Inorg. Chem. **1998,** *37,* 5299−5305

Platinum Group Metal Complexes of Macrocyclic Oxathiaethers. The Crystal Structures of $18S_4O_2$, $[Pt(9S_2O)_2](PF_6)_2{\cdot}2CH_3NO_2$, $[Pt(18S_4O_2)](PF_6)_2$, and $[Pd(9S_2O)_2](PF_6)_2{\cdot}2CH_3CN$

Gregory J. Grant,*,[†] David F. Galas,[†] Myron W. Jones,[†] Kristi D. Loveday,[†] William T. Pennington,[‡] George L. Schimek,[‡] Cassandra T. Eagle,[§] and Donald G. VanDerveer[||]

Department of Chemistry, The University of Tennessee at Chattanooga, Chattanooga, Tennessee 37403, Department of Chemistry, Clemson University, Clemson, South Carolina 29634, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332, and Department of Chemistry, Appalachian State University, Boone, North Carolina 28608

Received December 16, 1997

Improved syntheses of the mixed oxathia crown ligands 1-oxa-4,7-dithiacyclononane ($9S_2O$) and 1,10-dioxa-4,7,13,16-tetrathiacyclooctadecane ($18S_4O_2$) are presented. The single-crystal X-ray structure of $18S_4O_2$ has also been obtained. Crystal data for $18S_4O_2$: $C_{12}H_{24}O_2S_4$; triclinic, space group $P\bar{1}$; $a = 7.188(3)$ Å, $b = 5.240(1)$ Å, $c = 10.743(3)$ Å; $\alpha = 99.30(2)°$, $\beta = 98.09(3)°$, $\gamma = 92.19(3)°$; $V = 394.57$ Å^3; $Z = 1$, $R = 0.067$, $R_w = 0.103$ for 2419 reflections. The ligand structure shows the two oxygen atoms point into the macrocycle cavity while the four sulfur atoms are oriented in an *exodentate* fashion. Therefore, this ligand is poorly preorganized for hexadentate complexation and will have to undergo substantial reorganization to be able to complex in a multidentate fashion using its sulfur atoms. The syntheses of homoleptic complexes for both of these macrocycles with the platinum group metal ions, Pd(II) and Pt(II), are also described. The single-crystal X-ray structures for three of the complexes have been obtained, and all show that only the sulfur atoms are bound to the metal center. Crystal data for $[Pt(9S_2O)_2](PF_6)_2{\cdot}2CH_3NO_2$: $C_{14}H_{30}N_2O_6F_{12}P_2S_4Pt$; triclinic, space group $P\bar{1}$; $a = 9.996(5)$ Å, $b = 11.019(3)$ Å, $c = 8.253(2)$ Å; $\alpha = 92.79(2)°$, $\beta = 110.18(2)°$, $\gamma = 64.04(2)°$; $V = 761.5(5)$ Å^3; $Z = 1$; $R = 0.0365$, $R_w = 0.0543$ for 2680 reflections. Crystal data for $[Pt(18S_4O_2)](PF_6)_2$: $C_{14}H_{24}O_2F_{12}P_2S_4Pt$; monoclinic, space group $P2_1/n$; $a = 11.110(3)$ Å, $b = 9.244(1)$ Å, $c = 12.642(2)$ Å; $\beta = 111.48(1)°$; $V = 1208.2(3)$ Å^3; $Z = 2$; $R = 0.0343$, $R_w = 0.0428$ for 1696 reflections. Crystal data for $[Pd(9S_2O)_2](PF_6)_2{\cdot}2CH_3CN$: $C_{14}H_{30}N_2O_6F_{12}P_2S_4Pd$; monoclinic, space group $C2/c$; $a = 12.535(2)$ Å, $b = 19.463(2)$ Å, $c = 12.127(2)$ Å; $\beta = 95.68(1)°$, $V = 2944.0(7)$ Å^3; $Z = 4$; $R = 0.0493$, $R_w = 0.0651$ for 1959 reflections. The oxygen atoms in all of the structures are oriented *exodentate* to the metal center and lie at too great of a distance (3.443(5), 3.730(5), or 3.379(5) Å, respectively) to exhibit the long-distance metal interactions exhibited in related crown thioether complexes. The effects of the lack of axial metal−oxygen interactions are seen in the absence of visible d−d electronic transitions, and the lack of any oxidation electrochemistry in the complexes. Additionally for the Pt(II) complexes, ^{195}Pt NMR chemical shifts are observed near −4650 ppm which are consistent with a square planar S_4 coordination environment around the platinum. The complexation behavior of these ligands toward Pt(II) and Pd(II) contrasts that of analogous crown thioethers ligands and mixed azathia macrocycles which show significant metal−axial donor atom interactions. The general ligand complexation characteristics of oxathia crowns are dominated by metal−ligand electronic interactions as opposed to ligand conformational factors.

Introduction

There has been a considerable recent interest in platinum group metal complexes of crown thioether ligands because of the unusual properties that they demonstrate.[1−4] Homoleptic complexes of these metal ions containing tridentate trithioethers such as 1,4,7-trithiacyclononane (9S3) and 1,4,7-trithiacyclodecane (10S3) have been shown to stabilize less common oxidation states such as Pt(III), Pd(III), Au(II), exhibit surprising electronic spectra which feature d−d visible absorption bands, and form exotic coordination geometries such as octahedral Rh(II).[5−13] For thioether complexes involving Pd(II) and Pt(II),

---

[†] The University of Tennessee at Chattanooga.
[‡] Clemson University.
[§] Appalachian State University.
[||] Georgia Institute of Technology.

(1) Blake, A. J.; Schröder, M. In *Advances in Inorganic Chemistry*; Sykes, A. G., Ed.; Academic Press: New York, 1990; Vol. 35, p 2.
(2) Cooper, S. R. *Acc. Chem. Res.* **1988**, *21*, 141.
(3) Cooper, S. R.; Rawle, S. C. *Struct. Bonding (Berlin)* **1990**, *72*, 1.
(4) Schröder, M. *Pure Appl. Chem.* **1988**, *60*, 517.
(5) Blake, A. J.; Holder, A. J.; Hyde, T. I.; Roberts, Y. V.; Lavery, A. J.; Schröder, M. *J. Organomet. Chem.* **1987**, *323*, 261.
(6) Blake, A. J.; Holder, A. J.; Hyde, T. I.; Schröder, M. *J. Chem. Soc., Chem. Commun* **1987**, 987.
(7) Blake, A. J.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Lavery, A. J.; Odulate, M. O.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1987**, 118.
(8) Grant, G. J.; Sanders, K. A.; Setzer, W. N.; VanDerveer, D. G. *Inorg. Chem.* **1991**, *30*, 4053.
(9) Chandrasekhar, S.; McAuley, A. *Inorg. Chem.* **1992**, *31*, 2663.
(10) Blake, A. J.; Crofts, R. D.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1993**, 2259.
(11) Blake, A. J.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1861.
(12) Cooper, S. R.; Rawle, S. C.; Yagbasan, R.; Watkin, D. J. *J. Am. Chem. Soc.* **1991**, *113*, 1600.
(13) Blake, A. J.; Greig, J. A.; Holder, A. J.; Hyde, T. I.; Taylor, A.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 197.

S0020-1669(97)01571-1 CCC: $15.00

these unusual properties have been shown to be a direct consequence of long distance interactions between the metal center and axial sulfur atoms.[14] In the absence of these interactions, more typical complex behavior is observed, and the presence of these long-distance interactions has been shown to be correlated with ligand structure. In particular, homoleptic Pt(II) complexes of 9S3, 10S3, and 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) have been shown to have a d−d absorption maximum near 430 nm and a reversible Pt^{II}/Pt^{III} couple near +0.35 V relative to Fc/Fc$^+$.[15] Similarly, several homoleptic crown thioether complexes of Pd(II) are an unusual green or blue color due to a d−d absorption maximum near 600 nm, and a reversible Pd^{II}/Pd^{III} couple is seen near +0.60 V relative to Fc/Fc$^+$.[5,8,9] These characteristics are lacking in Pt(II) or Pd(II) complexes with larger crown thioethers such as 20S6 or in acyclic thioethers.[14]

The focus for this current report is the nine-membered mixed oxathia crown, 1-oxa-4,7-dithiacyclononane (9S$_2$O), and the eighteen-membered oxathia crown, 1,10-dioxa-4,7,13,16-tetrathiacyclooctadecane (18S$_4$O$_2$). Both of these ligands were first prepared by Izatt, Bradshaw, and co-workers at Brigham Young, but surprisingly, their transition metal chemistry has received little attention.[16] In fact, reports of complexes with the ligands have been limited to lanthanide and main group metals,[17−19] and a very recent initial report of complexation with d-block metals.[20] We are interested in exploring their complexation chemistry with transition metal ions since they are intrinsic analogues to the well-studied 9S3 and 18S6 crown ligand systems. Notable differences in ligand behavior may be reflected in the replacement of the softer sulfur donor atoms with the harder oxygen atoms in the mixed O−S donor crowns. For these oxathia ligands, differences in coordination between the two distinct donor types may be observed. That is, will softer transition metal ions of the platinum group be simultaneously bound by both the sulfur and oxygen donor atoms present in the macrocycle? An important consideration is the difference in conformational preferences between C−O and C−S bonds.[21] The anti conformation is known to be preferred for C−O bonds, while C−S bonds prefer gauche conformations. Several other reports dealing with a few complexes of other macrocyclic oxathioethers have appeared.[22−29] However, the two ligands discussed here make a more facile comparison for complexation behaviors because they, like 9S3 and 18S6, form exclusively five-membered chelate rings bridged only by methylene carbons.

There may be both stereochemical as well as electronic factors which can differentiate the coordination behavior between these ligands and related crown thioethers and mixed azathia crowns. In the present work, we were interested in contrasting the properties of the homoleptic Pt(II) and Pd(II) complexes of the two mixed oxathia ligands with their all-sulfur analogues. In particular, will the unusual structural, spectroscopic, and electrochemical properties observed for the crown thioether and related ligand complexes of these two metal ions be repeated for the mixed oxathia crowns? We report the synthesis of the four platinum group metal complexes with these ligands including the molecular structure determination of three of them by single-crystal X-ray diffraction.[30]

Experimental Section

Materials. All solvents and reagents were purchased from Aldrich Chemical Co. and used as received except for 1,2-dichloroethane, 1,2-dibromoethane, and bis(2-mercaptoethyl)ether which were distilled prior to use. Inorganic salts were used as received.

Measurements. Analyses were performed by Atlantic Microlab, Inc., (Atlanta, GA). Fourier transform infrared spectra were obtained using a Galaxy FT IR 5000 spectrophotometer and ultraviolet−visible spectra were obtained on a Varian DMS 200 UV−visible spectrophotometer. Carbon-13 and proton NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer using either CD$_3$NO$_2$, DMSO-d_6, or CDCl$_3$ for both the deuterium lock and reference. All observed carbon resonances were confirmed to be methylene resonances via DEPT (Distortionless Enhancement by Polarization Transfer) experiments. Platinum-195 NMR spectra were recorded at 64.208 MHz using aqueous solutions of [PtCl$_6$]$^{2-}$ (0 ppm) as an external reference and delay time of 0.01 s. Referencing was verified versus authentic samples of [PtCl$_4$]$^{2-}$ which was found to have a chemical shift at −1626 ppm, in agreement with the reported value of −1624 ppm.[31] Molecular mechanics calculations were carried out using CAChe software from Oxford Molecular, Inc. A Princeton Applied Research model 273 polarographic analyzer was used for electrochemical measurements. The supporting electrolyte was 0.1 M (Bu)$_4$NBF$_4$ in CH$_3$NO$_2$, and sample concentrations were 1 mM. All voltammograms were recorded at a scan rate of 100 mV/s. The standard three-electrode configuration was as follows: platinum working electrode, Pt-wire auxiliary electrode, and Ag/AgCl reference electrode. All potentials were referenced against a Fc/Fc$^+$ couple.

Preparation of 1-Oxa-4,7-dithiacyclononane. The method used was based upon the Cooper synthesis of 1,4,7-trithiacyclononane.[32] A 2000-mL three-necked round-bottom flask equipped with a 125-mL pressure equalizing dropping funnel, magnetic stir bar, thermometer, and nitrogen inlet−outlet, was charged with a slurry of 1000 mL of dimethylformamide and cesium carbonate (52.12 g, 160 mmol). In the funnel was prepared a solution of freshly distilled bis(2-mercaptoethyl) ether (19.91 g, 144 mmol), 1,2-dichloroethane (11.35 mL, 14.25 g, 144 mmol), and 600 mL of DMF. The solution was added to the rapidly stirred, heated (100 °C) DMF/Cs$_2$CO$_3$ slurry at the rate of about 1 drop/6 s. After completion of the addition (48 h), the mixture was cooled to room temperature and stirred for an additional 48 h. A colorless supernatant solution and a white precipitate of CsCl had formed. The CsCl was filtered, and the solvent was removed in vacuo

---

(14) Grant, G. J.; Spangler, N. S.; Setzer, W. N.; VanDerveer, D. G. *Inorg. Chim. Acta* **1996**, *246*, 41.

(15) Blake, A. J.; Gould, R. O.; Lavery, A J.; Schröder, M. *Angew. Chem., Int Ed. Engl.* **1986**, *25*, 274.

(16) Bradshaw, J. S.; Hui, J. Y.; Haymore, B. L.; Christensen, J. J. Izatt, R. M. *J. Heterocycl. Chem.* **1974**, *10*, 1.

(17) Nazarneko, A. Y.; Dalley, N. K.; Lamb, J. D. 213th ACS National Meeting, San Francisco, CA; Division of Inorganic Chemistry, Paper Number 812.

(18) Singh, H.; Kumar, M.; Singh, P.; Kumar, S. *Indian J. Chem.* **1991**, *30*, 237.

(19) Ciampolini, M.; Mealli, C.; Nardi, N. *J. Chem. Soc., Dalton Trans.* **1980,** 376.

(20) Lucas, C. R.; Liang, W.; Miller, D. O.; Bridson, J. N. *Inorg. Chem.* **1997**, *36*, 4508.

(21) Wolf, R. E.; Hartman, J. A. R.; Storey, J. M. E.; Foxman, B. M.; Cooper, S. R. *J. Am Chem. Soc.* **1987**, *109*, 4328. Raithby, P. R.; Shields, G. P.; Allen, F. H. *Acta Crystallogr.* **1997**, *B53*, 241.

(22) Blake, A. J.; Reid, G.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1990**, 3849.

(23) Blake, A. J.; Reid, G.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1992**, 1074.

(24) Lucas, C. R.; Liu, S.; Bridson, J. N. *Can. J. Chem.* **1995**, *73*, 1023.

(25) Blake, A. J.; Gould, R. O.; Radek, C.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1995**, 4045.

(26) Kicham, J. E.; Loeb, S. J. *Organometallics* **1995**, *14*, 3584.

(27) de Groot, B.; Jenkins, H. A.; Loeb, S. J.; Murphy, S. L. *Can. J. Chem.* **1995**, *73*, 1102.

(28) Drexler, H.-J.; Reinke, H.; Holdt, H.-J. *Chem Ber.* **1996,** *129*, 807.

(29) Ashton, P. R.; Burns, A. L.; Claessens, C. G.; Shimizu, G. H.; Small, K.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1997**, 1493.

(30) This work was originally presented at at the XIX International Symposium on Macrocyclic Chemistry, June 12−17, 1994, Lawrence, KS; Paper Number ST9.

(31) Pregosin, P. S. In Pregosin, P. S., Ed.; *Transition Metal Nuclear Magnetic Resonance*; Elsevier: New York, 1991; p 251 and references therein.

(32) Blower, P. J.; Cooper, S. R. *Inorg. Chem.* **1987**, *26*, 2009.

leaving a brown yellow oil. The brown yellow oil was taken up in 100 mL of CH_2Cl_2, and the mixture was filtered. The CH_2Cl_2 solution was washed with 100 mL of water, 2 × 100 mL of 0.1 M NaOH, 2 × 100 mL of water again, and dried over anhydrous $MgSO_4$. The drying agent was filtered, and the CH_2Cl_2 was removed in vacuo. The brown oil was distilled under vacuum to yield 12.148 g (51.3%) of 1-oxa-4,7-dithiacyclononane as an amber oil, bp 61−63° at 0.1 mm. ^1H NMR ($CDCl_3$ δ), 3.96 (4 H, $-OCH_2CH_2S-$), 3.09 (4 H, $-OCH_2CH_2S-$), 2.81(4 H, $-SCH_2$ CH_2S-). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 73.90, 34.85, 33.36 ppm.

Preparation of 1,10-Dioxa-4,7,13,16-tetrathiacyclooctadecane. The method used was based upon the reported synthesis of 1,4,7,11,-14,17-hexathiacycloeicosane.[33] A 2000 mL three-necked round-bottom flask, fitted with a 125 mL pressure equalizing dropping funnel, a magnetic stir bar, a thermometer, a nitrogen inlet−outlet and was charged with a 1500 mL volume of absolute ethanol. To this volume, freshly distilled 2-mercaptoethyl ether (13.824 g, 100 mmol) was added and stirred. Next, a mass of sodium metal (4.60 g, 200 mmol) was added to the stirring mixture under nitrogen. The solution was then heated to reflux. After all of the sodium metal had reacted, a volume of 1,2-dibromoethane (18.800 g, 100 mmol) was dropped into the refluxing ethanol solution over 1.5 h. at the rate of 1 drop/s. After the completion of the addition, the mixture was stirred and cooled to room temperature for about 1 h. A white solid was present along with a yellow supernatant. The white solid, NaBr, was removed by filtration and washed with 3 × 50 mL of chloroform. The ethanol−chloroform extracts were rotary evaporated to leave a brown viscous oil. The brown residue was taken up in 200 mL of CH_2Cl_2, and the mixture was filtered. The CH_2Cl_2 solution was washed with 200 mL of water, 2 × 100 mL of 0.1 M NaOH, 2 × 100 mL of water again, and dried over anhydrous $MgSO_4$. The drying agent was filtered, and the CH_2Cl_2 was removed in vacuo leaving a yellow oily liquid. The yellow oily liquid was chromatographed on a silica gel gravity column (3 cm diameter × 50 cm length), eluting with 10% ethyl acetate/hexane to give 5.87 g (35.7% yield) of 1,10-dioxa-4,7,13,16-tetrathiacyclooctadecane as a white, crystalline solid, mp, 125−126 °C. ^1H NMR ($CDCl_3$, δ): 3.72 (8 H, $-OCH_2CH_2S-$), 2.90 (8 H, $-SCH_2CH_2O-$), 2.79 (8 H, $-SCH_2CH_2S-$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 71.90, 32.40, 31.11 ppm. Also obtained as separated products from the column were 1-oxa-4,7-dithiacyclononane (0.467 g, 3.0%) and 1-oxa-4,7,10-trithiacyclodecane (5.32 g, 32.4%).[16,34] The remaining mass (4.75 g), presumably a polymeric material, was insoluble in all common solvents.

Preparation of $[Pt(9S_2O)_2](PF_6)_2 \cdot 2CH_3NO_2$. A mixture of K_2PtCl_4 (125 mg, 0.301 mmol) and $9S_2O$ (100 mg, 0.608 mmol) was refluxed for 24 h in 27 mL of 2:1 MeOH−water. The solution was hot filtered and rotary evaporated to about $^2/_3$ volume. Next, a mass of NH_4PF_6 (43 mg, 0.265 mmol) was added, and the solution chilled. Off-white crystals were vacuum filtered, and the solid product was washed with ether (2 × 30 mL). The product (202 mg) was further purified via recrystallization from nitromethane/ether to yield a mass of 136 mg (48.5%) of colorless crystals. Anal. Calcd for $C_{14}H_{30}S_4F_{12}P_2N_2O_6Pt$: C, 17.97 H, 3.23; S, 13.71. Found: C, 18.25; H, 3.12; S, 13.79. The electronic absorption spectrum measured in acetonitrile showed two λ_{max}s at 313 nm (ϵ = 594) and 242 nm (ϵ = 10 700). FT-IR (KBr, cm^{-1}): 2920, 2871, 1479, 1425, 1310, 1135, 1020, 844 (s, PF_6^-), 664 (C−S). ^1H NMR (CD_3NO_2): complex, overlapping peaks, δ 3.9−3.5 ppm. $^{13}C\{^1H\}$ NMR(CD_3NO_2): δ 76.56 ($^3J_{PtC}$ = 47.4 Hz), 43.67, 43.55 ppm. $^{13}C\{^1H\}$ NMR (DMSO-d_6 δ): 74.89 ($^3J_{PtC}$ = 48 Hz), 41.85, 41.42 ppm. $^{195}Pt\{^1H\}$ NMR (CD_3NO_2), $\delta(\nu_{1/2})$: −4739 ppm (557 Hz).

Preparation of $[Pt(18S_4O_2)](PF_6)_2$. This compound was prepared using an identical synthesis to the above procedure and reacting 100 mg (305 mmol) of the $18S_4O_2$ ligand and 125 mg (305 mmol) of K_2PtCl_4. After metathesis to the PF_6^- salt, isolation, and recrystallization from nitromethane/ether, a yield of 61 mg (24.6%) of colorless crystals of $[Pt(18S_4O_2)](PF_6)_2$ were obtained. Anal. Calcd for $C_{12}H_{24}S_4F_{12}P_2Pt$: C, 17.72; H, 2.97; S, 15.67. Found: C, 17.99; H, 2.85; S, 15.49. FT-IR (KBr, cm^{-1}): 2975, 2932, 2874, 1415, 1299, 1111, 1062, 1040, 836 (s, PF_6^-), 657 (C−S), 557. The electronic absorption spectrum measured in acetonitrile shows a single λ_{max} at 235 nm(ϵ = 3980). ^1H NMR (CD_3NO_2): complex, overlapping pattern δ 4.0−3.0 ppm. $^{13}C\{^1H\}$ NMR (CD_3NO_2, δ): 65.69, 42.17, 41.69 ppm. $^{195}Pt\{^1H\}$ NMR (CD_3NO_2), $\delta(\nu_{1/2})$: −4571 ppm (84 Hz).

Preparation of $[Pd(9S_2O)_2](PF_6)_2 \cdot 2CH_3CN$. A mass of 1-oxa-4,7-dithiacyclononane ($9S_2O$) (100 mg, 0.609 mmol) and K_2PdCl_4, (99 mg, 0.303 mmol) was placed in 15 mL of a 2:1 methanol/water solution. The mixture was refluxed for 1 h. Next, yellow crystals of the complex were isolated by the addition of NH_4PF_6 (150 mg, 0.920 mmol) followed by the dropwise of addition of 20 mL of ether to the chilled mixture. These yellow crystals were collected by vacuum filtration and washed with ether (2 × 10 mL). The complex was further purified by the diffusion of ether into an acetonitrile solution yielding 78.9% yield (192 mg) of $[Pd(9S_2O)_2](PF_6)_2 \cdot 2CH_3CN$. IR (KBr, cm^{-1}): 2998, 2932, 2874, 1474, 1413, 1294, 1129, 1009, 837 (s, PF_6^-), 557. The electronic absorption spectrum measured in acetonitrile showed a single λ_{max} at 302 nm (ϵ = 10 600). Anal. Calcd for $C_{18}H_{30}S_4O_2P_2F_{12}PdN$: C, 23.81; H, 3.73; S, 16.30. Found: C, 23.81; H, 3.75; S, 16.09. ^1H NMR (CD_3NO_2): 4.97−4.49 (8 H), 4.29−3.87 (16 H) ppm. $^{13}C\{^1H\}$ NMR (CD_3NO_2): 72.42 ($-O-CH_2-CH_2-S-$), 42.40 ($-O-CH_2-CH_2-S-$), 41.39 ppm ($-S-CH_2-CH_2-S-$).

Preparation of $[Pd(18S_4O_2)](PF_6)_2$. The above procedure was employed using a mass of 1,10-dioxa-4,7,13,16-tetrathiacyclooctadecane (18S4O2) (100 mg, 0.304 mmol) and K_2PdCl_4 (99 mg, 0.303 mmol). A mass of 45.2 mg (20.6%) of yellow crystals of $Pd(18S_4O_2)](PF_6)_2$ were isolated. IR (KBr, cm^{-1}) 2973, 2917, 2878, 2858, 1479, 1412, 1299, 1109, 932 (s, PF_6^-), 619, 558, 529. The electronic absorption spectrum measured in acetonitrile showed a single λ_{max} at 296 nm (ϵ = 9150). Anal. Calcd for $C_{12}H_{24}S_4O_2P_2F_{12}Pd$: C, 19.88; H, 3.34; S, 17.69. Found: C, 19.93; H, 3.33; S, 17.79. ^1H NMR (DMSO-d_6): broad, overlapping resonances 4.5−3.1 ppm. $^{13}C\{^1H\}$ NMR (DMSO-d_6, δ): 65.7 ($-O-CH_2-CH_2-S-$), 39.6 ($-O-CH_2-CH_2-S-$), 30.8 ppm ($-S-CH_2-CH_2-S-$).

X-ray Crystallographic Analysis. Single crystals for the two Pt(II) complexes were grown by vapor diffusion of Et_2O into a nitromethane solution. Similarly, crystals of $[Pd(9S_2O)_2](PF_6)_2 \cdot 2CH_3CN$ were obtained by ether diffusion into an acetonitrile solution. A colorless needle of $18S_4O_2$ suitable for X-ray diffraction was grown by diffusion of hexane into a chloroform solution. The crystallographic data as well as the details of the solution are presented in Table 1. Selected bond distances and bond angles for all four structures are presented in Table 2.

Intensity data were measured with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 22 ± 1 °C by using $\omega/2\theta$ scans ($2\theta_{max}$ = 50°) on either a Nicolet $R3mV$ diffractometer (for $[Pt(18S_4O_2)](PF_6)_2$) or a Rigaku AFC7R diffractometer (for $[Pt(9S_2O)_2](PF_6)_2 \cdot 2CH_3NO_2$ and $[Pd(9S_2O)_2](PF_6)_2 \cdot 2CH_3CN$). An empirical absorption correction based on azimuthal scans of several moderately intense reflections were applied to the data for both compounds, as were Lorentz and polarization corrections. The intensities of three check reflections measured periodically throughout data collection declined by 10.7% over the course of the experiment for $[Pt(18S_4O_2)](PF_6)_2$ and 7.4% for $[Pd(9S_2O)_2](PF_6)_2 \cdot 2CH_3CN$; a linear correction was applied to the data to correct for crystal decomposition. No decay correction was needed for $[Pt(9S_2O)_2](PF_6)_2 \cdot 2CH_3NO_2$. The structures were solved by direct methods and refined by using full-matrix least-squares techniques. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in calculated positions (d_{C-H} = 0.96 Å) with a refined group thermal parameter (U = 0.070(9) Å^2 for $[Pt(18S_4O_2)](PF_6)_2$; U = 0.071(8) Å^2 for $[Pt(9S_2O)_2](PF_6)_2 \cdot 2CH_3NO_2$; U = 0.095(5) Å^2 for $[Pd(9S_2O)_2](PF_6)_2 \cdot 2CH_3CN$). Structure solution, refinement and the calculation of derived results were performed with the SHELXTL[35] package of computer programs. Neutral atom scattering factors were those of Cromer and Waber,[36] and the real and imaginary anomalous dispersion corrections were those of Cromer.[37] For the $18S_4O_2$ ligand

---

(33) Riley, D. P.; Oliver, J. D. *Inorg. Chem.* **1983**, *22*, 3361.

(34) Dalley, N. K.; Larson, S. B.; Smith, J. S.; Matheson, K. L.; Izatt, R. M.; Christensen, J. J. *J. Heterocycl. Chem.* **1981**, *18*, 463. Dalley, N. K.; Smith, J. S.; Larson, S. B.; Matheson, K. L.; Izatt, R. M.; Christensen, J. J. *J. Chem. Soc., Chem Commun.* **1975**, 84.

(35) Sheldrick, G. M. *SHELXTL*: *Crystallographic Computing System*; Nicolet Instruments Division: Madison, WI, 1986.

Table 1. Crystallographic Data for $[Pt(18S_4O_2)](PF_6)_2$, $[Pt(9S_2O)_2](PF_6)_2 \cdot 2CH_3NO_2$, $18S_4O_2$, and $[Pd(9S_2O)_2](PF_6)_2 \cdot 2CH_3CN$

	$[Pt(18S_4O_2)](PF_6)_2$	$[Pt(9S_2O)_2](PF_6)_2 \cdot 2CH_3NO_2$	$18S_4O_2$	$[Pd(9S_2O)_2](PF_6)_2 \cdot 2CH_3CN$
empirical formula	$C_{12}H_{24}O_2F_{12}P_2S_4Pt$	$C_{14}H_{30}N_2O_6F_{12}P_2S_4Pt$	$C_{12}H_{24}O_2S_4$	$C_{14}H_{30}N_2O_2F_{12}P_2S_4Pd$
fw, amu	813.58	935.67	328.45	807.00
lattice	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a, Å	11.110(3)	9.996(5)	7.188(3)	12.535(2)
b, Å	9.244(1)	11.019(3)	5.240(1)	19.463(2)
c, Å	12.642(2)	8.253(2)	10.743(3)	12.127(2)
α deg	90	92.79(2)	99.30°(2)	90
β deg	111.48(1)	110.18(2)	98.09°(3)	95.68(1)
γ, deg	90	64.04(2)	92.19°(3)	90
V, Å^3	1208.2(3)	761.5(5)	394.57	2944.0(7)
Z	2	1	1	4
radiation (λ, Å)	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	2.24	2.04	1.383	1.82
μ, mm^{-1}	6.39	5.09	0.57	1.12
T, °C	22	22	22	22
R^a	0.0343	0.0365	0.067	0.0493
$R_w{}^b$	0.0428	0.0543	0.105	0.0651

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Pt(18S_4O_2)](PF_6)_2$, $[Pt(9S_2O)_2](PF_6)_2 \cdot 2CH_3NO_2$, $[Pd(9S_2O)_2](PF_6)_2 \cdot 2CH_3CN$, and $18S_4O_2$

	$[Pt(18S_4O_2)](PF_6)_2$	$[Pt(9S_2O)_2](PF_6)_2 \cdot 2CH_3NO_2$	$[Pd(9S_2O)_2](PF_6)_2 \cdot 2CH_3CN$
M−S(1)	2.317(2)	2.308(2)	2.310(2)
M−S(2)	2.316(2)	2.302(3)	2.317(2)
M−O(1)	3.730(5)	3.443(5)	3.379(5)
S(1)−M−S(2)	91.0(1)	89.2(1)	89.3(1)
S(1)−M−S(2a)	89.0(1)	90.8(1)	90.7(1)

$18S_4O_2$

Sl−C2	1.813(5)	C8−C9	1.504(7)	C6−C5	1.501(7)
Sl−C9	1.802(5)	O7−C8	1.410(6)	C6−O7	1.412(6)
C2−C3	1.500(8)	C3−S4	1.816(6)	C5−C6	1.501(7)
S4−C5	1.811(6)				
C2−Sl−C9	99.99(25)	Sl−C2−C3	112.9(4)	C6−O7−C8	112.1(4)
O7−C8−C9	107.9(4)	C2−C3−S4	113.2(4)	Sl−C9−C8	109.9(3)
C3−S4−C5	104.8(3)	S4−C5−C6	117.3(4)	C5−C6−O7	108.8(4)

intensity data were measured with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 22 ± 1 °C by using $\omega/2\theta$ scans ($2\theta_{max}$ = 60°) on a Syntex P2$_1$ diffractometer using the ω scan mode. Unit cell parameters were determined by a least-squares refinement of the settings angle for 15 reflections in the range of 16.44−24.56°. No correction was made for absorption. The last least-squares cycle was calculated with 21 atoms, 83 parameters, and 1562 out of 2305 reflections. Weights based on counting statistics were used. A final difference map had extremes of +0.500 e and −0.500 e Å^{-3}. Structure solution, refinement, and the calculation of derived results were performed with the NCRVAX[38] package of computer programs.

Results and Discussion

Syntheses. Cesium carbonate cyclization reactions were employed by Cooper to improve the yield for the preparation of 9S3.[32] We have used this method to prepare $9S_2O$ with an improved yield, and the larger macrocycle $18S_4O_2$ also formed as a secondary product. If the $18S_4O_2$ ligand alone is desired, the sodium cyclization route can be employed more efficiently, but a large quantity of the macrocycle $12S_3O$ is formed via intramolecular cyclization reactions decreasing the overall yield.[16] A small quantity of $9S_2O$ is also formed as a byproduct in this reaction. The properties of both compounds agree well with their published values, and we further include additional characterization with ^{13}C DEPT NMR and the crystal structure of the $18S_4O_2$ macrocycle (see below). The metal compounds are readily prepared by reaction between the appropriate ligands and starting tetrachloro complexes and isolated as crystalline hexafluorophosphate salts.

Structures. Molecular mechanics calculations on both the $9S_2O$ and the $18S_4O_2$ ligands suggested that lower energy conformations are obtained when the O atoms are oriented in an *endodentate* fashion while the S atoms are positioned *exodentate*. This same orientation has been observed crystallographically in other macrocyclic oxathiaethers.[34] To examine a solid-state structure, a crystal structure on the $18S_4O_2$ ligand was obtained (the $9S_2O$ ligand is a viscous liquid). A structural perspective of the ligand is shown in Figure 1. In agreement with the molecular mechanics calculations, the two oxygen atoms are indeed placed endodentate to the macrocyclic cavity while the four sulfur atoms point outward. Therefore, the ligand is not well preorganized to complex a metal ion in multidentate fashion, and a substantial conformation change will be required for the ligand to complex using its sulfur atoms as ligating atoms.

In the ligand structure the two C−O bond lengths average 1.411(6) Å, the four C−S bond lengths average 1.811(6) Å, and the C−C bond lengths average 1.501(6) Å. As expected, the C−C−O−C bonds all adopt an anti conformation within an average 3° deviation. Half of the O−C−C−S bonds are

---

(36) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(37) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(38) Gabe, E. J.; Lee, F. L.; Page, Y. L. In *Crystallographic Computing 3*: *Structure Detemination, Proteins, and Databases*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds. Clarendon Press: Oxford, 1985; pp 167−174.

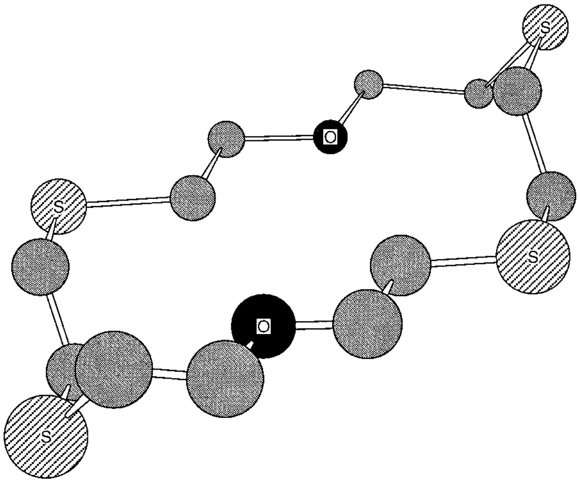

Figure 1. Structural perspective of $18S_4O_2$.

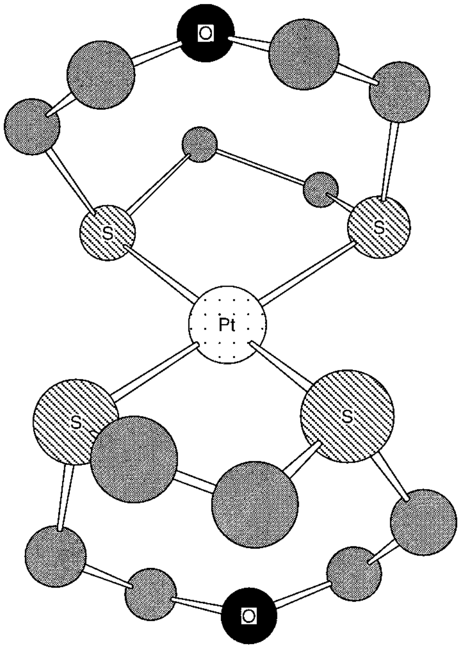

Figure 2. Structural perspective of $[Pt(9S_2O)_2](PF_6)_2 \cdot 2CH_3NO_2$.

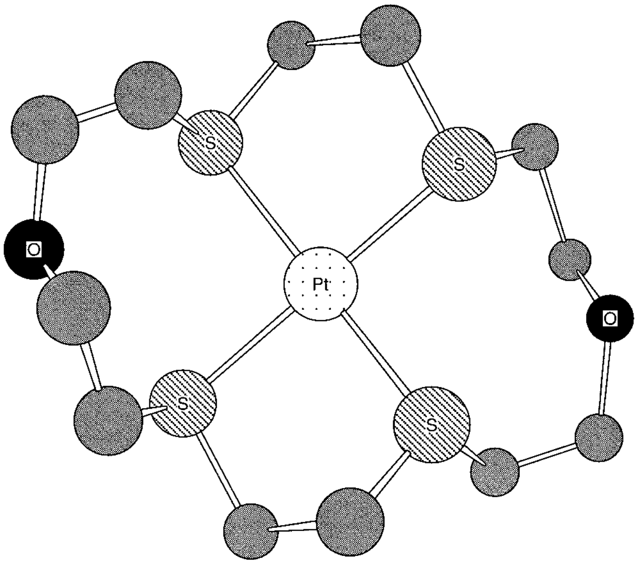

Figure 3. Structural perspective of $[Pt(18S_4O_2)](PF_6)_2$.

gauche, and the other half are anti, a compromise between the conformational preferences of the individual C—O and C—S bonds. Three-quarters of the C—C—S—C bonds are gauche (within an 8° deviation), and all of the S—C—C—S bonds are anti. The structure of $18S_4O_2$ contrasts that of $18S_4N_2$ which has sulfur atoms that are neither exodentate or endodentate but instead contains C—S—C triangles almost perpendicular to the macrocycle plane.[39]

Both Pt(II) structures exhibit similar complexation behavior by the two mixed oxathia crowns, and structural perspectives for each are shown in Figures 2 and 3. In both platinum structures, the Pt(II) lies at an inversion center surrounded by a distorted square planar array of four sulfur atoms. In each complex, the two oxygen atoms lie trans to each other and oriented away from the Pt center, precluding any Pt—O interactions. In fact, the distance between the Pt and the O atoms in the $9S_2O$ complex is 3.443(5) Å, greater than the sum of the van der Waals radii for the two atoms (3.3 Å).[40] The four Pt—S bond lengths in the complex average 2.305(3) Å while the equatorial S—Pt—S angles average 90.0(1)°. These equatorial Pt—S bond lengths are typical for bond lengths observed in other crown thioether complexes of platinum(II).[14] In our structure the platinum(II) ion lies 0.011 Å above the mean plane of the four sulfur atoms.

In the complex $[Pt(18S_4O_2)]^{2+}$, the S—O—S unit adopts a meridional rather than facial coordination mode, consistent with other structures of complexes involving this ligand and in contrast to complexes of 18S6 which exclusively forms facial stereoisomers.[41] The Pt—O distance in the $18S_4O_2$ complex is 3.730(5) Å, about 0.3 Å longer than observed in the $9S_2O$ complex, but again far too great to allow any Pt—O interactions. The Pt—S bond lengths average 2.317(2) Å, also somewhat longer than the $9S_2O$ complex, and matching more the slightly longer Pt—S bond lengths found in the crystal structure of $[Pt(16S4)]^{2+}$.[42] The equatorial S—Pt—S bond angles again average 90.0(1)°. In the structure the platinum(II) ion lies 0.018 Å above the mean plane of the four sulfur atoms, slightly more above than in the $9S_2O$ structure. Schröder and co-workers have reported a series of Pd(II) and Pt(II) complexes with mixed ether—thioether macrocycles (e.g., $18S_2O_4$), all of which show complexation by exodentate sulfur atoms and oxygen atoms pointed away from the palladium(II) center.[22,25] In those structures, all of the O—S macrocycles are already preorganized for complexation. In contrast however, our Pt(II) structure of the $18S_4O_2$ macrocycle confirms that the ligand does have the ability to turn “inside out” in order to complex a metal center and is able to achieve the large conformational change required to do so. The similarity between the two Pt(II) structures of the mixed oxygen—sulfur macrocycles shows that their complexation behavior is due to electronic metal—ligand interactions and not ligand conformational factors.

The Pd(II) complex of the $9S_2O$ ligand shows a similar structure to the analogous Pt(II) complex, and a structural perspective is given in Figure 4. The four sulfur atoms form a square plane around the Pd(II) center, and both oxygen atoms are again

---

(39) Reid, G.; Schröder, M. *Chem. Soc. Rev.* **1990**, *19*, 239.

(40) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Harper Collins: New York, 1993; p 292.

(41) Grant, G. J.; Jones, M. W.; VanDerveer, D. G.; Pennington, W. P.; Mehne, L. F., manuscript in preparation.

(42) Blake, A. J.; Bywater, M. J.; Crofts, R. D.; Gibson, A. M.; Reid, G.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1996,** 2979.

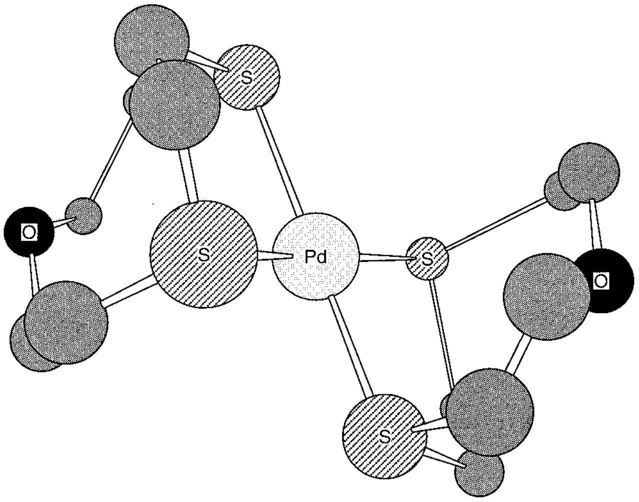

Figure 4. Structural perspective of $[Pd(9S_2O)_2](PF_6)_2{\cdot}2CH_3CN$.

directed away from the palladium. The Pd−S bond lengths average 2.313(2) Å, comparable to other Pd(II) complexes of crown thioether and mixed oxathia crowns.[14,22] The Pd−O distance in $[Pd(9S_2O)_2]^{2+}$ is 3.379(5) Å, exceeding the sum of the van der Waals radii and far too great to allow any Pd−O interactions.[40] The equatorial S−Pd−S bond angles again average 90.0(1)°. The palladium(II) ion lies 0.028 Å above the mean plane of the four sulfur atoms, and more displaced from the mean square plane than in the two Pt(II) structures.

Our bis($9S_2O$) Pd(II) crystal structure provides an interesting contrast to the recently published crystal structure of the $[Pd(9S_2O)Cl_2]$ complex.[20] In that structure, the single oxygen atom of the $9S_2O$ ligand is oriented in an unusual *endodentate* fashion and points toward the Pd center. The conformation adopted by the $9S_2O$ ligand in $[Pd(9S_2O)Cl_2]$ is the [234] conformation whereas the [12222] conformation is seen in both the bis Pt(II) and Pd(II) complexes. The Pd−O distance is 2.968(3) Å, much shorter than in our structure. Both of our $9S_2O$ structures do incorporate solvent molecules, acetonitrile for the Pd(II), nitromethane for the Pt(II) while the $[Pd(9S_2O)Cl_2]$ complex shows no solvent present in the solid state. Solvent interactions in the complex $[Pd(10S3)_2]^{2+}$ did result in the crystallization of two distinct linkage isomers.[8,9] Molecular mechanics calculations suggest only a small energy difference (∼2 kcal) between these two coordination modes of $9S_2O$. Thus, changes in solvent incorporation or crystal packing forces are factors which may switch *endodentate* and *exodentate* coordination of platinum group metals with these ligands. The Pd−S bond lengths are somewhat longer (by 0.050 Å) in the bis($9S_2O$) complex than in $[Pd(9S_2O)Cl_2]$. This lengthening could be a consequence of enhanced π back-bonding between the sulfur atoms and the palladium center due to increased π donation by the coordinated chlorides. Similar structural observations were seen in the two related Pd(II) complexes of $18S_2O_4$.[25] This enhanced Pd−S π back-bonding in the dichloride complex could also be responsible for the atypical *endodentate* structure of $[Pd(9S_2O)Cl_2$.

Spectra and Electrochemistry. The ^{195}Pt NMR spectra for both Pt complexes show a single peak with a chemical shift near −4650 ppm. We believe that the presence of a square planar array of four sulfur atoms around a Pt(II) center is confirmed by a 195-Pt NMR signal at this value, and similar chemical shifts have been reported for other platinum tetrathioether complexes with S_4 structures.[42] Thus, our Pt NMR chemical shift data support our structural data regarding the lack of platinum−oxygen interactions in either Pt(II) complex.

The carbon NMR spectra for all four complexes show simple three line spectra, consistent with a centrosymmetric ligand binding and in agreement with our three reported crystal structures. No other isomers are observed in solution. An interesting feature of the ^{13}C NMR spectrum of $[Pt(9S_2O)_2]_2{}^{2+}$ is the observed vicinal platinum−carbon coupling, $^3J_{PtSCC}$, which has a value of 47 Hz. No platinum−carbon coupling is present in the $18S_4O_2$ complex which we believe is due to the differences in complex stereochemistry between the larger and smaller ligands. Indeed, the PtSCC dihedral angles vary by 39° in the two structures. A close contact of only 2.26 Å between a methylene hydrogen from C_2 and the oxygen is observed in the structure. A similar interaction of 2.42 Å is seen in the analogous Pd(II) complex, but palladium does not have a nonquadrupolar nucleus such as platinum. The $18S_4O_2$ Pt(II) complex does not show this same close H−O contact, and thus, no coupling is observed. Conformational dependency of vicinal coupling constants between platinum and carbon has been documented previously.[43] This value of $^3J_{PtSCC}$ is somewhat larger than previously reported values of vicinal platinum−carbon coupling which typically range up to 45 Hz. However, these couplings were found in complexes involving carbon, amine, and halide ligands, and to our knowledge, this is the first example of vicinal platinum−carbon coupling over a thioether bond linkage.

The value of this coupling constant does not change upon heating to 80 °C, indicating no dynamic processes are occurring. We also would like to suggest that the presence of the Pt−C coupling is a source of the line broadening of the Pt resonance in the $9S_2O$ complex relative to Pt in the $18S_4O_2$ complex. A three-line ^{13}C NMR spectrum is also obtained for both Pd(II) complexes indicating a centrosymmetric binding of both the $9S_2O$ and $18S_4O_2$ ligands. This spectrum is consistent with the crystal structure obtained for the $[Pd(9S_2O)_2]^{2+}$ complex. The downfield methylene resonance (adjacent to the O atom) is broadened for the two complexes, possibly due to ^{105}Pd, a quadrupolar nucleus.

All four complexes show a complex proton spectrum consistent with an *ABCD* splitting pattern for the methylene hydrogens. Interestingly, this same splitting pattern is observed in $[Pd(9S_2O)Cl_2]$ which shows an *endodentate* conformation with the oxygen.[20] Thus, ^{1}H NMR cannot differentiate between these two coordination modes of $9S_2O$. The proton and carbon NMR spectrum of $[Pt(9S_2O)_2]^{2+}$ in CD_3NO_2 solvent remains unchanged upon heating from 25° to 80 °C. Since intermolecular ligand exchange processes for the complex $[Pd(9S_2O)Cl_2]$ were observed upon heating in DMSO,[20] we also examined the proton and carbon-13 NMR spectrum of $[Pt(9S_2O)_2]^{2+}$ in this solvent. In contrast to $[Pd(9S_2O)Cl_2]$, we observed no changes in either the proton or carbon NMR spectrum upon heating in DMSO. The same value of $^3J_{Pt-C}$ coupling for the complex is also observed in DMSO (47 Hz), and this coupling constant remains unaffected by temperature.

Cyclic voltammetry in nitromethane reveals that the $9S_2O$ ligand exhibits an irreversible oxidation wave at +1.074 V vs Fc/Fc^+. In contrast, the larger $18S_4O_2$ is electrochemically silent over the range of −1.0 to +2.0 V. Cyclic voltammograms for both platinum(II) complexes reveal that each is electrochemically silent over this range. Likewise, the two Pd(II) complexes exhibit no oxidative activity up to +2.0 V. We believe our electrochemical results are in agreement with our structural data which show the oxygen atoms are at too great of a distance to

---

(43) Pregosin, P. S.; Sze, S. N.; Salvadori, P.; Lazzaroni, R. *Helv. Chim. Acta* **1977**, *60*, 2514.

Table 3. Summary of Structural, Spectroscopic, and Electrochemical Data for Pd(II) and Pt(II) Macrocyclic Thioether and Mixed Thioether Complexes

complex	geometry	solution color (λ max, visible)	$E°$ (V) vs Fc/Fc^+ oxidation	reference
		Pd(II) Complexes		
$[Pd(9S_2O)_2]^{2+}$	S_4	yellow (none)	none	this work
$[Pd(9S3)_2]^{2+}$	$S_4 + S_2$	blue-green (615 nm)	+0.605 V	5
$[Pd(10S3)_2]^{2+}$	$S_4 + S_2$	blue-green (603 nm)	+0.606 V	8
$[Pd(9N_2S)_2]^{2+}$	$N_4 + S_2$	brick red (NR)	+0.30 V	46
$[Pd(9S_2N)_2]^{2+}$	$S_2N_2 + S_2$	purple-blue (NR)	+0.43 V	45
$[Pd(18S_4O_2)]^{2+}$	S_4	yellow (none)	none	this work
$[Pd(18S_2O_4)_2]^{2+}$	S_4	yellow (none)	NR[a]	25
$[Pd(15S_2O_3)_2]^{2+}$	S_4	yellow (none)	none	22
$[Pd(18S_4N_2)]^{2+}$	$S_2N_2 + S_2$	purple (514 nm)	+0.57 V	44
$[Pd(18S_4NMe_2)]^{2+}$	S_4	orange (none)	none	44
$[Pd(20S6)]^{2+}$	S_4	yellow (none)	none	14
		Pt(II) Complexes		
$[Pt(9S_2O)_2]^{2+}$	S_4	colorless (none)	none	this work
$[Pt(9S3)_2]^{2+}$	$S_4 + S_1$	orange (432 nm)	+0.39 V	7
$[Pt(10S3)_2]^{2+}$	$S_4 + S_2$	orange (430 nm)	+0.324 V	14, 10
$[Pt(9N_2S)_2]2+$	N_4	colorless (none)	none	46
$[Pt(18S_4O_2)]2+$	S_4	colorless (none)	none	this work
$[Pt(20S6)]^{2+}$	S_4	colorless (none)	none	14

[a] NR, not reported.

interact effectively with the Pt and Pd center, and thereby stabilize the trivalent oxidations states of these metals. As seen in Table 3, whenever Pt(III) or Pd(III) can be generated electrochemically (such as 9S3 and 10S3 complexes), the axially ligating atom was within 3.13 Å of the metal center, considerably closer than the oxygen atoms in any of these complexes. The inability of the oxygen atom to function as a long distance axial donor precludes the ability of the platinum or palladium center to be oxidized. Reductive electrochemical activity is observed for both Pd(II) complexes. For $[Pd(9S_2O)_2]^{2+}$, an irreversible one electron reduction is observed at −645 mV vs Fc/Fc^+ which is assigned as a Pd^{II}/Pd^{I} reduction. Similar reduction behavior is seen in Pd(II) complexes of mixed oxathia and azathia crowns.[22,44] A second irreversible one electron reduction is seen at −1.43 V vs Fc/Fc^+ which is assigned as a Pd^{I}/Pd^{0} reduction. For $Pd(18S_4O_2)]^{2+}$ a single poorly resolved, irreversible reduction is seen at −1.20 V vs Fc/Fc^+.

Although charge-transfer bands are observed in the ultraviolet, all four complexes lack d−d electronic transitions in the visible region, another consequence of the inability of the oxygen to interact with the Pt(II) or Pd(II) center. This distinctly contrasts the behavior of crown thioether Pt(II) complexes whose orange colors are due to d−d transitions near 430 nm and Pd(II) complexes which exhibit a blue or green color due to transitions near 600 nm. Also, mixed donor macrocyclic complexes, in particular $18S_4N_2$ and $9S_2N$, exhibit similar unique colors so the inability to form appears to be a function of the structure of these oxa-thia complexes. As summarized in Table 3, the electrochemical and spectroscopic properties of Pd(II) and Pt(II) complexes with these two and related macrocycles are a consequence of their structures, in particular the long distances between the metal center and the axial donor oxygen atoms. The complex structures themselves are determined by the metal−donor electronic interactions and not by ligand conformational factors since the ligand linkages are the same in all complexes.

Conclusions

In contrast to crown thioether ligands and mixed azathia macrocycles, the two mixed crown oxathiaether ligands, $9S_2O$ and $18S_4O_2$, form exclusively square planar complexes with Pt(II) and Pd(II) in which only the four sulfur atoms are coordinated. The oxygen atoms in these complexes are oriented away from the precious metal center, and the hard donor sites do not interact with it. Our results show that replacement of sulfur or nitrogen by oxygen in these macrocycles produces significant changes in complex stereochemistry. Accordingly, the ^{195}Pt NMR chemical shift for both Pt(II) complexes is observed near −4650 ppm, consistent with four bound sulfur atoms to Pt(II). An unusual vicinal platinum−carbon coupling is observed in the $9S_2O$ complex, a consequence of the conformation adopted by the ligand. The complexes do not exhibit reversible oxidations to Pt(III) and Pd(III), a consequence of the large distance between the metal and oxygen which effectively prevents any axial interactions from occurring. The colors and visible electronic absorption spectra associated with Pd(II) and Pt(II) crown thioether complexes are also not observed. The similarity among all of the platinum group metal compounds show that the general coordination chemistry of these ligands is dominated by specific metal−ligand interactions and not by ligand conformational factors.

Acknowledgment. This research was generously supported by grants from the Research Corporation, the Council on Undergraduate Research, the Wheeler Odor Center, and the Grote Chemistry Fund at UTC. The support of the National Science Foundation ILI Program is also acknowledged for the purchase of a Gemini 300 MHz NMR Spectrometer. The assistance of Ivan Poullaos and Melissa Gunderson in the synthetic work, Pavle Repovic, Chris Brandow, and Larry Mehne for the electrochemical and NMR measurements, and Mary Jo Gray for some of the molecular mechanics calculations is also appreciated.

Supporting Information Available: Complete listings for $[Pt(18S_4O_2)](PF_6)_2$ and $[Pt(9S_2O)_2](PF_6)_2 \cdot 2CH_3NO_2$, $18S_4O_2$, and $[Pt(9S_2O)_2](PF_6)_2 \cdot 2CH_3CN$: crystallographic data, atomic coordinates, bonding distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (21 pages). Ordering information is given on any current masthead page.

IC9715714

---

(44) Blake, A. J.; Reid, G.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1990**, 3363.

(45) Blake, A. J.; Crofts, R. D.; De Groot, B.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1993**, 485.

(46) Hoffmann, P.; Mattes, R. *Z. Naturforsch.* **1988**, *43B*, 261. Additional Pd(II) and Pt(II) complexes have been reported by the Mattes Group (*Inorg. Chim. Acta* **1992**, *194*, 157), but no spectroscopic or electochemical data were available for comparison.