# Synthesis, electrochemistry and luminescence of $[Pt{4'-(R)trpy}(CN)]^+$ (R = Ph, *o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, *o*-ClC<sub>6</sub>H<sub>4</sub> or *o*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; trpy = 2,2':6',2''-terpyridine): crystal structure of $[Pt{4'-(Ph)trpy}(CN)]BF_4 \cdot CH_3CN$

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The synthesis and characterization of  $[Pt{4'-(R)trpy}(CN)]X$  (R = Ph, X = BF<sub>4</sub> or SbF<sub>6</sub>; R = o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, X = SbF<sub>6</sub>; R = o-ClC<sub>6</sub>H<sub>4</sub>, X = SbF<sub>6</sub>; or R = o-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, X = SbF<sub>6</sub>) are described where trpy = 2,2':6',2''-terpyridine. Single crystals of [Pt{4'-(Ph)trpy}(CN)]BF<sub>4</sub>·CH<sub>3</sub>CN were grown by vapour diffusion of diethyl ether into an acetonitrile solution of [Pt{4'-(Ph)trpy}(CN)]BF<sub>4</sub>. An X-ray crystal structure determination of the solvated complex confirms the near linear coordination of the cyanide ligand to the platinum centre. The cation is almost planar as evidenced by a twist of only 1.9° of the phenyl group out of the plane of the terpyridyl moiety. Cyclic voltammograms were recorded in DMF/0.1 M TBAH for the  $[Pt{4'-(R)trpy}(CN)]^+$  cations. Two quasi-reversible one-electron reduction (cathodic) waves are observed with  $E_{1/2}$  values that show the trend expected for an increasingly lower  $C_{6}H_{4}$ trpy(CN)]<sup>+</sup> < [Pt{4'-(o-ClC\_{6}H\_{4})trpy}(CN)]<sup>+</sup> < [Pt{4'-(o-CF\_{3}C\_{6}H\_{4})trpy}(CN)]<sup>+</sup>. All the  $[Pt(4'-(R)trpy](CN)]^+$  cations are photoluminescent in dichloromethane. Emission by  $[Pt{4'-(Ph)trpy}(CN)]^+$  is from an excited state with largely <sup>3</sup>MLCT orbital parentage, but with some intraligand  ${}^{3}\pi - \pi^{*}$  character mixed-in ( $\tau = 0.1 \,\mu$ s). In contrast, the other three cations display emission that appears exclusively intraligand  ${}^{3}\pi-\pi^{*}$  in origin ( $\tau \sim 0.8 \,\mu$ s). Emission spectra have been recorded in a low concentration frozen DME {1 : 5 : 5 (v/v) DMF–MeOH–EtOH} glass. For the R = o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, o-ClC<sub>6</sub>H<sub>4</sub> and o-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub> cations the envelope of vibronic structure and energies of the vibrational components are essentially the same as that recorded in dichloromethane. However, for the  $[Pt{4'-(Ph)trpy}(CN)]^+$  cation, there is a blue-shift in the energies of the vibrational components as compared to that recorded in dichloromethane, as well as a change in the envelope of vibronic structure to a more "domed" pattern; this has been interpreted in terms of a higher percentage of intraligand  ${}^{3}\pi$ - $\pi^*$  character in the emitting state for the glass. Increasing the concentration of the glass invariably leads to aggregation of the cations and the consequent development of new low energy bands, such that at 0.200 mM broad peaks centred at ca. 650 and 700 nm dominate the spectrum; these bands are assigned to excimeric  ${}^{3}\pi - \pi^{*}$  and  ${}^{3}MMLCT$  emission, respectively.

## Introduction

Terpyridyl or substituted 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.<sup>1-15</sup> Similarly, a number of reports have appeared that describe the photoluminescence properties of compounds where a  $\sigma$ -acetylide ligand is bound to a Pt(trpy) unit.<sup>16-20</sup> However, only one report has appeared to date on the photophysics of platinum terpyridine complexes that include the strong-field cyanide ion as a co-ligand.<sup>21</sup> Their luminescence properties vary according to the substituent in the 4'-position of the terpyridyl ligand. Thus, whereas [Pt(trpy)(CN)]<sup>+</sup> and [Pt{(4'-(CN)trpy}(CN)]<sup>+</sup> emit weakly in dichloromethane (DCM) from an intraligand  ${}^{3}\pi-\pi^{*}$  state, [Pt{4'-(dma)trpy}(CN)]<sup>+</sup> (dma = dimethylamino) emits strongly in DCM from a largely ligand-based charge-transfer excited state with an unusually long lifetime of 22 µs.<sup>21</sup> Here we report the electrochemical and photoluminescence properties of the [Pt{4'-(R)trpy}(CN)]<sup>+</sup> cations where R = Ph, *o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, *o*-ClC<sub>6</sub>H<sub>4</sub> or *o*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub> *i.e.*, a phenyl or *ortho*-substituted phenyl group. Also reported, for the first time, is the crystal structure of a terpyridyl ligand complex of platinum(II) with the cyanide ion as a co-ligand, in particular of [Pt{4'-(Ph)trpy}(CN)]BF<sub>4</sub>·CH<sub>3</sub>CN.

### **Results and discussion**

The compounds  $[Pt{4'-(R)trpy}(CN)]SbF_6$  (R = Ph, yellow; *o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, red; *o*-ClC<sub>6</sub>H<sub>4</sub>, orange or *o*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, yellow) and  $[Pt{4'-(Ph)trpy}(CN)]BF_4$  (yellow) were synthesized in good yields by means of a metathesis reaction in which the chloride ion precursor,  $[Pt{4'-(R)trpy}Cl]SbF_6$  or  $[Pt{4'-(Ph)trpy}Cl]BF_4$ , was

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reacted in refluxing acetonitrile with one equivalent of silver cyanide. The compounds were characterised by means of elemental analysis, IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy. These data are listed in the Experimental section.

#### Crystal structure of [Pt{4'-(Ph)trpy}(CN)]BF<sub>4</sub>·CH<sub>3</sub>CN

Yellow needle-shaped single crystals of [Pt{4'-(Ph)trpy}-(CN)]BF<sub>4</sub>·CH<sub>3</sub>CN were grown by slow diffusion of diethyl ether into a concentrated solution of the compound in acetonitrile. A perspective view of the cation in [Pt{4'-(Ph)trpy (CN)]BF<sub>4</sub>·CH<sub>3</sub>CN is given in Fig. 1 with a selection of intramolecular bond lengths and angles being listed in the caption. None of these shows any unusual features and are similar to those measured for other terpyridyl ligand complexes of platinum(II).<sup>1,2,4,5,7,16,19</sup> As expected the Pt−C≡N linkage is nearly linear with a Pt–C(22)–N(4) angle of  $176.1(8)^{\circ}$ . The phenyl ring is only slightly twisted out of the plane of the terpyridyl moiety as evidenced by (i) a dihedral angle between the mean planes through the phenyl ring carbon atoms and the non-hydrogen atoms of the central pyridine ring of 2.1° and (ii) a C(9)-C(8)-C(16)-C(17) torsion angle of 1.9°. The corresponding torsion angles calculated from crystal structure determinations of the free 4'-(Ph)trpy ligand,<sup>22</sup> and for the cation in [Pt{4'-(Ph)trpy}Cl]BF<sub>4</sub>·CH<sub>3</sub>CN,<sup>4</sup> are considerably larger at 10.9 and 33.4°, respectively. Presumably crystal packing effects are responsible for these differences. Noteworthy is that the packing of the cations in  $[Pt{4'-(Ph)trpy}(CN)]BF_4 \cdot CH_3CN$  is very different from that for the chloride analogue, [Pt{4'-(Ph)trpy}Cl]BF<sub>4</sub>·CH<sub>3</sub>CN.<sup>4</sup> Thus, whereas in the former the cations are well-separated (the shortest intermolecular Pt  $\cdots$  Pt distance is 4.766 Å) in the latter they are stacked as an extended chain of tetramers with  $Pt \cdots Pt$  distances within the tetramers of *ca.* 3.3 Å.<sup>4</sup> The upper Pt  $\cdots$  Pt distance limit for significant  $d_{z^2}(Pt)-d_{z^2}(Pt)$  orbital interactions is about 3.5 Å.<sup>23</sup> Clearly,  $d_{z^2}(Pt) - d_{z^2}(Pt)$  orbital interactions are absent



Fig. 1 ORTEP view of the cation in  $[Pt{4'-(Ph)trpy}(CN)]$ -BF<sub>4</sub>·CH<sub>3</sub>CN. Non-hydrogen atoms are drawn as 50% ellipsoids while the hydrogen atoms are drawn as spheres of arbitrary radius. Interatomic distances (Å) and angles (°): Pt–N(1) 2.026(6), Pt–N(2) 1.936(5), Pt–N(3) 2.028(6), Pt–C(22) 2.048(8); N(1)–Pt–N(2) 80.6(2), N(1)–Pt–N(3) 161.0(3), N(2)–Pt–N(3) 80.5(2), Pt–C(22)–N(4) 176.1(8).

in  $[Pt{4'-(Ph)trpy}(CN)]BF_4\cdot CH_3CN$ , consistent with its yellow colour. On the other hand,  $[Pt{4'-(Ph)trpy}Cl]BF_4\cdot CH_3CN$  is red, the colour often associated with the presence of  $d_{z^2}(Pt)-d_{z^2}(Pt)$  orbital interactions in the crystal; see ref. 24 and 25 for example.

#### Electrochemistry

Cyclic voltammograms of the hexafluoroantimonate salt of the  $[Pt{4'-(Ph)trpy}(CN)]^+$  cation were recorded in dimethylformamide (DMF) as a function of scan rate; the results obtained for a 1 mM solution are shown in Fig. 2. At 1000 mV s<sup>-1</sup> two quasi-reversible reduction waves are observed with the first somewhat broader than the second. Other related platinum(II) terpyridine complexes similarly exhibit a pair of quasi-reversible reduction waves that are assigned as one-electron transfers to a largely ligand-based orbital.<sup>5,11,21,26</sup> Accordingly, we make the same assignment and calculate  $E_{1/2}$  (vs. Fc<sup>+/0</sup>) values of -1.14 and -1.68 V for the two waves. These values are significantly anodic of the corresponding  $E_{1/2}$  values of -1.22 and -1.76 V measured in DMF for the chloride ion analogue, [Pt{4'-(Ph)trpy}Cl]<sup>+</sup>.<sup>5</sup> The implication is that the energy of the largely terpyridyl ligandbased LUMO for the cyanide ion complex,<sup>27</sup> is lower than that for the chloride ion species, an expected result in view of the fact that the cyanide ion is strongly electron-withdrawing whereas the chloride ion is considered a  $\pi$ -donor ligand. The  $E_{1/2}$  values are also anodic of those recorded in DMF for the parent cyanide complex, [Pt(trpy)(CN)]+ but only marginally so; the latter values are -1.16 and -1.72 V<sup>21</sup> Though the anodic shift is small it is consistent with the extended  $\pi$ -delocalisation and hence lower energy of the terpyridyl ligand-based LUMO brought about by the presence of phenyl group in the 4'-position of the terpyridyl moiety.



**Fig. 2** Cyclic voltammograms of [Pt{4'-(Ph)trpy}(CN)]\* (1 mM in DMF containing 0.1 M TBAH) as a function of scan rate.

We now discuss the cyclic voltammograms recorded at lower scan rates for the  $[Pt{4'-(Ph)trpy}(CN)]^+$  cation. As shown in Fig. 2, an additional irreversible wave *ca*. 0.14 V cathodic of the first wave is clearly visible at a scan rate of 100 mV s<sup>-1</sup>. Note that its height decreases as the scan rate increases such that at 1000 mV s<sup>-1</sup> it is no longer discernable as a distinct peak. A similar peak was observed in the cyclic voltammogram recorded for  $[Pt(trpy)(CN)]^+$ also in DMF.<sup>21</sup> A likely explanation for the peak is that a chemical process is coupled to the first reduction step, in particular dimer formation due to a rapid reaction at the electrode surface between  $[Pt{4'-(Ph)trpy}(CN)]$  and  $[Pt{4'-(Ph)trpy}(CN)]^+$  to form  $[Pt{4'-(Ph)trpy}CN]_2^+$ ; and that it is the reduction of the latter that gives rise to the additional peak. Certainly, other workers have invoked dimer formation to explain the spectroelectrochemical results obtained for  $[Pt(trpy)Cl]^+$ .<sup>26</sup> Note that doubling the concentration to 2 mM has as a result that the additional cathodic wave increases in height relative to that for the first wave for a given scan rate. This is also consistent with dimer formation.<sup>28</sup>

With regard to the cyclic voltammograms recorded in DMF of the other cations viz  $[Pt{4'-(o-CH_3C_6H_4)trpy}(CN)]^+$ ,  $[Pt{4' (o-ClC_6H_4)trpy\}(CN)]^+$  and  $[Pt\{4'-(o-CF_3C_6H_4)trpy\}(CN)]^+$ , they all display two reversible one-electron reduction waves over the full scan rate range of 100 to 1000 mV s<sup>-1</sup>; note that they are not complicated by the intervention of an additional wave cathodic of the first reduction wave. The implication is that dimer formation does not occur on reduction of these cations. We speculate that, due to steric interactions with adjacent hydrogens of the terpyridyl moiety, the ortho-substituent of the 4'-phenyl group forces the phenyl group out of the plane of the terpyridyl moiety, thus rendering the cation as a whole non-planar. The upshot is that the cations do not  $\pi$ -stack as easily as the flat [Pt{4'-(Ph)terpy}(CN)]+ cation, thus hindering dimer formation. A summary of the electrochemical data for all four cations is given in Table 1. Note the trend in  $E_{1/2}$  values:  $[Pt{4'-(Ph)trpy}(CN)]^+ \sim [Pt{4'-(o-1)}]^+ \sim [Pt{4'-(o-1)}]^+ \sim [Pt{4'-(o-1)}]^+$  $CH_{3}C_{6}H_{4})trpy (CN)]^{+} < [Pt{4'-(o-ClC_{6}H_{4})trpy}(CN)]^{+} < [Pt{4' (o-CF_3C_6H_4)$ trpy(CN)<sup>+</sup>. The order reflects an increasingly lower energy for the largely  $\pi^*$ -trpy LUMO of the complex and is the expected one, given an order of electron-withdrawing ability of o-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub> > o-ClC<sub>6</sub>H<sub>4</sub> > o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> ~ Ph.

 Table 1
 Electrochemical data in DMF with 0.1 M TBAH

Complex	$E_1^{a}/V$ (vs. Fc <sup>+/0</sup> )	$E_2^a/V$ (vs. Fc <sup>+/0</sup> )
[Pt{4'-(Ph)trpy}Cl]+ (ref. 5)	$-1.21 (88, 1.2)^{b,c}$	$-1.75(68, 1.0)^{b}$
[Pt(trpy)(CN)] <sup>+</sup> (ref. 21)	$-1.16(90, 0.9)^{b,c}$	$-1.72(60, 1.2)^{b}$
$[Pt{4'-(Ph)trpy}(CN)]^+$	$-1.14(126, 1.3)^{b,d}$	$-1.68(66, 1.0)^{b}$
$[Pt{4'-(o-CH_3C_6H_4)trpy}(CN)]^+$	$-1.14(108, 1.1)^{b,e}$	$-1.68(60, 1.0)^{b}$
$[Pt{4'-(o-ClC_6H_4)trpy}(CN)]^+$	$-1.10(100, 1.1)^{b,e}$	$-1.74(64, 1.0)^{b}$
$[Pt{4'-(o-CF_3C_6H_4)trpy}(CN)]^+$	$-1.08 (98, 1.1)^{b,e}$	$-1.62(64, 1.0)^{b}$

 $^a$   $E_{1/2} = (E_{\rm pa} + E_{\rm pc})/2$  where  $E_{\rm pa}$  and  $E_{\rm pc}$  are the peak anodic and peak cathodic potentials, respectively.  $^b$   $E_{\rm pa}-E_{\rm pc}$  separation in mV and  $i_c/i_a$  ratio in brackets.  $^c$  Scan rate = 50 mV s<sup>-1</sup>.  $^d$  Scan rate = 100 mV s<sup>-1</sup>.

#### Photophysics

The absorption spectrum measured in dichloromethane (DCM) for [Pt{4'-(Ph)trpy}(CN)]+ is representative and is shown in Fig. 3; a listing of the wavelengths of the absorption maxima for all the cations is given in Table 2. Typical of platinum(II) terpyridine complexes is the presence of mainly intraligand  $\pi$ - $\pi^*$  absorptions at shorter wavelengths and weaker metal-to-ligand charge-transfer [ $^{1}MLCT/^{1}d-\pi^{*}(trpy)$ ] absorptions bands in the range 350-450 nm.<sup>1,3,12,21</sup> In DCM the latter occur at 365 and 380 nm *i.e.*, at a significantly higher energy than the corresponding bands at 397 and 412 nm measured for the chloride ion analogue,  $[Pt{4'-(Ph)trpy}Cl]^+$ .<sup>5</sup> A likely explanation for the blue shift is that the stronger  $\pi$ -acceptor properties of the cyanide (as compared to the chloride) causes a larger ligand field splitting of the dorbitals and a concomitant stabilization of the  $d\pi$  orbitals of the metal (more correctly molecular orbitals with significant  $d\pi(Pt)$ ) atomic orbital character).29 Note that this effect must dominate the energy of the <sup>1</sup>MLCT absorption since, as discussed above, the electrochemical data suggest that the energy of the trpy ligandbased LUMO is actually lower for the cyanide ion complex. The corresponding <sup>1</sup>MLCT absorptions of the parent cyanide complex, [Pt(trpy)(CN)]+, occur at 360 and 375 nm i.e., at slightly higher energies than those shown in Fig. 1.21 This is consistent with the



Fig. 3 Absorption spectrum of  $[Pt\{4^\prime\mathchar`-(Ph)trpy\}(CN)]^*$  in dichloromethane solution.

 Table 2
 Photophysical data for platinum terpyridine complexes in DCM at room temperature

Complex	$\lambda^{abs}_{max}{}^{a}/nm$	$\lambda^{\rm em}{}_{\rm max}{}^{b}/{ m nm}$	$\tau^c/\mu s$	$\phi^{d}$	$k_{\rm r} = (\phi/\tau)^e/{\rm s}^{-1}$
$ [Pt{4'-(Ph)trpy}Cl]^{+} (ref. 5)  [Pt(trpy)(CN)]^{+} (ref. 21)  [Pt{4'-(Ph)trpy}(CN)]^{+}  [Pt{4'-(o-CH_{3}C_{6}H_{4})trpy}(CN)]^{+f}  [Pt{4'-(o-CIC_{6}H_{4})trpy}(CN)]^{+f}  [Pt{4'-(o-CF_{3}C_{6}H_{4})trpy}(CN)]^{+f} $	283, 309, 322, 336; 397sh, 412 298, 312, 330, 345; 360sh, 375 245, 275, 309, 322, 344; 365, 380 247, 277, 302sh, 316, 328, 345; 365, 379 244, 278, 315, 331, 346; 367, 377 245, 279, 314, 330, 346: 362, 377	535, 570sh, 608sh 465, 500, 530, 570sh 490, 525, 575 465, 500, 540 471, 504, 535 468, 501, 534	0.085 0.015 0.1 0.7 0.8 0.8	0.0031 0.0004 0.0028 0.0008 0.0003 0.0003	$\begin{array}{c} 3.6\times10^{4}\\ 2.6\times10^{4}\\ 2.8\times10^{4}\\ 1.1\times10^{3}\\ 3.8\times10^{2}\\ 6.3\times10^{2} \end{array}$

<sup>*a*</sup> Absorption maxima; semicolon sets off CT bands. <sup>*b*</sup> Emission maxima. Italic values refer to the most intense band. <sup>*c*</sup> Excited state lifetime  $\pm 10\%$ . <sup>*d*</sup> Emission yield  $\pm 10\%$ . <sup>*e*</sup> Estimate of radiative rate constant, see ref. 32. <sup>*f*</sup> Emission spectra in DCM have not been recorded for the chloride ion analogue of these complexes.

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comparison of  $E_{1/2}$  values made above *i.e.*, the energy of the trpy ligand-based LUMO for  $[Pt{4'-(Ph)trpy}(CN)]^+$  is slightly lower than that of  $[Pt(trpy)(CN)]^+$ .

The [Pt{4'-(Ph)trpy}(CN)]+ complex also exhibits photoluminescence in DCM as shown in Fig. 4. Well resolved vibrational components attributable to the 0-0 and 0-1 transitions appear at 490 and 525 nm along with a shoulder at 575 nm. Increasing the excitation wavelength from 340 to 390 nm results in a gradual decrease in the intensity of the emission but has no effect on the positions of the peaks. We assign the emission as mainly <sup>3</sup>MLCT in origin. Consistent with this assignment, the envelope of vibronic structure shows a monotonic decrease in intensity with increase in wavelength.<sup>1,3,5,21</sup> However, the Huang–Rhys ratio (*i.e.*,  $I_{0-1}/I_{0-0}$ ) of 0.96 is close to 1.0, which indicates that the emitting state has significant intraligand  ${}^{3}\pi-\pi^{*}$  character mixed-in as well.<sup>1,3,5,21</sup> The emission exhibited by the  $[Pt{4'-(Ph)trpy}(CN)]^+$  complex in fluid solution is the more interesting because it differs from that of the parent species [Pt(trpy)(CN)]<sup>+</sup> which emits from an intraligand  ${}^{3}\pi-\pi^{*}$  state at higher energy (see Table 2). As previously noted,<sup>21</sup> it is possible to observe  ${}^{3}\pi - \pi^{*}$  emission from [Pt(trpy)(CN)]<sup>+</sup>, even though the lowest energy absorption has  ${}^{1}d-\pi^{*}$  character, because the singlet-triplet splitting is comparatively small for  $d-\pi^*$  excitation.<sup>30,31</sup> What makes the [Pt{4'-(Ph)trpy}(CN)]<sup>+</sup> system different is an appreciably lower energy  ${}^{1}d-\pi^{*}$  absorption. The chloride analogue [Pt{4'-(Ph)trpy}Cl]<sup>+</sup> also exhibits <sup>3</sup>MLCT emission in DCM,5 consistent with the low energy of the CT absorptions recorded for the complex (see Table 2). The radiative rate constants in Table 2 tend to support the proposed state assignments. Note that the  $k_r$  value for the triplet emission drops by more than an order of magnitude as the participation of the heavy metal decreases and the orbital parentage changes from predominantly  ${}^{3}d-\pi^{*}$  to predominantly  ${}^{3}\pi-\pi^{*}$  in character. The  $k_r$  value calculated for [Pt(trpy)(CN)]<sup>+</sup> in Table 2 is anomalously high, but note that the reported lifetime is an extrapolated value, as opposed to a directly measured quantity.<sup>21</sup> Also, for this system the simple kinetic model that gives rise to the  $k_r = \phi/\tau$  equation may not be applicable if the  ${}^{3}\pi - \pi^{*}$  emitting state is in equilibrium with a nearby deactivating state, vide infra.32



**Fig. 4** Emission spectrum of  $[Pt{4'-(Ph)trpy}(CN)]^+$  in dichloromethane solution;  $\lambda_{ex} = 340$  nm.

In contrast, the emission spectra recorded for the  $[Pt{4'-(o-CH_3C_6H_4)trpy}(CN)]^+$ ,  $[Pt{4'-(o-ClC_6H_4)trpy}(CN)]^+$  and  $[Pt{4'-(o-CF_3C_6H_4)trpy}(CN)]^+$  cations clearly exhibit  ${}^3\pi-\pi^*$  character; see Fig. 5 for the signal from the 4'-(o-CH\_3C\_6H\_4)trpy complex. Here the envelope of the vibronic structure has a 'domed'



Fig. 5 Emission spectrum of  $[Pt{4'-(o-CH_3C_6H_4)trpy}(CN)]^+$  in dichloromethane solution:  $\lambda_{ex} = 340$  nm.

shape *i.e.*, a longer wavelength vibronic component becomes the most intense transition (see Table 2). Also significant is that the energy spacing within the progression is of the order of 1400 cm<sup>-1</sup> which is typical of the C-C and C-N stretching motion of the terpyridine framework. As others have discussed, a Franck-Condon envelope of this type is the signature for polypyridine-centred  ${}^{3}\pi-\pi^{*}$  emission.  ${}^{30,33-35}$  Accordingly, the emissions exhibited by the  $[Pt{4'-(o-CH_3C_6H_4)trpy}(CN)]^+$ ,  $[Pt{4'-(o-CH_3C_6H_4)trpy}(CN)]^+$  $ClC_6H_4$ )trpy}(CN)]<sup>+</sup> and  $[Pt{4'-(o-CF_3C_6H_4)trpy}(CN)]^+$  cations have similar energies as that recorded for the parent [Pt(trpy)(CN)]<sup>+</sup> complex (see Table 2). The difference in the emission energy relative to [Pt{4'-(Ph)trpy}(CN)]+ is probably due to the planarity of the latter; crystal structure determinations of  $[Pt{4'-(o-CH_3C_6H_4)trpy}Cl]SbF_6,^7 [Pt{4' (o-CH_3C_6H_4)trpy$ Cl]BF<sub>4</sub>,<sup>7</sup> [Pt{4'-(o-ClC\_6H\_4)trpy}Cl]SbF<sub>6</sub>,<sup>9</sup> and  $[Pt{4'-(o-CF_3C_6H_4)trpy}Cl]SbF_6,^7$  reveal that the other cations must be markedly non-planar.

Insofar as the room-temperature excited state lifetimes are concerned, those measured for the  $[Pt{4'-(R)trpy}(CN)]^+$  cations as well as for  $[Pt{4'-(Ph)trpy}Cl]^+$ , follow the pattern expected from the prediction of the energy-gap law,<sup>36</sup> in that the emission lifetimes decrease as the energy of the emission decreases (see Table 2). The trend is remarkable because the orbital parentage is also changing. One anomaly is that the lifetime of  $0.015 \ \mu s$ for the emitting state of the parent [Pt(trpy)(CN)]<sup>+</sup> cation is low by comparison with the lifetimes of 0.1-0.8 µs measured for the  $[Pt{4'-(R)trpy}(CN)]^+$  cations. The relatively short excited state lifetime of the [Pt(trpy)(CN)]+ complex has been rationalized in terms of the thermal population of a non-radiative <sup>3</sup>d-d state,<sup>21</sup> in accordance with findings for related transition metal coordination compounds.37 However, if that were the case, the complexes with an ortho-substituted phenyl group in the 4'-position of the terpyridyl ligand might also be expected to exhibit short lifetimes. Other work on complexes of platinum(II) with aryl substituents in the 4'position of the terpyridyl ligand *i.e.*,  $[Pt{4'-(R')trpy}Cl]^+$  systems where  $\mathbf{R}' = 1$ -naphthyl, 2-naphthyl or 1-phenanthrenyl, may be relevant in this regard.5 The dramatically enhanced lifetimes of up to 64 µs within that series have been explained in terms of emitting states having an admixture of aryl-to-trpy intraligand charge-transfer (ILCT) character. Perhaps, a similar effect is at work in the complexes with the *ortho*-substituted phenyl groups in the 4' position of the trpy ligand. Another possibility is that the thermally assisted decay of the photoexcited [Pt(trpy)(CN)]+

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complex occurs *via* a higher lying vibrational level of the emitting state rather than a <sup>3</sup>d–d excited state.<sup>38</sup> With that type of pathway, the efficiency could be very dependent on the ligand structure.

Emission spectra have been recorded in a frozen DME {1:5:5 (v/v) DMF-MeOH-EtOH} glass as a function of concentration for the hexafluoroantimonate salts of the  $[Pt{4'-(R)trpy}(CN)]^+$ cations. The spectra obtained for the [Pt{4'-(Ph)trpy}(CN)]+ cation are shown in Fig. 6. At the lowest concentration of 0.005 mM, a structured band is observed with vibrational components at 478, 505 and 543 nm. There is no measurable difference in the intensities of the first two (0-0 and 0-1) components, and the band positions are slightly blue-shifted when compared to those recorded for the  $[Pt{4'-(Ph)trpy}(CN)]^+$  cation in DCM (see Table 2). The blue-shift in energy as well as the change in emission profile towards a more "domed" envelope suggests that there is more  ${}^{3}\pi - \pi^{*}$  character in the dilute glass emission, though the emitting state remains one of mixed  ${}^{3}MLCT/{}^{3}\pi-\pi^{*}$  orbital parentage. Increasing the concentration of the glass results in the development of two new longer wavelength bands; in particular bands at 653 and 713 nm. These bands are associated with different types of aggregates that form when the concentration is increased. At the suggestion of a Referee, excitation spectra of a concentrated solution of the  $[Pt{4'-(Ph)trpy}(CN)]^+$  cation were recorded at 77 K in a DME glass. At an emission wavelength of 505 nm, the excitation spectrum revealed charge-transfer excitation bands in the vicinity of 390 nm, similar to what has been observed in fluid solution at room temperature. This observation establishes that the monomeric complex is present in the glass. However, other species are also present because the same bands do not appear in the excitation spectrum obtained while monitoring at 720 nm. In their stead, the excitation spectrum shows a broad band centred at around 440 nm which is attributable to aggregated species *i.e.*, oligomers of an undetermined length. Consistent with the excitation data, the sample was virtually colorless at room temperature but clearly took on a reddish hue at 77 K. Similar aggregation effects have been observed in the high concentration glass spectra recorded for [Pt{4'-(Ph)trpy}Cl]<sup>+</sup> in butyronitrile,<sup>4</sup> and  $[Pt(trpy)Cl]^+$  in DME.<sup>2</sup> The emission from the 4'-(o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)trpy ligand complex in a low-temperature glass appears in Fig. 7. At low concentrations ( $\leq 0.013$  M) the spectrum consists of a structured 'domed' pattern with vibronic components at 465, 496 and 534 nm and a weak progression at 576 nm. As such it is very



**Fig. 6** Emission spectra of  $[Pt{4'-(Ph)trpy}(CN)]^+$  in DME at 77 K as a function of concentration:  $\lambda_{ex} = 340$  nm.



**Fig. 7** Emission spectra of  $[Pt{4'-(o-CH_3C_6H_4)trpy}(CN)]^+$  in DME at 77 K as a function of concentration:  $\lambda_{ex} = 340$  nm.

similar to that recorded for the [Pt{4'-(o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)trpy}(CN)]<sup>+</sup> cation in DCM (see Table 2 and Fig. 5). Thus, the same assignment of emission from a terpyridyl ligand-based  ${}^{3}\pi$ - $\pi$ \* state applies. As for the [Pt{4'-(Ph)trpy}(CN)]<sup>+</sup> cation, increasing the concentration of [Pt{4'-(o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)trpy}(CN)]<sup>+</sup> in frozen DME leads to aggregate formation and hence to the development of two new low energy bands, in particular at 647 and 711 nm, the latter as a shoulder. Finally, the frozen DME glass emission spectra have also been recorded as a function of concentration for the [Pt{4'-(o-ClC<sub>6</sub>H<sub>4</sub>)trpy}(CN)]<sup>+</sup> cations, but since these display essentially the same features as those shown in Fig. 7 for the [Pt{4'-(o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)trpy}(CN)]<sup>+</sup> cation, they are not discussed further here.

#### Experimental

#### Methods

The 4'-phenyl-2,2':6',2"-terpyridine was prepared by the method of Constable,22 4'-o-methylphenyl-2,2':6',2"-terpyridine and 4'o-trifluoromethylphenyl-2,2':6',2"-terpyridine by the Kröhnke method described in ref. 7, and 4'-o-chlorophenyl-2,2':6',2"terpyridine by the Kröhnke method described in ref. 9. The chloride ion platinum complex precursors were prepared according to procedures described in the literature: [Pt{4'-(Ph)trpyCl]SbF<sub>6</sub> and  $[Pt{4'-(Ph)-trpy}Cl]BF_4$  (ref. 4);  $[Pt{4' (o-CH_3C_6H_4)trpy$ Cl]SbF<sub>6</sub> and [Pt{4'- $(o-CF_3C_6H_4)trpy$ Cl]SbF<sub>6</sub> (ref. 7) and  $[Pt{4'-(o-ClC_6H_4)trpy}Cl]SbF_6$  (ref. 9). The acetonitrile used as the solvent and for the purposes of crystal growth was purified by the method of Carlsen and co-workers.<sup>39</sup> Other solvents were dried and purified using standard procedures.<sup>40</sup> The silver cyanide was obtained from FLUKA chemicals and used as received. The tetrabutylammonium hexafluorophosphate (TBAH) used for the electrochemistry studies was of electrochemical grade (FLUKA); the DMF of Biotech grade (ALDRICH).

 $[Pt{4'-(R)trpy}(CN)]SbF_6 (R = Ph, o-CH_3C_6H_4, o-ClC_6H_4 or o-CF_3C_6H_4)$ . To a suspension of  $[Pt{4'-(R)trpy}Cl]SbF_6$  (100 mg) in acetonitrile (10 mL) was added an equimolar amount of AgCN dissolved in 10 mL of boiling acetonitrile and the mixture heated to reflux for 24 h. After cooling to room temperature the resulting AgCl precipitate was removed by filtration, and the volume of the solvent reduced *in vacuo* to induce the precipitation of

 $[Pt{4'-(R)trpy}(CN)]SbF_6$  as a microcrystalline solid. The precipitate was collected by filtration and washed with a minimum amount of ice-cold acetonitrile and finally dried in vacuo. The resultant solid was purified by extraction into hot acetonitrile that was then allowed to slowly cool to room temperature, a process that afforded a pure crystalline solid that was collected by filtration and dried in vacuo. Analytical and spectroscopic data are as follows.  $[Pt{4'-(Ph)trpy}(CN)]SbF_6$ : Yield 83 mg (86%). Colour, yellow. Anal. Calc. for C<sub>22</sub>H<sub>15</sub>N<sub>4</sub>F<sub>6</sub>PtSb: C, 34.5; H, 2.0; N, 7.3%. Found: C, 34.1; H, 1.9; N, 6.9%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ  $9.02(2H, s, H_{3'/5'}), 8.87(2H, d, H_{6/6''}), 8.85(2H, d, H_{3/3''}), 8.55(2H, H_{3/3''})), 8.55(2H, H_{3/3''}), 8.55(2H, H_{3/3''})), 8.55(2H, H_{3/3''}))), 8.5(2H, H_{3/3''}))), 8.5(2H, H_{3/3''})))$ m, H<sub>4/4"</sub>), 8.18-8.16 (phenyl H's), 7.90 (2H, m, H<sub>5/5"</sub>), 7.70-7.69 (phenyl H's). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$  158.2 (1C, s, pyridyl quat. C4'), 155.0 (2C, s, C6/6"), 154.6-154.2 (4C, singlets, C2/2'/6'/2"), 142.8 (2C, s, C<sub>4/4"</sub>), 134.8 (1C, s, phenyl quat. C<sub>1""</sub>), 131.8 (phenyl C's), 130.4 (2C, s, C<sub>5/5"</sub>), 129.5–128.1 (phenyl C's), 126.4 (2C, s, C<sub>3/3"</sub>), 121.4 (2C, s,  $C_{3'/5'}$ ), 120.5 (1C, s, quat.  $C_{CN}$ ). IR (KBr, cm<sup>-1</sup>): v[C=N]: 2145ms; v[4'-(Ph)trpy]: 1607s, 1557ms, 1477ms, 1415s, 883m;  $v[SbF_6^-]$ : 652vs. [Pt{4'-(o-CH\_3C\_6H\_4)trpy}(CN)]SbF\_6: Yield 89.3 mg (90%). Colour, red. Anal. Calc. for  $C_{23}H_{17}N_4F_6PtSb$ : C, 35.4; H, 2.2; N, 7.2. Found: C, 35.6; H, 2.3; N, 7.0%]. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  8.93 (2H, d, H<sub>6/6''</sub>), 8.78 (2H, s, H<sub>3'/5'</sub>), 8.75 (2H, d, H<sub>3/3"</sub>), 8.54 (2H, m, H<sub>4/4"</sub>), 7.92 (2H, m, H<sub>5/5"</sub>), 7.52-7.46 (4H, m, phenyl H's), 2.43 (3H, s, HCH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$  158.4 (1C, s, pyridyl quat. C<sub>4</sub>), 156.4–155.1 (4C, singlets, quat. C<sub>2/2'/6'/2"</sub>), 154.2 (2C, s, C<sub>6/6"</sub>), 142.9 (2C, s, C<sub>4/4"</sub>), 136.9 (1C, s, phenyl quat. C<sub>1"</sub>), 135.4 (1C, s, phenyl quat. C<sub>2"</sub>), 130.4 (2C, s, C<sub>5/5"</sub>), 130.1-126.6 (singlets, phenyl C's), 126.4 (2C, s,  $C_{\scriptscriptstyle 3/3''}),\,124.8\;(2C,\,s,\,C_{\scriptscriptstyle 3'/5'}),\,119.9\;(1C,\,s,\,quat.\;C_{\scriptscriptstyle CN}),\,19.87\;(1C,\,s,\,$ CCH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): v[C $\equiv$ N]: 2137m; v[4'-(o-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)trpy]: 1607s, 1558w, 1478m, 1418s, 885m; v[SbF<sub>6</sub><sup>-</sup>]: 652vs. [Pt{4'-(o- $ClC_6H_4$ )trpy}(CN)]SbF\_6: Yield 78.8 mg (89%). Colour, orange. Anal. Calc. for C<sub>22</sub>H<sub>14</sub>N<sub>4</sub>F<sub>6</sub>ClPtSb: C, 33.0; H, 1.8; N, 7.0%. Found: C, 32.6; H, 1.7; N, 6.6%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ 8.91 (2H, s, H<sub>3'/5'</sub>), 8.89 (2H, d, H<sub>6/6"</sub>), 8.74 (2H, d, H<sub>3/3"</sub>), 8.54 (2H, m, H<sub>4/4"</sub>), 7.91 (2H, m, H<sub>5/5"</sub>), 7.79–7.65 (4H, m, phenyl H's). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$  158.1 (1C, s, pyridyl quat. C<sub>4'</sub>), 155.1 (2C, s, C6/6"), 154.3-153.4 (4C, singlets, quat. C2/2'/6'/2"), 142.9 (2C, s, C<sub>4/4"</sub>), 135.7 (1C, s, phenyl quat. C<sub>1""</sub>), 132.0 (1C, s, phenyl quat. C<sub>2'''</sub>), 131.5–131.0 and 130.3–128.1 (4C, singlets, phenyl C's), 130.4 (2C, s, C<sub>5/5"</sub>), 126.4 (2C, s, C<sub>3/3"</sub>), 125.1 (2C, s, C<sub>3'/5'</sub>), 120.3 (1C, s, quat.  $C_{CN}$ ). IR (KBr, cm<sup>-1</sup>):  $v[C \equiv N]$ : 2136ms;  $v[4'-(o-ClC_6H_4)trpy]$ : 1609s, 1558w, 1478ms, 1415s, 1032ms; v[SbF<sub>6</sub><sup>-</sup>]: 654vs. [Pt{4'-(o- $CF_3C_6H_4$ )trpy}(CN)]SbF<sub>6</sub>: Yield 86.0 mg (92%). Colour, yellow. Anal. Calc. for C<sub>23</sub>H<sub>14</sub>N<sub>4</sub>F<sub>9</sub>PtSb: C, 33.1; H, 1.7; N, 6.7%. Found: C, 32.7; H, 1.6; N, 6.3%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ 8.97 (2H, d, H<sub>6/6"</sub>), 8.84 (2H, s, H<sub>3'/5'</sub>), 8.72 (2H, d, H<sub>3/3"</sub>), 8.55 (2H, m, H<sub>4/4"</sub>), 8.21 (1H, d, phenyl H's), 7.95 (2H, m, H<sub>5/5"</sub>), 7.88-7.66 (m, phenyl H's). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$  158.0 (1C, s, pyridyl quat. C<sub>4'</sub>), 155.2 (2C, s, C<sub>6/6"</sub>), 154.2–154.1 (4C, singlets, quat. C<sub>2/2'/6'/2"</sub>), 142.9  $(2C, s, C_{4/4''})$ , 135.9 (2C, s, phenyl quat.  $C_{1'''/2'''}$ ), 133.0–130.5 (3C, singlets, phenyl C's), 130.4 (2C, s, C<sub>5/5"</sub>), 126.6 (1C, s, phenyl C), 126.3 (2C, s, C<sub>3/3"</sub>), 124.5 (2C, s, C<sub>3'/5'</sub>), 120.3 (1C, s, quat. C<sub>CN</sub>). IR (KBr, cm<sup>-1</sup>):  $\nu$ [C=N]: 2139ms;  $\nu$ [4'-(o-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)trpy]: 1608s, 1480s, 1420s, 1316s, 1073m, 1034s, 887w; v[SbF<sub>6</sub><sup>-</sup>]: 658vs.

[Pt{4'-(Ph)trpy}(CN)]BF<sub>4</sub>. The same procedure was followed as described above for the SbF<sub>6</sub><sup>-</sup> salts except that the starting complex was [Pt{4'-(Ph)trpy}Cl]BF<sub>4</sub>. Yield 82.9 mg (86%). Colour,

yellow. Anal. Calc. for  $C_{22}H_{15}BF_4N_4Pt$ : C, 42.8; H, 2.5; N, 9.1%. Found: C, 43.2; H, 2.6; N, 9.1%. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  9.04 (2H, s,  $H_{3'/5'}$ ), 8.91 (2H, d,  $H_{6/6''}$ ), 8.87 (2H, d,  $H_{3/3''}$ ), 8.57 (2H, m,  $H_{4/4''}$ ), 8.19–8.17 (phenyl H's), 7.91 (2H, m,  $H_{5/5''}$ ), 7.71–7.69 (phenyl H's). <sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$  158.3 (1C, s, pyridyl quat. C<sub>4'</sub>), 155.0 (2C, s, C<sub>6/6''</sub>), 154.7–154.2 (4C, singlets, C<sub>2/2'/6'/2''</sub>), 142.8 (2C, s, C<sub>4/4''</sub>), 134.9 (1C, s, phenyl quat. C<sub>1'''</sub>), 131.7 (phenyl C's), 130.3 (2C, s, C<sub>5/5''</sub>), 129.5–128.1 (phenyl C's), 126.4 (2C, s, C<sub>3/3''</sub>), 121.5 (2C, s, C<sub>3'/5'</sub>), 120.7 (1C, s, quat. C<sub>CN</sub>). IR (KBr, cm<sup>-1</sup>):  $\nu$ [C $\equiv$ N]: 2139ms;  $\nu$ [4'-(Ph)trpy]: 1607s, 1557m, 1479ms, 1417s, 894vw;  $\nu$ [BF<sub>4</sub><sup>-</sup>]: 1055vs.

The [Pt{4'-(R)trpy}(CN)]SbF<sub>6</sub> complexes are soluble in DCM as the TFPB salts after metathesis with Na[TFPB]·nH<sub>2</sub>O where TFPB = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. The UV-vis absorption and emission spectra were recorded on deoxy-genated DCM solutions of the complexes obtained in this way. An excitation wavelength of 340 nm was used to record the DCM fluid and DME glass emission spectra, unless otherwise stated. A long-wave-pass filter of 400 nm was used to remove scattered light. The method of determining lifetimes has been described previously.<sup>41</sup> The method used for measuring quantum yields is described in ref. 21.

For voltammetry, the electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) in DMF. The working electrode was a platinum disc (diameter = 6.0 mm) and the auxiliary electrode a spiral platinum wire. The pseudo-reference electrode used during the experiments was a Ag/AgCl spiral wire sealed in a glass tube fitted with a frit and containing the 0.1 M TBAH in DMF solution. The primary scans were made relative to this electrode; however, ferrocene was added at the end of each experiment as an internal standard. Thus, the potentials given in Table 1 and in Fig. 2 are shown relative to the Fc<sup>+/0</sup> couple.

#### Instrumentation

Microanalyses for %C, H and N were performed by Galbraith Laboratories Inc., Knoxville, Tennessee, USA. <sup>1</sup>H (500 MHz) and <sup>13</sup>C (125 MHz) NMR spectra were recorded on a Varian UNITY INOVA 500 spectrometer at 25 °C with chemical shifts referenced to the solvent. IR spectra were recorded as KBr discs on a Perkin Elmer Spectrum One FTIR spectrometer. UV/vis absorption spectra were recorded at 22 °C using a Shimadzu-2101PC scanning spectrophotometer and the spectrofluorimeter was a Varian Cary Eclipse. A finger-Dewar filled with liquid nitrogen permitted measurements in a frozen DME glass. See previous work for a description of the nitrogen-pumped dye laser and associated equipment used for lifetime determinations.<sup>42</sup> The cyclic voltammetry unit was a BAS100B Electrochemical Analyser.

#### Crystallography

Intensity data were obtained for single crystals of [Pt{4'-(Ph)trpy}(CN)]BF<sub>4</sub>·CH<sub>3</sub>CN on an Oxford Diffraction Xcalibur 2 CCD four circle diffractometer in the range  $4 \le \theta \le 32^{\circ}$  using graphite monochromated Mo-K $\alpha$  radiation. The intensity data collection, as well as the determination of the unit cell parameters and the data reduction were processed by the CrysalisRED v. 170 software supplied by Oxford Diffraction.<sup>43</sup> Lorentz and

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Table 3 Crystal structure data and refinement details for [Pt{4'-(Ph)trpy(CN) $BF_4 \cdot CH_3CN$ 

	Formula	$C_{24}H_{18}BF_4N_5Pt \\$
	М	658.33
	T/K	280
	Crystal size/mm	$0.60 \times 0.20 \times 0.16$
	Crystal system	Triclinic
	Space group	$P\overline{1}$
	a/Å	7.304(3)
	b/Å	13.015(3)
	c/Å	13.057(3)
	a/°	72.15(2)
	β/°	76.32(2)
	y/°	81.03(2)
	$U/Å^3$	1143.2(6)
	Ζ	2
	$D_{\rm c}/{ m g~cm^{-3}}$	1.912
	$\mu/\mathrm{mm}^{-1}$	6.193
	F(000)	632
	Reflections measured	11424
	Unique reflections	7010
	Reflections with $F^2 \ge 2\sigma(F^2)$	5941
	$R_{\rm int}$	0.0335
	$R_1, wR_2 \left[ F^2 \ge 2\sigma(F^2) \right]^a$	0.0553, 0.1540
	$R_1, wR_2$ (all data) <sup><i>a</i></sup>	0.0644, 0.1599
	No. refined parameters,	318,0
	restraints	1 102
	Goodness-of-fit on $F^2$	1.103
	Max. $\Delta \rho / e A^{-3}$	3.85 (Pt)
	Min. $\Delta \rho / e A^{-3}$	-1.96 (Pt)
$R_1 =$	$\sum   F_{o}  -  F_{c}   / \sum  F_{o} . w$	$R_2 = [(\sum [w(F_0^2 - F_0^2)^2])^2]$

$${}^{a}R_{1} = \sum_{i} ||F_{o}| - |F_{c}|| / \sum_{i} |F_{o}|. wR_{2} = [(\sum_{i} [w(F_{o}^{2} - F_{o}^{2})^{2}]) / (\sum_{i} [w(F_{o}^{2})^{2}]]^{1/2}. w = 1 / [(\sigma^{2}(F_{o}^{2}) + (0.1P)^{2}] \text{ where } P = (F_{o}^{2} + 2F_{c}^{2}) / 3.$$

polarization as well as absorption corrections, the latter by means of a numerical face-indexing method, were also effected using the same software. Crystal data and details of the refinement are reported in Table 3. To attain the temperature of 280 K the crystal was cooled in a stream of nitrogen supplied by an Oxford Instruments cryostat cooling system, fitted with a thermocouple and temperature controller, which allowed the temperature of the nitrogen in the immediate vicinity of the crystal to be measured. The intensities of selected reflections were monitored from three reference frames spanning the period of time (ca. 14 h) required to collect a complete intensity data set. No statistically significant variation in the intensities of these standard reflections was observed indicating that no crystal decomposition had occurred. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares using SHELX-97,44 with all non-hydrogen atoms assigned anisotropic temperature factors and with the hydrogen atoms (in calculated positions) assigned a single overall isotropic temperature factor. The crystal structure diagram was produced by the ORTEP32 program.<sup>45</sup>

CCDC reference number 616745.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611244g

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