phenyl rings were constrained to a regular hexagon with *d*(C–C) of 1.392 Å. All the hydrogen atoms were included in idealized positions [with *d*(C–H) of 0.95 Å] in structure factor calculations. Common thermal parameters were assigned for methylene and methyl and for phenyl ring hydrogen atoms, and these values were refined.

An inspection of F_o and F_c suggested that an extinction parameter should be included. In the final cycles, employing 8884 observations with $I > 3\sigma(I)$, and weights of the form $w = k/[(\text{sig } F_o)^2 + gF_o^2]$, where $k = 0.3564$ and $g = 0.005\,924$, refinement of 363 variables converged at agreement factors $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.049$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.088$. The maximum shift/esd of 0.97 was for *y* of atom C(37). In a total difference Fourier synthesis, there were ten peaks with electron densities in the range 1.911–1.163 e Å^{-3}, and of these, eight were associated with the Au and Pt atoms at distances from 1.03 to 1.19 Å. The extinction parameter refined to 1.41 (14) × 10^{-4}.

The crystal data and experimental conditions are summarized in Table IV and Table SI (supplementary material). Positional and *U*(equiv) thermal parameters are given for selected atoms in Table V and for all atoms in Table SII (supplementary material). Tables of hydrogen atom parameters, anisotropic thermal parameters, root-mean-square amplitudes of vibration, additional dimensions, a weighted least-squares plane, and structure amplitudes have been deposited as supplementary material (Tables SIII–SVIII).

Acknowledgment. We thank the NSERC of Canada for financial support.

Supplementary Material Available: Tables of X-ray structure determination parameters, positional and thermal parameters, anisotropic thermal parameters, hydrogen atom parameters, root-mean-square amplitudes of vibration, additional interatomic dimensions, and a weighted least-squares plane and dihedral angles (Tables SI–SVII) and figures showing the ^{31}P NMR spectrum (121.4 MHz) of complex **10a**, the ^{31}P NMR spectrum (121.4 MHz) of complex **11**, and the ^{13}C NMR spectrum (75.4 MHz) of complex **12*** (^{13}CO enriched) (Figures S1–S3) (16 pages); a listing of structure amplitudes (Table SVIII) (44 pages). Ordering information is given on any current masthead page.

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Synthesis and Crystal Structure of Bis(1,4,7-trithiacyclodecane)palladium(II) Hexafluorophosphate[1]

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We wish to report the synthesis and X-ray crystal structure of the crown thioether complex bis(1,4,7-trithiacyclodecane)palladium(II) hexafluorophosphate, $[\text{Pd}(10\text{S}3)_2](\text{PF}_6)_2$. The two 10S3 ligands are arranged around the palladium in pseudooctahedral fashion to yield the *meso* stereoisomer. Four of the six sulfur atoms from the 10S3 ligands form a square-planar arrangement around the palladium (mean Pd–$\text{S}_{\text{equatorial}}$ bond distance = 2.27 Å). The remaining two sulfurs are coordinated axially at a much greater distance from the Pd (Pd–S_{axial} = 3.11 Å). Despite this long distance, the axial sulfur atoms do influence the electronic absorption spectrum for the complex resulting in a blue-green solid with a single d–d absorption band at 602 nm. The palladium complex crystallizes with two nitromethane solvent molecules per palladium atom. Crystal data for $[\text{Pd}(10\text{S}3)_2](\text{PF}_6)_2\cdot 2\text{CH}_3\text{NO}_2$: $\text{C}_{16}\text{H}_{34}\text{PdS}_6\text{P}_2\text{F}_{12}\text{N}_2\text{O}_4$, monoclinic, space group *C*2/*c*; $a = 22.473$ (9) Å, $b = 12.071$ (4) Å, $c = 11.186$ (3) Å, $\beta = 94.14$ (3)°, $V = 3026.53$ Å^3, $Z = 4$, $R = 0.046$, $D = 1.991$ g/cm^3, 2836 reflections measured. The complex undergoes a chemically reversible one-electron oxidation in nitromethane at +1.03 V vs Ag/AgCl.

Introduction

Research involving the coordination chemistry of thioether ligands, especially crown thioethers, is currently very active with several research groups examining the complexation behavior of thioether ligands such as 1,4,7-trithiacyclononane (9S3) and 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) (see Chart I).[3-6] Our research interests have focused on the effects that structural alterations on mesocyclic trithioether ligands might have on the ease of complex formation, complex stability, and complex structure. We have recently reported the synthesis of the 10-membered mesocyclic (medium-sized ring) thioether 1,4,7-trithiacyclodecane (10S3) and presented some complexation studies with divalent first-row transition metals, heavy-metal ions, and zerovalent metals.[7,8] This ligand typically complexes in tridentate fashion forming bis octahedral complexes in which all six sulfur atoms are coordinated. One distinctive feature in the complexation characteristics of 10S3 when compared to 9S3 is that, in the free ligand, one of the sulfur atoms in 10S3 is exodentate while all three sulfur atoms in 9S3 are endodentate.[9] Therefore, the 10S3 ligand has to undergo a conformational change in order to complex as a tridentate ligand whereas the 9S3 ligand does not.

Due to its electronic requirements, palladium(II) typically forms square-planar complexes that are usually yellow-orange in color.[10] Interestingly, Schroder and Wieghardt have independently reported X-ray crystal structures of the $(9\text{S}3)_2$ complex of Pd(II) in which the 9S3 complexes in an unusual pseudooctahedral or $[\text{S}_4 + \text{S}_2]$ fashion.[11,12] In the reported structures, four sulfur atoms from two 9S3 ligands form a square-planar arrangement around the Pd (mean Pd–$\text{S}_{\text{equatorial}}$ bond length = 2.32 Å) while the two axial sulfur atoms are coordinated at a distance of 2.95 Å from

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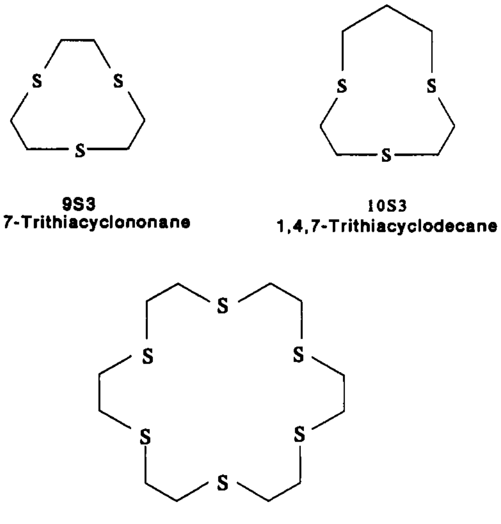
Chart I. Crown Thioether Ligands Discussed in This Paper



9S3
1,4,7-Trithiacyclononane

10S3
1,4,7-Trithiacyclodecane

18S6
1,4,7,10,13,16-Hexathiacyclooctadecane

the palladium atom. Despite this long bond distance, there is an electronic interaction between the palladium ion and the axial sulfur atoms resulting in a green complex (λ_{max} = 615 nm), an atypical color for palladium(II) complexes. The behavior of the 18S6 ligand toward palladium(II) follows a more anticipated pattern. The four sulfur atoms from the 18S6 ligand form a square-planar array around the palladium (mean Pd–$S_{equatorial}$ bond length = 2.31 Å) while the remaining two sulfur atoms are at a distance of 3.27 Å.[3,13] This distance is apparently too large for the axial sulfur atoms to influence the absorption spectrum of the palladium complex since the color is brown, and there are no bands near 600 nm.

We have recently reported several X-ray crystal structures in which 10S3 complexes as a bis tridentate ligand forming octahedral metal complexes.[1,7,8] Therefore, there will be an interesting interplay between the preferred octahedral coordination of the trithioether ligand and the preferred square-planar geometry of Pd(II). Since the conformational stereochemistry and complexation properties of 10S3 are different from the two previously studied crown thioethers,[9] the coordination of the ligand to Pd(II) is an intriguing problem for study.

Experimental Section

Materials. Nitromethane was dried by using common methods.[14] All other materials were used as received without additional purification. The 10S3 ligand was prepared by the reported method.[7]

Measurements. Analyses were performed by Atlantic Microlab, Inc., Atlanta, GA. Fourier transform infrared spectra were obtained by using a Beckman FT 1100 infrared spectrophotometer. Solution ultraviolet–visible spectra were obtained on a Varian DMS 200 UV–vis spectrophotometer. Magnetic susceptibility measurements on the solid complex were obtained with a Johnson-Matthey-Evans magnetic susceptibility balance, and standard diamagnetism correction factors were included. Cyclic voltammograms were recorded by using a Princeton Applied Research Model 384B polarographic analyzer. The supporting electrolyte was 0.1 M $(Bu)_4NBF_4$ in CH_3NO_2, and sample concentrations were approximately 1 mM. All voltammograms were recorded at a scan rate of 100 mV/s. The standard three-electrode configuration was as follows: glassy-carbon working electrode, Pt-wire auxiliary electrode, and Ag/AgCl reference electrode. A Syntex $P2_1$ auto diffractometer was used for the crystallographic study.

Synthesis of [Pd(10S3)$_2$](PF$_6$)$_2$. The $[Pd(10S3)_2](PF_6)_2$ complex was prepared by using the method of Schroder.[12] A mixture containing $K_2[PdCl_4]$ (50.0 mg, 0.153 mmol) and 10S3 (60.0 mg, 0.309 mmol) was refluxed in 15 mL of a 2:1 MeOH/water solution for 30 min. A dark blue solution resulted. The solution was concentrated to two-thirds of its original volume. Addition of NH_4PF_6 (58.0 mg, 0.337 mmol) and cooling yielded green crystals of $[Pd(10S3)_2](PF_6)_2$. The crystals were washed three times with 10 mL of MeOH, three times with anhydrous ether, and air-dried. Clear dark blue crystals were grown by solvent diffusion of a nitromethane solution with anhydrous diethyl ether to give 83.0 mg (69.2% yield) of bis(1,4,7-trithiacyclodecane)palladium(II) hexafluorophosphate. IR (KBr, cm^{-1}): 2950, 2912, 1442, 1418, 1415, 1289, 924, 888–815 (s, PF_6^-), 742, 712, 696, 677, 655, 616, 558. The visible electronic spectrum measured in nitromethane showed a single absorption with λ_{max} at 602 nm (ϵ = 80). The ultraviolet electronic spectrum measured in water showed two absorptions with λ_{max} at 309 nm (ϵ = 11 600) and λ_{max} at 279 nm (ϵ = 12 800). Magnetic susceptibility measurements on the complex showed that it was diamagnetic. Anal. Calcd for $C_{16}H_{34}PdS_6P_2F_{12}N_2O_4$: C, 21.42; H, 3.60; S, 24.50. Found: C, 21.51; H, 3.62; S, 24.44.

Table I. Crystallographic Data and Details of Refinement for $[Pd(10S3)_2](PF_6)_2 \cdot 2CH_3NO_2$

formula	$C_{16}H_{34}PdS_6P_2F_{12}N_2O_4$
fw	643.26 amu
color and habit	blue prisms
cryst size, mm	0.61 × 0.41 × 0.34
cryst syst	monoclinic
space group	*C*2/*c*
a, Å	22.473 (9)
b, Å	12.071 (4)
c, Å	11.186 (3)
V, Å^3	3026.53
β, deg	94.14 (3)
D(calcd), g cm^{-3}	1.991
Z	4
μ, cm^{-1}	1.19
no of reflcns measd	2836
no of unique reflcns measd	2681
no of indep reflcns with $I \geq 3.0\sigma(I)$	2402
F(000)	1824.00
R	0.046
R_w	0.058

Upon drying, the clear dark blue crystals to an opaque green solid, presumably due to loss of nitromethane solvent. The process can be reversed by redissolving the green solid in nitromethane. The complex is highly soluble in nitromethane and slightly soluble in water and readily dissolves in acetonitrile with a noticeable color change to yellow.

X-ray Crystal Structure of [Pd(10S3)$_2$](PF$_6$)$_2$·2CH$_3$NO$_2$. A clear blue crystal suitable for X-ray diffraction and having approximate dimensions 0.61 × 0.41 × 0.34 mm was mounted on an auto diffractometer equipped with a scintillation counter, Mo Kα radiation (λ = 0.710 73 Å), and a graphite monochromator. The automatic centering, indexing, and least-squares routines were carried out on 15 independent reflections in the range $18.32 < 2\theta < 25.95°$ to obtain the unit cell dimensions, which are given in Table I. The ω-scan technique over the range $4° \leq 2\theta \leq 50°$ was used to collect the data of which those with $I \geq 3.0\sigma(I)$ were considered observed. No correction was made for absorption.

The structure was solved by the heavy-atom method. The position of the palladium atom was located from a three-dimensional Patterson map, and the remaining atoms were located by subsequent structure factor calculations and difference electron density maps.[15] The structure was refined by full-matrix least-squares techniques. The hydrogen atoms were located by difference maps and were isotropically refined (positional parameters were not refined). All non-hydrogen atoms were refined anisotropically converging at

$$R = \sum||F_o| - |F_c||/\sum|F_o| = = 0.046$$

$$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.058$$

$$\mathrm{GOF} = [\sum w(|F_o| - |F_c|)^2(\text{no. of reflections} - \text{no. of parameters})]^{1/2} = 4.108$$

The final atomic parameters for $[Pd(10S3)_2](PF_6)_2 \cdot 2CH_3NO_2$ with their standard deviations are given in Table II. Selected bond distances and bond angles are given in Table III.

The unit cell contains eight nitromethane solvent molecules, and they are present in two special positions. One molecule is disordered with an inversion center between the nitrogen and the carbon atoms. This was refined with occupancies of 0.5 for the oxygen atoms and by assigning the carbon scattering factor for the C/N position. The second nitro-

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Table II. Atomic Positional Parameters for Non-Hydrogen Atoms and Thermal Parameters with Esd's in Parentheses

atom	x	y	z	B_{iso},[a] Å^2
Pd	$^1/_4$	$^1/_4$	0	1.893 (24)
S1	0.33263 (6)	0.15664 (12)	0.06852 (13)	2.25 (5)
C2	0.39149 (24)	0.2480 (5)	0.0328 (6)	2.72 (25)
C3	0.1275 (3)	0.1326 (5)	−0.0303 (6)	2.80 (24)
S4	0.19374 (6)	0.10663 (11)	0.06155 (13)	2.19 (5)
C5	0.17255 (23)	0.1366 (5)	0.2120 (5)	2.50 (23)
C6	0.2210 (3)	0.1238 (5)	0.1284 (7)	4.4 (3)
C7	0.2190 (3)	0.2946 (5)	0.3375 (5)	3.1 (3)
S8	0.26624 (6)	0.10411 (12)	−0.22464 (14)	2.71 (6)
C9	0.3366 (3)	0.0612 (5)	−0.1655 (6)	2.85 (25)
C10	0.3403 (3)	0.0390 (5)	−0.0297 (6)	2.79 (24)
P	0.91073 (8)	0.20140 (15)	0.92206 (16)	3.23 (7)
F1	0.9642 (3)	0.1342 (7)	0.9606 (7)	12.3 (5)
F2	0.8651 (3)	0.2682 (6)	0.8860 (9)	12.8 (6)
F3	0.9418 (4)	0.2573 (6)	0.8207 (6)	11.7 (5)
F4	0.8792 (3)	0.1421 (5)	1.0210 (6)	10.2 (4)
F5	0.8918 (3)	0.1088 (5)	0.8326 (5)	10.0 (4)
F6	0.9278 (4)	0.2946 (5)	1.0138 (6)	10.9 (4)
C11	0	0.0663 (10)	$^1/_4$	5.9 (6)
N	0	0.1888 (8)	$^1/_4$	4.1 (4)
O1	0.04015 (522)	0.2361 (5)	0.2117 (6)	5.9 (3)
CN	−0.0073 (4)	0.5003 (7)	0.1845 (7)	4.5 (4)
O2	0.0298 (5)	0.4749 (10)	0.1117 (11)	5.6 (6)
O3	−0.0499 (5)	0.5203 (12)	0.1558 (14)	7.7 (7)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

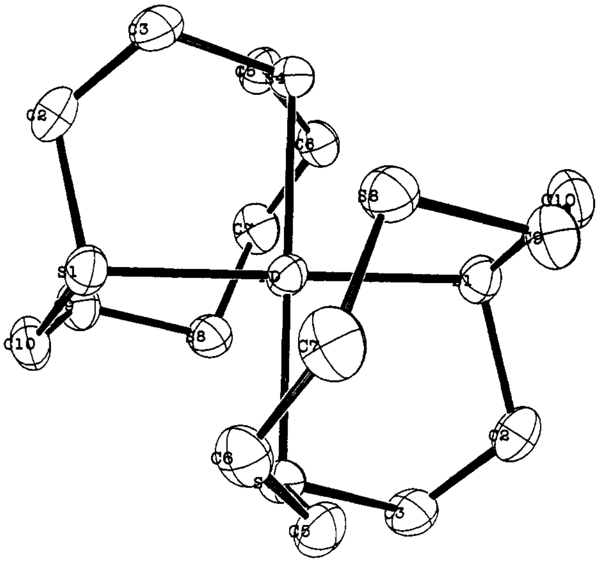


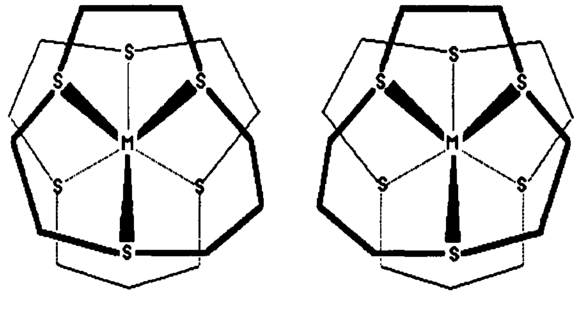
Figure 1. ORTEP perspective of $[Pd(10S3)_2](PF_6)_2$.

methane has a 2-fold axis along the C–N bond, causing the hydrogen atoms to be disordered. As a consequence of these disorders, no hydrogen atoms were located on the nitromethane molecules.

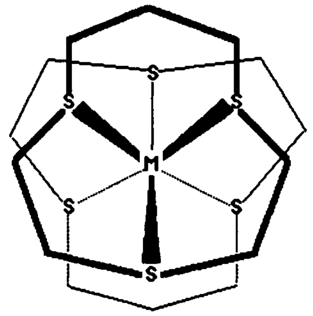
Results and Discussion

Structural Studies. The $[Pd(10S3)_2](PF_6)_2$ complex is isomorphous with the analogous 9S3 complex, crystallizing in the same space group ($C2/c$). The complex cation is centrosymmetric with two equivalent 10S3 ligands coordinating facially in tridentate fashion. A view of the complex is shown in Figure 1. The complex involves a tetragonally distorted pseudooctahedral environment of sulfur atoms $[S_4 + S_2]$ about the palladium. The two sulfur atoms between the two ethylene bridges in each 10S3 molecule lie in a trans arrangement to each other. The ligand adopts a [2233] conformation in which all three sulfur atoms are necessarily syn endodentate, and the six-membered chelate ring is nearly in a chair form.[8,9] Four sulfur atoms (two from each of the two 10S3 ligands) form a square-planar arrangement around the palladium with an average Pd–S bond distance of 2.27 Å. This distance is considerably shorter than the sum of the covalent radii, which is 2.35 Å.[16] A recent review reports Pd–S lengths in several structures ranging from 2.26 to 2.30 Å, indicating that the Pd–S bonds in the 10S3 complex are short.[16] These equatorial Pd–S bonds are considerably shorter (<0.04 Å) than the equatorial Pd–S bonds in the 18S6 and 9S3 complexes.[11-13] In our structure the axial sulfur atoms, one from each 10S3 ligand, are at a surprisingly large distance from the palladium atom, 3.11 Å. Interestingly, this is almost the mean for the Pd–S_{axial} bond distances in the 18S6 and 9S3 complexes.

Chart II. Stereoisomers of $(10S3)_2$ Octahedral Complexes



Δ Enantiomer **Λ Enantiomer**



***meso* Stereoisomer**

The Pd–$S_{equatorial}$ bond angles average 88.8°, which are almost identical with the values reported in the 9S3 structure.[11,12] The C–C bond distances in the 10S3 complex average 1.51 Å (9S3 structure: C–C = 1.51 Å), and the C–S bond distances average 1.79 Å (9S3 structure: C–S = 1.82 Å). The angle between the axial sulfur atoms and the plane formed by the palladium and the four equatorial sulfur atoms is 80.1°. In a tetragonally elongated octahedral geometry, this angle should be 90°. In the $[Pd(9S3)_2]^{2+}$ structure this angle is 84°, and in the $[Pd(18S6)]^{2+}$ structure this angle is 75°.[11-13] Again, the value obtained for the 10S3 complex lies between those of the 9S3 and 18S6 complex, reflecting the differences in conformational factors of the three ligands. The conformational preferences of the 10S3 ligand are therefore seen in longer axial Pd–S bonds, shorter equatorial Pd–S bonds, and the deviation from octahedral bond angles for the axial sulfur atoms. Because of the strong preference of Pd(II) for square-planar coordination, conformational differences among the three crown thioethers strongly influence the binding of the axial sulfur atoms.

The three possible stereoisomers for the facial octahedral coordination of 1,4,7-trithiacyclodecane are illustrated in Chart II. The first two stereoisomers have an enantiomeric relationship, and the third stereoisomer is a *meso* compound. Note that in the *meso* stereoisomer the two six-membered chelate rings form an anti arrangement in the two trigonal faces whereas they have a gauche arrangement in the pair of enantiomers. In this structure, the *meso* stereoisomer is the one obtained with the two propylene bridges from the 10S3 ligands occupying trans positions around the palladium center. We have recently determined the crystal structures for both the gauche and *meso* forms of $[Fe(10S3)_2](ClO_4)_2$.[8,17] The gauche stereoisomer of the iron(II) complex surprisingly crystallized into optically active enantiomers,

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Table III. Selected Bond Lengths (Å) and Bond Angles (deg)

		Bond Lengths			
Pd–S1	2.2584 (15)	S1–C2	1.790 (6)	C2–C3	1.502 (9)
Pd–S4	2.2789 (14)	S1–C10	1.811 (6)	C3–S4	1.775 (6)
S4–C5	1.819 (6)	C5–C6	1.483 (8)	S8–C9	1.747 (6)
C6–C7	1.523 (9)	C7–S8	1.805 (5)	C9–C10	1.539 (9)
		Bond Angles (deg)			
S1–Pd–S1	179.9	S1–Pd–S4	88.80 (6)	S1–Pd–S4	91.20 (6)
Pd–S1–C2	102.67 (20)	Pd–S1–C10	107.31 (20)	C2–S1–C10	104.1 (3)
S1–C2–C3	112.5 (4)	C2–C3–S4	113.9 (4)	Pd–S4–C3	98.73 (20)
Pd–S4–C5	108.45 (19)	C3–S4–C5	103.6 (3)	S4–C5–C6	116.4 (4)
C5–C6–C7	115.8 (5)	C7–S8–C9	105.0 (3)	S8–C9–C10	114.1 (4)
S1–C10–C9	117.5 (4)	C6–C7–S8	116.6 (4)		

Table IV. Comparison of Data for Pd(II)–Crown Thioether Complexes[a]

complex	mean equat Pd–S, Å	ax Pd–S, Å	color	ref
$[Pd(9S3)_2]^{2+}$	2.32	2.95	green	11, 12
$[Pd(10S3)_2]^{2+}$	2.27	3.11	blue-green	this work
$[Pd(18S6)]^{2+}$[b]	2.31	3.27	brown	13
$[Pd(18S6)]^{2+}$[c]	2.33	3.01	green	4
$[Pd(L1)]^{2+}$	2.33	none	yellow-orange	18
$[Pd(L2)]^{2+}$	2.33	2.95, 3.00	green	18

[a] Ligand abbreviations: L1 = $Me_2[18]aneN_2S_4$, 7,16-dimethyl-1,4,10,13-tetrathia-7,16-diazacyclooctadecane; L2 = $[18]aneN_2S_4$, 1,4,10,13-tetrathia-7,16-diazacyclooctadecane. [b] Tetraphenylborate salt. [c] Hexafluorophosphate salt.

a rare example of the spontaneous resolution of a coordination complex into conglomerates.

Absorption Spectra, Electrochemistry, and Magnetic Properties. A single absorption band is observed in the visible region at 602 nm, and it is this band that accounts for the unusual blue-green color of the palladium(II) complex. The value of the extinction coefficient demonstrates that the band is indeed a d–d transition. There are also two charge-transfer bands which appear at 309 and 279 nm. Table IV illustrates the relationship between six reported palladium crown thioether complexes and their observed spectral properties. In the 9S3 complexes, the charge-transfer bands lie between 400 and 470 nm, possibly due to the shorter axial Pd–S bond lengths. A very recent report by Schroder and co-workers describes two new palladium(II) complexes with potentially hexadentate macrocyclic ligands, which exhibit characteristics similar to those of the complex described here.[18] One of these complexes is green in color with palladium–axial sulfur bond lengths of 3.00 Å. In addition, Schroder has also recently reported the X-ray crystal structure of the hexafluorophosphate salt of $[Pd(18S6)]^{2+}$, which is also green in color with similar (3.00 Å) axial bond lengths.[4] This illustrates the influence that anion effects can have on the preferred geometry of these types of complexes.

Cyclic voltammetry is nitromethane shows a cathodic half-wave potential at +0.97 V vs Ag/AgCl and an anodic peak potential at +1.09 V vs Ag/AgCl. Square-wave voltammetry of the complex in nitromethane shows a single peak at +1.03 V vs Ag/AgCl, which corresponds with the $E_{1/2}$ at +1.03 V. The peak-to-peak separation was 63 mV, and the process is chemically reversible with i_{pa}/i_{pc} equal to 0.98. This reversible process is assigned to the oxidation of the Pd(II) center to Pd(III). The oxidation process does appear to be metal based since the 10S3 ligand shows only an irreversible oxidation wave in nitromethane at +1.33 V vs Ag/AgCl. Schroder and co-workers have noted similar oxidation behavior for the 9S3 complex, and they have been able to isolate an unusual Pd(III) complex of 9S3 by oxidation of the Pd(II) complex and have reported its crystal structure.[12,19] On the basis of its redox behavior, the 10S3 complex should form a similar stable Pd(III) complex, and we are currently pursuing this interest. The observed electrochemical behavior of the 10S3 ligand is similar to that reported for 9S3.[20] A chemically irreversible reduction wave is also observed for the $[Pd(10S3)_2]^{2+}$ complex in nitromethane at −0.482 V vs Ag/AgCl.

There is a noticeable color change from blue-green to yellow when the 10S3 complex is dissolved in acetonitrile. However, the 9S3 complex retains its green color in a variety of solvents.[11,12] This process is reversible for $[Pd(10S3)_2]^{2+}$, yielding green crystals upon evaporation of solvent. We believe that this and other noted color changes (i.e.; clear blue to opaque green with loss of solvent) are due to changes in the weak axial sulfur–palladium interactions, which probably influence the positions of the charge-transfer bands. This interaction is sensitive to changes in solvent and counterion. Room-temperature magnetic susceptibility measurements on the complex showed that it was diamagnetic as expected. The synthetic procedure is an additional unusual example of substitution of chloride ligands by a crown thioether.[5]

Conclusions

The tridentate ligand, 10S3, complexes palladium(II) in pseudooctahedral fashion. Four of the six sulfur atoms surround the palladium in square-planar fashion while the remaining two sulfurs are at a much greater distance, more than 0.9 Å longer. This long axial bond length relative to the 9S3 complex is due to the greater conformational freedom of the 10S3 ligand. However, despite this long Pd–S bond length, the axial S–Pd interaction still results in a d–d absorption band at 602 nm, causing the complex to be an unusual blue-green color.

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Supplementary Material Available: Listings of complete bond lengths and bond angles, complete atom positional parameters, anisotropic thermal parameters, and torsional angles (11 pages); a listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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