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Inorganic Chemistry Communications 6 (2003) 598-603

Inorganic Chemistry Communications

www.elsevier.com/locate/inoche

# The structures and decomposition products of palladium(II) and platinum(II) terpyridine phenoxide complexes

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Received 4 December 2002; accepted 27 January 2003

#### Abstract

A series of complexes of formula  $[Pd(OR)(terpy)]BF_4$  and  $[Pt(OR)(terpy)]BF_4$  (ROH = a substituted phenol; terpy = 2,2':6',2''-terpyridine) have been prepared by reaction of  $[M(OH)(terpy)]BF_4$  (M = Pd, Pt) with ROH. One Pd(II) and one Pt(II) complex in this series have been structurally characterised. These compounds are very acid sensitive; decomposition products resulting from recrystallisation of two of these compounds from MeNO<sub>2</sub> or MeCN have been crystallographically characterised. © 2003 Elsevier Science B.V. All rights reserved.

Keywords: Palladium complexes; Platinum complexes; Phenoxide complexes; Crystal structure

# 1. Introduction

A large number of different Pd(II) and Pt(II) complexes have been reported of formula  $[MX(terpy)]^+$  or  $[{M(terpy)}_2(\mu-Y)]^{3+}$  (M = Pd, Pt), where  $X^{-1}$  is a monodentate ligand such as Cl<sup>-</sup> [1-5], OH<sup>-</sup> [6,7], OCH<sub>3</sub><sup>-</sup> [7], NCS<sup>-</sup> [7], SR<sup>-</sup> [8], CH<sub>2</sub>R<sup>-</sup> [5,9–11], C<sub>3</sub>H<sub>3</sub>R<sub>2</sub><sup>-</sup> [12],  $C \equiv CR^{-}$  [13],  $NHR^{-}$  [14] or  $N \equiv CNR^{-}$  [15] (not a comprehensive list); or,  $Y = SR^{-}$  [16,17], *cis*-[Pd(SC<sub>2</sub>  $H_4NH_2$ )<sub>2</sub>] [18], Et<sub>2</sub>NCS<sub>2</sub><sup>-</sup> [19], guanadinide [20,21], amidinate [22] or pyrazolide [23]. Several  $[MZ(terpy)]^{2+}$ derivatives with neutral N- or O-donor Z coligands are also known [4,6,16,24]. The optical and emission spectra of many of the Pt complexes have been widely studied, since these are very dependent on the mode of intermolecular association of the  $[Pt(terpy)]^+$  centres in the solid state [25]; or, in the binuclear species, on the proximity of the two  $[Pt(terpy)]^+$  moieties to each other [19,21,26]. Several  $[PtX(terpy)]^+$  derivatives have also been shown to bind strongly to DNA [27] and to proteins [28].

We have recently prepared a series of hydroxy [3.3]cyclophanes, whose conformations can be controllably switched between a fluxional chair-boat form, in which the two annelated benzo groups lie far apart; and, a rigid twin-chair form, in which the benzo rings are now stacked upon each other [29]. While these compounds were originally intended to model a biological phenoxyl radical cofactor, we have been interested to explore alternative aspects of their chemistry. Since complexes of formula  $[Pd(OR)(terpy)]^+$  and  $[Pd(OR) (terpy)]^+$  (R = aryl) have not yet been reported, we have synthesised the new complexes  $[PdL(terpy)]BF_4$  (HL = HL<sup>1</sup>, 1; HL = HL<sup>2</sup>, 2; HL = HL<sup>3</sup>, 3) and  $[PtL(terpy)]BF_4$  (HL = HL<sup>1</sup>, 4; HL = HL<sup>2</sup>, 5; HL = HL<sup>3</sup>, 6). Complexes of  $[L^1]^-$  were also studied, as a control.



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# 2.1. Syntheses of the complexes

The syntheses of all of the complexes followed the same basic procedure, as described here for 1. To a suspension of  $[Pd(terpy)(OH)]BF_4$  (0.050 g,  $1.12 \times$  $10^{-4}$  mol) [6] in freshly distilled CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>) was added HL<sup>1</sup> (0.016 g,  $1.34 \times 10^{-4}$  mol). The mixture was refluxed for 1 h, until almost all of the solid had dissolved, affording a deep red solution. Insoluble materials were removed, and the filtrate concentrated to ca. 2 cm<sup>3</sup>. Diffusion of  $Et_2O$  vapour into this solution afforded a red polycrystalline product. Similar reactions using  $HL^2$  [29] or  $HL^3$  [29] afforded 2 and 3, respectively. Yields of 1-3 ranged from 80% to 90%. An identical method starting from  $[Pt(terpy)(OH)]BF_4$ [7] was used for the Pt complexes, except that the mixture was kept refluxing for 7 days. Yields of 4-6 were lower at 50-75%.

For  $[Pd(L^1)(terpy)]BF_4$  (1): Found: C, 50.4; H, 4.1; N, 7.4%. Calcd. for  $C_{23}H_{20}BF_4N_3OPd$ : C, 50.2; H, 4.2; N, 7.6%. FAB mass spectrum: m/z 460  $[^{106}Pd(L^1)(terpy)]^+$ , 339  $[^{106}Pd(terpy)]^+$  with correct isotopic distributions. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ , nm ( $\varepsilon_{max}$ , M<sup>1</sup> cm<sup>-1</sup>) 244 (56,300), 277 (33,600), 306 (21,900), 328 (13,900), 344 (14,600), 360 (11,700), 436 (sh).

For  $[Pd(L^2)(terpy)]BF_4$  (2): Found: C, 57.1; H, 4.2; N, 5.6%. Calcd. for  $C_{34}H_{28}BF_4N_3O_2Pd$ : C, 58.0; H, 4.0; N, 5.9%. FAB mass spectrum: *m/z* 616  $[^{106}Pd(terpy)L^2]^+$ , 339  $[^{106}Pd(terpy)]^+$ , 278  $[L^2]^+$  with correct isotopic distributions. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ , nm ( $\epsilon_{max}$ , M<sup>-1</sup> cm<sup>-1</sup>) 245 (43,400), 276 (29,000), 306 (18,700), 329 (12,600), 344 (13,000), 361 (11,000), 429 (sh).

For  $[Pd(L^3)(terpy)]BF_4$  (3): Found: C, 57.6; H, 4.5; N, 5.4%. Calcd. for  $C_{36}H_{32}BF_4N_3O_3Pd$ : C, 57.8; H, 4.3; N, 5.6%. FAB mass spectrum: m/z 660  $[^{106}Pd(L^3)(terpy)]^+$ , 339  $[^{106}Pd(terpy)]^+$  with correct isotopic distributions. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ , nm ( $\varepsilon_{max}$ ,  $M^{-1}$  cm<sup>-1</sup>) 244 (43,300), 274 (28,600), 306 (17,700), 328 (11,100), 344 (11,300), 360 (8,900), 447 (sh).

For  $[Pt(L^1)(terpy)]BF_4$  (4): Found: C, 43.2; H, 3.4; N, 6.5%. Calcd. for  $C_{23}H_{20}BF_4N_3OPt$ : C, 43.4; H, 3.2; N, 6.6%. FAB mass spectrum: m/z 550  $[^{195}Pt(L^1)(terpy)]^+$ , 428  $[^{195}Pt(terpy)]^+$  with correct isotopic distributions. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ , nm  $(\varepsilon_{max}, M^{-1} \text{ cm}^{-1})$  243 (29,200), 258 (29,100), 282 (28,200), 307 (12,400), 320 (13,300), 331 (13,300), 348 (8,400), 388 (sh), 540 (850).

For  $[Pt(L^2)(terpy)]BF_4$  (5): Found: C, 50.8; H, 3.7; N, 5.0%. Calcd. for  $C_{34}H_{28}BF_4N_3O_2Pt$ : C, 51.4; H, 3.6; N, 5.3%. FAB mass spectrum: m/z 705  $[^{195}Pt(L^2)(terpy)]^+$ , 428  $[^{195}Pt(terpy)]^+$  with correct isotope distributions. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ , nm ( $\varepsilon_{max}$ ,  $M^{-1}$  cm<sup>-1</sup>) 253 (38,200), 282 (34,000), 305 (15,000), 318 (15,700), 331 (15,500), 348 (11,600), 392 (sh), 515 (1,400).

For [Pt(L<sup>3</sup>)(terpy)]BF<sub>4</sub> (6): Found: C, 51.0; H, 4.0; N, 4.7%. Calcd. for C<sub>36</sub>H<sub>32</sub>BF<sub>4</sub>N<sub>3</sub>O<sub>3</sub>Pt: C, 51.7; H, 3.9; N, 5.0%. FAB mass spectrum: m/z 749 [<sup>195</sup>Pt(L<sup>3</sup>)(terpy)]<sup>+</sup>, 428 [<sup>195</sup>Pt(terpy)]<sup>+</sup>, 322 [L<sup>3</sup>]<sup>+</sup> with correct isotopic distributions. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$ , nm ( $\varepsilon_{max}$ , M<sup>-1</sup> cm<sup>-1</sup>) 234 (32,100), 259 (32,300), 282 (30,600), 318 (14,600), 332 (14,200), 370 (sh), 385 (sh), 567 (740).

### 2.2. Single crystal X-ray structure determinations

Thin red plates of  $[Pd(L^1)(terpy)]BF_4$  (1) and  $[Pt(L^{1})(terpy)]BF_{4}$  (4) were grown from  $CH_{2}Cl_{2}/Et_{2}O/$ hexanes. Recrystallisation of 5 from MeNO<sub>2</sub>/Et<sub>2</sub>O led to its clean conversion to yellow crystals of  $[Pt(CH_2NO_2)]$ (terpy)]BF<sub>4</sub>. Recrystallisation of 1 from MeCN/Et<sub>2</sub>O afforded a small number of yellow crystals of [{Pd (terpy)<sub>2</sub> $(\mu$ -NHC}CH<sub>3</sub>)][BF<sub>4</sub>]<sub>3</sub> · 2CH<sub>3</sub>CN (8 · 2CH<sub>3</sub>CN), contaminated by an excess of a yellow powder. Experimental details from the structure determinations are given in Table 1. All structures were solved by direct methods (SHELXS 86 [33]) and refined by full matrix least squares on  $F^2$  (SHELXL 97 [34]). The X-ray datasets from 1 and, particularly, 4 and 7 suffer from absorption problems leading to several intense residual Fourier peaks around the heavy metal atoms. These could be a reflection of their heavily anisotropic morphologies; 1 and 4 crystallise as thin plates, while 7 has a needle morphology.

No disorder was detected during refinement of any of these structures, and no restraints were applied. All non-H atoms were refined anisotropically. For 1, 4 and 7 all H atoms were placed in calculated positions and refined using a riding model. However, for 8 all H atoms in the complex trication were located in the difference map and allowed to refine freely, while the H atoms on the  $CH_3CN$  molecules in this structure were placed in calculated positions and refined using a riding model.

### 2.3. Other measurements

UV/Visible spectra were obtained with a Perkin– Elmer Lambda 12 spectrophotometer, operating between 100 and 200 nm, in 1 cm quartz cells. Positive ion fast atom bombardment mass spectra were performed on a VG Autospec MS890 spectrometer, employing a 3-NOBA matrix. CHN microanalyses were performed by the University of Leeds Department of Chemistry microanalytical service.

### 3. Results and discussion

Attempted syntheses of **1–6** by reacting [MCl(terpy)]  $BF_4$  (M = Pd, Pt) with the appropriate phenol under neutral or basic conditions did not yield clean products. However, reaction of [M(OH)(terpy)]  $BF_4$  (M = Pd, Pt)

|  | $[Pd(L^1)(terpy)]BF_4$ (1) | $[Pt(L^1)(terpy)]BF_4 \ \textbf{(4)}$ | $[Pt(CH_2NO_2) (terpy)]BF_4$ (7) | $\begin{array}{l} [\{Pd(terpy)\}_2(\mu\text{-}NHC\{O\}CH_3)][BF_4]_3 \cdot \\ 2CH_3CN(\textbf{8}\cdot 2CH_3CN) \end{array}$ |
|--|----------------------------|---------------------------------------|----------------------------------|---|
| Formula                                      | $C_{23}H_{20}BF_4N_3Opd$   | $C_{23}H_{20}BF_4N_3OPt$              | $C_{16}H_{13}BF_4N_4O_2Pt$       | $C_{36}H_{32}B_3F_{12}N_9OPd_2$   |
| $M_{ m r}$                                   | 547.63                     | 636.32                                | 575.20                           | 1079.94   |
| Crystal system                               | Monoclinic                 | Monoclinic                            | Monoclinic                       | Triclinic   |
| Space group                                  | $P2_1/n$                   | $P2_1/n$                              | $P2_1/n$                         | $P\bar{1}$  |
| a (Å)  | 10.6077(1)                 | 10.6014(1)                            | 8.2868(1)                        | 12.3743(1)  |
| $b(\mathbf{A})$                              | 13.2571(1)                 | 13.2489(1)                            | 10.6173(2)                       | 13.0949(1)  |
| c (Å)  | 30.4366(4)                 | 30.4958(4)                            | 19.0328(3)                       | 14.4584(2)  |
| α (°)  | _                          | _                                     | _                                | 64.3486(5)  |
| β (°)  | 95.1621(5)                 | 95.0067(5)                            | 92.4214(7)                       | 72.5261(5)  |
| γ (°) ,                                      | _                          | _                                     | _                                | 83.5104(4)  |
| $V(\dot{A})$                                 | 4262.86(8)                 | 4267.00(8)                            | 1673.08(5)                       | 2013.95(4)  |
| Z  | 8                          | 8                                     | 4                                | 2   |
| $D_{\rm c} \ ({\rm mg} \ {\rm m}^{-3})$      | 1.707                      | 1.981                                 | 2.284                            | 1.781   |
| $\mu$ (Mo-K $\alpha$ , mm <sup>-1</sup> )    | 0.927                      | 6.633                                 | 8.451                            | 0.993   |
| $T(\mathbf{K})$                              | 150(2)                     | 150(2)                                | 150(2)                           | 150(2)  |
| Measured reflections                         | 66080                      | 38715                                 | 28163                            | 37133   |
| Unique reflections                           | 9758                       | 9688                                  | 3847                             | 9044  |
| R <sub>int</sub>                             | 0.090                      | 0.139                                 | 0.102                            | 0.060   |
| No. of parameters                            | 599                        | 599                                   | 253                              | 672   |
| $R(F)^{\mathrm{a}}$ , $wR(F^2)^{\mathrm{b}}$ | 0.051, 0.140               | 0.074, 0.221                          | 0.035, 0.093                     | 0.033, 0.088  |
| GOF  | 1.024                      | 1.026                                 | 1.066                            | 1.037   |

Table 1 Experimental details for the single crystal structure determinations in this study

 ${}^{a}R = \sum [|F_{0}| - |F_{c}|] / \sum |F_{0}|.$  ${}^{b}wR = \left[ \sum w(F_{0}^{2} - F_{c}^{2}) / \sum wF_{0}^{4} \right]^{1/2}.$ 

with  $HL^{1}-HL^{3}$  in acid-free  $CH_{2}Cl_{2}$  did afford **1**–**6** in moderate-to-good yields. All these complexes are airand moisture-stable red solids, which are air-stable in solution but very sensitive to the presence of acid. Thus, **1**–**6** decompose over periods of hours when dissolved in weakly acidic solvents like MeNO<sub>2</sub>, MeCN and acetone (see below), but can be safely handled in air in acid-free  $CH_{2}Cl_{2}$ ,  $CHCl_{3}$  or toluene. The UV/Vis spectra of **1**–**6** in  $CH_{2}Cl_{2}$  are complex, showing a highest wavelength band at  $\lambda_{max} = 429-447$  nm (M = Pd) and 515–567 nm (M = Pt). The wavelength of this peak is dependent on the phenoxide ligand present, following the trend in  $\lambda_{max}$ of  $[L^{3}]^{-} > [L^{1}]^{-} > [L^{2}]^{-}$  for both series of complexes. This transition is therefore assigned as a  $[OR]^{-} \rightarrow M$ (M = Pd, Pt) charge transfer.

Of the above compounds, only 1 and 4 form crystals that are suitable for X-ray structure determination. These crystals are isomorphous, with two crystallographically independent molecules in the asymmetric unit that have almost identical molecular structures (Table 2, Fig. 1). The complexes adopt the expected approximately square-planar geometry. The M-O (M = Pd, Pt) bond lengths are typical for phenoxide ligands to these metal ions trans to a N-donor [30], although the Pt-O distances in 4 are slightly longer than the Pd–O bonds in 1 (Table 1). All the other metric parameters are very similar in the two structures. The dihedral angles between the least squares planes of the  $[L^1]^-$  and terpy ligands bound to M(1) and M(29) are, respectively, 71.30(9)° and 73.49(9)° in 1, and 70.43(17)° and  $71.82(17)^{\circ}$  in 4. The high deviation of these angles

Table 2 Selected bond lengths (Å) and angles (°) for  $[Pd(L^1)(terpy)]BF_4$  (1) and  $[Pt(L^1)(terpy)]BF_4$  (4)

|                    | 1 [M = Pd] | 4 [M = Pt] |
|--------------------|------------|------------|
| M(1)–N(2)          | 1.944(4)   | 1.935(7)   |
| M(1)–N(9)          | 2.007(4)   | 2.010(7)   |
| M(1)–N(15)         | 2.041(4)   | 2.016(7)   |
| M(1)–O(20)         | 1.979(3)   | 2.009(6)   |
| M(29)–N(30)        | 1.930(3)   | 1.933(7)   |
| M(29)-N(37)        | 2.020(4)   | 1.999(8)   |
| M(29)–N(43)        | 2.033(3)   | 2.017(7)   |
| M(29)-O(48)        | 1.988(3)   | 2.010(5)   |
| N(2)–M(1)–N(9)     | 81.17(16)  | 81.0(4)    |
| N(2)-M(1)- N(15)   | 80.80(15)  | 82.2(3)    |
| N(2)-M(1)-O(20)    | 175.62(13) | 175.3(3)   |
| N(9)-M(1)-N(15)    | 161.95(16) | 163.2(3)   |
| N(9)-M(1)-O(20)    | 96.09(15)  | 95.9(3)    |
| N(15)-M(1)-O(20)   | 101.97(14) | 100.9(3)   |
| N(30)-M(29)-N(37)  | 80.87(15)  | 80.8(3)    |
| N(30)-M(29)- N(43) | 81.11(15)  | 81.3(3)    |
| N(30)-M(29)-O(48)  | 175.60(13) | 175.9(3)   |
| N(37)-M(29)-N(43)  | 161.95(15) | 162.0(3)   |
| N(37)-M(29)-O(48)  | 101.49(14) | 101.3(3)   |
| N(43)-M(29)-O(48)  | 96.56(14)  | 96.6(3)    |



Fig. 1. View of the two crystallographically independent  $[Pd(L^1) (terpy)]^+$  cations in the crystal structure of 1, showing the atom numbering scheme employed. Thermal ellipsoids are drawn at the 50% probability level. For clarity, all C-bound H atoms have been omitted. The  $[Pt(L^1)(terpy)]^+$  cations in 4 are visually indistinguishable from those of 1, and employ the same atom numbering scheme with Pd(1) and Pd(29) replaced by Pt(1) and Pt(29).

from  $0^{\circ}$  or  $90^{\circ}$  suggests that there is no significant  $\pi$ -bonding between the metal ions and phenoxide ligands.

The two molecules in 1 and 4 are almost coparallel in the crystal, and pack in 1-D stacks parallel to the crystallographic *a* direction (in the setting  $P2_1/n$ , Fig. 2); the dihedral angles between the [MN<sub>3</sub>O] (M = Pd, Pt) least squares planes on adjacent molecules in these stacks is 5.88(16)° for 1, and 5.4(4)° for 4. Despite the formal aggregation of these columns into crystallographically unique dimers, the two sets of unique intermolecular distances within each stack are almost equal, as shown



Fig. 2. View of the association of the complex cations in 1 (M = Pd) into 1-D stacks. The intermolecular distances quoted (Å) are: the shortest  $C \cdots C$  distance between each adjacent terpy ligand; the shortest  $O \cdots C$  intermolecular contact made by the phenoxide O-donors; and, the metal  $\cdots$  metal distance. The figures in square brackets are the corresponding parameters for 4 (M = Pt).

in Fig. 2. The distances of 3.3–3.4 Å between each terpy ligand are consistent with an attractive  $\pi$ – $\pi$  interaction between each molecule in the columns. However, adjacent molecules in the stacks are offset by 4.10–4.12 Å, so that the M · · · M distances are 5.3 Å (Fig. 2). This rules out significant overlap between the d<sub>z<sup>2</sup></sub> orbitals on adjacent Pd or Pt centres, which is a feature of many red crystals of Pt(II)/imine complexes [31].

As described earlier, 1-6 decompose upon dissolution in weakly acidic organic solvents, as evidenced by a colour change from red to yellow. We were able to crystallise decomposition products from two of the resultant solutions. First, dissolution of 5 in MeNO<sub>2</sub> resulted in its clean conversion to yellow  $[Pt(CH_2NO_2)(terpy)]BF_4$  (7). The molecular structure of 7 is identical to that of the  $BPh_{4}^{-}$ salt of the same complex cation [11]. The Pt(II) centres in 7 associate into coparallel dimers related by the centre of symmetry 1 - x, -v, 1 - z; these dimers aggregate further into 1-D stacks via a second inversion centre -x, -y, 1 - z. In 7, the intradimer  $Pt(1) \cdots Pt(1') = 5.2473(3)$  A while the intermolecular separation is 3.36 A. The corresponding interdimer distances are  $Pt(1) \cdots Pt(1'') =$ 5.1986(3) and 3.53 Å. Hence, adjacent molecules within the stacks are offset with respect to each other, by 4.0 and 3.8 Å, respectively. This contrasts with the 1-D stacking motif in  $[Pt(CH_2NO_2)(terpy)]BPh_4$ , where individual molecules are still related by inversion centres but are not now offset, so that the Pt · · · Pt separation within the chain is 3.4039(4) A. This accounts for the different colours of 7 (yellow) and the  $BPh_4^-$  salt (red) [11].

Secondly, recrystallisation of 1 from MeCN/Et<sub>2</sub>O yielded a large amount of an unknown yellow powder, together with a small number of yellow crystals that were identified by X-ray crystallography as [{Pd(terpy)}<sub>2</sub>  $(\mu$ -NHC{O}CH<sub>3</sub>)][BF<sub>4</sub>]<sub>3</sub> (8). The acetamidate bridging ligand in 8 must arise from hydrolysis of MeCN with adventitious water, promoted either by the presence of phenoxide base, or by coordination to Pd after initial hydrolysis of the  $Pd-[L^1]^-$  bond. The Pd(II)-effected hydrolysis of nitriles is unusual, but does have literature precedent [32]. Unfortunately, our attempts to obtain 8 in pure form by reaction of [Pd(OH)(terpy)]  $BF_4$  [6] with MeCN at room temperature or under reflux yielded impure product contaminated by an excess of unreacted starting material, which we were unable to remove by recrystallisation. Hence, we were unable to characterise 8 beyond determining its crystal structure.

The complex cation of **8** consists of two square-planar Pd(II) centres, linked by a 1,3-acetamidato bridge (Table 2, Fig. 3). The dihedral angle between the two [PdN<sub>3</sub>Y] (Y = N or O) planes in the molecule is 17.94(8)°, which reflects the small bite distance of the acetamidate group,  $O(41) \cdots N(42) = 2.292(2)$  Å, compared to the Pd(1)  $\cdots$  Pd(20) distance of 3.0570(2) Å. The two [Pd(terpy)Y] moieties are also slipped with respect to each other, the



Fig. 3. View of the hydrogen-bonded  $[\{Pd(terpy)\}_2(\mu-NHC \{O\}CH_3)]^{3+}$  trication and  $BF_4^-$  anion in the crystal structure of  $\mathbf{8} \cdot 2CH_3CN$ , showing the atom numbering scheme employed. Details as for Fig. 1. Selected bond lengths (Å) and angles (°): Pd(1)–N(2) 1.9331(17), Pd(1)–N(9) 2.0310(18), Pd(1)–N(15) 2.0323(17), Pd(1)–O(41) 2.0215(14), Pd(20)–N(21) 1.9433(17), Pd(20)–N(28) 2.0288(18), Pd(20)–N(34) 2.0315(18), Pd(20)–O(42) 2.0174(18), N(2)–Pd(1)–N(9) 81.14(7), N(2)–Pd(1)– N(15) 81.10(7), N(2)–Pd(1)–O(41) 177.30(6), N(9)–Pd(1)–N(15) 162.23(7), N(9)–Pd(1)–O(41) 96.94(7), N(15)–Pd(1)–O(41) 100.79(7), N(21)–Pd(20)–N(28) 80.88(7), N(21)–Pd(20)–N(34) 80.78(7), N(21)–Pd(20)–N(42) 173.97(7), N(28)–Pd(20)–N(34) 160.86(8), N(28)–Pd(20)–N(42) 100.42(7), N(34)–Pd(20)–N(42) 98.39(7).

torsion angle N(2)–Pd(1) ··· Pd(20)–N(21) being 14.47(7)°. Two complex molecules are associated into coparallel  $\pi$ – $\pi$  dimers separated by 3.19 Å, with a Pd(1) ··· Pd(1') distance of 3.2328(3) Å (related by 1 – x, 1 – y, 1 – z). Similar aggregation at the other face of the molecule is blocked by a hydrogen bond between the acetamido N–H group and a BF<sub>4</sub> anion (Fig. 3). Compound **8** is the first crystallographically characterised Pd(II) analogue of the well-known series of [{Pt(terpy)}<sub>2</sub>( $\mu$ -Z)]<sup>3+</sup> complexes, where Z<sup>-</sup> is a 1,3-bridging ligand [17–22]. The Pd(1) ··· Pd(20) distance in **8** is at the low end of the range previously observed in the Pt compounds [19]. Despite this, its yellow colouration suggests that there is no significant 4d<sub>z<sup>2</sup></sub>–4d<sub>z<sup>2</sup></sub> overlap between the Pd centres in **8**.

In summary, we have prepared the first complexes of type  $[Pd(OR)(terpy)]^+$  and  $[Pt(OR)(terpy)]^+$  (R = aryl). These represent a new extension to the well-established Pd(II) and Pt(II) terpyridine chemistry, whose emissive and electrochemical properties are likely to be of interest. These complexes are sensitive to weak organic acids, and we have characterised two unusual decomposition products. One of these is the first Pd(II) analogue of the well-known series of diplatinum face-to-face complexes, containing two  $[M(terpy)]^{2+}$  (M = Pd, Pt) centres linked by a 1,3-bridging ligand.

# Supplementary data

Full crystallographic data for the structure analysis in this study are available on request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk), quoting deposition numbers 198482 (1), 198483 (4), 198484 (7) and 198485 ( $8 \cdot 2CH_3CN$ ).

### Acknowledgements

The authors gratefully acknowledge funding by The Royal Society (M.A.H.), the EPSRC (X.L., S.L.R.) and the University of Leeds.

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