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Synthesis, crystal structure and solid state photoluminescence of [Pt(trpy)(C=CPh)]SbF₆ (trpy=2,2':6',2"-terpyridine)

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Abstract

The synthesis and characterisation of an orange polymorph of $[Pt(trpy)(C \square CPh)]SbF_6$ is described where trpy = 2,2':6',2"-terpyridine. An X-ray crystal structure determination at 293 K reveals that the cations are planar and stacked head-to-tail with alternating Pt···Pt distances of 3.604(1) and 4.412(1) Å. The perpendicular distances between successive cation planes are constant along the stack at a value of 3.33 Å. Crystal structure determinations at 240 and 200 K show that reducing the temperature to 200 K has no significant effect on the cation arrangement. However, below 200 K there is a phase change that we have not been able to characterise, but which has an effect on the solid state photoluminescence exhibited by $[Pt(trpy)(C \square CPh)]SbF_6$. Thus, whereas at temperatures of ≥ 200 K, a broad peak with two components at *ca*. 566 and 597 nm is observed, below 200 K a longer wavelength peak develops that red-shifts as the temperature is lowered $[\lambda(em)_{max} = 637$ nm at 80 K]. We assign the ≥ 200 K emission as ³MLLCT in origin, since the X-ray data show that ligand–ligand (LL) and not metal–metal (MM) interactions are important at $T \ge 200$ K. On the other hand, the long wavelength emission observed below 200 K is typical of ³MMLCT emission, suggesting that the phase change leads to $d_{z^2}(Pt)-d_{z^2}(Pt)$ orbital interactions. Of particular interest is that the cation exhibits ³MLCT emission in dichloromethane that maximizes at 619 nm, *i.e.*, the high temperature solid state emission occurs at a *shorter* wavelength, an unexpected result since intermolecular interactions in the solid usually cause the emission to occur at *longer* wavelengths. A possible explanation for this unexpected result is given.

Keywords: Luminescence; Platinum complexes; Terpyridine complexes

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 five reports have appeared on the photophysics of complexes where a σ -acetylide ligand is bound to a Pt(trpy) unit [15–19]; and one report on the photophysics of cyanide ligand complexes of the type [Pt{4'(R)-trpy}(CN)]⁺ (R = H, CN, or NMe₂) [20]. A recurring theme in the reports by Yam and co-workers, is that the luminescence properties of mononuclear Pt(trpy)(σ -acetylide) derivatives are markedly dependent on the extent to which the lumaphores aggregate in fluid solution and in the solid state [15,18]. One example is of direct relevance here. The purple [Pt(trpy)($\Box \equiv CPh$)]-PF₆ complex exhibits monomeric ³MLCT emission in acetonitrile but, due to $d_{z^2}(Pt)-d_{z^2}(Pt)$ orbital interactions, exhibits ³MMLCT (MMLCT = metal-metal bond-to-ligand charge-transfer) emission at a much longer wavelength of *ca.* 800 nm in the solid state [15]. This observation has prompted this report on the crystal structure and solid state photophysics of the hexafluoroantimonate salt of the same cation, *i.e.*, [Pt(trpy)(C $\equiv CPh$)]SbF₆, a salt that is both

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different in colour (orange) and that exhibits very different emission behaviour to that reported for the purple hexafluorophosphate salt in the solid state [15].

2. Experimental

2.1. Materials

The organic solvents used in the syntheses were of HPLC grade, and with the 2,2':6',2"-terpyridine, phenylacetylene, "Bu₃SnCl and butyllithium (1.6 M solution in hexanes) came from Aldrich Chemicals and were used as received. The [Pt(PhCN)₂Cl₂] and AgSbF₆ were obtained from Strem Chemicals and also used as received. The [Pt(trpy)Cl]SbF₆ was synthesized by the reaction in acetonitrile of [Pt(PhCN)₂Cl₂] with an equimolar amount of AgSbF₆ followed by addition of 2,2':6',2''-terpyridine, as described in the literature [7]. The DMSO- d_6 used for recording the NMR spectra, as well as the acetonitrile and dichloromethane used for the infrared, UV-Vis absorption and solution emission measurements, were of spectroscopic grade and obtained from Merck Chemicals. For the UV-Vis absorption and solution emission measurements the solvents were deoxygenated prior to use by a stream of argon.

2.2. Synthesis of ${}^{n}Bu_{3}SnC \equiv CPh$

Butyllithium (5.35 ml of a 1.6 M solution in hexanes, 8.56 mmol) was added dropwise over a period of 10 min to a vigorously stirred solution of phenylacetylene (0.75 ml, 6.85 mmol) in dry THF (20 ml) at -78 °C. The mixture was stirred for a further 10 min after which ^{*n*}Bu₃SnCl (2.78 ml, 10.28 mmol) added dropwise over a period of *ca*. 30 min. The reaction mixture was then allowed to warm up to room temperature and its volume reduced to *ca*. 5 ml. The remaining liquid was extracted into *n*-hexane (2 × 20 ml) and the combined extracts filtered under dinitrogen using a P4 frit. The volume of the filtrate was reduced to a minimum (*ca*. 2 ml) *in vacuo* to afford the product as a clear light-yellow liquid. Yield: 1.61 g (60%). IR (CH₂Cl₂, cm⁻¹): v(C=CPh): 2132m.

2.3. Synthesis of $[Pt(trpy)(C \equiv CPh)]SbF_6$

Two equivalents of ${}^{n}Bu_{3}SnC \equiv CPh (0.17 \text{ g}, 0.42 \text{ mmol})$ were added to a suspension of [Pt(trpy)Cl]SbF₆ (0.15 g, 0.21 mmol) in acetonitrile (10 ml) and the mixture heated under reflux for 6 h. After allowing the mixture to cool to room temperature, the product precipitated out as an orange microcrystalline solid that was isolated by filtration, washed successively with *n*-hexane, cold acetonitrile and diethyl ether and dried *in vacuo*. Yield: 0.12 g (70%). *Anal*. Calc. for C₂₃H₁₆F₆N₃PtSb: C, 36.10; H, 2.11; N, 5.49. Found: C, 36.10; H, 2.25; N, 5.71%. IR (KBr, cm⁻¹): $v(C \equiv CPh)$: 2128w; v(trpy): 1605s, 1487m, 1478m, 1454s, 1439s, 1400s, 1035m, 772s; $v(SbF)_{6}^{-}$ 658vs. ¹H NMR (DMSO-*d*₆): δ 8.69 (2H, d, H_{6,6"}) 8.26 (2H, s, H_{3,3"}) 8.22 (2H, s, H_{3',5'}) 8.04 (2H, t, H_{4,4"}) 7.68 (2H, m, H_{5,5"}) 7.46– 7.24 (5H, m, C₆*H*₅) 2.50 (1H, s, H_{4'}). ¹³C NMR (DMSO*d*₆): δ 160.0–154.2 (4C, m, C_{2,2',6',2"}) 144.8 (2C, s, C_{4,4"}) 142.2 (1C, s, C_{4'}) 142.0 (1C, s, C_{2"}) 144.0 (2C, s, C_{6,6"}) 129.8 (2C, s, C_{5,5"}) 128.9–126.8 (6C, m, C₆H₅C=C) 126.5 (2C, s, C_{3,3"}) 124.8 (2C, s, C_{3',5'}) 103.7 and 98.6 (2C, s, C₆H₅C=C). UV–Vis (50 µM in MeCN): λ_{max}/nm (ε , M⁻¹ cm⁻¹) 244 (2.5 × 10⁴); 259 (6.1 × 10³); 311 (8.3 × 10³); 330 (9.0 × 10³); 343 (9.2 × 10³); 430 (2.5 × 10³).

2.4. 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 and ¹³C NMR spectra were recorded at 298 K using a Varian Unity Inova 500 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-500 C 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 350 nm, with the scattered light removed by a 400 nm long-wave-pass filter.

2.5. Crystal structure determinations

The crystal and refinement data for $[Pt(trpy)-(C = CPh)]SbF_6$ obtained at 293, 240 and 200 K are summarized in the Table 1. X-ray intensity data from an orange needle-shaped crystal were collected with CRYSALIS CCD 170 [21] on an Oxford Diffraction Xcalibur 2CCD four-circle diffractometer fitted with an Oxford Instruments Cryojet and temperature controller. Absorption corrections were applied using a numerical face-indexing method and the data reduced with the program CRYSALIS RED 170 [21]. The structure was solved using the program sHELXS97 [22]. All non-hydrogen atoms were assigned anisotropic displacement parameters and the hydrogen atoms (in calculated positions) a single overall isotropic displacement parameter. The plots were obtained using the ORTEP program [23].

3. Results and discussion

The σ -acetylide complex [Pt(trpy)(C=CPh)]SbF₆ was synthesised in a good yield by means of a metathesis reaction in which the chloro-analogue, [Pt(trpy)Cl]SbF₆, was reacted in acetonitrile under reflux with two equivalents of "Bu₃SnC=CPh. The compound was isolated as an orange microcrystalline solid by rapidly cooling the reaction mixture to room temperature. Single crystals suitable for the purposes of an X-ray diffraction study were grown by dissolving the compound in acetonitrile at room temperTable 1

C_{1} vstar and remember data for $ F_{1} D_{1} C_{-}$	Crvstal	and refinement	t data for	[Pt(trpy)(C=CPh)]	SbF_6^a
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Temperature (K)	293	240	200
a (Å)	7.521(4)	7.521(1)	7.501(1)
b (Å)	14.691(4)	14.640(2)	14.604(2)
<i>c</i> (Å)	20.755(6)	20.683(3)	20.632(2)
β (°)	91.35(3)	90.74(1)	90.57(1)
$V(Å^3)$	2293(1)	2277(1)	2260(1)
$D_{\rm c} ({\rm g}{\rm cm}^{-3})$	2.217	2.232	2.249
$\mu (\mathrm{mm}^{-1})$	7.34	7.39	7.44
Total number of reflections measured	19385	19471	19259
Independent reflections	7165	7111	7053
R _{int}	0.102	0.067	0.064
Reflections observed $[I \ge 2\sigma(I)]$	3403	4076	4341
$R_1^{\text{b}}[I \ge 2\sigma(I)]$	0.066	0.060	0.058
R_1^{b} , wR_2^{c} (all data)	0.146, 0.231	0.115, 0.176	0.106, 0.177
Number of refined parameters, ^d restraints	308, 0	308, 0	308, 0
(shift/esd) _{max}	0.000	0.000	0.000
Maximum, minimum $\Delta \rho$ (e Å ⁻³)	2.63(Pt), -2.29(Pt)	3.49(Pt), -2.03(Pt)	4.13(Pt), -2.20(Pt)

^a Crystal data common to all temperatures: formula (fw), $C_{23}H_{16}F_6N_3PtSb$ (765.23 S); crystal system, monoclinic; space group, $P2_1/n$ (no. 14); Z, 4; F(000), 1432.

$$\sum_{n=1}^{\infty} w_{n} \sum_{n=1}^{\infty} [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}]^{1/2} \text{ where } w = 1/[\sigma^{2}(F_{o}^{2}) + (0.1P)^{2}] \text{ and } P = (F_{o}^{2} + 2F_{c}^{2})/3.$$

^d Refinement on F^2 .

ature and allowing the solvent to evaporate slowly over a period of days. Note that when the orange compound is dissolved in refluxing acetonitrile and the solution allowed to cool slowly to room temperature, *i.e.*, over a period of days, a purple crystalline material forms at the bottom of the flask along with a few orange crystals. However, despite repeated attempts including hand selection of crystals, it was not possible to separate an analytically pure purple compound; nor could single crystals suitable for an X-ray diffraction study be isolated. Nevertheless, an infrared spectrum of the purple compound recorded as a KBr disc showed a peak at ca. 2130 cm⁻¹ that is clearly assigned to the stretching frequency of the C=C triple bond of the phenylacetylide ligand. Thus, we suspect (but cannot prove) that the purple material is a second polymorph of $[Pt(trpy)(C \equiv CPh)]SbF_6.$

3.1. Crystal structure of orange $[Pt(trpy)(C \equiv CPh)]SbF_6$ at 293 K

A perspective view of the cation in $[Pt(trpy)(C \equiv CPh)]$ -SbF₆ 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) [2–4,7,14,24]. The phenyl ring of the acetylide ligand is almost co-planar with the Pt(trpy) moiety as evidenced by a dihedral angle between these two units of only 1.1°. In fact the cation as a whole is essentially planar, with a maximum deviation of any one atom from a mean plane through all the non-hydrogen atoms of 0.10 Å. Insofar as the packing of the cations in crystals of $[Pt(trpy)-(C \equiv CPh)]SbF_6$ is concerned, it is very different to that reported for the purple hexafluorophosphate salt, $[Pt(trpy)-(C \equiv CPh)]PF_6$ [15]. In the latter salt, the cations are stacked head-to-tail with the Pt···Pt distances alternating between 3.363 and 3.375 Å in a zig-zag chain [15]. As noted by the authors, these distances are short enough to support extended $d_{z^2}(Pt)-d_{z^2}(Pt)$ orbital interactions along the platinum atom chain [15]. Fig. 2 gives a side-on view of the cation stack in [Pt(trpy)(C=CPh)]SbF₆. Here the cations are also stacked head-to-tail, but with alternating Pt···Pt



Fig. 1. Perspective view of the cation in $[Pt(trpy)(C = CPh)]SbF_6$. Selected interatomic distances (Å) and angles (°): Pt–N(1) 2.04(1), Pt–N(2) 1.95(1), Pt–N(3) 2.06(1), Pt–C(16) 1.97(1); N(1)–Pt–N(2) 80.5(2), N(1)–Pt–N(3) 160.7(4), N(1)–Pt–C(16) 99.1(4), N(2)–Pt–N(3) 80.3(4), N(2)–Pt–C(16) 179.5(4), N(3)–Pt–C(16) 100.1(5). Atom positions are plotted using the 293 K data and the program *ORTEP* with 50% displacement ellipsoids.

^b $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|.$



Fig. 2. View of a cation stack in $[Pt(trpy)(C \equiv CPh)]SbF_6$. Successive cations are related by centres of inversion on the [a]-axis of the unit cell. The $Pt \cdots Pt$ distances shown are those obtained from the 293 K data.

distances that are not only much longer than those observed for [Pt(trpy)(C=CPh)]PF₆, but also very different in length viz 3.604(1) and 4.412(1) Å. The upper $Pt \cdots Pt$ distance limit for significant $d_{r^2}(Pt) - d_{r^2}(Pt)$ orbital interactions is about 3.5 Å [25]. As a result, the $Pt \cdot \cdot Pt$ distances in crystals of [Pt(trpy)(C=CPh)]SbF₆ are too long to allow for finite $d_{z^2}(Pt)-d_{z^2}(Pt)$ orbital overlap, with the result that orange $[Pt(trpy)(C \equiv CPh)]SbF_6$ and purple [Pt(trpy)-(C=CPh)]PF₆ exhibit very different emission behaviour in the solid state (see below). The perpendicular distances (or interplanar spacings) between successive mean planes through the non-hydrogen atoms of the cation in $[Pt(trpy)(C \equiv CPh)]SbF_6$ are constant at a value of 3.33 Å. Thus, the difference between the two interaction Pt···Pt distances observed for $[Pt(trpy)(C \equiv CPh)]SbF_6$ can be attributed to the different extents to which adjacent platinum atoms are slipped with respect to a line drawn perpendicular to the cation planes; the greater the slippage the longer the $Pt \cdot \cdot Pt$ distance. This is illustrated in Fig. 3. Note that an interplanar spacing of 3.33 Å is well within the upper distance limit of about 3.8 Å for π - π interactions in organic species [26].

3.2. Crystal structures of orange $[Pt(trpy)(C \equiv CPh)]SbF_6$ at lower temperatures

As the data in Table 1 show, there is no phase change on cooling crystals of $[Pt(trpy)(C = CPh)]SbF_6$ to 240 and 200 K but there is the expected systematic decrease in the unit cell volume. Insofar as the structural parameters relevant to the discussion of the solid emission behaviour of $[Pt(trpy)(C = CPh)]SbF_6$ are concerned these are as follows. At 240 K, the Pt···Pt distances alternate between 3.607(1) and 4.443(1) Å while the interplanar spacing is 3.32 Å. At 200 K, the Pt···Pt distances alternate between 3.603(1) and 4.454(1) Å while the interplanar spacing is 3.31 Å. The Pt···Pt distances are not significantly different to those obtained at 293 K and, therefore, $d_{z^2}(Pt)-d_{z^2}(Pt)$ orbital interactions are not expected to play a role in determining



Fig. 3. View perpendicular to the plane defined by the three nitrogen atoms of the two types of cation interaction in $[Pt(trpy)(C \equiv CPh)]SbF_6$. (a) $Pt \cdots Pt = 3.604(1)$ Å (at 293 K), (b) 4.412(1) Å (at 293 K).

the solid emission by the compound at 240 and 200 K. However, as at 293 K, π - π interactions *are* expected to influence the photoluminescence by [Pt(trpy)(C=CPh)]-SbF₆ in the solid state (see below).

Attempts were made to collect intensity data sets at temperatures below 200 K, specifically at 160, 120 and 80 K, but without success. It became apparent that the crystal underwent a phase change below 200 K, as evidenced by the fact that the unit cell on which the data were indexed at 293, 240 and 200 K, did not appear as an option for the data obtained at the lower temperatures. In fact, it was not possible to discern using the CRYSALIS CCD 170 software, a unit cell on which a full sphere of reflections could be indexed. Interestingly, warming the crystal from temperatures below 200 K back up to 200, 240 and 293 K and recollecting the intensities, gave data sets that solved for the same structures as summarized in Table 1.

3.3. Photophysical properties of $[Pt(trpy)(C \equiv CPh)]SbF_6$

The UV–Vis absorption spectrum of [Pt(trpy)(C \equiv CPh)]-SbF₆ measured in acetonitrile exhibits an intense peak at 244 nm with a shoulder at 259 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(π – π^*) transitions of the terpyridyl ligand [2,3,15,20]. Two possibilities exist for the assignment of the broad low

energy band, a $d\pi(Pt) \rightarrow \pi^*(trpy)$ metal-to-ligand chargetransfer (¹MLCT) transition or an acetylide-to-terpyridine ligand-to-ligand charge-transfer (¹LLCT) transition. We tentatively make the ¹MLCT 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 terpyridyl ligand complexes of platinum(II) with a σ -acetylide as the co-ligand [15–17].

The emission spectra of $[Pt(trpy)(C \equiv CPh)]SbF_6$ measured in acetonitrile and dichloromethane at room temperature are shown in Fig. 4. The emission is broad. asymmetric and unstructured in both solvents but there are differences in the peak intensities and maxima. Specifically, the signal in acetonitrile is weaker and maximizes at 608 nm, whereas the more intense peak recorded in dichloromethane maximizes at 619 nm. These observations are consistent with a ³MLCT assignment to the emission in fluid solution, since (1) the emissions from planar complexes of platinum(II) tend to be quenched in a coordinating solvent (like acetonitrile), and (2) the wavelength of the emission maximum for ³MLCT emission is dependent on the polarity of the solvent [27]. In fact, a similar assignment has been offered for the emission recorded in acetonitrile from $[Pt(trpy)(C \equiv CPh)]PF_6$ [15] as well as $[Pt(trpy)(C \equiv CPh)]$ -ClO₄ [16].

Solid state emission spectra of a microcrystalline sample of orange [Pt(trpy)(C=CPh)]SbF₆were recorded at 40 K intervals over the temperature range 80–280 K and are shown in Fig. 5. At 280 K the solid emission spectrum comprises a broad peak with two barely discernable components at *ca*. 566 and 597 nm of near equal intensity and separated in energy by *ca*. 900 cm⁻¹. The emission intensity increases on lowering the temperature to 200 K, and the resolution improves with little or no shift in the band maxima. However, below 200 K, a longer wavelength component develops as shown in Fig. 5. This component is different in that the maximum shifts to longer wavelength as the temperature decreases. In assigning the solid emission at temperatures of ≥ 200 K, we first note that it is clear from the X-ray structural data that *neither* component can



Fig. 4. Room temperature emission spectra of $[Pt(trpy)(C = CPh)]SbF_6$ in degassed CH_2Cl_2 (a) and CH_3CN (b).



Fig. 5. Solid state emission spectra recorded on the orange polymorph of $[Pt(trpy)(C \equiv CPh)]SbF_6$ at 40 K intervals over the temperature range 80 K (a) to 280 K (f).

be assigned to emission from a ³MMLCT state since the Pt...Pt distances of >3.6 Å are too long to support finite $d_{z^2}(Pt) - d_{z^2}(Pt)$ orbital overlap [25]. On the other hand, the interplanar spacings of *ca.* 3.3 Å indicate that there are extended π - π interactions between adjacent terpyridyl moieties at all temperatures investigated. To the extent that intermolecular forces influence the solid-state emission, the emission has ³MLLCT character because ligand-ligand (LL) interactions, not metal-metal (MM) interactions, influence the transition energies. We note that the 900 cm⁻¹ spacing in the solid-state emission spectrum of $[Pt(trpy)(C \equiv CPh)]SbF_6$ is smaller than the vibrational progressions of 1300–1500 cm⁻¹ normally associated with the v(CC) and v(CN) stretching modes of a terpyridyl ligand [2,3,15,19]. This may mean that the two components observed at 200, 240 and 280 K have different origins. Another possibility is that the 900 cm^{-1} spacing corresponds to a 'beat frequency' associated with two higher frequency components [28]. Either way, it is interesting that the solid-state emission occurs at a *shorter* wavelength than that recorded in fluid solutions. Usually, intermolecular interactions in the solid or a concentrated glass cause the emission to occur at a *longer* wavelength [3,7,29-31]. One possible explanation is as follows. Recall that the cations are planar and that any one cation is sandwiched between two others oriented in the opposite direction (see Fig. 3). In view of the dipole moments, this arrangement is stabilizing for the ground state, but it may be destabilizing for the excited state which has a different charge distribution.

We now turn to the changes in the solid emission that manifest at temperatures below 200 K. As already noted, a long wavelength emission appears and the maximum shifts from 602 nm at 160 K to 637 nm at 80 K. Accompanying this red shift is a narrowing of the bandwidth such that, at 80 K, the full-width-at-half-maximum (fwhm) value is *ca*. 1500 cm⁻¹. This kind of behaviour is associated with ³MMLCT emission, *i.e.*, where there *is* a finite $d_{z^2}(Pt)-d_{z^2}(Pt)$ orbital interaction that increases as the temperature decreases due to further shortening of the Pt...Pt distance [2,3,9,15]. Unfortunately, we do not have the requisite X-ray crystal structure determinations at 80, 120 and 160 K to support this conclusion, but it is likely that the Pt \cdots Pt distances shrink to less than 3.5 Å as a result of the phase change that occurs around 200 K.¹

4. Conclusions

This work has demonstrated that changing the counterion from the hexafluorophosphate to the larger hexafluoroantimonate anion, causes a dramatic change in the colour and solid state emission of their salts with the $[Pt(trpy)(C \equiv CPh)]^+$ cation. Thus, whereas the former is purple the latter is orange and, whereas the solid emission exhibited by the hexafluorophosphate salt is characterized by a long wavelength band at 800-830 nm [15], there is no evidence for such a band in the emission spectra recorded for [Pt(trpy)(C=CPh)]SbF₆ (see Fig. 5). However, this change is not clear-cut since, as described above, $[Pt(trpy)(C \equiv CPh)]SbF_6$ can be induced to crystallize in a purple form by slow cooling of a solution of the compound in hot acetonitrile. Though the purple sample thus obtained is not analytically pure, we have been able to record emission spectra of the purple sample as a function of temperature that can be regarded as genuinely representative of the purple polymorph. These spectra are dominated by a broad band that increases in intensity as the temperature is lowered and which maximizes at ca. 780 nm at 80 K. As such, its solid state photoluminescence is similar to that recorded for the purple hexafluorophosphate salt $[Pt(trpy)(C = CPh)]PF_6$ [15]. We have also recorded the excitation spectrum of the purple polymorph and note that is dominated by absorption bands that appear towards the red end of the spectrum, *i.e.*, at about 600 nm. This accounts for the purple colour.

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¹ Based on previous studies in our laboratories [9], we speculate that on cooling the crystal below 200 K the platinum atoms shift their positions within the cation plane, i.e., the interplanar spacings remain essentially unchanged. In so doing the platinum atoms of successive cations adopt new positions that are more eclipsed with respect to a line drawn perpendicular to the cation stack with the result that the $Pt \cdots Pt$ distances shorten.