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Notes

Coordination Chemistry of the Tetrathiacyclophane Ligand 2,5,14,17-Tetrathia[6.6]-*o*-cyclophane, TT[6.6]OC. Synthesis and Structures of TT[6.6]OC and [Pt(TT[6.6]OC)][BF$_4$]$_2$

Stephen J. Loeb* and Karen D. L. Smith

Department of Chemistry and Biochemistry,
University of Windsor, Windsor, Ontario, Canada N9B 3P4

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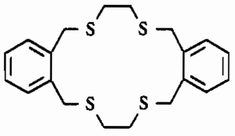
Perhaps more than any other type of macrocyclic ligand, the ability of tetradentate thioether macrocycles to complex transition metal ions can be directly related to the free ligand conformation.[1-4] This derives from several important conformational criteria. First is the strong preference of CS–CC and SC–CS bonds to favor *gauche* and *anti* dispositions respectively.[5,6] This results in cyclic ligands containing the $-SCH_2CH_2SCH_2CH_2S-$ linkage invariably having exodentate conformations with sulfur lone pairs directed away from the macrocyclic cavity.[4,5] Second is the fact that to a lesser extent CC–CS and CC–CC bonds also favor *anti* conformations which means that the introduction of extra methylene groups into the backbone of the macrocycle will have little overall effect on the exodentate conformation.[4,10] For example, 1,4,7,10-tetrathiacyclododecane,[5,7] 12S4 and 1,4,8,11-tetrathiacyclotetradecane,[8] 14S4 both have quadrangular structures with all four S atoms exodentate. Thirdly, the introduction of a *gem*-dimethyl group in place of the central methylene group of a propyl linkage to give $-SCH_2C(CH_3)_2CH_2S-$ markedly effects the 1,4 repulsions at *gauche* C–S bonds and favors endodentate S atoms.[9,10] The result is that 6,6-dimethyl-1,4,8,-11-tetrathiacyclotetradecane, Me$_2$14S4, contains two exodentate and two endodentate S atoms and 6,6,13,13-tetramethyl-1,5,9,-13-tetrathiacyclohexadecane, Me$_4$16S4, has all four S donor atoms endodentate.[10]

Our studies on the coordination chemistry of thiacyclophane molecules has shown that introduction of an *o*-xylyl fragment has a similar, if less dramatic, effect on the macrocyclic conformation as that exhibited by the *gem*-dimethyl groups.[11-15] Herein, we describe the synthesis and structure of the tetrathiacyclophane 2,5,14,17-tetrathia[6.6]-*o*-cyclophane, TT[6.6]OC, as well as the synthesis of homoleptic square planar complexes with Pd(II) and Pt(II) including the X-ray structure of [Pt(TT[6.6]OC)][BF$_4$]$_2$.



TT[6.6]OC

Experimental Section

α,α′-Dibromo-*o*-xylene, *o*-xylene-α,α′-dithiol, 2-mercaptoethanol and all deuterated solvents were purchased from Aldrich and used as received. All reactions were conducted under an atmosphere of N$_2$ using standard Schlenk techniques and all solvents were degassed prior to use. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 300.1 and 75.4 MHz respectively, on a Bruker AC300 spectrometer locked to the deuterated solvent. Infrared spectra were recorded on a Nicolet 5DX FTIR spectrometer. Elemental analyses were performed by Microanalytical Services, New Westminister, British Columbia, Canada.

Preparation of *o*-Xylylenebis(1-hydroxy-3-thiapropane). 2-Mercaptoethanol (14.8 g, 0.189 mol) was added to anhydrous ethanol (300 mL) in which Na metal (4.36 g, 0.189 mol) had been dissolved and this solution stirred for one hour. α,α′-Dibromo-*o*-xylene (25.0 g, 0.095 mol) dissolved in anhydrous ethanol (250 mL) was added dropwise over two hours while the solution was maintained at reflux. The reaction mixture was then refluxed for a further two hours, cooled to room temperature, filtered, and the solvent removed in vacuo yielding an orange-yellow oil which was extracted with diethyl ether (400 mL). The ether extracts were filtered and the solvent removed to yield a colorless oil which solidified upon standing at 10 °C to give a waxy solid. Yield: 22.1 g (90%). IR (neat): ν(OH) 3380 cm^{-1} (vs, br). ^{1}H NMR (CDCl$_3$): δ 7.23 (m, 4H, aromatic), 3.90 (s, 4H, benzylic), 3.69 (q, 4H, CH$_2$O), 2.86 (t, 2H, OH), 2.67 (t, 4H, SCH$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 135.95, 130.50, 127.42 (aromatic), 60.61 (CH$_2$O), 34.82 (CH$_2$S), 33.29 (benzylic). Anal. Calcd for $C_{12}H_{18}O_2S_2$: C, 55.78; H, 7.02; S, 24.81. Found: C, 55.76, H, 7.07, S, 25.00.

Preparation of *o*-Xylylenebis(1-chloro-3-thiapropane). *Extreme Caution! This compound is a severe vesicant!* The diol *o*-xylylenebis(1-hydroxy-3-thiapropane), prepared as described above, (17.74 g, 0.069 mol) was dissolved in CH$_2$Cl$_2$ (30 mL). Thionyl chloride (19.60 g, 0.165 mol; 20% excess) was added slowly via syringe and the mixture stirred for one hour. A saturated solution of NaHCO$_3$ (30 mL) was added and this mixture was stirred vigorously for a further hour. The two-phase reaction mixture was then filtered through phase separation paper and the organic layer dried over anhydrous MgSO$_4$. After filtration, the solvent was removed in vacuo yielding an orange oil. Due to the dangerous nature of this compound, no further purification procedures or elemental analysis were attempted. From ^{1}H NMR, it was estimated that the material prepared in this manner was >98% pure. Yield: 18.0 g (88%). ^{1}H NMR (CDCl$_3$): δ 7.26 (m, 4H, aromatic), 3.95 (s, 4H, benzylic), 3.56 (t, 4H, CH$_2$Cl), 2.82 (t, 4H, SCH$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 135.76, 130.65, 127.72 (aromatic), 43.01 (CH$_2$Cl), 33.80 (benzylic), 33.29 (SCH$_2$).

Preparation of 2,5,14,17-Tetrathia[6.6]-*o*-cyclophane, TT[6.6]OC. Cs$_2$CO$_3$ (3.83 g, 11.74 mmol) was suspended in DMF (700 mL) under an atmosphere of N$_2$(g). To this mixture was added a solution of *o*-xylylenebis(1-chloro-3-thiapropane) (1.784 g, 5.87 mmol) and *o*-xylene-α,α′-dithiol (1.00 g, 5.87 mmol) in DMF (125 mL). The addition was over a period of 20 h with the reaction temperature maintained at 55–60 °C. After addition, the mixture was cooled to room temperature and stirred for a further 12 h. The DMF was removed under vacuum and the resulting residue extracted with CH$_2$Cl$_2$ (150 mL). The CH$_2$Cl$_2$ solution was then washed with 0.1 M NaOH (2 × 50 mL) and the organic fractions dried over anhydrous MgSO$_4$. After filtration and removal of the solvent, the residue was recrystallized from acetone. Yield: 1.87 g

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Table I. Crystallographic Data for TT[6.6]OC and $[Pt(TT[6.6]OC)][BF_4]_2$

chem formula	$C_{20}H_{24}S_4$	$C_{20}H_{24}B_2F_8PtS_4$
fw	392.72	761.42
a, Å	23.885(5)	22.413(8)
b, Å	4.707(2)	10.633(3)
c, Å	8.578(3)	11.514(5)
β, deg	91.47(3)	106.62(3)
space group	*C*2 (No. 5)	*C*2 (No. 5)
V, Å^3	964.1(9)	2629(3)
ρ, g/cm^{3}	1.352	1.923
Z	2	4
μ, cm^{-1}	4.725	57.609
λ, Å	0.710 69	0.710 69
T, °C	24	24
$R(F_o)$, %	6.21	4.69
$R_w(F_o)$, %	6.87	4.83

^{a} $R = \sum||F_o| - |F_c|/\sum|F_o||$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$ and $w = 1/\sigma^2(F)$.

(81%). Mp: 142–142.5 °C (lit.[16] mp 142–144 °C). ^{1}H NMR ($CDCl_3$): δ 7.19–7.33 (m, 4H, aromatic), 3.90 (s, 4H, benzylic), 2.85 (s, 4H, SCH_2CH_2S). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 135.72, 130.14, 127.83 (aromatic), 38.33 (benzylic), 37.12 (SCH_2CH_2S). Anal. Calcd for $C_{20}H_{24}S_4$: C, 61.16; H, 6.17; S, 32.66. Found: C, 61.11, H, 6.11, S, 32.58.

Preparation of $[Pd(TT[6.6]OC)][BF_4]_2$. TT[6.6]OC (0.221 g, 0.563 mmol) dissolved in CH_2Cl_2 (5 mL) was added to a solution of $[Pd(CH_3CN)_4][BF_4]_2$ (0.250 g, 0.563 mmol) dissolved in acetonitrile (10 mL). The reaction mixture instantly turned color from yellow to orange-brown and after stirring for one hour, a pale orange-brown precipitate formed. The solid was then isolated by filtration yielding a tan colored product. Yield: 0.341 g (90%). ^{1}H NMR ($CDCl_3$): δ 7.48–7.67 (m, 4H, aromatic), 5.16 (d, 2H, ^2J = 12.5 Hz, benzylic), 4.51 (d, 2H, ^2J = 12.5 Hz, benzylic), 3.77 (s, br, 4H, SCH_2CH_2S). Anal. Calcd for $C_{20}H_{24}S_4B_2F_8Pd$: C, 35.70; H, 3.60. Found: C, 35.80, H, 3.71.

Preparation of $[Pt(TT[6.6]OC)][BF_4]_2$. TT[6.6]OC (0.210 g, 0.535 mmol) dissolved in CH_2Cl_2 (5 mL) was added to a solution of $Pt(COD)Cl_2$ (0.200 g, 0.535 mmol) and NH_4BF_4 (0.112 g, 1.70 mmol) in MeCN (10 mL). Over a three hour time period, the initially colorless solution turned to a creamy yellow color with an off-white precipitate. The solid was then isolated by filtration yielding a white colored product. Yield: 0.383 g (94%). ^{1}H NMR ($CDCl_3$): δ 7.45–7.69 (m, 4H, aromatic), 5.41 (d, 2H, ^2J = 12.3 Hz, benzylic), 4.84 (d, 2H, ^2J = 12.3 Hz, benzylic), 3.67 (s, br, 4H, SCH_2CH_2S). Anal. Calcd for $C_{20}H_{24}S_4B_2F_8Pt$: C, 31.55; H, 3.18. Found: C, 31.47, H, 3.09.

General X-ray Diffraction Data Collection, Solution, and Refinement. Diffraction experiments were performed on a four-circle Rigaku AFC6S diffractometer with graphite-monochromatized Mo Kα radiation. The unit cell constants and orientation matrices for data collection were obtained from 25 centered reflections (15° < 2θ < 35°). Machine parameters, crystal data, and data collection parameters are summarized in Tables I and S-1. The intensities of three standard reflections were recorded every 150 reflections and showed no statistically significant changes over the duration of the data collections. The intensity data were collected using the ω–2θ scan technique, in four shells (2θ < 30, 40, 45, and 50°). Absorption corrections (empirical) were applied to the data based on psi-scan data. The data were processed using the TEXSAN software package running on a VAX 3520 computer.[17] Refinements were carried out by using full-matrix least-squares techniques on *F* by minimizing the function $\sum w(|F_o|-|F_c|)^2$, where $w = 1/\sigma^2(F_o)$ and F_o and F_c are the observed and calculated structure factors. Atomic scattering factors[18] and anomalous dispersion[19,20] terms were taken from the usual sources. Fixed H-atom contributions were included with C–H distances of 0.95 Å and thermal parameters 1.2 times the isotropic thermal parameter of the bonded C atoms. No H atoms were refined, but all values were updated as refinement continued.

Table II. Selected Positional Parameters and *B*(eq) Values (Å^2) for TT[6.6]OC

atom	*x*	*y*	*z*	*B*(eq)
S1	0.50381(10)	0.7133	0.2753(4)	3.9(1)
S2	0.33316(10)	0.4787(12)	0.4022(4)	4.2(1)
C7	0.5513(4)	0.469(4)	0.1981(13)	4.0(2)
C8	0.4438(4)	0.482(2)	0.3122(11)	3.2(2)
C9	0.3971(4)	0.670(3)	0.3769(12)	3.2(2)
C10	0.3457(5)	0.321(3)	0.5918(13)	4.2(3)

Table III. Selected Bond Distances and Angles for TT[6.6]OC

	Distances (Å)		
S1–C7	1.758(13)	S1–C8	1.833(12)
S2–C9	1.791(11)	S2–C10	1.806(12)
C6–C7	1.49(2)	C8–C9	1.54(2)
C1–C10′	1.47(2)		
	Angles (deg)		
C7–S1–C8	101.0(7)	C9–S2–C10	101.2(5)
C1–C6–C7	125.5(12)	C2–C1–C10′	117.8(9)
C5–C6–C7	114.5(10)	C6–C1–C10′	124.9(9)
C6–C7–S1	112.9(11)	S1–C8–C9	107.4(8)
C8–C9–S2	112.6(8)	S2–C10–C1′	116.0(10)

Table IV. Selected Positional Parameters and *B*(eq) Values (Å^2) for $[Pt(TT[6.6]OC)][BF_4]_2$

atom	*x*	*y*	*z*	*B*(eq)
Pt	0.08248(4)	0.0091	–0.00011(8)	2.55(3)
S1	0.0407(7)	0.182(2)	–0.1279(11)	2.6(5)
S2	0.1283(7)	0.169(2)	0.149(2)	2.7(5)
S3	0.1245(9)	–0.137(2)	0.134(2)	4.4(7)
S4	0.0402(8)	–0.144(2)	–0.130(2)	3.9(6)
C7	0.038(2)	0.147(5)	–0.282(4)	5(1)
C8	0.101(2)	0.293(4)	–0.068(4)	2.7(9)
C9	0.106(2)	0.313(4)	0.039(3)	3.4(8)
C10	0.209(2)	0.166(4)	0.166(4)	5(1)
C17	0.213(2)	–0.118(3)	0.152(3)	2.5(7)
C18	0.106(1)	–0.286(3)	0.071(3)	2.6(7)
C19	0.097(2)	–0.273(6)	–0.084(4)	6(1)
C20	0.047(2)	–0.129(4)	–0.283(4)	1.9(8)

Structure of TT[6.6]OC. Colorless crystals of TT[6.6]OC were grown by slow evaporation of a benzene solution of the compound. A statistical analysis of intensity distributions and a determination of observed extinctions were consistent with space group C2 and this was confirmed by a successful solution refinement. A total of 973 reflections were collected and 531 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The positions of the sulfur atoms were determined by direct methods from the *E*-map with highest figure of merit. The remaining carbon atoms were located from a difference Fourier map calculation. In the final cycles of refinement, the sulfur atoms were assigned anisotropic thermal parameters and the carbon atoms were assigned isotropic thermal parameters. This resulted in $R = 0.0621$ and $R_w = 0.0687$ at final convergence. The Δ/σ value for any parameter in the final cycle was less than 0.001. A final difference Fourier map calculation showed no peaks of chemical significance; the largest was 0.403 electrons/Å^3 and was associated with the C3–C4 bond. Selected atomic positional parameters are summarized in Table II and selected bond distances and angles are summarized in Table III. Positional parameters (Table S-II), non-essential bond distances and angles (Table S-III), thermal parameters (Table S-IV) and hydrogen atom parameters (Table S-V) are deposited as supplementary material.

Structure of $[Pt(TT[6.6]OC)][BF_4]_2$. Colorless crystals of $[Pt(TT[6.6]OC)][BF_4]_2$ were grown by slow evaporation of an acetonitrile solution of the complex. A statistical analysis of intensity distributions and a determination of observed extinctions were consistent with space group *C*2 and this was confirmed by a successful solution refinement. A total of 2463 reflections were collected and 1496 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. The position of the platinum atom was determined by conventional Patterson techniques and the remaining non-hydrogen-atoms were located from difference Fourier map calculations. In the final cycles of refinement, the platinum, sulfur, fluorine and boron atoms were all assigned anisotropic thermal parameters and the carbon atoms were assigned isotropic thermal parameters. This resulted in $R = 0.0469$ and $R_w = 0.0483$ at final convergence. The Δ/σ value for any parameter in the final cycle was less than 0.001. A final

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Table V. Selected Bond Distances and Angles for $[Pt(TT[6.6]OC)][BF_4]_2$

	Distances (Å)		
Pt–S1	2.38(2)	S2–C9	1.96(4)
Pt–S2	2.43(2)	S2–C10	1.76(5)
Pt–S3	2.20(2)	S3–C17	1.94(4)
Pt–S4	2.23(2)	S3–C18	1.74(4)
S1–C7	1.80(5)	S4–C19	1.85(6)
S1–C8	1.77(5)	S4–C20	1.82(4)
	Angles (deg)		
S1–Pt–S2	84.7(6)	S3–Pt–S4	88.2(8)
S1–Pt–S3	174.1(7)	C7–S1–C8	109(2)
S1–Pt–S4	97.6(3)	C9–S2–C10	99(2)
S2–Pt–S3	89.5(3)	C18–S3–C19	104(2)
S2–Pt–S4	177.3(7)	C19–S3–C20	96(2)

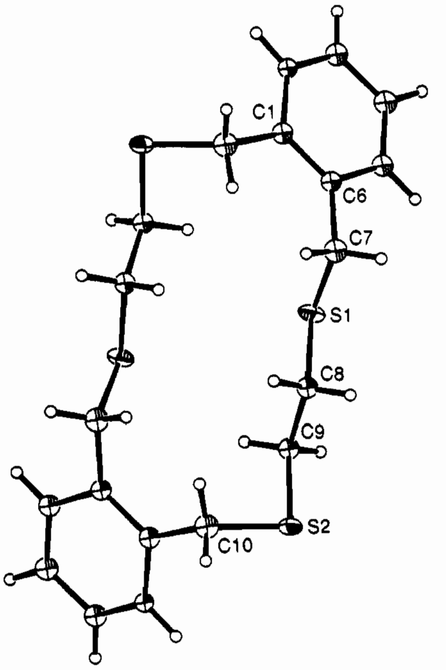
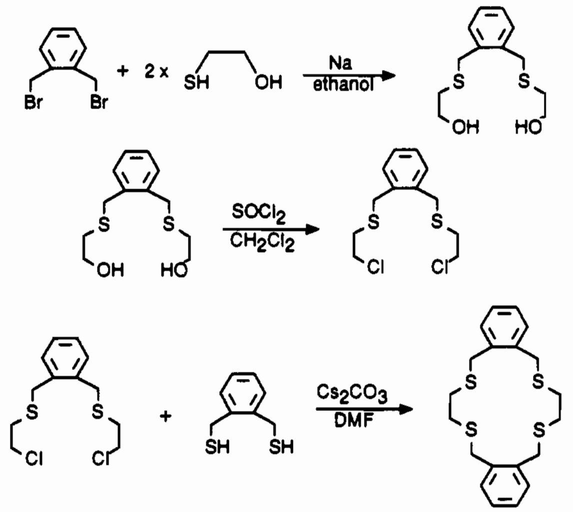


Figure 1. Perspective ORTEP drawing of TT[6.6]OC showing the atom-numbering scheme.

Scheme I



difference Fourier map calculation showed no peaks of chemical significance; the largest was 0.917 electrons/Å^3 and was associated with the Pt atom. Selected atomic positional parameters are summarized in Table IV and selected bond distances and angles are summarized in Table V. Positional parameters (Table S-VI), non-essential bond distances and angles (Table S-VII), thermal parameters (Table S-VIII) and hydrogen atom parameters (Table S-IX) are deposited as supplementary material.

Table VI. Selected Torsional Angles (deg) for TT[6.6]OC and $[Pt(TT[6.6]OC)][BF_4]_2$

angle[a]	TT[6.6]OC	$[Pt(TT[6.6]OC)][BF_4]_2$
C1–C6–C7–S1	108.0(13)	–85(6)
C6–C7–S1–C8	–169.8(9)	–164(4)
C7–S1–C8–C9	–178.4(6)	–177(4)
S1–C8–C9–S2	174.6(6)	62(4)
C8–C9–S2–C10	84.2(8)	79(4)
C9–S2–C10–C1	71.5(9)	174(3)
S2–C10–C11–C16[b]	–111.9(12)	48(6)
C10–C11–C16–C17		39(7)
C11–C16–C17–S3		–102(3)
C16–C17–S3–C18		–138(2)
C17–S3–C18–C19		–80(3)
S3–C18–C19–S4		–53(3)
C18–C19–S4–C20		171(3)
C19–S4–C20–C1		167(3)
S4–C20–C1–C6		91(5)

[a] Sign is positive for a clockwise rotation of 1 to 4 viewed down the 2–3 bond. [b] For TT[6.6]OC, this is the angle S2–C10–C1′–C6′ which includes appropriate symmetry-related atoms.

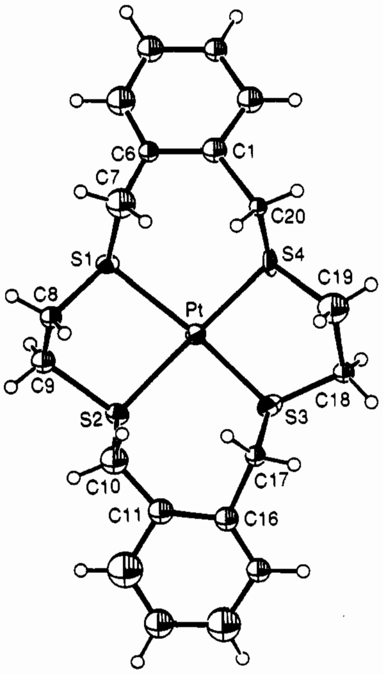


Figure 2. Perspective ORTEP drawing of the $[Pt(TT[6.6]OC)]^{2+}$ cation showing the atom-numbering scheme.

Results and Discussion

The tetrathiacyclophane TT[6.6]OC can be prepared in high yield using a three step synthetic route as outlined in Scheme I. The final ring closure reaction proceeds in good yield employing Kellogg's Cs^+ mediated cyclization method.[21] TT[6.6]OC was previously prepared in 5% yield by the direct reaction of α,α′-dibromo-*o*-xylyene with the disodium salt of ethanedithiol.[16] The three step synthesis outlined herein provides a significant improvement on this with an over yield of 72%. TT[6.6]OC is quite soluble in a number of organic solvents such as benzene, $CHCl_3$, CH_2Cl_2, CH_3CN, and is easily recrystallized from acetone. The ^1H NMR spectrum of TT[6.6]OC shows three distinct sets of resonances, a multiplet for the aromatic protons, 7.19–7.33 ppm, and pair of singlets for the benzylic and methylene groups at 3.90 and 2.85 ppm respectively. The X-ray structure of TT[6.6]OC (Figure 1) shows that the ligand conformation is one with two S atoms exodentate and two S atoms endodentate. The overall conformation is the familiar quadrangular shape found

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[21] (a) Buter, J.; Kellogg, R. M. *J. Org. Chem.* **1981**, 4481–4486. (b) Buter, J.; Kellogg, R. M. *Org. Synth.* **1987**, *65*, 150–152.

for 12S4 and 14S4 and the $-SCH_2CH_2S-$ torsional angle is 174.6(6)° (Table VI) demonstrating the propensity for this linkage to adopt an *anti* conformation. However, the *o*-xylyl fragments occupy two of the corners of the quadrangle and the introduction of this aromatic spacer allows an endodentate orientation for two of the S donors.

Preparation of the Pd(II) and Pt(II) complexes was straightforward employing $[Pd(CH_3CN)_4][BF_4]_2$ and $PtCl_2(COD)$ as sources of these metal ions. In both cases, relatively short reaction times of one to three hours in acetonitrile gave high yields of the metal complex with only volatile side products that were easily removed in vacuum. Upon complexation, the most significant change in the ^1H NMR spectra was the splitting of the benzylic resonance into a pair of doublets due to the presence of axial and equatorial positions in the seven-membered chelate ring. This is consistent with the formation of the expected square planar $[MS_4]^{2+}$ type complexes and was verified by a single crystal X-ray diffraction study of $[Pt(TT[6.6]OC)][BF_4]_2$ (Figure 2). The Pt complex has square planar geometry with the central metal atom bonded to the four S-donors of TT[6.6]OC; Pt–S1 2.38(2), Pt–S2 2.43(2), Pt–S3 2.20(2) and Pt–S4 2.23(2) Å. The S1–Pt–S2 and S3–Pt–S4 angles associated with the five-membered chelate rings are 84.7(6) and 88.2(3)° while the S2–Pt–S3 and S1–Pt–S4 angles spanned by the *o*-xylyl group are 97.6(3) and 89.5(3)° respectively. The macrocycle adopts a *syn* conformation in which both xylyl rings are on the same side of the metal. This is the conformation most often observed for tetradentate macrocycles of second and third row metals and is related to the larger size of these metals as compared to first row metals which usually adopt an *anti* conformation.[4] The Pt atom lies 0.024 Å above the least square plane defined by the four S atoms; the mean deviation from planarity is 0.006 Å.

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Supplementary Material Available: Listings of crystallographic data collection parameters, positional parameters, thermal parameters, nonessential bond distances and angles, and hydrogen atom parameters (Tables S-I–S-IX) (6 pages). Ordering information is given on any current masthead page.