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Low temperature emission spectra of 2-pyridyl-substituted platinum-1,2-enedithiolates

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Abstract

The emissions from the 2-pyridyl- and 2-pyridinium-substituted platinum-1,2-enedithiolate complexes, $L_2Pt\{S_2C_2(2\text{-pyridyl(ium)})(R)\}$ where L = PPh_3, PPh_2Me, $PPhMe_2$, $P(propyl)_3$ and L_2 = dppm, dppe, and dppp were studied in DMM ($DMF-CH_2Cl_2-MeOH$, 1:1:1, v/v/v) glasses at 77 K. All of the pyridyl-substituted complexes have an emission between 18,600 and 17,900 cm^{-1} with pronounced 1200 cm^{-1} vibronic structure. The lifetimes of the pyridyl-substituted complexes are 216–350 µs. The pyridinium-substituted complexes have emissions in the range of 16,600–16,100 cm^{-1} with less resolved vibronic structure than their pyridyl counterparts. The lifetimes of the pyridinium-substituted complexes are 158–290 µs. The emission at 77 K from both the pyridyl- and pyridinium-substituted complexes contrasts with the room temperature studies where only selected pyridinium complexes were emissive.

Keywords: Low-temperature; Platinum-1,2-enedithiolate; Dual emitter

1. Introduction

Platinum-1,2-enedithiolates have emerged as a important new class of room temperature solution lumiphores [1–13]. Our group has focused on the study of heterocyclic-substituted platinum-1,2-enedithiolate complexes of the type $L_2Pt\{S_2C_2(Het)(R)\}$, $[L_2Pt\{S_2C_2(HetH)(R)\}]^+$, and $[L_2Pt\{S_2C_2(CH_2CH_2\text{-}N\text{-}2\text{-pyridnium})\}]^+$ where L is a mono- or L_2 a bidentate phosphine and Het(H) = quinoxalyl(ium), 2- or 4-pyridyl(ium), pyrazyl(ium) and (R = H, CH_3, and CH_2CH_2OH) [1–10]. Several of these complexes are unique inorganic lumiphores since they are dual-emitters at room temperature. The room temperature emissions from these complexes have been assigned to a short-lived intraligand charge transfer singlet, $^1ILCT^*$ and long-lived triplet $^3ILCT^*$. Given that the lifetimes of the two excited states allows the use of ratiometric detection methods, these complexes have broad analytical applications [5–13]. At present these dual-emitters are under development as pH probes and luminescent tags and $[L_2Pt\{S_2C_2(CH_2CH_2\text{-}N\text{-}2\text{-pyridnium})\}]^+$ is used as the sensor for a commercially available oxygen detector [5,6,11–14].

In previous studies of the $L_2Pt\{S_2C_2(Het)(R)\}$ complexes, it was demonstrated that the 1,2-enedithiolate appended R-group, ancillary phosphine ligand(s) and the protonation state of the heterocycle all had a profound effect upon the solution emission from these complexes. [1–4] This study at low temperature (77 K) in DMM glass ($DMF-CH_2Cl_2-MeOH$, 1:1:1, v/v/v) extends our fundamental knowledge of this new class of emitters and compliments the previous room temperature and transient absorption studies [1–10].

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2. Experimental

2.1. Materials

The complexes (dppe)Pt{S_2C_2(2-pyridine)(H)}, (dppe)Pt{S_2C_2(2-pyridine)(CH_2CH_2OH)}, [(dppe)-Pt{S_2C_2 (CH_2CH_2-*N*-2-pyridinium)}][BPh_2] were prepared as previously described [1,5,10]. (dppm)Pt$(Cl)_2$ [15–17], (dppp)Pt$(Cl)_2$ [15–17], and $(PPh_3)_2Pt(SH)_2$ [18] (where dppp = diphenyldiphosphinopropane, dppm = diphenyldiphosphinomethane, and PPh_3 = triphenyl phosphine) and 1-pyridin-2-yl-2-bromoethanone [19] were prepared according to the literature procedures. All reactions were performed under an atmosphere of nitrogen using standard Schlenk line techniques. Workups were performed in air unless stated otherwise. Dichloromethane, acetonitrile, and pentane were dried over calcium hydride and distilled under nitrogen. Diethyl ether, tetrahydrofuran, and dioxane were dried over Na/benzophenone and distilled under nitrogen. Triethylamine was dried over potassium hydroxide and vacuum distilled. DMSO and DMF were dried over calcium hydride and vacuum distilled. Neutral activated alumina, 80–325 mesh, was purchased from EM Science, Cherry Hill, NJ and treated with 6% H_2O by weight to generate the Brockmann activity 3 material used throughout these studies.

2.2. Physical measurements

UV–Vis spectra were recorded on a Perkin–Elmer Lamda 2S spectrometer. Low temperature (77 K) emission spectra were acquired with a SLM AB2 fluorescence spectrometer. Emission spectra were corrected for instrumental response using factors supplied by the manufacturer. Low temperature emission spectra were made on 10^{-4}–10^{-5} M solutions of all complexes in DMM glass (DMF–CH_2Cl_2–MeOH, 1:1:1, v/v/v) in a 5 mm diameter glass tubes placed in a liquid nitrogen Dewar with quartz windows.

Low temperature emission lifetimes (τ) were determined using a SLM AB2 fluorescence spectrometer with a 25 µs gate width and a 10 µs minimum flash period. The pulse delay was varied in 25 µs intervals from 0 to 350 µs using software provided by the manufacturer. The system was verified using $Ru(bpy)_3Cl_2$ in ethanol–methanol glass (4:1, v/v) as a standard [20]. Lifetimes were calculated from the slope of I_{max} versus pulse delay and were fit with a least-squares analysis using $\tau =$ (pulse delay)/$[I_{max} - I_{max(t=0)}]$. Lifetimes (τ) are reported at the 95% confidence limit which was propagated from the standard error of the slope and the estimated uncertainties in τ.

2.3. Physical measurements

NMR spectra were acquired with a Brüker AF 200, AM 400, DRX 400 or a DRX 500. IR spectra were collected either with a Perkin–Elmer 1600 or a Nicolet 5 DXL FT-IR Spectrometer. UV–Vis spectra were recorded on either a Perkin–Elmer Lambda 2S or a Hewlet Packard 8452A spectrometer. EI and FAB mass spectral data were collected on a Magnetic Sector VG 7070E. Room temperature excitation and emission spectra were acquired with a SLM AB2 fluorescence spectrometer.

3. Synthesis

3.1. (dppm)Pt$(SH)_2$

A 0.27 M sodium hydrogensulfide solution was prepared by adding Na (0.09 g, 3.85 mmol) to 15 ml of absolute EtOH. After the Na dissolved, the solution was exposed to H_2S (1 atm) for 1 h. To this solution was added (dppm)PtCl_2 (1.00 g, 1.54 mmol). The mixture was stirred under an H_2S atmosphere for 24 h. The resulting solid was collected by filtration and washed with water (2 × 20 ml), ethanol (2 × 20 ml) and ether (2 × 20 ml). (dppm)Pt$(SH)_2$ was isolated in 70% yield (0.69 g, 1.08 mmol). ^1H NMR (DMSO-d_6): δ 7.84 (m, 8H, C_6H_5P), 7.51 (m, 12H, C_6H_5 P), 4.90 (t, $J_{P-P} = 10$ Hz, 2H, PCH_2P), −0.49 (d, second order spectrum with line spacing of 4 Hz and Pt satellites, $J_{Pt-H} = 28$ Hz, 2H, SH). ^{31}P NMR (DMSO-d_6): δ −50.9 (s with Pt satellites, $J_{Pt-P} = 2430$ Hz). IR (thin film, cm^{-1}): 3849 (w), 3049 (w), 2966 (w), 1435 (s), 1261 (m), 1100 (s). High resolution mass spectrum (FAB) calc. $m/z =$ 645.04425 for $C_{25}H_{24}P_2S_2{}^{195}Pt$; found 645.04332.

3.2. (dppp)Pt$(SH)_2$

Prepared and isolated as described for complex (dppm)Pt$(SH)_2$ using Na (85 mg, 3.68 mmol) and dpppPtCl_2 (1.00 g, 1.46 mmol). (dppp)Pt$(SH)_2$ was isolated in 65% yield (0.59 g, 0.88 mmol). ^1H NMR (DMSO-d_6): δ 7.66 (m, 8H, C_6H_5P), 7.44 (m, 12H, C_6H_5 P), 3.32 (m, 4H, C_3H_6P), 2.71 (m, 2H, C_3H_6P), −1.0 (d, second order spectrum with line spacing of 7 Hz and Pt satellites, $J_{Pt-H} = 26$ Hz, 2H, SH). ^{31}P NMR (DMSO-d_6): δ −0.97 (s with Pt satellites, $J_{Pt-P} = 2754$ Hz). IR (thin film, cm^{-1}): 3849 (w), 3049 (w), 2917 (w), 1434 (s), 1262 (m), 1100 (s). High resolution mass spectrum (FAB) calc. $m/z = 673.07556$ for $C_{27}H_{28}P_2S_2{}^{195}Pt$; found 673.07656.

3.3. (dppm)Pt{C_2S_2(2-pyridine)(H)}

To a DMF (5 ml) solution of (dppm)Pt$(SH)_2$ (250 mg, 0.156 mmol) was added 1-pyridin-2-yl-2-bromoethanone (46 mg, 0.233 mmol). The orange solution was stirred for 2 h becoming purple. The DMF was removed in vacuo and the solid was chromatographed on a 1 × 20 cm alumina column where the product eluted with CH_2Cl_2. The elutent was evaporated to dryness to give (dppm)Pt{C_2S_2(2-pyridine)(H)} as a yellow crystalline solid in 52% yield (60 mg, 0.080 mmol). ^{1}H NMR (DMF-d_7): δ 8.53 (d, 1H, C_5H_4N, $J_{H-H} = 6$ Hz), 8.21 (d with ^{195}Pt satellites, 1H, J_{P-H}, 6 Hz, S_2C_2H), $J_{Pt-H} = 98$ Hz), 7.91–7.81 (m, 8H, PC_6H_5 and 1H, C_5H_4N), 7.70 (m, 1H, C_5H_4N), 7.55 (d, 1H, C_5H_4N, $J_{H-H} = 6$ Hz), 7.38–7.36 (m, 12H, PC_6H_5), 7.08 (m, 1H, C_5H_4N), 6.97 (d, 1H, C_5H_4N, $J_{H-H} = 6$ Hz), 4.70 (t, 2H, PCH_2,P $J_{P-H} = 11$ Hz). ^{31}P NMR (DMF-d_7): δ −45.7 (q, second order spectrum with line spacings of 74 and 67 Hz and Pt satellites, $J_{Pt-P} = 2314$ Hz). IR (thin film, cm^{-1}): 3049 (w), 2959 (w), 1579 (m), 1461 (s), 1436 (s), 1276 (m), 1101 (s). High resolution mass spectrum (FAB) calc. $m/z = 746.07080$ for $C_{32}H_{27}NP_2S_2^{195}Pt$; found 746.07334. UV–Vis (λ (nm), ε, CH_2Cl_2): (dppm)Pt{C_2S_2(2-pyridine)(H)}, 355 (5000), 415 (900); [(dppm)Pt{C_2S_2(2-pyridinium)(H)]$^+$ 334 (6500), 449 (5100).

3.4. (dppp)Pt{C_2S_2(2-pyridine)(H)}

Prepared and isolated as described for (dppm)Pt{C_2S_2(2-pyridine)(H)} using (dppp)Pt$(SH)_2$ (100 mg, 0.149 mmol) and 1-pyridin-2-yl-2-bromoethanone (44 mg, 0.223 mmol). (dppp)Pt{C_2S_2(2-pyridine)(H)} was isolated as a yellow crystalline solid in in 81% yield (93 mg, 0.12 mmol). ^{1}H NMR ($CDCl_3$): δ 8.34 (m, 1H, C_5H_4N), 8.17 (d with ^{195}Pt satellites, S_2C_2H, $J_{P-H} = 5$, $J_{Pt-H} = 88$ Hz), 7.61–7.51 (m, 8H, PC_6H_5), 7.72 (m, 1H, C_5H_4N), 7.43–7.26 (m, 12H, PC_6H_5 and 1H, C_5H_4N), 6.84 (m, 1H, C_5H_4N), 2.69 (m, 4H, PC_2H_2), 2.57 (m, 2H, PC_2H_2). ^{31}P NMR (DMF-d_7): δ −3.85 (q, second order spectrum with line spacings of 7 and 37 Hz and Pt satellites, $J_{Pt-P} = 2642$ Hz). IR (thin film, cm^{-1}): 3049 (w), 2943 (m), 1644 (s), 1579 (m), 1520 (w), 1460 (w), 1435 (s), 1264 (m), 1102 (s). High resolution mass spectrum (FAB) calc. $m/z = 775.10992$ for $C_{34}H_{32}NP_2S_2^{195}Pt$; found 775.10790. UV–Vis (λ (nm), ε, CH_2Cl_2): (dppp)Pt{C_2S_2(2-pyridine)(H)}, 355 (6400), 410 (800); [(dppp)Pt{C_2S_2(2-pyridinium)(H)}]$^+$, 334 (7000), 464 (5300).

3.5. $(Ph_3P)_2$Pt{C_2S_2(2-pyridine)(H)}

Prepared and isolated as described for (dppm)Pt{C_2S_2(2-pyridine)(H)} using $(Ph_3P)_2$Pt$(SH)_2$ (250 mg, 0.318 mmol) and 1-pyridin-2-yl-2-bromoethanone (95 mg, 0.478 mmol). $(Ph_3P)_2$Pt{C_2S_2(2-pyridine)(H)} was isolated as a yellow crystalline solid in in 60% yield (169 mg, 0.19 mmol). ^{1}H NMR ($CDCl_3$): δ 8.34 (m, 1H, C_5H_4N), 7.65 (m, 1H, C_5H_4N), 7.53–7.42 (m, 15H, PC_6H_5 and 1H, C_5H_4N), 7.28–7.26 (m, 8H, PC_6H_5 and 1H, S_2C_2H), 7.17–7.12 (m, 15H, PC_6H_5 and 1H, C_5H_4N). ^{31}P NMR ($CDCl_3$): δ 20.2 (q, second order spectrum with line spacings of 27 and 65 Hz and Pt satellites, $J_{Pt-P} = 2868$ Hz). IR (thin film, cm^{-1}): 3060 (w), 2955 (w), 1672 (m), 1578 (m), 1525 (m), 1455 (w), 1435 (s), 1261 (s), 1094 (s), 1020 (m). High resolution mass spectrum (FAB) calc. $m/z = 887.14124$ for $C_{43}H_{36}NP_2S_2^{195}Pt$; found 887.14452. UV–Vis (λ (nm), ε, CH_2Cl_2): $(Ph_3P)_2$Pt{C_2S_2(2-pyridine)(H)}, 359 (6100), 415 (1400); [$(Ph_3P)_2$Pt{C_2S_2(2-pyridinium)(H)}]$^+$, 335 (6800), 472 (5400).

3.6. $((Propyl)_3P)_2$Pt{C_2S_2(2-pyridine)(H)}

To a DMF (1 ml) solution of $(Ph_3P)_2$Pt{C_2S_2(2-pyridine)(H)} (20 mg, 0.02 mmol) was added tri-n-propylphosphine (23 μl, 0.11 mmol). The solution was heated at 80 °C for 1 h. The DMF was removed in vacuo and the solid was chromatographed on a 1 × 5 cm alumina column where the product eluted with CH_2Cl_2. The elutent was evaporated to dryness to give $((propyl)_3P)_2$Pt{C_2S_2(2-pyridine)(H)} as a crystalline solid in 52% yield (7 mg, 0.01 mmol). ^{1}H NMR ($CDCl_3$): δ 8.53 (m, 1H, C_5H_4N), 7.76–7.45 (m, 2H, C_5H_4N and S_2C_2H), 7.35 (m, 1H, C_5H_4N), 7.04 (m, 1H, C_5H_4N), 2.11–1.94 (m, 12H, CH_2P), 1.63–1.53 (12H, CH_2), 1.08–1.01 (m, 18H, CH_3). ^{31}P NMR ($CDCl_3$): δ −2.85 (q, second order spectrum with line spacings of 33 and 27 Hz and Pt satellites, $J_{Pt-P} = 2714$ Hz). IR (thin film, cm^{-1}): 2960 (w), 2929 (w), 2870 (w), 1698 (m), 1651 (m), 1575 (m), 1520 (m), 1455 (w), 1458 (s), 1076 (s). High resolution mass spectrum (FAB) calc. $m/z = 683.23511$ for $C_{25}H_{48}NP_2S_2^{195}Pt$; found 683.23566. UV–Vis (λ (nm), ε, CH_2Cl_2): $((Propyl)_3P)_2$Pt{C_2S_2(2-pyridine)(H)}, 356 (4000), 412 (5600); [$((Propyl)_3P)_2$Pt{C_2S_2(2-pyridinium)(H)}]$^+$, 339 (1200), 464 (4500).

3.7. $(Ph_2MeP)_2$Pt{C_2S_2(2-pyridine)(H)}

Prepared and isolated as described for $(Pr_3P)_2$Pt{C_2S_2(2-pyridine)(H)} using $(Ph_3P)_2$Pt-{C_2S_2(2-pyridine)(H), (20 mg, 0.02 mmol) and diphenylmethylphosphine (21 μl, 0.11 mmol). $(Ph_2MeP)_2$Pt{C_2S_2(2-pyridine)(H)} was isolated as a crystalline solid in 47% yield (7 mg, 0.009 mmol). ^{1}H NMR ($CDCl_3$): δ 8.61 (m, 1H, C_5H_4N), 7.96 (m, 1H, C_5H_4N), 7.76–7.60 (m, 8H, PC_6H_5 and 1H, S_2C_2H), 7.57–7.28 (m, 12H, PC_6H_5 and 1H, C_5H_4N), 7.09 (m, 1H, C_5H_4N), 1.85–1.69 (6H, CH_3P). ^{31}P NMR ($CDCl_3$): δ −1.21 (q, second order spectrum with line spacings of 30 and 24 Hz and Pt satellites, $J_{\mathrm{Pt-P}} = 2813$ Hz). IR (thin film, cm^{-1}): 3051 (w), 2962 (w), 1596 (m), 1508 (m), 1437 (m), 1380 (m), 1262 (m), 1028 (m), 825 (m). 747 (m). High resolution mass spectrum (FAB) calc. $m/z = 763.10992$ for $C_{33}H_{32}NP_2S_2^{195}Pt$; found 763.10729. UV–Vis (λ (nm), ε, CH_2Cl_2): $(Ph_2MeP)_2Pt\{C_2S_2(2\text{-pyridine})(H)\}$, 355 (4700), 415 (1100); $[(Ph_2MeP)_2Pt\{C_2S_2(2\text{-pyridinium})(H)\}]^+$, 334 (4400), 462 (4000).

3.8. *$(Me_2PhP)_2Pt\{C_2S_2(2\text{-pyridine})(H)\}$*

Prepared and isolated as described for $(Pr_3P)_2Pt\{C_2S_2(2\text{-pyridine})(H)\}$ using $(Ph_3P)_2Pt\{C_2S_2(2\text{-pyridine})(H)$ (20 mg, 0.02 mmol) and dimethylphenylphosphine (16 mg, 0.011 mmol). $(Me_2PhP)_2Pt\{C_2S_2(2\text{-pyridine})(H)\}$ was isolated as a crystalline solid in 56% yield (8 mg, 0.01 mmol). ^1H NMR ($CDCl_3$): δ 8.61 (m, 1H, C_5H_4N), 8.05 (m, 1H, C_5H_4N), 7.76–7.28 (m, 10H, PC_6H_5, 1H, C_5H_4N, and 1H S_2C_2H), 7.07 (m, 1H, C_5H_4N), 1.90–1.61 (12H, CH_3P). ^{31}P NMR ($CDCl_3$): δ −17.4 (q, second order spectrum with line spacings of 31 and 29 Hz and Pt satellites, $J_{\mathrm{Pt-P}} = 2762$ Hz). IR (thin film, cm^{-1}): 3049 (w), 2966 (w), 1578 (m), 1522 (s), 1437 (s), 1381 (s), 1262 (m), 1105 (m), 1028 (m), 911 (m). 743 (m). High resolution mass spectrum (FAB) calc. $m/z = 639.07861$ for $C_{23}H_{28}NP_2S_2^{195}Pt$; found 639.08279. UV–Vis (λ (nm), ε, CH_2Cl_2): $(Me_2PhP)_2Pt\{C_2S_2(2\text{-pyridine})(H)\}$, 351 (1700), 409 (506); $[(Me_2PhP)_2Pt\{C_2S_2(2\text{-pyridinium})(H)\}]^+$, 355 (1600), 457 (1600).

4. Results and discussion

4.1. Complex studies

The 2-pyridyl substituted platinum-1,2-enedithiolates used in this study are shown in Scheme 1. The complexes $L_2Pt\{S_2C_2(2\text{-pyridine})(H)\}$, L_2 = dppm, dppe, dppp, $(dppe)Pt\{S_2C_2(2\text{-pyridine})(CH_2CH_2OH)\}$, $[(dppe)Pt\{S_2C_2\ (CH_2CH_2\text{-}N\text{-}2\text{-pyridinium})\}][BPh_2]$ were prepared according to the literature procedure [1,5,10]. The complexes $L_2Pt\{S_2C_2(2\text{-pyridine})(H)\}$, L = PPh_3, PPh_2Me, $PPhMe_2$, $P(propyl)_3$ were prepared by phosphine substitution of $(PPh_3)_2Pt\{S_2C_2(2\text{-pyridine})(H)\}$ (Scheme 2).

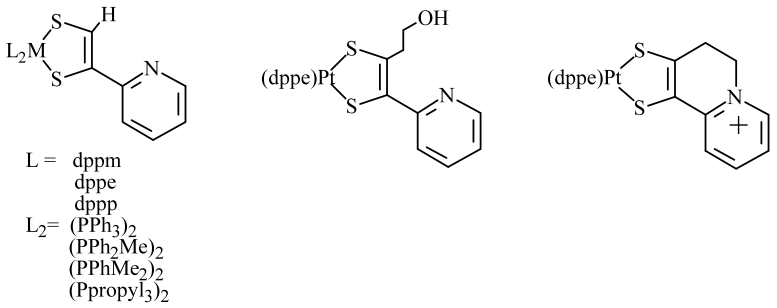
4.2. UV–Visible spectra

All of the complexes have a UV or visible band assignable to a 1,2-enedithiolate π to pyridyl(ium) π* intraligand charge-transfer transition (ILCT). The ILCT band in the neutral complexes is found between 28,100 and 26,900 cm^{-1}, while in the cationic complexes the band is found between 23,200 and 21,500 cm^{-1}, (Table 1, DMM Glass). The ILCT assignment was established in previous studies and was based upon the similarity in the energy of the bands in the corresponding Ni, Pd, and Pt complexes, the solvent dependence of the energy of these bands, and the red shift of these bands upon protonation or alkylation of the appended heterocycle [1,3,5,21–24].

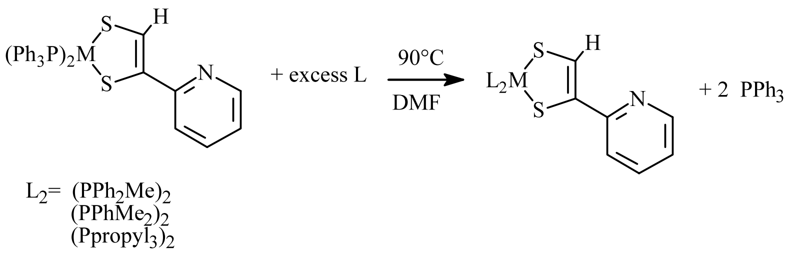
In the platinum complexes, a low energy shoulder at ~410 nm of the ILCT band was assigned to a d to d (d to σ*) transition. Given the low extinction coefficient of this band and its proximity to the ILCT band, the energy of the d to d transition is difficult to accurately determine. In the corresponding Ni and Pd analogs of $(dppe)Pt\{S_2C_2(Het)(H)\}$, where the d to d (d to σ*) is substantially red shifted from the transition in the Pt complexes and easily assigned, it was shown that the d to d transition was essentially unaffected by varying or protonating the appended heterocycle [1–5].

4.3. Low-temperature emission spectra

At room temperature, the luminescent pyridinium complexes have two emissive states, assigned to the ILCT* singlet and triplet (Fig. 1). The solution singlet quantum yields are 10^{-5}, while the triplet quantum yields range from 10^{-4} to 10^{-3}. None of the pyridyl-substitued complexes are emissive. However at 77 K, both the pyridyl and pyridinium complexes are emissive but only the triplet emission is easily observed. The pyridyl substituted complexes have a strong emission between 18,600 and 17,900 cm^{-1} while the pyridinium-substituted complexes have emissions between 16,600



Scheme 1.



Scheme 2.

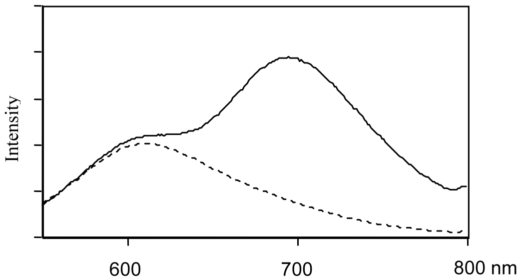


Fig. 1. Emission spectra of $[(dppe)Pt\{S_2C_2(CH_2CH_2\text{-}N\text{-}2\text{-}pyridnium)\}]^+$ in DMSO at 298 K prior to instrument correction: solid line air free; dashed line, in air.

and 16,100 cm^{-1} (Table 1). There is pronounced 1200 cm^{-1} vibronic structure in the pyridyl-substituted complexes that is somewhat less resolved in the pyridinium-substituted complexes (Figs. 2 and 3). The ^{3}ILCT* lifetime of the pyridinium complexes are 136–290 μs while the pyridyl complexes have lifetimes of 216–350 μs (Fig. 4). These lifetimes are 20–30 times the values of the room temperature lifetimes [3,4,7,8]. As is generally the case, thermal modes of deactivation are eliminated at 77 K and the ^{3}ILCT* lifetimes and quantum yields increase. The large increase in ^{3}ILCT* quantum yield leads to an inability to easily observe the singlet emission which in room temperature solutions is generally found in the 16,400–14,800 cm^{-1}.

The triplet emissions for all of the complexes have a vibrational progression of 1200 cm^{-1} (DMM 1:1:1 v/v/v). This vibronic progression has been assigned to the C=C stretch of the excited state given that the symmetric and asymmetric C=C stretches of the ground state $L_2Pt\{S_2C_2(2\text{-pyridyl(ium)})(R)\}$ are found at ~1460 and ~1430 cm^{-1} in the IR spectrum, respectively. This assignment is in agreement with that for the structurally related Pt(diimine)(1,2-enedithiolate) and $[Pt(L)(mnt)]^{-1}$ L = diimine, tertiary phosphine or phosphite, COD [25–27]. In the IR the localized C=C stretch of Pt(diimine)(1,2-enedithiolate) and $[Pt(L)(mnt)]^{-1}$ L = diimine, tertiary phosphine or phosphite, COD complexes are found at 1450–1500 cm^{-1} while the low temperature emission spectra had vibronic structure of 1200–1300 cm^{-1} [25–27].

Contrary to the fluid emissions, low temperature emissions from glasses are not particularly sensitive to the steric bulk of either the 1,2-enedithiolate appended R-group, the ancillary ligands (L_2) or the protonation state of the heterocycle. None of the pyridyl complexes are emissive at room temperature. In addition, $[L_2Pt\{S_2C_2(2\text{-pyridinium})(H)\}]^+$, $L_2 = PPh_3$, PPh_2Me,

Table 1
2-Pyridyl substituted platinum 1,2-enedithiolate complexes emission maxima and lifetimes in DMM [a] glass at 77 K

Compound	Neutral			Protonated			
	Ex_{max} (nm)	Em_{max} (nm)	$\tau_{77\ K}$ (μs) [b]	Ex_{max} (nm)	Em_{max} (nm)	$\tau_{77\ K}$ (μs) [b]	$\tau_{298\ K}$ (μs) [c]
$L_2Pt\{S_2C_2(2\text{-pyridyl})(H)\}$							
L_2 = dppm	362	538, 579, 640		433	608, 655		0.71
dppe	360	550, 586, 640	311±15	430	612, 652	158±9	2.01
dppp	358	550, 588, 640		433	612, 656		[d]
(PPh_3)	371	558, 588, 640	216±9	435	616, 660	136±8	[d]
(PPh_2Me)	365	547, 585, 640		435	617, 660		[d]
($PPhMe_2$)	365	546, 586, 640	249±9	436	608, 657	144±5	[d]
($propyl_3P$)	360	548, 591, 640	248±6	435	619, 661	138±7	[d]
$dppePt\{S_2C_2(2\text{-pyridyl})\text{-}(CH_2CH_2OH)\}$	355	555 (broad)	350±12	440	601 (broad)	166±9	[d]
$[dppePt\{S_2C_2(CH_2CH_2\text{-}N\text{-}2\text{-pyridinium})\}][BPh_4]$				464	618, 660	290±9	8.66

[a] DMM glass is 1:1:1 methylene chloride; methanol; DMF.
[b] The uncertainties are reported at the 95% confidence limits.
[c] DMSO, from Ref. [10].
[d] Not emissive at room temperature.

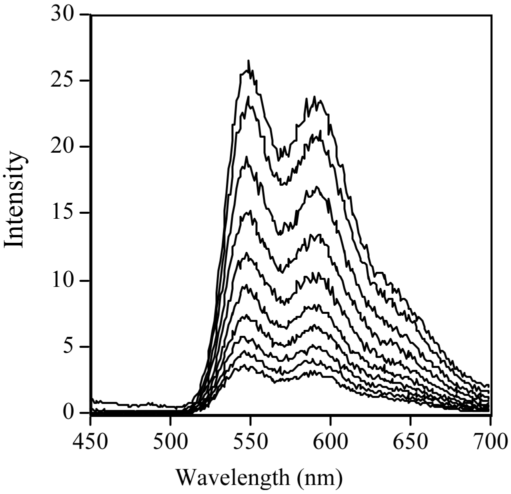


Fig. 2. Emission decay profile of $(propyl_3P)_2Pt\{S_2C_2$(2-pyridine)(H)$\}$at 77 K in DMM, 360 nm excitation. The pulse delay was varied from 50 to 275 μs in 25 μs intervals.

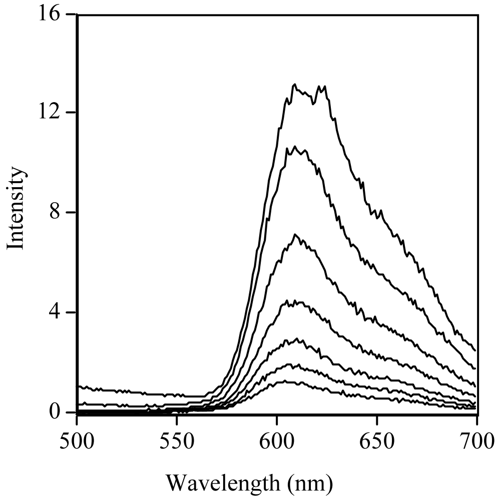


Fig. 3. Emission decay profile of $[(propyl_3P)_2Pt\{S_2C_2$(2-pyridinium)(H)$\}]^+$ at 77 K in DMM, 435 nm excitation. The pulse delay was varied from 50 to 200 μs in 25 μs intervals.

$PPhMe_2$, $(Ppropyl_3)_2$, and $[(dppe)Pt\{S_2C_2$(2-pyridinium)$(CH_2CH_2OH)\}]^+$ are not emissive at room temperature [4,14]. The presence of non-emissive excited states at room temperature for these complexes was precluded by transient absorption spectroscopy [10]. The lack of emission from rigid polymer films (such as cellulose acetate) would suggest that emissions at 77 K can be attributed to the population of lower lying vibronic and rotational states within the excited state manifold. This would suggest that thermal repopulation of a non-emitting state occurs at room temperature. Given that subtle changes in the ancillary ligands lead to an annihilation of the room temperature emission, it is likely that metal-based atomic orbitals contribute strongly to this deactivation as is the case in many metal containing emitters [7,8,25–27].

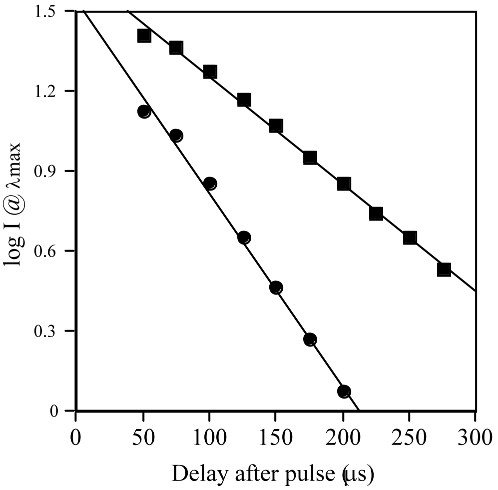
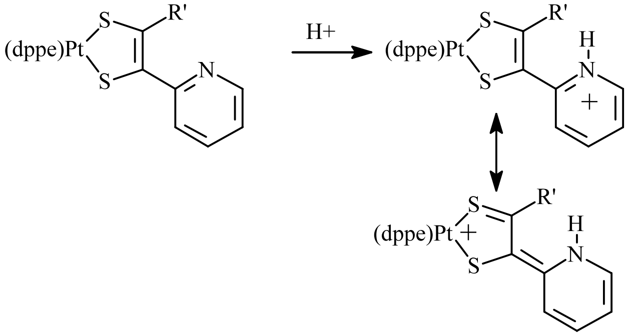


Fig. 4. A plot of the log of the emission intensity versus pulse delay (μs). Lifetimes were calculated from the inverse of the slope. (a) $(propyl_3P)_2Pt\{S_2C_2$(2-pyridine)(H)$\}$, with a lifetime of 248 μs. (b) $[(propyl_3P)_2Pt\{S_2C_2$(2-pyridinium)(H)$\}]^+$, with a lifetime of 138 μs.

5. Conclusion

In this study we have investigated the low temperature emissive properties of 2-pyridyl substituted platinum 1,2-enedithiolates, $L_2Pt\{S_2C_2$(2-pyridyl(ium))(R)$\}$ and $[L_2Pt\{S_2C_2(CH_2CH_2$-*N*-2-pyridnium)$\}]^+$ in DMM glass. All of the complexes studied, both neutral and cationic, were emissive at 77 K independent of the R-group bulk or appended phosphine. This is in stark contrast to the room temperature emissions where selected pyridinium complexes were emissive. The lifetime at 77 K of the pyridinium complexes is approximately half that of the corresponding pyridyl complexes. A finding that was counter-intuitive from solution studies but expected from the Energy Gap Law given that pyridinium emissions are red shifted from the pyridyl complexes [28]. The room temperature solution emissions of the cationic complexes, $[L_2Pt\{S_2C_2$(2-pyridinium)(R)$\}]^+$, and $[L_2Pt\{S_2C_2(CH_2CH_2$-*N*-2-pyridnium)$\}]^+$ are controlled by the steric bulk of the enedithiolate R-groups and the ancillary phosphine ligands. In the ILCT* excited state, the charge transfer formally oxidizes a 1,2-enedithiolate sulfur and reduces the pyridinium nitrogen. Stabilization of this excited state occurs with the generation of an exocylcic double bond between the dithiolate and the heterocycle (Scheme 3). Such a configuration requires a coplanar 1,2-enedithiolate and pyridine. Such resonance forms have also been evoked to justify the 3 pK_a unit increase in the ground state basicity of the 2- and 4-pyridyl substituted 1,2-enedithiolate complexes relative to pyridine and the large increase in the excited state basicity of $(dppe)Pt\{S_2C_2$(2-quinoxaline)(H)$\}$ relative to the ground state. This likely accounts for the sensitivity of



Scheme 3.

the room temperature emissions to ancillary ligands and R-group bulk.

Given that the neutral complexes are emissive at 77 K but not in room temperature solutions it would appear that the silmilarity in the energy of the ILCT band and d to d states leads to deavtiation of the emissive states [1–10]. This is clearly a temperature effect and not a solvent interaction effect since there is no emission from the neutral complexes in rigid polymeric media [5,7,8]. At 77 K such thermal repopulation is far less likely and hence a strong emission is observed. In contrast, emission from the protonated complexes is sufficiently lower in energy such that thermal repopulation of the d to d band is less likely even in room temperature solution. Even though an emission is observed for the pyridinium complex at room temperature, substantial depopulation of the excited state occurs as is evidenced by the 20–30-fold increase in emission lifetime at 77 K. A similar argument has been proposed for several Pt(diimine)(mnt) complexes [21–23].

6. Supplementary material

The material is available from the authors on request.

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