption band can most likely be assigned to a p(S)/d(Pt)→π^*(Mnt) transition with some degree of IL – MLCT character.

Thus, the electrochemical data and the order of the spin-allowed electronic transitions suggest that the energy of the π^*-orbitals of the cyclometalated ligand is lower than that of the π^*-orbitals of the dithiolate ligand. This leads to the following order for the lowest singlet excited states of [Pt(C^N)Mnt]$^-$ complexes: ^{1}LLCT < ^{1}(IL–MLCT) < ^{1}MLCT. As expected, however, the singlet–triplet splitting of the LLCT state looks smaller than that of the MLCT and particularly the IL state [25,45].

Electronic spectroscopy data obtained show that the lowest energy spin-forbidden transitions of [Pt(C^N)Mnt]$^-$ complexes do not show a notable solvatochromic effect. The energy and the band shape of the emission spectra are very similar to the previously reported spectra of the related [PtL$_1$L$_2$Mnt]^z complexes, and the same electronic assignment for the ^{3}(p(S)/d(Pt)→π^*(Mnt)) is suggested [19,24,27,31,32]. The [Pt(Tpy)Mnt]$^-$ shows detectable luminescence in DMF solution at room temperature. The value of the radiative lifetime, 150 ms, is consistent with a dipole-allowed but spin-forbidden ^{3}(p(S)/d(Pt)→π^*(Mnt)) transition. The emission from [Pt(Ppy)Mnt]$^-$ in fluid solution is too weak to be measured, but both of the [Pt(C^N)Mnt]$^-$ complexes show strong and structured emissions at lower temperature, see Fig. 3.

From the absorption and the emission data of [Pt(C^N)Mnt]$^-$ one may conclude that the difference in the singlet–triplet splitting for the LLCT, MLCT and IL–MLCT excited states of [Pt(C^N)Mnt]$^-$ leads to different ordering for the singlet excited state ^{1}LLCT < ^{1}(IL/MLCT) < ^{1}MLCT and for the triplet excited state ^{3}(IL/MLCT) < ^{3}MLCT, ^{3}LLCT.

2.3. Excited state properties

Based upon the spectroscopic and electrochemical data, the redox potentials of the excited state of [Pt(C^N)XY]^z complexes can be estimated, Table 2. The data show that the lowest long-lived excited state of the cyclometalated Pt(II) complexes are both good reductants and oxidants. Given the high luminescence quantum yields

and long lifetimes of $[Pt(Tpy)XY]^z$ and some of $[Pt(Ppy)XY]^z$ complexes in fluid solution at room temperature, it is not difficult to envisage that these compounds are promising candidates for photoinduced energy and electron transfer processes.

The emission of the $[Pt(C^N)XY]^z$ complexes in fluid solutions is most efficiently quenched by oxygen, the quenching constant being of the order of $10^9\ M^{-1}\ s^{-1}$ [36]. Moreover, the $[Pt(Ppy)En]^+$ complex shows self-quenching processes in aqueous solution. 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 $6.7 \times 10^8\ M^{-1}\ s^{-1}$ can be obtained from a linear Stern–Volmer plot [36]. 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 [35,44]. The planar structure of the $[Pt(Ppy)En]^+$ complex [46] 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 state dimer, an excimer. Formation of excimer species from the cyclometalated Pt(II) complexes has recently been suggested [47].

Like bis-cyclometalated Pt(II) complexes [8], in halocarbon solvents the $[Pt(C^N)XY]^z$ complexes undergo photo-oxidative addition reactions. As one can see, Fig. 4, the irradiation of the $[Pt(C^N)En]^+$ complexes caused the disappearance of the MLCT band and other spectral changes with clean isosbestic points. At the end of the photoreaction, only one species was present, which can most probably be identified as an addition product $[Pt(C^N)En(CHCl_2)Cl]^+$.

3. Conclusions

Combined photophysical, photochemical, and electrochemical studies of mixed-ligand cyclometalated $[Pt(C^N)XY]^z$ complexes indicate that this class of coordina-

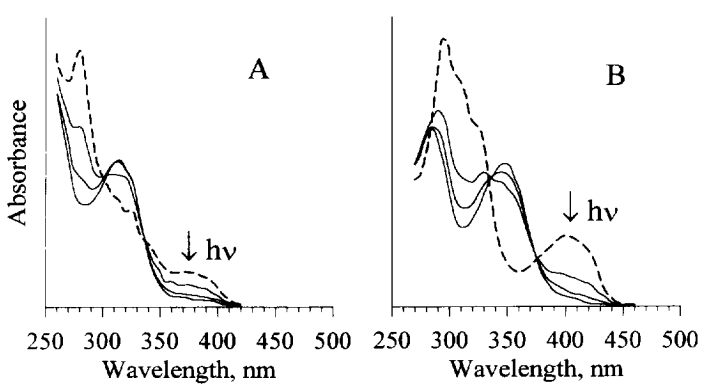

Fig. 4. Spectral changes for a $[Pt(Ppy)En]^-$ (A) and $[Pt(Tpy)En]^+$ (B) in deaerated $CHCl_3$ solution on irradiation with 313 nm.

tively unsaturated four-coordinated complexes provides a useful basis for the study of the effects of a variation of the donor and acceptor properties of the ligands on the nature and properties of the electronic excited states. Given the high luminescence quantum yields and long lifetimes of $[Pt(Tpy)XY]^z$ and some of $[Pt(Ppy)XY]^z$ complexes in fluid solution at room temperature, and the ability to tune their redox properties, size and hydrophilicity through variation in the X,Y-ligands, it is not difficult to envisage that these systems will possess rich photochemistry.

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