(16) This may seem like an extremely high decomposition level for intensity data collection, but we never had more than three crystals of diffraction quality. One was used up for the photographic data and the two remaining were used for intensity data collection.

(17) Patterson and electron density syntheses were calculated using "ERFR-3, a Three-Dimensional Fourier Summation Program Adapted for the IBM 7040 from ERFR-2 of Sly, Shoemaker, and van den Hende", by D. R. Harris. These (by different programs) calculations are now done on the IBM 370/168.

(18) In space group $P2_1$ (a polar space group) in the presence of anomalous dispersion it is possible to determine the chirality of the crystal. No attempt was made to do so in the present instance for the following reasons: (1) the anomalous dispersion correction for Cu with Mo Kα radiation is small; (2) two different crystals were used for the intensity data and they were not sufficiently well formed so that it could be certain they were both mounted in an identical manner. However, four possibilities could have been tested involving the two sign permutations on k for each crystal. This was rejected out of hand as a waste of computing time because of the general limitations of the intensity data as well as the fact that the different crystals represented data from different 2θ shells. Under these conditions it would have been better to have neglected $\Delta f''$ in the refinement, the general shortcoming of the intensity data indicated in text.

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Platinum and Palladium Complexes of Thienylpyridine. 2. Quasi-Octahedral Divalent-Metal Compounds

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Received September 27, 1977

In this paper we report the syntheses and structures of complexes of divalent platinum and palladium with 2-(2′-thienyl)pyridine (TP). The general formulas are $M(TP)_2X_2$ ($X^- = Br^-, Cl^-$). The crystal structure of $Pd(TP)Br_2$ was determined from three-dimensional X-ray diffraction data collected by counter methods. The compound $Pd(C_{18}H_{14}N_2S_2)Br_2$ was found to crystallize in the monoclinic space group $P2_1/c$ with $a = 6.328$ (1) Å, $b = 16.536$ (4) Å, $c = 9.267$ (2) Å, $\beta = 99.85$ (2)°, and $Z = 2$ molecules/cell. The structure was refined by standard methods to final $R_1 = 4.4\%$ and $R_2 = 4.8\%$ for 1244 nonzero reflections. The palladium atom is located on an inversion center and is coordinated to two nitrogen atoms (2.021 Å) and two bromine atoms (2.431 Å) in typical square-planar fashion. In addition, the two thiophene sulfur atoms are located above and below the coordination atom (3.05 Å), making the complex quasi-octahedral. The implications of this unusual geometry are discussed in the light of the structural and spectroscopic properties. The synthesis and characterization of *cis*- and *trans*-$Pd(TP)_2Cl_2$ and *trans*-$Pt(TP)_2Cl_2$ are also described. The geometries of these monomeric complexes have been determined by far-infrared measurements and analogy to the structure of $Pd(TP)_2Br_2$. The electronic spectra of the palladium complexes are similar to those of other four-coordinate, square-planar complexes of palladium(II). The electronic spectrum of the platinum complex contains an intense low-energy d–d band indicative of metal–thiophene axial interactions and is similar to the previously described complexes Pt(TP)(TP-H)I and Pt(TP)(TP-H)Br. A thiophene-based band at 850 cm^{-1} in the infrared spectrum of the free ligand is not significantly shifted in the palladium complexes but is shifted to 875 cm^{-1} in the platinum complex. The data pertinent to the metal binding ability of thiophene are summarized, and estimates are made of the strength of this interaction.

Introduction

We have previously reported the results of our initial investigations on the ligating properties of 2-(2′-thienyl)pyridine (TP).[1] In that earlier paper we described the ease with which the thiophene moiety forms metal–carbon bonds by loss of a hydrogen (TP-H). We now report on a series of compounds of formula $M(TP)_2X_2$ (M = Pd, Pt; X = Cl, Br) in which no new carbon bonds are formed. In these compounds two thiophene groups are located above and below the coordination plane at somewhat ambiguous distances with respect to bonding.

The complexes of formula $M(TP)_2X_2$ are analogous to the well-known dihalobis(pyridine) complexes of platinum(II) and palladium(II). We have previously noted similarities of the electronic and infrared spectra of Pt(TP)(TP-H)I and Pt(TP)(TP-H)Br with the spectrum of *trans*-$Pt(TP)_2Cl_2$, which we ascribed to interactions between the metal atom and a thiophene ring in an axial position. Here we will describe more fully the syntheses and characterizations of *trans*-$Pt(TP)_2Cl_2$, *cis*- and *trans*-$Pd(TP)_2Cl_2$, and *trans*-$Pd(TP)_2Br_2$, as well as the X-ray crystal structure of the latter.

These data provide some answers to questions regarding the binding tendency of thiophene, which were the original impetus for this work.

Experimental Section

Infrared spectra (4000–450 cm^{-1}), electronic spectra, conductivity measurements, and X-ray powder photographs were obtained by methods previously described.[1] Far-infrared spectra (450–100 cm^{-1}) were obtained on a Digilab Fourier transform spectrometer. A Nujol mull between polyethylene sheets was used for the sample and reference cells.

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The dielectric constants of benzene solutions of *trans*-$Pt(TP)_2Cl_2$ were measured using a WTW Type DMO1 dipolmeter, refractive indices were measured with a Bausch and Lomb precision refractometer, and the dipole moment was calculated from these data by the method of Mark, et al.[2]

Microanalyses were determined by Spang Microanalytical Laboratories, Ann Arbor, Mich., and the molecular weight of *trans*-$Pt(TP)_2Cl_2$ was determined in dimethylformamide by Galbraith Laboratories, Inc., Knoxville, Tenn.

Susceptibilities of the solid samples were determined by the Faraday method.[3] The magnetic field was supplied by a Varian V-3400 9-in. electromagnet, equipped with Heyding pole pieces and a Varian Mark I field dial. Weights were determined on a Cahn R-100 electrobalance. The standard used for calibration was $(NH_4)_2NiSO_4 \cdot 6H_2O$ ($\chi_g = 3065/T + 0.5 \times 10^{-6}$ cgs units).[4] The susceptibilities were corrected for the diamagnetism of the metal and ligands.

Synthesis. The preparation of 2-(2′-thienyl)pyridine has been described.[1] The *trans*-$Pd(py)_2Cl_2$ was prepared by the reaction of pyridine with K_2PdCl_4 and recrystallized by Soxhlet extraction with methylene chloride.

Anal. Calcd for $(C_5H_5N)_2PdCl_2$: C, 35.82; H, 2.98. Found: C, 35.78; H, 3.08. Dichlorobis(benzonitrile)palladium(II) used in this investigation was prepared by the method of Kharasch[5] from $PdCl_2$ and benzonitrile.

Preparation of *cis*-Dichlorobis[2-(2′-thienyl)pyridine]palladium(II). Dichlorobis(benzonitrile)palladium(II), 0.171 g (0.5 mmol), was dissolved in 50 mL of benzene and the mixture filtered. TP, 0.18 g (1.1 mmol), dissolved in 10 mL of benzene was added. A yellow precipitate appeared immediately. The mixture was stirred for 15 min. The precipitate was then collected by filtration, washed with benzene followed by ethyl ether and 30–60 °C petroleum ether, and air-dried; yield 45%.

Anal. Calcd for $Pd(C_9H_7NS)_2Cl_2$: C, 43.29; H, 2.81. Found: C, 43.34; H, 2.79.

The infrared absorption spectrum of *cis*-$Pd(TP)_2Cl_2$ from 900 to 650 cm^{-1} showed maxima at 870, 850 (m), 840 (w), 830 (w), 780 (s), 760 (s), 720 (s), 690 (s) cm^{-1}.

Preparation of *trans*-Dichlorobis[2-(2′-thienyl)pyridine]palladium(II). A sample of *cis*-dichlorobis[2-(2′-thienyl)pyridine]palladium(II) was dissolved in the minimum amount of acetone. The solution was transferred to a glass-stoppered Erlenmeyer flask and allowed to stand for 24 h. Small yellow crystals of product began to appear after several hours. The solid was collected by filtration, washed two times each with 15-mL portions of acetone, ethyl ether, and 30–60 °C petroleum ether, and air-dried; yield 80%.

Anal. Calcd for $Pd(C_9H_7NS)_2Cl_2$: C, 43.29; H, 2.81. Found: C, 43.27; H, 2.85.

The infrared absorption spectrum of *trans*-$Pd(TP)_2Cl_2$ from 900 to 650 cm^{-1} showed maxima at 850 (s), 840 (s), 755 (s), 740 (s), 705 (s) cm^{-1}.

Preparation of *trans*-Dibromobis[2-(2′-thienyl)pyridine]palladium(II). Potassium tetrachloropalladate, 0.163 g (0.5 mmol), was dissolved in 20 mL of water along with 0.25 g (2.1 mmol) of potassium bromide. The mixture was stirred for 5 h and TP, 0.18 g (1.1 mmol), dissolved in 40 mL of acetone, was added and the reaction mixture was stirred for 6 h more. The resulting yellow solid was collected by filtration, washed in the same manner described above, and air-dried. During Soxhlet extraction with methylene chloride, the product crystallized in the collection flask. It was collected by filtration, washed, and dried; yield 15%.

Anal. Calcd for $Pd(C_9H_7NS)_2Br_2$: C, 36.70; H, 2.38. Found: C, 36.68; H, 2.58.

The infrared absorption spectrum of *trans*-$Pd(TP)_2Br_2$ from 900 to 650 cm^{-1} showed maxima at 850 (s), 840 (s), 755 (s), 740 (s), 705 (s) cm^{-1}.

Preparation of *trans*-Dichlorobis[2-(2′-thienyl)pyridine]platinum(II). Potassium tetrachloroplatinate, 0.208 g (0.5 mmol), was dissolved in 20 mL of water. Acetone, 10 mL, was added followed by 0.18 g (1.1 mmol) of TP dissolved in 30 mL of a 1:1 v/v acetone–water mixture. The mixture was stirred for 24 h. A yellow-orange precipitate began to appear after 20 min. The product was collected by filtration and was washed two times each with 15-mL portions of water, ethanol, ethyl ether, and 30–60 °C petroleum ether, and air-dried. The product was then dissolved in the minimum amount of methylene chloride and eluted with acetone through a column packed with 60–100 mesh Florisil. The product which passed readily through the column was reprecipitated by the stripping of ca. two-thirds of the solvent and trituration of the remainder with 30–60 °C petroleum ether. The resulting yellow-orange solid was washed in the same manner as the preceding compound and air-dried. It was then heated in vacuo at 80 °C for 2 h to remove coordinated acetone; yield 35%.

Anal. Calcd for $Pt(C_9H_7NS)_2Cl_2$: C, 36.73; H, 2.38; mol wt, 588. Found: C, 36.87; H, 2.43; mol wt measured in *N,N*-dimethylformamide, 620.

The infrared absorption spectrum of *trans*-$Pt(TP)Cl_2$ from 900 to 650 cm^{-1} showed maxima at 875 (s), 845 (m), 770 (s), 740 (m), 715 (s), 705 (s) cm^{-1}.

Crystal Structure Determination of $PdBr_2(TP)_2$. Data Collection. Single crystals of $PdBr_2(TP)_2$ were grown as described above. A well-formed crystal of dimensions 0.211 × 0.120 × 0.086 mm was mounted on a $P\bar{1}$ Syntex diffractometer such that the long axis of the crystal (the 100 axis) was slightly misaligned from the spindle axis. The space group was determined to be $P2_1/c$ from axial photographs and systematic absences. The lattice parameters were measured using 15 centered reflections in a least-squares refinement and found to be $a = 6.328$ (1) Å, $b = 16.536$ (4) Å, $c = 9.267$ (2) Å, and $\beta = 99.85$ (2)°. The cell volume is 955.4 (4) $Å^3$. The density was measured by flotation in a mixture of CCl_4 and CH_3I. The observed density of 2.03 g/cm^3 is comparable to the value of 2.05 g/cm^3 calculated for a molecular weight of 588.3 with $Z = 2$.

Intensity data were collected using Mo Kα monochromatized radiation from a graphite crystal set perpendicular to the sample diffraction plane. The data were collected using the θ–2θ technique with a variable scan rate based on intensity of 2.4–15.0°/min. Background counts were measured at the edges of each scan for a period of 0.8 times the scan time. The scan range was Mo $K\alpha_1 - 0.8$ to Mo $K\alpha_2 + 0.8°$. Three standard reflections were measured every 50 reflections. The standard deviation of three reflections during the collection of data to a 2θ maximum of 55° was less than 4%.

The data were reduced according to previously described procedures.[6] The crystal faces were indexed and measured and the data were corrected for absorption using routine procedures.[7] The linear absorption coefficient of 53.06 cm^{-1} gave a maximum correction factor of 2.037 and a minimum correction factor of 1.489. A total of 2650 reflections were collected of which 1244 had $F^2 \geq 3\sigma(F^2)$ and were used in the solution and refinement.

Solution and Refinement of the Structure. The structure was solved using standard Fourier and least-squares refinement procedures.[6] The function $\sum w(|F_o| - |F_c|)^2$ was minimized where $|F_o|$ and $|F_c|$ are observed and calculated structure factor amplitudes, respectively. The atomic scattering factors were taken from ref 8. Corrections for anomalous scattering were made for palladium and bromine.

The Patterson function located the S and Br atoms relative to the palladium atom which was placed at 0, 0.5, 0.5. A standard difference Fourier revealed the position of all of the nonhydrogen atoms. Two least-squares refinement cycles gave $R_1 = \sum[|F_o| - |F_c|]/\sum(F_o) = 0.081$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.089$, where $w = 4F_o^2/\sigma^2(F_o^2)$. Two cycles of refinement on all nonhydrogen atoms using individual anisotropic thermal parameters and correcting palladium and bromine for anomalous scattering gave $R_1 = 0.047$ and $R_2 = 0.055$. The hydrogen atom positions were calculated and they were added as fixed contributions to the structure in the final cycle of refinement. The final cycle gave $R_1 = 0.044$ and $R_2 = 0.048$ with 1244 observed reflections and 115 variables. All shifts were less than one standard deviation and the average deviation of an observation of unit weight was 1.36. The largest peak in the final difference map which was not a palladium or bromine residual was 0.67 e/$Å^3$.

Final atomic positional parameters with their estimated standard deviations are given in Table I. Anisotropic thermal parameters with their estimated standard deviations are given in Table II. The basic structure of $PdBr_2(TP)_2$ is shown in Figure 1. Figure 2 is a stereo-drawing of the molecule showing thermal ellipsoidal motion of the atoms. Figure 3 shows the packing of the molecules in the unit cell. Table III is a listing of distances and angles in the molecule. The palladium atom is located at a crystallographic inversion center which requires the palladium, nitrogen, and bromine atoms to be planar.

Discussion

The palladium complexes *cis*-$Pd(TP)_2Cl_2$ (I), *trans*-$Pd(TP)_2Cl_2$ (II), and *trans*-$Pd(TP)_2Br_2$ (III) are yellow, crystalline solids which are slightly soluble in polar organic solvents

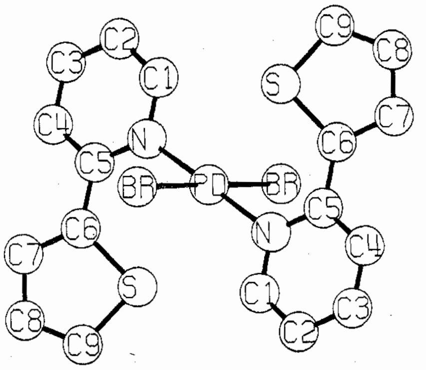

Figure 1. The molecular structure of $PdBr_2(TP)_2$.

Table I. Final Position Parameters for $PdBr_2(TP)_2$

Atom	x	y	z
Pd	0.0 (0)	0.5000 (0)	0.5000 (0)
Br	0.2325 (2)	0.4006 (1)	0.6407 (1)
S	−0.3418 (4)	0.3719 (1)	0.4062 (3)
N	0.0738 (10)	0.4544 (4)	0.3126 (7)
C1	0.2073 (15)	0.4990 (6)	0.2482 (10)
C2	0.2786 (17)	0.4753 (7)	0.1233 (11)
C3	0.2136 (17)	0.4037 (7)	0.0602 (11)
C4	0.0761 (17)	0.3570 (6)	0.1230 (10)
C5	0.0036 (13)	0.3831 (5)	0.2494 (9)
C6	−0.1499 (14)	0.3334 (5)	0.3099 (9)
C7	−0.1783 (16)	0.2526 (5)	0.2917 (11)
C8	−0.3508 (16)	0.2213 (6)	0.3518 (12)
C9	−0.4531 (15)	0.2790 (6)	0.4172 (11)
H1	0.2612 (17)	0.5530 (6)	0.2953 (11)
H2	0.3778 (17)	0.5117 (6)	0.0771 (11)
H3	0.2691 (17)	0.3837 (6)	−0.0301 (13)
H4	0.0248 (18)	0.3026 (6)	0.0773 (11)
H5	−0.0806 (17)	0.2167 (6)	0.2406 (12)
H6	−0.3971 (17)	0.1623 (6)	0.3443 (11)
H7	−0.5801 (18)	0.2673 (6)	0.4685 (11)

and insoluble in water. Orange, crystalline *trans*-$Pt(TP)_2Cl_2$ (IV) is not only more soluble in polar organic solvents than the palladium complexes but is also soluble in benzene. Examination of X-ray powder patterns shows that II and III are isomorphous. Complexes II and IV are not isomorphous although similar in composition.

The analytical data indicate empirical formula $M(TP)_2X_2$ for all four complexes. Nitromethane solutions of I and IV are poor conductors ($\Lambda < 10$ mhos) indicating that the chlorine atoms are bonded to the metal atoms and are not ionic chlorides. The molecular weight of IV is consistent with formulation as a monomer. The compounds I, II, and III were too insoluble for molecular weights to be determined.

The geometries of I and II can be determined from the M–Cl stretches observed in the far-infrared region. The spectrum of I has bands at 317 and 332 cm^{-1} corresponding to Pd–Cl symmetric and asymmetric stretches, whereas the spectrum of the trans dichloro complex has one band at 342 cm^{-1} assigned to the Pd–Cl asymmetric stretch. These were readily assigned by analogy to the Pd–Cl symmetric and asymmetric stretches which appear at 333 and 342 cm^{-1} in the spectrum of *cis*-$Pd(py)_2Cl_2$ and the Pd–Cl asymmetric stretch which appears at 358 cm^{-1} in the spectrum of *trans*-$Pd(py)_2Cl_2$.[9] In addition, compound II is known to be trans from its isomorphism with III.

It is apparent from changes in the far-infrared spectrum with time that the cis isomer always has some trans in it which

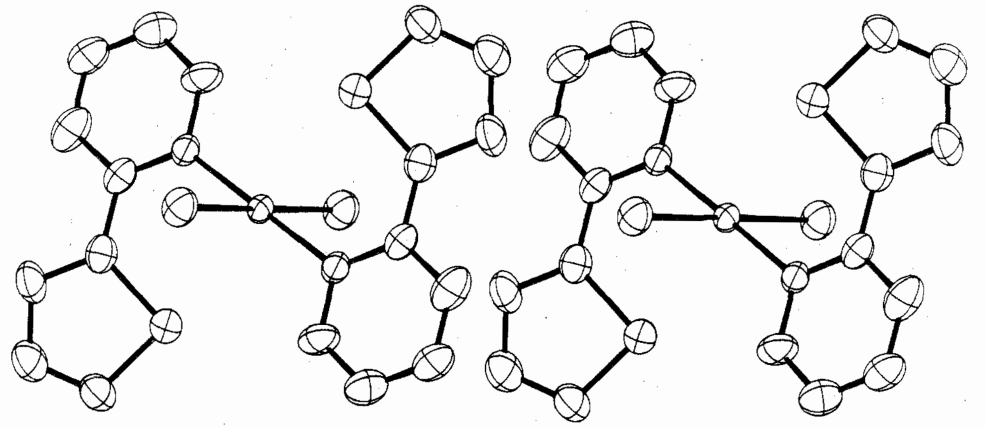

Figure 2. Stereoview of anisotropic thermal motion in $PdBr_2(TP)_2$.

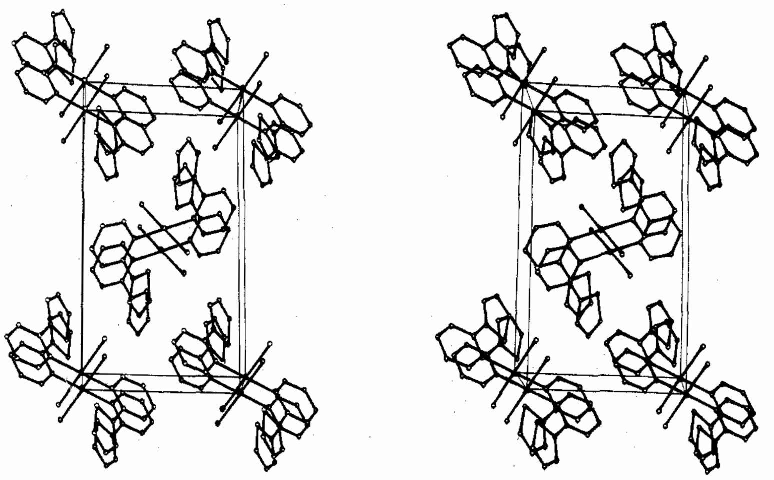

Figure 3. The unit cell of $PdBr_2(TP)_2$.

Table II. Final Thermal Parameters for $PdBr_2(TP)_2$ ($\times 10^3$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{iso}, Å^2
Pd	2.7 (1)	2.1 (1)	2.2 (1)	0.1 (1)	0.9 (1)	−0.1 (1)	2.2 (1)
Br	4.1 (1)	3.6 (1)	3.6 (1)	0.9 (1)	0.8 (1)	0.6 (1)	3.7 (1)
S	3.7 (1)	3.1 (1)	5.5 (1)	−0.2 (1)	1.7 (1)	−0.8 (1)	3.8 (0)
N	3.1 (3)	2.5 (3)	2.7 (3)	0.4 (3)	1.0 (3)	0.2 (3)	2.6 (1)
C1	4.3 (4)	4.0 (4)	3.7 (4)	0.1 (4)	1.9 (4)	0.5 (4)	3.6 (1)
C2	5.9 (6)	4.9 (5)	4.1 (5)	−0.6 (4)	2.9 (5)	0.2 (4)	4.3 (2)
C3	5.6 (6)	5.9 (6)	3.3 (4)	−0.1 (5)	2.6 (4)	−0.8 (4)	4.1 (2)
C4	5.6 (6)	4.6 (5)	3.0 (4)	0.6 (4)	1.0 (4)	−0.9 (4)	4.1 (2)
C5	2.9 (4)	3.4 (4)	2.2 (3)	0.9 (3)	0.1 (3)	−0.0 (3)	2.7 (1)
C6	3.6 (4)	3.1 (4)	2.6 (4)	0.1 (3)	0.2 (3)	−0.7 (3)	3.0 (2)
C7	4.8 (5)	2.9 (4)	4.5 (5)	−0.3 (4)	1.1 (4)	−1.1 (4)	3.8 (2)
C8	4.6 (5)	3.3 (5)	5.8 (6)	−1.1 (4)	0.6 (4)	−0.9 (4)	4.3 (2)
C9	3.7 (4)	3.6 (5)	5.4 (5)	−0.8 (4)	1.1 (4)	−0.2 (4)	4.0 (2)

Table III. Bonding Distances (Å) and Angles (deg) for $PdBr_2(TP)_2$

Pd-Br	2.431 (1)	C1-C2	1.36 (1)
Pd-S	3.046 (3)	C2-C3	1.35 (1)
Pd-N	2.020 (6)	C3-C4	1.36 (1)
S-C6	1.745 (9)	C4-C5	1.39 (1)
S-C9	1.700 (9)	C5-C6	1.46 (1)
N-C1	1.34 (1)	C6-C7	1.36 (1)
N-C5	1.36 (1)	C7-C8	1.41 (1)
		C8-C9	1.35 (1)

Br-Pd-N	90.1 (2)	C4-C5-N	120.0 (9)
N-Pd-Br	89.9 (2)	C4-C5-C6	120.0 (9)
N-Pd-S	75.6 (2)	N-C5-C6	120.6 (6)
Br-Pd-S	91.04 (6)	C5-C6-C7	126.3 (8)
C1-N-Pd	115.8 (6)	C5-C6-S	124.0 (6)
C5-N-Pd	126.1 (5)	C7-C6-S	109.5 (7)
C1-N-C5	117.6 (6)	C6-C7-C8	114.1 (8)
N-C1-C2	123.0 (9)	C7-C8-C9	112.4 (8)
C1-C2-C3	119.8 (9)	C8-C9-S	112.1 (7)
C2-C3-C4	118.6 (8)	C9-S-C6	91.9 (4)
C3-C4-C5	120.5 (9)		

increases as the sample ages over a period of weeks (Figure 4).

It has been reported that the Pt–Cl asymmetric stretch in complexes of formula *trans*-PtL_2Cl_2 appear at 337–342 cm^{-1}.[10] Product IV is thus assigned trans geometry because of its single intense band at 337 cm^{-1}. In order to confirm this assignment, an attempt was made to determine the dipole moment of IV. Dipole moments for cis and trans complexes of formula PtL_2Cl_2 (L = large group of neutral ligands) are in the ranges 5–13 and 0–3 D, respectively.[11] Benzene solutions of IV have dielectric constants consistent with a dipole moment of less than 2 D. More precise measurements were not possible due to limited solubility.

The question of whether a particular reaction will result in cis or trans products is a complicated one. Kinetic factors including the bulkiness of the ligand and the trans effect appear to be governing in most cases which lead to cis products,[12,13] whereas it is likely that the trans product is generally the more stable isomer.[14,15] Related compounds are observed in both forms,[16] and in the absence of detailed kinetic results, further speculation is unwarranted.

The visible–ultraviolet absorptions of the complexes of TP are listed in Table IV. The spectra of II and III are similar to spectra of complexes such as $Pd_2Br_6^{2-}$, $Pd_2Cl_6^{2-}$, and $Pd(NH_3)_4^{2+}$ which have moderately weak bands assigned to d–d transitions and intense bands assigned to ligand–metal charge transfers.[17] The bands assigned to the transition $^1A_{1g} \rightarrow {}^1E_g$ (d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$) appear at 2.06 (848), 2.49 (490), and 3.36 μm^{-1} (212), respectively. (Molar extinction coefficients are given in parentheses.) These results are in accord with increasing ligand field strength $Br^- > Cl^- > NH_3$. Similarly, the electronic spectra of II and III contain bands at 2.56 (240) and 2.40 μm^{-1} (300) which are assigned as d–d transitions. Furthermore, the lowest energy band in the spectrum of *trans*-$Pd(py)_2Cl_2$ appears at the same frequency as the lowest energy band in II, indicating that the thiophene rings of TP have little influence on the spectral properties of II. The lower frequency of the d–d band in III is a result of the weaker ligand field produced by bromide ions. Other d–d bands present at higher frequencies in the spectra of II and III are obscured by the intense band at ca. 3.30 μm^{-1} also found in free TP.

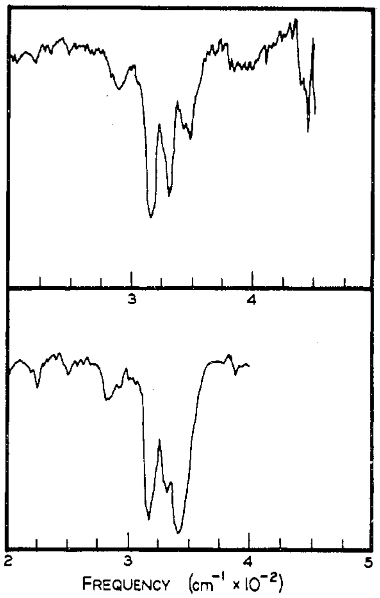

Figure 4. Far-infrared spectrum of fresh $Pd(TP)_2Cl_2$ (top) and spectrum of an aged sample (bottom).

Table IV. Visible–Ultraviolet Absorption Spectra[a]

TP	33.3 (140), 37.8 (80) sh, >41.7 (140)
I, *cis*-$Pd(TP)_2Cl_2$	33.3 (180), 37.0 (210), >41.7 (>280)
II, *trans*-$Pd(TP)_2Cl_2$	25.6 (2.4), 32.5 (120), 37.0 (260), >41.7 (250)
III, *trans*-$Pd(TP)_2Br_2$	24.0 (3.0), 33.3 (160), 40.0 (360), >41.7 (210)
IV, *trans*-$Pt(TP)_2Cl_2$	17.2 (0.15), 19.8 (0.35) sh, 24.5 (40), 33.4 (220)

[a] All values are in $cm^{-1} \times 10^3$. The values in parentheses are molar extinction coefficients $\times 10^{-2}$. Key: sh = shoulder.

The spectrum of IV resembles in part the spectra of other square-planar complexes of divalent platinum. Electronic spectra of $PtCl_4^{2-}$, $PtBr_4^{2-}$, and $Pt(NH_3)_{4-x}Cl_x^{(2-x)+}$ contain weak bands ($\epsilon < 30$) assigned to spin-forbidden d–d transitions.[17,18] Stronger bands at higher energies are assigned to spin-allowed d–d transitions and intense ligand–metal charge-transfer bands. The frequencies of the d–d bands are higher than the frequencies of corresponding bands in analogous palladium complexes. The band assigned $^1A_{1g} \rightarrow {}^1E_g$ (d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$) appears at 2.95 μm^{-1} (66) in $PtCl_4^{2-}$, 2.69

Table V. Corrected Molar Susceptibilities at 298 K[a]

Compound	Relative field strengths 1.38	2.15	3.11
I, *cis*-$Pd(TP)_2Cl_2$	2840	2300	1910
II, *trans*-$Pd(TP)_2Cl_2$	920	700	530
III, *trans*-$Pd(TP)_2Br_2$	4700	4000	3300
IV, *trans*-$Pt(TP)_2Cl_2$	1530	1090	960

[a] All values × 10^6 cgsu.

μm^{-1} (187) in $PtBr_4^{2-}$, and 2.49 μm^{-1} (490) in $Pd_2Cl_6^{2-}$. The spectrum of IV contains an intense asymmetric band at a lower frequency, 2.45 μm^{-1} (4000), than any band in the spectra of II, *trans*-$Pt(py)_2Cl_2$, or *trans*-$Pt(NH_3)_2Cl_2$.[18,19] A similar band appeared in the spectrum of Pt(TP)(TP-H)I and was tentatively assigned to the transition (d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$).[1] The unusually low frequency and high intensity of this band 2.42 μm^{-1} (3400) presumably result from the interaction between the metal and the thienyl moiety of the unchelated TP. This thiophene ring is positioned such that the metal–sulfur distance is 2.99 (3) Å. Gray noted that intense low-energy bands are characteristic of five-coordinate square-pyramidal complexes.[20] The observation of a nearly identical band in IV suggests a similar interaction between sulfur and platinum atoms. The lack of a similar perturbation in any of the spectra of palladium compounds suggests a greatly reduced metal–sulfur interaction, even though the distances are comparable. This is consistent with general expectations regarding orbital extension in 5d vs. 4d elements.

Further evidence which distinguishes the platinum from the palladium complexes is offered by a band appearing at 850 cm^{-1} in the infrared spectrum of TP which was previously assigned to thiophene modes.[1] The shift of this band to 875 cm^{-1} in Pt(TP)(TP-H)I was taken as evidence of metal–thiophene axial interactions. In the spectra of the palladium complexes this band is not significantly shifted, whereas this band is shifted to 875 cm^{-1} in the infrared spectrum of IV.

One can conceive of the possibility that quasi-octahedral complexes of palladium and platinum, by analogy to the well-known octahedral nickel species, might be paramagnetic even though five-coordinate complexes of these metals are diamagnetic. Accordingly, susceptibility measurements were obtained on a Faraday system as a function of magnetic field and temperature.

The complexes I–IV were observed to have limited paramagnetism which was approximately temperature independent and which decreased with increasing magnetic field (Table V). As a check, the susceptibilities of $CuSO_4 \cdot 5H_2O$, $VO(SO_4)H_2O$, and $CoHg(SCN)_4$ were measured using our instrument. The susceptibilities were in good agreement with values expected[3] and there were no significant changes in susceptibility with field strength.

There appears to be a correlation of these susceptibilities with the strength of the in-plane ligand field. The palladium chloride and bromide compounds are isostructural and have similar infrared and electronic spectra. The susceptibility of the bromo complex is ca. 5 times that of the chloro complex, however. It is likely that a TP group chelating through carbon would produce a stronger ligand field than an N-bonding monodentate pair of TP's. The previously described complexes which contain a chelating TP through carbon all have very low susceptibilities. Although the relationship of a weak in-plane ligand field to the paramagnetism of these complexes seems clear, the out-of-plane field must also be important. The compounds $Pt(benzonitrile)_2I_2$ and K_2PtCl_4 presumably have weak in-plane ligand fields, but our measurements confirm that they are diamagnetic. Eventoff[21] observed a high susceptibility for a platinum complex with steric crowding out-of-plane and weak ligands in-plane.

It has been suggested that although the ground state may remain a singlet in this type of compound, the paramagnetism could be due to a low-lying thermally populated triplet.[22] Our data are too limited to test this proposal directly, although it is interesting to note that such a triplet would be further above the ground state for Pt(II) than for Pd(II), due to the greater crystal field splitting, in the absence of other factors. Under this model, our observation of higher susceptibility for IV than for II thus would require assignment of greater metal–sulfur interaction in the platinum complex, which is consistent with our other measurements.

Susceptibilities as high as those we have observed have occasionally been ascribed to temperature-independent paramagnetism (TIP).[23] Although this may be a reasonable explanation of our data also, it is nevertheless striking how much variation is found in the susceptibilities of "diamagnetic" platinum and palladium complexes. On the other hand, our magnetic data does not demand that these complexes be treated analogously to octahedral nickel species nor does it require the assignment of a metal–sulfur bond.

This investigation began with the motive of discovering the coordinating tendencies (if any) of thiophene. It was clear from the outset that those tendencies would be weak. The use of thienylpyridine, as a vehicle for the study of a potentially chelating system, was suggested by certain results obtained in solution.[24] In our first report on this work we described the formation of metal–carbon bonds as an unexpected alternative to metal–sulfur bond formation. In this paper we have described complexes, in which metal–carbon bonds are not formed, and the strength of the metal–sulfur interaction can be inferred from the perturbations of the typically square-planar situation—hence, the name quasi-octahedral. The results of our structural, spectral, and synthetic data indicate that the palladium–sulfur interaction energy is very small, whereas the platinum–sulfur interaction, though small, is slightly larger as indicated by infrared absorption shifts, new visible–ultraviolet absorptions, and interatomic distances. In neither case can a bond truly be said to form, and the interaction is probably too small to fit the definition of "semicoordination" proposed by Hathaway.[25]

Hathaway suggests that bonds between Cu(II) and first-row atoms as much as 0.6 Å longer than normal (~2.0 Å) be considered links of "semicoordination". In the present case, even allowing for the greater covalent radius of a second-row atom (sulfur), the Pd–S distance of 3.046 (3) Å seems long for this rule-of-thumb. Use of this bond length in Pauling's formula[26] for estimating bond order leads to a similar conclusion.

Registry No. I, 66513-15-3; II, 66416-89-5; III, 66416-88-4; IV, 66416-87-3; dichlorobis(benzonitrile)palladium(II), 14220-64-5; *trans*-$Pd(py)_2Cl_2$, 14052-12-1; K_2PdCl_4, 10025-98-6.

Supplementary Material Available: Listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of [α-*N*-(*o*-Hydroxybenzyl)-L-histidinato](L-alaninato)cobalt(III) Dihydrate[1]

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Received October 4, 1977

The crystal and molecular structure of [α-*N*-(*o*-hydroxybenzyl)-L-histidinato](L-alaninato)cobalt(III) dihydrate has been determined by three-dimensional X-ray analysis. The compound crystallizes in the orthorhombic space group $P2_12_12_1$, with $a = 13.188$ (2) Å, $b = 18.140$ (2) Å, $c = 7.842$ (1) Å, and $Z = 4$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures to a final discrepancy factor $R = 0.059$ for 3553 observed reflections ($I_{\text{obsd}} \geq 3\sigma_I$). The geometry around the cobalt ion is distorted octahedral. The α-*N*-(*o*-hydroxybenzyl)-L-histidinato ligand is tetradentate, bonding through the imidazole nitrogen, carboxylate oxygen, secondary amino nitrogen, and phenolate oxygen atoms. The histidinate fragment of the tetradentate ligand occupies one face of the coordination octahedron with the phenolate oxygen of the *o*-hydroxybenzyl substituent occupying the position trans to the histidinate carboxyl oxygen. The bidentate L-alaninate ligand is attached with its amino nitrogen trans to the imidazole nitrogen and its carboxylate oxygen trans to the secondary amino nitrogen of the tetradentate ligand. The L-alaninato five-membered chelate ring adopts the conformation of an asymmetric envelope.

Introduction

A realization of the importance of transition metal ions in biological processes[1] has led to a dramatic growth in the number of investigations of interactions between amino acids and transition metal ions. As part of a program designed to investigate stereoselective effects that might occur in mixed (ternary) transition metal complexes of optically active amino acids, we have synthesized the potentially tetradentate α-*N*-(*o*-hydroxybenzyl)-L-histidine ligand (L-OHBH) as well as its mixed Co(III) complexes, [(L-OHBH)(AA)Co$^{\text{III}}$], where AA = L-, D-, DL-alaninate, or α-aminoisobutyrate.[2] In these complexes the tridentate histidine portion of the L-OHBH ligand could, because of geometric constraints, occupy only a face of the coordination octahedron; however, examination of molecular models indicated that the phenolate oxygen of the *o*-hydroxybenzyl group could coordinate trans to either the carboxylate oxygen or imidazole nitrogen donor atoms of the histidinate fragment. In addition, the orientation of the other amino acidate ligand in the coordination sphere was unknown. In order to interpret spectral features of this and related complexes,[2] an investigation of the structure of [(L-OHBH)(L-Ala)Co$^{\text{III}}$]·2H_2O was undertaken.

Experimental Section

Preparation. The preparation, purification, and characterization of [Co(L-OHBH)(L-Ala)]·2H_2O are described elsewhere.[2]

Crystal Data. The crystals were obtained, by recrystallization from hot water, in the form of dark red prismatic rods. A single crystal of approximate dimensions 0.2 × 0.2 × 0.4 mm was chosen and mounted on the end of a glass fiber with Duco cement. The crystal was placed on a four-circle diffractometer and initial ω-oscillation photographs were taken using a Polaroid cassette. The photographs indicated that the crystal was indeed single, and from these photographs the coordinates of 15 reflections were then input into our automatic indexing program.[3] The reduced cell and reduced cell scalars that resulted from this program indicated orthorhombic symmetry. Subsequent Polaroid oscillation pictures around each of the three axes in turn verified the presence of *mmm* Laue symmetry. Observed layer line spacings agreed, within experimental error, with those predicted for this cell by the indexing routine. A least-squares refinement of the lattice constants based on the $\pm 2\theta$ measurements of 17 strong high-angle reflections determined by left–right, top–bottom beam splitting on the previously aligned four-circle diffractometer (Mo Kα radiation, λ 0.709 54 Å), at 25 °C, yielded $a = 13.188$ (2), $b = 18.140$ (2), and $c = 7.842$ (1) Å.

Collection and Reduction of X-ray Intensity Data. Data were collected at room temperature using an automated four-circle diffractometer designed and built in the Ames Laboratory and previously described by Rohrbaugh and Jacobson.[4] Within a 2θ sphere of 50° ($(\sin\theta)/\lambda = 0.596$ Å^{-1}) all data in the *hkl* and $hk\bar{l}$ octants were measured. Of these 3880 reflections, 3553 had $I_{\text{obsd}} \geq 3\sigma_I$ and were considered observed. The estimated deviations in the structure factors were calculated by the finite difference method.[5]

The intensity data were then corrected for Lorentz–polarization effects, but no absorption correction was made ($\mu = 9.84$ cm^{-1}). The maximum transmission factor was less than 0.82 while the minimum exceeded 0.67. The estimated error in each intensity was calculated by

$$\sigma_I^2 = C_{\text{T}} + 2C_{\text{B}} + (0.03C_{\text{T}})^2 + (0.03C_{\text{B}})^2$$

where C_{T} and C_{B} represent the total count and background count, respectively, and the factor 0.03 represents an estimate of nonstatistical errors.

Solution and Refinement of Structure. Observed systematic extinctions of *h*00, $h = 2n + 1$, 0*k*0, $k = 2n + 1$, and 00*l*, $l = 2n + 1$, uniquely determine the space group to be $P2_12_12_1$. The position of the cobalt atom was obtained by analysis of a three-dimensional Patterson function. The remaining atoms were found by successive structure factor[6] and electron density map calculations.[7] In addition to positional parameters for all nonhydrogen atoms, the anisotropic

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