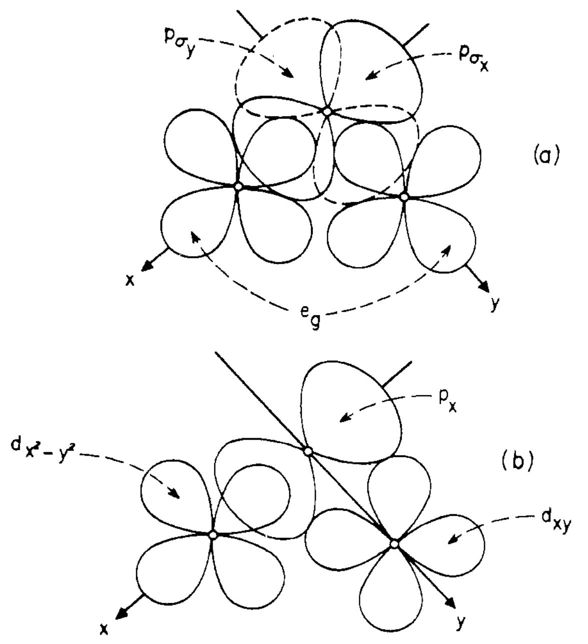

Figure 6.—The orientation of $p\sigma_x$ and $p\sigma_y$ orbitals on oxygen with respect to e_g and t_{2g} orbitals on two nickel atoms arranged at right angles.

interaction must be antiferromagnetic superexchange. It is also possible to orient the p_π orbitals to overlap the d_{xy} orbitals on the terminal Ni atoms. However,

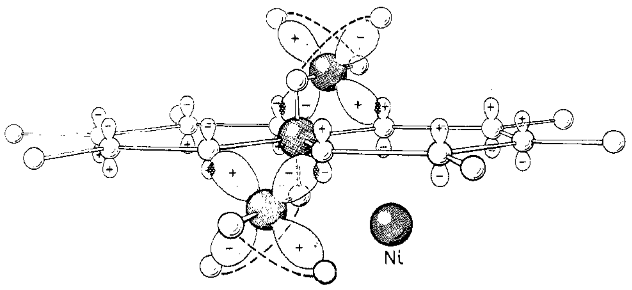

Figure 7.—Superexchange pathway between e_g orbitals centered on atoms Ni_1 and Ni_3 and the π system of the bridging acetylacetonate ligands.

since these are both filled orbitals, there is no exchange effect. There is no orientation of the π system which will result in the simultaneous overlap of the $d_{x^2-y^2}$ orbital of one terminal Ni atom with the d_{xy} of the other. Accordingly, ferromagnetic coupling by electron transfer plus intraatomic direct exchange is precluded. The net interaction between the end members of the trimer is therefore expected to be antiferromagnetic as is observed experimentally.

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Rates and Mechanism of Substitution Reactions of Sterically Hindered Palladium(II) Complexes

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The preparation and characterization of the complexes $Pd(dien)SO_3$, $Pd(Et_4dien)SO_3$, $Pd(Et_4dien)S_2O_3$, $Pd(MeEt_4dien)S_2O_3$, $Pd(Me_5dien)S_2O_3$, $[Pt(Et_4dien)NH_3][PtCl_4]\cdot H_2O$, and $[Pt(Et_4dien)NH_3]Cl_2$[1] are described, as well as the *in situ* preparation of $[Pd(Et_4dien)H_2O](ClO_4)_2$. In these complexes, the amine is tridentate and the other ligand is unidentate. The kinetics of the reaction of sulfite ion with $[Pd(Et_4dien)Br]Br$ and of thiosulfate ion with $[Pd(Et_4dien)Br]Br$, $[Pd(Me_5dien)Cl]PF_6$, and $[Pd(MeEt_4dien)Cl]Cl$ were investigated. The sulfite ion reaction follows the same first-order path as found previously for other ligands with this substrate, yet the thiosulfate ion reactions are described by both a ligand-dependent and a ligand-independent path. The kinetics of the reaction of $[Pd(Et_4dien)H_2O](ClO_4)_2$ with a series of nucleophiles was studied by the stopped-flow method; all reactions were fast and were first order in both substrate and reagent.

Introduction

The rates of substitution reactions of the sterically hindered complexes $Pd(amine)X^+$ (amine = Et_4dien, $MeEt_4dien$, or Me_5dien; X = Cl or Br) with various nucleophiles have been shown to be independent of the concentration of entering nucleophile, even for good nucleophiles such as I^- and SCN^-.[2] This type of kinetic behavior is similar to that for octahedral complexes and was explained by a solvent-assisted dissociative mechanism

$$Pd(amine)X^+ + H_2O \xrightarrow{slow} Pd(amine)H_2O^{2+} + X^- \quad (1)$$

$$Pd(amine)H_2O^{2+} + Y^{n-} \xrightarrow{fast} Pd(amine)Y^{(2-n)+} + H_2O \quad (2)$$

The one exception to this kinetic behavior occurs when the amine is Et_4dien and the nucleophile is hydroxide ion; in this case a hydroxide ion dependence is found. This was explained by postulating the removal of a

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[1] dien = $HN(C_2H_4NH_2)_2$; Et_4dien = $HN[C_2H_4N(C_2H_5)_2]_2$; $MeEt_4dien$ = $CH_3N[C_2H_4N(C_2H_5)_2]_2$; Me_5dien = $CH_3N[C_2H_4N(CH_3)_2]_2$.

[2] W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, **88**, 2944 (1966).

proton by hydroxide from the central amine nitrogen, yielding the somewhat more reactive conjugate base species.[2]

In the present study, the reactions of sulfite ion with $Pd(Et_4dien)Br^+$ and of thiosulfate ion with $Pd(Et_4dien)Br^+$, $Pd(MeEt_4dien)Cl^+$, and $Pd(Me_5dien)Cl^+$ have been investigated. The sulfite ion reaction follows the same first-order kinetics as for the other ligands studied previously,[2] and the thiosulfate ion reactions are explained by the same rate law with a thiosulfate-dependent term added.

It was also the purpose of this study to obtain rate constants for eq 2 for a series of nucleophiles when amine = Et_4dien. These anation reactions are rapid and were studied mainly by the stopped-flow technique. The reactions were all found to be first-order in both substrate and reagent, second order over-all.

Experimental Section

Materials.—Palladium chloride (Engelhard Industries, Inc.) was the starting material in the preparation of the palladium compounds.

Diethylenetriamine was from Matheson Coleman and Bell, technical grade. The amines Et_4dien and $MeEt_4dien$ were obtained from the Ames Laboratories, Milford, Conn., and Me_5dien was purchased from Columbia Organic Chemicals Co., Inc., Columbia, S. C. They were used without further purification.

Analyses.—C, H, and N analyses were performed by H. Beck of this department. Analyses of Pd and Pt were done by burning the complex to the metal. Chloride ion was determined *via* the indirect Volhard method[3] after the complex had been decomposed with hydrazine hydrate and NaOH.

Spectra.—All uv spectra were taken on a Cary 14 spectrophotometer. The ir spectra were taken as Nujol mulls or KBr disks on a Perkin-Elmer 337 (range 4000–400 cm^{-1}).

Kinetics.—The kinetics of the reactions of $Pd(Et_4dien)Br^+$ and $Pd(MeEt_4dien)Cl^+$ were followed with a Beckman DU spectrophotometer or with a Cary 14 if $t_{1/2} < 5$ min. Both were equipped with water-jacketed cell compartments. Reactions of $Pd(Me_5dien)Cl^+$ and $Pd(Et_4dien)H_2O^{2+}$ were observed by the stopped-flow technique, which is described elsewhere.[4] All of the kinetics were followed by recording absorbance with time at a uv wavelength where the spectral change is large. The products (except the acetato and thiourea complexes) either have been made before or were prepared here by an independent method. In all cases the uv spectra of the kinetic products were in agreement with the spectra of the available complexes. Rate constants from the stopped-flow data were calculated by a least-squares computer program. The rate constants for the conditions given are accurate within 10%.

Preparation and Description of the Compounds.—The preparation and description of $[Pd(Et_4dien)X]X$, where X = Cl, Br, I, or SCN, and of $[Pd(Me_5dien)Cl]PF_6$ were reported earlier.[2] The reaction of Et_4dien with $Na_2[Pd(NO_2)_4]$ in acetone solution yields $[Pd(Et_4dien)NO_2]NO_2$.[5] Its uv spectrum has one peak at 217 mμ (ε 22,000). Reaction of $MeEt_4dien$ with an H_2PdCl_4 solution yields an oil on evaporation, but yellow crystals of $[Pd(MeEt_4dien)Cl]Cl$ are obtained by cooling a hot acetone solution of this oil.[5] The preparation of the PF_6^- salt of this complex was reported earlier.[2]

$[Pd(Et_4dien)H_2O](ClO_4)_2$.—A typical preparation of the aquo complex used for the kinetics follows. To 4 g of freshly prepared Ag_2O in a flask was added 0.3 g of $[Pd(Et_4dien)Br]Br$ (accurately weighed) in 20 ml of water. The flask was stoppered and covered with aluminum foil to minimize carbonate formation and decomposition of the silver compounds. The mixture was stirred magnetically for 3 hr, filtered to remove Ag_2O and AgBr, and titrated to pH 5.1 using 0.1 *N* perchloric acid and a Corning Model 7 pH meter. The yellow solution was then diluted quantitatively to 100 ml; the molarity was based on the original amount of $[Pd(Et_4dien)Br]Br$ used. No attempts were made to isolate the aquo complex as a pure compound. The K_a for the reaction

$$Pd(Et_4dien)H_2O^{2+} \rightleftharpoons Pd(Et_4dien)OH^+ + H^+ \qquad (3)$$

was determined by potentiometeric titration with $HClO_4$ to be 3.2×10^{-8} ($pK_a = 7.5$). A uv spectrum of the aquo complex has absorption maxima at 329 mμ (ε 1140) and 231 mμ (ε 11,100); that of the hydroxo complex has bands at 322 mμ (ε 728) and 212 mμ (ε 17,900).

$Pd(H_2O)_2SO_3$.—The preparation of the triaquo complex $Pd(H_2O)_3SO_3$ was described by Earwicker.[6] Reportedly the same method was used by Eskenazi, Raskovan, and Levitus,[7] who obtained the diaquo complex $Pd(H_2O)_2SO_3$. The same method was used in this work, and the Pd analysis agreed with the formulation $Pd(H_2O)_2SO_3$. The ir spectrum of the diaquo complex obtained in this work also did not agree with the published infrared spectrum of $Pd(H_2O)_3SO_3$.[8] Hence it is probable that the diaquo and triaquo species are two distinct compounds, each obtainable depending on the extent to which water is removed at reduced pressure. It is also probable that in water solution both compounds exist as the triaquo complex, $Pd(H_2O)_3SO_3$. *Anal.* Calcd for $Pd(H_2O)_2SO_3$: Pd, 47.5. Found: Pd, 47.2, 47.3.

Ir spectrum (cm^{-1}):[9] 3400 (s, b), 1620 (w), 1135 (s), 1085 (s), 997 (s), 940 (m), 840 (w), 640 (s), 555 (w, sh), 500 (m), 485 (m).

$Pd(Et_4dien)SO_3$.—To 0.57 g of $Pd(H_2O)_2SO_3$ in 5 ml of water was added 2 ml of Et_4dien at room temperature; an exothermic reaction took place. The solution was filtered to remove some finely powdered palladium present in the starting material. The complex was precipitated from solution by acetone and was reprecipitated several times from alcohol by the addition of acetone to obtain a light yellow powder. The powder was placed *in vacuo* overnight using a mercury diffusion pump; yield 0.34 g (33%). *Anal.* Calcd for $Pd(Et_4dien)SO_3$: C, 35.87; H, 7.28; N, 10.46; Pd, 26.5. Found: C, 35.91; H, 7.52; N, 10.21; Pd, 26.2.

A uv spectrum of an aqueous solution of the complex has maxima at 273 mμ (ε 13,900) and 232 mμ (ε 11,250). The complex is stable in aqueous solution at room temperature, with essentially no hydrolysis occurring in a period of 6 hr.

Ir spectrum (cm^{-1}):[9] sulfite peaks: 1120 (s), 1080 (s), 967 (s), 638 (s), 510 (m), 502 (m), 469 (m). Others: 3070 (m), 1315 (w), 1295 (w), 1205 (w), 1153 (s), 1103 (s), 1096 (m), 1038 (m), 1012 (m), 978 (s), 910 (m), 860 (m), 840 (m), 830 (m), 762 (m), 756 (m), 580 (w). The peaks in the C–H stretch region (*ca.* 2900 cm^{-1}) and C–H deformation region (*ca.* 1450 cm^{-1}) are obscured by the Nujol. Assignments of the sulfito bands are made by subtracting the spectrum of $[Pd(Et_4dien)Br]Br$ and also on the basis of other sulfito complexes. The sulfito peaks agree well with those of other unidentate sulfur-bonded sulfito complexes.[8]

$Pd(dien)SO_3$.—Preparation of this complex is completely analogous to that of $Pd(Et_4dien)SO_3$. The complex $Pd(dien)SO_3$ was prepared to compare its ir spectrum and mode of sulfite bonding with the Et_4dien sulfito complex. To 1.07 g of $Pd(H_2O)_2SO_3$ in 10 ml of water was added 3 ml of dien. As with the Et_4dien complex, the reaction solution became quite hot. The solution was filtered and the complex precipitated with acetone. The compound was reprecipitated from water with acetone, then

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[3] L. F. Hamilton and S. G. Simpson, "Quantitative Chemical Analysis," 11th ed, The Macmillan Co., New York, N. Y., 1958, p 296.

[4] R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **5**, 1523 (1966).

[5] K. J. Weidenbaum, private communication.

[6] G. W. Earwicker, *J. Chem. Soc.*, 2620 (1960).

[7] R. Eskenazi, J. Raskovan, and R. Levitus, *J. Inorg. Nucl. Chem.*, **27**, 371 (1965).

[8] G. Newman and D. B. Powell, *Spectrochim. Acta*, **19**, 213 (1963).

[9] s, strong; m, medium; w, weak; b, broad; sh, shoulder.

with 95% ethanol (this complex is much less soluble in ethanol than is the Et$_4$dien analog). With each precipitation, the solid became lighter in color. Finally the complex was allowed to crystallize slowly by addition of 95% ethanol to a water solution and by cooling in ice. White platelets separated. After drying for some time in a desiccator, the crystals had crumbled to a white powder; yield 1.11 g (80%). *Anal.* Calcd for Pd(dien)SO$_3$: C, 16.59; H, 4.52; N, 14.51; Pd, 36.74. Found: C, 16.20; H, 4.39; N, 14.25; Pd, 36.94.

A uv spectrum of the complex in water solution has maxima at 250 mμ (ϵ 14,300) and 194 mμ (ϵ 11,500).

Ir spectrum (cm^{-1}):[9] sulfite peaks: 1640 (m), 1112 (s), 1080 (s), 992 (s), 653 (s), 510 (m), 500 (m), 482 (m). Others: 3230 (s), 3120 (s), 1595 (m), 1320 (w), 1275 (m), 1164 (m), 1152 (m), 1140 (m), 1045 (s), 1015 (m), 910 (m), 892 (m), 862 (m), 836 (m), 810 (m), 600 (m), 538 (m). Peaks in the 2900- and 1450-cm^{-1} regions are obscured by Nujol. Assignments are made by subtracting the spectrum of [Pd(dien)I]I, and also on the basis of spectra of other sulfito complexes. Again, the sulfite peaks match those of other unidentate sulfur-bonded sulfito complexes.[8]

Pd(Et$_4$dien)S$_2$O$_3$.—This complex was prepared quite easily by the addition of Et$_4$dien to the complex Pd(NH$_3$)$_3$S$_2$O$_3$. The Pd(NH$_3$)$_3$S$_2$O$_3$ was prepared by Riabchikov's method.[10] To 0.33 g of Pd(NH$_3$)$_3$S$_2$O$_3$ was added 10 ml of water and 1 ml of Et$_4$dien. The mixture was heated gently with stirring. Within a few minutes, the insoluble Pd(NH$_3$)$_3$S$_2$O$_3$ had reacted, producing an orange solution with a strong ammonia odor. The solution was evaporated, the excess amine was extracted several times with anhydrous ether, and the orange powder was air dried and then dried overnight *in vacuo* with a mercury diffusion pump. *Anal.* Calcd for Pd(Et$_4$dien)S$_2$O$_3$: C, 33.22; H, 6.74; N, 9.68; Pd, 24.52. Found: C, 32.83; H, 6.52; N, 9.35; Pd, 24.48.

A uv spectrum of the aqueous complex has a peak at 263 mμ (ϵ 14,430) and a shoulder at 240 mμ. At 5×10^{-5} *M*, an increase in this peak height of only 2.3% occurs with addition of excess thiosulfate, indicating very little hydrolysis.

Ir spectrum (cm^{-1}):[9] thiosulfate peaks: 1197 (s), 1172 (s), 1008 (s), 635 (s), 535 (s). Others: 3090 (s), 1210 (s), 1157 (s), 1107 (m), 1082 (m), 1059 (m), 1045 (m), 1028 (m), 990 (m), 905 (w), 861 (m), 840 (m), 825 (m), 810 (w), 762 (m), 750 (m), 586 (w), 570 (w), 505 (m), 460 (w). The regions *ca.* 2900 and 1450 cm^{-1} are obscured by Nujol. Assignments are made by subtracting the spectrum of [Pd(Et$_4$dien)Br]Br and also on the basis of spectra of other thiosulfato complexes. The thiosulfate peak positions agree quite well with those found in unidentate Co(III) thiosulfato complexes.[11] From the chemical inertness of these cobalt thiosulfato complexes, they were assumed to be linked *via* sulfur rather than oxygen. If the sulfur–metal linkage exists in these relatively hard Co(III) complexes, then it would certainly be expected for a soft Pd(II) complex.[12]

[Pd(MeEt$_4$dien)S$_2$O$_3$]·H$_2$O.—This compound was prepared in a manner strictly analogous to the Et$_4$dien compound preparation. To 0.41 g of Pd(NH$_3$)$_3$S$_2$O$_3$ and 20 ml of water was added 1.2 ml of MeEt$_4$dien. The solution was stirred and warmed, and within a few minutes the yellow solid had completely dissolved, forming a deep orange solution. Evaporation of the solution to near dryness yielded an orange oil. An orange powder was obtained by extracting the water and excess MeEt$_4$dien with anhydrous ether several times. The ether was evaporated, and attempts to remove the water of hydration at reduced pressure with a mercury diffusion pump were not successful; yield 0.54 g (77%). *Anal.* Calcd for [Pd(MeEt$_4$dien)S$_2$O$_3$]·H$_2$O: C, 33.51; H, 7.14; N, 9.02; Pd, 22.83. Found: C, 32.99; H, 7.12; N, 8.85; Pd, 22.73.

A uv spectrum of the aqueous complex after addition of 1:1 excess Na$_2$S$_2$O$_3$ has a peak at 272 mμ (ϵ 16,160) and a shoulder centered at 245 mμ. Addition of 1:1 excess thiosulfate increased the peak height by only 2% and did not change the peak position.

Ir spectrum (cm^{-1}):[9] thiosulfate peaks: 1210 (s), 1175 (s), 1017 (s), 635 (s), 530 (s). Others: 3550 (s), 3450 (s), 1660 (m), 1310 (w), 1280 (m), 1196 (s), 1189 (s), 1150 (m), 1080 (m), 1072 (m), 1060 (m), 1043 (m), 1033 (m), 967 (m), 925 (w), 900 (m), 840 (w), 820 (w), 800 (w, sh), 790 (s), 750 (m), 740 (m), 707 (w), 565 (m), 520 (m), 475 (w). Peaks in the 2900- and 1450-cm^{-1} regions are obscured by Nujol. The assignments of the thiosulfato bands are made by subtracting the spectrum of [Pd(MeEt$_4$dien)Cl]Cl and also on the basis of the spectra of other thiosulfato complexes. As with the Et$_4$dien analog, the thiosulfato peak positions indicate unidentate sulfur-bonded linkage.[11]

[Pd(Me$_5$dien)S$_2$O$_3$]·H$_2$O.—Preparation was similar to the Et$_4$dien and MeEt$_4$dien analogous preparations. To 0.51 g of Pd(NH$_3$)$_3$S$_2$O$_3$ was added 10 ml of water and 1.5 ml of Me$_5$dien. The mixture was warmed gently and stirred magnetically until all of the solid had dissolved. The solution was heated for 30 min, then evaporated until an orange oil separated. The water and excess Me$_5$dien were extracted with anhydrous ether, and the remaining oil changed to a powder on scratching the sides of the vessel. In this preparation, evaporation of the ether caused the powder to become somewhat oily, yet exposure to the atmosphere for a few minutes caused the material to revert to a yellow-orange powder; yield 0.63 g (82%). Heating the compound at 65° under reduced pressure did not remove the water of hydration. *Anal.* Calcd for [Pd(Me$_5$dien)S$_2$O$_3$]·H$_2$O: C, 26.38; H, 6.15; N, 10.25; Pd, 25.96. Found: C, 25.83; H, 6.15; N, 10.60; Pd, 26.05.

A uv spectrum of the aqueous complex after addition of 1:1 excess Na$_2$S$_2$O$_3$ has maxima at 262 mμ (ϵ 14,610) and 224 mμ (ϵ 11,140). Addition of this 1:1 excess thiosulfate ion increased peak heights only about 2% and did not change their positions.

Ir spectrum (cm^{-1}):[9] thiosulfate peaks: 1200 (s), 1168 (s), 1010 (s), 640 (s), 530 (m). Others: 3515 (s), 3440 (s), 3260 (m), 3150 (s), 1630 (m), 1300 (m), 1225 (m), 1190 (sh), 1152 (s), 1122 (m), 1097 (m), 1070 (m), 1058 (m), 1040 (m), 1025 (sh), 971 (m), 958 (m), 945 (m), 938 (w), 860 (m), 815 (m), 795 (m), 782 (s), 765 (m), 648 (sh), 503 (w), 480 (m). Peaks in the 2900- and 1450-cm^{-1} regions are obscured by Nujol. Assignments of the thiosulfato bands are made by subtracting the spectrum of [Pd(Me$_5$dien)Cl]PF$_6$ and also on the basis of spectra of other thiosulfato complexes. As with the Et$_4$dien and MeEt$_4$dien analogs, unidentate sulfur-bonded linkage is evident.[11]

[Pt(Et$_4$dien)NH$_3$][PtCl$_4$]·H$_2$O.—To 1.02 g of *cis*-Pt(NH$_3$)$_2$Cl$_2$ was added 1.68 g of Et$_4$dien previously adjusted to pH 5 with 6 *N* HCl. The volume was increased to 20 ml with water, and the mixture was refluxed 14 hr. The solution was then cooled in ice and filtered to remove small amounts of platinum and unreacted *cis*-Pt(NH$_3$)$_2$Cl$_2$. The solution was warmed to 50°, and to it was added a solution of 1.41 g of K$_2$PtCl$_4$ (theoretical amount) in 20 ml of water. A pink precipitate formed at once. The suspension was stirred 10 min while warm, then filtered, washed with water and acetone, and air dried; yield 1.60 g (60%). Solubility *ca.* 1 g/l. in water at 25°. *Anal.* Calcd for [Pt(Et$_4$dien)NH$_3$][PtCl$_4$]·H$_2$O: C, 18.42; H, 4.38; Cl, 18.12; N, 7.16; Pt, 49.87. Found: C, 19.18; H, 4.39; Cl, 17.91; N, 7.16; Pt, 49.90.

Ir spectrum (KBr disk) (cm^{-1}):[9] 3450 (s), 3230 (s), 3170 (m), 3085 (s), 2970 (s), 2930 (m), 2880 (s), 1630 (s), 1460 (s), 1448 (s), 1390 (s), 1380 (s), 1360 (s), 1345 (s), 1305 (w), 1275 (w), 1253 (w), 1213 (w), 1192 (w), 1180 (w), 1138 (m), 1108 (w), 1080 (m), 1043 (m), 1022 (m), 1003 (m), 903 (w), 863 (w), 828 (w), 798 (w), 750 (m), 550 (w, b).

[Pt(Et$_4$dien)NH$_3$]Cl$_2$.—To 0.71 g of [Pt(Et$_4$dien)NH$_3$][PtCl$_4$]·H$_2$O was added 20 ml of water and 0.32 g of [Pt(NH$_3$)$_4$]Cl$_2$·H$_2$O (theoretical amount). The mixture was stirred and heated 4 hr, at which time the formation of the green Magnus salt [Pt(NH$_3$)$_4$][PtCl$_4$] seemed complete. The solution was filtered and evaporated to near dryness, and the resulting oil was dissolved in 20 ml of ethanol. The solution was filtered, the alcohol evaporated,

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(10) D. I. Riabchikov and A. P. Issakova, *Dokl. Akad. Nauk SSSR*, **41**, 161 (1943).

(11) A. V. Babaeva, I. B. Baranovskii, and Yu. Ya. Kharitonov, *Russ. J. Inorg. Chem.*, **8**, 307 (1963); *Zh. Neorgan. Khim.*, **8**, 604 (1963).

(12) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

and the oil converted to a white powder by extracting the residual solvent with dry ether and by scratching the sides of the vessel. The compound was placed *in vacuo* for 24 hr to remove water of crystallization, using a mercury diffusion pump; yield 0.45 g (99%). *Anal.* Calcd for $[Pt(Et_4dien)NH_3]Cl_2$: C, 28.92; H, 6.47; Cl, 14.23; N, 11.24; Pt, 39.14. Found: C, 28.35; H, 6.63; Cl, 14.40; N, 10.45; Pt, 38.79.

A uv spectrum of the aqueous complex has maxima at 245 mμ (ε 590) and 220 mμ (ε 680).

Ir spectrum (KBr disk) (cm^{-1}):[9] 3450 (s), 3250 (m), 3180 (s), 3125 (s), 3035 (s), 2980 (s), 2945 (m), 2880 (s), 2625 (w), 2515 (w), 2430 (w), 2320 (w), 2200 (w), 1645 (s), 1580 (m), 1480 (s), 1470 (s), 1400 (s), 1385 (s), 1375 (s), 1350 (w), 1340 (w), 1330 (w), 1310 (w), 1275 (w), 1250 (w), 1210 (w), 1197 (w), 1177 (w), 1140 (m), 1115 (m), 1085 (m), 1045 (m), 1020 (m), 990 (w), 940 (w), 900 (w), 865 (w), 823 (m), 800 (m), 750 (m), 550 (w, b).

Results

Reactions of $Pd(amine)X^+$.—In order to supplement the previous work,[2] reaction 4 was carried out in water

$$Pd(Et_4dien)Br^+ + SO_3^{2-} \longrightarrow Pd(Et_4dien)SO_3 + Br^- \quad (4)$$

at 25°. The reaction was buffered to maintain an appreciable concentration of both SO_3^{2-} and HSO_3^-. The rate constant obtained (Table I) was independent of sulfite ion (and bisulfite ion) concentration.

TABLE I

EXPERIMENTAL FIRST-ORDER RATE CONSTANTS FOR REACTIONS OF SUBSTRATES $Pd(amine)X^+$ WITH NUCLEOPHILES Y IN WATER AT 25°

$10^3[Y]$, *M*	10^3k_{obsd}, sec^{-1}
5.0×10^{-5} *M* $Pd(Et_4dien)Br^{+\,a}$	
1.00 sulfite[b]	1.52
2.00 sulfite[b]	1.52
5.00 sulfite[b]	1.53
5.7×10^{-5} *M* $Pd(Et_4dien)Br^{+\,c}$	
0.100 $S_2O_3^{2-}$	1.97
0.200 $S_2O_3^{2-}$	2.75
0.350 $S_2O_3^{2-}$	3.59
0.500 $S_2O_3^{2-}$	4.72
0.750 $S_2O_3^{2-}$	5.98
1.00 $S_2O_3^{2-}$	7.47
1.30 $S_2O_3^{2-}$	8.87
1.60 $S_2O_3^{2-}$	10.4
2.00 $S_2O_3^{2-}$	12.2
4.8×10^{-5} *M* $Pd(MeEt_4dien)Cl^{+\,d}$	
1.00 $S_2O_3^{2-}$	0.700
2.00 $S_2O_3^{2-}$	0.744
5.00 $S_2O_3^{2-}$	0.898
10.0 $S_2O_3^{2-}$	1.18
15.0 $S_2O_3^{2-}$	1.42
20.0 $S_2O_3^{2-}$	1.75
4.8×10^{-5} *M* $Pd(MeEt_4dien)Cl^{+\,e}$	
1.00 $S_2O_3^{2-}$	0.642
10.0 $S_2O_3^{2-}$	0.858
20.0 $S_2O_3^{2-}$	1.18
50.0 $S_2O_3^{2-}$	2.05
75.0 $S_2O_3^{2-}$	3.05
100.0 $S_2O_3^{2-}$	4.31
13.6×10^{-5} *M* $Pd(Me_5dien)Cl^{+\,f}$	
2.00 $S_2O_3^{2-}$	265
5.00 $S_2O_3^{2-}$	305
10.0 $S_2O_3^{2-}$	366
15.0 $S_2O_3^{2-}$	429
20.0 $S_2O_3^{2-}$	497

[a] 0.04 *M* phosphate buffer, pH 7.0. [b] Concentration listed is sum of $[SO_3^{2-}]$ and $[HSO_3^-]$. [c] Ionic strength 0.0060 ($NaClO_4$). [d] Ionic strength 0.060 ($NaClO_4$). [e] Ionic strength 0.300 ($NaClO_4$). [f] Ionic strength 0.060 ($NaClO_4$).

Thiosulfate ion substitution reactions were also studied.

$$Pd(amine)X^+ + S_2O_3^{2-} \longrightarrow Pd(amine)S_2O_3 + X^- \quad (5)$$

Here amine = Et_4dien, $MeEt_4dien$, or Me_5dien, and X = Br or Cl. In all of these cases, the rates showed a *dependence* on thiosulfate ion concentration (Table I). With the substrate $Pd(Et_4dien)Br^+$, decomposition is appreciable and good kinetics are difficult to obtain at $[S_2O_3^{2-}] > 2 \times 10^{-3}$ *M*. The same is true with $Pd(MeEt_4dien)Cl^+$ at $[S_2O_3^{2-}] > 0.05$ *M*.

Reactions of $Pd(Et_4dien)H_2O^{2+}$.—The reactions of this complex with various nucleophiles

$$Pd(Et_4dien)H_2O^{2+} + Y^{n-} \xrightarrow{k_2} Pd(Et_4dien)Y^{(2-n)+} + H_2O \quad (6)$$

are fairly fast and have a first-order rate dependence on both the substrate and Y. The data obtained are shown in Table II.

TABLE II

EXPERIMENTAL FIRST-ORDER RATE CONSTANTS FOR THE REACTION OF $Pd(Et_4dien)H_2O^{2+}$ WITH Y IN WATER AT 25° AND IONIC STRENGTH 0.02 ($NaClO_4$)

$10^4[Pd(Et_4dien)H_2O^{2+}]$, *M*	$10^3[Y]$, *M*	k_{obsd}, sec^{-1}
0.955	0.833 $S_2O_3^{2-}$	1.45
	1.67 $S_2O_3^{2-}$	2.77
	2.50 $S_2O_3^{2-}$	4.72
	3.33 $S_2O_3^{2-}$	6.05
1.33[a]	2.66 HSO_3^-	1.35 (0.0203)[b]
	3.99 HSO_3^-	2.00 (0.0217)[b]
1.91	2.50 SCN^-	0.184
	5.00 SCN^-	0.373
	7.50 SCN^-	0.536
	10.0 SCN^-	0.771
1.35[c]	2.70 NO_2^-	0.0326
	4.05 NO_2^-	0.0503
	5.40 NO_2^-	0.0707
	6.75 NO_2^-	0.0829
1.91	5.00 Cl^-	0.0368
	10.0 Cl^-	0.0726
	15.0 Cl^-	0.114
	20.0 Cl^-	0.144
1.91	5.00 Br^-	0.0308
	10.0 Br^-	0.0559
	15.0 Br^-	0.0917
	20.0 Br^-	0.119
1.91	5.00 I^-	0.0232
	10.0 I^-	0.0427
	15.0 I^-	0.0654
	20.0 I^-	0.0912
1.35	5.00 CH_3COO^-[d]	0.0265
	10.0 CH_3COO^-[d]	0.0372
	15.0 CH_3COO^-[d]	0.0493
	20.0 CH_3COO^-[d]	0.0590
0.53	5.00 thiourea[e]	0.00725
	7.50 thiourea[e]	0.0112
	10.0 thiourea[e]	0.0133

[a] Acetate buffer (0.02 *M* CH_3COO^-, 0.004 *M* CH_3COOH), pH 5.14. [b] k_{obsd} for the slower reaction. [c] Final pH 6.3–6.8. [d] Acetate:acetic acid = 5:1 (pH 5.11). [e] Kinetic study *via* Cary 14 at 270, 274 mμ.

Thiosulfate Ion.—Ultraviolet spectra show $Pd(Et_4dien)S_2O_3$ to be apparently the sole product of the reaction of $Pd(Et_4dien)H_2O^{2+}$ with $S_2O_3^{2-}$, yet a slower reaction was seen on the oscilloscope trace after the rapid reaction. The rapid reaction was the principal reaction, and its rate was first order in both thiosulfate ion and aquo complex; consequently, its rate constants are the ones listed in Table II. The infinity absorbance reading was calculated *via* computer for the least-squares line which gave the best fit to the data. Consistent results were achieved by this method. The slower reaction is apparently not due to impurities, since changing both aquo complex and thiosulfate ion stock solutions did not eliminate it. It also occurs if the reaction solution is made either slightly acidic (pH 5) or slightly basic (pH 8.3). However, the thiosulfato complex does decompose at pH ≤ 5 in the presence of excess thiosulfate ion. For the kinetics, the reaction solutions were not buffered, yet the pH was always close to 6.5.

Bisulfite Ion.—Reactions of $Pd(Et_4dien)H_2O^{2+}$ with sodium bisulfite were run in a sodium acetate–acetic acid buffer at pH 5.14. The buffer was used to keep the reagent mainly in the form HSO_3^-, since the pK_a of bisulfite ion is 7. It should be noted, however, that the uv spectrum of the product agreed with the spectrum of the nonprotonated $Pd(Et_4dien)SO_3$.

Since acetate ion also reacts with the aquo complex (see below), the buffer was added to both the reagent and the substrate solutions to establish the aquo–acetato equilibrium before mixing. With 0.02 *M* sodium acetate, used for ionic strength as well as for the buffer, and 1.33×10^{-4} *M* aquo complex, the equilibrium mixture contained approximately 70% acetato and 30% aquo complex, as determined from the oscilloscope traces. Thus these traces showed a rapid reaction, first order in both aquo complex and bisulfite ion, followed by a much slower reaction, first order in aquo complex and zero order in bisulfite ion. The fast reaction was assumed to be that of the aquo complex with HSO_3^- and the slower reaction, that of the acetato complex with HSO_3^-, both giving the product $Pd(Et_4dien)SO_3$. The computer program which was used to calculate k_{obsd} first subtracts the slower reaction from the oscilloscope trace and then homes in by specified increments on the infinity absorbance for which the sum of the squares of the deviations from the least-squares plot of log $|A_\infty - A|$ *vs.* *t* is the least. Good agreement was obtained.

If the reaction of aquo complex with sodium bisulfite is carried out without buffer, the reaction rates are qualitatively the same as those of the fast reaction, yet the product decomposes quickly as the solution becomes quite acidic. If, however, one goes to a more basic medium in which $[SO_3^{2-}]$ is not insignificant compared with $[HSO_3^-]$, a *decrease* in rate is observed. For instance, using a 1:1 Na_2SO_3–$NaHSO_3$ buffer (pH *ca.* 7.0) gives $k_2 = k_{obsd}/[Y] = 320\ M^{-1}\ sec^{-1}$; with 4:1 Na_2SO_3–$NaHSO_3$ (pH *ca.* 7.6), $k_2 = 76\ M^{-1}\ sec^{-1}$.

Thiocyanate Ion.—Since thiocyanate ion reacts with $Pd(Et_4dien)H_2O^{2+}$ to give both N- and S-bonded isomers,[5] the *over-all* reaction rate constants are the ones listed in Table II. From other studies it has been found that the aquo complex reacts with SCN^- to give 85% N-bonded isomer.[5]

Nitrite, Chloride, Bromide, and Iodide Ions.—The reactions of sodium nitrite, chloride, bromide, and iodide with $Pd(Et_4dien)H_2O^{2+}$ were all of roughly the same rate (Table II). The reaction solutions were not buffered; the pH was always near 6.5, and in the case of nitrite, the pH fell in the range 6.3–6.8.

Acetate Ion.—No attempts were made to isolate the acetato complex $Pd(Et_4dien)CH_3COO^+$, yet there is little doubt of its existence.

The uv spectra of $Pd(Et_4dien)H_2O^{2+}$ with and without added 0.02 *M* sodium acetate and 0.004 *M* acetic acid (pH 5.11) are the same at wavelengths greater than 237 mμ, but below this wavelength an increase in absorbance over that of the two reactants is observed; this increase is greatest at about 220 mμ, at which wavelength the stopped-flow kinetics were followed. The kinetics did depend on acetate ion concentration (Table II), yet the plot of the observed rate constant k_{obsd} in sec^{-1} *vs.* $[CH_3COO^-]$ has a positive intercept, instead of a zero intercept as with all of the other Y listed in Table II. This is consistent with the equilibrium

$$CH_3COO^- + Pd(Et_4dien)H_2O^{2+} \underset{k_r}{\overset{k_2}{\rightleftharpoons}} Pd(Et_4dien)CH_3COO^+ + H_2O \quad (7)$$

Here $k_2 = (k_{obsd} - k_r)/[CH_3COO^-]$. The plot of k_{obsd} *vs.* $[CH_3COO^-]$ (Figure 1) gives a straight line of slope $k_2 = 2.18\ M^{-1}\ sec^{-1}$ and intercept $k_r = 0.0154\ sec^{-1}$. The equilibrium constant for acetato complex formation is then $K_{eq} = k_2/k_r = 142\ M^{-1}$.

Thiourea.—Attempts to isolate $Pd(Et_4dien)SC(NH_2)_2^{2+}$ as a salt met with failure because of the rapid decomposition of the amine complex at high thiourea concentrations, even if $SC(NH_2)_2:Pd \leq 1$. This decomposition was noticed in the kinetics, but reasonably good infinities were obtained as decomposition here is relatively slow because of the low concentrations. In all cases, the final product uv spectrum of the kinetic runs had a peak at 381 mμ ($\epsilon \simeq 580$). This peak is not present in the spectrum of $Pd(Et_4dien)H_2O^{2+}$ or of $Pd(SC(NH_2)_2)_4^{2+}$ and was assumed to result from the formation of $Pd(Et_4dien)SC(NH_2)_2^{2+}$. The second-order nature of the reaction supports this assumption.

Sulfate Ion.—A uv spectral study did not detect any absorbance changes resulting from the addition of sodium sulfate to a solution of $Pd(Et_4dien)H_2O^{2+}$. A reaction was looked for by the stopped-flow technique at 220 and 209 mμ without success. If there is a reaction, it is either quite slow or involves only a very small spectral change.

High Concentrations of Halide Ions.—In an effort to establish the dependence of rate on nucleophile concentration even at high molarity, reactions of $Pd(Et_4dien)H_2O^{2+}$ with 0.500 and 2.00 *M* sodium chloride, with 3.00 *M* sodium bromide, and with 0.500 *M* sodium iodide were investigated. The complex $Pd(Et_4dien)Cl^+$ is quite stable in the presence of 2.00 *M* NaCl at the experimental conditions of the kinetic runs. The complex $Pd(Et_4dien)Br^+$ decomposes rather rapidly in the 3 *M* excess Br^-, yet the decomposition is sufficiently slow compared with the

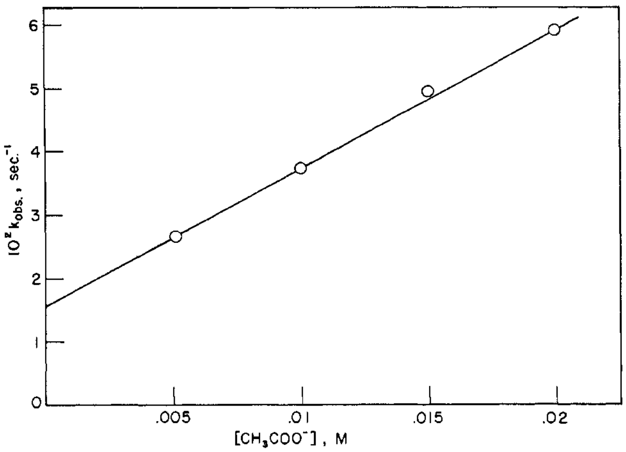

Figure 1.—Plot of k_{obsd} vs. [CH_3COO^-] for the reaction of 1.35 × 10^{-4} M Pd(Et_4dien)H_2O^{2+} with sodium acetate at pH 5.1, 25°, and ionic strength 0.02.

desired reaction, permitting meaningful kinetics to be obtained. The complex Pd(Et_4dien)I^+ in 0.5 M NaI decomposes too rapidly to obtain good kinetic data, so the reaction with iodide ion was not studied further. The data, given in Table III, show a strict first-order dependence of rate on ligand even at high concentration.

TABLE III
RATE CONSTANTS FOR THE REACTION OF Pd(Et_4dien)H_2O^{2+} WITH Y^- AT HIGH IONIC STRENGTH IN WATER AT 25°

[Y^-], M	k_{obsd}, sec^{-1}	k_2, M^{-1} sec^{-1} [b]
μ[a] 0.500 M		
0.00500 Cl^-	0.0128	2.57
0.0100 Cl^-	0.0224	2.24
0.0250 Cl^-	0.0578	2.31
0.0500 Cl^-	0.117	2.35
0.100 Cl^-	0.231	2.31
0.150 Cl^-	0.353	2.35
0.200 Cl^-	0.488	2.44
0.250 Cl^-	0.706	2.82
0.350 Cl^-	0.885	2.53
0.500 Cl^-	1.24	2.47
μ[a] 2.00 M		
0.0100 Cl^-	0.0154	1.54
0.0200 Cl^-	0.0298	1.49
0.0500 Cl^-	0.0735	1.47
0.100 Cl^-	0.147	1.47
0.250 Cl^-	0.355	1.42
μ[a] 2.00 M (*Contd*)		
0.500 Cl^-	0.751	1.50
1.00 Cl^-	1.44	1.44
1.50 Cl^-	2.01	1.34
2.00 Cl^-	2.75	1.37
μ[a] 3.00 M		
0.0100 Br^-	0.0127	1.27
0.0250 Br^-	0.0275	1.10
0.0500 Br^-	0.0551	1.10
0.100 Br^-	0.110	1.10
0.250 Br^-	0.273	1.09
0.500 Br^-	0.529	1.06
1.00 Br^-	1.28	1.28
2.00 Br^-	2.35	1.18
3.00 Br^-	2.90	0.97

[a] Ionic strength adjusted with $NaClO_4$. [b] $k_2 = k_{obsd}/[Y^-]$.

Discussion

Reactions of Pd(amine)X^+.—The reaction of sulfite ion with Pd(Et_4dien)Br^+ is zero order in [SO_3^{2-}], a behavior found previously for all other nucleophiles except hydroxide ion.[2] The rate dependence on hydroxide ion was explained by a rapid acid–base equilibrium followed by the reaction of the conjugate base (SN1CB mechanism). This mechanism could not be operative with complexes containing amines such as MeEt$_4$dien and Me$_5$dien which have no N–H hydrogen, and indeed no dependence of rate on hydroxide ion was found in these systems. However, reactions of all three of these amine–halogeno complexes with thiosulfate ion did depend on [$S_2O_3^{2-}$] (Figures 2–4). This apparently anomalous behavior of $S_2O_3^{2-}$ in these reactions is in accord with the rate law

$$-d[\mathrm{Pd(amine)X^+}]/dt = \{k_1 + k_2[\mathrm{S_2O_3^{2-}}]\}[\mathrm{Pd(amine)X^+}] \quad (8)$$

Such a two-term rate law is reminiscent of the usual behavior of square-planar substitution reactions.[13] The values of k_1 and k_2 (Table IV) are obtained, respectively, from the intercept and slope of a plot of k_{obsd} vs. [$S_2O_3^{2-}$]. As can be seen from Figures 2–4, the k_1 values (intercepts) of the thiosulfate reactions coincide with the k_1 values of the other reagents. Thus it appears that rate law 8 is valid for all the nucleophiles used, but the k_2 term (reagent-dependent path) is too small to be measured at the reagent concentrations used, except for thiosulfate ion.

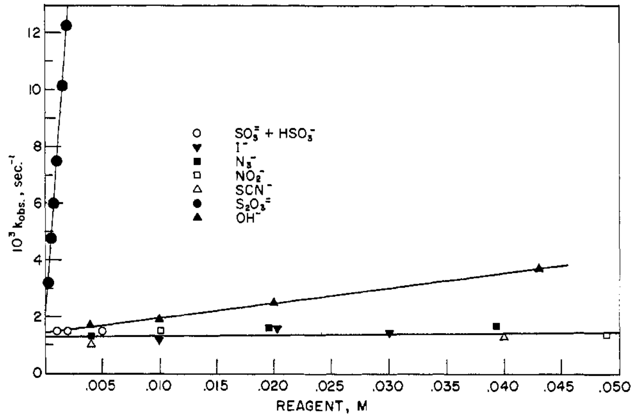

Figure 2.—Plot of k_{obsd} vs. reagent concentration for reactions of Pd(Et_4dien)Br^+ with various nucleophiles in water at 25°. Data (except for sulfite and thiosulfate ions) are from ref 2.

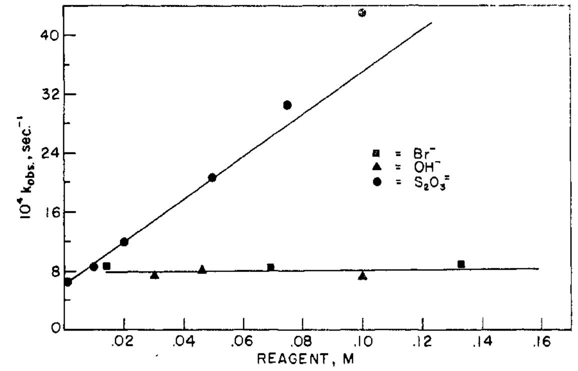

Figure 3.—Plot of k_{obsd} vs. reagent concentration for reactions of Pd(MeEt$_4$dien)Cl^+ with various nucleophiles in water at 25°. Data (except for thiosulfate ion) are from ref 2.

For a mechanistic path involving attack of the halogeno complex by thiosulfate ion, a five-coordinate transition state containing both halide and thiosulfate must exist. This is attributed to the fact that thiosulfate ion has a large nucleophilic reactivity constant (n_{Pt})[14] and to the fact that it is doubly charged,

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(13) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 377.

(14) H. Sobel, J. Songstad, and R. G. Pearson, *J. Am. Chem. Soc.*, **90**, 319 (1968).

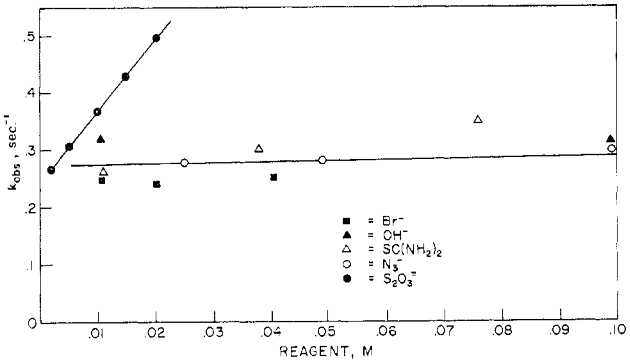

Figure 4.—Plot of k_{obsd} *vs.* reagent concentration for reactions of $Pd(Me_5dien)Cl^+$ with various nucleophiles in water at 25°. Data (except for thiosulfate ion) are from ref 2.

TABLE IV

RATE CONSTANTS FOR THE REAGENT-INDEPENDENT AND REAGENT-DEPENDENT PATHS OF THE REACTION OF $Pd(amine)X^+$ WITH $S_2O_3^{2-}$ IN WATER AT 25°

10^5[substrate], M	Ionic strength[a]	k_1, 10^3 sec^{-1}	k_2, M^{-1} sec^{-1}
5.7 $Pd(Et_4dien)Br^+$	0.0060	1.50	5.9
4.8 $Pd(MeEt_4dien)Cl^+$	0.060	0.65	0.052
4.8 $Pd(MeEt_4dien)Cl^+$	0.300	0.62	0.0285
13.6 $Pd(Me_5dien)Cl^+$	0.060	240	12.6

[a] Ionic strength adjusted with $NaClO_4$.

aiding ion-pair formation. It has also been found that the five-coordinate complex $Ni(Et_4dien)Cl_2$ is a stable entity in organic solvents containing excess chloride ion,[15] indicating that the fitting of a fifth ligand around the sterically hindered palladium atom is possible. In addition, recent X-ray studies[16] have shown that $Co(Et_4dien)Cl_2$ is a five-coordinated complex.

Reactions of $Pd(Et_4dien)H_2O^{2+}$.—It was found without exception that anation reactions 6 are second order, first order in both substrate and nucleophile. The rate law is

$$-d[Pd(Et_4dien)H_2O^{2+}]/dt = k_2[Pd(Et_4dien)H_2O^{2+}][Y^{n-}] \quad (9)$$

The second-order rate constant $k_2 = k_{obsd}/[Y]$. These rate constants, together with the nucleophilic reactivity constants,[14] are listed in Table V.

From Table V, it is seen that good nucleophiles, such as thiourea and iodide ion, need not have large rate constants, nor does the doubly charged sulfate ion have a large rate constant. However, a combination of these two properties, exhibited in the thiosulfate ion, does give a large k_2. This behavior suggests a mechanism which involves ion pairing (where charge is important), but one which also depends on the nucleophilicity of the reagent. The ion-pair associative ligand interchange mechanism (SN2IP[17a] or I_a[17b]) fulfills these requirements and is given by the reactions

$$Pd(Et_4dien)H_2O^{2+} + Y^{n-} \overset{K_{IP}}{\rightleftharpoons} Pd(Et_4dien)H_2O^{2+},Y^{n-} \quad (10)$$

$$Pd(Et_4dien)H_2O^{2+},Y^{n-} \xrightarrow{k} Pd(Et_4dien)Y^{(2-n)+} + H_2O \quad (11)$$

TABLE V

SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF $Pd(Et_4dien)H_2O^{2+}$ WITH Y IN WATER AT 25°, IONIC STRENGTH 0.02, AND n_{Pt} VALUES OF Y

Y	n_{Pt}[a]	k_2, M^{-1} sec^{-1}	Y	n_{Pt}[a]	k_2, M^{-1} sec^{-1}
$S_2O_3^{2-}$	7.34	1780	Br^-	4.18	5.95
HSO_3^-	5.79[b]	505	I^-	5.42	4.46
SCN^-	5.65	75.1[c]	CH_3COO^-	2.0	2.18
NO_2^-	3.22	12.5	Thiourea	7.17	1.42
Cl^-	3.04	7.36	SO_4^{2-}	...	Nr[d]

[a] Reference 14. [b] Value of n_{Pt} listed is for SO_3^{2-}. [c] This is the sum of the k_2's for N- and S-bonded isomer formation; 85% (k_2 = 63.8) is attributed to N-bonded isomer formation; 15% (k_2 = 11.3) is attributed to the S-bonded isomer.[5] [d] No observable reaction.

Reaction 10, the rapid formation of the ion pair, is followed by reaction 11, the collapse of the ion pair to form the product. For this mechanism and reactions containing excess Y^-, one obtains

$$k_{obsd} = kK_{IP}[Y]/(1 + K_{IP}[Y]) \quad (12)$$

For reaction 6, $k_2 = kK_{IP}$.

If eq 12 is valid, a graph of k_{obsd} *vs.* [Y] should be purely second order for $K_{IP}[Y] << 1$, first order for $K_{IP}[Y] >> 1$, and curved for $K_{IP}[Y] \sim 1$. In all of the reactions studied, however, no deviation from second-order behavior was ever observed. Unfortunately, in most cases the complexes are unstable in a large excess of nucleophile, which precluded studies at high [Y]. Such was not the case with chloride and bromide ions, however, but even with 2 M Cl^- and 3 M Br^-, no deviation from second-order behavior is seen (Table III). This means that for Cl^- and Br^-, and perhaps for most of the 2+,1− ion pairs, $K_{IP} <$ 0.05.

Estimates of ion-pair formation constants can be made from the theoretical Fuoss equation.[18] At 25° for an assumed distance of closest approach of the ions in the ion pair of 5 Å, for ionic strength 0.02, K_{IP} = 33 for 2+,2− pairs and 3.2 for 2+,1− pairs. For ionic strengths of 2.0 and 3.0 (pertinent to the data of Table III), K_{IP} = 0.75 and 0.67, respectively, for 2+,1− pairs. There seems little doubt that in the latter case, K_{IP} is at least a factor of 10 below these estimates. That the K_{IP}'s for these systems are lower than those found for octahedral systems may in part result from a lack of hydrogen-bonding sites on the complex; hydrogen bonding has been shown to be an important factor in ion-pair formation.[19-21]

Ultraviolet spectral studies have been used quite successfully to observe ion pairing and to determine ion-pair formation constants.[22] Since rapid rates of reaction precluded measurements of ion-pair formation constants for $Pd(Et_4dien)H_2O^{2+}$ and even for the

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(15) Z. Dori and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 1394 (1966).

(16) Z. Dori, R. Eisenberg, and H. B. Gray, *Inorg. Chem.*, **6**, 483 (1967).

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analogous Pt(Et$_4$dien)H$_2$O^{2+}, the more inert Pt(Et$_4$dien)NH$_3$$^{2+}$ ion was used in a spectral study at a concentration of *ca.* 10^{-3} *M*. Unfortunately, 0.5 *M* NaI and 0.01 *M* Na$_2$S$_2$O$_3$ reacted slowly even with this complex; however, no significant *instantaneous* spectral shifts were seen at wavelengths where the reagents were transparent ($\lambda > 280$ mμ). At $\lambda > 235$ mμ, 0.5 *M* NaBr does not shift the spectrum, nor does 0.5 *M* Na$_2$SO$_4$ at $\lambda > 210$ mμ. Measurements below these wavelengths are difficult to make because of the significant anion absorbance. With 0.5 *M* NaCl, small increases in absorbance (*ca.* 5%) are seen in the range 215–230 mμ, indicating perhaps a small percentage of ion-pair formation.

It is also seen that for the halide ion rate constants in Table V, Cl > Br > I. This is the opposite of what is expected for the attack on a soft Lewis acid like Pd(II), yet it is the order expected for ion-pair formation constants. Steric reasons might also be important, however, as the bulky Et$_4$dien may hinder the attack of the larger bromide and iodide ions relative to chloride ion. Hewkin and Poë have found[23] that for reaction 13, the equilibrium constant $K_{eq} = 90$ when amine = dien, but $K_{eq} = 10$ when amine = Et$_4$dien. This destabilization of the iodo complex relative to the chloro complex in going from dien to Et$_4$dien was attributed to steric hindrance. Steric arguments have also been used to explain the fact that the five-coordinate complex Ni(Et$_4$dien)I$_2$ does not exist in organic solvents containing excess I$^-$; the complex Ni(Et$_4$dien)Cl$_2$, however, forms readily under the same conditions.[15]

$$\text{Pd(amine)Cl}^+ + \text{I}^- \overset{K_{eq}}{\rightleftharpoons} \text{Pd(amine)I}^+ + \text{Cl}^- \qquad (13)$$

It is true, of course, that the kinetics of these anation reactions given in Table V are described by rate law 9 without invoking ion pairing; yet the ion-pair concept seems necessary to explain the otherwise strange order of the rate constants.

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Complexes of Zinc(II) with Tris(2-aminoethyl)amine

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Complexes of the potentially tetradentate ligand tris(2-aminoethyl)amine (tren), of the types trenZn(ClO$_4$)$_2$, trenZnX$_2$, and tren(ZnX$_2$)$_2$ (where X = Cl, Br, I), have been characterized. On the basis of infrared data, conductivity and molecular weight measurements, and metathetical reactions with B(C$_6$H$_5$)$_4$$^-$, it is proposed that all of these complexes are derivatives of five-coordinate [Zn(tren)A]$^+$ cations where A may be either a halide or a monodentate perchlorato group. The additional ZnX$_2$ unit in the tren(ZnX$_2$)$_2$ complexes appears to be associated with the anionic portion of these complexes, presumably as either solvated or halo-bridged (ZnX$_3$$^-$)$_x$ species.

Introduction

The compound tris(2-aminoethyl)amine (tren) and its close relative tris(2-dimethylaminoethyl)amine (Me$_6$tren) have received considerable attention in recent years as ligands which produce five-coordinate, high-spin complexes with the divalent, 3d transition metal ions. Me$_6$tren complexes of this type have been reported for all of the transition metal ions from Cr(II) to Zn(II).[2] However, in the case of tren the structure of the complex is apparently more sensitive to the size and electronic configuration of the metal ion as well as the availability of other donor groups, and both five- and six-coordinate complexes have been identified.

The nickel(II)–tren derivatives are apparently *cis* octahedral both in solution and in the solid state, as indicated by spectral evidence[3] and X-ray studies,[4] whereas both five-[5] and six-coordinate[6] copper(II) complexes of this ligand have been characterized. A five-coordinate, trigonal-bipyramidal structure has recently been assigned to the Co(SCN)$_2$ and CoI$_2$ derivatives on the basis of spectral evidence and conductivity measurements.[7] In addition, indirect evidence for six-coordinate Mn(II) and Fe(II) and five-coordinate zinc(II) complexes of tren has been obtained from an analysis of the entropy change upon complex

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