$(C_4H_7)(PMe_2Ph)_2]^+PF_6^-$ were prepared by adding an acetone solution of $AgPF_6$ to *trans*-$PtHBr(PMe_2Ph)_2$ in acetone while allene or butadiene was bubbled through the solution (yield 65 and 75%). The proton nmr spectra in CD_2Cl_2 are as follows: for the former compound, τ(P–CH$_3$) 8.21 (doublet), J(P–H) = 10.0 Hz, J(Pt–H) = 36.5 Hz; τ(anti H) 7.07 (doublet of doublets), J(H–H) = 13 Hz, J(P–H) = 8 Hz, J(Pt–H) = 42 Hz; τ(syn H) 5.70 (doublet), J(H–H) = 7 Hz; τ(2-H) 4.75 (multiplet); for the latter compound, τ(P–CH$_3$) 8.09 (doublet), J(P–H) = 10.5 Hz, J(Pt–H) = 39. Hz; τ(P–CH$_3$) 8.32 (doublet), J(P–H) = 9.5 Hz, J(Pt–H) = 35 Hz; τ(1-CH$_3$) 8.73 (multiplet) and overlapped by the phosphine methyl; other resonances, τ 7.21 (quartet), 6.45 (multiplet), 5.95 (broad), 4.97 (multiplet).

Other Reactions.—Reactions of ethylene with *trans*-$[PtH(PPh_2Me)_2L]^+PF_6^-$ (L = 2,4,6-trimethylpyridine, *p*-$CH_3C_6H_4NC$, PPh_2Me)[16] were attempted under conditions similar to those used for the reaction of *trans*-$[PtH(PPh_2Me)_2(acetone)]^+$ (1 hr, room temperature). However, no reaction occurred in every case as shown by the unchanged infrared spectra of the reaction mixtures.

Reactions of *trans*-$[PtH(PPh_2Me)_2(acetone)]^+PF_6^-$ with *cis*-butene-2, vinyl fluoride, and methyl vinyl ether were attempted under conditions similar to those for (3) or (4) (1 hr). 2,4,6-Trimethylpyridine was added to the reaction mixture; however, the infrared spectra of the solid products obtained after evaporating the solvent were identical with that of *trans*-$[PtH(PPh_2Me)_2(B)]^+PF_6^-$[16] (B = 2,4,6-trimethylpyridine).

CONTRIBUTION FROM THE E. F. SMITH LABORATORY OF CHEMISTRY AND THE LABORATORY FOR RESEARCH ON THE STRUCTURE OF MATTER, UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA, PENNSYLVANIA 19104

Palladium(II) and Platinum(II) Alkyl Sulfoxide Complexes. Examples of Sulfur-Bonded, Mixed Sulfur- and Oxygen-Bonded, and Totally Oxygen-Bonded Complexes

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A series of Pd(II) and Pt(II) cationic complexes of the form $[PdL_4](BF_4)_2$ [L = dimethyl sulfoxide (DMSO), tetramethylene sulfoxide (TMSO), diethyl sulfoxide (DESO), di-*n*-propyl sulfoxide (NPSO), di-*n*-butyl sulfoxide (NBSO), and diisoamyl sulfoxide (IASO)] has been prepared and the general structural features of the complexes have been studied by ir spectrometry. Many new complexes, including $[Pt(DMSO)_4](ClO_4)_2$, which contain mixed S- and O-coordination sites, are reported. Proton nmr studies of $[Pt(DMSO)_4](ClO_4)_2$ demonstrate that two S-bonded and two O-bonded sulfoxides are retained in CH_3NO_2 solution. O-Bonded sulfoxides are found to exchange rapidly with free ligand, while the S-bonded sulfoxides are relatively kinetically stable. Steric effects are manifested in both the cationic and neutral chloride complexes of diisoamyl sulfoxide. The complex $[Pd(IASO)_4](BF_4)_2$ is the first example of a completely oxygen-bonded palladium(II) sulfoxide complex. Cationic Pd(II) and Pt(II) complexes of 2,5-dithiahexane 2,5-dioxide ($DTHO_2$) are prepared and polymeric structures with all sulfur and mixed sulfur and oxygen coordination are proposed.

Introduction

Sulfoxide ligands have two potential donor sites. The lighter or more highly charged metal ions favor oxygen coordination while a few heavier metals prefer the sulfur donor site.[1,2] We recently proposed $[Pd(DMSO)_2]X_2$ (X^- = BF_4^-, ClO_4^-) as the first example of a complex which contains both S- and O-bonded sulfoxide ligands. Two S-bonded and two O-bonded ligands in a cis array were inferred primarily from ir spectra.[3,4] These structural features have now been confirmed by a complete X-ray study.[5] Interest in determining the factors which govern the donor site and consequently the complex configuration prompted us to investigate a series of alkyl sulfoxide donors with Pd(II)[6] and to extend these studies to Pt(II). The ligands were selected to reveal the influence of steric effects on the donor site and examples of sulfur-bonded, mixed sulfur- and oxygen-bonded, and totally oxygen-bonded complexes are reported.

Results and Discussion

Neutral Complexes of Pd(II) and Pt(II) with Sulfoxide Donors.—A trans S-bonded structure for solid $[Pd(DMSO)_2Cl_2]$ has been proven by single-crystal X-ray studies[7] while a cis S-bonded structure for $[Pt(DMSO)_2Cl_2]$ is indicated by ir studies.[1] The proton nmr spectrum for the latter complex in CD_3NO_2 is shown in Figure 1a. A single methyl proton resonance at −1.00 ppm relative to free DMSO with ^{195}Pt satellites ($J_{^{195}Pt-^1H}$ = 23.1 Hz) indicates the absence of detectable ligand dissociation and retention of the S-bonded structure in this solvent. Similar, although time-dependent, results were obtained for this complex by Kitching, *et al.*, when pyridine was used as the solvent.[8] If the cis configuration is maintained in solution, then the methyl group equivalence probably indicates rapid rotation about both the Pt–S and C–S bonds. Intermolecular exchange has been shown to be slow on the nmr time scale by addition of excess free ligand.

In the palladium complexes $[PdL_2Cl_2]$ (L = di-*n*-ethyl, di-*n*-propyl, di-*n*-butyl, diisoamyl, and tetra-

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[1] F. A. Cotton, R. Francis, and W. D. Horrocks, Jr., *J. Phys. Chem.*, **64**, 1534 (1960).

[2] F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, **82**, 2986 (1960).

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[4] B. B. Wayland and R. F. Schramm, *Inorg. Chem.*, **8**, 971 (1969).

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TABLE I
PRINCIPAL INFRARED FREQUENCIES FOR PALLADIUM(II) AND PLATINUM(II) SULFOXIDE COMPLEXES

Complex	ν_{SO}, cm^{-1}		ν_{M-L},[g] cm^{-1}		ν_{M-X},[g] cm^{-1}
	S bonded	O bonded	S[a]	O	($X^- = Cl^-$ or Br^-)
[Pd(DMSO)$_2$Cl$_2$]	1116[b,c]		415		355
[Pd(DMSO)$_2$Br$_2$]	1116		417		293
[Pt(DMSO)$_2$Cl$_2$]	1157, 1134[c]		450, 430		334, 309
[Pd(DMSO)$_4$](BF$_4$)$_2$[d]	1150, 1140	920, 905	437, 420	493	
[Pt(DMSO)$_4$](ClO$_4$)$_2$	1154, 1143	897, 879	455, 438	517	
[Pd(DESO)$_2$Cl$_2$]	1131		407		375
[Pt(DESO)$_2$Cl$_2$]	1147, 1122		433, 415		339, 332
[Pd(DESO)$_4$](ClO$_4$)$_2$	1132	918	420	504, 490	
[Pd(TMSO)$_2$Cl$_2$]	1119[e]		374		357
[Pd(TMSO)$_2$Br$_2$]	1120		364		292
[Pt(TMSO)$_2$Cl$_2$]	1150, 1136		368, 355		337, 321
[Pd(TMSO)$_4$](BF$_4$)$_2$	1154, 1141	920, 901	365, 354	473, 458	
[Pt(TMSO)$_4$](ClO$_4$)$_2$	1150, 1137	895, 879	379, 370	480, 469	
[Pd(NPSO)$_2$Cl$_2$]	1136		416		372
[Pt(NPSO)$_2$Cl$_2$]	1136, 1117		452, 434		357, 343
[Pd(NPSO)$_4$](BF$_4$)$_2$	1134	914, 905	441	495	
[Pd(NPSO)$_4$](PF$_4$)$_2$	1139	915, 906	438	505	
[Pt(NPSO)$_4$](ClO$_4$)$_2$	1140	921, 896	451	512	
[Pd(NBSO)$_2$Cl$_2$]	1136		444		359
[Pt(NBSO)$_2$Cl$_2$]	1143, 1129		472, 465		352, 332
[Pd(NBSO)$_4$](BF$_4$)$_2$[f]	1135	942, 925			
[Pd(IASO)$_2$Cl$_2$]	1134		425		370
[Pt(IASO)$_2$Cl$_2$]	1142		428		356
[Pd(IASO)$_4$](BF$_4$)$_2$		918		478	
[Pd(IASO)$_4$](PF$_6$)$_2$		914		478	
[Pd(α-DTHO$_2$)Cl$_2$]	1155, 1138, 1135		(427)		325, 316
[Pt(α-DTHO$_2$)Cl$_2$]	1148, 1128		(441)		332, 315
[Pd(α-DTHO$_2$)$_2$](BF$_4$)$_2$	1163		(433)		
[Pt(α-DTHO$_2$)$_2$](ClO$_4$)$_2$	1156		(450)		
[Pd(β-DTHO$_2$)$_2$Cl$_2$]	1149, 1130		(428)		333, 318
[Pt(β-DTHO$_2$)$_2$Cl$_2$]	1155, 1143		(440)		338, 322
[Pd(β-DTHO$_2$)$_2$](BF$_4$)$_2$	1143	908	(430)	503	
[Pt(β-DTHO$_2$)$_2$](ClO$_4$)$_2$	1159	904	(448)	517	

[a] The DTHO$_2$ complexes exhibit bands in both the 355–382- and 427–450-cm^{-1} regions which could be attributed to ν_{M-S} modes. However, the presence of ligand bands in these regions makes any assignments tentative. [b] F. A. Cotton and R. Francis, *J. Amer. Chem. Soc.*, **82**, 2986 (1960). [c] F. A. Cotton, R. Francis, and W. D. Horrocks, Jr., *J. Phys. Chem.*, **64**, 1534 (1960). [d] B. B. Wayland and R. F. Schramm, *Inorg. Chem.*, **8**, 971 (1969). [e] D. W. Meek, W. E. Hatfield, R. S. Drago, and T. S. Piper, *ibid.*, **3**, 1637 (1964). [f] This complex was isolated as an oil which gave an unresolved far-ir spectrum. [g] In planar complexes of the type [MX$_2$L$_2$] single ν_{M-X} and ν_{M-L} are consistent with a trans configuration while two bands in each of the ν_{M-X} and ν_{M-L} regions indicates a cis configuration.

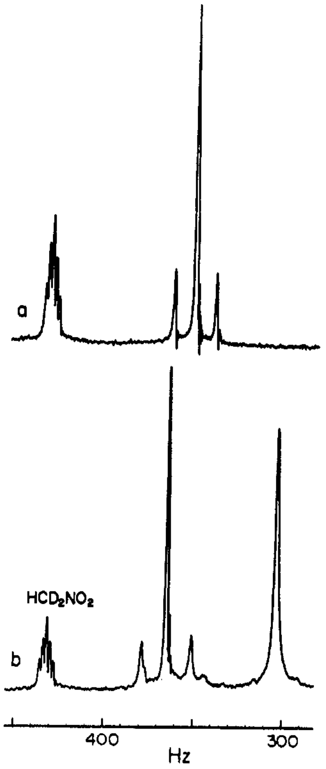

Figure 1.—Proton nmr spectra for platinum(II) dimethyl sulfoxide complexes in CD$_3$NO$_2$: (a) Pt(CMSO)$_2$Cl$_2$; (b) [Pt(DMSO)$_4$](ClO$_4$)$_2$.

methylene sulfoxide[9]), near- and far-ir data are consistent with a trans sulfur-bonded configuration in every case (Table I). Palladium–sulfur stretching modes have been generally assigned to the 400–440-cm^{-1} region (Table I); however, the neutral complex Pd(TMSO)$_2$Br$_2$ contains no bands in the far-ir region from 528 to 364 cm^{-1}. We conclude that the metal–sulfur stretching mode in this species is attributable to the strong 364-cm^{-1} band. Similarly, Pd(TMSO)$_2$Cl$_2$ contains no bands from 526 to 374 cm^{-1}. The strong bands near 357 cm^{-1}, which probably derive most of their intensity from metal–chlorine stretching, may also include the metal–sulfur stretching mode.

In the analogous [PtL$_2$Cl$_2$] complexes, ir data support a cis configuration when the ligand is diethyl, di-*n*-propyl, di-*n*-butyl, or tetramethylene sulfoxide, but a trans configuration is indicated for the diisoamyl sulfoxide complex [Pt(IASO)$_2$Cl$_2$] (Table I).

The preference of Pt(II) and Pd(II) for the sulfur donor site when steric influences are not prohibitive is suggested by the observation that every neutral complex is exclusively sulfur bonded in the solid. In the Pd(II) chlorides, the enhanced (d–d)π bonding in the cis geometry is apparently insufficient to overcome the interligand repulsions which are larger in the cis configuration, and all of the complexes have the trans structure. In the corresponding [PtL$_2$Cl$_2$] complexes

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(9) D. W. Meek, W. E. Hatfield, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **3**, 1637 (1964)

(d–d)π bonding is apparently more effective and cis structures are obtained for all the complexes except with the most sterically demanding ligand, diisoamyl sulfoxide, which yields *trans*-$[Pt(IASO)_2Cl_2]$.

Cationic Complexes of Pd(II) and Pt(II). Dimethyl Sulfoxide Complexes of Pd(II) and Pt(II).—The cationic complex $[Pd(DMSO)_4]X_2$ ($X^- = BF_4^-, ClO_4^-$) is now known to contain both S- and O-bonded DMSO in a cis configuration in the solid state.[3–5] The ir spectrum for $[Pt(DMSO)_4](ClO_4)_2$ (Figure 2) is very similar to that of the palladium complex with two strong bands in both the S-bonded (1155, 1143 cm^{-1}) and O-bonded (897, 879 cm^{-1}) ν_{SO} regions (Table I). The far-ir spectrum contains bands at 517, 455, and 438 cm^{-1} which are assigned to Pt–ligand stretching frequencies. These data support a cis configuration of two oxygen- and two sulfur-bonded ligands. This structure probably results from more favorable Pt-S (d–d)π bonding in the cis configuration. The proton nmr spectrum of this complex in CD_3NO_2 consists of two equal-intensity resonances centered at −1.139 and −0.525 ppm relative to uncoordinated DMSO (Figure 1b). The narrow lower field resonance has ^{195}Pt satellites (J_{Pt-^1H} = 27.9 Hz) consistent with S-bonded DMSO. We assign the somewhat broader higher field resonance, on which ^{195}Pt coupling is not resolved, to O-bonded DMSO. Addition of excess ligand shifts this reasonance upfield but has no effect on the S-bonded methyl reasonance at 40°. These nmr spectra are consistent with retention of two S-bonded and two O-bonded DMSO ligands in CH_3NO_2. Rapid O-bonded ligand exchange leaves open the possibility of slight O-bonded DMSO dissociation in nitromethane solution. The kinetic instability of the oxygen-coordinated sulfoxide may be used to prepare mixed-ligand complexes of the form $[Pt(DMSO)_2L_2]^{2+}$.

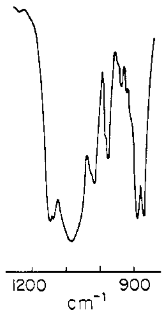

Figure 2.—Infrared spectrum of $[Pt(DMSO)_4](ClO_4)_2$ in the ν_{SO} region.

Tetramethylene Sulfoxide Complexes of Pd(II) and Pt(II).—The near-ir spectrum of $[Pd(TMSO)_4](BF_4)_2$ contains strong doublets in both the sulfur-bonded and the oxygen-bonded regions (Table I) suggesting a cis configuration. The far-ir spectrum contains two nonligand bands at 473 and 458 cm^{-1} which we ascribe to Pd–O stretching modes. The metal–sulfur modes can be ascribed to the 365- and 354-cm^{-1} bands in this species considering the tentative assignments of ν_{Pd-S} in $[Pd(TMSO)_2Br_2]$ and $[Pd(TMSO)_2Cl_2]$ (Table I). The near- and far-ir data are thus consistent with a cis configuration of S- and O-bonded ligands in $[Pd(TMSO)_4](BF_4)_2$. Virtually identical spectral features are found for $[Pt(TMSO)_4](ClO_4)_2$ which is assigned the same structure as the Pd(II) complex in the solid state. The proton nmr of $[Pt(TMSO)_4](BF_4)_2$ in CD_3NO_2 shows two sets of equal-intensity resonances which are associated with equal numbers of S- and O-bonded TMSO ligands.

Di-*n*-ethyl, Di-*n*-propyl, Di-*n*-butyl, and Diisoamyl Sulfoxide Complexes.—The series of complexes $[Pd(L_4)]X_2$ (L = DESO, NPSO, NBSO, IASO; $X^- = BF_4^-, PF_6^-$) and $[Pt(NPSO)_4](ClO_4)_2$ were prepared to assist in evaluating the effects of varying the ligand alkyl groups. The knowledge that $[Pd(DMSO)_4]^{2+}$ contains two S- and O-bonded ligands in a cis configuration and the likelihood that both electronic and ligand steric effects influence this structure prompted us to examine the above series of complexes. The possibilities of providing the proper conditions for observing sets of linkage isomers and inducing changes in complex configuration were of primary interest.

Mull spectra for $[Pd(L)_4](PF_6)_2$ (L = DESO, NPSO, NBSO; $X^- = BF_4^-, PF_6^-$) clearly show the presence of both S- and O-bonded sulfoxides in each complex. Although there are fewer bands in the ν_{SO} and ν_{M-L} regions than found in the cis complex $[Pd(DMSO)_4]^{2+}$, each of these complexes has at least one more band in these regions than expected for a trans configuration. Since these spectral features are maintained in CH_2Cl_2 and CH_3NO_2 solutions, a cis configuration is more consistent with the spectra. Similarly $[Pt(NPSO)_4](ClO_4)_2$ contains one band in the ν_{SO} (S bonded), ν_{Pt-S}, and ν_{Pt-O} regions and two bands in the ν_{SO} (O bonded) region in both mull and solution spectra. These spectra clearly demonstrate the presence of both S- and O-bonded NPSO but are not definitive in distinguishing between several possible isomers. There is no evidence for mixtures of geometric or linkage isomers in any of the isolated solid complexes.

The proton nmr spectrum of $[Pt(NPSO)_4](ClO_4)_2$ in CD_3NO_2 has not been completely interpreted because of the superposition of resonances due to sulfur- and oxygen-coordinated ligands and the second-order nature of the methylene proton resonances. The methyl resonances, however, have a relatively simple six-line pattern which can be attributed to overlap of two triplets of equal intensity, one due to sulfur- and the other to oxygen-coordinated NPSO. When excess ligand is added to the sample, the higher field triplet shifts toward the free ligand methyl resonance position suggesting that these resonances are attributable to the oxygen-coordinated ligands. The remaining three resonances, which are unaffected by ligand addition, are attributed to sulfur-bonded ligand. These nmr data clearly demonstrate that $[Pt(NPSO)_4](ClO_4)_2$ has equal numbers of S- and O-bonded NPSO ligands in CH_3NO_2 solution but does not assist in determining whether a cis or trans configuration is present.

Diisoamyl Sulfoxide Complex of Pd(II).—Diisoamyl sulfoxide is the most sterically demanding ligand studied and it forms a cationic complex which is distinctly different from the others investigated. The ir spectrum of $[Pd(IASO)_4](BF_4)_2$ reveals a strong, broad peak at 918 cm^{-1} indicative of oxygen coordination (Figure 3b). The complex spectrum contains sharp, medium weak bands at 1133 and 1121 cm^{-1} which on the basis of intensity were tentatively assigned to ligand bands which occur at 1134 and 1115 cm^{-1}. In all other

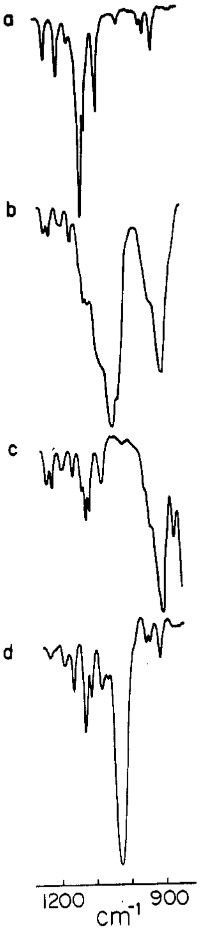

Figure 3.—Infrared spectra for diisoamyl sulfoxide complexes in the ν_{SO} region: (a) *trans*-Pd(IASO)$_2$Cl$_2$ (S bonded); (b) [Pd(IASO)$_4$](BF$_4$)$_2$; (c) [Pd(IASO)$_4$](PF$_6$)$_2$; (d) IASO ligand.

cationic complexes of Pd(II) which we have prepared, the ν_{SO} bands attributed to sulfur coordination are of comparable intensity with those attributed to oxygen coordination.

Since the very broad ν_3 band of BF$_4^-$ centered at 1053 cm^{-1} partially obscures examination of the ν_{SO} S-bonded region, [Pd(IASO)$_4$]$^{2+}$ was prepared with the hexafluorophosphate anion which is completely transparent in the 900–1200-cm^{-1} region. [Pd(IASO)$_4$](PF$_6$)$_2$ has a strong, broad ν_{SO} band at 914 cm^{-1}, associated with oxygen-bonded ligand. Sharp bands also appear at 1143, 1132, and 1122 cm^{-1}, but their medium weak intensity clearly associates them with ligand modes (Figure 3c). It is thus concluded that [Pd(IASO)$_4$]$^{2+}$ is the first example of a totally oxygen-bonded palladium(II) sulfoxide complex.

Further evidence for exclusive oxygen bonding is found in the far-ir spectrum which exhibits a single strong band (478 cm^{-1}) attributable to Pd–O stretching. The spectrum of [Pd(IASO)$_4$](BF$_4$)$_2$ in dichloromethane is virtually identical with the mull spectrum suggesting configuration retention in this solvent. The high dichloromethane solubility of [Pd(IASO)$_4$](BF$_4$)$_2$ permitted further evaluation of the complex by nmr. Only one type of ligand is observed in the nmr from +40 to −45°, and all of the coordinated ligands exchange rapidly with excess ligand. All accessible lines of evidence suggest that [Pd(IASO)$_4$]$^{2+}$ contains only oxygen-bonded sulfoxide.

2,5-Dithiahexane 2,5-Dioxide Complexes of Pd(II) and Pt(II).—2,5-Dithiahexane 2,5-dioxide (CH$_3$S(O)-CH$_2$CH$_2$S(O)CH$_3$) contains two asymmetric sulfur atoms and is obtained in both racemic and meso diastereomeric forms.[10] There are no data in the literature on the assignment of these isomers. We have examined the proton nmr in optically active solvents,[11] but this has not yet proven useful in making these isomer assignments. Madan, *et al.*, have previously used the higher melting α isomer to prepare several divalent metal complexes, including [Pd(α-DTHO$_2$)-Cl$_2$] and [Pt(α-DTHO$_2$)Cl$_2$].[12] It was concluded from the increase in ν_{SO} that the sulfur donor sites were utilized in forming five-membered rings with these metals. We have prepared the corresponding complexes with β-DTHO$_2$ and also have found exclusive sulfur bonding (Table I).

Studies of palladium and platinum sulfoxide complexes indicate that sulfur is the preferred donor site when steric requirements are not too large. In DTHO$_2$ the –CH$_2$–CH$_2$– segment between the two sulfoxide donor sites is less sterically restricting than are adjacent methyl groups on two DMSO ligands. This reduced interligand repulsion along with the increased kinetic stability expected of a chelate suggested that an entirely sulfur-coordinated cationic species might be isolated.

The complexes [M(β-DTHO$_2$)$_2$]$^{2+}$ [M = Pt(II), Pd(II)] have one band in each of the sulfur- and oxygen-bonded ν_{SO} regions as well as single bands in the ν_{M-O} and ν_{M-S} regions (Table I). These data are most consistent with a trans sulfur- and oxygen-bonded configuration (effective C_{2h} symmetry) in the cationic complexes of each metal. These complexes can be formulated either as monomers or as polymers in which each β-DTHO$_2$ (CH$_3$S(O)CH$_2$–CH$_2$S(O)CH$_3$) utilizes one sulfur- and one oxygen-coordination site.

The Pd(II) and Pt(II) cationic complexes of α-DTHO$_2$ each show a single strong ν_{SO} band attributable to sulfur coordination but no strong bands associated with oxygen-coordinated sulfoxide (Table I). In each case far-ir data show a single band attributable to M–S but no bands associated with M–O stretching. These data are consistent with an entirely sulfur-coordinated cationic species in both cases. If there is a ν_{SO} band associated with oxygen bonding, it must appear at a substantially higher frequency than in related complexes. The single ν_{SO} and M–S stretching frequencies indicate an effective D_{4h} symmetry, which is most consistent with a polymer resulting from each DTHO$_2$ bridging adjacent metal sites.

The insolubility of these complexes, which has prohibited characterization by nmr, is consistent with formulating the complexes as polymers.

Experimental Section

Materials.—Sponge palladium and nitrosyl tetrafluoroborate (vacuum sublimed before use) were purchased from K & K Laboratories. Dimethyl sulfoxide (DMSO), di-*n*-propyl sulfoxide (NPSO), di-*n*-butyl sulfoxide (NBSO), diisoamyl sulfoxide (IASO), and tetramethylene sulfoxide (TMSO) were obtained from Aldrich Chemical Co., Inc. The DMSO and NPSO were dried over 4A Linde Molecular Sieves and vacuum distilled. The NBSO and TMSO were dried over molecular sieves and used without further purification. 2,5-Dithiahexane 2,5-dioxide

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[10] E. V. Bell and G. M. Bennett, *J. Chem. Soc.*, 1798 (1927).

[11] W. H. Pirkle and S. D. Beare, *J. Amer. Chem. Soc.*, **90**, 6250 (1968).

[12] S. K. Madan, C. M. Hull, and L. J. Herman, *Inorg. Chem.*, **7**, 491 (1968)

(DTHO$_2$) was synthesized by the method of Bell and Bennett,[10] from 2,5-dithiahexane. The α (mp 163°) and β (mp 128°) isomers were separated by repeated fractional crystallizations from acetonitrile in which the β isomer has the greater solubility.

Instrumentation.—The infrared spectra were obtained as Nujol mulls of the solids using sodium chloride and silver chloride plates. The spectrum from 4000 to 600 cm^{-1} was recorded using a Perkin-Elmer Model 421 spectrometer. The spectrum from 600 to 200 cm^{-1} was recorded using a Perkin-Elmer 225 spectrometer. Nmr spectra were recorded on Varian HA 100 and HA 60 spectrometers.

Preparation of Complexes. [PdL$_2$X$_2$] (X = Cl, Br).—The neutral palladium sulfoxide complexes where L = DMSO, TMSO, NPSO, NBSO, or IASO were prepared by dissolving 0.2500 g of PdCl$_2$ in 5 ml of the respective sulfoxide at 50°. The DMSO, TMSO, and NPSO complexes precipitated upon addition of anhydrous ether with stirring. The NBSO and IASO complexes precipitated upon addition of cyclohexane and subsequent cooling of the solution at −78° for 1 hr. The complexes were dried *in vacuo* for 5 hr.

Anal. Calcd for [Pd(DESO)$_2$Cl$_2$]: C, 24.66; H, 5.17. Found: C, 24.92; H, 5.23. Calcd for [Pd(NPSO)$_2$Cl$_2$]: C, 32.33; H, 6.33. Found: C, 32.44; H, 6.37. Calcd for [Pd(NBSO)$_2$Cl$_2$]: C, 38.29; H, 7.23. Found: C, 38.41; H, 7.30. Calcd for [Pd(TMSO)$_2$Cl$_2$]: C, 24.92; H, 4.18. Found: C, 24.59; H, 4.28. Calcd for [Pd(TMSO)$_2$Br$_2$]: C, 20.25; H, 3.40. Found: C, 20.46; H, 3.55. Calcd for [Pd(IASO)$_2$Cl$_2$]: C, 43.05; H, 7.95. Found: C, 43.25; H, 8.09. Calcd for [Pd(DMSO)$_2$Br$_2$]: C, 11.37; H, 2.86. Found: C, 11.48; H, 2.90.

[PtL$_2$Cl$_2$].—The neutral platinum sulfoxide complexes were prepared by adding 0.009 mol of the respective sulfoxide to an aqueous solution of 0.003 mol of K$_2$[PtCl$_4$] in 10 ml of water and allowing the solution to stand at room temperature until yellow crystals precipated. The complexes were filtered, washed with water, ethanol, and ether, and dried *in vacuo* for 4 hr.

Anal. Calcd for [Pt(DMSO)$_2$Cl$_2$]: C, 11.38; H, 2.86. Found: C, 11.58; H, 2.91. Calcd for [Pt(DESO)$_2$Cl$_2$]: C, 20.08; H, 4.21. Found: C, 19.96; H, 4.06. Calcd for [Pt(NPSO)$_2$Cl$_2$]: C, 26.96; H, 5.28. Found: C, 26.88; H, 5.38. Calcd for [Pt(NBSO)$_2$Cl$_2$]: C, 32.54; H, 6.14. Found: C, 32.31; H, 6.07. Calcd for [Pt(TMSO)$_2$Cl$_2$]: C, 20.26; H, 3.40. Found: C, 20.02; H, 3.27. Calcd for [Pt(IASO)$_2$Cl$_2$]: C, 37.14; H, 6.85. Found: C, 36.95; H, 6.74.

[Pd(NPSO)$_4$](BF$_4$)$_2$.—A 0.2500-g sample of [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ was dissolved in 2 ml of NPSO to give an orange-brown solution. Upon heating for 12 hr at 47° under vacuum, the excess ligand was removed by volatilization yielding clear light brown crystals. *Anal.* Calcd for [Pd(NPSO)$_4$](BF$_4$)$_2$: C, 35.28; H, 6.91. Found: C, 36.11; H, 6.91.

[Pd(NPSO)$_4$](PF$_6$)$_2$.—A 0.2500-g sample of [Pd(CH$_3$CN)$_4$](PF$_6$)$_2$ was dissolved in 2 ml of NPSO. Anhydrous ether was added dropwise over 15 min to the solution with stirring. The resulting orange precipitate was dried *in vacuo* for 4 hr. *Anal.* Calcd for [Pd(NPSO)$_4$](PF$_6$)$_2$: C, 30.89; H, 6.05. Found: C, 31.53; H, 6.18.

[Pd(NBSO)$_4$](BF$_4$)$_2$.—A 0.2500-g sample of [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ was dissolved in 2 ml of NBSO to give an orange-brown solution. After heating at 50° under vacuum in a 100-ml round-bottom flask for 3 hr, the volatile excess ligand condensed on the upper walls of the flask. The reaction solution was then transferred to a new flask and the process was repeated. After seven or eight such cycles, a viscous dark brown oil of the complex remained. *Anal.* Calcd for [Pd(NBSO)$_4$](BF$_4$)$_2$: C, 41.36; H, 7.81. Found: C, 41.08; H, 8.02.

[Pd(IASO)$_4$](BF$_4$)$_2$.—A 0.2500-g sample of [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ was dissolved in 2 ml of diisoamyl sulfoxide warmed to 50°. To the resulting orange solution 20 ml of cyclohexane was added. Anhydrous ether was added dropwise over 15 min with vigorous stirring. The oil which precipitated was converted to a crystalline solid by continued stirring for 12 hr. The resulting yellow-brown precipitate was dried *in vacuo* for 5 hr. *Anal.* Calcd for [Pd(IASO)$_4$](BF$_4$)$_2$: C, 46.13; H, 8.52. Found: C, 45.82; H, 8.95.

[Pd(IASO)$_4$](PF$_6$)$_2$.—A 0.2500-g sample of [Pd(CH$_3$CN)$_4$](PF$_6$)$_2$ was dissolved in 2 ml of diisoamyl sulfoxide warmed to 50°, and 5 ml of cyclohexane was added to the resulting solution. Anhydrous ether was then added dropwise while stirring for 15 min. The resulting orange yellow crystals were filtered in air, and vacuum dried for 2 hr. *Anal.* Calcd for [Pd(IASO)$_4$](PF$_6$)$_2$: C, 41.50; H, 7.67. Found: C, 40.85; H, 7.49.

[Pd(TMSO)$_4$](BF$_4$)$_2$.—A 0.2500-g sample of [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ was dissolved in 2 ml of TMSO and the resulting orange solution was diluted to 40 ml with CH$_2$Cl$_2$. Anhydrous ether was added very slowly dropwise to the solution over 3 hr with vigorous stirring. The fine orange-brown precipitate which formed was filtered in air and dried *in vacuo* for 5 hr. *Anal.* Calcd for [Pd(TMSO)$_4$](BF$_4$)$_2$: C, 27.58; H, 4.63. Found: C, 27.66; H, 4.85.

[PtL$_4$](ClO$_4$)$_2$.—Cationic platinum(II) complexes with DMSO, NPSO, and TMSO were prepared by adding 0.006 mol of anhydrous silver perchlorate to a solution of 0.003 mol of the neutral [PtL$_2$Cl$_2$] complex in 10 ml of the respective ligand. The resulting silver chloride was filtered off, and anhydrous ether was added to the filtrate, precipitating a yellow oil. The complexes crystallized from the oil upon addition of chloroform. They were dried *in vacuo* for 4 hr.

Anal. Calcd for [Pt(DMSO)$_4$](ClO$_4$)$_2$: C, 13.60; H, 3.42. Found: C, 13.81; H, 3.42. Calcd for [Pt(NPSO)$_4$](ClO$_4$)$_2$: C, 30.96; H, 6.06. Found: C, 30.76; H, 5.97. Calcd for [Pt(TMSO)$_4$](ClO$_4$)$_2$: C, 23.70; H, 3.97. Found: C, 23.42; H, 3.81.

[Pd(DTHO$_2$)Cl$_2$] and [Pt(DTHO$_2$)Cl$_2$] were prepared according to the methods of Madan.[12] *Anal.* Calcd for [Pd(DTHO$_2$)Cl$_2$]: C, 14.49; H, 3.04. Found for α isomer: C, 15.15; H, 2.91. Found for β isomer: C, 15.93; H, 3.27. Calcd for [Pt(DTHO$_2$)Cl$_2$]: C, 11.43; H, 2.40. Found for α isomer: C, 11.84; H, 2.44. Found for β isomer: C, 12.08; H, 2.58.

[Pd(DTHO$_2$)$_2$](BF$_4$)$_2$.—A 0.1036-g (0.000233-mol) sample of [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ and 0.1395 g (0.000905 mol) of the α isomer of DTHO$_2$ were blended in a mortar. The resulting mixture was heated under vacuum in a closed-end tube at 83° for 12 hr to yield an orange-brown solid which was washed with CH$_2$Cl$_2$ and dried *in vacuo* 5 hr. The β isomer complex was prepared similarly. *Anal.* Calcd for [Pd(DTHO$_2$)$_2$](BF$_4$)$_2$: C, 16.33; H, 3.43. Found for α isomer: C, 16.40; H, 3.57. Found for β isomer: C, 16.27; H, 3.20.

[Pt(DTHO$_2$)$_2$](ClO$_4$)$_2$.—A 0.1010-g (0.000108-mol) sample of [Pt(NPSO)$_4$](ClO$_4$)$_2$ and 0.0680 g (0.000441 mol) of DTHO$_2$ were blended in a mortar. The resulting mixture was treated as in the above preparation. *Anal.* Calcd for [Pt(DTHO$_2$)$_2$](ClO$_4$)$_2$: C, 13.68; H, 2.87. Found for α isomer: C, 13.72; H, 3.10. Found for β isomer: C, 13.85; H, 3.20.

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