An Alternative Route to Highly Luminescent Platinum(II) Complexes: Cyclometalation with N^C^N-Coordinating Dipyridylbenzene Ligands

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The remarkable luminescence properties of the platinum(II) complex of 1,3-di(2-pyridyl)benzene, acting as a terdentate N^C^N-coordinating ligand cyclometalated at C2 of the benzene ring ([PtL^1-Cl]), have been investigated, together with those of two new 5-substituted analogues [PtL^{2}Cl] and [PtL^{3}Cl] {HL^2 = methyl-3,5-di(2-pyridyl)benzoate; HL^3 = 3,5-di(2-pyridyl)toluene}. All three complexes are intense emitters in degassed solution at 298 K (λ_{max} 480–580 nm; ϕ_{lum} = 0.60, 0.58, and 0.68 in CH$_2$Cl$_2$), displaying highly structured emission spectra in dilute solution, with lifetimes in the microsecond range (7.2, 8.0, and 7.8 μs). On the basis of the very small Stokes shift, the highly structured profiles, and the relatively long lifetimes, the emission is attributed to an excited state of primarily $^3\pi$–π* character. At concentrations >1 × 10^{-5} M, structureless excimer emission centered at ca. 700 nm is observed. The X-ray crystal structure of [PtL^{2}Cl] is also reported.

In the field of luminescent transition metal complexes, advances with d^8 metal ions have lagged behind those with d^6 metals. Many Pt(II) complexes with simple bipyridine or terpyridine ligands are scarcely emissive at room temperature, often because their metal-centered (d–d) states are subject to efficient nonradiative deactivation, providing a decay pathway for the emissive state.[1] On the other hand, the square planar coordination geometry of such platinum systems offers possible reactivity not available to six-coordinate d^6 complexes, by way of axial interactions. These include self-quenching and cross-quenching,[2,3] and photochemical reactivity,[4] and render those Pt(II) complexes which are emissive of particular interest. Complexes with cyclometalated ligands, such as 2-phenylpyridine and analogues,[5–7] often fall into this category, since the very strong ligand field of the cyclometalated carbon raises the energy of the d–d states, diminishing their deactivating effect. Such a strategy has led to Pt(II) complexes which are emissive in solution at room temperature, either from states of primarily π–π* character, or from MLCT states. For example, the complex [Pt(ppy)-(bpy)]$^+$, where ppy is cyclometalated 2-phenylpyridine, displays emission from an MLCT state,[5a] while [Pt(biphenyl)-(CH$_3$CN)$_2$] is an example of a bright $^3\pi$–π* emitter, with an emission quantum yield of 0.18.[7] Aside from these complexes with bidentate (N^C or C^C) coordination, two main classes of terdentate cyclometalating ligands have been investigated, comprising N^N^C or C^N^C coordination modes. The N^N^C ligand 6-phenyl-2,2′-bipyridine combines the cyclometallating ability of ppy with the π-acceptor property of bpy, leading to emission from a charge-transfer excited state,[8] while the luminescence of complexes with C^N^C coordination has been assigned to a metal-perturbed $^3\pi$–π* state.[9] Luminescence from the third possible class of complex, with ligands offering N^C^N coordination, has not been investigated hitherto, and only one example of such a compound has been synthesized previously.[10]

In this contribution, we report on the remarkably high luminescence quantum yields exhibited by cyclometalated Pt(II) complexes of the N^C^N-coordinating ligand 1,3-di-(2-pyridyl)benzene and two 5-substituted derivatives.
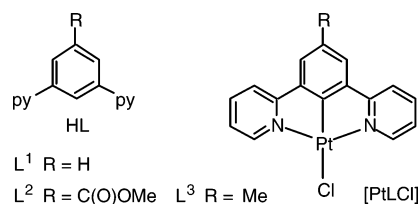
Ligands HL^1–HL^3 were prepared by palladium-catalyzed Stille cross-coupling reactions. Thus, 1,3-dibromobenzene

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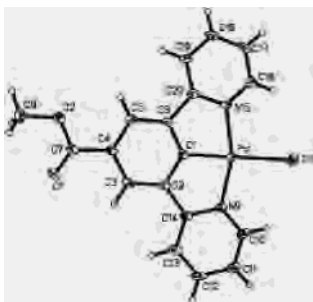
Figure 1. The molecular structure of [PtL²Cl], with displacement ellipsoids at 50% probability level. Selected bond lengths (Å) and angles (deg): Pt-(1)−C(1) 1.903(4); Pt(1)−N(9) 2.035(3); Pt(1)−N(15) 2.036(3); Pt(1)−Cl(1) 2.405(1); N(9)−Pt(1)−N(15) 161.29(13); C(1)−Pt(1)−Cl(1) 178.30-(10); C(1)−Pt(1)−N(9) 80.63(14); C(1)−Pt(1)−N(15) 80.68(13) (see Supporting Information).

reacted with 2-tri-*n*-butylstannyl-pyridine (>2 equiv) in toluene, in the presence of [Pd(PPh₃)₂Cl₂] and LiCl, to generate HL¹ as described previously,[10] while HL³ and the new ligand HL² were prepared in the same way from 3,5-dibromotoluene and methyl-3,5-dibromobenzoate, respectively (see Supporting Information). [PtL²Cl] was prepared by adding an aqueous solution of K₂[PtCl₄] to a solution of HL² in acetonitrile and refluxing the aerated yellow-orange mixture for 3 days. The other two complexes could not be prepared by this route (see Supporting Information). Since [PtL¹Cl] has been synthesized previously in acetic acid under argon,[10] these conditions were employed here, and also allowed [PtL³Cl] to be obtained from HL³. The compounds precipitated as yellow solids, and the cycloplatinated structures were confirmed by ¹H NMR, mass spectrometry, and X-ray crystallography for [PtL²Cl].

The X-ray structure of [PtL²Cl][15] (Figure 1) is similar to that reported for the square-planar unsubstituted compound [PtL¹Cl].[10] Significantly, as in [PtL¹Cl], the Pt−C bond length {1.903(4) Å} in [PtL²Cl] is markedly shorter than that in Pt(II) complexes of 6-phenyl-2,2′-bipyridine and its derivatives, and the Pt−N bond lengths {2.036(3) Å} are also somewhat shorter than typical.[11]

Cyclic voltammetry demonstrates similar electrochemical properties for [PtL¹⁻³Cl] (Table 1). The E^{ox}_p of irreversible oxidation follows the electron-donating properties of the ligand. For [PtL¹Cl] and [PtL³Cl], the $E_{red}^{1/2}$ values are essentially identical, which may arise from the LUMO being dominated by the pyridyl rings, while a significantly less negative $E_{red}^{1/2}$ for [PtL²Cl] may indicate a greater contribution to the LUMO from the phenyl ring.

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(11) A search in the CCD reveals a mean value of 2.04 Å for the Pt−C bond length in six N^N^C complexes, 2.14 Å for the lateral Pt−N bond, and 1.97 Å for the bond to the central N.

Table 1. Photophysical and Electrochemical Parameters for [PtL¹⁻³Cl] at 293 K, in Dichloromethane unless Otherwise Stated

	[PtL¹Cl]	[PtL²Cl]	[PtL³Cl]
absorbance λ_{max}/nm (ϵ/L mol⁻¹ cm⁻¹)[a]	332 (6510)	329 (7560)	335 (5710)
	380 (8690)	380 (9990)	381 (6900)
	401 (7010)	397 (7880)	412 (6780)
	454 (270)	446 (180)	460 (190)
	485 (240)	478 (200)	495 (130)
emission[b] λ_{max}/nm	491, 524, 562	481, 513, 550	505, 539, 578
ϕ_{lum} degassed (aerated)[c]	0.60 (0.039)	0.58 (0.067)	0.68 (0.024)
τ_0 degassed (aerated)/μs[d]	7.2 (0.5)	8.0 (0.6)	7.8 (0.3)
τ excimer/μs[e]	0.10	0.30	0.25
k_Q/M⁻¹ s⁻¹	5.3 × 10⁹	3.6 × 10⁹	3.3 × 10⁹
$E_{red}^{1/2}$/V (ΔE/mV)[f]	−2.140 (70)	−2.040 (60)	−2.150 (70)
E_p^{ox}/V[f]	0.350	0.390	0.290

[a] Beer−Lambert law obeyed at concentrations <2 × 10⁻⁴ M. [b] Emission maxima at <10⁻⁶ M. [c] Value quoted is the mean obtained from measurements using three standards, [Ru(bpy)₃]Cl₂ in H₂O (ϕ = 0.028),[13a] fluorescein in 0.1 M NaOH (ϕ = 0.90),[13b] and quinine sulfate in 1 M H₂SO₄ (ϕ = 0.546),[13c] uncertainty ±15%. [d] The lifetime at infinite dilution as determined using eq 1 (±10%). [f] In CH₃CN/0.2 M [Bu₄N][BF₄], in the potential range −2.4 to +1.0 V; E_p^{ox} = peak potential of chemically irreversible oxidation; $E_{red}^{1/2}$ = half-wave potential of the reduction process. At low scan rates, the return wave associated with this reduction is diminished, implying chemical irreversibility. ΔE = cathodic-to-anodic peak separation; potentials were measured vs SCE, reported vs Fc⁺/Fc couple ($E_{1/2}$ = +0.424 V), scan rate 300 mV s⁻¹.
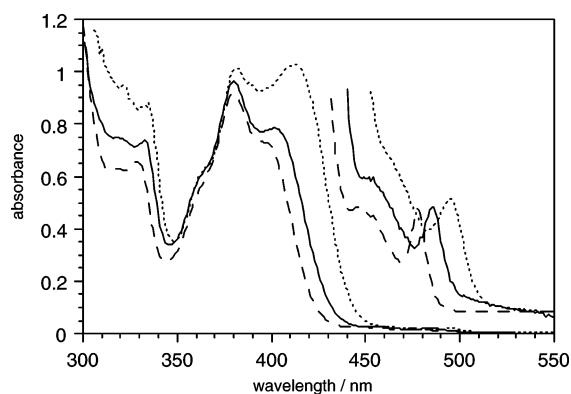

Figure 2. Absorption spectra of [PtL¹Cl] (−), [PtL²Cl] (- - -), and [PtL³-Cl] (···) in CH₂Cl₂ at 295 K. The weak, long wavelength bands are shown on an expanded scale for clarity.

The absorption spectra of [PtL¹⁻³Cl] in solution (Figure 2, Table 1) display very intense bands at wavelengths below 300 nm, assigned to ¹π−π* transitions of the ligands. The absorption envelope at 350−440 nm comprises at least three absorption bands. The component band at lowest energy is subject to a red-shift as the 4-substituent becomes more electron-donating, and exhibits pronounced negative solvatochromic behavior, typical of charge-transfer transitions (shifting, for example, for [PtL³Cl], from 379 nm in CH₃-CN to 434 nm in CCl₄), with a concomitant increase in the half-width (see Supporting Information). These observations suggest that there are at least two overlapping transitions responsible for this absorption band, one a ¹π−π* (little affected by solvent) and the other a charge-transfer transition. The very weak bands at lower energy (478−495 nm, Figure 2) are attributed to direct population of ³π−π* states facilitated by the high spin−orbit coupling associated with the Pt(II) ion.
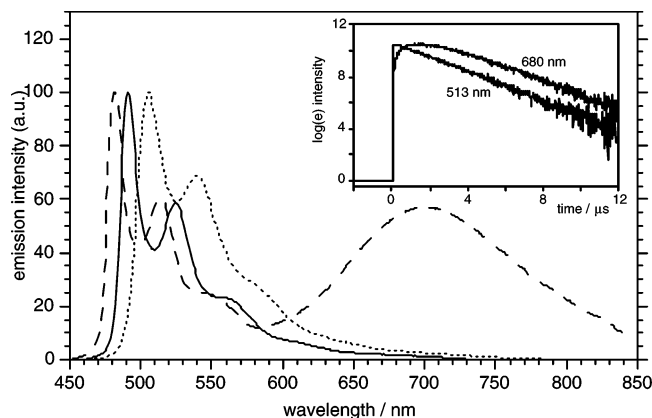
Figure 3. (a) Emission spectra of [PtL^{1}Cl] (—) and [PtL^{3}Cl] ($\cdots$) in dilute solution in CH$_2$Cl$_2$ (2.5 × 10^{-6} M), and of [PtL^{2}Cl] (- - -) at higher concentration (1.0 × 10^{-4} M). λ_{ex} = 401, 412, and 397 nm, respectively; excitation and emission band-passes of 2.0 nm, 293 K. (b) The emission kinetic traces for the solution of [PtL^{2}Cl], registered at 515 nm (monomer) and 680 nm (excimer), obtained using 355 nm excitation (3rd harmonic of a Nd:YAG laser).

All three complexes are highly luminescent in solution, with quantum yields in the range 0.58−0.68 in degassed dichloromethane (Figure 3, Table 1). The emission spectra are highly structured, with the highest energy band almost coincident with the weak, lowest energy absorption band, e.g., 481 and 478 nm, respectively, for [PtL^{2}Cl]. The emission maxima are slightly red-shifted in the order CO$_2$-CH$_3$ < H < CH$_3$, but as this trend is also observed in the low energy absorbance maxima, the Stokes shifts remain small. The pronounced vibrational structure is typical of emission from a $\pi-\pi*$ excited state, and the very small Stokes shifts are incompatible with emission from a charge-transfer excited state, indicating that the emission originates from a state of primarily $^3\pi-\pi*$ character.

Further evidence in support of this assignment comes from the relatively long emission lifetimes (7.2−8.0 μs, Table 1). Efficient quenching of the emission of each complex by dioxygen is observed, with quenching rate constants of the order of 10^9 M^{-1}s^{-1} (see Supporting Information). Many square planar Pt(II) complexes are also subject to self-quenching, sometimes accompanied by excimer formation.[3] For [PtL$^{1-3}$Cl], an increase in concentration leads to a decrease in the observed lifetime and the appearance of a new, broad structureless emission band centered at ca. 700 nm, indicative of excimer formation. The emission decay registered in the 480−538 nm region, where no significant contribution from the excimer emission can be anticipated, remains monoexponential over the whole range of concentrations used. The emission kinetic trace registered near the maximum of the excimer emission shows a monoexponential growth followed by a monoexponential decay with the same rate constant as that of the monomer (Figure 3b). The emission lifetime of the monomer at infinite dilution, τ_0, and the apparent[12] rate constant of self-quenching, k_Q, were determined (eq 1, Table 1) from the linear variation of the observed emission decay rate constant, k_{obs}, as a function of

the concentration of the complex, [Pt]. The high values of

$$k_{obs} = 1/\tau_0 + k_Q[Pt] \text{ (eq 1)}^{3a} \qquad (1)$$

k_Q indicate very efficient excimer formation. The excimer lifetime was estimated by extrapolation of a plot of $1/k_{obs}$ versus 1/[Pt] to infinite concentration[3a] and gave values of 100−300 ns. Such excimer emission has been observed in [Pt(diimine)(CN)$_2$] complexes[3a] and some Pt(II) acetylide systems,[3b] but not previously in complexes of N^N^C or C^N^C ligands.

The unambiguous switch from MLCT to $\pi-\pi*$ character in passing from N^N^C to N^C^N-chelation is evidently due to a change in the nature of the HOMO, from being primarily metal-centered to ligand-centered. The relatively long lifetimes and extremely high emission quantum yields are considerably superior to those of the analogous N^N^C complexes (e.g., for [Pt(phbpy)Cl], ϕ = 0.025 and τ = 0.51 μs[8]). It is likely that the stronger ligand field exerted by the N^C^N chelate, with its significantly shorter Pt−C bond compared to the N^N^C, serves to further raise the energy of the d−d excited state, effectively cutting off this pathway of nonradiative deactivation. Thus, as a strategy for obtaining highly emissive Pt(II) complexes, N^C^N coordination offers an alternative to the switch from MLCT to ILCT emission achieved by appending [Pt(tpy)Cl]$^+$ with electron-rich aromatic groups,[14] which is also accompanied by dramatic increases in quantum yield and lifetime.

In summary, the three compounds reported represent a new class of highly luminescent square planar Pt(II) complexes, in which the emission energy can be fine-tuned via the *para* substituent on the phenyl ring of the N^C^N ligand. The luminescence quantum yields in solution are of a magnitude apparently very large for Pt(II) complexes. These compounds may offer potential in a variety of applications, from molecular sensors to electroluminescence, and further properties are under investigation.

Supporting Information Available: Details of synthetic procedures, electrochemistry and crystallography; luminescence decay rate constants as a function of concentration; and absorption and emission data in solvents of different polarities. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Crystal data for [PtL^{2}Cl]: C$_{18}$H$_{13}$ClN$_2$O$_2$Pt, M = 519.84, monoclinic, a = 7.4042(5) Å, b = 12.9869(9) Å, c = 16.4071(12) Å, β = 91.482(1)°, U = 15.77.1(3) Å^3, T = 150(2) K, space group $P2_1/c$ (No. 14), Z = 4, D_c = 2.190 g cm^{-3}, μ(Mo Kα) = 9.08 mm^{-1}, 3697 unique reflections measured and used in all calculations. Final R$_1$ [3165F > 4$\sigma(F)$] = 0.0216, and wR(all F^2) was 0.0576.