Intermolecular interactions and electronic properties in phosphino-(oligothiophene) palladium(II) and platinum(II) complexes

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Abstract: A series of Pt(II) and Pd(II) complexes containing diphenylphosphino-substituted oligothiophene ligands ranging from 1 to 3 thiophene rings in length have been prepared. Crystal structures of four of these complexes were determined via single X-ray crystal diffraction and the solid-state packing arrangements found to vary with both the metal and the thiophene-containing ligand. In some cases, π -stacking between thiophene rings are found for the oligothiophene ligands. Solution and solid-state absorption spectra of these complexes are reported.

Key words: oligothiophenes, metal complexes, structural properties, electronic spectra.

Résumé : On a préparé une série de complexes du Pt(II) et du Pd(II) contenant des ligands oligothiophènes substitués par des groupes diphénylphosphino dans lesquels le nombre de noyaux thiophènes varie de un à trois. On a déterminé les structures cristallines de quatre de ces complexes par diffraction des rayons X par un cristal unique et on a observé que les arrangements de l'empilement à l'état solide varient en fonction de la nature du métal ainsi que du ligand contenant le thiophène. Dans quelques cas, on a observé un empilement π pour les ligands oligothiophènes. On a aussi mesuré les spectres d'absorption en solution et à l'état solide de ces complexes.

Mots-clés : oligothiophènes, complexes métalliques, propriétés structurales, spectres électroniques.

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Introduction

Conjugated oligomers are of significant interest for application in electroluminescent devices (1), solar cells (2), and field-effect transistors based on molecular materials (3). Solid-state packing and intermolecular interactions are known to influence the emission properties (4) and charge mobility (5) of these materials. In π -conjugated oligomers such as oligothiophenes, π -stacking (6, 7) has been shown to influence the charge mobility as well as the excitation and emission energy of the material (4, 8). The degree of conjugation may also be influenced by solid-state packing, and unsubstituted oligothiophenes adopt a planar, fully conjugated arrangement in the solid state (5).

The solid-state packing of conjugated oligomers, such as oligothiophenes, can be influenced by the use of different organic substituents (5, 9–12) or by a combination of electronrich and electron-poor groups (13). A novel approach in controlling the solid-state packing is through the use of coordination chemistry where the conjugated groups are positioned as ligands on metal complexes giving a defined local geometrical arrangement, which may predispose the molecule towards specific packing arrangements. Intramolecular geometry may be controlled with coordination chemistry approaches; for example, our group has recently reported the use of pendant Ru(II) complexes to control the coplanarity of rings in a terthiophene derivative (14, 15). In the present work, we have selected palladium(II)- and platinum(II)bis(phosphine) complexes to further explore these effects. These were chosen because they are readily synthesized, are stable in air, crystallize easily (16), and exist in both cis- and trans-substituted square planar geometries (16–22). Our group has previously reported the synthesis and characterization of several β -substituted phosphinothiophene palladium(II) complexes (23–25). The metal was found to affect both the electronic properties and the structure of the oligothiophene. Au(I) complexes of the α -phosphinothiophene ligands used here have also been reported (26).

Metal centers may create quenching sites within the crystal (27, 28) thus limiting the immediate utility of these materials for application in optoelectronic devices; however, these studies still allow exploration of solid-state effects. The crystal structures of a series of phosphinothiophene palladium(II) and platinum(II) complexes are reported in this paper. The effects of the metal geometry and the length of the thiophene ligand on the structure and electronic spectra are explored. Gray and co-workers (29) recently reported the third-order nonlinear optical behavior of one of the Pd com-

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pounds $(Pd(PT_3)_2Cl_2)$ and one of the Pt compounds $(Pt(PT_3)_2Cl_2)$ described here; however, the solid-state structures of these complexes have not been reported.

Experimental

General

¹H and ³¹P{¹H} NMR experiments were performed on either a Bruker AV-300 or a Bruker AV-400 spectrometer. Spectra were referenced to a residual solvent (¹H) or external 85% H_3PO_4 (³¹P). Isomer ratios were determined from ³¹P NMR spectra obtained with a delay time of 2 s. Electronic spectra were obtained on a Cary 5000 in HPLC grade CH₂Cl₂. Solid-state absorption spectra were obtained by drop casting the compound from a CH₂Cl₂ solution onto a quartz slide. Microanalyses were performed at UBC. Electrospray mass spectra were obtained by infusion of 10 μ mol/L of a methanol solution at ~10 μ L/min into the electrospray source of a Bruker Esquire ion trap mass spectrometer. The spectra were acquired in positive ion mode. MALDI-TOF mass spectra were obtained on a Bruker Biflex IV mass spectrometer. Samples were prepared from dichloromethane in a dithranol matrix. PdCl₂ and K₂PtCl₄ were purchased from Strem and used as received. THF was dried over Na and benzophenone and was distilled before use. CH₂Cl₂ was dried by passing over an alumina column. Acetonitrile was dried over 3 Å molecular sieves and was degassed by sparging with N₂ for 20 min. No special precautions for the exclusion of oxygen were taken during synthesis. The phosphine ligands 2-diphenylphosphinothiophene (PT), 2-diphenylphosphino-5,2'-bithiophene (PT₂) and 2diphenylphosphino-5,2':5',2''-terthiophene (PT₃) were prepared as described previously (30, 31).

Synthesis

$Pd(PT)_{2}Cl_{2}(1)$

PdCl₂ (0.033 g, 0.19 mmol) was dissolved in an HCl–H₂O solution (0.2:3 ν/ν), which was then added dropwise to a solution of 0.10 g (0.39 mmol) PT dissolved in an ethanol–acetonitrile mixture (5:4 ν/ν). A yellow precipitate formed immediately, and the yellow slurry was stirred for 1 h. The solvent was then removed via rotary evaporation, and the resulting sticky material was dissolved in CH₂Cl₂ and acetone, then filtered, and a yellow powder was precipitated in hexanes. The product was recrystallized in hexanes–CH₂Cl₂, yielding an analytically pure product. Yield 80%. Anal. calcd. for C₃₂H₂₆Cl₂P₂PdS₂: C 53.83, H 3.67; found: C 53.67, H 3.67. ¹H NMR (CDCl₃) δ : 7.80 (m, 1H), 7.69–7.62 (m, 5H), 7.46–7.34 (m, 6H), 7.13 (m, 1H). ³¹P{¹H} NMR (CDCl₃) δ : 13.6 (s), 23.9 (s).

$Pd(PT_2)_2Cl_2$ (2)

PdCl₂ (0.025 g, 0.14 mmol) and PT₂ (0.10 g, 0.29 mmol) were mixed together in a 1:2 mixture of CH₃CN–CH₂Cl₂ for 3 h. The solvent was removed, and the resulting yellow powder was dissolved in CH₂Cl₂, gravity filtered, and precipitated with hexanes. The product was recrystallized in hexanes–CH₂Cl₂. Yield 40%. Anal. calcd. for C₄₀H₃₀Cl₂P₂PdS₄: C 54.71, H 3.44; found: C 54.31, H 3.58. ¹H NMR (CD₂Cl₂) δ : 7.73–7.66 (m, 5H), 7.47–7.38 (m, 6H), 7.31 (dd, J = 5.0,

1.2 Hz, 1H), 7.18 (dd, J = 1.2, 3.5 Hz, 2H), 6.98 (dd, J = 5.0, 3.6 Hz, 1H). ³¹P{¹H} NMR (CDCl₃) δ : 14.0 (s), 24.2 (s).

$Pd(PT_{3})_{2}Cl_{2}$ (3)

Results obtained by using a different synthesis were previously reported by our group (24). PdCl₂ (0.021 g, 0.12 mmol) was dissolved in an HCl-H₂O solution (0.2:3 v/v). This was added dropwise to a solution of 0.10 g (0.23 mmol) of PT₃ in THF, and a yellow precipitate began to form almost immediately. The yellow slurry was stirred for 1 h, and the solvent was then removed via rotary evaporation. The resulting sticky material was dissolved in CH₂Cl₂, filtered, and precipitated in hexanes. The product, a bright yellow powder, was recrystallized in hexanes-CH₂Cl₂. Yield 86%. Anal. calcd. for $C_{48}H_{34}Cl_2P_2PdS_6$: C 55.30, H 3.29; found: C 55.06, H 3.29. ¹H NMR (CDCl₃) δ : 7.70– 7.63 (m, 4H), 7.46-7.38 (m, 6H), 7.28-7.20 (m, 6H, includes CHCl₃), 7.18 (d, J = 3.6 Hz, 1H), 7.15 (d, J = 3.6 Hz, 1H), 7.08 (d, J = 3.6 Hz, 1H), 7.04 (d, J = 3.6 Hz, 1H), 6.99 (dd, J = 5.2, 3.6 Hz, 1H). ³¹P{¹H} NMR (CD₂Cl₂) δ : 14.3 (s), 24.4 (s).

General procedure for the synthesis of $\text{Pt}(\text{PT}_n)_2\text{Cl}_2$ complexes

The appropriate ligand was dissolved in 50 mL of CH_2Cl_2 and stirred with a solution of 0.5 equiv. of K_2PtCl_4 in 10 mL of H_2O . The reaction was monitored both by the disappearance of the red color in the H_2O layer due to K_2PtCl_4 and by the disappearance of the ligand via TLC. When the reaction was complete the layers were separated, the organic layer was dried over MgSO₄ and gravity filtered, and the solvent was removed via rotary evaporation. A minimal amount of CH_2Cl_2 was added to dissolve the resulting solid, which was then precipitated in 300 mL hexanes. The resulting powder was collected via suction filtration and either dried under vacuum or recrystallized from CH_2Cl_2 –hexanes to yield an analytically pure sample.

$Pt(PT)_2Cl_2$ (4).

Yield 67%. Anal. calcd. for $C_{32}H_{26}Cl_2P_2PtS_2$: C 47.89, H 3.27; found: C 47.78, H 3.57. ¹H NMR (CDCl₃) δ : 7.65–7.59 (m, 2H), 7.47–7.41 (m, 4H), 7.32–7.28 (m, 2H), 7.17–7.13 (m, 4H), 7.04–7.01 (m, 1H). ³¹P{¹H} NMR (CDCl₃) δ : 5.6 (s), ¹ J_{P-Pt} = 3680 Hz. MS (MALDI-TOF) *m/z*: 766 (MW-Cl).

$Pt(PT_{2})_{2}Cl_{2}$ (5)

Yield 73%. Anal. calcd. for $C_{40}H_{30}Cl_2P_2PtS_4$: C 49.69, H 3.13; found: C 49.72, H 3.39. ¹H NMR (CDCl₃) δ : 7.58–7.53 (m, 4H), 7.43–7.40 (dd, J = 7.7, 3.8 Hz, 1H), 7.36–7.32 (m, 2H), 7.24–7.19 (m, 6H, includes CHCl₃), 7.07 (dd, J = 3.6, 0.9 Hz, 1H), 7.01 (dd, J = 3.6, 1.1 Hz, 1H), 6.97 (dd, J = 5.1, 3.7 Hz, 1H). ³¹P{¹H} NMR (CDCl₃) δ : 5.1 (s), ¹ $J_{P-Pt} = 3690$ Hz. MS (ESI) m/z: 931 (MW-Cl).

$Pt(PT_3)_2Cl_2$ (6).

Previously reported by Gray and co-workers (29). Yield 81%. Anal. calcd. for $C_{48}H_{34}Cl_2P_2PtS_6$: C 50.97, H 3.03; found: C 50.61, H 3.27. ¹H NMR (CD₂Cl₂) δ : 7.68–7.57 (m, 8H), 7.51–7.38 (m, 6H), 7.32–7.19 (m, 11H), 7.15 (dd, J =

3.51, 1.1 Hz, 2H), 7.07–6.98 (m, 7H). ³¹P{¹H} NMR (CD₂Cl₂) δ : 4.9 (s), ¹*J*_{P-Pt} = 3700 Hz. MS (ESI) *m*/*z*: 1095 (MW-Cl).

X-ray Crystallography

Suitable crystals of **2**, **3**, **5**, and **6** were mounted in oil on a glass fiber, and the data for each compound were collected at 173(1) K. The structures were solved using direct methods (32, 33) and refined using SHELXL-97 (34). All measurements were made on a Bruker X8 APEX diffractometer with graphite monochromated Mo K α radiation. For each of the four structures, one terminal thiophene ring was disordered in two orientations. In each case, the disordered fragments were modeled using the simple restraints (SADI or SAME) found in SHELXL.

The data for 2 were collected to a maximum 2θ value of 55.8°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 10.0 s exposures. Data were collected and integrated using the Bruker SAINT (35) software package and were corrected for absorption effects using the multiscan technique (SADABS) (36). The data were corrected for Lorentz and polarization effects. The material crystallizes with one half-molecule residing on an inversion center. One thiophene ring in the asymmetric unit is disordered and was modeled in two orientations. The atoms of the major disordered fragment were refined anisotropically, while the atoms of the minor fragment (with a relative population of approximately 0.23) were refined isotropically. Restraints were used to ensure the disordered thiophene fragments had reasonable geometries. All other nonhydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined.

The data for **3** were collected to a maximum 2θ value of 55.6°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 10.0 s exposures. Data were collected and integrated using the Bruker SAINT (35) software package and were corrected for absorption effects using the multiscan technique (SADABS) (36). The data were corrected for Lorentz and polarization effects. All nonhydrogen atoms were refined anisotropically, while all hydrogen atoms were included in calculated positions but not refined. The terminal thiophene ring containing S(3) was disordered and modeled in two orientations with relative populations of 0.77 and 0.23 for the major and minor fragments, respectively.

The data for **5** were collected to a maximum 2θ value of 50.2°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 20.0 s exposures. Data were collected and integrated using the Bruker SAINT (35) software package, were corrected for absorption effects using the multiscan technique (SADABS) (36), and were corrected for Lorentz and polarization effects. One thiophene ring is disordered in two orientations. All atoms except the two sulfur fragments and one carbon were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined.

The data for **6** were collected to a maximum 2 θ value of 52.8°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 12.0 s exposures. Data were collected and integrated using the Bruker SAINT (35) software package. Data were corrected for absorption effects using the

Scheme 1.

$$\begin{array}{c} H & \begin{pmatrix} S \\ \end{pmatrix} & PPh_2 \\ n \\ \hline PdCl_2 (1-3) \\ PT \\ n = 1 \\ PT_2 \\ n = 2 \\ PT_3 \\ n = 3 \end{array} \xrightarrow{PdCl_2 (1-3)} \begin{array}{c} Ph_2P & \begin{pmatrix} S \\ \end{pmatrix} & H \\ H \\ DCl_2 \\ Ph_2P \\ \begin{pmatrix} S \\ \end{pmatrix} & H \\ Ph_2P \\ H \\ Ph_2P \\ H \\ n \end{array} \xrightarrow{Ph_2P} \begin{array}{c} H \\ H \\ Ph_2P \\ H \\ Ph_2P \\ H \\ n \end{array} \xrightarrow{Ph_2P} \begin{array}{c} H \\ H \\ Ph_2P \\ H \\ Ph_2P \\ H \\ n \end{array} \xrightarrow{Ph_2P} \begin{array}{c} H \\ H \\ Ph_2P \\ H \\ Ph_2P \\ H \\ n \end{array} \xrightarrow{Ph_2P} \begin{array}{c} H \\ H \\ Ph_2P \\ H \\ Ph_2P \\ H \\ Ph_2P \\ H \\ n \end{array} \xrightarrow{Ph_2P} \begin{array}{c} H \\ Ph_2P \\ \\ Ph_2P$$

multiscan technique (SADABS) (36). The data were corrected for Lorentz and polarization effects. All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The thiophene ring containing S (6) was disordered and modeled in two orientations with the populations of the major and minor fragments refined to an approximate 2:1 ratio.

Results and discussion

Synthesis of complexes

The palladium complexes 1-3 were synthesized by one of two methods. The ligand and PdCl₂ were either stirred together in a mixture of CH₂Cl₂ and CH₃CN, or PdCl₂ was dissolved in dilute HCl and subsequently added dropwise to a solution of the ligand in an appropriate solvent (Scheme 1). The crude products were crystallized in CH₂Cl₂-hexanes to yield analytically pure materials in reasonable yields. Complex 1 has been reported previously (37, 38), and the synthesis and structure of 3 was previously communicated by our group (39). Palladium bis(phosphine) complexes of this type are known to exhibit cis-trans equilibria in solution (20), which can be observed by 31 P NMR spectroscopy. The ³¹P NMR signals for the trans complexes are generally found at a lower chemical shift than those of the cis isomer (40–45). The 31 P NMR spectra of 1–3 in CD₂Cl₂, CDCl₃, and DMSO indicate that although both cis and trans isomers exist in solution, the trans isomer predominates in these solvents (as determined by integration of ³¹P NMR spectra).

As a single species is desirable for solution characterization, we also chose to synthesize the more inert Pt (16, 46) analogs **4–6**. These were prepared by stirring together a solution of K₂PtCl₄ in H₂O and the appropriate ligand dissolved in CH₂Cl₂. The progress of the reaction was monitored by the disappearance of the dark red color of [PtCl₄]⁻ in the water layer. The crude product obtained was either crystallized in CH₂Cl₂-hexanes or dried under vacuum. Complex **4** has been previously synthesized (37, 38, 47), and the synthesis of **6** was reported by Gray and coworkers (29).

The ¹⁹⁵Pt satellites in the ³¹P NMR spectra of **4–6** may be used to determine the geometry at the metal (18, 48). Complexes **4** (δ 6), **5**(δ 5), and **6** (δ 6) have ¹⁹⁵Pt–³¹P coupling constants of 3681, 3685, and 3700 Hz, respectively, which indicate that these are cis-substituted complexes. A second less intense peak was observed in the ³¹P NMR spectra of analytically pure **6** at δ 11.5. This peak is assigned to the trans isomer, expected to appear downfield to the signal from the cis isomer (48). However, because of the low intensity, no ¹⁹⁵Pt satellites are observed for this signal. It may be

 Table 1. Selected crystal structure data for 2, 3, 5, and 6.

Compound	2	3	5	6
Formula	$C_{40}H_{30}Cl_2P_2S_4Pd$	$C_{48}H_{34}P_2S_6Cl_2Pd$	$C_{40}H_{30}P_2S_4Cl_2Pt$	$C_{48}H_{34}S_6P_2PtCl_2$
Colour, habit	Yellow, plate	Orange, rod	Colorless, prism	Yellow-orange, plate
Dimension (mm)	$0.15 \times 0.05 \times 0.02$	$0.25 \times 0.10 \times 0.10$	$0.25 \times 0.20 \times 0.08$	$0.25 \times 0.25 \times 0.10$
T (K)	173	173	173	173
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (#14)	$P2_1/n$ (#14)	$P2_1/c$ (#14)	$P2_1/n$ (#14)
a (Å)	9.489(1)	11.8648(8)	14.7543(5)	11.749(1)
b (Å)	17.637(2)	20.875(1)	14.7758(2)	29.282(2)
<i>c</i> (Å)	11.2772(9)	18.270(1)	17.5571(6)	12.609(1)
α (°)	90.0	90.0	90.0	90
β (°)	100.667(4)	98.054(4)	107.868(1)	93.704(3)
γ (°)	90.0	90.0	90.0	90
V (Å ³)	1854.7(3)	4480.4(4)	3642.9(2)	4328.9(6)
Ζ	2	4	4	4
$D_{\text{calc}} \text{ (g cm}^{-3})$	1.572	1.545	1.763	1.735
Unique data	4056	10 054	6425	8887
μ (Mo K α) (cm ⁻¹)	9.86	9.20	43.46	37.65
$R(F)^a \ (I > 2\sigma(I))$	0.098	0.033	0.064	0.041
$R_w(F^2)^b$ (all data)	0.093	0.074	0.078	0.094

 ${}^{a}R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|$ ${}^{b}R_{w} = (\Sigma (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2})^{1/2}$

that the increased steric bulk of the terthienyl group results in the formation of some trans isomer.

Molecular solid-state structures

Four of the complexes have been characterized by single crystal X-ray diffraction and selected data is shown in Table $1.^2$ Complex **3** was reported in a preliminary communication; however, comparisons are included here. The molecular structures of the four complexes are shown in Fig. 1.

All four complexes 2, 3, 5, and 6 are close to a square planar geometry at the metal center. The largest distortion is observed in 5 where one of the Cl-Pt-P angles is 170.85(5)°. In the two Pd complexes the ligands are arranged in trans geometry, whereas the Pt complexes both exhibit cis geometry at the metal. The metal-Cl, metal-P, and P-C bond lengths are similar to those observed for other complexes of this type. The bond lengths in the thiophene rings range from 1.666(8) to 1.752(7) Å for the S-C bonds and from 1.332(8) to 1.519(10) Å for the C-C bonds. The arrangement and coplanarity of adjacent thiophene rings can be assessed by the S-C-C-S torsion angle. A syn coplanar arrangement is indicated by an S-C-C-S angle of 0°, while an anti coplanar arrangment gives an angle of 180°. Unsubstituted thiophene oligomers typically crystallize in a nearly completely anti coplanar arrangement (5). In all the structures here, adjacent thiophene rings are not completely coplanar (S–C–C–S angle is between $7.6(7)^{\circ}$ and $175.40(14)^{\circ}$), and both syn and anti arrangements are found, sometimes Fig. 1. Molecular structures of complexes (a) 2, (b) 3, (c) 5, and (d) 6.



within the same molecule. Table 2 summarizes these angles. The largest deviation from coplanarity between adjacent rings is found in **6** where rings containing S2 and S3 have an interannular angle of approximately 40° .

²Supplementary data for this article are available on the journal Web site (http://canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 5158. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 252088, 626550, 626551, and 626552 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via http://www.ccdc.cam.ac.uk/conts/retrieving.html (Or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

Complex	Bonds	Torsion angle (°)
2	S1C4C5S2	10(2)
3	S1-C4-C5-S2	24.4(3)
3	S2-C8-C9-S3	162.21(16)
3	S4-C28-C29-S5	169.15(14)
3	S5-C32-C33-S6	175.40(14)
5	S1-C4-C5-S2	14.1(8)
5	S3-C24-C25-S4	153.8(4)
6	S1-C4-C5-S2	22.9(7)
6	S2-C8-C9-S3	140.4(4)
6	S4-C28-C29-S5	7.6(7)
6	S5-C32-C33-S6	8.3(8)

Table 2. S–C–C–S torsion angles for complexes 2, 3, 5, and 6.

Solid-state packing of Pd complexes

Complex 2 crystallizes in the $P2_1/n$ point group. The bithienyl groups are arranged on opposite sides of the plane passing through the Pd, P, and Cl atoms (Fig. 2*a*). The bithiophene groups are arranged in interlocking stacks with adjacent bithienyl groups twisted relative to one another by approximately 90°. When the structure is examined looking down the *c* axis (Fig. 2*b*), it is apparent that the phenyl groups form a tube surrounding the bithienyl stacks, separating the stacks from each other. No π -stacking of thiophene rings is observed in this structure. Short S–S interactions are believed to be important in facilitating charge-transfer in the oligothiophenes (5), however here the shortest intermolecular S–S distance is ~5.6 Å, precluding any interactions between sulfur atoms.

Complex 3 was previously reported but the solid-state packing is discussed here for comparative purposes. This complex crystallizes in the $P2_1/n$ point group. In contrast to 2, the terthienyl groups are oriented on the same side of the metal plane in this case. In the crystal lattice, the arrangement of the terthienyl groups may be examined by considering the crystallographically distinct terthienyl groups A and B (Fig. 3). Pairs of terthienyl groups A are arranged with interplanar distances, for the inner thiophene rings of the terthienyl groups, within the range of π -stacking (3.65 Å) (13, 49). The π orbital overlap between aromatic groups is greatest if they are arranged in a stack perpendicular to the molecular plane. The two A groups are slightly slipped relative to one another, with the slip greater along the short axis of the groups. The degree of slip along the long and short axis may be quantified via pitch and roll angles, as discussed for organic conjugated oligomers by Curtis et al. (13). The interactions between the other pair of coplanar terthienyl groups (B and B) are much weaker, since these groups are slipped much more substantially (large roll angle) relative to each other despite having little slip along the long axis (small pitch angle). Pairs of groups A and B are arranged face-to-edge, similar to the motif found in herringbone stacks of organic oligomers (13). The shortest S-S distance in the lattice is 4.13 Å, again too long for any significant S-S interactions in this structure (5).

Solid-state packing of Pt complexes

Complex 5 crystallizes in the $P2_1/c$ point group. The structure shows some similarities to that of the Pd terthienyl

Fig. 2. Packing diagrams of 2 showing (a) the arrangement of bithienyl and phenyl groups with the hydrogen atoms omitted and (b) looking down the c axis, with the hydrogen atoms omitted.



Fig. 3. Packing diagram for **3**, viewed down the long molecular axis of the terthienyl groups. Phenyl groups and hydrogen atoms are omitted for clarity.



complex 3. The bithienyl groups in 5 are also arranged on the same side of the plane containing the metal, and weak intermolecular π -stacking (3.76 Å) between the outer thienyl

Fig. 4. Packing diagram of **5** viewed (*a*) down the long molecular axis of the bithienyl groups and (*b*) down the short molecular axis of bithienyl groups **A**. Phenyl groups and hydrogen atoms are omitted for clarity.



rings in group **B** on adjacent molecules is observed (Fig. 4*a*). However, these groups show substantial slip along the long molecular axis (large pitch angle) relative to what is observed in **3** (Fig. 4*b*). The **A** groups are rather far apart in the structure and do not interact. Some intramolecular π -stacking of phenyl groups is observed (not shown), with a plane-to-plane distance between the centroids of the rings of 3.63 Å.

Complex 6 crystallizes in the $P2_1/n$ point group. The terthienyl groups (A) in this structure are arranged in an approximately coplanar fashion to each other with an intermolecular plane-to-plane distance (between the centroids of the rings) of 3.45 Å (Fig. 5). The rings are slightly slipped along both the long and short molecular axis. The other terthienyl groups (B) are arranged so that the edges of the pair of A groups point towards the plane of B with the A and B groups twisted 90° relative to each other. Thus in Fig. 5 the view is down the long axes of the two A groups, with the long axis of the B groups perpendicular to these. Intramolecular π -stacking is also observed between thienyl and phenyl rings (Fig. 6), with a plane-to-plane distance between the centroids of the rings of 3.52 Å.

Absorption spectra

The solution and solid-state absorption spectra of complexes 1-6 are shown in Figs. 7 and 8 respectively, and the data is summarized in Table 3. Although both cis and trans isomers are present in solutions of the Pd complexes 1-3, Fig. 5. Packing diagram of 6. Phenyl groups and hydrogen atoms are omitted for clarity.



Fig. 6. Intramolecular stacking between phenyl ring and inner thiophene ring in group B of 6. Hydrogen atoms are omitted for clarity.



Fig. 7. Solution absorption spectra of palladium and platinum complexes 1–6.



Table 3. Solution and solid-state absorption data for 1-6.

Complex	λ_{max} (nm), ϵ_{max} (mol/L cm)^{-1}	λ_{max} (nm) (solid state)
1	267 (sh), 1.4×10^4 ; 296 (sh), 5.7×10^3 ; 352, 1.9×10^4	269 (sh), 355
2	264 (sh), 1.8×10^4 ; 322, 3.7×10^4 ; 374 (sh), 2.3×10^4	328, 384 (sh)
3	264 (sh), 2.2×10^4 ; 372, 5.5×10^4 ; 415 (sh), 3.9×10^4	380, 428 (sh)
4	269 (sh), 1.6×10^4 ; 277 (sh), 1.2×10^4	250 (sh)
5	270 (sh), 1.7×10^4 ; 277 (sh), 1.5×10^4 ; 331, 3.6×10^4	250 (sh), 340, 364 (sh)
6	269 (sh), 2.1×10^4 ; 277 (sh), 1.6×10^4 ; 377, 5.8×10^4	270 (sh), 396

Fig. 8. Solid-state absorption spectra of palladium complexes 1-6.



the amount of cis is low in CH₂Cl₂ (ca. 5% as determined by integration of the ³¹P NMR spectrum) and should not significantly affect the spectra. In the solution spectrum of 1, there are shoulders between 250 and 300 nm and a distinct peak at 352 nm. The higher energy bands are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the ligands and are not substantially shifted from the spectra of the uncoordinated PT (31). The band at 352 nm is not seen in the spectra of PT or in the analogous gold (26) or platinum (4) complexes. A band at comparable energy and molar absorptivity is seen in the spectra of other dichlorobis(phosphine) palladium complexes (40, 50-55) and is usually assigned to a LMCT transition (Cl \rightarrow Pd). The energy of charge transfer bands typically change with the polarity of the solvent (56); however, for 1 no significant shift was observed for this band when comparing the spectra in toluene, CH₂Cl₂, and CH₃CN (Fig. 9). In the solid state the band does shift slightly (3 nm).

Two overlapping bands can be seen in both the solution (322 nm and 374 nm) and solid-state (328 and 384 nm) absorption spectra of **2**. Presumably, one of these peaks is due to a $\pi \rightarrow \pi^*$ transition in the bithienyl group and the other to a Cl \rightarrow Pd charge transfer band, similar to that seen in the spectrum of **1**. The higher energy band is assigned as the $\pi \rightarrow \pi^*$ transition, as it is very similar in energy to PT₂ ($\lambda_{max} = 333$ nm) (31). The Pd center appears to have little effect on the absorbance of the thiophene group. The lower energy band is assigned to the LMCT transition, which is shifted by 22 nm when compared with the spectrum of **1**. This indicates that the phosphinothiophene ligand has some influence on the LMCT transition. Although the shift is sur-

Fig. 9. Solution absorption spectra of palladium complexes 1, 2, and 3 in CH_3CN (dotted line), CH_2Cl_2 (broken line), and toluene (solid line).



prisingly large, it is known that there is a significant contribution from triphenylphosphine to the LMCT band of *trans*dichlorobis(triphenylphosphine) palladium (II), as determined by resonance Raman spectroscopy (51). When the solution spectra for **2** taken in toluene, CH_2Cl_2 , and CH_3CN are compared, (Fig. 9) a shift in energy and a change in the intensity of the lower energy band are observed.

The solution spectrum of 3 consists of a broad band at 372 nm with a shoulder at 415 nm. The peak is assigned to a terthiophene-based $\pi \rightarrow \pi^*$ transition. As in the spectrum of 2, it is very similar in energy to the ligand ($\lambda_{max} = 374$ nm), indicating little influence of the Pd center on the conjugated moiety. This has also been noted by Gray and co-workers (29). The solid-state spectrum of $\mathbf{3}$ appears much the same as the solution spectrum, but the peak broadens and shifts to lower energy (380 and 428 nm). These effects may be due to the π -stacking of the terthienyl groups observed in the crystal structure or to the increased planarity of the terthienyl groups in the solid state (57–60). As was seen in the β -substituted phosphinothiophene palladium(II) complexes previously reported (24), no distinct LMCT band is observed here. It is likely that this band overlaps with the terthienyl $\pi \rightarrow \pi^*$ transition, which would also indicate some phosphinothiophene character in the LMCT. There appears to be a small decrease in the energy of the band, as the polarity of the solvent is increased and the shoulder at 415 nm becomes more prominent (Fig. 9). This may be due to conformational effects or, if the LMCT overlaps with the terthienyl $\pi \rightarrow \pi^*$

transition, it may be solvatochromism of the LMCT transition.

The spectra of platinum complexes **4–6** are dominated by the $\pi \rightarrow \pi^*$ transitions of the oligothiophene moieties. The spectra of these complexes in solution and in the solid state are very similar to those of the corresponding ligands, indicating little electronic effect of the metal center on the thienyl moiety. The shoulders in the spectra of **5** and **6** have been assigned to conformational effects (57, 60).

Conclusions

The series of palladium (II) and platinum (II) phosphinothiophene complexes reported here show interesting variation in their solid-state crystal structures. Although both cis and trans species are observed in the ³¹P NMR spectra of the palladium complexes 1–3, the isolated crystals of both 2 and 3 exhibit trans geometry exclusively. The platinum complexes 4–5 exist in solution only as the cis isomer, as evidenced by their respective ³¹P-¹⁹⁵Pt coupling constants, while 6 appears to have a small amount of the trans isomer present. Only cis isomers are seen in the solid state.

We have focused on the intermolecular interactions between the oligothiophene groups and have found that in contrast to most organic oligothiophenes that pack in a herringbone fashion (5), these metal complexes adopt a variety of structures in the solid state depending on both the metal and the oligothiophene ligand. Interestingly, we find similarities in the structures of **3** and **5**, both of which pack with the oligothiophene groups interlocked and on the same side of the metal plane. The overlap between the terthienyl groups is greater in **3** and it is tempting to speculate that if the bithienyl groups in **5** were extended by one ring, the overlap would improve to give a structure similar to **3**. However, this is not observed and the Pt terthienyl complex **6** exhibits quite a different structure, although also one in which π -stacking between terthienyl groups is observed.

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