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Preparation and Structural Characterization of a Platinum Catecholate Complex Containing Two 3-Ethynylthiophene Groups

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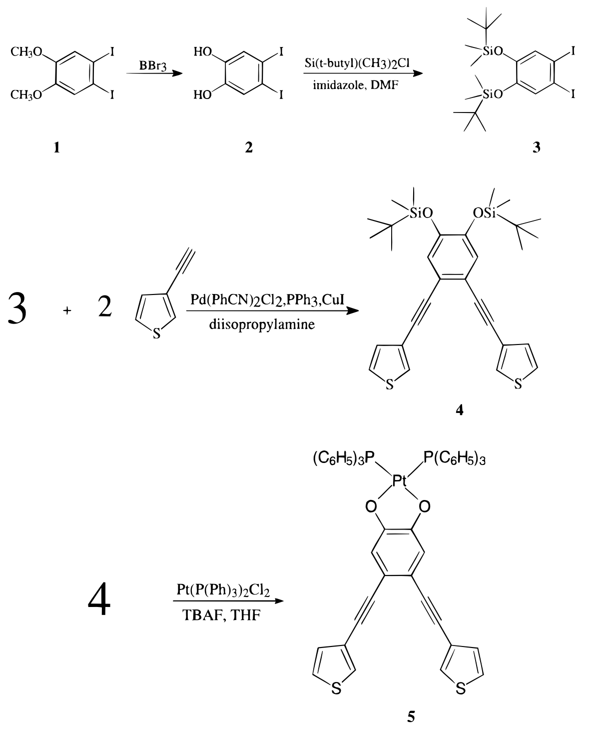
*Summary: The reaction of 1,2-bis(tert-butyldimethylsiloxy)-3,4-bis(3-ethynylthiophene-yl)benzene (**4**) with Pt-(P(Ph)$_3$)$_2$Cl$_2$ and tetrabutylammonium fluoride produces a novel platinum catecholate complex.*

The catechol group can coordinate to a variety of transition and main group metals in a wide range of oxidation states.[1] Catechols and metal catecholates have been intensively studied for their unique structural,[2] electronic,[3] magnetic,[4] and catalytic activity.[5] The incorporation of metal catecholates into a conducting polymer matrix provides the opportunity for the construction of modified electrodes that may have interesting electrocatalytic behavior. In this paper, the synthesis, characterization, and electrochemical properties of a platinum catecholate complex containing two 3-ethynylthiophene groups are described.

The synthesis of the platinum catecholate complex **5** is illustrated in Scheme 1. The synthesis of **1** was accomplished by the procedure developed by Kajigaeshi and co-workers.[6] Treatment of **1** with BBr$_3$ in acetic acid produced the diiodocatechol **2** (94% yield). To prevent the catechol group from complexing the palladium catalyst used in the alkyne coupling reaction, the catechol was protected by reacting **2** with *tert*-butyldimethylsilyl chloride to form **3** (69% yield). The *tert*-butyldimethylsilyl group was chosen due to its reported stability to a variety of reaction conditions and its facile removal by fluoride ion.[7] Reaction of **3** with 2 equiv of 3-ethynylthiophene[8] in the presence of a palladium catalyst produced the disubstituted product **4** (62% yield).

Scheme 1



The formation of metal catecholates normally proceeds by treating a catechol with strong base (e.g., KOH) in the presence of a metal dichloride. However, the platinum catecholate complex **5** formed in high yield (94%) by combining **4** with a THF solution of tetra-*n*-butylammonium fluoride and Pt(PPh$_3$)$_2$Cl$_2$. Thus, it was unnecessary to deprotect **4** to form the catechol before reaction with the metal dichloride. The infrared spectrum of **5** showed an intense absorption at 1284 cm^{-1}, indicating a C−O stretching vibration, which is indicative of a metal catecholate structure. The thermal stability of **5** was examined with thermal gravimetric analysis (TGA). A 5% weight loss was observed for **5** at 307 °C in N$_2$.

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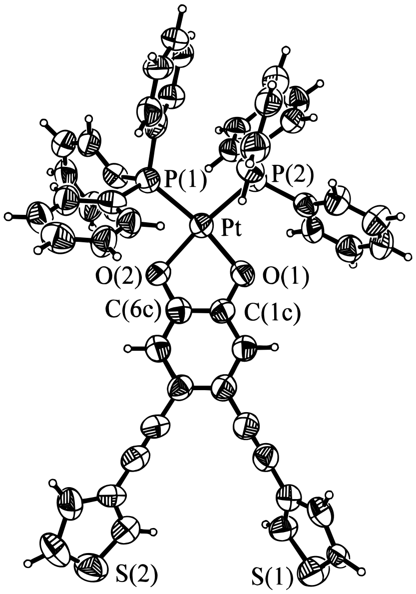

Figure 1. Thermal ellipsoid of **5** drawn at 50% probability. Selected bond distances (Å) and angles (deg): Pt−O(1), 2.028 (8); Pt−O(2), 2.052(9); C(6c)−O(2), 1.333(16); C(1c)−O(1), 1.348(15); P(1)−Pt−O(2), 87.9(3); P(2)−Pt−O(1), 90.5(3); P(2)−Pt−P(1), 98.6(1).

Crystals of **5** were grown by slow concentration of **5** in methylene chloride. The crystal structure of **5**, showing the thermal ellipsoids, is shown in Figure 1. A molecule of methylene chloride is also present in the asymmetric unit. Crystals of **5** were air stable. However, the crystals slowly lost solvent over time, which degraded the quality of the crystals. The geometry of the ligands around the platinum atom is square planar. The thiophene ring containing sulfur atom S1 is twisted (57.7°), and the thiophene ring containing sulfur atom S2 is twisted (29.6°) out of the plane defined by the platinum catecholate structure. The Pt−O bond distances of 2.028(8) and 2.052(9) Å and the C−O bond distances of 1.348(15) and 1.333(16) Å are typical for metal catecholate complexes.

Many thiophene systems can be anodically electropolymerized to form electrically conducting polymers with conductivities as high as 10^2 (Ω·cm)$^{-1}$. Substituents in the β position on the thiophene ring have a strong influence on both the conductivity and the extent of polymerization of the thiophene monomers. Roncali and co-workers found that when a bulky substituent such as an isopropyl group is attached to the β position on the thiophene ring polymerization can be prevented. By adding two (CH_2) units as spacers between the thiophene and isopropyl groups, polymerization occurred.[9]

The cyclic voltammetry of **5** in 0.1 M TBAP−CH_2Cl_2 is shown in Figure 2. Two one-electron reversible (ΔE = 82 mV, $i_a/i_c = 1$) oxidation waves at 0.266 and 0.870 V [vs Ag/Ag$^+$ (CH_3CN)] were observed. Attempts at electropolymerization of **5** failed in CH_2Cl_2 and in a mixture of 1:1 CH_2Cl_2−nitrobenzene. This may be due to steric effects around the thiophene rings. Future work will concentrate on synthesizing new metal catecholate complexes analogous to **5** and examining the electrochemical and optical properties of these new systems.

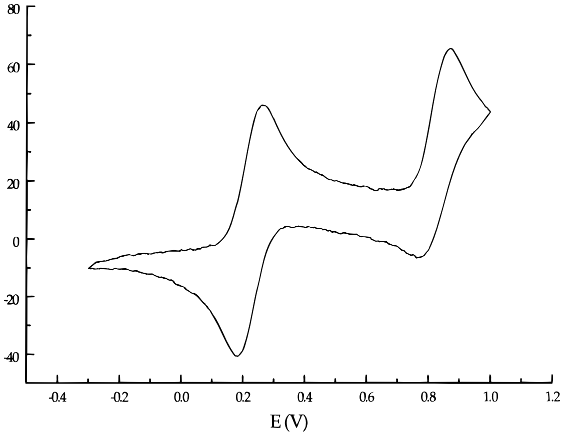

Figure 2. Cyclic voltammogram of **5** (1 mM) in 0.1 M TBAP−CH_2Cl_2. Scan rate was 100 mV s^{-1}.

Experimental Section

Materials. All manipulations were performed using standard inert atmosphere techniques[10] unless otherwise specified. Literature procedures were used to prepare 4,5-diiodoveratrole,[6] 3-ethynylthiophene,[8] and dichlorobis(benzonitrile)palladium(II).[11] Diisopropylamine was distilled from BaO, CH_2Cl_2 from CaH_2, and tetrahydrofuran (THF) from sodium−benzophenone ketyl. Tetrabutylammonium perchlorate (TBAP, Kodak) was recrystallized twice from ethyl acetate−pentane and dried for 48 h at 100 °C (10^{-3} Torr) before use.

Apparatus. NMR spectra were recorded on either a Bruker AC200 or AM300 spectrometer. X-ray diffraction data were collected on a Syntex P2$_1$ single-crystal diffractometer. IR data were collected on a Nicolet 510P FT-IR spectrometer. An EG&G Princeton Applied Research Model 273A potentiostat/galvanostat controlled by the EG&G Princeton Applied Research Model 270 software package was used to monitor the electrochemical measurements. Mass spectra were recorded on a Kratos MS25RFA mass spectrometer. Thermogravimetric analysis was collected on a Perkin-Elmer TGS2-II thermal gravimetric analyzer.

Synthesis of 4,5-Diiodocatechol (2). 4,5-Diiodoveratrole (10.074 g, 26 mmol) was dissolved in $CHCl_3$ and cooled to −60 °C. BBr_3 (9.72 mL, 103 mmol) was slowly added via syringe. After warming to room temperature the mixture was allowed to stir for 6 h and was then poured into ice water. The product was extracted with ether and dried with $MgSO_4$. Evaporation of the solvent produced 8.75 g (94% yield) of **2** as a white powder. ^1H NMR (acetone-d_6, 200 MHz): δ 8.41, 7.35. ^{13}C NMR (acetone-d_6, 300 MHz): δ 147.47, 126.50, 94.50. FT-IR (KBr): 3245(s), 3048(m), 1595(m), 1477(s), 1408(s), 1307(m), 1224(s), 870(s), 701(s) cm^{-1}. HRMS calcd 361.8300, obsd 361.8294.

Synthesis of 1,2-Bis(*tert*-butyldimethylsilyloxy)-4,5-diiodobenzene (3). A solution of imidazole (8.411 g, 124 mmol) and *tert*-butyldimethylsilyl chloride (9.32 g, 62 mmol) dissolved in 50 mL of DMF was added via cannula to 11.193 g (31 mmol) of 4,5-diidocatechol dissolved in 100 mL of DMF. After stirring for 48 h the mixture was poured into water, extracted with ether, and dried with $MgSO_4$. Evaporation of the solvent followed by column chromatography on silica gel eluting with hexane produced 12.54 g (69% yield) of **3** as a white powder. ^1H NMR (acetone-d_6, 200 MHz): δ 7.38, 0.99, 0.23. ^{13}C NMR (acetone-d_6, 300 MHz): δ 148.86, 132.15, 97.14, 26.29, 19.12, −3.94. FT-IR (neat): 2955(s), 2930(s), 2858(s), 1564(w), 1542(m), 1472(s), 1390(m), 1338(s), 1292(s), 1255(s), 1005(w), 932(s) cm^{-1}. HRMS calcd 590.0030, obsd 590.0027.

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Table 1. Crystallographic Data for 5

formula	$C_{55}H_{40}Cl_2O_2P_2PtS_2$
formula wt	1124.9
space group	$P2_1/c$
crystal system	monoclinic
cell constants	
a (Å)	18.556(4)
b (Å)	13.562(3)
c (Å)	20.524(4)
β (deg)	110.69(3)
V (Å^3)	4832(2)
Z	4
D (calcd) (g cm^{-3})	1.546
absorp coeff (mm^{-1})	3.221
F(000)	2240.00
temp (K)	133
2θ range (deg)	3.5−45.0
scan type	ω
scan speed (deg/min in ω)	8.72
scan range (ω) (deg)	1.80
no. of reflns collcd	4976
no. of indep reflns	3984 (R_{int} = 2.74%)
refinement method	full-matrix least-squares
no. of obsd reflns	3362 ($F > 4.0\sigma(F)$)
no. of params refined	578
R(*F*) (%)	5.86
$R_w(F)$ (%)	7.33
GOF	1.14

Synthesis of 1,2-Bis(*tert*-butyldimethylsilyloxy)-4,5-bis(3-ethynylthiophene-yl)benzene (4). Diisopropylamine (150 mL) was added to 0.4547 g (1.2 mmol) of $Pd(Cl)_2(PhCN)_2$, 0.6224 g (2.4 mmol) of PPh_3, 0.1142 g (0.6 mmol) of CuI, and 7.0 g (12 mmol) of **3**. To this solution was added 2.8 g (26 mmol) of 3-ethynylthiophene slowly via syringe. The mixture was heated to 60 °C for 1 h and then cooled to room temperature and stirred for 11 h. The mixture was filtered and the solvent was evaporated. Chromatography on silica gel eluting with a 1:9 CH_2Cl_2−hexane mixture produced 4.0465 g (62% yield) of **4** as a yellow powder. ^1H NMR (acetone-d_6, 300 MHz): δ 7.70 (dd, 1 H), 7.53 (dd, 1 H), 7.21 (dd, 1 H), 7.05 (s, 1 H), 1.02 (s, 9 H), 0.28 (s, 3 H). ^{13}C NMR (acetone-d_6, 300 MHz): 148.42, 130.57, 129.63, 127.00, 123.29, 120.40, 88.22, 26.22, 26.37, 19.15, −3.74. FT-IR (KBr): 3106(w), 2954(s), 2930(s), 2858(s), 1594(w), 1529(s), 1494(s), 1492(s), 1362(w), 1331(s), 1255(s), 932(s), 838(s), 781(s) cm^{-1}. HRMS calcd 550.1852, obsd 550.1840.

Synthesis of [4,5-Bis(3-ethynylthiophene-yl)-1,2-benzenediolato(2−)-*O*,*O*′]bis(triphenylphosphine)platinum(II) (5). THF (20 mL) was added to a flask containing 1.001 g (1.8 mmol) of **4** and 1.437 g (1.8 mmol) of $Pt(P(Ph)_3)_2Cl_2$. A sample of 7.2 mL of a 1 M tetrabutylammonium fluoride−THF solution was added via syringe. The mixture was allowed to stir for 48 h. After filtration the solvent was removed and the oily residue was washed with hexane. The compound was recrystallized from CH_2Cl_2 to produce 1.758 g (94% yield) of **5** as yellow crystals. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.58−7.06 (m), 6.54 (s). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 164.43, 134.77 (dd), 130.79, 130.11, 128.76 (dd), 127.94 (dd), 126.43, 124.54, 124.08, 117.93, 113.46, 90.63, 84.16. FT-IR (KBr): 2203(w), 1483(m), 1437(s), 1284(s), 1231(s), 1098(s), 781(m) cm^{-1}. Anal. Calcd for $C_{55}H_{40}O_2P_2PtS_2Cl_2$: C, 58.72; H, 3.58; S, 5.70. Found: C, 59.16; H, 4.00; S, 5.70.

Electrochemical Measurements. A three-compartment electrochemical cell (~25 mL capacity) was used for electrochemical measurements. A coiled Pt wire was used as a counter electrode and separated from the working electrode compartment by a glass frit. The reference electrode was Ag/Ag$^+$ (CH_3CN, 0.1 M TBAP). The working electrode was a platinum disk (diameter = 5 mm). The concentration of **5** was 1.0×10^{-3} M in 0.10 M TBAP−CH_2Cl_2.

Table 2. Atomic Coordinates (×10^5) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^4)

	x	*y*	*z*	*U*(eq)[a]
Pt(1)	20807(3)	9618(4)	7994(3)	630(3)
P(2)	18558(20)	6912(27)	−3323(18)	666(15)
P(1)	18123(21)	25779(26)	7434(17)	665(14)
O(2)	23500(50)	10499(61)	18575(45)	686(38)
C(5B)	18993(83)	−22866(116)	−4173(72)	803(69)
O(1)	24250(48)	−4567(63)	10237(44)	681(38)
C(1D)	8411(70)	6961(87)	−9074(65)	583(55)
C(2I)	42223(73)	−10296(107)	52647(74)	703(66)
C(3)	39736(85)	−9300(100)	45314(101)	807(81)
C(2D)	6547(85)	4222(95)	−15897(72)	741(68)
C(2H)	47971(82)	−39381(102)	35427(71)	742(65)
C(5A)	22215(85)	43799(109)	−6851(74)	785(69)
C(5D)	−5006(84)	7916(98)	−10702(79)	731(69)
C(1A)	16986(70)	32929(85)	−394(67)	586(57)
C(6B)	1771(79)	−13208(113)	−2932(66)	711(64)
C(2A)	10315(73)	32213(96)	−6114(68)	659(58)
C(2)	39458(89)	−23829(125)	30134(75)	736(68)
C(1I)	42642(88)	−18993(130)	56104(82)	976(78)
C(6A)	22941(88)	38662(103)	−740(80)	776(68)
C(3C)	35046(74)	−15415(107)	27267(73)	709(65)
C(6E)	7302(80)	22282(115)	13561(75)	812(66)
C(3A)	9512(86)	37239(105)	−12243(77)	752(67)
C(4C)	34203(73)	−7900(103)	31521(74)	678(65)
C(1H)	46397(75)	−45476(108)	40175(72)	775(62)
C(4)	37378(78)	−8521(98)	39107(89)	728(70)
C(2E)	5670(85)	37679(104)	7619(75)	761(66)
C(4B)	24268(83)	−24697(109)	−7379(75)	798(67)
C(3I)	44660(97)	−2630(124)	57513(82)	1020(81)
C(2B)	26387(81)	−7682(107)	−7942(74)	736(67)
C(6D)	2758(86)	8665(86)	−6264(72)	703(65)
C(1E)	9523(69)	28727(112)	9520(64)	668(56)
C(1C)	27508(67)	−5696(98)	17191(69)	609(60)
C(4D)	−6863(82)	5477(110)	−17469(82)	791(70)
C(3D)	−1222(82)	3414(106)	−20059(71)	783(66)
C(6C)	26941(70)	2131(111)	21446(71)	665(65)
C(1)	43548(94)	−30578(121)	32372(75)	800(70)
C(1B)	21253(76)	−5629(97)	−4905(62)	626(54)
C(5C)	30215(70)	963(104)	28542(73)	699(63)
C(2C)	31401(72)	−14224(97)	19962(71)	658(60)
C(3B)	28080(80)	−17232(123)	−9207(78)	850(72)
C(4A)	15428(84)	42824(100)	−12644(67)	688(62)
C(3H)	54595(76)	−42910(105)	34116(67)	723(61)
C(2F)	32002(74)	15851(97)	−2541(66)	660(57)
C(1G)	26041(82)	31903(105)	14101(67)	745(66)
C(6F)	21702(78)	18666(88)	−13370(72)	654(60)
C(3F)	36895(84)	21037(117)	−5024(83)	831(70)
C(2G)	24963(91)	39716(107)	18209(82)	801(70)
C(5F)	26944(90)	23582(102)	−15782(78)	777(68)
C(5E)	1125(85)	24549(1109)	15668(81)	824(72)
C(1F)	24317(75)	14644(91)	−6963(67)	627(61)
C(6G)	33495(83)	28844(102)	15447(70)	740(63)
C(5G)	39689(82)	32987(107)	20255(81)	789(66)
C(4G)	38662(100)	40770(134)	23987(87)	940(82)
C(4F)	34310(93)	24835(96)	−11695(83)	757(74)
C(3G)	31087(121)	43925(122)	23052(81)	1001(88)
C(5)	17019(98)	67725(151)	16913(166)	1993(199)
Cl	13095(46)	63465(77)	23209(37)	2015(45)
Cl(1)	10944(37)	65283(45)	8784(33)	1442(32)
C(3E)	−127(98)	40034(113)	9968(85)	884(75)
C(4E)	−2757(90)	33500(122)	13708(78)	859(73)
S(1)	52702(25)	−54664(34)	42833(24)	1010(21)
S(2)	45603(41)	−17690(58)	64545(33)	1090(33)
C(4I)	47290(57)	−6691(85)	65163(45)	1107(50)
C(4H)	57854(58)	−52023(100)	38115(54)	585(50)

[a] Equivalent isotropic *U* is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

X-ray Crystallographic Data for 5. Crystals of **5** were grown by slow concentration of a CH_2Cl_2 solution. A yellow crystal measuring 0.4 × 0.4 × 0.4 was mounted on a glass fiber and aligned on the diffractometer. Final unit cell parameters were determined by least-squares refinement of 25 reflection with 20° < 2θ < 30°. Crystal data, data collection and reduction, and structure refinement details are listed in Table 1. Crystal stability was monitored by measuring three standard reflections every 97 measurements. Data were corrected for Lorentz and polarization factors and reduced to unscaled *F* values. Crystallographic calculations were performed by using the Siemens SHELXTYLPLUS (PC version)[12] program library. The positions of all non-hydrogen atoms were determined by direct methods. Hydrogen atoms were included using a riding model with $d(\mathrm{C-H}) = 0.95$ Å, and the isotropic thermal parameters were fixed at 0.08 Å^2. A disorder model for sulfur atom S2 and carbon atom C4I was used. The final agreement factors for the 3362 data ($|F_o| > 4.0\sigma(|F_o|)$) were $R_f = 5.86$ and $R_{wf} = 7.33$ and GOF = 1.14.

Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, and anisotropic displacement coefficients (17 pages). Ordering information is given on any current masthead page.

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[12] Nicolet Instrument Corp., Madison, WI, 1988.