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Palladium Complexes of 21-Thiaporphyrin: Syntheses and Characterization

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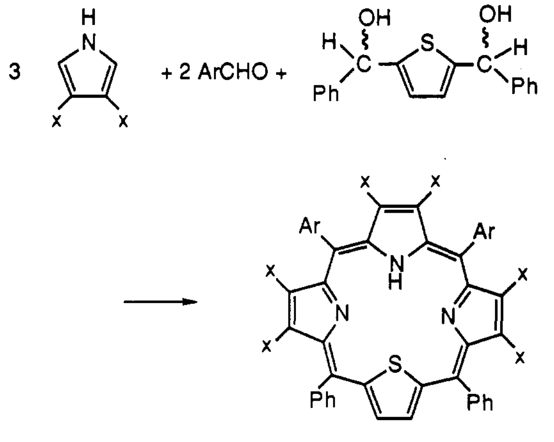
Treatment of tetraphenyl-21-thiaporphyrin (STPPH) with palladium(II) chloride in acetonitrile yields diamagnetic [Pd^{II}(STPP)]Cl. The electronic and ^{1}H NMR spectra are reported. [Pd^{II}(STPP)]Cl undergoes one-electron reduction ($E°_{1/2}$ = −0.28 vs SCE) to give Pd(STPP). The product of the chemical reduction was isolated and characterized. The nature of the reduced species was examined by EPR and NMR spectroscopy. The EPR spectrum displays a rhombic pattern (g_1 = 2.042; g_2 = 2.009; g_3 = 1.962). This asymmetry suggests an electronic structure with a considerable ligand radical anion contribution. The spin density distribution has been established by ^{2}H NMR spectroscopy. The observed pattern of paramagnetic shifts (pyrrole positions −9.9, 7.1 ppm; 10,15 phenyl meta 17.7, ortho −8.2, para −1.2 ppm) is consistent with thiaporphyrin based localization of the unpaired electron. Pd(SDPDTP) crystallizes in the monoclinic space group $P2_1/c$ with a = 15.625(5) Å, b = 16.039(4) Å, c = 15.519(6) Å, and β = 112.47(3)° at 130 K with Z = 4. Refinement of 3104 reflections and 409 parameters yielded R = 0.097. The palladium is four-coordinate with bonds to three pyrrole nitrogen atoms (Pd–N distances 2.085(11), 1.999(15), 2.061(11) Å) and the thiophene sulfur (Pd–S 2.208(5) Å). The palladium atom lies in the plane of the three nitrogen atoms while the thiophene is sharply tilted out of the plane. The thiophene group is bound to palladium through pyramidal sulfur in the usual η^1(S) fashion. The thiophene ring is bent so the dihedral angle between the $C_\alpha SC_\alpha$ and $C_\alpha C_\beta C_\beta C_\alpha$ planes is 15.6°. The structure is compared to those of the related four-, five-, and six-coordinate metallothiaporphyrins.

Introduction

Core modification of porphyrins by introduction of various heteroatoms (O, S, Se) in place of the pyrrole nitrogen atoms allows for the preparation of a series of new heterocycles that have interesting properties in terms of both their aromatic character and their ability to bind metal ions. Reports on the preparation of 21-oxaporphyrin[1] and a series of diheterosubstituted porphyrins (21,23-dithiaporphyrin, 21,23-diselenaporphyrin, 21-selena-23-telluraporphyrin, 21-thia-23-selenaporphyrin, and 21-thia-23-telluraporphyrin)[2] have appeared. The tetraoxaporphyrin and tetrathiaporphyrin dications have been synthesized and their electronic structures discussed in context of the aromatic character of annulenes.[3]

Recently our laboratories reported a reasonable synthesis (eq 1) and characterization of a new macrocyclic ligand, 5,10,15,-20-tetraphenyl-21-thiaporphyrin, in which one of the pyrrole moieties is replaced by thiophene.[4–6] This ligand forms five-coordinate complexes with the first-row transition-metal ions—Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}.[5–10] These all have an anionic axial ligand that completes the metal ion coordination. Tetraphenyl-21-thiaporphyrin also forms six-coordinate complexes with Rh^{III} [11] and Ni^{II}, [9] which have two axial ligands, and four-, five-, and six-coordinate complexes with Ni^{I}.[12,13]



(1)

1 STPPH, Ar = C_6H_5, x = H

STPPH-d_{10}, Ar = C_6D_5, x = H

STPPH-d_6, Ar = C_6H_5, x = D

SDPDTPH, Ar = p-$CH_3C_6H_5$

The incorporation of a thiophene ring into a porphyrin core alters the character of the macrocycle significantly, and the

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coordination properties of this modified porphyrin are of the substantial interest. The presence of the large sulfur atom shrinks the core size of the thiaporphyrin relative to those of other porphyrins. Although thiophene itself is capable of binding metal ions in a variety of ways,[14] the thiophene ring in the thiaporphyrins binds the metal ion in one common way, through a pyramidal sulfur atom in an η^1(S) fashion, in all structurally characterized complexes. As a result, the thiophene ring is sharply bent out of the mean plane of the porphyrin and is usually folded with respect to the thiophene C_α–C_α axis. The relationship between the metal ionic radius and the geometry of metallothiaporphyrins has been reported.[7,11,13]

The replacement of nitrogen by sulfur in the porphyrin core also has a profound effect on the stability of lower oxidation states of metal ions within a macrocyclic framework. The formation of a Ni^I thiaporphyrin complex has been demonstrated by a group of X-ray, EPR, and NMR studies.[12,13] In light of the interesting properties of nickel thiaporphyrins, we have decided to prepare their palladium analogs and to examine properties of these complexes. Here we report the characterization of a palladium(II) complex of thiaporphyrin and its one-electron-reduction product, which could contain Pd(I). Complexes of palladium(I) generally contain short (~2.6 Å) Pd–Pd bonds,[15] but it appeared unlikely that the tetraarylthiaporphyrin ligand could accommodate any Pd–Pd bonding. Consequently the nature of the one-electron reduced complex deserved study.

Results and Discussion

Formation and Characterization of Palladium(II) Complexes. Addition of palladium(II) chloride to STPPH (and its analogs) in acetonitrile results in formation of $[Pd^{II}(STPP)]Cl$ in 90% yield. The presence of acetonitrile is essential for metalation and presumably facilitates the reaction by producing soluble forms of palladium(II). The complex $[Pd^{II}(STPP)]Cl$ is stable as a solid and in solution. It has good solubility in dichloromethane and chloroform and moderate solubility in benzene and toluene. $[Pd^{II}(STPP)](ClO_4)$ was formed by treating $[Pd^{II}(STPP)]Cl$ with silver perchlorate in acetonitrile solution.

The electronic absorption spectrum of $[Pd^{II}(STPP)]Cl$ is shown in trace A of Figure 1 (solid line). A porphyrin-like pattern is clearly present with a strong, but split, Soret-like band (421 and 474 nm (log ϵ 4.53 and 4.69)) and weaker Q bands at lower energies (562 (3.73), 636 (3.67), and 663 nm (log ϵ 3.63)). The spectral pattern resembles those of other thiaporphyrin complexes where generally a split Soret band and three Q bands have been observed.[4,7,8,11] Due to the reduced symmetry of the palladium(II) thiaporphyrin complex, the low-energy portion of the spectrum is more complex than is found for the corresponding porphyrin complex.[16] The electronic spectra of $[Pd^{II}(STPP)]Cl$ in chloroform, dichloromethane, benzene, and toluene solutions are nearly identical. Additionally, the electronic spectra of $[Pd^{II}(STPP)]Cl$ and $[Pd^{II}(STPP)](ClO_4)$ are similar. These similarities suggest that the anion is not coordinated to the palladium and that the anion does not affect the electronic structure of the complex. Potentially coordinating solvents, acetonitrile, methanol, or pyridine, also produce relatively minor shifts in the electronic spectra of these complexes. This is in contrast with observations on the related complex $Ni^{II}(STPP)Cl$, whose electronic absorption spectra show pronounced solvent effects that are associated with the formation of five- and six-coordinate species.[9]

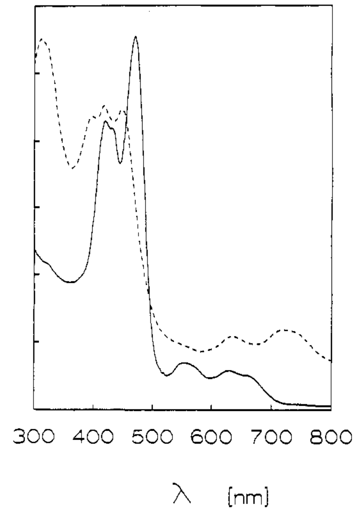

Figure 1. UV/vis absorption spectra of $[Pd^{II}(STPP)]Cl$ (solid line) and Pd(STPP) (dashed line) in chloroform solution. The absorbance scale is arbitrary.

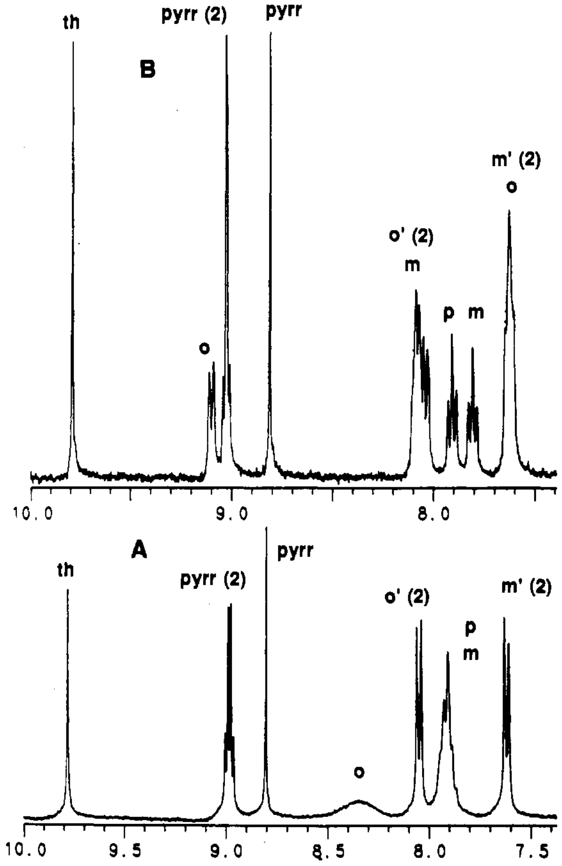

Figure 2. 360-MHz ^1H NMR spectra of $[Pd^{II}(SDPDTP)]Cl$ in chloroform-*d* at (A) 298 and (B) 213 K. Resonance assignments: th, thiophene H; pyrr, pyrrole H; o, m, and p, ortho, meta, and para H of the phenyl rings; o′ and m′, ortho and meta H of the *p*-tolyl rings.

The ^1H NMR spectra of these palladium(II) complexes show features that indicate that rotation of the aryl rings that are closest to the thiophene ring is facile. Relevant data for a chloroform-*d* solution of $[Pd^{II}(SDPDPT)]Cl$ are shown in Figure 2. Trace A shows the spectrum at 298 K, where the broad resonance at 8.35 ppm indicates clearly that a dynamic exchange process is occurring. Upon cooling of the sample to 213 K, the spectrum shown in trace B is obtained. At this temperature, the rotation has slowed so that all resonances are narrow. This spectrum has been fully assigned as shown in Figure 2 through a set of double-resonance experiments. The broad resonance at

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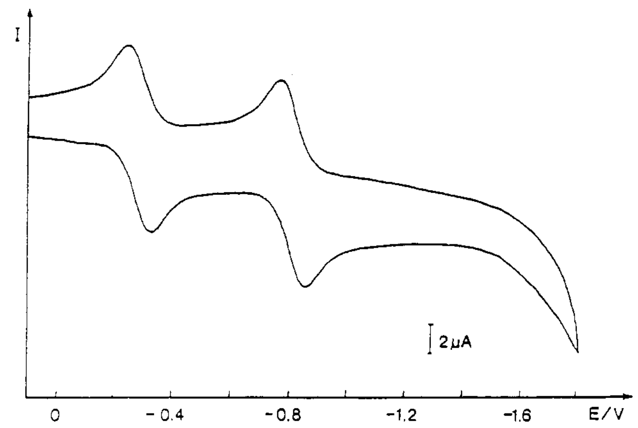

Figure 3. Cyclic voltammogram of $[Pd^{II}(STPP)]Cl$ in 1,2-dichloroethane with 0.10 M tetrabutylammonium perchlorate as supporting electrolyte and a scan rate of 100 mV s^{-1}.

8.35 ppm in trace A has resolved into two remarkably shifted doublets, one at 9.1 ppm and one at 7.6 ppm, which is coincident with two doublets due to the meta protons of the *p*-tolyl group. Additionally, at 213 K the ill-resolved meta resonance that was present at 7.9 ppm in trace A has become resolved into a triplet at 7.8 ppm and a second triplet at 8.1 ppm which overlaps the ortho resonances of the phenyl ring. The relative ease of rotation of the phenyl group in this complex must be a consequence of the tilting of the thiophene ring out of the porphyrin plane. This reduces steric congestion at the periphery of the macrocycle and facilitates rotation of these phenyl groups.

Reduction of $[Pd^{II}(STPP)]Cl$. The cyclic voltammogram of $[Pd^{II}(STPP)]Cl$ in 1,2-dichloroethane (with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte) is shown in Figure 3. The half-wave potentials for the reduction processes are $E^1_{1/2} = -0.28$ V and $E^2_{1/2} = -0.81$ V vs SCE. The reversible nature of the reduction waves suggests that the two complexes, $[Pd(STPP)]^+$ and Pd(STPP), have the same coordination geometry. The first reduction potential for $[Pd^{II}(STPP)]Cl$ is close to the first reduction potentials of $Ni^{II}(STPP)Cl$ and $Cu^{II}(STPP)Cl$, while the half-wave potential for the first reduction of the free base, STPPH, is -1.065 V in 1,2-dichloroethane.[8] This shift in the reduction potential upon coordination of palladium suggests either that the reduction is metal centered or that coordination strongly perturbs the energies of the ligand orbitals. Additionally, $[Pd^{II}(STPP)]Cl$ undergoes a two-electron oxidation at $E_{1/2} = 1.78$ V.

Moderate reducing agents should be sufficient to generate the one-electron-reduction product of $[Pd^{II}(STPP)]Cl$. Reduction with sodium anthracenide, sodium dithionite, sodium sulfite, zinc powder, or sodium thiosulfate produced Pd(STPP), which was isolated as a dark green solid. With sodium anthracenide, the reduction was carried out in homogeneous solution whereas, with the other reducing agents, the reaction was performed under heterogeneous conditions with a variety of solvents (acetonitrile, toluene, pyridine, dichloromethane). Since some of the reducing agents listed above are capable of two-electron reduction of $[Pd^{II}(STPP)]Cl$, the redox titrations were conveniently followed by electronic spectroscopy, and isosbestic points were observed during the first, one-electron reduction. The absorption spectrum of Pd(STPP) is shown in Figure 1. The spectrum is characterized by a split Soret band (λ_{max} 401 nm (log ϵ 4.45) and 454 (4.51)) and two visible bands (638 nm (log ϵ 3.66) and 720 (3.76)). The Soret bands are blue-shifted relative to $[Pd^{II}(STPP)]Cl$, but a red shift of the Q bands is observed. Similarly a blue shift of the Soret bands was observed in the $Ni^{II}(STPP)Cl/Ni^{I}(STPP)$ couple.[12]

The chemical reduction is reversible. Pd(STPP) is reoxidized to $[Pd^{II}(STPP)]^+$ with diiodine or dioxygen. The oxidation with dioxygen is slow in benzene or toluene (1 h) but faster in chlorinated solvents. Pd(STPP) does not react with alkyl chlorides in the absence of dioxygen.

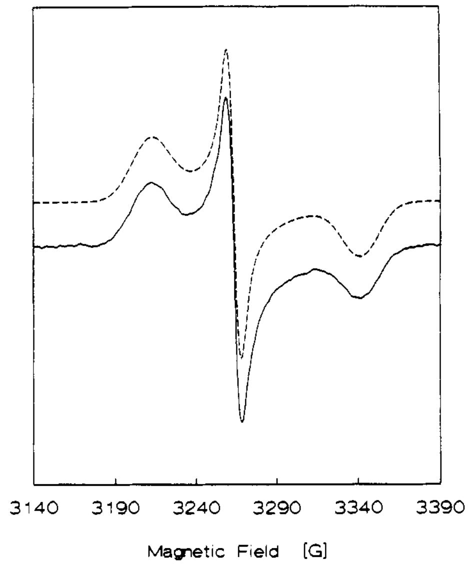

Figure 4. EPR spectrum of Pd(STPP) in dichloromethane (77 K, X-band): solid line, experimental; dashed line, simulated with $g_x = 2.042$, $g_y = 2.009$, $g_z = 1.962$, with line widths of $s_x = 23.5$ G, $s_y = 6.8$ G, $s_z = 22.0$ G, and unresolved hyperfine coupling of about 3.5 G for *x* and *z* components and 1 G for the *y* component due to 8 protons and 8, 9, 0 G, respectively, due to 3 nitrogen nuclei.

Electrochemical measurements for Pd(STPP) produced a voltammogram that is similar to that shown in Figure 3.

The EPR spectrum of Pd(STPP) as a frozen dichloromethane solution at 77 K is shown in Figure 4. A rhombic pattern is observed with $g_1 = 2.042$, $g_2 = 2.009$, and $g_3 = 1.962$. Nearly identical spectra have been obtained from frozen dichloromethane, toluene, and pyridine solutions of the radical. This suggests that, contrary to the situation with $Ni^{I}(STPP)$, there is no coordination of Pd(STPP) by pyridine.

The **g** tensor anisotropy is smaller than that expected for a typical d^9 complex with a single electron in the $d_{x^2-y^2}$ orbital.[17] Although monomeric, d^9 Pd^{I} complexes are rare,[15] it is possible to compare Pd(STPP) to $[Pd^{I}(1,4,8,11\text{-tetramethyl-}1,4,8,11\text{-tetraazacyclotetradecane})]^+$, which has a planar Pd^{I} center coordinated by four tertiary amines.[18] The EPR spectrum of this complex has axial symmetry with $g_{\parallel} = 2.302$ and $g_{\perp} = 2.076$ (values which are not dissimilar from those of the more common planar Cu^{II} complexes). Moreover, hyperfine coupling to ^{105}Pd ($I = {}^5/_2$, 22.2% natural abundance) with $A_{\parallel} = 53$ G and $A_{\perp} = 40$ G is observed. In contrast, no coupling to ^{105}Pd could be observed in the EPR spectrum of Pd(STPP) and the range of *g* values is much smaller. It is also significant to note that the *g* value anisotropy for Ni(STPP) ($g = 2.030, 2.040, 2.109$)[12,13] is larger than that for Pd(STPP). Thus, although the **g** tensor anisotropy for Pd(STPP) is larger than that expected for a pure ligand radical, it must be concluded that the orbital containing the unpaired spin is not the Pd $d_{x^2-y^2}$ orbital and that orbital contains only a small contribution from the metal. Indeed, it should be noted that simple sulfur radicals show **g** tensor anisotropies that are as large as that of Pd(STPP). For example the cystinyl radical has $g_1 = 2.002$, $g_2 = 2.029$, and $g_3 = 2.056$.[19]

^2H NMR Studies of Pd(STPP). Because the ^1H NMR spectrum of paramagnetic Pd(STPP) is broad and difficult to interpret, we chose to examine the ^2H NMR spectra of two specifically deuterated samples where identification of individual

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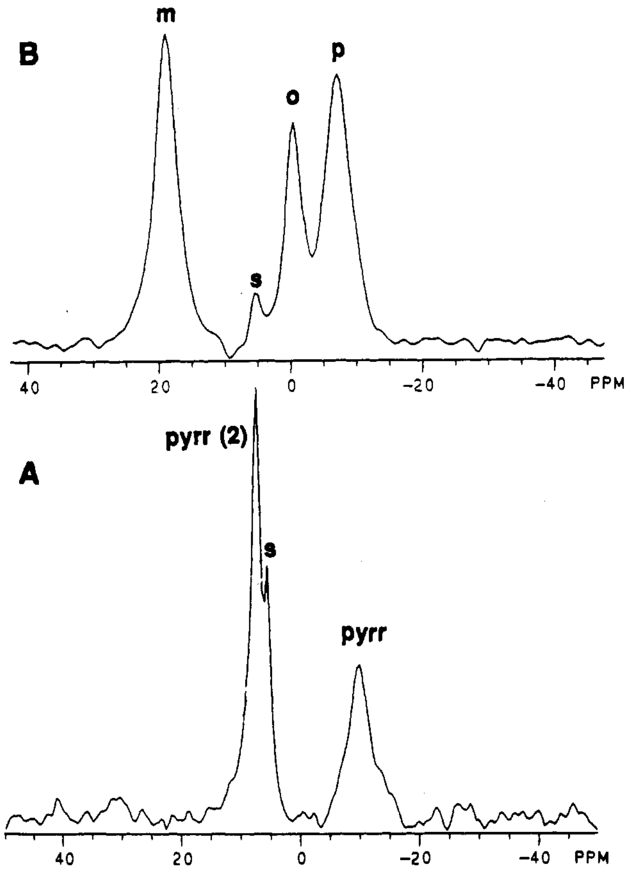

Figure 5. ^{2}H NMR spectrum of (A) Pd(STPP-d_6) and (B) Pd(STPP-d_{10}) in chloroform at 298 K. Resonances are labeled as described in the caption of Figure 2.

resonances would be facilitated. Representative ^{2}H NMR spectral data are presented in Figure 5. Trace A of Figure 5 shows a spectrum of Pd(STPP-d_6) with specific deuteration of the pyrrole positions. One upfield pyrrole resonances is seen at −9.9 ppm, while the second pyrrole resonance shows a smaller upfield shift. Its intensity is twice that of the resonance at −9.9 ppm. Trace B of Figure 5 shows the ^{2}H NMR spectrum of Pd(STPP-d_{10}). The resonance at −1.2 ppm is readily assigned to the phenyl para protons on the basis of its intensity. If, as we suspect, the unpaired spin density in this radical resides in an orbital with π symmetry that is able to conjugate with these aryl groups, then it is reasonable to assign the other upfield shift resonance at −8.2 ppm to the phenyl ortho protons and the downfield shifted resonance at 17.7 ppm to the phenyl meta protons. Thus the overall pattern with two resonances with upfield shifts and one with a downfield shift is wholly consistent with π radical character for this reduced complex.

Plots of the chemical shifts versus $1/T$ for the upfield pyrrole resonance and the three phenyl resonances for Pd(STPP-d_6) and Pd(STPP-d_{10}) are linear. The extrapolated shifts at infinite temperature are near the anticipated diamagnetic reference positions.

The pattern of the phenyl resonances shows a shift direction alternation for the phenyl protons that is characteristic of π-spin density delocalization onto the rings by removing the orthogonality of the phenyl and porphyrin π-systems. Consequently, the dipolar contribution to the isotropic shift of the pyrrole and thiophene resonances is expected to be negligible and the measured isotropic shift is a direct indication of the spin delocalization in the thiaporphyrin skeleton.

Crystal and Molecular Structure of Pd(SDPDTP)·0.5CH$_2$Cl$_2$. Table 1gives the atomic positional parameters, while Table 2 contains selected interatomic distances and angles. Figure 6 shows a perspective view of the complex which is monomeric and lacks any Pd–Pd bonding. The introduction of unsymmetrical substituents on the thiaporphyrin periphery resulted in sufficient asymmetry, so disorder involving the sulfur position, which was frequently observed for metallothiaporphyrins,[4,11,13] was not encountered. The geometry of Pd(SDPDTP) resembles that of other thiaporphyrin complexes and is very similar to that of four-coordinate Ni$^{\text{I}}$(SDPDTP).[13]

The geometry of the complex reflects the balance among constraints of the macrocycle ligand, the size of the palladium ion, and the requirement of the palladium for the planar geometry. The thiaporphyrin has had to distort to accommodate bonding the palladium. Although 21-thiaporphyrin free bases are planar,[4,6] the macrocycle in Pd(SDPDTP) is nonplanar with the thiapor-

Table 1. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Pd(SDPDTP)

	x	y	z	U(eq)[a]
Pd	4081(1)	3900(1)	4081(1)	29(1)
S	5417(3)	4316(3)	4051(3)	32(2)
N(1)	4750(10)	3747(7)	5518(8)	29(6)
N(2)	2831(9)	3719(7)	4119(7)	27(6)
N(3)	3534(9)	3996(8)	2648(7)	31(6)
C(1)	4282(13)	3759(9)	6116(10)	28(8)
C(2)	3309(13)	3730(9)	5840(9)	28(7)
C(3)	2636(13)	3692(9)	4935(11)	35(8)
C(4)	1617(14)	3598(10)	4614(12)	47(10)
C(5)	1238(14)	3654(11)	3689(11)	47(9)
C(6)	1978(12)	3755(10)	3368(10)	34(8)
C(7)	1881(12)	3832(10)	2430(10)	34(7)
C(8)	2619(12)	3995(10)	2139(10)	30(7)
C(9)	2450(15)	4084(10)	1163(12)	49(9)
C(10)	3298(13)	4144(9)	1117(10)	34(8)
C(11)	4016(13)	4065(9)	2037(11)	35(8)
C(12)	4969(12)	3985(10)	2229(10)	28(7)
C(13)	5651(13)	3957(10)	3108(11)	37(8)
C(14)	6552(12)	3662(10)	3441(10)	33(8)
C(15)	6959(12)	3562(10)	4382(9)	31(7)
C(16)	6350(13)	3814(10)	4838(11)	44(8)
C(17)	6435(12)	3664(8)	5724(10)	26(7)
C(18)	5689(12)	3729(9)	6042(10)	25(8)
C(19)	5780(14)	3772(10)	6993(10)	37(8)
C(20)	2923(7)	3735(6)	6601(6)	32(7)
C(22)	3158	3110	7277	37(8)
C(23)	2793	3123	7968	47(8)
C(24)	2192	3761	7983	44(8)
C(25)	1956	4386	7307	38(8)
C(26)	2322	4373	6616	43(8)
C(27)	1754	3738	8765	67(10)
C(28A)	906(15)	3721(16)	1763(16)	27(19)
C(29A)	229	4327	1641	64(12)
C(30A)	−646	4237	935	64(12)
C(31A)	−845	3541	352	40(19)
C(32A)	−168	2935	475	37(9)
C(33A)	708	3025	1180	46(10)
C(28B)	903(13)	3785(14)	1663(14)	20(20)
C(29B)	490	4488	1142	29(8)
C(30B)	−412	4443	476	57(11)
C(31B)	−900	3693	331	35(17)
C(32B)	−487	2990	852	51(10)
C(33B)	415	3035	1519	23(7)
C(34)	−1836(13)	3553(12)	−370(12)	58(9)
C(35)	5254	3915	1400	27(6)
C(36)	4870(6)	3318(6)	705(6)	27(7)
C(37)	5159	3269	−40	36(8)
C(38)	5831	3818	−90	42(8)
C(39)	6214	4415	605	44(9)
C(40)	5926	4464	1350	33(8)
C(41)	7345	3392	6435	40(8)
C(42)	8118(10)	3909(6)	6652(9)	67(10)
C(43)	8985	3630	7258	86(13)
C(44)	9079	2835	7648	92(14)
C(45)	8307	2318	7431	49(9)
C(46)	7440	2597	6824	38(8)
Cl(1)	313(9)	9512(8)	−93(10)	87(7)
Cl(2)	−672(8)	11037(8)	−561(8)	79(6)

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

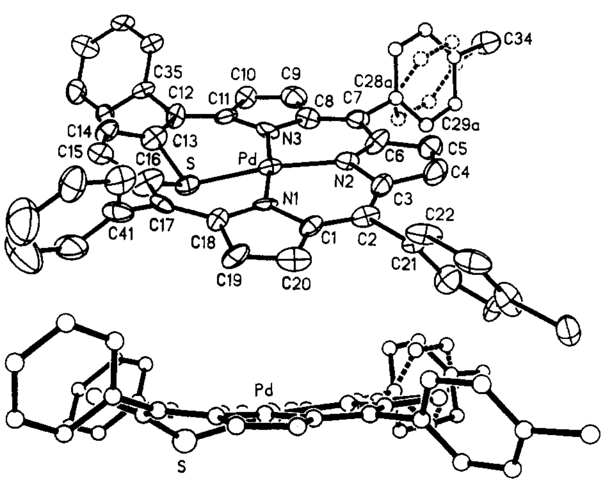

Figure 6. Perspective view of Pd(SDPDTP) with 50% thermal contours for all non-hydrogen atoms and a second view that shows deviations from planarity. The position of the second form of the disordered *p*-tolyl group is shown with a dashed line.

Table 2. Selected Bond Lengths and Angles for Pd(SDPDTP).

	Bond Lengths (Å)		
Pd–S	2.208(5)	Pd–N(1)	2.085(11)
Pd–N(2)	1.999(15)	Pd–N(3)	2.061(11)
S–C(13)	1.736(20)	S–C(16)	1.703(16)
	Bond Angles (deg)		
S–Pd–N(1)	88.1(5)	N(1)–Pd–N(2)	92.7(6)
S–Pd–N(2)	170.8(4)	N(1)–Pd–N(3)	174.3(6)
S–Pd–N(3)	87.8(4)	Pd–S–C(13)	115.0(6)
N(2)–Pd–N(3)	92.0(5)	C(13)–S–C(16)	92.9(9)
Pd–S–C(16)	113.5(7)	Pd–N(1)–C(18)	128.2(13)

phyrin ring characteristically bent out of the N(1), N(2), N(3), C(1)–C(11), C(18)–C(20) plane. The out-of-plane displacements are as follows: Pd, 0.022 Å; S, 0.482 Å; C(13), –0.27 Å; C(14), -0.81 Å; C(15), –0.88 Å; C(16), –0.32 Å. The angle between the C(13)SC(16) plane and the Pd–S bond is 53.4°. This structural parameter is larger than for Ni^{I}(SDPDTP) (45.9°)[13] but smaller than found for five-coordinate and six-coordinate complexes: Ni^{II}(STPP)Cl (63.3°);[7] Cu^{II}(STPP)Cl (65.6°);[7] Fe^{II}(STPP)Cl (69.5°);[7] Rh^{III}(STPP)Cl (61.2°).[11] Moreover, the thiophene ring is no longer planar. The dihedral angle between the C(13)C(14)C(15)C(16) plane and the C(13)SC(16) plane is 15.6°. The folding is similar, as established for four-and five-coordinate complexes (Ni^{I}(SDPDTP) (14.6°), Ni^{II}(STPP)Cl (15.2°), Fe^{II}(STPP)Cl (11.8°)) but smaller than determined for six-coordinate Rh^{III}(STPP)Cl (26.4°).[7,11,13] The bending and tipping of the thiophene ring allows the sulfur to coordinate the palladium in pyramidal, side-on fashion. The geometry of the sulfur resembles that established for the other η^1-thiophene complexes. The palladium ion has nearly planar geometry. The Pd–N distances (2.085(11), 1.999(15), 2.061(11) Å) fall near the range of distances (2.00–2.02 Å) seen for palladium porphyrins.[20] The Pd–S bond length, 2.208(5) Å, is considerably shorter than the sum of covalent radii, which is 2.35 Å.[21] The Pd–S bond lengths in other structures typically range from 2.26 to 2.30 Å.[21,22] Thus the Pd–S bond in Pd(SDPDTP) is short.

Conclusions

The redox-related pair of complexes [Pd^{II}(STPP)]$^+$ and its one-electron-reduction product Pd(STPP) have been characterized. While the former is a conventional d^8 planar complex with a diamagnetic ground state, the latter is paramagnetic with its unpaired electron in an orbital which both EPR and NMR studies indicate is largely ligand based and of π-symmetry. The geometry of Pd(STPP) as shown by an X-ray crystal structure is nearly planar, with the major out-of-plane distortions caused by the need to accommodate the thiophene ring and η^1-bonding of the pyramidal sulfur. These features are characteristic of a number of thiaporphyrin complexes.

Experimental Section

Preparation of Compounds. Tetraaryl-21-thiaporphyrin derivatives were synthesized as described previously.[10] Selectively deuterated 5,20-diphenyl-10,15-di(phenyl-d_5)-21-thiaporphyrin (STPPH-d_{10}) was synthesized using benzylaldehyde-d_5, which was obtained by oxidation of toluene-d_8 with $Ce(SO_4)_2$.[23] STPPH-d_6 (deuterated at the pyrrole β-positions) was prepared from pyrrole-d_5.[24]

[Pd^{II}(STPP)]Cl. A 63 mg sample of STPPH (0.1 mmol) and 100 mg of palladium(II) chloride (0.56 mmol) were added to 450 mL of acetonitrile. The mixture was heated under reflux for 10 h. After cooling, the remaining solid palladium(II) chloride was removed by filtration, and the solvent was then removed under reduced pressure. The solid residue, dissolved in dichloromethane, was subjected to chromatography on a silica gel column (3 × 30 cm). Elution with chloroform gave a yellow-brown fraction of STPPH. Further elution with chloroform/methanol (5/1 v/v) produced a green fraction that was recovered as a solid after evaporation of solvent under vacuum. Recrystallization of this solid from dichloromethane/*n*-hexane (1/1 v/v) produced 70 mg (90%) of [Pd^{II}(STPP)]Cl. Mass by liquid secondary ion mass spectroscopy: m/z 736 (M – Cl). The ^{1}H NMR spectrum of the complex is shown in Figure 2. The thiophene resonance has been observed to show unusual broadening that appears to depend on the chloride concentration.

[Pd^{II}(STPP)](ClO$_4$). The metathesis of a 5-mg sample of [Pd^{II}(STPP)]Cl was carried out in toluene (10 mL) by addition of Ag^{I}(ClO$_4$)·3CH$_3$CN. The precipitate of silver chloride was removed by filtration, the solution volume was reduced, and the product was precipitated by the addition of hexane. ^{1}H NMR (chloroform-*d*), δ: 9.78 ppm, thiophene H; 9.00 (d), 8.98 (d), 8.80 ppm, pyrrole H.

Pd(STPP). All operations were done under a dinitrogen atmosphere through the use of Schlenck techniques. [Pd^{II}(STPP)]Cl, 46 mg (0.054 mmol), was dissolved in acetonitrile (10 mL). Sodium dithionite (100 mg) dissolved in water (5 mL) was added to the [Pd^{II}(STPP)]Cl solution. This mixture was vigorously stirred for 1 h. In the course of the reaction, the dark-green reduction product precipitated. The solid material was collected by filtration, washed with water, dried in vacuum for 8 h, and recrystallized from dichloromethane/acetonitrile. The yield was 85%. Anal. Calcd for Pd(STPP)·CH$_2$Cl$_2$, C$_{44}$H$_{30}$N$_3$SCl$_2$Pd: C, 65.38; H, 3.66; N, 5.08. Found: C, 65.71; H, 3.70; N, 5.45.

Instrumentation. ^{1}H NMR and ^{2}H NMR spectra were recorded on a Bruker AMX 300 (^{1}H, 300 MHz; ^{2}H, 46.06 MHz) spectrometer or a Nicolet 360 (^{1}H, 360 MHz) spectrometer operating in a quadrature detection mode.

Electrochemical measurements were performed in dichloromethane and acetonitrile with tetra-*n*-butylammonium perchlorate (TBAP) as a supporting electrolyte. Cyclic voltam-

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Table 3. Crystallographic Data for Pd(SDPDTP)·$0.5CH_2Cl_2$

empirical formula	$C_{46.5}H_{33}ClN_3PdS$
color, habit	dark-green plates
fw	807.7
crystal system	monoclinic
space group	$P2_1/c$
a, Å	15.625(5)
b, Å	16.039(4)
c, Å	15.519(6)
β, deg	112.47(3)
V, Å^3	3594(2)
T, K	130
Z	4
cryst dimens, mm	0.10 × 0.14 × 0.16
d_{calcd}, g cm^{-3}	1.49
radiation λ, Å	0.710 73
μ(Mo Kα), mm^{-1}	0.68
range of transm factors	0.91–0.94
R^a	0.097
$R_w{}^b$	0.083

[a] $R = \sum||F_o| - |F_c||/|F_o|$. [b] $R_w = \sum||F_o| - |F_c||/|F_o|w^{1/2}/\sum|F_o w^{1/2}|$; $w = 1/\sigma^2(F_o)$.

mograms were recorded for the potential scan rate that ranged from 0.02 to 0.5 V s^{-1}. A Pt-disk working electrode, Pt-foil auxiliary electrode, and SCE reference electrode were used.[7] The system was thermostated at 298 K, and an inert-gas atmosphere was maintained during the measurements.

X-ray Data Collection and Refinement for Pd(SDPDTP)·$^1/_2CH_2Cl_2$. Crystals of Pd(SDPDTP) were obtained by slow diffusion of hexane into a dichloromethane solution of the complex. Data were collected at 130 K on a Siemens P4/R4 diffractometer that was equipped with a Siemens LT-2 low-temperature apparatus. Two check reflections showed random (less than 2%) variation during data collection. The data were corrected for Lorentz and polarization effects. Crystal data are compiled in the Table 3. Calculations were performed on a DEC VAX station 3200 with the programs of SHELXTL Plus v 4.21. Scattering factors for neutral atoms and corrections for anomalous dispersion were taken from a standard source.[25] An absorption correction was applied to the structure.[26] The solution of the structure was obtained by direct methods. There is disorder in the orientation of the *p*-tolyl group that involves C(28)–C(33). It was modeled with two rigid phenyl rings at occupancies 0.50 and 0.50 for sets "A" and "B".

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Supplementary Material Available: Tables of bond distances, bond angles, anisotropic thermal parameters, hydrogen atom coordinates, and crystal structure refinement data for Pd(STPP) (7 pages). Ordering information is given on any current masthead page.

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