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Optical Resolution and Circular Dichroism Spectra of Mixed-diamine Palladium(II) Complexes with Configurational Chirality

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Six square-planar complexes, $[PdL(\textit{meso}\text{-stien})](ClO_4)_2$ (*meso*-stien=*meso*-1,2-diphenyl-1,2-ethanediamine; L=*N*,*N*-diethylethylenediamine, *N*,*N*-dimethylethylenediamine, 2-methyl-1,2-propanediamine, N^2,N^2-dimethyl-2-methyl-1,2-propanediamine, *N*,*N*-dimethyl-1,3-propanediamine, and (2*S*)-N^1,N^1-diethyl-1,2-propanediamine), were prepared and optically resolved (or separated in the case of the last named ligand) using diacetyl-*d*-tartaric anhydride as the resolving agent. Their electronic absorption and CD spectra were measured. A definite additivity has been confirmed between the configurational CD caused by the chiral configuration and the vicinal CD due to the asymmetric carbon atom in the (2*S*)-N^1,N^1-diethyl-1,2-propanediamine complex. Absolute configurations of this and the other five complexes have been assigned by examining molecular models and the CD spectra.

Circular dichroism (CD) of a metal complex in the d-d transition region generally arises from two kinds of main chirality, *i.e.*, the configurational one of the whole complex, and the vicinal one due to the asymmetric atoms of the ligands, the latter including the so-called conformational chirality of the chelate rings, if any. Although many kinds of Pt(II) and Pd(II) complex show d-d CD spectra owing to the vicinal effect,[1] only a limited number of square-planar complexes have been found to have the configurational chirality. The well-known complexes [M(2-methyl-1,2-propanediamine) (*meso*-stien)]$^{2+}$ (M=Pt[2] and Pd[3]) are unique examples of a successful optical resolution of the configurationally chiral complexes with square-planar coordination geometry. These complexes have a particular kind of configurational chirality, which arises from a combination of two types of bidentate ligands, an h-type which has a symmetry plane coplanar to the coordination square but none perpendicular to it in the conformationally averaged state, and a v-type which has the latter kind of symmetry plane but not the former kind (Fig. 1).

This paper reports the preparation, optical resolution, CD spectra, and absolute-configuration assignment of a series of such complexes, [Pd(h-type diamine) (*meso*-stien)]$^{2+}$. The ligands are given in Table 1. The complex [Pd(N^1,N^1-Et$_2$-(*S*)-pn) (*meso*-stien)]$^{2+}$ containing both kinds of chirality due to the asymmetric carbon atom and to the configuration was also examined in order to establish a criterion for the assignment of absolute configuration.

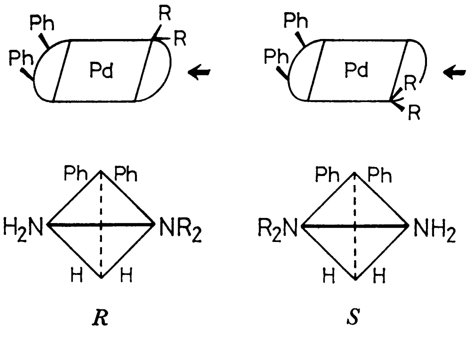


Fig. 1. Absolute configuration of the complex; the lower drawing shows the complex which is viewed along the arrow and regarded as a tetrahedron.

Table 1. Abbreviations and classification of the ligands

Abbreviation	Rational formula	Classification
N,*N*-Et$_2$en	$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!NCH_2CH_2NH_2$	h-type
N^1,N^1-Et$_2$-(*S*)-pn	$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>\!NCH_2\overset{CH_3}{\overset{\mid}{C}}HNH_2$	——
N,*N*-Me$_2$en	$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!NCH_2CH_2NH_2$	h-type
C,*C*-Me$_2$en[a]	$H_2NC(CH_3)_2CH_2NH_2$	h-type
N,*N*,*C*,*C*-Me$_4$en[b]	$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!NC(CH_3)_2CH_2NH_2$	h-type
N,*N*-Me$_2$tn	$\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!NCH_2CH_2CH_2NH_2$	h-type
meso-stien	$H_2N\overset{Ph}{\overset{\mid}{C}}H\ \overset{Ph}{\overset{\mid}{C}}HNH_2$	v-type
en	$H_2NCH_2CH_2NH_2$	——

a) 2-Methyl-1,2-propanediamine; the abbreviation is based on the name for a substituted ethylenediamine, specifying the atom to which the substituents attach. b) N^2,N^2-Dimethyl-2-methyl-1,2-propanediamine; abbreviation as in a).

Experimental

Ligands. *(1)* N,N,C,C-*Me$_4$en*: 2-Dimethylamino-2-methylpropanenitrile[4] (bp 54.3 °C/3.13 kPa; 56.6 g) in 130 cm^3 of anhydrous ether was added dropwise with stirring (at *ca.* −5 °C) to 25 g of lithium tetrahydridoaluminate suspended in 950 cm^3 of anhydrous ether. After the mixture had been stirred in an ice-bath for five hours, 28 cm^3 of water and 24 cm^3 of a 20% aqueous solution of potassium hydroxide were successively added with vigorous stirring. The ether layer was decanted from the slurry, from which the residue was extracted three times with 150 cm^3 portions of boiling ether. The combined mother liquor and extracts were treated with dry hydrogen chloride gas in an ice-bath. The white precipitate was mixed with a large excess of potassium hydroxide and a small amount of water, and the oil separated was extracted several times with boiling ether. The combined ether extracts were dried over potassium hydroxide pellets and then with sodium wire, and fractionally distilled. The fraction boiling at 61—62 °C/5.20 kPa was collected. Yield: 38.3 g.

(2) C,C-*Me$_2$en*: 2-Amino-2-methylpropanenitrile was obtained according to the method reported;[5] bp 61.5—62.0 °C/

3.60 kPa. The subsequent procedure was the same as described in *(1)*. bp 41.5 °C/2.87 kPa.

(3) Other Ligands: The following ligands were prepared by the methods reported: N^1,N^1-Et_2-(*S*)-pn[6] (bp 145—152 °C/100 kPa) and *meso*-stien[2,7] (Found: C, 79.25; H, 7.57; N, 13.19%).

Resolving Agent. Diacetyl-*d*-tartaric anhydride was obtained by the method of Chattaway and Parkes[8] (Found: C, 43.85; H, 3.88%).

[$PdCl_2L$]-type Complexes. *(1) L*=N,N-*Et_2en and* N^1,N^1-*Et_2-(*S*)-pn*: These complexes were prepared by a method similar to that of Suzuki and Nishida.[6] Found: C, 24.36; H, 5.52; N, 9.55%. Calcd for [$PdCl_2$(*N*,*N*-Et_2en)]=$C_6H_{16}N_2Cl_2Pd$: C, 24.55; H, 5.49; N, 9.54%. Found: C, 27.30; H, 5.92; N, 9.11%. Calcd for [$PdCl_2$(N^1,N^1-Et_2-(*S*)-pn)]=$C_7H_{18}N_2Cl_2Pd$: C, 27.34; H, 5.90; N, 9.11%.

(2) L=N,N-*Me_2en*, C,C-*Me_2en*, N,N,C,C-*Me_4en*, *and* N,N-*Me_2tn*: These complexes were obtained by a method similar to that for [$PdCl_2$(en)][9] as light orange to yellow crystals. Found: C, 18.01; H, 4.58; N, 10.56%. Calcd for [$PdCl_2$(*N*,*N*-Me_2en)]=$C_4H_{12}N_2Cl_2Pd$: C, 18.10; H, 4.56; N, 10.55%. Found: C, 18.09; H, 4.56; N, 10.65%. Calcd for [$PdCl_2$(*C*,*C*-Me_2en)]=$C_4H_{12}N_2Cl_2Pd$: C, 18.10; H, 4.56; N, 10.55%. Found: C, 23.06; H, 5.81; N, 8.97%. Calcd for [$PdCl_2$(*N*,*N*,*C*,*C*-Me_4en)]·H_2O=$C_6H_{18}N_2Cl_2OPd$: C, 23.13; H, 5.82; N, 8.99%. Found: C, 21.54; H, 5.07; N, 9.96%. Calcd for [$PdCl_2$(*N*,*N*-Me_2tn)]=$C_5H_{14}N_2Cl_2Pd$: C, 21.49; H, 5.05; N, 10.02%.

(3) L=meso-*stien*: When a methanol solution of *meso*-stien was mixed with an aqueous solution of $K_2[PdCl_4]$ at *ca.* 60 °C (molar ratio 2 : 1), an ivory-colored insoluble precipitate was obtained. After two hours of heating and stirring, hydrochloric acid (equimolar with the *meso*-stien) was added to the mixture. The precipitate which had turned pale yellow was collected and washed with boiling water several times in order to remove *meso*-stien·2HCl (only slightly soluble). Found: C, 43.09; H, 4.15; N, 7.18%. Calcd for [$PdCl_2$(*meso*-stien)]=$C_{14}H_{16}N_2Cl_2Pd$: C, 43.16; H, 4.14; N, 7.19%.

[$Pd(N)_4$]-type Complexes. *(1) [Pd(*N,N-*Et_2en)(*meso-*stien)]$(ClO_4)_2$*: A hot methanol-solution (3 cm^3) containing 0.76 g of *meso*-stien was added (at *ca.* 55 °C) to an aqueous solution (30 cm^3) of [$PdCl_2$(*N*,*N*-Et_2en)] (1.05 g). The almost colorless solution was filtered and treated with an aqueous solution of sodium perchlorate (1.2 g), at *ca.* 50 °C with stirring. The desired complex precipitated during the course of addition of perchlorate drop by drop. The mixture was allowed to stand at room temperature and then in a refrigerator overnight. Very pale yellow crystals were collected, washed with water, and dried *in vacuo*. Yield: 2.0 g. This product is sparingly soluble in water, being more soluble in methanol. Found: C, 37.82; H, 5.12; N, 8.92%. Calcd for $C_{20}H_{32}N_4Cl_2O_8Pd$: C, 37.90; H, 5.09; N, 8.84%.

(2) [Pd(N^1,N^1*-Et_2-(*S*)-pn)(*meso-*stien)]$(ClO_4)_2$*: This was prepared by the same method as described in *(1)*. The crude product was purified by conversion into the corresponding chloride with an anion-exchange resin (Dowex 1×8, 200—400 mesh, Cl^- form) and then by reconversion into the perchlorate crystals. The yield was good. The product, labeled **2′**, is a mixture of *R*(*S*) and *S*(*S*) isomer, neither a pseudo racemate nor an equilibrium mixture. Found: C, 38.96; H, 5.35; N, 8.71%. Calcd for $C_{21}H_{34}N_4Cl_2O_8Pd$: C, 38.93; H, 5.29; N, 8.65%.

*(3) [Pd(*N,N-*Me_2en)(*meso-*stien)]$(ClO_4)_2$·H_2O*: To a suspension of [$PdCl_2$(*N*,*N*-Me_2en)] (1.00 g) in 35 cm^3 of water was added (at *ca.* 60 °C) 0.80 g of *meso*-stien dissolved in hot methanol (4 cm^3). When the mixture was stirred for a few minutes, the starting material was dissolved, the solution turning almost colorless. An aqueous solution of sodium perchlorate (1.2 g) was added to the filtered solution, at *ca.* 55 °C with stirring. The resulting cloudy solution was allowed to stand at room temperature for three hours, a powder product (very pale yellow; 0.82 g) being collected. The residual glassy solid adhering to the bottom of the beaker was dissolved again in the mother liquor at 70—75 °C, and the solution was allowed to stand at room temperature and then in a refrigerator overnight; an additional amount of the product was obtained (0.36 g). After removal of the potassium chloride by methanol extraction, further crops (0.52 and 0.31 g) were obtained from the mother liquor. Total yield: 2.01 g. The complex is more soluble in water and in methanol than the corresponding *N*,*N*-Et_2en complex. Found: C, 34.76; H, 4.83; N, 8.89%. Calcd for $C_{18}H_{30}N_4Cl_2O_9Pd$: C, 34.66; H, 4.85; N, 8.98%.

*(4) [Pd(*C,C-*Me_2en)(*meso-*stien)]$(ClO_4)_2$*: This was prepared by a method similar to that described in *(3)*, but is more difficult to crystallize. The yield was 1.63 g for 1.00 g of the starting material [$PdCl_2$(*C*,*C*-Me_2en)]. The solubility (in water and in methanol) is comparable to that of the corresponding *N*,*N*-Me_2en complex. Found: C, 35.67; H, 4.72; N, 9.22%. Calcd for $C_{18}H_{28}N_4Cl_2O_8Pd$: C, 35.69; H, 4.66; N, 9.25%.

*(5) [Pd(*N,N,C,C-*Me_4en)(*meso-*stien)]$(ClO_4)_2$*: This was obtained in the same way as described in *(3)*, and is more difficult to crystallize than the corresponding *C*,*C*-Me_2en complex. It tended to disproportionate to [Pd(*N*,*N*,*C*,*C*-Me_4en)$_2$]$^{2+}$ and [Pd(*meso*-stien)$_2$]$^{2+}$ during the course of preparation. The yield was 1.63 g for 1.30 g of the starting material [$PdCl_2$(*N*,*N*,*C*,*C*-Me_4en)]. Found: C, 38.09; H, 5.11; N, 8.77%. Calcd for $C_{20}H_{32}N_4Cl_2O_8Pd$: C, 37.90; H, 5.09; N, 8.84%.

*(6) [Pd(*N,N-*Me_2tn)(*meso-*stien)]$(ClO_4)_2$·0.5H_2O*: A methanol solution (3 cm^3) containing 0.26 g of *N*,*N*-Me_2tn was added to 0.985 g of [$PdCl_2$(*meso*-stien)] suspended in a water (23 cm^3)–methanol (7 cm^3) mixture. After the reaction mixture had been stirred at *ca.* 50 °C for 1.5 h, undissolved material was filtered off. The filtrate was treated with an aqueous solution of sodium perchlorate (0.80 g), and evaporated under reduced pressure to give a sirup. The sodium chloride was removed by extracting the complex with methanol, *ca.* 25 cm^3 of water being added to the extract (*ca.* 15 cm^3). The warmed mixture was allowed to stand at room temperature. The desired product was obtained as pale yellow needles (1.00 g). Total yield was 1.18 g, including another crop from the mother liquor. Found: C, 36.17; H, 4.99; N, 8.83%. Calcd for $C_{19}H_{31}N_4Cl_2O_{8.5}Pd$: C, 36.29; H, 4.97; N, 8.91%.

The anhydrous salt, [Pd(*N*,*N*-Me_2tn)(*meso*-stien)]$(ClO_4)_2$ (pale yellow blocks), was also obtained by using [$PdCl_2$(*N*,*N*-Me_2tn)] as a starting material, the yield being low. Found: C, 36.91; H, 4.89; N, 8.96%. Calcd for $C_{19}H_{30}N_4Cl_2O_8Pd$: C, 36.82; H, 4.88; N, 9.04%.

(7) [Pd(N^1,N^1*-Et_2-(*S*)-pn)(en)]Cl_2·H_2O* (**7**): An aqueous solution containing 0.12 g of ethylenediamine was added at *ca.* 65 °C to 0.61 g of [$PdCl_2$(N^1,N^1-Et_2-(*S*)-pn)] suspended in 16 cm^3 of water. The reaction was fast. The almost colorless solution was filtered and evaporated under reduced pressure. The resulting sirup was dissolved in a small amount of ethanol and mixed with 15 cm^3 of acetone. The mixture was cooled in a refrigerator overnight to give very pale yellow needles. Yield: 0.60 g. The compound can be recrystallized from 95% ethanol by adding acetone, when necessary. Found: C, 28.02; H, 7.25; N, 14.63%. Calcd for $C_9H_{28}N_4Cl_2OPd$: C, 28.03; H, 7.32; N, 14.53%.

Optical Resolution and Separation. The diacetyl-*d*-tartrate salts of all the configurationally chiral complexes were obtained as a sirup as follows.

General Procedure: A suspension of racemic perchlorate salt[10] (1.80 mmol) in 50 cm^3 of water was stirred with an anion-exchange resin (Dowex 1×8, 200—400 mesh, Cl$^-$ form) for one hour. After removal of the resin the reaction mixture was treated with silver carbonate (2.0 mmol) at room temperature for two hours in the dark. The silver chloride was filtered off and diacetyl-*d*-tartaric anhydride (1.75 mmol) was dissolved in the filtrate. The solution was evaporated under reduced pressure to give a sirup.

The subsequent procedure for individual complexes is as follows.

*(1) $(+)^{\mathrm{CD}}_{220}$-$[\mathrm{Pd}(N,N\text{-}\mathrm{Et_2en})(meso\text{-}\mathrm{stien})](\mathrm{ClO_4})_2$ (**1**)*: The sirup obtained by the general procedure was dissolved in methanol (6 cm^3) and mixed with 20 cm^3 of acetone. Almost white powder was deposited on scratching the wall of the beaker. It was collected and recrystallized twice from 90% methanol by adding acetone. An additional amount of the product was obtained from the mother liquor and repeatedly recrystallized. A high yield (91% based on the half of the racemate) was attained in total because of the moderately fast shift of the equilibrium ($R \rightleftharpoons S$) in the mother liquor. Found: C, 48.84; H, 6.18; N, 8.13%. Calcd for $(+)^{\mathrm{CD}}_{220}$-$[\mathrm{Pd}(N,N\text{-}\mathrm{Et_2en})(meso\text{-}\mathrm{stien})](\text{diac-}d\text{-tart})\cdot\mathrm{H_2O}$[11]$=\mathrm{C_{28}H_{42}N_4O_9Pd}$: C, 49.09; H, 6.18; N, 8.18%. The less-soluble diastereomer (0.18 g) was dissolved in 7 cm^3 of water and treated with an aqueous solution (2 cm^3) of sodium perchlorate (0.09 g). Very pale yellow crystals were collected after several hours, washed with water, and dried *in vacuo*. Yield: 0.135 g. Found: C, 37.93; H, 5.10; N, 8.84%. Calcd for $\mathrm{C_{20}H_{32}N_4Cl_2O_8Pd}$: C, 37.90; H, 5.09; N, 8.84%.

*(2) $(+)^{\mathrm{CD}}_{220}$-$[\mathrm{Pd}(N^1,N^1\text{-}\mathrm{Et_2}\text{-}(S)\text{-}\mathrm{pn})(meso\text{-}\mathrm{stien})](\mathrm{ClO_4})_2$ (**2**)*: The sirup obtained by the general procedure was crystallized from a 90% ethanol–acetone (2 : 1) mixture, giving a crude less-soluble diastereomer (diac-*d*-tart salt), which was recrystallized three times from 90% ethanol by adding acetone. Found: C, 48.38; H, 6.29; N, 7.79%. Calcd for $(+)^{\mathrm{CD}}_{220}$-$[\mathrm{Pd}(N^1,N^1\text{-}\mathrm{Et_2}\text{-}(S)\text{-}\mathrm{pn})(meso\text{-}\mathrm{stien})](\text{diac-}d\text{-tart})\cdot 2\mathrm{H_2O}=\mathrm{C_{29}H_{46}N_4O_{10}Pd}$: C, 48.57; H, 6.47; N, 7.81%. The resolving agent was removed by the same method as described in *(1)*. Found: C, 38.92; H, 5.29; N, 8.65%. Calcd for $\mathrm{C_{21}H_{34}N_4Cl_2O_8Pd}$: C, 38.93; H, 5.29; N, 8.65%.

*(3) $(+)^{\mathrm{CD}}_{220}$-$[\mathrm{Pd}(N,N\text{-}\mathrm{Me_2en})(meso\text{-}\mathrm{stien})](\mathrm{ClO_4})_2\cdot 0.5\mathrm{H_2O}$ (**3**)*: A crude less-soluble diastereomer (diac-*d*-tart salt) was obtained from the corresponding sirup in the same manner as described in *(2)* and recrystallized twice from the same solvent as in *(1)*. Found: C, 47.66; H, 5.68; N, 8.48%. Calcd for $(+)^{\mathrm{CD}}_{220}$-$[\mathrm{Pd}(N,N\text{-}\mathrm{Me_2en})(meso\text{-}\mathrm{stien})](\text{diac-}d\text{-tart})\cdot\mathrm{H_2O}=\mathrm{C_{26}H_{38}N_4O_9Pd}$: C, 47.53; H, 5.83; N, 8.53%. The compound free from the resolving agent was obtained by the same method as in *(1)* but from a more concentrated solution. Found: C, 35.06; H, 4.63; N, 9.13%. Calcd for $\mathrm{C_{18}H_{29}N_4Cl_2O_{8.5}Pd}$: C, 35.17; H, 4.75; N, 9.11%.

*(4) $(-)^{\mathrm{CD}}_{220}$-$[\mathrm{Pd}(C,C\text{-}\mathrm{Me_2en})(meso\text{-}\mathrm{stien})](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$ (**4**)*: A less-soluble diastereomer (diac-*d*-tart salt) was obtained by the method of Lidstone and Mills[3] with a slight modification. At first almost racemic[12] diacetyl-*d*-tartrate salt was obtained from the corresponding sirup in 95% ethanol by scratching the wall of the beaker, and recrystallized several times from the minimum quantity of water by adding ethanol, giving the corresponding optically pure salt. Found: C, 45.79; H, 6.23; N, 7.91%. Calcd for $(-)^{\mathrm{CD}}_{220}$-$[\mathrm{Pd}(C,C\text{-}\mathrm{Me_2en})(meso\text{-}\mathrm{stien})](\text{diac-}d\text{-tart})\cdot 3\mathrm{H_2O}=\mathrm{C_{26}H_{42}N_4O_{11}Pd}$: C, 45.06; H, 6.11; N, 8.08%. The resolving agent was removed by the same method as in *(3)*. Found: C, 34.67; H, 4.82; N, 9.02%. Calcd for $\mathrm{C_{18}H_{30}N_4Cl_2O_9Pd}$: C, 34.66; H, 4.85; N, 8.98%.

*(5) $(+)^{\mathrm{CD}}_{220}$-$[\mathrm{Pd}(N,N,C,C\text{-}\mathrm{Me_4en})(meso\text{-}\mathrm{stien})](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$ (**5**)*: The sirup obtained by the general procedure was crystallized from a water–ethanol–acetone (1 : 3 : 14) mixture, giving a less-soluble diastereomer (diac-*d*-tart salt). Recrystallization was carried out four times from water by adding an ethanol–acetone (1 : 2) mixture. Found: C, 47.68; H, 6.48; N, 7.58%. Calcd for $(+)^{\mathrm{CD}}_{220}$-$[\mathrm{Pd}(N,N,C,C\text{-}\mathrm{Me_4en})(meso\text{-}\mathrm{stien})](\text{diac-}d\text{-tart})\cdot 3\mathrm{H_2O}=\mathrm{C_{28}H_{46}N_4O_{11}Pd}$: C, 46.64; H, 6.43; N, 7.77%. The product free from the resolving agent was obtained by the same method as in *(3)* but in water–methanol. Found: C, 37.06; H, 5.14; N, 8.59%. Calcd for $\mathrm{C_{20}H_{34}N_4Cl_2O_9Pd}$: C, 36.85; H, 5.26; N, 8.60%.

*(6) $(-)^{\mathrm{CD}}_{220}$-$[\mathrm{Pd}(N,N\text{-}\mathrm{Me_2tn})(meso\text{-}\mathrm{stien})]\mathrm{Cl_2}$ Solution (**6**)*: A crude less-soluble diastereomer (diac-*d*-tart salt) was obtained from the corresponding sirup in a 90% ethanol–acetone (4 : 5) mixture, and recrystallized four times from the same solvent as described in *(5)*. Found: C, 49.47; H, 5.86; N, 8.56%. Calcd for $(-)^{\mathrm{CD}}_{220}$-$[\mathrm{Pd}(N,N\text{-}\mathrm{Me_2tn})(meso\text{-}\mathrm{stien})](\text{diac-}d\text{-tart})=\mathrm{C_{27}H_{38}N_4O_8Pd}$: C, 49.66; H, 5.87; N, 8.58%. No corresponding optically active perchlorate salt was obtained by a method similar to that for **1**, **3**, or **5**; the diastereomer was converted into the corresponding optically active chloride with a column containing an anion-exchange resin (Dowex 1×8, 200—400 mesh, Cl$^-$ form). The CD spectrum of this complex was measured with the eluate, the concentration being calculated from the molar absorption coefficient of the corresponding racemic perchlorate.

Measurements. Electronic absorption spectra were recorded with a Hitachi 330 spectrophotometer and CD spectra with a JASCO MOE-1 spectropolarimeter. All the measurements were made in aqueous solutions at room temperature, except the electronic absorption spectrum of *meso*-stien measured in methanol and a water–methanol (9 : 1) mixture. A 10-cm cell was employed for the CD measurements in the long wavelength region. No spectral change was observed during the course of measurements.

Results and Discussion

Absolute Configuration. The enantiomeric configurations are denoted by *R* and *S* (Fig. 1) from analogy with the axial chirality[13] of organic compounds. The absorption spectrum of **2** is almost identical with that of **1** (Table 2 and Fig. 2). Both these optically pure complexes were derived from the less-soluble diastereomers. The CD spectra of both **1** and **2** contain a configurational contribution; in addition that of **2** contains the vicinal contribution due to the asymmetric carbon atom. Assuming the additivity of the configurational and vicinal contributions, a calculated vicinal CD curve can be obtained by subtracting the CD of **1** from that of **2**. The same configurational chirality of **1** and **2** was also assumed in the calculation, and justified by comparing the calculated vicinal CD with the CD spectrum of **7** containing the same asymmetric carbon atom as in **2** (Fig. 3); these two curves are of a similar pattern to each other, differing slightly in intensity.

The spectrum of **2′**[14] recorded immediately after dissolution can be reproduced by adding 0.25 part of the CD of **1** to the calculated vicinal CD of **2** (Fig. 4); this demonstrates the additivity of the configurational and vicinal CD. The CD spectrum of **2′** (*ca.* 10^{-3} mol dm^{-3}, in water) became constant in about five days at *ca.* 17 °C, indicating that the solution attained

TABLE 2. ABSORPTION DATA OF THE COMPLEXES

No.	Complex	Spin-forbidden d-d	Spin-allowed d-d	d-p or CT[a)]
		$\frac{\sigma_{\max}{}^{b)}}{10^3\ \mathrm{cm}^{-1}}$	$\left(\log\frac{\varepsilon}{\mathrm{mol}^{-1}\ \mathrm{dm}^3\ \mathrm{cm}^{-1}}\right)$	
1	$(+)^{\mathrm{CD}}_{220}$-[Pd(*N*,*N*-Et$_2$en)(*meso*-stien)]$^{2+}$	*ca.* 28.5sh (2.0)	34.2(2.79)	*ca.* 44.5sh
2	$(+)^{\mathrm{CD}}_{220}$-[Pd(N^1,N^1-Et$_2$-(*S*)-pn)(*meso*-stien)]$^{2+}$	*ca.* 28.5sh (2.0)	34.1(2.81)	*ca.* 44.5sh
3	$(+)^{\mathrm{CD}}_{220}$-[Pd(*N*,*N*-Me$_2$en)(*meso*-stien)]$^{2+}$	*ca.* 29sh (2.0)	34.5(2.75)	*ca.* 44.5sh
4	$(-)^{\mathrm{CD}}_{220}$-[Pd(*C*,*C*-Me$_2$en)(*meso*-stien)]$^{2+}$	*ca.* 29sh (1.5)	34.9(2.65)	*ca.* 44.5sh
5	$(+)^{\mathrm{CD}}_{220}$-[Pd(*N*,*N*,*C*,*C*-Me$_4$en)(*meso*-stien)]$^{2+}$	*ca.* 28.5sh (2.0)	34.3(2.77)	*ca.* 44.5sh
6	$(-)^{\mathrm{CD}}_{220}$-[Pd(*N*,*N*-Me$_2$tn)(*meso*-stien)]$^{2+}$	*ca.* 28sh (2.0)	33.5(2.82)	*ca.* 44.5sh
7	[Pd(N^1,N^1-Et$_2$-(*S*)-pn)(en)]$^{2+}$	*ca.* 28.5sh (1.8)	34.2(2.65)	49.9(4.26)

a) See text. b) sh: shoulder.

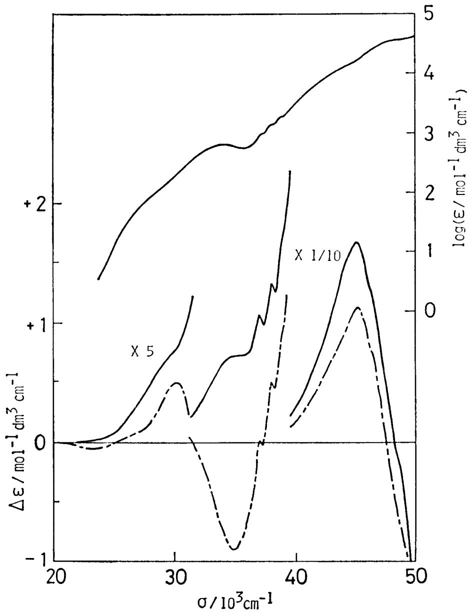


Fig. 2. Absorption and CD spectra of $(+)^{\mathrm{CD}}_{220}$-[Pd(*N*,*N*-Et$_2$en)(*meso*-stien)]$^{2+}$, **1** (——) and CD spectrum of $(+)^{\mathrm{CD}}_{220}$-[Pd(N^1,N^1-Et$_2$-(*S*)-pn)(*meso*-stien)]$^{2+}$, **2** (——).

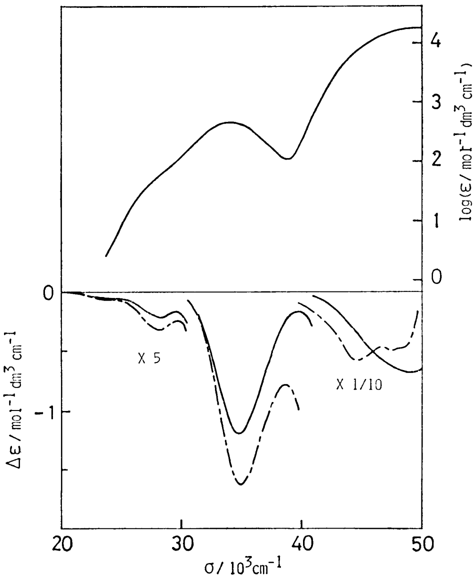


Fig. 3. Absorption and CD spectra of [Pd(N^1,N^1-Et$_2$-(*S*)-pn)(en)]$^{2+}$, **7** (——) and vicinal CD curve calculated from [Δε(**2**)−Δε(**1**)] (— — —).

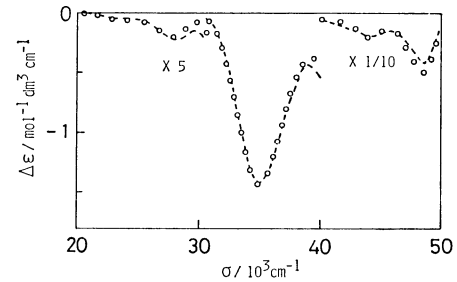
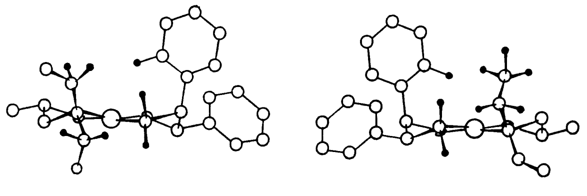


Fig. 4. CD spectrum of [Pd(N^1,N^1-Et$_2$-(*S*)-pn)(*meso*-stien)]$^{2+}$, **2′**, recorded immediately after dissolution (-----) and CD curve calculated from [0.25 Δε(**1**)+ calcd $\Delta\varepsilon_{\mathrm{vicinal}}$] (∘∘∘∘∘∘). The calcd $\Delta\varepsilon_{\mathrm{vicinal}}$ is given in Fig. 3.

equilibrium. However, the CD spectrum could not be accurately measured in the region of wavelengths shorter than 250 nm because of the low intensity. This can be expained by the cancellation between the vicinal and the increasing configurational CD contribution. The CD additivity, therefore, was examined with the solution of **2′** immediately after dissolution over the range 500—200 nm. The configuration of the predominant isomer both in solid **2′** and in the equilibrium mixture is found to be the same as the absolute configuration of **1** from a comparison of the configurational CD. The abundance of the diastereomers in **2′** was estimated on the basis of CD additivity as follows: *R*(*S*), 62.5 and *S*(*S*), 37.5%[15] immediately after dissolution; *R*(*S*), 67.5 and *S*(*S*), 32.5% at equilibrium. The abundance at equilibrium was evaluated from $\Delta\varepsilon_{\mathrm{ext}}$ at about 35000 cm^{-1}.

The absolute configuration predominating in aqueous solutions can be assigned by considering the steric



R(*S*) *S*(*S*)

Fig. 5. A pair of diastereomers of [Pd(N^1,N^1-Et$_2$-(*S*)-pn)-(*meso*-stien)]$^{2+}$. Hydrogen atoms which are less concerned with the steric repulsions are omitted; one of two possible conformations of *meso*-stien is shown.

repulsions between the phenyl groups on *meso*-stien and one of the ethyl groups on N^1,N^1-Et$_2$-(*S*)-pn (Fig. 5). The ligand N^1,N^1-Et$_2$-(*S*)-pn is likely to be in almost pure δ-form, because of the repulsion between the *C*(*S*)-methyl and one of the two *N*-ethyl groups. As a result, the orientations of the two *N*-ethyl groups might be restricted. The steric interactions between the *N*-ethyl and the two phenyl groups should differ between the *R*(*S*) and the *S*(*S*) isomer. Thus, the repulsive interaction in *R* configuration is concluded to be smaller than that in *S*, and the predominant configuration in solid **2′** and in the equilibrium mixture can be assigned to *R*; consequently complex **1** has *R* configuration.

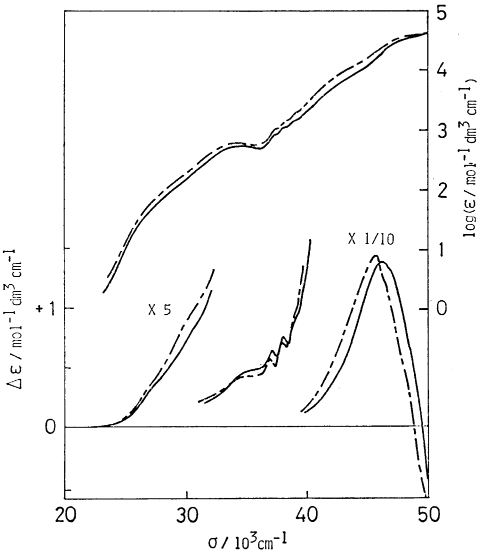


Fig. 6. Absorption and CD spectra of $(+)^{\rm CD}_{220}$-[Pd(*N*,*N*-Me$_2$en)(*meso*-stien)]$^{2+}$, **3** (——) and $(+)^{\rm CD}_{220}$-[Pd(*N*,*N*,*C*,*C*-Me$_4$en)(*meso*-stien)]$^{2+}$, **5** (——).

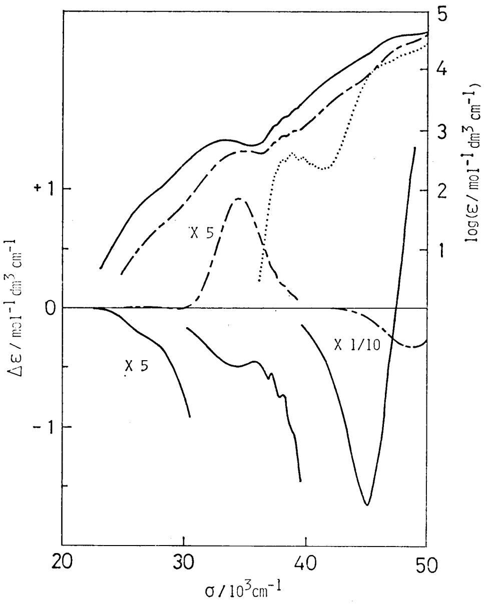


Fig. 7. Absorption and CD spectra of $(-)^{\rm CD}_{220}$-[Pd(*C*,*C*-Me$_2$en)(*meso*-stien)]$^{2+}$, **4** (– – –) and $(-)^{\rm CD}_{220}$-[Pd(*N*,*N*-Me$_2$tn)(*meso*-stien)]$^{2+}$, **6** (——); absorption spectrum of *meso*-stien in methanol (······).

The absolute configuration of **3** is easily assigned to *R* by comparing its CD curve with that of **1**; both CD patterns are very similar to each other throughout the range 500—200 nm, though the CD intensity is somewhat different (Figs. 2 and 6). However, the absolute configuration of **4** cannot be easily determined. The sign of the major CD band in the region of spin-allowed d-d transitions is the same as that for **1** or **3**, whereas the sign of the band at *ca.* 49000 cm^{-1} is opposite (Figs. 2, 6, and 7). In order to solve this problem complex **5** was prepared. The ligand *N*,*N*,*C*,*C*-Me$_4$en has four methyl substituents: two on a nitrogen, the other two on the carbon adjacent to the nitrogen atom (Table 1). From the fact complex **4** displays remarkably weak CD in comparison with **3**, the CD pattern of **5** is expected to be similar to that of **3**. Figure 6 shows the *R* configuration of **5**, indicating the validity of the expectation. The small deviation (from the CD curve of **3**) associated with the introduction of the *C*-methyl groups is considered to have a pattern similar to that of the CD spectrum of *R*-[Pd(*C*,*C*-Me$_2$en) (*meso*-stien)]$^{2+}$. Upon comparing the CD curves of **3** and **5**, the difference between their ligand-field-strengths should be taken into account. Quantitative estimation of the difference is not only difficult but also unnecessary. It is approximated by the energy difference in the d-d absorption maxima. In practice, the CD curve of **3** (27000—37000 cm^{-1}) is displaced to the side of lower energies by the difference (240 cm^{-1}) and then compared with the intact CD curve of **5** (Fig. 8). The positive (*ca.* 30000 cm^{-1}) and the negative (*ca.* 35000 cm^{-1}) deviation of the CD curve of **5** from that of **3** are visualized; the sign pattern is opposite that of the CD spectrum of **4** in the region. It is concluded that complex **4** has *S* configuration.

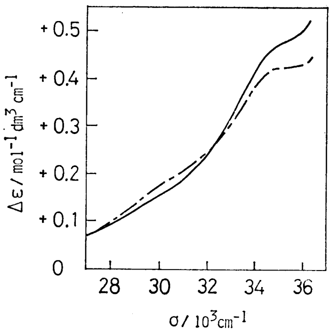


Fig. 8. CD curve of **3**, shifted by 240 cm^{-1} to the side of lower energies (——) and intact CD curve of **5** (——).

Complex **6** was similarly derived from the corresponding less-soluble diastereomer using the same resolving agent as used for **1**—**5**. The entire CD pattern, however, is enantiomeric to those of **1**, **3**, and **5**. No marked change is found in the CD pattern with increase in chelate-ring size (Figs. 6 and 7); we conclude that complex **6** has *S* configuration. The absolute configuration of the above six complexes are given in Table 3. The results can be summarized as follows: Positive sign of the first CD band in the region of wave numbers larger than 40000 cm^{-1} indicates *R* configuration.

TABLE 3. CD DATA OF THE COMPLEXES

No.	Complex	Spin-forbidden d-d	Spin-allowed d-d	d-p or CT[a]
		$\sigma_{\rm ext}$[b] / 10^3 cm^{-1} ($\Delta\varepsilon$ / mol^{-1} dm^3 cm^{-1})		
1	$R(+)^{\rm CD}_{220}$-[Pd(*N*,*N*-Et$_2$en)(*meso*-stien)]$^{2+}$		*ca.* 30sh (*ca.*+0.15) *ca.* 35sh (+0.73)	45.2 (+16.8)
2	$R(+)^{\rm CD}_{220}$-[Pd(N^1,N^1-Et$_2$-(*S*)-pn)(*meso*-stien)]$^{2+}$	23.3 (−0.010) *ca.* 26.5sh (*ca.*+0.014)	30.2 (+0.10) 35.0 (−0.90)	45.2 (+11.3)
2′[c]	$(-)^{\rm CD}_{220}$-[Pd(N^1,N^1-Et$_2$-(*S*)-pn)(*meso*-stien)]$^{2+}$	24sh (−0.011) 28.0 (−0.046)	35.0 (−1.42)	44.5 (−2.0) 48.5 (−4.2)
3	$R(+)^{\rm CD}_{220}$-[Pd(*N*,*N*-Me$_2$en)(*meso*-stien)]$^{2+}$	*ca.* 27.5sh (+)	*ca.* 30.5sh (*ca.*+0.16) *ca.* 35.5sh (+0.48)	46.2 (+13.9)
4	$S(-)^{\rm CD}_{220}$-[Pd(*C*,*C*-Me$_2$en)(*meso*-stien)]$^{2+}$	26.7 (+0.002)	29.4 (−0.001) 34.6 (+0.18)	49.0 (−3.2)
5	$R(+)^{\rm CD}_{220}$-[Pd(*N*,*N*,*C*,*C*-Me$_4$en)(*meso*-stien)]$^{2+}$	*ca.* 27.5sh (+)	*ca.* 30.5sh (*ca.*+0.18) *ca.* 35.5sh (+0.43)	45.7 (+14.2)
6	$S(-)^{\rm CD}_{220}$-[Pd(*N*,*N*-Me$_2$tn)(*meso*-stien)]$^{2+}$	*ca.* 27sh (−)	34.4 (−0.49)	45.3 (−16.6)
7	[Pd(N^1,N^1-Et$_2$-(*S*)-pn)(en)]$^{2+}$	*ca.* 24.5sh (−0.010) 28.2 (−0.042)	34.8 (−1.19)	49.0 (−6.8)

a) See text. b) sh: shoulder. c) Recorded immediately after dissolution.

CD and Absorption Spectra. Absorption and CD data of the complexes are given in Tables 2 and 3, respectively, those concerning π-π^* intraligand transitions in Table 4. The complexes generally exhibit four configurational-CD bands (27000, 30000, 35000, and beyond 45000 cm^{-1}) within the range 20000—50000 cm^{-1}. The CD pattern of the complexes with *N*-alkyl substituents, however, is different from that for the *C*-alkyl analog. In the former complexes all of the four bands have the same sign (*i.e.*, plus for *R* isomer), whereas in the latter the sign pattern is −, +, −, and + (from the side of smaller wave numbers) for *R* isomer. For all of these complexes, the first band is assigned to a spin-forbidden d-d transition and the second and third to spin-allowed d-d transitions. The last band should be assigned to either d-p transition or nitrogen-σ-to-metal-d charge-transfer transition.

In the present series of complexes, h-type ligands were varied with the v-type ligand unchanged; the relative intensity of configurational CD varied in the following order: *N*,*N*-Et$_2$en>*N*,*N*-Me$_2$tn>*N*,*N*-Me$_2$en >*C*,*C*-Me$_2$en. This result indicates three factors determining the intensity, the size of alkyl substituent, the location of alkyl substituent and the size of chelate ring: (1) The CD intensity increases with increasing bulkiness of substituents. (2) Alkyl groups on the nitrogen atom cause CD intensity higher than those on the carbon atom. (3) The increase in chelate-ring size from five to six is accompanied by an increase in the CD intensity. The finding (1) can be explained in terms

TABLE 4. ABSORPTION AND CD DATA OF π-π^* INTRALIGAND TRANSITIONS

No.	Complex	α-bands			*p*-bands	
		Absorption		CD	Absorption	CD
		$\sigma_{\rm sh}$[a] / 10^3cm^{-1}	$\sigma_{\rm ext}$[a] / 10^3cm^{-1}	($\Delta\varepsilon$ / mol^{-1} dm^3 cm^{-1})	$\sigma_{\rm sh}$[a] / 10^3cm^{-1}	$\sigma_{\rm sh}$[a] / 10^3cm^{-1}
1	$R(+)^{\rm CD}_{220}$-[Pd(*N*,*N*-Et$_2$en)(*meso*-stien)]$^{2+}$	*ca.* 37.4sh *ca.* 38.2sh *ca.* 39.0sh		37.1 (+1.07) 38.1 (+1.33) *ca.* 39sh (*ca.*+1.8)	*ca.* 47.3sh *ca.* 48.2sh	*ca.* 46.3sh *ca.* 48.5sh
2	$R(+)^{\rm CD}_{220}$-[Pd(N^1,N^1-Et$_2$-(*S*)-pn)(*meso*-stien)]$^{2+}$	*ca.* 37.4sh *ca.* 38.2sh *ca.* 39.0sh		37.1 (+0.01) 38.1 (+0.49) *ca.* 39sh (*ca.*+0.9)	*ca.* 47.3sh *ca.* 48.2sh	*ca.* 46.3sh *ca.* 48.5sh
3	$R(+)^{\rm CD}_{220}$-[Pd(*N*,*N*-Me$_2$en)(*meso*-stien)]$^{2+}$	*ca.* 37.4sh *ca.* 38.2sh *ca.* 39.0sh		37.1 (+0.65) 38.0 (+0.76) *ca.* 39sh (*ca.*+0.92)	*ca.* 47.4sh *ca.* 48.3sh	*ca.* 46.5sh *ca.* 48.5sh
4	$S(-)^{\rm CD}_{220}$-[Pd(*C*,*C*-Me$_2$en)(*meso*-stien)]$^{2+}$	*ca.* 37.4sh *ca.* 40.0sh	38.2(2.90)[b] 39.0(2.98)[b]	*ca.* 37sh (+) *ca.* 38sh (+)	*ca.* 47.4sh *ca.* 48.3sh	
5	$R(+)^{\rm CD}_{220}$-[Pd(*N*,*N*,*C*,*C*-Me$_4$en)(*meso*-stien)]$^{2+}$	*ca.* 37.4sh *ca.* 38.2sh *ca.* 39.0sh		36.9 (+0.56) 37.9 (+0.69) *ca.* 39sh (*ca.*+1.0)	*ca.* 47.3sh *ca.* 48.2sh	*ca.* 46.3sh *ca.* 48.3sh
6	$S(-)^{\rm CD}_{220}$-[Pd(*N*,*N*-Me$_2$tn)(*meso*-stien)]$^{2+}$	*ca.* 37.4sh *ca.* 38.2sh *ca.* 39.0sh		37.0 (−0.59) 37.9 (−0.75) *ca.* 39sh (*ca.*−1.0)	*ca.* 47.3sh *ca.* 48.1sh	*ca.* 46.1sh *ca.* 47.3sh

a) sh: shoulder. b) log ($\varepsilon_{\rm max}$/mol^{-1} dm^3 cm^{-1}).

of the symmetry of complex cations. Although the present complexes have a square-planar coordination geometry around the central metal ion, the distribution of the peripheral substituents can be regarded as a tetrahedron: $\mathrm{Pd}(\overline{\mathrm{Ph}_2)(\mathrm{H}_2})(\overline{\mathrm{NR}_2)(\mathrm{NH}_2})$ (Fig. 1). Thus the configurational-CD intensity increases with the bulkiness of R. Care should be taken for simultaneous operations of the factors producing mutually opposite CD signs. For example, complex **5** has a larger degree of the pseudo-tetrahedral chirality than **3**, but it exhibits a smaller CD intensity than the latter in *ca.* 34000—38500 cm^{-1}. This can be attributed to the *C*-methyl and *N*-methyl groups contributing to opposite CD signs in the region.

The CD intensity in the region of π-π^* intraligand transitions seems to depend upon another factor. The CD intensity of *C*-alkyl-substituted complex **4** considerably differs from those of the *N*-alkyl analogs **1**, **3**, and **6**. The former complex shows only very weak CD bands (shoulders) in the 36000—40000 cm^{-1} region, whereas the latter complexes show rather strong bands (Figs. 2, 6, and 7; Table 4). These bands have been assigned to α-bands[16] relating to the π-π^* transitions. The *N*-alkyl-substituted complexes give additional CD bands assigned to *p*-bands[16] in the 45000—49000 cm^{-1} region as very weak shoulders. In these complexes, the two phenyl groups are expected to interact with the *N*-alkyl group in a different way. It seems that the disposition of the two phenyl groups acquires a chirality, giving a strong CD in the region of the π-π^* intraligand transitions. For the *C*-methyl-substituted complex, however, no such a chirality around the two phenyl groups is expected since the *C*-methyl groups are remote from both phenyl groups; therefore complex **4** should exhibit only weak π-π^* CD as actually observed.

The vicinal CD due to the asymmetric carbon atom comprises four bands, as well as the configurational CD, in the range 20000—50000 cm^{-1}, but the band assignments in the two cases slightly differ. The weak CD bands at *ca.* 24500 and 28200 cm^{-1} and the strong band at 34800 cm^{-1} of complex **7** can be assigned to the spin-forbidden and -allowed d-d transitions, respectively, by comparing their positions with those of the corresponding absorption bands. Another CD band at 49000 cm^{-1}, which corresponds to the absorption peak at 49900 cm^{-1}, should be assigned to either d-p transition or nitrogen-σ-to-metal-d charge-transfer transition. The intensity of this CD band is significantly smaller than that of the corresponding bands in the configurational CD. This is fortunate in the assignment of absolute configuration for the complexes with asymmetric carbon atoms, such as **2**.

The absorption spectra apparently consist of three bands except those due to the π-π^* intraligand transitions. A shoulder at 28000—29000 cm^{-1} and a peak at 33500—35000 cm^{-1} can be assigned to the spin-forbidden and -allowed d-d transitions, respectively (Table 2). A bulge at *ca.* 45000 cm^{-1} is considered to be an apparent shoulder produced by the overlap of the *p*-bands with the band which has the same origin as the 49900 cm^{-1} band of **7**. In the absorption spectra of the present series of complexes the α-bands shift only slightly to lower energies and the *p*-bands by about 2000 cm^{-1} to higher energies than the absorption bands of *meso*-stien in a methanol solution[17] (Fig. 7). The bands in a water–methanol (9 : 1) mixture appear at almost the same places as in methanol. It is thus concluded that the shifts are caused by coordination and not by a solvent effect.

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10) Diastereomeric mixture **2′** was used in the case of N^1,N^1-Et_2-(*S*)-pn complex.

11) diac-*d*-tart=diacetyl-*d*-tartrate=$\mathrm{C_8H_8O_8}^{2-}$.

12) With respect to the complex cation.

13) *J. Org. Chem.*, **35**, 2849 (1970).

14) See Experimental.

15) The *R*(*S*) isomer content increases with the increasing yield in the preparation of **2′**. This suggests that solid **2′** is a mixture of *R*-[Pd(N^1,N^1-Et_2-(*S*)-pn)(*meso*-stien)]$(\mathrm{ClO_4})_2$ and pseudo racemic [Pd(N^1,N^1-Et_2-(*S*)-pn)(*meso*-stien)]$(\mathrm{ClO_4})_2$.

16) E. Clar, "Aromatische Kohlenwasserstoffe," 2 Aufl., Springer (1952), p. 25.

17) The *meso*-stien ligand is only slightly soluble in water.