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Dependence of Complex Structure on Ligand Conformation in Palladium(II) Complexes of the Crown Thioether Ligands 2,5,8-Trithia[9]-*o*-benzenophane (TT[9]OB) and 2,5,8-Trithia[9]-*m*-benzenophane (TT[9]MB). Structures of $PdCl_2$(TT[9]OB)·DMSO and $PdCl_2$(TT[9]MB)

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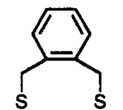
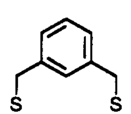
The tridentate crown thioether ligands 2,5,8-trithia[9]-*o*-benzenophane, TT[9]OB, and 2,5,8-trithia[9]-*m*-benzenophane, TT[9]MB, are known to have exodentate conformations in the uncomplexed form. These ligands react with $PdCl_2(PhCN)_2$ to give complexes of the general formula $PdCl_2L$, where L = TT[9]OB and TT[9]MB. ^1H NMR spectra indicate that TT[9]MB acts as a bidentate ligand via two adjacent S atoms forming a single five-membered chelate ring and the third S atom remains exodentate to the macrocyclic ring. Similar spectra for complexes of TT[9]OB are fluxional at room temperature, suggesting the incorporation of a third endodentate S atom into the coordination sphere. The complex $PdCl_2$(TT[9]MB) crystallized in the space group $P2_1/c$ with a = 14.411 (2) Å, b = 8.247 (1) Å, c = 13.749 (2) Å, β = 106.45 (1)°, V = 1567.2 (2), and Z = 4. The structure refined to R = 3.61% and R_w = 4.07% for 1672 reflections with $F_o^2 > 3\sigma(F_o^2)$. The Pd atom is in a square-planar environment defined by two Cl atoms and two adjacent ligand S atoms (Pd–S1 = 2.259 (2) Å and Pd–S2 = 2.266 (2) Å), which form a five-membered chelate ring. The third S atom is exodentate to the macrocyclic ring and oriented away from the metal centre at a distance of 5.122 (2) Å. The complex $PdCl_2$(TT[9]OB)·DMSO crystallized in the space group $P2_1/c$ with a = 13.636 (5) Å, b = 11.005 (3) Å, c = 13.911 (4) Å, β = 113.91 (2)°, V = 1908.5 (10), and Z = 4. The structure refined to R = 4.83% and R_w = 4.65% for 1930 reflections with $F_o^2 > 3\sigma(F_o^2)$. The Pd atom is in a square-planar environment defined by two Cl atoms and two adjacent ligand S atoms (Pd–S1 = 2.259 (3) Å and Pd–S2 = 2.266 (3) Å), which form a five-membered chelate ring. The third S atom is in an apical position above the $PdCl_2S_2$ plane at a distance of 3.076 (3) Å.


TT[9]OB


TT[9]MB

We have previously shown that the crown thioether ligands 2,5,8-trithia[9]-*o*-benzenophane (TT[9]OB) and 2,5,8-trithia[9]-*m*-benzenophane (TT[9]MB) have exodentate conformations in the free ligand with the sulfur atoms oriented out of the macrocyclic cavity.[1] In spite of this, TT[9]OB will bind facially to a single metal center in either a tetrahedral or octahedral geometry, as shown by the structural characterizations of $Mo(CO)_3$(TT[9]OB),[1] Cu(NCS)(TT[9]OB),[2] [Cu(PPh_2Me)(TT[9]OB)][ClO_4],[3] [Ag(PPh_3)(TT[9]OB)][ClO_4],[3] and [Ag(TT[9]OB)$_2$][CF_3SO_3].[4] In particular, the fluxional nature of [Ag(TT[9]OB)$_2$][CF_3SO_3], which contains TT[9]OB bound in both the endodentate and exodentate conformations, shows that the metal-assisted interconversion of these two conformations is relatively facile.[4] In contrast to the rich coordination chemistry of TT[9]OB, we have found no case in which TT[9]MB acted as a ligand to a transition metal.

Although the electronic structure of Pd(II) dictates a preference for square-planar geometry, it is of interest to investigate the coordination of these S_3 macrocycles to metals which are not generally compatible with facial coordination. We report herein an investigation of the coordination chemistry of TT[9]OB and TT[9]MB with Pd(II). Significant results include the first preparation and structural characterization of a complex of TT[9]MB and the structure of $PdCl_2$(TT[9]OB), in which TT[9]OB coordinates facially to Pd(II).

Experimental Section

$PdCl_2(PhCN)_2$,[5] TT[9]OB,[1,3] and TT[9]MB[1] were prepared by the literature methods. $PdCl_2$, all organic reagents, and all 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. ^1H NMR spectra were recorded at 300.1 MHz on a Bruker AC300 spectrometer locked to the deuterated solvent. Infrared spectra were recorded on a Nicolet 5DX FTIR spectrometer. Elemental analysis were performed by Microanalytical Services, New Westminister, British Columbia, Canada.

Table I. Crystallographic Data for $PdCl_2$(TT[9]OB)·DMSO and $PdCl_2$(TT[9]MB)

chem formula	$C_{14}H_{22}Cl_2OPdS_4$	$C_{12}H_{16}Cl_2PdS_3$
fw	511.96	433.74
a, Å	13.636 (5)	14.411 (2)
b, Å	11.005 (3)	8.247 (1)
c, Å	13.911 (4)	13.749 (2)
β, deg	113.91 (2)	106.45 (2)
space group	$P2_1/c$	$P2_1/c$
v, Å^3	1908.5 (10)	1567.2 (8)
ρ(calcd), g/cm^{-3}	1.78	1.84
Z	4	4
μ, cm^{-1}	16.62	18.78
λ, Å	0.71069	0.71069
T, °C	24	24
$R(F_o)$,[a] %	4.65	3.61
$R_w(F_o)$,[a] %	4.83	4.07

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

Preparation of $PdCl_2L$ (L = TT[9]OB, TT[9]MB). In a typical preparation, a solution of $PdCl_2(PhCN)_2$ (0.802 mmol) in CH_3CN (10 mL) was added dropwise to TT[9]OB or TT[9]MB (206 mg, 0.802 mmol) dissolved in CH_3CN (5 mL). No visible change occurred as the two solutions were mixed. The solution was stirred for 12 h at room temperature, during which time a precipitate formed. The solution was filtered and the solid washed with CH_2Cl_2 (3 × 5 mL) and then dried in vacuo. $PdCl_2$(TT[9]OB) was recrystallized from DMSO/diethyl ether resulting in red-brown crystals of the DMSO adduct. Yield: 337 mg (82%). ^1H NMR (DMSO-d_6): δ 7.27–7.32 (m, br, 4 H, aromatic), 4.13 (br, 4 H, benzylic), 3.32 (br, 8 H, SCH_2CH_2S). Anal. Calcd for $C_{14}H_{22}Cl_2OPdS_4$: C, 32.84; H, 4.34; S, 25.06. Found: C, 32.78; H, 4.44; S, 24.94. $PdCl_2$(TT[9]MB) was recrystallized from DMSO, resulting in bright yellow-orange crystals. Yield: 306 mg (88%). ^1H NMR (DMSO-d_6): δ 8.55 (s, 1 H, aromatic), 7.47 (m, 2 H, aromatic), 7.26 (m, 1 H, aromatic), 4.63 (d, 1 H, ^2J = 13.4 Hz, benzylic), 4.06 (d, 1 H, ^2J = 13.4 Hz, benzylic), 4.00 (d, 1 H, ^2J = 13.5 Hz, benzylic), 3.80 (d, 1 H, ^2J = 13.5 Hz, benzylic), 3.10 (m, 2 H), 3.02 (m, 1 H), 2.95 (m, 2 H), 2.41 (dt, 1 H), 2.18 (dt, 1 H), 1.35 (dt, 1 H). Anal. Calcd for $C_{12}H_{16}Cl_2PdS_3$: C, 33.22; H, 3.73; S, 22.18. Found: C, 33.54; H, 3.87; S, 22.29.

General X-ray Diffraction Data Collection, Solution, and Refinement. Cell constants and orientation matrices for data collection were obtained from least-squares refinements using the setting angles of 25 centered reflections. Machine parameters, crystal data, and data collection pa-

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Table II. Selected Positional Parameters and B(eq)[a] Values for $PdCl_2$(TT[9]OB)·DMSO

atom	x	y	z	B(eq), Å^2
Pd	0.1660 (6)	0.13901 (7)	0.95249 (6)	2.01 (3)
Cl1	0.3628 (2)	0.0433 (2)	0.7906 (2)	3.2 (1)
Cl2	0.5593 (2)	0.2380 (2)	0.9333 (2)	3.2 (1)
S1	0.2876 (2)	0.0365 (2)	0.9814 (2)	2.2 (1)
S2	0.4755 (2)	0.2195 (2)	1.1046 (2)	2.7 (1)
S3	0.3106 (2)	0.3908 (2)	0.8966 (2)	2.7 (1)
C1	0.1249 (8)	0.272 (1)	0.7777 (8)	2.7 (4)
C2	0.0865 (8)	0.286 (1)	0.6703 (9)	3.4 (5)
C3	0.0513 (9)	0.186 (1)	0.6048 (8)	4.0 (5)
C4	0.0510 (9)	0.073 (1)	0.6458 (8)	3.8 (5)
C5	0.0880 (8)	0.059 (1)	0.7529 (8)	3.5 (5)
C6	0.1260 (6)	0.1578 (9)	0.8203 (7)	2.1 (4)
C7	0.1681 (7)	0.132 (1)	0.9376 (7)	2.7 (4)
C8	0.3336 (7)	0.049 (1)	1.1239 (7)	2.6 (4)
C9	0.3753 (8)	0.175 (1)	1.1647 (7)	2.9 (4)
C10	0.4593 (8)	0.3838 (9)	1.1036 (7)	2.9 (4)
C11	0.3499 (9)	0.4343 (8)	1.0338 (8)	3.0 (4)
C12	0.1636 (7)	0.383 (1)	0.8459 (8)	3.4 (5)

[a] $B(\mathrm{eq}) = 8\pi^2/3\sum^3_{i=1}\sum^3_{j=1}U_{ij}a^*_ia^*_j\vec{a}_i\cdot\vec{a}_j$.

Table III. Selected Bond Distances and Angles for $PdCl_2$(TT[9]OB)·DMSO

	Distances (Å)		
Pd–Cl1	2.319 (3)	Pd–Cl2	2.337 (3)
Pd–S1	2.259 (3)	Pd–S2	2.266 (3)
Pd–S3	3.076 (3)	S1–C7	1.826 (9)
S1–C8	1.827 (9)	S2–C9	1.818 (9)
S2–C10	1.82 (1)	S3–C11	1.82 (1)
S3–C12	1.84 (1)	C1–C12	1.50 (1)
C6–C7	1.52 (1)	C8–C9	1.52 (1)
C10–C11	1.52 (1)		
	Angles (deg)		
Cl1–Pd–Cl2	92.9 (1)	Cl1–Pd–S1	89.04 (9)
Cl1–Pd–S2	175.7 (1)	Cl1–Pd–S3	103.45 (9)
Cl2–Pd–S1	175.8 (3)	Cl2–Pd–S2	87.7 (1)
Cl2–Pd–S3	83.06 (9)	S1–Pd–S2	90.05 (9)
S1–Pd–S3	100.06 (8)	S2–Pd–S3	80.82 (9)
C7–S1–C8	100.6 (4)	C9–S2–C10	102.7 (5)
C11–S3–C12	103.1 (5)	S1–C7–C6	111.2 (6)
S1–C8–C9	112.8 (6)	S2–C9–C8	109.2 (6)
S2–C10–C11	118.3 (7)	S3–C11–C10	111.7 (7)
S3–C12–C1	109.3 (7)		

rameters are summarized in Table I and detailed in Table S-I (deposited as supplementary material). The intensities of three standard reflections were recorded every 150 reflections and showed no statistically significant changes over the duration of the data collections. Empirical absorption corrections, based on ψ-scan data, were applied to the data. The data were processed by using the TEXSAN software package[6] running on a VAX 3520 workstation. Refinements were carried out by using full-matrix least-squares techniques on F minimizing the function $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$ and F_o and F_c are the observed and calculated structure factors. Atomic scattering factors[7] and anomalous dispersion terms.[8,9] 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 IV. Selected Positional Parameters and B(eq)[a] Values for $PdCl_2$(TT[9]MB)

atom	x	y	z	B(eq), Å^2
Pd	0.13337 (6)	–0.00964 (6)	0.05312 (4)	1.99 (2)
Cl1	0.1875 (2)	–0.0168 (3)	–0.0897 (1)	3.65 (8)
Cl2	0.1294 (2)	0.2713 (2)	0.0540 (2)	3.77 (9)
S1	0.1306 (1)	–0.2834 (2)	0.0466 (1)	2.27 (7)
S2	0.0803 (1)	–0.0153 (2)	0.19327 (12)	2.32 (7)
S3	0.3626 (2)	0.1267 (3)	0.4022 (2)	3.48 (8)
C1	0.3589 (5)	–0.1674 (9)	0.2019 (5)	2.8 (3)
C2	0.4135 (5)	–0.1358 (10)	0.3004 (6)	3.0 (3)
C3	0.4375 (6)	–0.2638 (11)	0.3679 (6)	3.7 (4)
C4	0.4047 (6)	–0.4169 (11)	0.3390 (6)	4.0 (4)
C5	0.3471 (6)	–0.4478 (10)	0.2426 (6)	3.5 (3)
C6	0.3224 (5)	–0.3212 (9)	0.1724 (5)	2.5 (3)
C7	0.2564 (5)	–0.3520 (8)	0.0688 (5)	2.7 (3)
C8	0.1017 (5)	–0.3471 (9)	0.1630 (5)	2.7 (3)
C9	0.0388 (5)	–0.2220 (8)	0.1937 (5)	2.3 (3)
C10	0.1880 (5)	–0.0174 (10)	0.3034 (5)	3.0 (3)
C11	0.2483 (5)	0.1326 (9)	0.3042 (5)	3.0 (3)
C12	0.4411 (5)	0.0362 (10)	0.3345 (6)	3.7 (4)

[a] $B(\mathrm{eq}) = 8\pi^2/3\sum^3_{i=1}\sum^3_{j=1}U_{ij}a^*_ia^*_j\vec{a}_i\cdot\vec{a}_j$.

Table V. Selected Bond Distances and Angles for $PdCl_2$(TT[9]MB)

	Distances (Å)		
Pd–Cl1	2.310 (2)	Pd–Cl2	2.318 (2)
Pd–S1	2.259 (2)	Pd–S2	2.266 (2)
S1–C7	1.841 (7)	S1–C8	1.840 (7)
S2–C9	1.807 (7)	S2–C10	1.836 (7)
S3–C11	1.809 (7)	S3–C12	1.818 (8)
C2–C12	1.51 (1)	C6–C7	1.494 (9)
C8–C9	1.511 (9)	C10–C11	1.51 (1)
Pd···S3	5.122 (2)		
	Angles (deg)		
Cl1–Pd–Cl2	92.56 (8)	Cl1–Pd–S1	86.99 (8)
Cl1–Pd–S2	177.35 (7)	Cl2–Pd–S1	177.33 (7)
Cl2–Pd–S2	90.09 (8)	S1–Pd–S2	90.37 (7)
C7–S1–C8	102.9 (3)	C9–S2–C10	101.1 (3)
C11–S3–C12	101.4 (3)	S1–C7–C6	115.9 (5)
S1–C8–C9	110.5 (5)	S2–C9–C8	114.7 (5)
S2–C10–C11	110.4 (5)	S3–C11–C10	112.6 (5)
S3–C12–C2	113.3 (5)		

Table VI. Ligand Torsional Angles[a] in $PdCl_2$(TT[9]OB)·DMSO and $PdCl_2$(TT[9]MB)

angle, deg	$PdCl_2$(TT[9]OB)·DMSO	$PdCl_2$(TT[9]MB)
C6–C7–S1–C8	168.6 (7)	–43.3 (6)
C7–S1–C8–C9	–68.9 (7)	142.7 (5)
S1–C8–C9–S2	–52.4 (8)	–47.5 (6)
C8–C9–S2–C10	148.5 (6)	–71.0 (5)
C9–S2–C10–C11	–57.6 (8)	167.0 (5)
S2–C10–C11–S3	63.7 (8)	–173.1 (4)
C10–C11–S3–C12	149.6 (7)	91.6 (6)
C11–S3–C12–C1[b]	137.5 (7)	–64.4 (6)

[a] This does not include torsional angles associated with the aromatic bonds of the xylyl groups. Sign is positive for a clockwise rotation of 1–4 viewed down the 2–3 bond. [b] This is C11–S3–C12–C2 for TT[9]-MB.

Structure of $PdCl_2$(TT[9]OB)·DMSO. Red-brown crystals of $PdCl_2$(TT[9]OB)·DMSO were grown by vapor diffusion of diethyl ether into a DMSO solution of the complex. The positions of the palladium atom, the chlorine atoms, and two of the four sulfur atoms were determined by direct methods from the E map with highest figure of merit. The remaining non-hydrogen atoms were located from a difference Fourier map calculation. In the final cycles of refinement, the palladium, chlorine, sulfur, oxygen, and carbon atoms were all assigned anisotropic thermal parameters. 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), nonessential bond distances and angles (Table S-III), thermal parameters (Table S-IV), hydrogen atom parameters (Table S-V), and values of $10|F_o|$ and $10|F_c|$ (Table S-X) are deposited as supplementary material.

Structure of $PdCl_2$(TT[9]MB). Orange crystals of $PdCl_2$(TT[9]MB) were grown by slow evaporation of a DMSO solution of the complex. The position of the palladium atom was determined by the Patterson method, and the remaining non-hydrogen atoms were located from difference Fourier map calculations. In the final cycles of refinement, the palladium, chlorine, sulfur, and carbon atoms were all assigned anisotropic thermal parameters. Selected atomic positional parameters are summarized in Table IV, and selected bond distances and angles are summarized in Table V. Ligand torsional angles are listed in Table VI. Positional parameters (Table S-VI), nonessential bond distances and

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(6) TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985.

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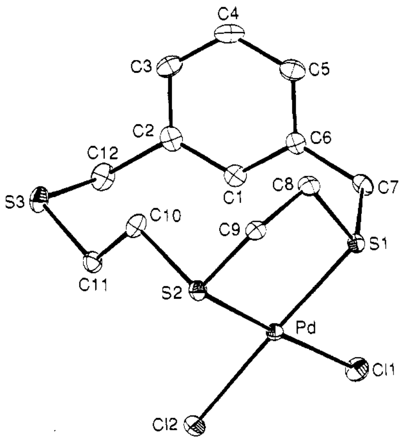


Figure 1. Perspective ORTEP drawing of $PdCl_2(TT[9]MB)$, showing the atom-numbering scheme. Thermal ellipsoids of 20% are shown.

angles (Table S-VII), thermal parameters (Table S-VIII), hydrogen atom parameters (Table S-IX), and values of $10|F_o|$ and $10|F_c|$ (Table S-XI) are deposited as supplementary material.

Results

The reactions of TT[9]OB and TT[9]MB with $PdCl_2(PhCN)_2$ result in the formation of mononuclear complexes of formula $PdCl_2L$, in which the thioether macrocycle has displaced the labile PhCN ligands. The complex $PdCl_2(TT[9]MB)$ is a bright yellow-orange crystalline material with only limited solubility in polar organic solvents. ^1H NMR spectra (300 K, DMSO-d_6) are consistent with coordination of TT[9]MB as a bidentate ligand and formation of a complex with a square-planar $PdCl_2S_2$ geometry. This results in nonequivalent halves for the macrocyclic ring and separate ^1H NMR resonances for each of the 12 hydrogen atoms. In symmetrical complexes of TT[9]OB in which this ligand bonds in a facial coordination mode, the benzylic protons appear as an AA'BB' pattern due to the formation of chelate rings.[1-3] In the complex $PdCl_2(TT[9]MB)$ two such patterns exist indicating that the benzylic groups are part of different chelate ring systems, emphasizing the asymmetric nature of the coordination mode. Seven of the eight hydrogen atoms of the $-SCH_2CH_2SCH_2CH_2S-$ linkage appear as separate resonance patterns in the ranges 3.80–2.18 ppm, while the remaining proton is shifted to comparably high field. This upfield resonance at 1.35 ppm is assigned to an H atom in the $-SCH_2CH_2SCH_2CH_2S-$ linkage which is oriented over the ring current of the aromatic π system.

The X-ray structure of $PdCl_2(TT[9]MB)$ (Figure 1) verifies the coordination mode proposed from NMR data. The square plane consists of two chloride ligands (Pd–Cl1 = 2.310 (2), Pd–Cl2 = 2.318 (2) Å) and two adjacent sulfur atoms (Pd–S1 = 2.259 (2), Pd–S2 = 2.266 (2) Å) which form a five-membered chelate ring with a S1–Pd–S2 angle of 90.37 (2)°. The remaining sulfur atom is in an exodentate conformation and is oriented away from the metal center at a distance of 5.122 (2) Å. The two SCH_2CH_2S portions of the TT[9]MB ligand show torsional angles of −47.5 (4)° for S1–C8–C9–S2 and −173.1 (4)° for S2–C9–C10–S3. One of the H atoms attached to C8 is oriented above the plane of the aromatic ring and can be assigned to the upfield resonance observed in the ^1H NMR spectrum.

The complex $PdCl_2(TT[9]OB)$ also exhibits limited solubility in polar organic solvents, but this material is a much darker and more intense red-brown color than the TT[9]MB analogue. This suggests the coordination environment for $PdCl_2(TT[9]OB)$ is different from the square-planar $PdCl_2S_2$ coordination observed for $PdCl_2(TT[9]MB)$. ^1H NMR spectra (300 K, DMSO-d_6) are also significantly different from those observed for $PdCl_2(TT[9]MB)$, showing only broad resonances in the aromatic, benzylic, and methylene regions. These observations suggest that TT[9]OB may act as a tridentate ligand to Pd(II), giving rise to a complex with a $PdCl_2S_3$ coordination sphere in which some fluxional process is occurring.

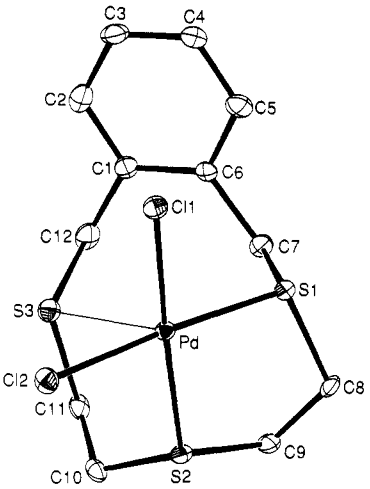
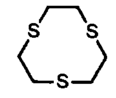


Figure 2. Perspective ORTEP drawing of $PdCl_2(TT[9]OB)$, showing the atom-numbering scheme. Thermal ellipsoids of 20% are shown.

The molecular structure of $PdCl_2(TT[9]OB)$ (Figure 2) was determined by an X-ray crystallographical study of the DMSO adduct. This verified that TT[9]OB does indeed assume a facial coordination mode on Pd(II). The square plane consists of two chloride ligands (Pd–Cl1 = 2.319 (3), Pd–Cl2 = 2.337 (3) Å) and two adjacent sulfur atoms (Pd–S1 = 2.259 (3), Pd–S2 = 2.266 (3) Å) which form a five-membered chelate ring with a S1–Pd–S2 angle of 90.05 (9)°. The position of the Pd atom deviates only 0.078 (2) Å from of the PdS_2Cl_2 least-squares plane. The remaining sulfur atom is oriented toward the Pd center above the square coordination plane (Pd–S3 = 3.076 (3) Å). The angles related to the positioning of S3 with respect to the square plane (Cl1–Pd–S3 = 103.45 (9), Cl2–Pd–S3 = 83.06 (8), S1–Pd–S3 = 100.06 (8), S2–Pd–S3 = 80.82 (9)°) show that the Pd–S3 bond is approximately perpendicular to the PdS_2Cl_2 plane. Therefore, the structure of $PdCl_2TT[9]OB{\cdot}DMSO$ is best described as having square-planar geometry with a weak apical Pd···S interaction.

Discussion

The crown thioether ligand 1,4,7-trithiacyclononane (9S3) forms transition-metal complexes of high thermodynamic and kinetic stability, and a number of these complexes display unusual electronic and redox behavior.[10] The exceptional coordinating ability of 9S3 is attributed to preorganization of the sulfur donor atoms and often results in coordination geometries dependent upon the ligand conformation rather than the electronic requirements of the metal.



9S3

Although the electronic structure of Pd(II) dictates a preference for square-planar geometry, the complexes $PdX_2(9S3)$ (X = Br, Cl)[12,13] and $[Pd(9S3)(L)][BF_4]$ (L = 2 PPh_3, bipyridyl, phenanthroline)[10] are pseudo-five-coordinate complexes, containing weak Pd···S interactions ranging from 2.877 (3) Å for L = PPh_3 to 3.140 (2) Å for X = Cl. Additional Pd···S interactions have been observed[14] for the complex $[Pd(9S3)_2]^{2+}$, and this contrasts

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with the behavior of $[Pd(9N3)_2][PF_6]_2$ (9N3 = 1,4,7-triazacyclononane) in which the apical nitrogen atoms are oriented away from the axial coordination sites.[15]

In contrast to 9S3, the S donor atoms of TT[9]OB are not preorganized in the free ligand, as the solution and solid-state structures show an exodentate conformation for the S donor atoms.[1] In spite of this, the structure of $PdCl_2$(TT[9]OB) demonstrates that TT[9]OB is able to achieve facial coordination[16] at Pd(II) similar to that observed for 9S3.[11-15] The positioning of the S3 atom in the coordination sphere of $PdCl_2$(TT[9]OB) and the temperature dependence of the ^1H NMR spectra are consistent with a fluxional process in solution which would interconvert S1 and S3 coordination to Pd via a pivot of the ligand about the Pd-S2 bond.[17] This process is not possible for the complex $PdCl_2$(TT[9]MB) because the *m*-xylyl unit imparts an increased rigidity to the complex and does not allow for the close approach of S3 to the Pd atom. The $-SCH_2CH_2SCH_2CH_2S-$ linkage of TT[9]MB has been shown to adopt a "bracket structure" in the free ligand which resembles a right angle in projection.[1] This feature is characterized in the solid state by S-C-C-S torsional angles of approximately 180°, and this has been shown to persist in solution.[1,3] It is proposed that upon coordination to Pd(II) only one of the SCH_2CH_2S units is rearranged from this anti placement to the gauche placement required for a five-membered chelate ring. Another interesting feature of $PdCl_2$(TT[9]MB) is the ligand conformation, which allows for simultaneous positioning of S donor atoms in exodentate *and* endodentate positions. The uncoordinated exodentate S3 atom could be employed in subsequent coordination to other metals or for aggregation of the mononuclear complex. This feature of TT[9]MB is the focus of current work.

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Registry No. $PdCl_2(PhCN)_2$, 114220-66-5; $PdCl_2$(TT[9]OB), 136822-80-5; $PdCl_2$(TT[9]MB), 136822-81-6.

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) (5 pages); listings of observed and calculated structure factors (Tables S-X and S-XI) (26 pages). Ordering information is given on any current masthead page.

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(16) We have recently found that TT[9]OB can enforce facial coordination and octahedral geometry at Ag(I) in the complex $[Ag(TT[9]OB)_2][ClO_4]$.

(17) For an example of similar fluxional behavior, see: Lui, S.; Lucas, C. R.; Newlands, M. J.; Charland, J. P. *Inorg. Chem.* **1990**, *29*, 4380-4385.

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Vibrational and Electronic Spectra of $[Pt_2(SO_4)_4]^{2-}$ Complexes

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The vibrational and electronic spectra of axially ligated sulfate-bridged binuclear platinum complexes ($[Pt_2(SO_4)_4L_2]^{n-}$: L = OH_2, DMSO, $n = 2$; L = Cl, Br, $n = 4$) have been studied. Raman spectra acquired with near-UV excitation show bands assigned to Pt-O(sulfate) stretching (300-350-cm^{-1} region) for all complexes, while bands assigned to Pt-Pt and Pt-L stretching are seen for complexes (L = Cl, Br) that display preresonance Raman scattering within intense near-UV absorption bands assigned to the $\sigma(L) \rightarrow \sigma^*(Pt_2)$ electronic transition. Weaker electronic absorptions are assigned as metal-metal $^1(\sigma \rightarrow \sigma^*)$ (near 220 nm for L = OH_2, Cl) and $d\pi \rightarrow d\sigma^*(Pt_2)$ (350-500 nm). Single-crystal polarized absorption spectra (L = OH_2, DMSO) show that the weak absorption system in the 350-500-nm region consists of three z-polarized (metal-metal axis) bands and an x,y-polarized band. The L = OH_2, Cl complexes show weak emission bands in the 695-750-nm region when excited at 77 K with near-UV light. These emission bands are similar to those observed for $[Pt_2(HPO_4)_4L_2]^{n-}$ (L = OH_2, $n = 2$; L = Cl, $n = 4$) complexes. The emission lifetimes for the sulfate-bridged complexes (450 ± 50 ns, L = OH_2; 290 ± 20 ns, L = Cl) are much shorter, and the emission intensities are much weaker, than the corresponding properties of the phosphate-bridged complexes.

Introduction

The structures and spectroscopic properties of d^7-d^7 complexes containing metal-metal single bonds have attracted much attention.[2-5] Extensive investigations of binuclear Pt(III) complexes have established that the relatively long Pt-Pt bond in bridging-pyrophosphite ($P_2O_5H_2^{2-}$) species is significantly perturbed by both axial and equatorial ligand interactions.[5-7] The effects of ligand variations on the vibrational and electronic spectra of $(Rh^{II})_2$ carboxylates[8] and $(Rh^{II})_2$ isocyanides[9] also have been studied in detail.

Binuclear Pt(III) complexes with bridging sulfate and phosphate ligands are of special interest because they possess relatively short Pt-Pt bonds;[10,11] indeed, a study of the electronic spectra of several phosphate-bridged species has already appeared.[12] We have now completed an extensive spectroscopic examination (absorption, emission, and vibrational spectra and single-crystal polarized electronic absorption spectra) of the sulfate-bridged compounds, and the results are reported herein.

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† Contribution No. 8442.

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