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Synthesis and luminescence properties of $[Pt{4'-(Np1)-trpy}(C \equiv CPh)]SbF_6$ and $[Pt{4'-(Np1)-trpy}{C \equiv C(CH_2)_2CH_3}]SbF_6$ [4'-(Np1)-trpy = 4'-(1-naphthyl)-2,2':6',2''-terpyridine]

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Abstract

The synthesis and characterisation of $[Pt{4'-(Np1)-trpy}(C = CPh)]SbF_6 (1)$ and $[Pt{4'-(Np1)-trpy}{C = C(CH_2)_2CH_3}]SbF_6 (2)$ [4'-(Np1)-trpy = 4'-(1-naphthyl)-2,2:6',2'-terpyridine] are described. Complexes 1 and 2 exhibit unimolecular ³MLCT (MLCT = metal-to-ligand charge transfer) emission in acetonitrile and in a low concentration 77 K glass solution in butyronitrile. The high concentration glass emission as well as the emission in the solid state is from a ³MMLCT (MMLCT, metal-metal-to-ligand charge transfer) excited state, reflecting the presence of $d_z^2(Pt)-d_z^2(Pt)$ interactions in these media. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Terpyridyl (trpy where trpy = 2,2':6',2''-terpyridine) ligand complexes of platinum (II) with a chloride ion as the fourth ligand bonded to platinum have received considerable attention insofar as their photoluminescence properties are concerned [1–14]. However, only four reports have appeared on the photophysics of complexes where a terminal-acetylide ligand is bound to a Pt(trpy) unit [15–18] and one report on the photophysics of complexes where two Pt(trpy) units are linked by a bridging-acetylide ligand [19]. We report the synthesis and photoluminescence properties of two new-acetylide complexes, [Pt{4'-(Np1)-trpy}(C=CPh)]SbF₆ (1) and [Pt{4'-(Np1)-trpy}{ $C \equiv C(CH_2)_2CH_3$ }]SbF₆ (2) (Np1 = 1-naphthyl). These complexes are distinguished by the presence of a 1-naphthyl group bonded to the 4-position of the 2,2':6',2"-terpyridyl moiety. As we have previously reported, the naphthyl group can influence dramatically the luminescence properties of terpyridyl ligand complexes of platinum (II) [5].

2. Experimental

2.1. Materials

All organic reagents and solvents were purchased from Aldrich Chemicals and used as received. The 4'-(1-naphthyl)-2,2:6',2"-terpyridine was prepared as described previously [5]. The [Pt(PhCN)₂Cl₂] and AgSbF₆

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were obtained from Strem Chemicals. The AgC \equiv CA [A = Ph or (CH₂)₂CH₃] salts were prepared by reaction of AgNO₃ with the appropriate alkyne using the method of Agawa [20]. The CD₃CN used for recording NMR spectra was of spectroscopic grade and obtained from Merck Chemicals. For the UV–Vis absorption and solution emission measurements spectroscopic grade solvents were used that were deoxygenated prior to use by a stream of argon.

2.2. Synthesis of $[Pt\{4'-(Np1)-trpy\}(C \equiv CA)]SbF_6$ [A = Ph (1) and A = $(CH_2)_2CH_3$ (2)]

A suspension of [Pt(PhCN)₂Cl₂] (100 mg, 0.21 mmol) in acetonitrile (20 ml) was treated with an equimolar amount of AgSbF₆ (73 mg, 0.21 mmol) dissolved in acetonitrile (5 ml). The reaction mixture was heated under reflux for 16 h, the AgCl precipitate removed by filtration and one equivalent of 4'-(1-naphthyl)-2,2:6',2"-terpyridine (76 mg, 0.21 mmol) added to the filtrate. The reaction mixture was heated under reflux for a further 24 h after which the volume of the solution was reduced in vacuo, resulting in the precipitation of [Pt{4'-(Np1)trpy{Cl]SbF₆. Subsequent purification involved washing the product with a minimum of acetonitrile and drying in vacuo. Yield: 0.12 g (70%). Anal. Calc. for C₂₅H₁₇ClF₆N₃PtSb: C, 36.37; H, 2.08; N, 5.09. Found: C, 36.71; H, 2.33; N, 5.30%. ¹H NMR (CD₃CN): δ 8.92 (m, 2H), 8.49 (m, 2H), 8.0–8.4 (7H), 7.6–7.9 (6H).

A suspension of $[Pt{4'-(Np1)-trpy}Cl]SbF_6$ (100 mg, 0.12 mmol) and AgC=CA (0.15 mmol, 25% excess) in pyridine (5 ml) was stirred for 48 h. Precipitation of the product was effected by the addition of chloroform. The solid material was washed thoroughly with chloroform and dried in vacuo. Purification of the crude product was achieved by its extraction into a minimum amount of boiling acetonitrile and subsequent filtration of the hot solution. Allowing the filtrate to cool to room temperature afforded both $[Pt{4'-(Np1)-trpy}(C=CPh)]$ SbF₆ and $[Pt{4'-(Np1)-trpy}{C=C(CH_2)_2CH_3}]SbF_6$ as orange microcrystalline solids.

[*Pt*{4'-(*Np1*)-*trpy*}(*C*=*CPh*)]*SbF*₆. Yield: 78 mg (73%). *Anal.* Calc. for C₃₃H₂₂F₆N₃PtSb: C, 44.77; H, 2.49; N, 4.71. Found: C, 44.40; H, 2.68; N, 4.81%. IR (KBr, cm⁻¹): v(C=*CPh*) 2120w; v(trpy) 1608s, 1486m, 1477m, 1418m, 1394mw, 1034w; $v(SbF_6^{-})$ 659vs. ¹H NMR (CD₃CN): δ 8.88 (m, 2H), 7.9–8.4 (8H), 7.5–7.8 (8H), 7.30 (m, 4H). UV–Vis (50 μ M in CH₃CN): λ_{max}/nm (ϵ , M⁻¹ cm⁻¹) 289(3.8 × 10⁴); 310(1.7 × 10³); 326(1.5 × 10³); 341(1.7 × 10³); 429(7.8 × 10³).

[*Pt*{4'-(*Np1*)-*trpy*}{*C* \equiv *C*(*CH*₂)₂*CH*₃}]*SbF*₆. Yield: 50 mg (49%). *Anal.* Calc. for C₃₀H₂₄F₆N₃PtSb: C, 42.03; H, 2.82; N, 4.90. Found: C, 42.40; H, 2.96; N, 5.07%. *v*[*C* \equiv *C*(*CH*₂)₂*CH*₃] 2128w; *v*(*trpy*) 1603m, 1475w, 1415w, 1337m, 1031w, 788m, 779m, 752m; *v*(*SbF*₆⁻) 661vs. ¹H NMR (CD₃CN): δ 9.89 (m, 2H), 7.9–8.4 (7H), 7.5–7.8 (4H), 7.33 (m, 4H), 2.64 (t, 2H, C=CH₂CH₂CH₂CH₃), 1.68 (m, 2H, CCH₂CH₂CH₃), 1.11 (t, 3H, CCH₂CH₂CH₃). UV–Vis (50 μ M in CH₃CN): λ_{max}/nm (ϵ , M⁻¹ cm⁻¹) 289(3.3 × 10⁴); 312(1.5 × 10³); 326(1.3 × 10³); 341(1.6 × 10³); 430(6.0 × 10³).

2.3. Instrumentation

Microanalysis for carbon, hydrogen and nitrogen was performed by Galbraith Laboratories, Knoxville, TN, USA. Infrared spectra were recorded using a Shimadzu FT IR 4300 spectrometer. ¹H NMR spectra were recorded at 303 K using a Varian Gemini 200 MHz spectrometer. UV-Vis spectra were recorded at 295 K using a Shimadzu UV-2101PC scanning spectrophotometer. Emission spectra were recorded on a SLM-Aminco SPF-500C spectrofluorometer. The cryostat was an Oxford Instruments model DN1704 liquid-nitrogen-cooled system complete with an Oxford Instruments model ITC4 temperature controller. The excitation wavelength was 330 nm, with the scattered light removed by a 400 nm long-wave-pass filter. The 337 nm line from a nitrogen laser served as the excitation source for the lifetime measurements, with a 337 nm band pass filter used to remove stray light from the beam. Lifetime data were analysed as described previously [21,22].

3. Results and discussion

The σ -acetylide complexes 1 and 2 were synthesised in good yields by means of a metathesis reaction in which the chloro-analogue, [Pt{4'-(Np1)-trpy}Cl]SbF₆, was reacted in pyridine with the silver salts AgC=CPh and AgC=C(CH₂)₂CH₃ respectively. Complexes 1 and 2 were isolated as orange microcrystalline solids by cooling a solution of the compound in hot acetonitrile. Unfortunately, despite repeated attempts, it was not possible to grow single crystals of 1 and 2 for the purposes of an X-ray diffraction study.

3.1. Photophysical properties of 1 and 2

The UV–Vis absorption spectra of **1** and **2** measured in acetonitrile are very similar with a peak at ~289 nm, a vibrationally structured band between 300 and 350 nm, and a broad band at ~430 nm. As is the case for other terpyridyl ligand complexes of platinum(II), the high energy peaks are assigned to ${}^{1}(\pi-\pi^{*})$ transitions of the 4'-(1-naphthyl)-2,2:6',2-terpyridyl ligand [2–19]. Two possibilities exist for the assignment of the broad low energy band, a $d\pi(Pt) \rightarrow \pi^{*}(trpy)$ metal-to-ligand charge transfer (MLCT) transition or an acetylide-to-terpyridine ligand-to-ligand charge transfer (LLCT) transition. We tentatively make the MLCT assignment, as indeed have other workers for the broad band that is observed in the 400–500 nm region of the absorption spectra of mononuclear σ -acetylide ligand complexes of platinum terpyridines [15–18].

The emission spectra of 1 and 2 measured in $CH_2Cl_2/$ CH₃CN (20:1) and CH₂Cl₂ solutions are shown in Fig. 1. The emission spectra in the mixed solvent system consist of a single asymmetric peak centred at 611 nm for 1 and 632 nm for 2, with excited state lifetimes of 1.80 and 0.55 µs, respectively. Both complexes exhibit more intense emission maxima at slightly lower energies when recorded in pure CH₂Cl₂, occurring at 616 and 638 nm for **1** and **2**, respectively. The excited state lifetimes (τ) are correspondingly longer, being 2.6 and 1.2 µs, respectively. The decrease of the emission intensity when a coordinating solvent (CH₃CN) is added, the change in emission energy with the polarity of the solvent and the emission profile, are all consistent with a ³MLCT assignment to the emitting state. The same assignment has been made for the fluid emission exhibited by the σ -acetylide complexes, $[Pt(trpy)(C \equiv CPh)]PF_6$ [15], $[Pt\{4'-R_1-trpy)$ $(C \equiv CR_2)$ ClO₄ (R₁ = *p*-tolyl; R₂ = CH₂OH, *n*-propyl, C_6H_4Cl-4 , C_6H_5 , $C_6H_4CH_3-4$) [16] and [Pt(trpy)(C=C) C_6H_4 -4-R]X (R = N(CH_3)₂, X = BF₄; R = N-15-monoazacrown-5, $X = ClO_4$) [17]. We note that the emission in dichloromethane exhibited by the analogous chloride compound [Pt{4'-(Np1)-trpy}Cl]SbF₆ [5], has a similar band profile to those shown in Fig. 1 for the σ -acetylide derivatives 1 and 2. However, the emission energy and excited state lifetime are higher $[\lambda_{em}(max) = 588 \text{ nm}]$ and $\tau = 16.6 \,\mu\text{s}$]. The unexpectedly long excited state lifetime for the chloride compound has been explained in terms of the configurational mixing of ³ILCT (ILCT = intraligand charge transfer) character in an emitting state that is primarily ³MLCT in origin [5]. This does not appear to be the case for compounds 1 and 2; moreover, the shorter lifetimes recorded for the σ -acetylide derivatives are consistent with the energy gap law [23,24] as their emission energies are lower than that recorded for $[Pt{4'-(Np1)-trpy}Cl]SbF_{6}[5]$.



Fig. 1. Emission spectra of 1 in $CH_2Cl_2/CH_3CN(20:1)$ (a) and CH_2Cl_2 (b). Emission spectra of 2 in $CH_2Cl_2/CH_3CN(20:1)$ (c) and CH_2Cl_2 (d).



Fig. 2. Solid state emission spectra of 1 as a function of cooling from (a) 280 K to (f) 80 K in 40 K steps.

The solid state emission spectra of 1 and 2 were recorded at 40 K intervals over the temperature range 80-280 K. The spectra recorded for 1 are shown in Fig. 2, those obtained for **2** being very similar.¹ The solid emission spectrum of 1 at 280 K consists of a relatively broad asymmetric band centred at 703 nm ($\tau = 360$ ns). On lowering the temperature to 80 K the band narrows and systematically increases in intensity ($\tau = 1.30 \ \mu s$). Furthermore, the emission maximum systematically shifts to the red as the solid is cooled reaching a value of 754 nm at 80 K. These features of the solid emission exhibited by 1 are characteristic of a ³MMLCT (metalmetal-to-ligand charge transfer) excited state as exhibited in the solid state by, for example, [Pt(trpy)Cl]CF₃ SO₃ [2], [Pt{4-(*o*-CH₃-Ph)-trpy}Cl]SbF₆ [7], [Pt{4-(*o*-Cl-Ph)-trpyCl]SbF₆ [9] and [Pt(trpy)(C \equiv CPh)]PF₆ [15]. The implication is that $d_z^2(Pt)-d_z^2(Pt)$ interactions are present in the solid and that these grow stronger as the solid is cooled [7,9,15]. However, in view of the absence of a crystal structure determination of 1 or 2 to confirm this conclusion, a study was made of the concentration dependence of the 77 K butyronitrile glass emission exhibited by 2; Fig. 3 gives the results. (The lower solubility of **1** in butyronitrile prevented the acquisition of a clean set of spectra over the full concentration range for this compound.) At the lowest concentration of 0.001 mM, a vibrationally structured band with components at 527 and 558 nm is observed. A Huang-Rhys ratio (I_{0-1}/I_{0-0}) of less than 1 is in line with an assignment that is predominantly ³MLCT in character. Indeed, the low concentration glass emission for 2 is very similar to that measured at 77 K in a butyronitrile glass for $[Pt(trpy)(C \equiv CPh)]PF_6$ and for which a ³MLCT assignment was made [15]. When the concentration is increased

 $^{^{1}}$ The solid emission maxima at 280 and 80 K for **2** occur at 680 (287 ns) and 729 nm (676 ns), respectively. (The lifetime of the emitting state is given in brackets.)



Fig. 3. Emission spectra of $\mathbf{2}$ at 77 K in a butyronitrile glass as a function of concentration.

a new low energy band develops such that at 0.260 M it appears as a broad, but well-pronounced band, centred at 691 nm. This band is reminiscent of the bands that appear between 680 and 729 nm in the solid state emission spectra of 2^1 . Clearly, aggregation of the [Pt{4'-(Np1)trpy}{C==C(CH_2)CH_3}]⁺ cations occurs at high concentrations of the complex with, presumably, the concomitant onset of $d_z^2(Pt)-d_z^2(Pt)$ interactions that give rise to ³MMLCT emission at a longer wavelength. Similar behaviour has been reported for the concentration dependence of the emission recorded in an EMD (EMD = EtOH:MeOH:dimethylformamide) glass for [Pt(trpy)Cl]PF₆ [3].

In summary, complexes 1 and 2 exhibit photoluminescence from a unimolecular ³MLCT excited state when the cationic luminophore is isolated; however, when aggregation occurs (either in a high concentration glass or in the solid state) emission is from a ³MMLCT state because of the presence of d_z^2 (Pt) $-d_z^2$ (Pt) interactions.

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