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Synthesis, Crystal Structure, and Magnetic Resonance of Dichloro- and Diiodo(5-methyl-1-thia-5-azacyclooctane)palladium(II)

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Treatment of 5-methyl-1-thia-5-azacyclooctane (TACO) with palladium chloride in CH_2Cl_2 gave the complex Pd(TACO)Cl_2. The X-ray crystal structure shows that the ligand is bidentate and adopts a boat–chair configuration. The yellow crystals of Pd($C_7H_{15}NS$)Cl_2 crystallize in the monoclinic system, of space group $P2_1/n$, with lattice constants $a = 7.916$ (4) Å, $b = 11.845$ (5) Å, $c = 11.362$ (5) Å, $\beta = 98.63$ (4)°, and $Z = 4$. Full-matrix least-squares refinement gave $R = 0.019$ for the 1238 reflections having $I > 3\sigma(I)$. This complex is the first example of a bidentate chelate in which both a thioether and a tertiary amine group are coordinated to a metal ion. Since the complex does not dissociate in CH_2Cl_2 and inversion at sulfur or nitrogen cannot occur, we were presented with a unique opportunity to carry out a detailed ^{13}C and ^1H analysis. Decoupling experiments and a 2DFT-J spectrum showed that the complex exhibits six coupled nonequivalent methylene protons and one methyl group. The spectrum was simulated, and all 15 coupling constants involving the methylene protons were determined. The crystal structure of the palladium iodide complex Pd($C_7H_{15}NS$)I_2 was also determined for comparison. The red-violet crystals of this complex belong to the orthorhombic space group *Pbca*, with $a = 12.054$ (3) Å, $b = 13.185$ (4) Å, $c = 15.352$ (3) Å, and $Z = 8$. Full-matrix least-squares refinement yielded $R = 0.075$ for the 1235 reflections having $I > 3\sigma(I)$. It exhibits the same molecular geometry, but the Pd–N and Pd–S bonds are 0.04 (2) and 0.055 (7) Å longer than the corresponding bonds in the chloride complex.

We have shown that mesocyclic molecules with transannular electron pair donors are useful chelating agents for first-row transition-metal ions.[2,3] Structures of complexes in which either secondary diamines or dithioethers are chelated to copper, nickel, and cobalt have been established by both chemical and crystallographic methods.[2,3] Recently, we obtained both a dichloro– and a diiodo–palladium complex of an eight-membered-ring amino thioether, 5-methyl-1-thia-5-azacyclooctane (TACO), and determined that both the tertiary amine and thioether groups are coordinated to palladium. This palladium complex, Pd(TACO)Cl_2, is the first example of a bidentate chelating agent in which both a tertiary amine and a thioether group are bonded to the same element. A planar complex of methionine with $PdCl_2$ is known,[4] but methionine contains a primary amine. Likewise a thiomorpholine (secondary amine) complex of $PdCl_2$ was reported, but due to the ring strain involved in forming the boat conformation of the six-membered ring, it was suggested that thiomorpholine bridges palladium ions to give a polymeric structure.[5]

Unlike previously reported examples of thioether and amine complexes, Pd(TACO)Cl_2 cannot invert about either the sulfur or the nitrogen atoms. Therefore we were presented with a unique opportunity to carry a detailed ^{13}C and ^1H NMR analysis.

Experimental Section

The visible spectra were recorded on a Cary 17 spectrophotometer and the infrared spectra were recorded on a Perkin-Elmer Model 180 grating infrared spectrophotometer.

Space Group Determination and Data Collection for Pd(TACO)Cl_2. Yellow needle-shaped crystals of Pd(TACO)Cl_2 were grown by slow evaporation of a dichloromethane solution. A crystal was cut to dimensions 0.150 × 0.125 × 0.100 mm and mounted along the long axis on the goniometer head of a Syntex $P2_1$ diffractometer equipped with a modified LT-1 low-temperature apparatus. With use of a combination of rotation and axial photographs and the automatic indexing program of the Data General/Nova software, the crystal lattice was determined to be primitive and the space group monoclinic. Quick scans of selected reflections revealed the conditions for reflections $0k0$, $k = 2n$, and $h0l$, $h + l = 2n$; thus the space group was assigned as $P2_1/n$. Careful centering of 20 reflections, including the equivalent $\bar{h}\bar{k}\bar{l}$, $\bar{h}k\bar{l}$, and $h\bar{k}l$ reflections in the range $20° < 2\theta < 40°$ yielded accurate cell dimensions (140 K) of $a = 7.916$ (4) Å, $b = 11.845$ (5) Å, $c = 11.362$ (5) Å, and $\beta = 98.63$ (4)°. For $Z = 4$, the calculated density (140 K) is 2.035 g cm^{-3}, as compared to the value of 2.04 g cm^{-3} (298 K) found by flotation methods.

Intensity data were collected at 140 K with use of graphite-monochromatized Mo Kα radiation of a $2\theta_{max}$ of 45°. Two check reflections monitored throughout data collection indicated no decay. A scan range of 1° and variable speed ω scan of 2–60° min^{-1} were chosen. Background measurements equal in time to the scan time and a 1° offset from peak center were used. A total of 1494 unique reflections were collected. Net intensities were computed from the relationship $I = [P - (LB + RB)]SR$, where P is the peak count, LB and RB are left and right background counts, and SR is the scan rate. The standard deviation in intensity is calculated as $\sigma(I) = ([P + LB + RB)^{1/2}Sr]^2 + (FI)^2)^{1/2}$, where F is the average of the standard deviation of check reflections ($F = 0.011$). Intensity data were corrected for Lorentz and polarization effects. For a crystal of the dimensions given and $\mu_{Mo\,K\alpha} = 23.5$ cm^{-1}, the range of absorption factors is 1.45–1.54, resulting in an error in F_o of ±3%; no absorption correction was applied.

Space Group Determination and Data Collection for Pd(TACO)I_2. Red-violet plates of Pd(TACO)I_2 were isolated from a dichloromethane solution. A crystal of dimensions 0.10 × 0.10 × 0.02 mm was selected for data collection and positioned in the cold stream of the diffractometer. Following the same procedure as for the chloride, and on the basis of the conditions limiting reflections $hk0$, $h = 2n$, $h0l$, $l = 2n$, and $0kl$, $k = 2n$, the space group was established as orthorhombic (*Pbca*). A least-squares fit of 20 reflections in the range $30° < 2\theta < 40°$ yielded cell dimensions of $a = 12.054$ (3) $b = 13.185$ (4), and $c = 15.352$ (3) Å. The calculated density (140 K) for $Z = 8$ is 2.75 g cm^{-3}, while that determined by flotation (298 K) is 2.71 g cm^{-3}. X-ray data were collected essentially the same as for the chloride, except that a 1.3° ω scan was employed, resulting in 1597 unique data. Although the absorption correction is more severe for this crystal ($\mu_{Mo\,K\alpha} = 67.2$ cm^{-1} and $A = 1.25$–3.0), no correction was applied to the data. The usual Lorentz and polarization corrections were applied.

NMR Parameters. Proton spectra were obtained at 360 MHz on a Nicolet NT360 NMR spectrometer in the pulse Fourier transform mode. Homonuclear $^1H\{^1H\}$ decoupling and variable temperature were computer controlled. Nuclear Overhauser experiments (NOE) employed 10° flip angles and 20-s delays with the second irradiation field turned off during the data acquisition. Samples were prepared for NOE experiments by Argon flush. NOE spectra were computed by subtracting an off resonance control from the on resonance irradiation experiment. Quadrature detection was employed and spectral

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(1) (a) Department of Chemistry. (b) Nuclear Magnetic Resonance Facility.

(2) Musker, W. K.; Hill, N. L. *Inorg. Chem.* **1972**, *11*, 710–717.

(3) Wolford, T. W. Ph.D. Dissertation, University of California, Davis, CA, 1977.

(4) Warren, R. C.; McConnell, J. F.; Stephenson, N. C. *Acta Crystallogr., Sect. B* **1970**, *B26*, 1402–1407.

(5) Allen, A.; Johnson, N. P.; Rosevear, D. T.; Wilkinson, W. *J. Chem. Soc. A* **1970**, 2137–2142.

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Table I. Final Atomic Fractional Coordinates and Temperature Factors[a] for $Pd(TACO)Cl_2$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	0.072 36 (4)	0.357 38 (2)	0.179 14 (3)	0.64 (2)	0.84 (2)	0.82 (2)	0.00 (1)	−0.07 (1)	−0.09 (1)
Cl(1)	0.064 75 (14)	0.470 60 (9)	0.343 23 (9)	1.63 (5)	1.73 (4)	1.45 (4)	0.28 (4)	−0.22 (4)	−0.70 (4)
Cl(2)	0.365 48 (13)	0.390 05 (9)	0.198 68 (9)	0.79 (4)	1.55 (4)	1.37 (4)	−0.18 (3)	−0.11 (3)	0.18 (3)
S	−0.215 60 (13)	0.345 51 (9)	0.167 42 (9)	0.80 (4)	1.34 (4)	1.30 (5)	0.02 (3)	0.10 (4)	−0.09 (3)

atom	x	y	z	B_{iso}, Å^2	atom	x	y	z	B_{iso}, Å^2
N	0.0607 (4)	0.2542 (3)	0.0274 (3)	0.92 (6)	H(5)	0.080 (5)	0.086 (3)	0.059 (4)	0.9 (8)
C(1)	−0.2712 (6)	0.1966 (4)	0.1478 (4)	1.40 (7)	H(6)	−0.087 (5)	0.119 (3)	−0.030 (4)	0.6 (8)
C(2)	−0.1166 (6)	0.1235 (4)	0.1454 (4)	1.34 (8)	H(7)	−0.415 (7)	0.403 (4)	0.016 (4)	2.4 (10)
C(3)	−0.0176 (6)	0.1396 (3)	0.0414 (4)	1.28 (8)	H(8)	−0.256 (7)	0.474 (4)	0.017 (4)	2.6 (11)
C(4)	−0.2887 (6)	0.3989 (4)	0.0193 (4)	1.34 (8)	H(9)	−0.266 (7)	0.377 (4)	−0.148 (5)	2.8 (11)
C(5)	−0.2271 (6)	0.3320 (4)	−0.0807 (4)	1.21 (7)	H(10)	−0.280 (6)	0.264 (4)	−0.086 (4)	2.0 (10)
C(6)	−0.0362 (5)	0.3192 (4)	−0.0755 (4)	1.16 (7)	H(11)	0.012 (5)	0.385 (4)	−0.073 (3)	0.3 (8)
C(7)	0.2312 (6)	0.2319 (4)	−0.0079 (4)	1.49 (8)	H(12)	−0.024 (6)	0.276 (4)	−0.152 (4)	2.1 (10)
H(1)	−0.350 (6)	0.187 (4)	0.077 (4)	1.6 (9)	H(13)	0.293 (5)	0.202 (3)	0.052 (4)	0.5 (8)
H(2)	−0.329 (6)	0.182 (4)	0.216 (4)	1.8 (10)	H(14)	0.284 (6)	0.308 (4)	−0.025 (4)	1.7 (9)
H(3)	−0.150 (5)	0.045 (4)	0.140 (4)	1.1 (8)	H(15)	0.222 (6)	0.180 (4)	−0.077 (4)	2.5 (11)
H(4)	−0.039 (6)	0.131 (3)	0.213 (4)	1.2 (9)					

[a] The anisotropic temperature factor is of the form $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + ... + 2klb^*c^*B_{23})]$.

resolution was 0.3 Hz for all spectra including two-dimensional J spectra. Temperature control was precise to ±0.1 °C and accurate to ±1 °C. Chemical shifts are referenced to Me_4Si (δ(methylene-d_2 chloride) 5.32).

Two-dimensional J spectra[6,7] were performed with use of the Hahn spin–echo method[8] with the delay incremented by 12.5 ms on each of 64 successive experiments (8 K data points each). Five-second pulse repetition was employed, and each spectrum was time averaged for 52 free induction decays. Prior to the first Fourier transformation (chemical shift domain), the time domain spectra were apodized with an exponential weighting function (0.5-Hz line broadening). Prior to the second Fourier transformation (coupling constant domain), the spectra were resolution enhanced with a sine function, zero filled once, Fourier transformed, and computed as amplitude spectra.

Carbon-13 spectra were obtained at 50 MHz on a Nicolet NT 200 wide-bore spectrometer and at 25 MHz with a JEOL 100 in the pulse Fourier transform mode. Broad-band proton decoupling was employed with two power levels. One low power was applied during the delay which was sufficient to sustain the nuclear Overhauser effect; another higher power level was applied during the aquisition period to decouple carbon resonances from protons. Spectral resolution was 1 Hz, and pulse recycle times were 2 s. Spectral simulations of 360-MHz proton spectra were computed with use of the Nicolet software adaptation of LACOON3.[9]

Synthesis of TACO. TACO was prepared by a modification of the method of Leonard and Yethon.[10] One of the reagents, 3-(dimethylamino)propanethiol hydrochloride, was a gift from Evans Chemetics, Inc. ^1H NMR (CD_2Cl_2): δ 1.82 (pent, 4, CH_2), 2.27 (s, 3, NCH_3), 2.53 (t, 4, CH_2S), 2.72 (t, 4, CH_2N). ^{13}C NMR (CD_3CN): δ 32.8 ($C_{2,8}$), 30.1 ($C_{3,7}$), 51.6 ($C_{4,6}$) 43.5 (CH_3N).

Synthesis of $Pd(TACO)Cl_2$. $Pd(TACO)Cl_2$ was prepared by treating a suspension of 1 equiv (0.172 g, 0.97 mmol) of $PdCl_2$ in dichloromethane (20 mL) with a solution of 1 equiv of 5-methyl-1-thia-5-azacyclooctane (0.162 g, 1.11 mmol) in 5 mL of dichloromethane. The mixture was stirred for 7 days. As the reaction proceeded, the solution became yellow-orange. Dichloromethane was removed by evaporation to leave a yellow residue. The residue was washed with ether and then placed in the thimble of a Soxhlet and extracted with CH_2Cl_2 to give a mixture of yellow and red crystals of $Pd(TACO)Cl_2$ in quantitative yield. The red crystals were twinned. IR (Nujol, CsI plates): 309, 317 cm^{-1} (PdCl). Vis (Nujol, quartz plates): λ_{max} = 392 nm. Vis (CH_2Cl_2): λ_{max} (ε): 392 (581), 323 nm (1075). ^1H NMR (CD_2Cl_2): δ 2.20 (m, 2), 2.45 (m, 4), 2.72 (m, 2) 2.92 (m, 5), 3.16 (m, 2). ^{13}C NMR (CH_2Cl_2 with 20% $CDCl_3$): δ 60.25 (2), 59.95 (1), 29.32 (2), 27.27 (2). Anal. Calcd for $PdC_7H_{15}NSCl_2$: C, 26.04; H, 4.65. Found: C, 26.46; H, 4.35.

Synthesis of $Pd(TACO)I_2$. $Pd(TACO)I_2$ was prepared by treating a suspension of 1 equiv of $Pd(TACO)Cl_2$ in 20 mL of dichloromethane with 10 equiv of KI. The solution rapidly became dark red. The solution was stirred for 24 h, filtered, and evaporated to leave a black-red residue. The residue was recrystalized from dichloromethane. ^1H NMR (CD_2Cl_2): δ 2.2 (s, NCH_3) 1.5–3.5 (br).

Solution and Refinement of the Structure of $Pd(TACO)Cl_2$. The scattering factors applied to the atoms were those for neutral Pd, Cl, S, N, and C given by Cromer and Waber,[11a] and those for H were from the tabulation of Stewart et al.[12] Corrections for anomalous scattering were applied to Pd, Cl, and S.[11b] The programs used in data reduction and refinement are from a locally developed program library. All computations were performed on a Data General Eclipse computer.

The position of the palladium atom was determined from a Patterson map, and the remaining nonhydrogen atoms were located on Fourier maps. Full-matrix least-squares refinement of these atomic positions using isotropic thermal parameters and a Hughes[13] weighting scheme yielded an $R = 0.037$. The function minimized during refinement is $\sum w(kF_o - |F_c|)^2$, where k is a scale factor and w is the weight. The agreement factor, R, is defined as $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. The use of anisotropic thermal parameters for Pd, Cl(1), Cl(2), and S resulted in an R of 0.030. Location of the 15 hydrogen atoms from a difference Fourier map and inclusion of these in full-matrix least-squares refinement resulted in a final of 0.019. The last shift in any parameter was less than $^1/_{10}$ the esd in the final cycle of refinement. The number of parameters being refined was 129; the number of reflections was 1238, including only those for which $I > 3\sigma(I)$. Final atomic fractional coordinates and thermal parameters, together with estimated standard deviations, are given in Table I.

Solution and Refinement of the Structure of $Pd(TACO)I_2$. The tabulations for scattering factors and anomalous dispersion were the same as for the chloride. Corrections for anomalous scattering were applied to Pd, I, and S. Solution of the structure of $Pd(TACO)I_2$ followed from an application of the Sayre[14] equation, as programmed by Long.[15] Successive Fourier maps revealed the positions of all the nonhydrogen atoms. Full-matrix least-squares refinement using anisotropic thermal parameters for Pd, I(1), I(2), and S yielded an R of 0.075. A total of 1235 reflections having $I > 3\sigma(I)$ was used in the refinement of these 69 parameters. No attempt was made to include hydrogen atoms since the crystal was of poorer quality and the absorption effects more severe than for the chloride. In the final cycle of refinement no parameter shifted more than 0.01 the ESD.

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(6) Aue, W. P.; Karhan, J.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 4226–4227.

(7) Bodenhausen, G.; Freeman, F.; Niedermeyer, R.; Turner, D. L. *J. Magn. Reson.* **1977**, *26*, 133–164.

(8) Hahn, E. L. *Phys. Rev.* **1950**, *80*, 580–594.

(9) Castellano, S.; Bothner-By, A. A. *J. Chem. Phys.* **1964**, *41*, 3863–3869.

(10) Leonard, N.; Yethon, A. *Tetrahedron Lett.* **1965**, 4259–4263.

(11) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) pp 99–101; (b) pp 149–150.

(12) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–3187.

(13) Hughes, E. W. *J. Am. Chem. Soc.* **1941**, *63*, 1737–1752.

(14) Sayre, D. *Acta Crystallogr.* **1952**, *5*, 60–65.

(15) Long, R. E. Ph.D. Dissertation, University of California, Los Angles, CA, 1965.

Table II. Final Atomic Fractional Coordinates and Temperature Factors for Pd(TACO)I_2

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	0.1406 (1)	0.1253 (1)	0.5589 (1)	1.43 (7)	0.50 (7)	3.11 (9)	0.08 (5)	−0.48 (6)	−0.27 (5)
I(1)	0.1268 (1)	0.1733 (1)	0.3934 (1)	1.86 (7)	2.06 (7)	2.8 (7)	−0.11 (5)	−0.33 (5)	−0.02 (5)
I(2)	−0.0225	0.2499 (1)	0.5882 (1)	1.61 (7)	1.47 (7)	4.26 (9)	0.33 (5)	0.44 (6)	−0.33 (5)
S	0.1450 (5)	0.1087 (5)	0.7095 (4)	2.7 (3)	2.8 (3)	3.2 (3)	0.3 (2)	−0.2 (2)	−0.2 (2)

atom	*x*	*y*	*z*	B_{iso}, Å^2	atom	*x*	*y*	*z*	B_{iso}, Å^2
N	0.259 (2)	0.004 (2)	0.552 (1)	2.5 (4)	C(4)	0.110 (2)	−0.025 (2)	0.726 (2)	3.3 (5)
C(1)	0.291 (2)	0.109 (2)	0.735 (2)	3.4 (5)	C(5)	0.192 (2)	−0.094 (2)	0.685 (2)	3.3 (5)
C(2)	0.367 (2)	0.119 (2)	0.656 (1)	1.5 (4)	C(6)	0.206 (2)	−0.091 (2)	0.587 (2)	3.0 (5)
C(3)	0.368 (2)	0.028 (2)	0.595 (2)	3.4 (5)	C(7)	0.290 (2)	−0.021 (2)	0.460 (2)	3.6 (5)

Table III. Distances (Å) between Selected Atoms in Pd(TACO)X_2 (X = Cl, I)

atoms	Pd(TACO)Cl_2	Pd(TACO)I_2
Pd–X(1)	2.305 (1)	2.601 (2)
Pd–X(2)	2.330 (1)	2.624 (2)
Pd–S	2.268 (1)	2.323 (7)
Pd–N	2.104 (3)	2.14 (2)
S–C(1)	1.823 (4)	1.81 (3)
S–C(4)	1.810 (4)	1.83 (3)
N–C(3)	1.510 (5)	1.51 (3)
N–C(6)	1.510 (5)	1.51 (3)
N–C(7)	1.489 (6)	1.49 (3)
C(4)–C(5)	1.524 (6)	1.48 (4)
C(5)–C(6)	1.510 (6)	1.51 (4)
C(1)–C(2)	1.503 (7)	1.52 (3)
C(2)–C(3)	1.524 (7)	1.53 (3)
S···N	3.087 (3)	3.11 (2)
Pd···C(2)	3.144 (5)	3.12 (2)
Pd···C(5)	3.510 (4)	3.53 (3)
Pd···C(7)	3.018 (5)	3.04 (3)

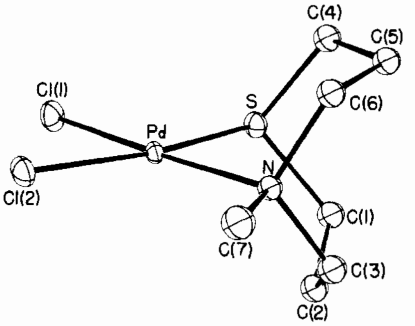

Figure 1. View of Pd(TACO)Cl_2 showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. The numbering scheme for Pd(TACO)I_2 is identical.

A difference map computed at this stage revealed some residual electron density in the vicinity of the heavy atoms but no other features larger than a hydrogen atom. Table II lists the atomic positional and thermal parameters for this complex.

Results

Crystal Structure of Pd(TACO)Cl_2. As shown in Figure 1 TACO acts as a bidentate ligand by coordinating to the palladium atom through both the nitrogen and sulfur atoms and adopting a boat–chair configuration. The four atoms Cl(1), Cl(2), S, and N are in a planar arrangement about the palladium atom. The calculated distances from the best least-squares plane to these five atoms are as follows: Pd, −0.033; Cl(1), −0.023; Cl(2), +0.038; N, −0.022; S, +0.040 Å. Tables III and IV list the bond distances and angles for this molecule.

The results of the crystal structure determination show that the N–Pd–Cl(2) angle is greater than 90° (95.5°). In contrast, the N–Pd–Cl angle in dichloro(methionine)palladium(II) is 85.3°.[4] The greater angle in Pd(TACO)Cl_2 may be attributed to a repulsion between the *N*-methyl group and the Cl(2) atom since H(14) of the methyl group is only 2.707 Å from Cl(2). The N···S distance of 3.08 Å as compared to 3.21 Å in the Pd(MtH)Cl_2 complex also reflects this difference. Other bond distances in the two complexes are quite similar, with the exception that the value of 2.104 (3) Å for the Pd–N distance in the TACO complex is 0.043 Å longer than that reported for the methionine complex. The Pd–Cl(2) distance is 0.025 (1) Å longer than the Pd–Cl(1) distance which may reflect the greater trans effect of sulfur than nitrogen, although the steric effect of the CH_3–Cl(2) interaction may also cause bond lengthening.

Table IV. Interatomic Angles (Deg) for Pd(TACO)X_2 (X = Cl, I)

atoms	Pd(TACO)Cl_2	Pd(TACO)I_2
X(1)–Pd–X(2)	88.4 (1)	88.1 (1)
X(1)–Pd–S	86.3 (1)	84.5 (2)
S–Pd–N	89.8 (1)	88.1 (6)
N–Pd–X(2)	95.5 (1)	99.8 (5)
X(1)–Pd–N	175.5 (1)	169.9 (5)
X(2)–Pd–S	173.4 (1)	171.1 (2)
C(4)–S–C(1)	100.8 (2)	102 (1)
C(1)–S–Pd	106.8 (2)	104 (1)
C(4)–S–Pd	102.2 (2)	103 (1)
C(3)–N–C(6)	111.8 (3)	112 (2)
C(3)–N–C(7)	105.8 (3)	104 (2)
C(6)–N–C(7)	104.9 (3)	105 (2)
C(3)–N–Pd	113.8 (2)	114 (2)
C(6)–N–Pd	107.1 (2)	109 (1)
C(7)–N–Pd	113.2 (3)	113 (2)
S–C(4)–C(5)	114.7 (3)	112 (2)
C(4)–C(5)–C(6)	117.0 (4)	119 (2)
C(5)–C(6)–N	118.0 (4)	115 (2)
N–C(3)–C(2)	117.4 (3)	115 (2)
C(3)–C(2)–C(1)	117.2 (4)	115 (2)
C(2)–C(1)–S	112.2 (3)	115 (2)

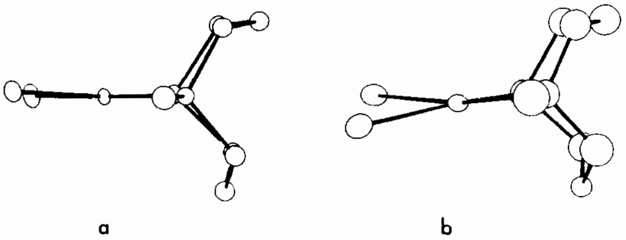

Figure 2. Edge-on views of (a) Pd(TACO)Cl_2 and (b) Pd(TACO)I_2.

The possibility of dimer formation prompted the synthesis and structure determination of Pd(TACO)I_2. Contrary to expectations, the complex is a monomer with TACO coordinated in the same manner as in Pd(TACO)Cl_2. Edge-on views of the two complexes are shown for comparison in Figure 2. The ellipsoids are scaled to enclose 50% probability. It can be seen than, while the iodide structure is less well determined, the overall geometry is quite similar in the two complexes. The other noticeable feature is the somewhat greater tetrahedral distortion of the least-squares plane surrounding the palladium atom. For the best plane comprised of these five atoms, the sum of the squares of the deviations

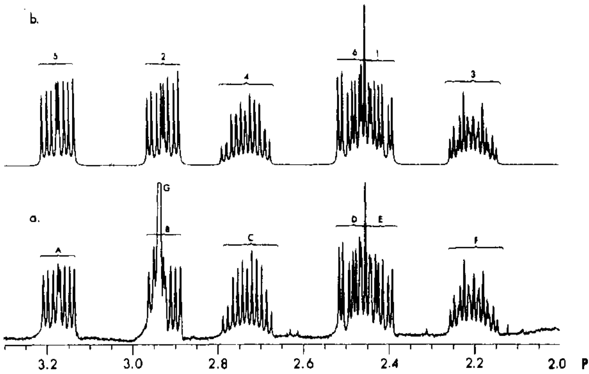

Figure 3. (a) 360-MHz ^1H NMR spectrum of $Pd(TACO)Cl_2$. (b) Computer-simulated ^1H NMR spectrum of $Pd(TACO)Cl_2$. The *N*-methyl group is not included in the simulation. See Figure 4 for proton numbering.

is 0.005 Å for the chloride and 0.065 Å for the iodide complex. The individual distances for the iodide complex alternate in going around the square as follows: I(1), −0.127; I(2), +0.104; N, −0.137; S, +0.136; Pd, −0.024 Å. This distortion probably arises from the intramolecular repulsion of cis iodide ligands rather than from packing forces, since no short intermolecular contacts occur. Selected angles and bond distances are found in Tables III and IV. The N–Pd–I angle (99.8°) is large and can again be attributed to a repulsion between the *N*-methyl group and the halogen. As with the chloride complex, the palladium–halogen distance trans to the sulfur is 0.023 (2) Å longer than the palladium–halogen distance trans to the nitrogen. The Pd–N and Pd–S distances in the iodide complex are 0.04 (2) and 0.055 (7) Å longer than the corresponding distances in the chloride complex. These larger distances are consistent with the larger trans effect of iodide compared to chloride.

NMR Data. The ^{13}C NMR spectrum of $Pd(TACO)Cl_2$ in dichloromethane exhibits three resonances of double intensity and one resonance of single intensity. The ^1H NMR spectrum of $Pd(TACO)Cl_2$ in CD_2Cl_2 is shown in Figure 3a. In contrast to the simple spectrum of the free ligand the palladium chloride complex exhibits an interesting and highly complicated splitting pattern. The pattern and chemical shifts are unchanged when the sample is cooled to −45 °C. Lowering the temperature to −80 °C resulted in coalescence of all of the multiplets.

The ^{13}C NMR spectrum clearly shows that the palladium complex does not isomerize or dissociate in solution since there are no additional resonances in the spectrum of the complex than there are in the free ligand and each resonance is shifted upon complexation. The fact that there are only three resonances for the ring carbons indicates that the ligand is fluxional in solution, and carbons 1–3 are magnetically equivalent to carbons 4–6, respectively.

The ^1H NMR spectrum of $Pd(TACO)Cl_2$ was analyzed in detail by use of decoupling experiments and the generation of a 2DFT-J spectrum.[6,7] The decoupling experiments suggest that there are seven types of resonances (A–G), with two resonances overlapping. See Figure 3a. Six resonances, A–F, are expected for the six nonequivalent hydrogens of the trimethylene bridge. The seventh resonance is due to the methyl group on the nitrogen atom. The 2DFT-J spectrum shown in Figure 4 clearly shows that resonances A, B, D, and E exhibit similar eight-line multiplets. Decoupling experiments show that resonance A is strongly coupled to D, weakly coupled to C and F, and not coupled to B or E. In a similar manner, resonance B is strongly coupled to E, weakly coupled to C and F, and not coupled to A or D. Resonance C is strongly coupled to resonance F. Therefore it is apparent that the pairs of resonances A and D, B and E, and C and F are each due to geminal protons. Since decoupling of resonances C and F affects resonances A, B, D, and E, resonances C and F must be due to the protons β to the nitrogen and sulfur atoms. A definitive assignment of resonances due to protons adjacent to the sulfur atoms and those which are due to the protons adjacent to the nitrogen atoms was accomplished by observing a nuclear Overhauser enhancement (NOE) between the *N*-methyl protons and resonances A and D. Saturation of the *N*-methyl group should affect the intensity of the adjacent protons. A positive NOE effects would be expected for small molecules whereas a negative NOE effect would be expected for large molecules.[16] Saturation of the *N*-methyl of the free ligand resulted in a positive NOE effect of approximately 9%. Saturation of the *N*-methyl of the palladium complex under identical conditions resulted in a positive NOE of approximately 5% for resonance A and of approximately 4% for resonance D. Therefore resonances A and D can be assigned to the protons adjacent to the nitrogen atom, and resonances B and E must be the protons adjacent to the sulfur atom.

Table V. Proton Chemical Shifts and Coupling Constants for $Pd(TACO)Cl_2$ in CD_2Cl_2 Referenced to Me_4Si

resonance	freq, ppm	resonance	freq, ppm
A	3.169	D	2.478
B	2.922	E	2.424
C	2.728	F	2.200

resonance		coupling const, Hz
exptl	assigned	
$J_{A,B}$	$J_{2,5}$	0.0
$J_{A,C}$	$J_{2,4}$	4.37
$J_{A,D}$	$J_{1,2}$	−14.50
$J_{A,E}$	$J_{2,6}$	0.0
$J_{A,F}$	$J_{2,3}$	8.30
$J_{B,C}$	$J_{4,5}$	3.77
$J_{B,D}$	$J_{1,5}$	0.0
$J_{B,E}$	$J_{5,6}$	−14.50
$J_{B,F}$	$J_{3,5}$	8.30
$J_{C,D}$	$J_{1,4}$	8.30
$J_{C,E}$	$J_{4,6}$	8.25
$J_{C,F}$	$J_{3,4}$	−15.90
$J_{D,E}$	$J_{1,6}$	0.0
$J_{D,F}$	$J_{1,3}$	3.50
$J_{E,F}$	$J_{3,6}$	3.00

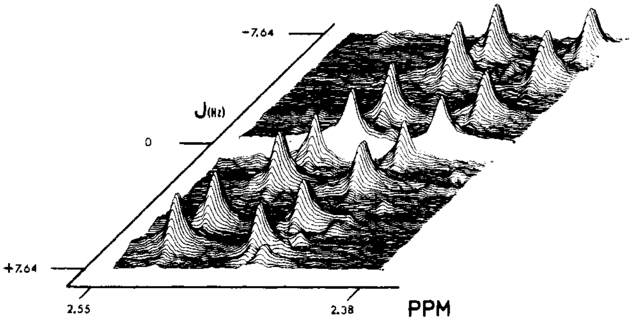

Figure 4. Section of 2DFT-J spectrum of $Pd(TACO)Cl_2$.

From the analysis discussed above and the 2DFT-J spectrum, the coupling constants could be easily measured. The coupling constants and chemical shifts are shown in Table V.

The ^1H NMR spectrum of the $Pd(TACO)I_2$ complex in dichloromethane exhibits broad absorptions, with the exception of one resonance, at δ 2.2, which is attributed to the *N*-methyl resonance. This resonance is not shifted from that of the free

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[16] (a) Balaram, P.; Bothner-By, A. A., Dadok, J. *J. Am. Chem. Soc.* **1972**, *94*, 4015–4017. (b) Balaram, P.; Bothner-By, A. A.; Breslow, E. *Ibid.* **1972**, *94*, 4017–4018. (c) Solomon, I. *Phys. Rev.* **1955**, *99*, 559–565.

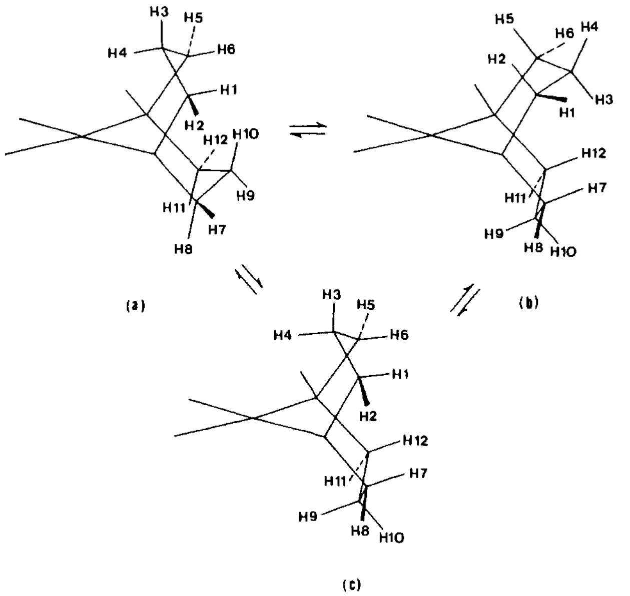

Figure 5. Possible conformations for Pd(TACO)Cl_2 in solution.

ligand, indicating that TACO behaves as a monodentate ligand with only the sulfur atom coordinated to palladium.

Discussion

Previous examples of palladium and platinum complexes having coordinated amine and thioether groups exhibit complicated proton NMR spectra. In these cases the complexity of the spectra has been attributed to an inversion process about either the sulfur or nitrogen atoms as well as to the nonequivalence of the hydrogen atoms.[17-20] Since TACO is both a cyclic and a bidentate ligand, there can be no inversion without prior dissociation of the ligand, and in this molecule no dissociation occurs.

The reason that each methylene proton is nonequivalent can be seen by an examination of the structure of the complex. Figure 5 shows the structure of the palladium complex including the hydrogen atoms.

Molecular models show that to minimize steric repulsions between hydrogen atoms either a boat–chair or a chair–chair conformation is required. It can be seen that the solution structure is in dynamic equilibrium since six rather than 12 resonances are observed. Further evidence for a dynamic equilibrium is obtained from the observation that all of the multiplets coalesce at −80 °C.

Since the magnitude of the coupling constants is proportional to the $\cos^2$ of the dihedral angle between vicinal protons,[21] an estimate of the conformation of the palladium complex can be made. The large coupling constants J(B, F), J(E, C), J(F, A), J(C, D) of 8.30, 8.25, 8.30, and 8.30 Hz, respectively, indicates that protons B and F, E and C, F and A, and C and D are periplanar. In a similar manner, the coupling constants J(B, C), J(E, F), J(F, D), and J(C, A) of 3.77, 3.00, 3.50, and 4.37 Hz, respectively, indicate that the protons B and C, E and F, F and D, and C and A are in an anticlinal relationship. Spectral simulation yielded an exact reproduction of the experimental spectrum (Figure 3b).

Table VI. Dihedral Angles (Deg)

atoms	conformation a	b	c
H(1)-H(3)	61.0	50.4	61.0
H(1)-H(4)	179.7	66.6	179.7
H(2)-H(3)	61.6	167.8	61.6
H(2)-H(4)	57.1	50.7	57.1
H(3)-H(6)	56.7	57.6	56.7
H(3)-H(5)	60.8	178.0	60.8
H(4)-H(5)	51.7	56.8	51.7
H(4)-H(6)	169.2	63.6	169.2
H(7)-H(10)	50.4	61.0	61.0
H(7)-H(9)	66.6	179.7	179.7
H(8)-H(10)	167.8	61.6	61.6
H(8)-H(9)	50.7	57.1	57.1
H(10)-H(12)	57.6	56.7	56.7
H(10)-H(11)	178.0	60.8	60.8
H(9)-H(11)	56.8	51.7	51.7
H(9)-H(12)	63.6	169.2	169.2

The assignment of proton resonances is based on the assumption that protons close to the palladium atom are less shielded. With use of this rationale, resonances A–C are assigned to protons 2, 5, and 4 (Figure 5). These assignments are consistent with the NOE and coupling constant data. Spectral simulation yielded an exact reproduction of the experimental spectrum (Figure 3b). The remaining spectral assignments are found in Table V.

The possible conformations that may exist for the Pd(TACO)Cl_2 complex in solution are shown in Figure 4. Considering the ligand itself, there are two possible boat–chain conformations, a and b, and one chair–chair conformation, c. Due to hydrogen repulsions the boat–boat conformation is less likely and not considered. In solution these three conformations may be in equilibrium. With use of the X-ray data in Table I dihedral angles were calculated for these conformations (Table VI). This data shows that for conformation a, H(1)–H(4) and H(4)–H(6) are periplanar, and for conformation b, H(2)–H(3) and H(3)–H(5) are periplanar. Hydrogen atoms H(1)–H(3), H(2)–H(4), H(3)–H(6), and H-(4)–H(5) are anticlinal in all conformations. The other six hydrogen atoms are equivalent on the NMR time scale so that H(1), H(2), H(3), H(4), H(5), and H(6) are equivalent to H(7), H(8), H(10), H(9), H(11), and H(12), respectively. Since the coupling constants are proportional to the $\cos^2$ of the dihedral angle, it can be seen that, if there were a significant amount of the chair–chair conformation c, the average coupling constant of $J_{H(1)-H(4)}$ and $J_{H(4)-H(6)}$ would be much larger than $J_{H(2)-H(3)}$ and $J_{H(3)-H(6)}$. Experimentally these coupling constants are similar, and conformation c can therefore be ruled out. With the same reasoning, the experimental coupling constants are best fitted by an equal population of conformations a and b. These results indicate that the boat–chair conformation exists in solution, as well as in the solid state.

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Registry No. Pd(TACO)Cl_2, 76998-86-2; Pd(TACO)I_2, 76998-85-1.

Supplementary Material Available: Listings of structure factors for Pd($C_7H_{15}NS$)Cl_2 and Pd($C_7H_{15}NS$)I_2 (19 pages). Ordering information is given on any current masthead page.

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(17) Hartley, F. R.; Murray, S. G.; Levason, W.; Soutter, H. E.; McAuliffe, C. A. *Inorg. Chim. Acta* **1979**, *35*, 265–277 and references therein.

(18) (a) Haake, P.; Turley, P. C. *J. Am. Chem. Soc.* **1967**, *89*, 4611–4616. (b) Turley, P. C.; Haake, P. *Ibid.* **1967**, *89*, 4617–4621.

(19) (a) Appleton, T. G.; Hall, J. R. *Inorg. Chem.* **1970**, *9*, 1807–1814. (b) Appleton, T. G.; Hall, J. R. *Ibid.* **1971**, *10*, 1717–1725.

(20) Jezowska-Trzebiatowska, B.; Allain, A.; Kozlowski, H. *Inorg. Nucl. Chem. Lett.* **1979**, *15*, 279–284.

(21) Kowaleski, J. "Progress in NMR Spectroscopy"; Emsley, Feeney, Sutcliff, Eds.; Pergamon Press: Oxford, 1977; Vol. II, pp 1–78.