*Bull. Chem. Soc. Jpn.*, *57*, *1240—1254 (1984)*

# Synthesis and Isomerism of Mixed (Amine)(carboxylato) Complexes with the $[Pd(N)_n(O)_{4-n}]$-type ($n$=1—4) and Their Circular Dichroism Spectra

Kazuhiko Nakayama,* Takashi Komorita, and Yoichi Shimura
*Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560*
(Received December 8, 1983)

A large number of mixed-ligand $[Pd(N)_n(O)_{4-n}]$-type complexes ($n$=1—4) which contain at least one optically active ligand were synthesized and isolated in a systematic manner. ($S$)-Propylenediamine, ($2S$)-$N^1$,$N^1$-diethyl-1,2-propanediamine, and ($S$)-amino carboxylates were employed as one ligand, which is optically active; ammonia, diamines, amino carboxylates, acetates, and dicarboxylates as the other ligand occupying the remaining coordination sites. Isomerism could be detected in the mixed complexes of an unsymmetrical diamine and an amino carboxylate and has been discussed on the basis of $^{13}$C NMR and CD spectra. Moreover, the influence of optically inactive ligands on the vicinal CD spectra has been examined, and also the additivity of vicinal CD contributions of two different optically active ligands has been demonstrated.

The electronic structure of d$^8$ square-planar complexes has been studied most extensively on $[MCl_4]^{2-}$ (M=Pt and Pd)[1] which are easy to deal with theoretically and experimentally. In a separate paper,[2] we reported on the electronic structures of *cis*- and *trans*-$[Pd(Cl)_2(N)_2]$-type complexes. An extension of the work to complexes containing nitrogen and oxygen atoms which are most popular as coordinating atoms is desirable to understand systematically the electronic structure of square-planar palladium(II) complexes. Although it is desired to use as simple ligands as possible in order to study the d-d absorption spectra, there have been known few examples of the isolation of mixed-ligand palladium(II) complexes comprising of such $N$- and/or $O$-ligands. This seems to be ascribed to the lability of palladium(II) complexes and to retarded development of systematized synthetic routes. Unavailability of ion exchange column chromatography, which serves as a very powerful tool for separating some chemical species in the case of cobalt(III), chromium(III), rhodium(III) complexes *etc.*, is also responsible for the situation.

In 1932, Drew *et al.*[3] isolated $[Pd(en)(NH_3)_2]Cl_2$, $[Pd(en)(py)_2]Cl_2$, and $[Pd(NH_3)_2(py)_2]Cl_2$ and observed that the former two complexes were obtained only by the action of ammonia or pyridine(py) on $[PdCl_2(en)]$, the action of ethylenediamine(en) on $[PdCl_2(NH_3)_2]$ or $[PdCl_2(py)_2]$ causing disproportionation to give $[Pd(NH_3)_4]Cl_2$ or $[Pd(py)_4]Cl_2$ as well as $[Pd(en)_2]Cl_2$, respectively. According to these investigations $[Pd(NH_3)_2(py)_2]Cl_2$ can be obtained either from $[PdCl_2(NH_3)_2]$ or from $[PdCl_2(py)_2]$, where excess pyridine is necessary in the case of the former starting material but in the latter case the calculated quantity of ammonia must be used because excess ammonia replaces the coordinated pyridine molecules. These observations suggest that the order of introduction of ligands is important in the synthesis of mixed-ligand palladium(II) complexes.

Although the kinetics of the mixed-ligand palladium(II) complexes of ethylenediamine and a variety of amino carboxylates has been systematically investigated by Lim,[4] no isolation and spectroscopic studies of the complexes have been undertaken at all. The examples of the isolation of $[Pd(N)_2(O)_2]$-type complexes with simple ligands are limited to $[Pd(ox)(NH_3)_2]$[5] and $[Pd(CH_3CO_2)_2L_2]$ (L=py, $NH(C_2H_5)_2$, $N(C_2H_5)_3$, and $(bipyridine)_{1/2}$)[6] except bis(amino carboxylato) complexes.[7,8] None of these complexes, however, are suited for investigation of d-d spectra because of low solubility, isomerization reaction, and/or the presence of the low energy intraligand transitions. As to the mixed-ligand palladium(II) complexes of an amino carboxylate and a (di)carboxylate, no reports could be found even on the preparation.

This paper deals with the synthesis and isolation of mixed-ligand $[Pd(N)_n(O)_{4-n}]$-type complexes ($n$=1—4) containing (di)amine(s) as an $N$-ligand, (di)carboxylate(s) as an $O$-ligand, and an amino carboxylate as an $N$,$O$-ligand. Then, the mixed-ligand complexes comprising of ($S$)-propylenediamine or ($2S$)-$N^1$,$N^1$-diethyl-1,2-propanediamine and an unsymmetrical bidentate ligand such as an amino carboxylate should exhibit isomerism; this could be actually detected in the amino carboxylato complexes, and has been discussed on the basis of $^{13}$C NMR and CD spectra. Moreover, we have examined the additivity of vicinal CD contributions of two optically active ligands and the influence of optically inactive ligands on the vicinal CD spectra. The following abbreviations are used for ligands in the present paper: $S$-pn, ($S$)-propylenediamine $NH_2CH_2CH(CH_3)NH_2$; tn, trimethylenediamine $NH_2CH_2CH_2CH_2NH_2$; $N^1$,$N^1$-Et$_2$-($S$)-pn, ($2S$)-$N^1$,$N^1$-diethyl-1,2-propanediamine $NH_2CH(CH_3)CH_2N(C_2H_5)_2$; $N$,$N$-Me$_2$en, $N$,$N$-dimethylethylenediamine $NH_2CH_2CH_2N(CH_3)_2$; $N$,$N$-Et$_2$en, $N$,$N$-diethylethylenediamine $NH_2CH_2CH_2N(C_2H_5)_2$; Hgly, glycine $NH_2CH_2CO_2H$; β-Hala, β-alanine $NH_2CH_2CH_2CO_2H$; $S$-Hala, ($S$)-alanine $NH_2CH(CH_3)CO_2H$; $S$-Hpro, ($S$)-proline $\overline{NHCH_2CH_2CH_2C}HCO_2H$; $S$-Hser, ($S$)-serine $NH_2CH(CH_2OH)CO_2H$; $S$-Hleu, ($S$)-leucine $NH_2CH\{CH_2CH(CH_3)_2\}CO_2H$; $S$-Hhpro, ($S$)-hydroxyproline $\overline{NHCH_2CH(OH)CH_2C}HCO_2H$; H($N$,$N$-Me$_2$gly), $N$,$N$-dimethylglycine $N(CH_3)_2CH_2CO_2H$; H$_2$ox, oxalic acid $HO_2CCO_2H$; H$_2$mal, malonic acid $HO_2CCH_2CO_2H$; Ham,amino carboxylic acid.

## Experimental

*[Pd(N)$_4$]-type Complexes.* *1) [Pd(S-pn)(NH$_3$)$_2$]Cl$_2$*: Concentrated aqueous ammonia (*ca.* 26.5%, 120 mg) was added to a suspension of 400 mg of [PdCl$_2$(*S*-pn)][2] in 15 cm$^3$ of water, with stirring at room temperature. The resulting clear solution was evaporated to 1—2 cm$^3$ under reduced pressure and then diluted with 5 cm$^3$ of methanol. After removal of a small amount of [PdCl$_2$(*S*-pn)] reproduced, the solution was mixed with one drop of concentrated aqueous ammonia and 3 cm$^3$ of ether, and allowed to stand at room temperature. White crystals were collected, washed with a mixture of methanol—ether, and dried in air. Yield: 310 mg. Found: C, 12.57; H, 5.65; N, 19.42%. Calcd for $C_3H_{16}N_4Cl_2Pd$: C, 12.62; H, 5.65; N, 19.62%.

*2) [Pd(S-pn)(en)]Cl$_2$*: An aqueous solution containing 73 mg of ethylenediamine was mixed with 300 mg of [PdCl$_2$(*S*-pn)] suspended in 10 cm$^3$ of water and the mixture was stirred at 40 °C. The resulting solution was filtered and concentrated to a small volume under reduced pressure. Addition of ethanol to the concentrate warmed gave white precipitate, which was collected, washed with a mixture of water–ethanol, and dried *in vacuo*. Yield: 290 mg. Found: C, 18.67; H, 5.92; N, 17.34%. Calcd for [Pd(*S*-pn)(en)]Cl$_2$·0.5H$_2$O=$C_5H_{19}N_4Cl_2O_{0.5}Pd$: C, 18.73; H, 5.97; N, 17.48%.

*3) [Pd(S-pn)$_2$]Cl$_2$*: This complex was obtained from [PdCl$_2$-(*S*-pn)] by the same method as in *2)*, in a 72% yield. The content of water of crystallization is different from that reported for [Pd(*R*-pn)$_2$]Cl$_2$.[9] Found: C, 21.68; H, 6.20; N, 16.81%. Calcd for [Pd(*S*-pn)$_2$]Cl$_2$·0.5H$_2$O=$C_6H_{21}N_4Cl_2O_{0.5}Pd$: C, 21.54; H, 6.33; N, 16.75%.

*4) [Pd(S-pn)(tn)]Cl$_2$*: An aqueous solution containing this complex was prepared in the same way as in *2)*. The solution was evaporated under reduced pressure to give a sirup, which was dissolved in ethanol. After filtration the ethanol solution was mixed with ether and allowed to stand in a refrigerator. The desired product was obtained as white crystals in an 82% yield. Found: C, 21.04; H, 6.37; N, 16.35%. Calcd for [Pd(*S*-pn)(tn)]Cl$_2$·H$_2$O=$C_6H_{22}N_4Cl_2OPd$: C, 20.97; H, 6.45; N, 16.31%.

*5) [Pd(N$^1$,N$^1$-Et$_2$-(S)-pn)(NH$_3$)$_2$]Cl$_2$*: A suspension of 610 mg of [PdCl$_2$(*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)][10] in 10 cm$^3$ of water was mixed with concentrated aqueous ammonia (*ca.* 26.5%, 300 mg) and the mixture was stirred at 40 °C. An evaporation of the resulting pale yellow solution gave a sirup, which was dissolved in a mixture of ethanol–ether and stored in a freezer for 4 d. Yellow blocks deposited were mechanically separated from a small amount of white powder and identified as [PdCl(NH$_3$)(*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)]Cl by the absorption spectrum and elemental analysis (yield: 370 mg). Found: C, 25.99; H, 6.48; N, 12.97%. Calcd for [PdCl(NH$_3$)(*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)]-Cl=$C_7H_{21}N_3Cl_2Pd$: C, 25.90; H, 6.52; N, 12.95%. Its electronic absorption(AB) and CD data in a 0.10 M KCl aqueous solution (1 M=1 mol dm$^{-3}$) were as follows in $\sigma_{max}/10^3$ cm$^{-1}$ ($\varepsilon$/mol$^{-1}$ dm$^3$ cm$^{-1}$) and $\sigma_{ext}/10^3$ cm$^{-1}$ ($\Delta\varepsilon$/mol$^{-1}$ dm$^3$ cm$^{-1}$), respectively; AB: 29.3 (346), 47.8 (17000) and CD: 23.6 (−0.027), 27.9 (+0.12), 32.0 (−0.73).

The monochloro complex (220 mg) was dissolved in a minimum quantity of warm water and diluted with 3 cm$^3$ of ethanol containing one drop of concentrated aqueous ammonia. The resulting almost colorless solution was mixed with ether to give faint yellow needles, which were washed with a mixture of 95%-ethanol-ether and dried in air. Yield: 140 mg. Found: C, 23.46; H, 7.33; N, 15.38%. Calcd for [Pd(*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)(NH$_3$)$_2$]Cl$_2$·H$_2$O=$C_7H_{26}N_4Cl_2OPd$: C, 23.38; H, 7.29; N, 15.58%. This complex is liable to decompose even in the crystalline state.

*6) [Pd(N$^1$,N$^1$-Et$_2$-(S)-pn)(tn)]Cl$_2$*: An aqueous solution of 130 mg of *N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn was added to 250 mg of [PdCl$_2$(tn)] suspended in 13 cm$^3$ of water, with stirring at *ca.* 55 °C. The resulting solution was evaporated to dryness and the residue was dissolved in a small amount of warm methanol. After filtration the methanol solution was mixed with acetone and allowed to stand in a refrigerator to give faint yellow crystals, which were washed with a mixture of water–acetone and dried *in vacuo*. Total yield: 300 mg. Found: C, 31.42; H, 7.38; N, 14.75%. Calcd for $C_{10}H_{28}N_4Cl_2Pd$: C, 31.47; H, 7.39; N, 14.68%.

*7) [PdL(S-pn)]Cl$_2$ (L=N$^1$,N$^1$-Et$_2$-(S)-pn and N,N-Et$_2$en)*: These complexes were prepared from [PdCl$_2$(*S*-pn)] by a method similar to that in *6)*, but crystallized from ethanol by adding acetone. Yield: 75—85%. Found: C, 28.77; H, 7.66; N, 13.46%. Calcd for [Pd(*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)(*S*-pn)]Cl$_2$·2H$_2$O=$C_{10}H_{32}N_4Cl_2O_2Pd$: C, 28.76; H, 7.72; N, 13.41%. Found: C, 27.71; H, 7.29; N, 14.29%. Calcd for [Pd(*N*,*N*-Et$_2$en)(*S*-pn)]-Cl$_2$·1.25H$_2$O=$C_9H_{28.5}N_4Cl_2O_{1.25}Pd$: C, 27.71; H, 7.36; N, 14.36%.

*8) [PdL(N$^1$,N$^1$-Et$_2$-(S)-pn)]Cl$_2$ (L=N,N-Et$_2$en and N,N-Me$_2$en)*: Each of these complexes was obtained from [PdCl$_2$L][11] in a manner similar to that in *6)*, but crystallization was performed from warm ethanol or methanol by adding ether. Yield: 80—85%. Found: C, 36.87; H, 8.06; N, 13.32%. Calcd for [Pd(*N*,*N*-Et$_2$en)(*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)]Cl$_2$=$C_{13}H_{34}N_4Cl_2Pd$: C, 36.85; H, 8.09; N, 13.22%. Found: C, 33.40; H, 7.60; N, 14.29%. Calcd for [Pd(*N*,*N*-Me$_2$en)(*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)]Cl$_2$=$C_{11}H_{30}N_4Cl_2Pd$: C, 33.39; H, 7.64; N, 14.16%.

*9) Other Complexes*: The complex [Pd(*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)$_2$]-Cl$_2$ was prepared according to the method reported,[10] but the content of water of crystallization was different. Found: C, 35.57; H, 8.47; N, 11.82%. Calcd for [Pd(*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)$_2$]-Cl$_2$·2H$_2$O=$C_{14}H_{40}N_4Cl_2O_2Pd$: C, 35.49, H, 8.51; N, 11.82%. The complex [Pd(*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)(en)]Cl$_2$ was prepared in our previous work.[11]

*[Pd(N)$_3$(O)]-type Complexes.* *1) [Pd(gly)(S-pn)]ClO$_4$*: A suspension of 400 mg of [PdCl$_2$(*S*-pn)] in 15 cm$^3$ of water was mixed with an aqueous solution (5 cm$^3$) containing 120 mg of glycine and 65 mg of sodium hydroxide. The mixture was stirred for 30 min at 45 °C to turn into a clear lemon yellow solution, which was treated with 200 mg of sodium perchlorate and evaporated to dryness under reduced pressure. After washing with cold water, the crude product was recrystallized from warm water by adding methanol. Yield: 270 mg. Found: C, 17.03; H, 4.01; N, 11.87%. Calcd for $C_5H_{14}N_3ClO_6Pd$: C, 16.96; H, 3.99; N, 11.87%.

*2) [PdL(en)]ClO$_4$ (L=S-ala and S-ser)*: These complexes were prepared from [PdCl$_2$(en)] by the same method as in *1)*, in a 75—80% yield. Found: C, 17.05; H, 4.08; N, 11.85%. Calcd for [Pd(*S*-ala)(en)]ClO$_4$=$C_5H_{14}N_3ClO_6Pd$: C, 16.96; H, 3.99; N, 11.87%. Found: C, 16.43; H, 3.89; N, 11.35%. Calcd for [Pd(*S*-ser)(en)]ClO$_4$=$C_5H_{14}N_3ClO_7Pd$: C, 16.23; H, 3.81; N, 11.36%.

*3) [Pd(S-ala)(tn)]ClO$_4$*: Silver oxide (380 mg) was mixed with 400 mg of [PdCl$_2$(tn)] suspended in 12 cm$^3$ of water and the mixture was stirred at room temperature for 20 min in the dark. After the silver chloride had been filtered off, perchloric acid (60%, 266 mg) and (*S*)-alanine (141 mg) were successively added to the filtrate. The reaction mixture was stirred for 20 min and evaporated to dryness. A water–methanol (1:9) solution of the residue was mixed with ether and allowed to stand in a refrigerator, giving pale yellow crystals, which were washed with a mixture of methanol–ether and dried *in vacuo*. Yield: 510 mg. Found: C, 18.83; H, 4.76; N, 10.91%. Calcd for [Pd(*S*-ala)(tn)]ClO$_4$·H$_2$O=$C_6H_{18}N_3ClO_7Pd$: C, 18.67; H, 4.70; N, 10.88%.

*4) [Pd(β-ala)(S-pn)]ClO$_4$*: This complex was prepared by a method similar to that in *3)*, but crystallization was performed in an aqueous medium by adding ethanol carefully and allowing to stand at room temperature for 4 d. Yield: 190 mg. Found: C, 19.33; H, 4.55; N, 11.12%. Calcd for [Pd(β-ala)-(*S*-pn)]ClO$_4$·0.5H$_2$O=C$_6$H$_{17}$N$_3$ClO$_{6.5}$Pd: C, 19.11; H, 4.54; N, 11.14%.

*5) [Pd(*S*-leu)(en)]ClO$_4$*: This was obtained in the same manner as in *3)*, but ethanol was used in place of ether in crystallization. Yield: 75%. Found: C, 24.34; H, 5.12; N, 10.54%. Calcd for C$_8$H$_{20}$N$_3$ClO$_6$Pd: C, 24.26; H, 5.09; N, 10.61%.

*6) [Pd(*S*-ala)(*S*-pn)]ClO$_4$*: Silver perchlorate (290 mg) and silver oxide (165 mg) were successively added to a suspension of 350 mg of [PdCl$_2$(*S*-pn)] in 12 cm$^3$ of water and the mixture was stirred at room temperature for 15 min in the dark. The silver chloride was filtered off and the filtrate was mixed with an aqueous solution (3 cm$^3$) containing 124 mg of (*S*)-alanine. After 20 min of stirring the mixture was evaporated under reduced pressure to give a sirup, which was dissolved in a methanol-ethanol (1:4) mixture (6 cm$^3$) and allowed to stand at room temperature. The desired product separated was washed with a mixture of methanol-ethanol and dried *in vacuo*. Yield: 370 mg. Found: C, 19.61; H, 4.40; N, 11.35%. Calcd for C$_6$H$_{16}$N$_3$ClO$_6$Pd: C, 19.58; H, 4.38; N, 11.42%.

*7) [Pd(*S*-pro)(*S*-pn)]ClO$_4$*: This complex was prepared by the same method as in *6)*, but a mixture of methanol-ethanol (1:1) was used as the solvent for crystallization. The crude product was recrystallized from warm water by adding acetone. Yield: 25%. Found: C, 24.48; H, 4.67; N, 10.65%. Calcd for C$_8$H$_{18}$N$_3$ClO$_6$Pd: C, 24.38; H, 4.60; N, 10.66%.

*8) [PdL(en)]ClO$_4$ (L=*S*-pro and *S*-hpro)*: Each of these complexes was prepared from [PdCl$_2$(en)] in the same way as in *6)*, but crystallized from hot water by adding ethanol. Yield: 85—90%. Found: C, 22.18; H, 4.28; N, 11.02%. Calcd for [Pd(*S*-pro)(en)]ClO$_4$=C$_7$H$_{16}$N$_3$ClO$_6$Pd: C, 22.12; H, 4.24; N, 11.06%. Found: C, 21.29; H, 4.13; N, 10.57%. Calcd for [Pd(*S*-hpro)(en)]ClO$_4$=C$_7$H$_{16}$N$_3$ClO$_7$Pd: C, 21.23; H, 4.07; N, 10.61%.

*9) [Pd(*N,N*-Me$_2$gly)(*N$^1$,N$^1$*-Et$_2$-(*S*)-pn)]ClO$_4$*: A suspension of 470 mg of [PdCl$_2$(*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)] in 15 cm$^3$ of water was treated with 320 mg of AgClO$_4$ and 180 mg of Ag$_2$O in the same manner as in *6)*. The resulting solution was mixed with an aqueous solution of 215 mg of *N,N*-dimethylglycine hydrochloride pre-neutralized with Ag$_2$O. The mixture was stirred at room temperature for 1 h and evaporated to dryness. The crude product was recrystallized from hot water; yield 410 mg. Found: C, 30.34; H, 5.95; N, 9.51%. Calcd for C$_{11}$H$_{26}$N$_3$ClO$_6$Pd: C, 30.15; H, 5.98; N, 9.59%.

*10) [Pd(β-ala)(*N$^1$,N$^1$*-Et$_2$-(*S*)-pn)]ClO$_4$*: This complex was obtained in the same manner as in *9)*, using β-alanine in place of *N,N*-dimethylglycine hydrochloride and silver oxide, in a 65% yield. Found: C, 28.19; H, 5.79; N, 9.82%. Calcd for C$_{10}$H$_{24}$N$_3$ClO$_6$Pd: C, 28.32; H, 5.70; N, 9.91%.

cis-*[Pd(N)$_2$(O)$_2$]-type Complexes.* *1) [Pd$_2$(μ-OH)$_2$(*S*-pn)$_2$]-(ClO$_4$)$_2$*: This complex could be isolated as an intermediate product in the preparation of [Pd(amino carboxylato)(*S*-pn)]ClO$_4$.

A suspension of 300 mg of [PdCl$_2$(*S*-pn)] in 12 cm$^3$ of water was treated with 250 mg of AgClO$_4$ and 145 mg of Ag$_2$O in the same way as described for [Pd(*S*-ala)(*S*-pn)]ClO$_4$. The resulting solution was evaporated to dryness under reduced pressure and the residue was dissolved in a small amount of methanol. After filtration the methanol solution was mixed with ethanol and chilled in an ice-bath to give yellow precipitate, which was collected after 1.5 h, washed with ethanol and ether, and dried *in vacuo*. Yield: 230 mg. Found: C, 12.18; H, 3.82; N, 9.11%. Calcd for C$_6$H$_{22}$N$_4$Cl$_2$O$_{10}$Pd$_2$: C, 12.13; H, 3.73; N, 9.43%. This complex, as well as the corresponding nitrate and hydrogencarbonate salts described below, tends to decompose in an ethanol solution and is sensitive to heat.

*2) [Pd$_2$(μ-OH)$_2$(*S*-pn)$_2$](NO$_3$)$_2$*: This was prepared by a method similar to that in *1)* using AgNO$_3$ in place of AgClO$_4$. Crystallization was performed from water by adding acetone at room temperature. The solubility of this complex exhibits a negative temperature gradient in a solvent system of water–acetone. Yield: 35%. Found: C, 13.78; H, 4.32; N, 15.87%. Calcd for C$_6$H$_{22}$N$_6$O$_8$Pd$_2$: C, 13.88; H, 4.27; N, 16.19%. The nitrate is most unstable among the three kinds of the dimer salts.

*3) [Pd$_2$(μ-OH)$_2$(*S*-pn)$_2$](HCO$_3$)$_2$*: The mixture [PdCl$_2$(*S*-pn)] (250 mg) and Ag$_2$CO$_3$ (95%, 290 mg) suspended in 15 cm$^3$ of water was stirred for 15 min at 55—60 °C. The AgCl was filtered off in hot and the filtrate was chilled in an ice-bath. Yellow crystals were collected, washed with cold water, methanol, and ether, and dried *in vacuo*. Yield: 100 mg. Found: C, 18.34; H, 4.50; N, 10.72%. Calcd for C$_8$H$_{24}$N$_4$O$_8$Pd$_2$: C, 18.58; H, 4.68; N, 10.83%. This complex was also obtained by adding aqueous solution of NaHCO$_3$ to that containing [Pd$_2$($\mu$-OH)$_2$(*S*-pn)$_2$](ClO$_4$)$_2$.

*4) [Pd(CH$_3$CO$_2$)$_2$(*S*-pn)]*: A suspension of 350 mg of [PdCl$_2$(*S*-pn)] in 10 cm$^3$ of water was stirred with 330 mg of Ag$_2$O for 15 min at room temperature. After removal of AgCl, to the solution was added 167 mg of acetic acid diluted with 2 cm$^3$ of water. The mixture was stirred for 15 min at *ca.* 55 °C and then evaporated to a small volume under reduced pressure and chilled in an ice-bath to give yellow crystals. The crystals were washed with cold methanol and ether, and dried *in vacuo*. Total yield: 320 mg. Found: C, 28.10; H, 5.40; N, 9.38%. Calcd for C$_7$H$_{16}$-N$_2$O$_4$Pd: C, 28.15; H, 5.40; N, 9.38%.

*5) [PdL(*S*-pn)] (L=ox and mal)*: These complexes were obtained by the same method as in *4)*, but crystallized from a more dilute solution. Yield: 75—80%. Found: C, 22.41; H, 3.75; N, 10.44%. Calcd for [Pd(ox)(*S*-pn)]=C$_5$H$_{10}$N$_2$O$_4$Pd: C, 22.36; H, 3.75; N, 10.43%. Found: C, 25.39; H, 4.25; N, 9.92%. Calcd for [Pd(mal)(*S*-pn)]=C$_6$H$_{12}$N$_2$O$_4$Pd: C, 25.50; H, 4.28; N, 9.91%. The oxalato complex was also obtained by a reaction of [PdCl$_2$(*S*-pn)] with silver oxalate.

*6) [Pd(ox)(*N$^1$,N$^1$*-Et$_2$-(*S*)-pn)]*: A suspension of 300 mg of [PdCl$_2$(*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)] in 15 cm$^3$ of water was treated with 300 mg of silver oxalate. The solution filtered was evaporated to dryness under reduced pressure and the crude product was recrystallized from a minimum amount of warm water by adding acetone; yield 110 mg. Found: C, 33.24; H, 5.60; N, 8.60%. Calcd for C$_9$H$_{18}$N$_2$O$_4$Pd: C, 33.29; H, 5.59; N, 8.63%.

*[Pd(N)(O)$_3$]-type Complexes.* *1) K[Pd(CH$_3$CO$_2$)$_2$(*S*-ala)]*: An aqueous solution (18 cm$^3$) containing K[PdCl$_2$(*S*-ala)][8] (360 mg) and acetic acid (144 mg) was cooled in an ice-bath and then stirred with 285 mg of freshly prepared silver oxide for 8 min in the dark. After removal of AgCl the solution was evaporated to a small volume and mixed with acetone. On standing in a refrigerator overnight, the desired product was obtained as orange-brown crystals, which were washed with a mixture of water-acetone and dried *in vacuo*. Total yield: 210 mg. Found: C, 23.64; H, 3.44; N, 4.00%. Calcd for C$_7$H$_{12}$NO$_6$KPd: C, 23.91; H, 3.44; N, 3.98%. This complex is thermally labile and decomposes gradually even at room temperature in an aqueous solution.

*2) K[Pd(mal)(*S*-ala)]*: The crude poduct was obtained in the same manner as in *1)* using malonic acid in place of acetic acid, and recrystallized from water by adding acetone; yield 30%. Found: C, 21.41; H, 2.47; N, 4.13%. Calcd for C$_6$H$_8$NO$_6$KPd: C, 21.47; H, 2.40; N, 4.17%

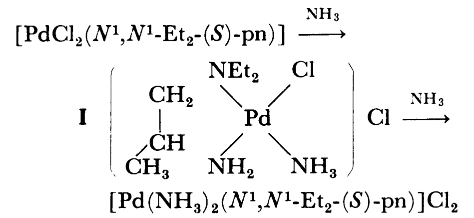
*Measurements.* Electronic absorption spectra were recorded with a Hitachi 330 spectrophotometer and CD spectra with a JASCO MOE-1 spectropolarimeter. Unless otherwise noted, all the measurements were made in aqueous solutions at room temperature. A 10-cm cell was employed for the CD measurements in the long wavelength region in order to acquire a higher precision. $^{13}C$ NMR spectra were taken on a JEOL FX-90Q NMR spectrometer in $D_2O$ containing 1,4-dioxane as an internal standard ($\delta$=67.40).

## Results and Discussion

*Synthesis of the Mixed-ligand Complexes.* In the synthesis of palladium(II) complexes comprising of two kinds of ligands, a ligand possessing higher affinity for palladium [which we will call a higher-affinity ligand hereafter] should be introduced firstly, as the study by Drew *et al.*[3] suggests. When the order is reversed, a disproportionation reaction tends to occur, affording the complexes each having one kind of ligands. Generally, *N*-ligands coordinate to palladium more strongly than *O*-ligands; then, $[Pd(N\text{-}O)(N\text{-}N)]^+$ and $[Pd(O\text{-}O)(N\text{-}N)]$ complexes should be synthesized from $[PdCl_2(N\text{-}N)]$, and $[Pd(O\text{-}O)(N\text{-}O)]^-$ should be from $[PdCl_2(N\text{-}O)]^-$. The order of the affinity with respect to diamine ligands was obtained from the observation of the disproportionation in the course of the synthesis of $[Pd(N)_4]$-type complexes, being as follows:

$$\text{en} \approx S\text{-pn} > \text{tn} > N,N\text{-Me}_2\text{en}$$
$$> N^1,N^1\text{-Et}_2\text{-}(S)\text{-pn} \approx N,N\text{-Et}_2\text{en} \gg NH_3.$$

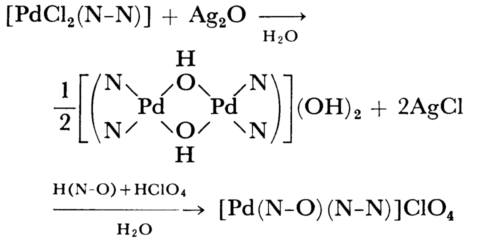
The disproportionation reaction proceeded also when excess lower-affinity ligand was allowed to react with a dichloro complex of higher-affinity ligands. All the $[Pd(N)_4]$-type complexes under investigation were obtained in accord with the above order of affinity. The reaction of ammonia with $[PdCl_2(N^1,N^1\text{-Et}_2\text{-}(S)\text{-pn})]$ apparently does not proceed by one step but by two steps [Eq. (1)], that is, the intermediate product $[PdCl(NH_3)(N^1,N^1\text{-Et}_2\text{-}(S)\text{-pn})]Cl$ was isolated. The action of twice the equimolar quantity of ammonia on the dichloro complex gave only the intermediate chloroammine complex, indicating that the remaining chloro ligand is resistant to the substitution with ammonia. Judging from this observation, the intermediate is supposed to possess structure **I** because an ammine ligand is considered to be more bulky than a chloro ligand.



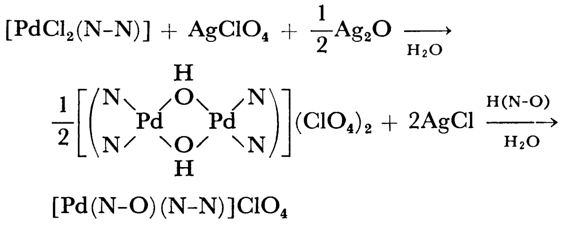
$$[PdCl_2(N^1,N^1\text{-Et}_2\text{-}(S)\text{-pn})] \xrightarrow{NH_3} \mathbf{I} \xrightarrow{NH_3} [Pd(NH_3)_2(N^1,N^1\text{-Et}_2\text{-}(S)\text{-pn})]Cl_2 \qquad (1)$$

$[Pd(N)_3(O)]$-type complexes were synthesized by the following three methods [Eqs. (2)—(4)]. The method of Eq. (2) is useful only when a desired product crystallizes with ease and is sufficiently less soluble than sodium chloride (*e.g.* $[Pd(gly)(S\text{-pn})]ClO_4$ and $[Pd(S\text{-ala})(en)]ClO_4$). When the complexes are highly soluble, the method of Eq. (3), where both perchloric acid and amino carboxylic acid are employed in an equimolar amount with the starting dichloro complex is effective. The method of Eq. (4) is essentially the same as that of Eq.(3), but it is noticed that all the reactions proceed under nearly neutral conditions.

$$[PdCl_2(N\text{-}N)] + H(N\text{-}O) + NaOH \xrightarrow[H_2O]{NaClO_4} [Pd(N\text{-}O)(N\text{-}N)]ClO_4 + 2NaCl \qquad (2)$$

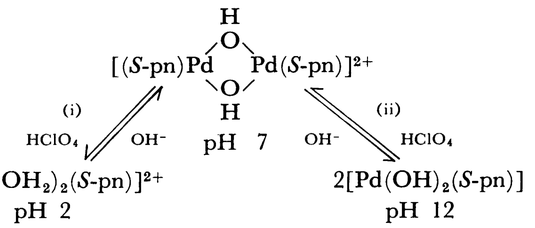


$$[PdCl_2(N\text{-}N)] + Ag_2O \xrightarrow[H_2O]{} \frac{1}{2}\left[(N\text{-}N)Pd(\mu\text{-}OH)_2Pd(N\text{-}N)\right](OH)_2 + 2AgCl \xrightarrow[H_2O]{H(N\text{-}O)+HClO_4} [Pd(N\text{-}O)(N\text{-}N)]ClO_4 \qquad (3)$$



$$[PdCl_2(N\text{-}N)] + AgClO_4 + \frac{1}{2}Ag_2O \xrightarrow[H_2O]{} \frac{1}{2}\left[(N\text{-}N)Pd(\mu\text{-}OH)_2Pd(N\text{-}N)\right](ClO_4)_2 + 2AgCl \xrightarrow[H_2O]{H(N\text{-}O)} [Pd(N\text{-}O)(N\text{-}N)]ClO_4 \qquad (4)$$

The di-$\mu$-hydroxo complex of *S*-pn, which is an intermediate in the reactions of Eqs.(3) and (4), could be isolated as nitrate and hydrogencarbonate, as well as perchlorate. The following equilibria with regard to the dimer perchlorate were confirmed by absorption and CD spectral measurements [See also Fig. 1; the shoulder at $45.5\times10^3$ cm$^{-1}$ of the dimer complex is assigned to a charge transfer transition, Pd← O($\mu$-OH)]. The equilibrium constant of equilibrium (i) for the corresponding en complexes has been determined by Lim and Martin.[12]



$$2[Pd(OH_2)_2(S\text{-pn})]^{2+}\ (pH\ 2) \underset{HClO_4}{\overset{OH^-}{\rightleftharpoons}}\text{(i)}\ [(S\text{-pn})Pd(\mu\text{-}OH)_2Pd(S\text{-pn})]^{2+}\ (pH\ 7)\ \text{(ii)} \underset{HClO_4}{\overset{OH^-}{\rightleftharpoons}} 2[Pd(OH)_2(S\text{-pn})]\ (pH\ 12)$$

The preparation of $[Pd(S\text{-ala})(NH_3)_2]ClO_4$ was attempted according to both Eqs. (3) and (4), but the contamination with the bis(alaninato) complex prevented the isolation of the pure product. The purity was not improved by recrystallization. This seems to be primarily caused by the mechanism that the ammonia liberated during the course of recrystallization promotes a disproportionation reaction.

*cis*-$[Pd(N)_2(O)_2]$-type complexes could not be obtained by the method of Eq. (5). The reaction proceeded only incompletely even by the use of excess dicarboxylate, which indicates high affinity of a chloro ligand over *O*-ligands for palladium. Thus it is necessary that chloride ions are removed from the

$$[PdCl_2(S\text{-pn})] + M_2(O\text{-}O) \xrightarrow[H_2O]{} [Pd(O\text{-}O)(S\text{-pn})] + 2MCl\ (M{=}\text{alkali metal}) \qquad (5)$$

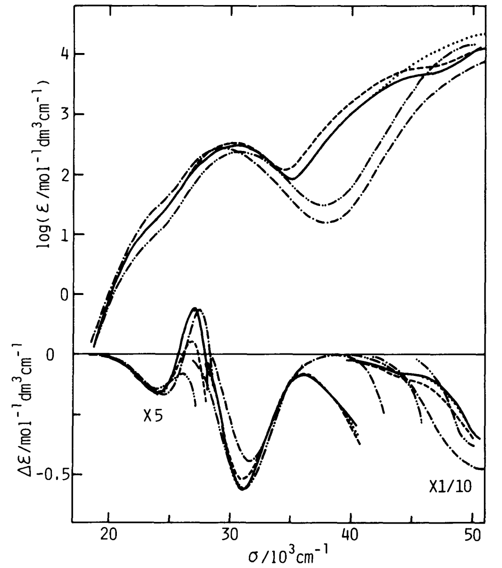


Fig. 1. Absorption and CD spectra of $[Pd_2(\mu\text{-OH})_2(S\text{-pn})_2]X_2$. ——: $X=ClO_4$ in $H_2O$, —·—: $X=ClO_4$ in 0.01 M $HClO_4$ $(=2\times[Pd(OH_2)_2(S\text{-pn})](ClO_4)_2)$, —··—: $X=ClO_4$ in 0.01 M NaOH $(=2\times[Pd(OH)_2(S\text{-pn})]$, ----, $X=HCO_3$ in $H_2O$, and ······: $X=NO_3$ in $H_2O$.

reaction system. The method of Eq. (6) satisfies this

$$[PdCl_2(S\text{-pn})] + Ag_2O \xrightarrow[H_2O]{} \frac{1}{2}[(S\text{-pn})Pd(\mu\text{-OH})_2Pd(S\text{-pn})](OH)_2 + 2AgCl \xrightarrow[H_2O]{H_2(O\text{-}O)} [Pd(O\text{-}O)(S\text{-pn})] \qquad (6)$$

requirement. The calculated quantity of a dicarboxylic acid is sufficient here, and a desired product can be isolated from the salt free system. The method of Eq. (7)

$$[PdCl_2(S\text{-pn})] + Ag_2(O\text{-}O) \xrightarrow[H_2O]{} [Pd(O\text{-}O)(S\text{-pn})] + 2AgCl \qquad (7)$$

was also effective for the synthesis of the oxalato complex. Attempts to synthesize the carbonato complex by this method, however, were unsuccessful, and the hydrogen carbonate salt of the same di-μ-hydroxo complex as is seen in Eq. (6) was obtained instead. The same material was also obtained by metathesis of an authentic sample of the corresponding perchlorate with sodium hydrogencarbonate.

$[Pd(N)(O)_3]$-type complexes could not be obtained by reaction (8) but by (9) in analogy with the case of

$$K[PdCl_2(S\text{-ala})] + M_2(O\text{-}O) \xrightarrow[H_2O]{} K[Pd(O\text{-}O)(S\text{-ala})] + 2MCl \qquad (8)$$

$$K[PdCl_2(S\text{-ala})] + Ag_2O + H_2(O\text{-}O) \xrightarrow[H_2O]{} K[Pd(O\text{-}O)(S\text{-ala})] + 2AgCl \qquad (9)$$

*cis*-$[Pd(N)_2(O)_2]$-type complexes. Chloro ligands must be removed in the presence of a dicarboxylic acid because otherwise some decomposition occurs and it seems to be concerned with the instability of the di-μ-hydroxo complex $[(S\text{-ala})Pd(\mu\text{-OH})_2Pd(S\text{-ala})]$ in a basic solution [Eq. (10)]. The malonato complex

$$K[PdCl_2(S\text{-ala})] + Ag_2O \xrightarrow[H_2O]{} \frac{1}{2}[(S\text{-ala})Pd(\mu\text{-OH})_2Pd(S\text{-ala})] + KOH + 2AgCl \qquad (10)$$

obtained according to Eq. (9) had been somewhat contaminated by the disproportionation products, but it could be purified by recrystallization. The use of oxalic acid in place of malonic acid gave only a mixture of the disproportionation products. The direct method where silver oxalate is used as in Eq. (7) also led to the same result.

*Isomerism.* As both *S*-pn and am⁻ are unsymmetrical bidentate ligands, their mixed-ligand complexes should exhibit geometrical isomerism. We will call the configurations of two isomers *cis*($CH_3$,*O*) and *trans*($CH_3$,*O*) by considering the relative positions between the methyl group of *S*-pn and the coordinating oxygen atom of am⁻. The $^{13}C$ NMR spectra of the β-ala, *S*-pro, and *S*-ala complexes varied with time, which was ascribed to the variation of distribution of such isomers: the β-ala and *S*-pro complexes comprise exclusively one isomer in the crystalline state and the *S*-ala complex also roughly so, whereas in solution each of them changes slowly into a mixture of the two isomers (approximately equimolar). The gly complex was found to be such a mixture even in the crystalline state. All the resonances were assigned on the basis of comparison with those of the related complexes[13] and by the INEPT method[14] (Table 1). The chelate ring carbons C(1) and C(2) of *S*-pn exhibit different

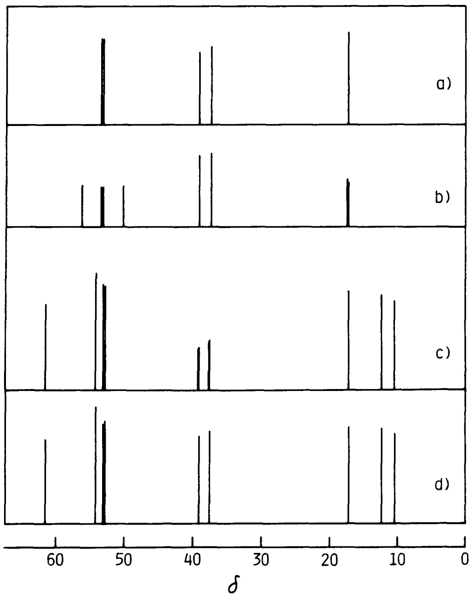


Fig. 2. Diagramatic representation of the $^{13}C$ NMR spectra of a) $[Pd(\beta\text{-ala})(S\text{-pn})]^+$ recorded immediately after dissolution, b) $[Pd(\beta\text{-ala})(S\text{-pn})]^+$ after 110 h, c) $[Pd(\beta\text{-ala})(N^1,N^1\text{-Et}_2\text{-}(S)\text{-pn})]^+$ recorded immediately after dissolution, and d) $[Pd(\beta\text{-ala})(N^1,N^1\text{-Et}_2\text{-}(S)\text{-pn})]^+$ after 120 h; the resonance for the carbonyl carbon being omitted.

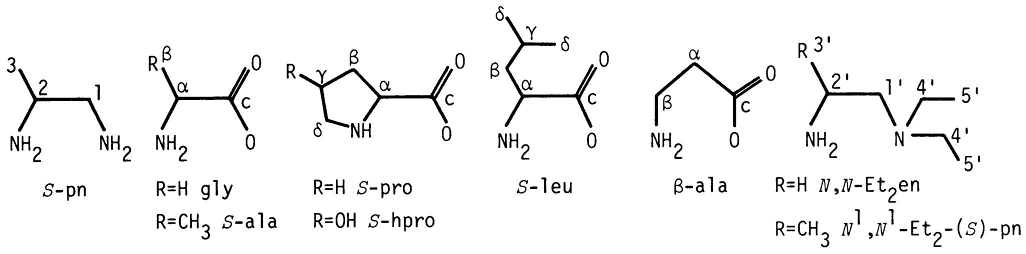
TABLE 1. $^{13}$C NMR CHEMICAL SHIFTS FOR SELECTED $[Pd(N)_4]$- AND $[Pd(N)_3(O)]$-TYPE COMPLEXES[a, j)]

| Complex[b)] $(L_1)(L_2)$ | | *S*-pn | | | am$^-$ | | | | | Others | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C(1) | C(2) | C(3) | C(α) | C(β) | C(γ) | C(δ) | C(c) | | |
| (gly)(*S*-pn) | | 50.52<br>52.58 | 55.78<br>53.72 | 17.31 | 47.27 | | | | {186.68<br>{186.73 | | |
| (*S*-ala)(*S*-pn) | c) | 50.55<br>52.50[e)] | 55.70<br>53.64[e)] | 17.39 | 54.67 | 19.67 | | | 187.57 | | |
| | d) | 50.55<br>52.50 | 55.75<br>53.69 | 17.39 | 54.67 | 19.67 | | | 187.57 | | |
| (*S*-pro)(*S*-pn) | c) | 52.45 | 53.48 | 17.44 | 64.85 | 30.34 | 25.68 | 52.61 | f) | | |
| | d) | 50.39<br>52.39 | 55.53<br>53.42 | 17.45 | 64.85 | 30.29 | 25.57 | 52.55 | 188.06 | | |
| (β-ala)(*S*-pn) | c) | 53.20 | 53.48 | 17.34 | 37.44 | 39.17 | | | 181.29 | | |
| | d) | 50.32<br>53.20 | 56.39<br>53.47 | 17.49<br>17.33 | 37.43 | 39.16 | | | 181.22 | | |
| (*S*-ala)(en) | | | | | 54.78 | 19.67 | | | 187.52 | 45.73[h)] | 47.79[h)] |
| (*S*-leu)(en) | | | | | 57.16 | 43.02 | 24.49 | 21.51<br>23.19 | 187.62 | 45.73[h)] | 47.73[h)] |
| (*S*-hpro)(en) | | | | | 63.39 | 38.58 | 70.71 | 59.16 | 187.62 | 45.62[h)] | 47.79[h)] |
| (en)(*S*-pn) | | 51.39 | 54.53 | 17.64 | | | | | | 46.57[h)] | |

| | *S*-pn | | | $N^1,N^1$-$Et_2$-(*S*)-pn (or *N*,*N*-$Et_2$en) | | | | | Others | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C(1) | C(2) | C(3) | C(1′) | C(2′) | C(3′) | C(4′) | C(5′) | | |
| (*N*,*N*-$Et_2$en)-(*S*-pn) | 51.01 | 54.75 | 17.58 | 57.19 | 43.94 | | 55.45 | 11.78<br>12.06 | | |
| ($N^1,N^1$-$Et_2$-(*S*)-pn)-(*S*-pn) | 51.28 | 54.59 | 17.69 | 62.66 | 52.42 | 17.55 | 55.86<br>56.35 | 11.43<br>12.79 | | |
| ($N^1,N^1$-$Et_2$-(*S*)-pn)-(*N*,*N*-$Me_2$en) | | | | 62.52 | 52.10 | 17.48 | 55.86<br>56.54 | 11.22<br>13.20 | 50.71[g)]<br>51.85[g)] | 42.78[h)]<br>66.42[i)] |

| | | am$^-$ | | | $N^1,N^1$-$Et_2$-(*S*)-pn | | | | | Others |
|---|---|---|---|---|---|---|---|---|---|---|
| | | C(α) | C(β) | C(c) | C(1′) | C(2′) | C(3′) | C(4′) | C(5′) | |
| (*N*,*N*-$Me_2$gly)-($N^1,N^1$-$Et_2$-(*S*)-pn) | | 68.32 | | 181.98 | 62.80 | 52.23 | 17.13 | 54.13<br>55.05 | 11.00<br>12.14 | 51.45[g)]<br>51.61[g)] |
| (β-ala)-($N^1,N^1$-$Et_2$-(*S*)-pn) | c) | 37.59<br>37.62 | 39.15<br>39.26 | 181.52 | 61.63 | 52.94 | 17.26 | 53.21<br>54.36 | 10.50<br>12.34 | |
| | d) | 37.56 | 39.12 | 181.46 | 61.60 | 52.94 | 17.23 | 53.22<br>54.37 | 10.49<br>12.34 | |

a) ppm from $Me_4Si$. b) $(L_1)(L_2)\equiv[Pd(L_1)(L_2)]^{n+}$. c) Recorded immediately after dissolution. d) Recorded in equilibrium (See text). e) Weak. f) Not scanned. g) $(\underline{C}H_3)_2N$-. h) $H_2N\underline{C}H_2$-. i) $(CH_3)_2N\underline{C}H_2$-. j) Ligand carbons are named as follows.



chemical shifts between a pair of isomers, and this is also the case for the carbonyl carbon C(c) of the gly complex and the methyl carbon C(3) of *S*-pn in the β-ala complex. For example, the $^{13}$C NMR spectrum of the β-ala complex showed six signals correspoding to six different carbons when it was recorded immediately after dissolution; whereas after equilibration (110 h) it showed three additional signals, which are assigned to C(1), C(2), and C(3) (Fig. 2 and Table 1). The variable distribution of the isomers could be also detected by CD spectra. The main negative CD band in the d-d transition region increased in intensity with time after dissolution in the β-ala and *S*-pro complexes, but decreased in the *S*-ala complex

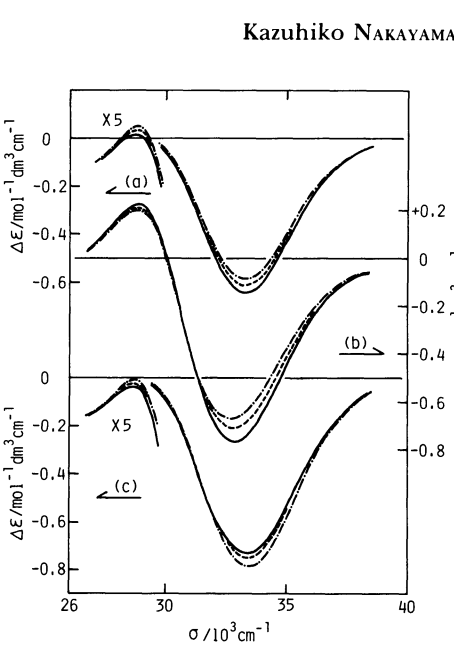
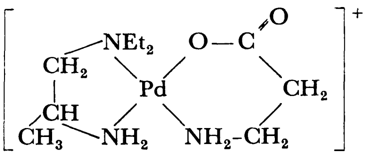


Fig. 3. CD spectral variation with time after dissolution for [PdL($S$-pn)]ClO$_4$. (a) L=β-ala; —·—: 0 h, ----: 24 h, and ——: 110 h (in equilibrium). (b) L=$S$-pro; —·—: 0 h, ----: 5 h, and ——: 30 h (in equilibrium). (c) L=$S$-ala; —·—: 0 h, ----: 5 h, and ——: 12 h (in equilibrium).

(Fig. 3). This suggests that the configuration of the isomer predominant in the crystalline state of the former complexes is different from that of the latter complex, which is compatible with the deduction from the $^{13}$C NMR spectra. In one isomer of every complex,the difference in chemical shifts between C(1) and C(2) is small (*ca.* 1.3, 1.0, and 1.2 ppm for the β-ala, $S$-pro, and $S$-ala complexes, respectively), and in the other isomer it is large (*ca.* 6.1, 5.1, and 5.2 ppm, respectively). The predominant isomer in the crystalline state is the former for the β-ala and $S$-pro complexes, and the latter for the $S$-ala complex (Table 1).

The configuration was determined by examination of the time-dependent $^{13}$C NMR and CD spectra of [Pd(β-ala)($N^1$,$N^1$-Et$_2$-($S$)-pn)]$^+$. In the NMR spectrum recorded immediately after dissolution, each of the α- and β-carbon of β-ala showed two signals; and after 120 h (in equilibrium) one of the two signals disappeared and the remaining one increased in intensity (Fig. 2). This fact suggests that the complex comprises a mixture of a pair of isomers in the crystalline state, but in solution isomerizes slowly to the more stable isomer.[15] The steric interaction between the amino group of β-ala and the diethylamino group of $N^1$,$N^1$-Et$_2$-($S$)-pn is expected to be more significant than that between the carboxyl oxygen of β-ala and the diethylamino group.[16] Therefore, structure **II** can be assigned to the more stable isomer.



**II** *trans*(CH$_3$,*O*)

Although the CD variation with time was unexpectedly small, it was reproducible: +0.021→+0.014 (at 350 nm) and −0.919→−0.903 (at 299 nm), given as $\Delta\varepsilon$/mol$^{-1}$ dm$^3$ cm$^{-1}$ for 0 h→120 h (See also Fig. 8). Thus, the main band varies in the positive direction. This variation can be correlated to the isomerization of the *cis*(CH$_3$,*O*) to the *trans*(CH$_3$,*O*) isomer on the basis of the above structural assignment. Therefore, the predominant isomer in the crystalline state of [Pd($S$-ala)($S$-pn)]ClO$_4$, which exhibits the same CD variation as [Pd(β-ala)($N^1$,$N^1$-Et$_2$-($S$)-pn)]ClO$_4$, is *cis*-(CH$_3$,*O*); and those of [Pd(β-ala)($S$-pn)]ClO$_4$ and [Pd-($S$-pro)($S$-pn)]ClO$_4$, which exhibit the reverse CD variation, are *trans*(CH$_3$,*O*). These results are summarized in Table 2.

It is worth noting that the complexes with a six-membered amino carboxylato chelate ring isomerize evidently more slowly than those with a five-membered one, and have comparable rate of isomerization (or racemization) with the [Pd(N)$_4$]-type complexes with two five-membered chelate rings.[11] Although [Pd(N)$_4$]-type complexes such as [Pd($N^1$,$N^1$-Et$_2$-($S$)-pn)($S$-pn)]$^{2+}$ should also exhibit similar isomerism, it could be detected by neither of $^{13}$C NMR nor CD spectra.

*$^{13}$C NMR Spectra.* A convenient rule concerning $^{13}$C NMR spectra is derived from the assignment of isomers given in the preceding section: A carbon atom adjacent to the coordinated $N$-atom resonates at *ca.* 1 ppm higher or lower magnetic field when an $O$-atom occupies the coordination site trans or cis to the $N$-atom, respectively, in comparison with the case that an $N$-atom occupies the same site instead of $O$-atom (Compare the data for a pair of isomers of [Pd(am)($S$-pn)]$^+$ with those for [Pd(en)($S$-pn)]$^{2+}$). Using this rule, two carbon signals of en in the [Pd($S$-am)(en)]$^+$ complexes can be readily assigned on reference to that of en in [Pd(en)($S$-pn)]$^{2+}$ (46.57

TABLE 2. ISOMERIZATION OF [Pd(N)$_3$(O)]-TYPE COMPLEXES[a)]

| Complex[b)] (L$_1$)(L$_2$) | Variation of distribution of isomers[c)] | Net change | Direction of CD variation[d)] |
|---|---|---|---|
| (β-ala)($S$-pn) | *trans* → [*trans*+*cis*(≈1:1)] | *trans* → *cis* | − |
| ($S$-pro)($S$-pn) | *trans* → [*trans*+*cis*(≈1:1)] | *trans* → *cis* | − |
| ($S$-ala)($S$-pn) | [*trans*<*cis*] → [*trans*+*cis*(≈1:1)] | *cis* → *trans* | + |
| (β-ala)($N^1$,$N^1$-Et$_2$-($S$)-pn) | [*trans*+*cis*(≈1:1)] → *trans* | *cis* → *trans* | + |

a) *trans*≡*trans*(CH$_3$,*O*) and *cis*≡*cis*(CH$_3$,*O*). b) (L$_1$)(L$_2$)≡[Pd(L$_1$)(L$_2$)]$^+$. c) In crystal→in solution at equilibrium. d) For the main band in the d-d transition region.

ppm). Accordingly, the signals at *ca.* 45.7 and 47.8 ppm are assigned to the carbon atom adjacent to the *N*-atom trans and cis to the *O*-atom, respectively.

*CD and Absorption Spectra.* *1) [Pd(N)$_4$]-type Complexes*: The spectra of the complexes containing *S*-pn and *N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn as an optically active ligand are shown in Figs. 4 and 5, respectively; the numerical data being given in Tables 3 and 4. The absorption curves are composed of an unsymmetrical broad band and a lower-lying shoulder in the d-d transition region, the latter being a spin-forbidden d-d band. The shape of the spin-allowed d-d band can be characterized by the half-value width parameters and the unsymmetry parameter.[2] These parameters for the complexes studied in this paper are listed in Table 5.

The CD spectra in the spin-forbidden d-d region show two negative bands, more distinctly in the *N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn complexes. In the spin-allowed d-d region, all complexes of the [Pd(N)$_4$]-type show only one negative band except the tn complexes, which exhibit an additional weak positive band in the lower energy side. The intensity of the main negative band is lower for the ammine complexes than for the en and tn complexes and it is almost equal for the latter two complexes, when compared within one of the series of *S*-pn or *N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn complexes (Figs. 4 and 5). The main CD band lies at higher energy by (0.5—1.1) $\times 10^3$ cm$^{-1}$ than the spin-allowed d-d absorption peak for all the complexes including the tn complexes. Thus, it is expected that the complexes other than the tn complexes also have another transition component in the lower energy side of the main band. The CD band for the lower energy component is, however, undetectable probably because of its low intensity. The minimum of $|\Delta\varepsilon|$ around $30\times 10^3$ cm$^{-1}$ seems to arise from such a CD band, and is included in Table 4. This and the main negative band

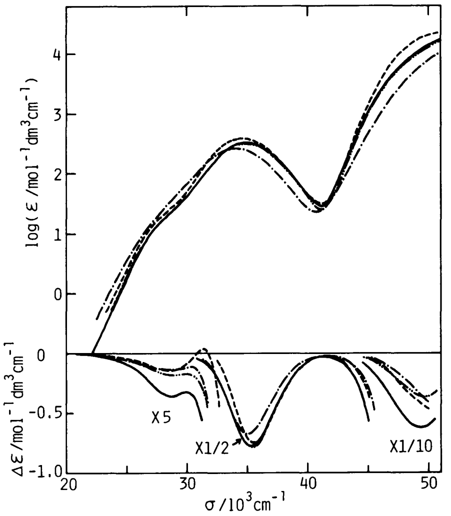


Fig. 4. Absorption and CD spectra of [PdL(*S*-pn)]Cl$_2$. ——: L=*S*-pn, —·—: L=(NH$_3$)$_2$, —··—: L=en, and ----: L=tn.

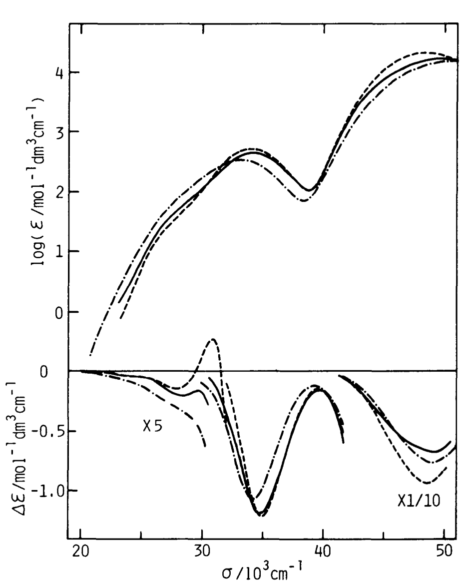


Fig. 5. Absorption and CD spectra of [PdL(*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)]Cl$_2$. ——: L=en, —·—: L=(NH$_3$)$_2$, and ----: L=tn.

Table 3. Absorption data[a] of [Pd(N)$_4$]-type complexes ([Pd(L$_1$)(L$_2$)]Cl$_2$·nH$_2$O)

| (L$_1$)(L$_2$) | *n* | $\sigma_{\max}/10^3$ cm$^{-1}$ ($\varepsilon$/mol$^{-1}$ dm$^3$ cm$^{-1}$) | | | |
|---|---|---|---|---|---|
| | | Spin-forbidden d-d | Spin-allowed d-d | Charge transfer | |
| (*S*-pn)(NH$_3$)$_2$ | 0 | 28.4 sh (30) | 34.08 (261) | | |
| (*S*-pn)(en) | 0.5 | 28.8 sh (23) | 34.86 (310) | | |
| (*S*-pn)$_2$ | 0.5 | 28.8 sh (24) | 34.89 (328) | | |
| (*S*-pn)(tn) | 1 | 28.6 sh (26) | 34.63 (387) | | |
| (*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)(NH$_3$)$_2$ | 1 | 27.4 sh (58) | 33.12 (337) | | |
| (*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)(en) | 1 | 28.2 sh (54) | 34.21 (443) | 49.90 (16600) | |
| (*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)(*S*-pn) | 2 | 28.2 sh (54) | 34.19 (481) | 49.85 (17300) | |
| (*N*,*N*-Et$_2$en)(*S*-pn) | 1.25 | 28.0 sh (54) | 34.15 (422) | 49.70 (16800) | |
| (*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)(tn) | 0 | 28.0 sh (39) | 33.97 (515) | 48.43 (20500) | |
| (*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)$_2$ | 2 | 27.4 sh (48) | 33.57 (603) | 44.48 (14600) | 48.2 sh (13300) |
| (*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)(*N*,*N*-Et$_2$en) | 0 | 27.6 sh (49) | 33.58 (579) | 44.39 (14400) | 48.4 sh (12200) |
| (*N*$^1$,*N*$^1$-Et$_2$-(*S*)-pn)(*N*,*N*-Me$_2$en) | 0 | 27.8 sh (47) | 33.83 (572) | 46.06 (15900) | 48.0 sh (15000) |

a) sh: Shoulder ($\varepsilon$ is for the value $\sigma$ given).

TABLE 4. CD DATA[a)] OF $[\mathrm{Pd(N)_4}]$-TYPE COMPLEXES ($[\mathrm{Pd(L_1)(L_2)]Cl_2}$)[b)]

| $(\mathrm{L_1})(\mathrm{L_2})$ | $\sigma_{\mathrm{ext}}/10^3\ \mathrm{cm^{-1}}$ ($\Delta\varepsilon/\mathrm{mol^{-1}\ dm^3\ cm^{-1}}$) | | |
|---|---|---|---|
| | Spin-forbidden d-d | Spin-allowed d-d | Charge transfer |
| ($S$-pn)($\mathrm{NH_3}$)$_2$ | 28.57 (−0.027) | 30.42m<br>35.06 (−0.68) | |
| ($S$-pn)(en) | 28.74 (−0.038) | 29.90m<br>35.34 (−0.79) | 49.41 (−3.7) |
| ($S$-pn)$_2$ | 24 sh (−0.012)<br>28.78 (−0.073) | 29.99m<br>35.36 (−1.55) | 49.26 (−6.3) |
| ($S$-pn)(tn) | 24.5 sh (−0.007)<br>28.53 (−0.030) | 31.35 (+0.005)<br>35.59 (−0.75) | 50.76 (−4.8) |
| ($N^1$,$N^1$-Et$_2$-($S$)-pn)($\mathrm{NH_3}$)$_2$ | 24 sh (−0.016)<br>28 sh (−0.062) | 34.25 (−1.07) | 48.9 (−7.7) |
| ($N^1$,$N^1$-Et$_2$-($S$)-pn)(en) | 24.5 sh (−0.010)<br>28.22 (−0.042) | 29.59m<br>34.82 (−1.19) | 49.02 (−6.8) |
| ($N$,$N$-Et$_2$en)($S$-pn) | 27.03 (−0.024) | 29.50m<br>34.77 (−0.85) | 48.6 (−1.8) |
| ($N^1$,$N^1$-Et$_2$-($S$)-pn)($S$-pn) | 24.5 sh (−0.021)<br>28.18 (−0.079) | 29.53m<br>34.97 (−2.10) | 47.62 (−8.9) |
| ($N^1$,$N^1$-Et$_2$-($S$)-pn)(tn) | 24.7 sh (−0.010)<br>28.00 (−0.029) | 30.86 (+0.053)<br>35.01 (−1.21) | 48.52 (−9.4) |
| ($N^1$,$N^1$-Et$_2$-($S$)-pn)($N$,$N$-Me$_2$en) | 23.5 sh (−0.009)<br>29.0 sh (−0.10) | 34.16 (−0.85) | 45.3 (−6.3)<br>47.8 (−6.5) |
| ($N^1$,$N^1$-Et$_2$-($S$)-pn)($N$,$N$-Et$_2$en) | 23.5 sh (−0.011)<br>27.14 (−0.032) | 28.61m<br>34.20 (−1.16) | 45.0 (−3.1)<br>47.8 (−3.6) |
| ($N^1$,$N^1$-Et$_2$-($S$)-pn)$_2$ | 23.5 sh (−0.025)<br>26.67 (−0.045) | 28.74m<br>34.13 (−2.85) | 44 sh (−6.9)<br>48.5 (−9.6) |

a) m: The minimum of $|\Delta\varepsilon|$ (See text); sh: shoulder ($\Delta\varepsilon$ is given for the value $\sigma$ given). b) Water of crystallization is omitted (See Table 3).

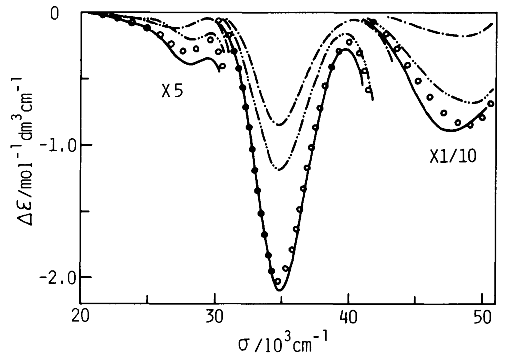


Fig. 6. CD spectra of $[\mathrm{Pd}(N,N\text{-Et}_2\mathrm{en})(S\text{-pn})]\mathrm{Cl}_2$ (—·—), $[\mathrm{Pd}(N,{}^1N^1\text{-Et}_2\text{-}(S)\text{-pn})(\mathrm{en})]\mathrm{Cl}_2$ (—··—), and $[\mathrm{Pd}(N^1,N^1\text{-Et}_2\text{-}(S)\text{-pn})(S\text{-pn})]\mathrm{Cl}_2$ (——); and CD curve calculated from [Δε(—·—)+Δε(—··—)] (oooo).

are assigned to $^1\mathrm{A_{2g}}$ and $^1\mathrm{E_g}\leftarrow{}^1\mathrm{A_{1g}}$ ($\mathrm{D_{4h}}$), respectively, and it is expected that the $^1\mathrm{B_{1g}}\leftarrow{}^1\mathrm{A_{1g}}$ transition, which is magnetic dipole forbidden, occurs at higher energy than the $^1\mathrm{E_g}\leftarrow{}^1\mathrm{A_{1g}}$ transition as in $[\mathrm{PdCl_4}]^{2-}$ and $cis$-$[\mathrm{Pd(Cl)_2(N)_2}]$-type complexes.[1,2)]

The CD spectrum of $[\mathrm{Pd}(N^1,N^1\text{-Et}_2\text{-}(S)\text{-pn})(S\text{-pn})]^{2+}$ comprising two different optically active ligands can be reproduced well by the sum of the CD curves of $[\mathrm{Pd}(N,N\text{-Et}_2\mathrm{en})(S\text{-pn})]^{2+}$ and $[\mathrm{Pd}(N^1,N^1\text{-Et}_2\text{-}(S)\text{-pn})(\mathrm{en})]^{2+}$, which have the same structure as the first complex except for the disposition of $C$-methyl group (Fig. 6). Thus the two optically active ligands contribute independently to the optical activity of $[\mathrm{Pd}(N^1,N^1\text{-Et}_2\text{-}(S)\text{-pn})(S\text{-pn})]^{2+}$. The complexes having two $N$,$N$-dialkylethylenediamine ligands exhibited a splitting with the absorption and CD bands which are assigned to Pd←N(σ) charge transfer(CT) transitions (Fig. 7). The complexes with only one $N$,$N$-dialkylethylenediamine

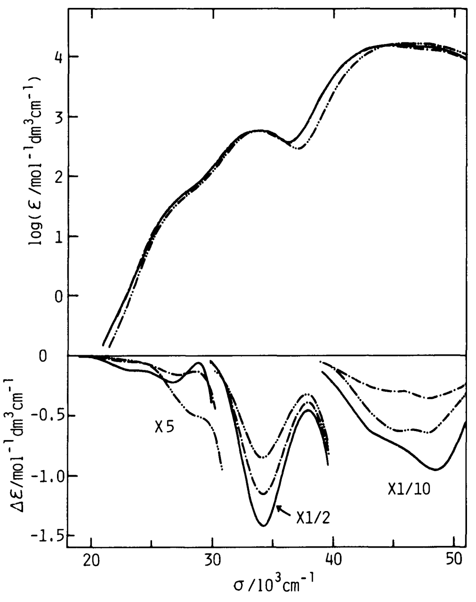


Fig. 7. Absorption and CD spectra of $[\mathrm{Pd}(N^1,N^1\text{-Et}_2\text{-}(S)\text{-pn})_2]\mathrm{Cl}_2$ (——), $[\mathrm{Pd}(N,N\text{-Et}_2\mathrm{en})(N^1,N^1\text{-Et}_2\text{-}(S)\text{-pn})]\mathrm{Cl}_2$ (—·—), and $[\mathrm{Pd}(N,N\text{-Me}_2\mathrm{en})(N^1,N^1\text{-Et}_2\text{-}(S)\text{-pn})]\mathrm{Cl}_2$ (—··—).

TABLE 5. BAND SHAPE PARAMETERS FOR THE SPIN-ALLOWED d-d BAND OF $[Pd(N)_n(O)_{4-n}]$-TYPE COMPLEXES ($n$=1—4)

| Complex | $\Delta\sigma^{-}$ a) / $10^3$ cm$^{-1}$ | $\Delta\sigma^{+}$ a) / $10^3$ cm$^{-1}$ | $\Delta\sigma_{1/2}$ a) / $10^3$ cm$^{-1}$ | Unsymmetry parameter b) |
|---|---|---|---|---|
| $[Pd(S\text{-pn})(NH_3)_2]^{2+}$ | 2.75 | 2.83 | 5.58 | 1.4 |
| $[Pd(S\text{-pn})(en)]^{2+}$ | 2.55 | 2.77 | 5.31 | 4.1 |
| $[Pd(S\text{-pn})_2]^{2+}$ | 2.53 | 2.74 | 5.27 | 4.0 |
| $[Pd(S\text{-pn})(tn)]^{2+}$ | 2.51 | 2.76 | 5.27 | 4.7 |
| $[Pd(N^1,N^1\text{-}Et_2\text{-}(S)\text{-pn})(NH_3)_2]^{2+}$ | 3.20 | 2.91 | 6.11 | −4.7 |
| $[Pd(N^1,N^1\text{-}Et_2\text{-}(S)\text{-pn})(en)]^{2+}$ | 2.73 | 2.68 | 5.42 | −0.9 |
| $[Pd(N^1,N^1\text{-}Et_2\text{-}(S)\text{-pn})(S\text{-pn})]^{2+}$ | 2.67 | 2.70 | 5.37 | 0.6 |
| $[Pd(N,N\text{-}Et_2en)(S\text{-pn})]^{2+}$ | 2.85 | 2.70 | 5.55 | −2.7 |
| $[Pd(N^1,N^1\text{-}Et_2\text{-}(S)\text{-pn})(tn)]^{2+}$ | 2.53 | 2.66 | 5.19 | 2.5 |
| $[Pd(gly)(S\text{-pn})]^{+}$ | 2.72 | 2.79 | 5.51 | 1.3 |
| $[Pd(\beta\text{-ala})(S\text{-pn})]^{+}$ | 2.45 | 2·73 | 5.18 | 5.4 |
| $[Pd(S\text{-ala})(en)]^{+}$ | 2.68 | 2.76 | 5.44 | 1.5 |
| $[Pd(S\text{-ala})(S\text{-pn})]^{+}$ | 2.64 | 2.74 | 5.38 | 1.9 |
| $[Pd(S\text{-ala})(tn)]^{+}$ | 2.53 | 2.83 | 5.37 | 5.6 |
| $[Pd(S\text{-pro})(en)]^{+}$ | 2.75 | 2.80 | 5.56 | 0.9 |
| $[Pd(S\text{-pro})(S\text{-pn})]^{+}$ | 2.78 | 2.80 | 5.58 | 0.4 |
| $[Pd(S\text{-ser})(en)]^{+}$ | 2.70 | 2.78 | 5.47 | 1.5 |
| $[Pd(S\text{-leu})(en)]^{+}$ | 2.71 | 2.76 | 5.46 | 0.9 |
| $[Pd(S\text{-hpro})(en)]^{+}$ | 2.70 | 2.79 | 5.49 | 1.6 |
| $[Pd(\beta\text{-ala})(N^1,N^1\text{-}Et_2\text{-}(S)\text{-pn})]^{+}$ | 2.65 | 2.79 | 5.44 | 2.6 |
| $[Pd(CH_3CO_2)_2(S\text{-pn})]$ c) | 2.60 | 3.08 | 5.68 | 8.5 |
| $[Pd(ox)(S\text{-pn})]$ | 2.59 | 2.74 | 5.33 | 2.8 |
| $[Pd(mal)(S\text{-pn})]$ | 2.88 | 2.83 | 5.70 | −0.9 |
| $[Pd_2(\mu\text{-}OH)_2(S\text{-pn})_2]^{2+}$ | 3.02 | 2.75 | 5.77 | −4.7 |
| $[Pd(OH_2)_2(S\text{-pn})]^{2+}$ d) | 2.53 | 3.09 | 5.62 | 10.0 |
| $[Pd(OH)_2(S\text{-pn})]$ e) | 2.94 | 2.97 | 5.91 | 0.5 |
| $[Pd(ox)(N^1,N^1\text{-}Et_2\text{-}(S)\text{-pn})]$ | 2.96 | 2.63 | 5.59 | −5.9 |
| $[Pd(CH_3CO_2)_2(S\text{-ala})]^{-}$ c) | 2.43 | 2.99 | 5.43 | 10.3 |
| $[Pd(mal)(S\text{-ala})]^{-}$ | 2.91 | 2.98 | 5.89 | 1.2 |

a) $\varepsilon=\varepsilon_{max}/2$ for $\sigma=\sigma_{max}-\Delta\sigma^{-}$ and for $\sigma=\sigma_{max}+\Delta\sigma^{+}$; and $\Delta\sigma_{1/2}=\Delta\sigma^{-}+\Delta\sigma^{+}$. b) unsymmetry parameter= $\{(\Delta\sigma^{+}-\Delta\sigma^{-})/\Delta\sigma_{1/2}\}\times 100$. c) In 0.50 M $CH_3CO_2Na$. d) $[Pd_2(\mu\text{-}OH)_2(S\text{-pn})_2](ClO_4)_2$ in 0.01 M $HClO_4$. e) $[Pd_2(\mu\text{-}OH)_2(S\text{-pn})_2](ClO_4)_2$ in 0.01 M NaOH.

TABLE 6. ABSORPTION DATA a) OF $[Pd(N)_3(O)]$-TYPE COMPLEXES ($[Pd(L_1)(L_2)]ClO_4$)

| $(L_1)(L_2)$ | $\sigma_{max}/10^3$ cm$^{-1}$ ($\varepsilon$/mol$^{-1}$ dm$^3$ cm$^{-1}$) Spin-forbidden d-d | Spin-allowed d-d | Charge transfer |
|---|---|---|---|
| $(gly)(S\text{-pn})$ | 26.2 sh (18) | 32.75 (270) | |
| $(\beta\text{-ala})(S\text{-pn})$ b) | 26.0 sh (16) | 32.48 (415) | 51.28 (21200) |
| $(S\text{-ala})(en)$ | 26.4 sh (18) | 32.89 (283) | |
| $(S\text{-ala})(S\text{-pn})$ | 26.4 sh (18) | 32.91 (308) | |
| $(S\text{-ala})(tn)$ c) | 26.4 sh (22) | 32.55 (384) | 50.45 (23200) |
| $(S\text{-pro})(en)$ | 26.6 sh (24) | 32.96 (292) | 51.18 (23400) |
| $(S\text{-pro})(S\text{-pn})$ | 26.6 sh (25) | 32.98 (299) | 51.18 (23900) |
| $(S\text{-ser})(en)$ | 26.4 sh (19) | 32.79 (280) | |
| $(S\text{-leu})(en)$ | 26.4 sh (19) | 32.88 (289) | |
| $(S\text{-hpro})(en)$ | 26.6 sh (23) | 32.91 (291) | 51.28 (22100) |
| $(\beta\text{-ala})(N^1,N^1\text{-}Et_2\text{-}(S)\text{-pn})$ | 26.0 sh (40) | 32.05 (609) | 49.14 (18000) |
| $(N,N\text{-}Me_2gly)(N^1,N^1\text{-}Et_2\text{-}(S)\text{-pn})$ | 26.0 sh (37) | 32.55 (516) | 44.5 sh (14400)<br>48.60 (17500) |

a) sh: Shoulder ($\varepsilon$ is for the value $\sigma$ given). b) Hemihydrate. c) Monohydrate.

ligand exhibited no such splitting (Fig. 5). Therefore, the splitting seems to be concerned with the structure that two dialkylamino groups occupy the trans sites. However, none of the complexes showed any splitting of the spin-allowed d-d band unlike the *trans*-$[Pd(Cl)_2(N)_2]$-type complexes.[2] The CD intensity of $[Pd(N,N\text{-}Et_2en)(N^1,N^1\text{-}Et_2\text{-}(S)\text{-}pn)]^{2+}$ is smaller than a half of that of $[Pd(N^1,N^1\text{-}Et_2\text{-}(S)\text{-}pn)_2]^{2+}$, additivity not holding (Fig. 7). This fact can be explained by supposing some difference between the ligand–ligand interactions of the two complexes. The explanation is also applicable to the significantly different CD curves of the *N,N*-Et2en and the *N,N*-Me2en complex.

*2) $[Pd(N)_3(O)]$-type Complexes*: The absorption and CD spectra are shown in Figs. 8—10 and the numerical data in Tables 6 and 7. It is noteworthy that the CD patterns of the complexes with *S*-pn or $N^1,N^1$-Et2-(*S*)-pn are very similar to those of the corresponding $[Pd(N)_4]$-type complexes. Namely, the CD patterns of $[Pd(gly)(S\text{-}pn)]^+$ and $[Pd(\beta\text{-}ala)(S\text{-}pn)]^+$ are similar to those of $[Pd(en)(S\text{-}pn)]^{2+}$and $[Pd(tn)(S\text{-}pn)]^{2+}$, respectively, and those of $[Pd(\beta\text{-}ala)(N^1,N^1\text{-}Et_2\text{-}(S)\text{-}pn)]^+$ and $[Pd(N,N\text{-}Me_2gly)(N^1,N^1\text{-}Et_2\text{-}(S)\text{-}pn)]^+$ to those of $[Pd(tn)(N^1,N^1\text{-}Et_2\text{-}(S)\text{-}pn)]^{2+}$ and $[Pd(N,N\text{-}Me_2en)(N^1,N^1\text{-}Et_2\text{-}(S)\text{-}pn)]^{2+}$, respectively. The intensity of the main CD band (in the spin-allowed d-d region) for the $[Pd(N)_3(O)]$-type complexes was *ca.* 60—80% comparing with the corresponding $[Pd(N)_4]$-type complexes. Thus, two types of complexes seem to possess much the same electronic structure, but their CD intensities are influenced not only by the kind of the coordinating atoms but also by the chelate ring size and the con-

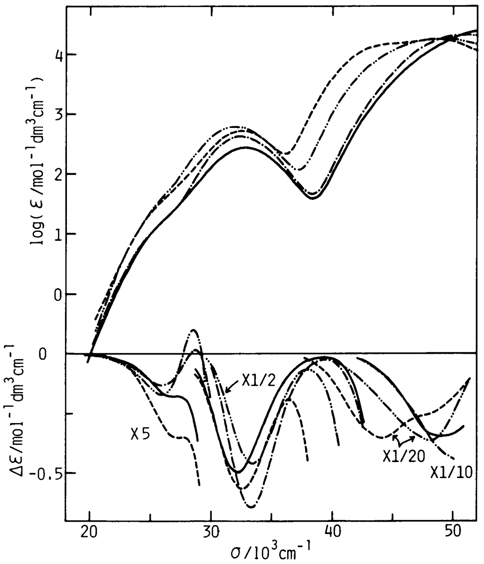


Fig. 8. Absorption and CD spectra of $[Pd(gly)(S\text{-}pn)]ClO_4$ (——), $[Pd(\beta\text{-}ala)(S\text{-}pn)]ClO_4$ (—·—), $[Pd(\beta\text{-}ala)(N^1,N^1\text{-}Et_2\text{-}(S)\text{-}pn)]ClO_4$ (—··—), and $[Pd(N,N\text{-}Me_2gly)(N^1,N^1\text{-}Et_2\text{-}(S)\text{-}pn)]ClO_4$ (----); the first two complexes being in the isomer equilibrium.

TABLE 7. CD DATA[a] OF $[Pd(N)_3(O)]$-TYPE COMPLEXES ($[Pd(L_1)(L_2)]ClO_4$)[b]

| $(L_1)(L_2)$ | $\sigma_{ext}/10^3\ cm^{-1}$ ($\Delta\varepsilon/mol^{-1}\ dm^3\ cm^{-1}$) | | |
|---|---|---|---|
| | Spin-forbidden d-d | Spin-allowed d-d | Charge transfer |
| (gly)(*S*-pn) | 22.5 sh (−0.006)<br>26.92 (−0.036) | 32.20 (−0.50) | 48.9 (−3.5) |
| (β-ala)(*S*-pn)[c] | 26.03 (−0.027) | 28.72 (+0.003)<br>33.31 (−0.64) | |
| (*S*-ala)(en) | 21.05 (+0.0007)<br>25.06 (−0.0061) | 30.10 (+0.077)<br>34.23 (−0.35) | 42.44 (+0.16)<br>48.1 sh (−2.4) |
| (*S*-ala)(*S*-pn)[c] | 22.5 sh (−0.005)<br>26.32 (−0.034) | 28.63 m<br>33.42 (−0.73) | 41.25 (+0.05)<br>50.51 (−8.4) |
| (*S*-ala)(tn) | 21.74 (+0.0007)<br>25.92 (−0.0079) | 29.57 (+0.017)<br>34.97 (−0.16) | 43.5 (+0.3) |
| (*S*-pro)(en) | 21.1 (−0.0006)<br>24.7 sh (+0.015) | 29.11 (+0.28)<br>33.52 (−0.30) | 46.36 (−2.6) |
| (*S*-pro)(*S*-pn)[c] | 21.83 (−0.0034)<br>25.28 (−0.0043) | 28.82 (+0.23)<br>32.86 (−0.77) | 46.19 (−4.6) |
| (*S*-ser)(en) | 24.34 (−0.0052) | 29.69 (+0.093)<br>33.94 (−0.49) | 46.34 (−1.6) |
| (*S*-leu)(en) | 25.19 (−0.010) | 28.67 (+0.027)<br>33.47 (−0.60) | 44.84 (−1.2) |
| (*S*-hpro)(en) | 20.51 (−0.0002)<br>24.7 sh (+0.015) | 29.15 (+0.27)<br>34.25 (−0.20) | 46.90 (−2.3) |
| (β-ala)($N^1,N^1$-Et2-(*S*)-pn)[d] | 25.94 (−0.035) | 28.56 (+0.021)<br>33.47 (−0.92) | 48.17 (−7.3) |
| (*N,N*-Me2gly)($N^1,N^1$-Et2-(*S*)-pn) | 27.25 (−0.070) | 32.57 (−0.57) | 44.21 (−7.1)<br>48.0 sh (−5.1) |

a) As in Table 4. b) Water of crystallization is omitted (See Table 6). c) In equilibrium (See Fig. 3). d) Immediately after dissolution.

formation of an optically inactive ligand.

The vicinal CD caused by an optically active amino carboxylate ligand possesses a pattern of + and − from lower energy in the spin-allowed d-d region for all the (*S*)-amino carboxylato complexes studied here, but the intensity ratio of the positive to the negative band is diverse (Figs. 9 and 10). The *S*-pro and *S*-hpro complexes exhibited a positive band with a high intensity relative to the other amino carboxylato complexes. This phenomenon is characteristic of the complexes with a coordinated asymmetric *N*-atom.[17,18] Moreover, the CD corresponding to the absorption band at *ca.* $51\times10^3\,\mathrm{cm}^{-1}$ also showed different features from those for the other complexes in agreement with the assignment of the band to a Pd←N(σ) CT transition.

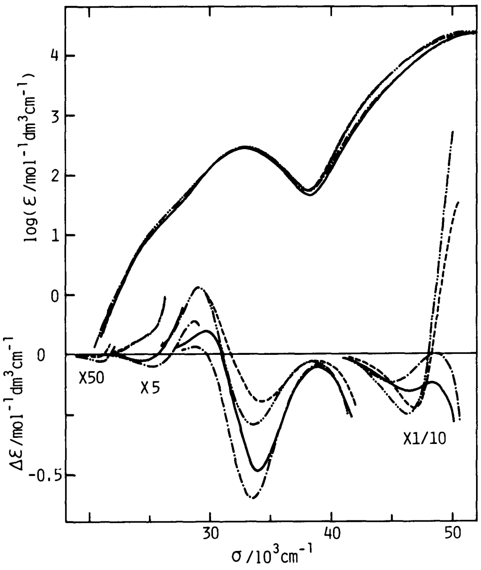


Fig. 9. Absorption and CD spectra of [PdL(en)]-$ClO_4$. ——: L=*S*-ser, —·—: L=*S*-leu, —··—: L=*S*-pro, and ----: L=*S*-hpro.

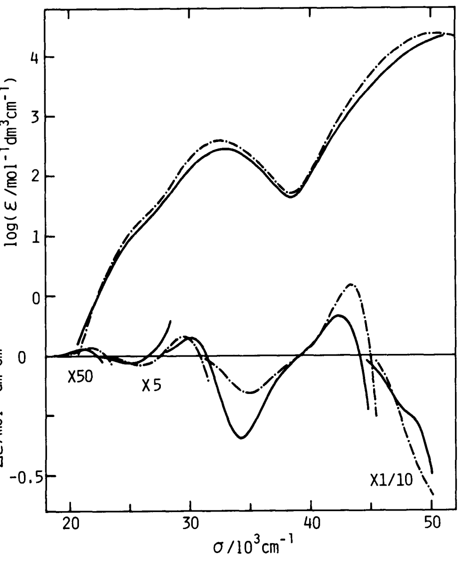


Fig. 10. Absorption and CD spectra of [Pd(*S*-ala)L]-$ClO_4$. ——: L=en and —·—: L=tn

The pattern of the vicinal CD of the *S*-ala complexes does not depend on the ring size of optically inactive diamine ligands, but the intensity does, particularly in the spin-allowed d-d region (Fig. 10). This situation contrasts with that in the corresponding *S*-pn complexes of [Pd(N)$_4$]-type (Fig. 4). A positive CD band occurring at the lower edge of the Pd←N(σ) CT absorption band is a general characteristic of the palladium(II) complexes containing *S*-ala. Although the corresponding absorption band was observed as a shoulder in [Pd(*S*-ala)$_2$],[19] it was hardly detected in the complexes containing only one *S*-ala ligand. The band is assigned to an orbitally-forbidden CT transition rather than a spin-forbidden CT one because the band differs in CD sign from the adjacent allowed CD band.

The additivity of the vicinal CD contributions of *S*-pn and *S*-am was demonstrated with regard to the *S*-ala and *S*-pro complexes (Fig. 11). The almost perfect additivity may be expected since a ligand-ligand interaction is considered to be smaller in these cases than in [Pd($N^1$,$N^1$-$Et_2$-(*S*)-pn)(*S*-pn)]$^{2+}$, even for which such an additivity holds. However, it should be noted that the CD data of [Pd(*S*-am)(*S*-pn)]$^+$ used in the analysis was taken for an approximately equimolar mixture of the geometrical isomers.

As [Pd(gly)(*S*-pn)]$^+$ and [Pd(*S*-ala)(en)]$^+$ are considered to have almost the same electronic energy level scheme, some informations will be obtained about the vicincal effects of *S*-pn and *S*-ala by comparing the CD spectra of the two complexes. We previously de-

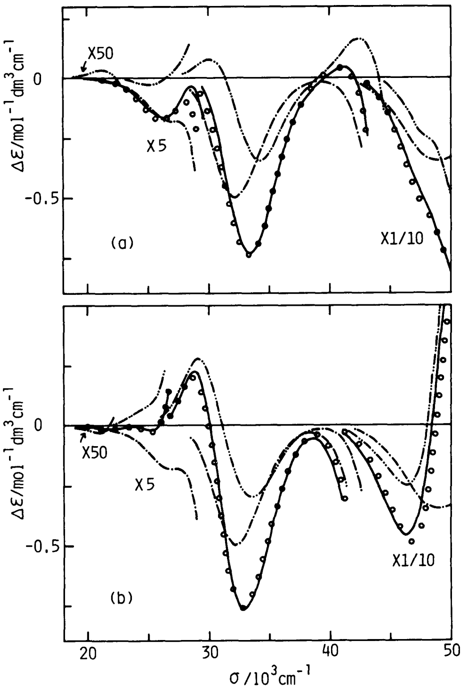


Fig. 11. CD spectra of [Pd(gly)(*S*-pn)]$ClO_4$ (—·—), [PdL(en)]$ClO_4$ (—··—), and [PdL(*S*-pn)]$ClO_4$ (——), all in the isomer equilibrium; and CD curves calculated from [Δε(—·—)+Δε(—··—)] (○○○○). (a) L=*S*-ala and (b) L=*S*-pro.

monstrated with regard to [$PdCl_2$(*S*-pn)] that the main negative CD band in the spin-allowed d-d region was primarily based on the $^1E_g \leftarrow {}^1A_{1g}$ transition, although it included a minor contribution by the $^1B_{1g} \leftarrow {}^1A_{1g}$ transition ($D_{4h}$).[2] This situation seems to be also the case for the *S*-pn complexes of various types, [Pd(*S*-pn)$(N)_n(O)_{2-n}$] ($n$=0—2), from an examination of the absorption and CD data (Figs. 4, 8, and 12). On the other hand, the main negative CD band of [Pd(*S*-ala)(en)]$^+$ shows a shift by *ca.* $2\times10^3\,cm^{-1}$ to higher energy than that of [Pd(gly)(*S*-pn)]$^+$, although the corresponding absorption band does not (Fig. 11a). Thus, it is reasonable to consider that the vicinal contribution by *S*-ala exhibits a dispersion pattern of + and − from lower energy for the $^1E_g \leftarrow {}^1A_{1g}$ transition ($D_{4h}$). The CD spectrum of [$Pd(CH_3CO_2)_2$(*S*-ala)]$^-$ supports this deduction (*vide infra*).

*3)* cis-*[Pd(N)$_2$(O)$_2$]-type Complexes*: The absorption and CD spectra are shown in Fig. 12 and the numerical data in Tables 8 and 9. The absorption and CD spectra of [$Pd(CH_3CO_2)_2$(*S*-pn)] measured in $H_2O$ are different from those in the aqueous solutions containing acetate ions. It seems that the coordinated acetate ions are released by aquation in $H_2O$, judging from the similarity of the absorption and CD spectra to those of [$Pd(OH_2)_2$(*S*-pn)]$^{2+}$ (Fig. 1). The enhancement of absorbance around $40\times10^3\,cm^{-1}$ in $H_2O$ is ascribable to the di-$\mu$-hydroxo complex formed partly.

The CD pattern in the spin-allowed d-d region is various, depending upon the optically inactive ligands: + and −; − and +; and − for the $CH_3CO_2$, ox, and mal complexes, respectively. The complexes containing monodentate ligands exhibit a positive CD band in the lower energy side of the main negative CD band. This situation differs from that found in the [$Pd(N)_4$]- and [$Pd(N)_3(O)$]-type complexes. The ox complex exhibits a positive CD band in the higher energy side of the main negative CD one, being unique in the series of *S*-pn complexes. It is reasonable to assign the CD band to the $^1B_{1g} \leftarrow {}^1A_{1g}$ transition ($D_{4h}$) from its position and low intensity. If this is true, it is a very unique example that the CD band for the transition was observed definitely. Although the corresponding band did not appear in [Pd(ox)($N^1$,$N^1$-$Et_2$-(*S*)-pn)], the CD features are very similar to those of [Pd(ox)(*S*-pn)] in the spin-allowed d-d region, particularly in the width of the main band. Thus it is likely that the CD band of interest is canceled out by the main band.

*4) [Pd(N)(O)$_3$]-type Complexes*: The absorption and CD spectra are shown in Fig. 13 and the numerical data

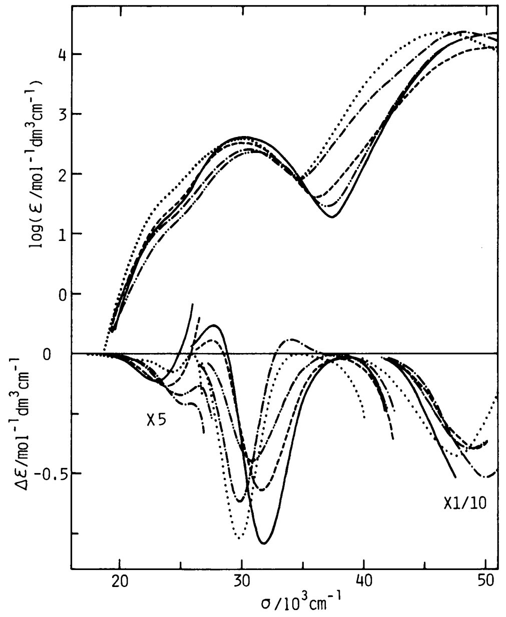


Fig. 12. Absorption and CD spectra of [PdL(*S*-pn)] and [Pd(ox)($N^1$,$N^1$-$Et_2$-(*S*)-pn)] (······). L=$(CH_3CO_2)_2$ in 0.50 M $CH_3CO_2Na$ (——) and in $H_2O$ (----); L=ox in $H_2O$ (—·—); and L=mal in $H_2O$ (—··—).

TABLE 8. ABSORPTION DATA[a] OF *cis*-[$Pd(N)_2(O)_2$]- AND [$Pd(N)(O)_3$]-TYPE COMPLEXES

| Complex | Solvent | $\sigma_{max}/10^3\,cm^{-1}$ ($\varepsilon$/mol$^{-1}$ dm$^3$ cm$^{-1}$) | | |
|---|---|---|---|---|
| | | Spin-forbidden d-d | Spin-allowed d-d | Charge transfer |
| [$Pd(CH_3CO_2)_2$(*S*-pn)] | 0.50 M $CH_3CO_2Na$ | 24.2 sh (23) | 30.09 (417) | |
| [Pd(ox)(*S*-pn)] | $H_2O$ | 24.4 sh (20) | 30.53 (258) | 48.19 (22600) |
| [Pd(mal)(*S*-pn)] | $H_2O$ | 24.8 sh (18) | 31.01 (234) | |
| [$Pd_2(\mu$-$OH)_2$(*S*-pn)$_2$]$(ClO_4)_2$[b,c] | $H_2O$ | 24.0 sh (20) | 30.47 (299) | 45.5 sh (4400) |
| | 0.01 M $HClO_4$ | 24.4 sh (37) | 29.24 (274) | |
| | 0.01 M NaOH | 24.0 sh (11) | 30.80 (234) | |
| [$Pd_2(\mu$-$OH)_2$(*S*-pn)$_2$]$(HCO_3)_2$[b,c] | $H_2O$ | 24.0 sh (20) | 30.21 (332) | 45.5 sh (4800) |
| | 0.01 M $HClO_4$ | 24.4 sh (37) | 29.25 (273) | |
| | 0.01 M NaOH | 24.0 sh (11) | 30.77 (230) | |
| [$Pd_2(\mu$-$OH)_2$(*S*-pn)$_2$]$(NO_3)_2$[b] | $H_2O$ | 24.0 sh (19) | 30.50 (300) | 51.84 (22800) |
| [Pd(ox)($N^1$,$N^1$-$Et_2$-(*S*)-pn)] | $H_2O$ | 23.8 sh (43) | 29.97 (388) | 46.43 (22900) |
| K[$Pd(CH_3CO_2)_2$(*S*-ala)] | 0.05 M $CH_3CO_2Na$ | 21.8 sh (17) | 27.92 (414) | |
| K[Pd(mal)(*S*-ala)][d] | $H_2O$ | 22.0 sh (9) | 28.86 (197) | 49.63 (26100) |

a) sh: Shoulder ($\varepsilon$ is for the value $\sigma$ given). b) Molar absorption coefficient is based on palladium. c) Another band was observed at *ca.* $39.5\times10^3\,cm^{-1}$ as a shoulder. d) Another band was observed at *ca.* $44\times10^3\,cm^{-1}$ as a shoulder.

Table 9. CD data[a)] of *cis*-[Pd(N)$_2$(O)$_2$]- and [Pd(N)(O)$_3$]-type complexes

| Complex | Solvent | $\sigma_{\text{ext}}/10^3\ \text{cm}^{-1}$ ($\Delta\varepsilon/\text{mol}^{-1}\ \text{dm}^3\ \text{cm}^{-1}$) | | |
|---|---|---|---|---|
| | | Spin-forbidden d-d | Spin-allowed d-d | Charge transfer |
| [Pd(CH$_3$CO$_2$)$_2$(*S*-pn)] | 0.50 M CH$_3$CO$_2$Na | 22.94 (−0.024) | 27.67 (+0.12)<br>31.80 (−0.79) | |
| [Pd(ox)(*S*-pn)] | H$_2$O | 21 sh (−0.005)<br>25.32 (−0.042) | 25.88 m<br>29.83 (−0.62)<br>34.01 (+0.06) | 50.00 (−5.2) |
| [Pd(mal)(*S*-pn)] | H$_2$O | 24.93 (−0.035) | 26.46 m<br>30.79 (−0.45) | 48.83 (−4.0) |
| [Pd$_2$($\mu$-OH)$_2$(*S*-pn)$_2$](ClO$_4$)$_2$[b)] | H$_2$O | 23.98 (−0.032) | 26.95 (+0.039)<br>30.96 (−0.56) | 44.5 sh (−0.8) |
| | 0.01 M HClO$_4$ | 24.45 (−0.033) | 27.42 (+0.038)<br>31.58 (−0.44) | 50.76 (−4.7) |
| | 0.01 M NaOH | 23.85 (−0.029) | 26.11 m<br>31.21 (−0.56) | |
| [Pd$_2$($\mu$-OH)$_2$(*S*-pn)$_2$](HCO$_3$)$_2$[b)] | H$_2$O | 23.91 (−0.031) | 26.80 (+0.011)<br>31.02 (−0.52) | 45 sh (−1.1) |
| | 0.01 M HClO$_4$ | 24.47 (−0.033) | 27.43 (+0.032)<br>31.65 (−0.43) | |
| | 0.01 M NaOH | 23.95 (−0.028) | 26.18 m<br>31.30 (−0.55) | |
| [Pd$_2$($\mu$-OH)$_2$(*S*-pn)$_2$](NO$_3$)$_2$[b)] | H$_2$O | 24.02 (−0.034) | 26.94 (+0.037)<br>30.96 (−0.56) | 44.5 sh (−0.8) |
| [Pd(ox)($N^1$,$N^1$-Et$_2$-(*S*)-pn)] | H$_2$O | 21 sh (−0.010)<br>24.31 (−0.031) | 25.93 m<br>29.80 (−1.54) | 47.62 (−8.5) |
| K[Pd(CH$_3$CO$_2$)$_2$(*S*-ala)] | 0.05 M CH$_3$CO$_2$Na | 17.9 (+0.001)<br>20.88 (−0.0044) | 25.91 (+0.081)<br>27.2 sh (+0.078)<br>31.31 (−0.14) | 39.5 (+0.03) |
| K[Pd(mal)(*S*-ala)] | H$_2$O | 20.37 (−0.0027) | 26.62 (+0.17)<br>30.61 (−0.27) | 39.7 (+0.07)<br>48.83 (−5.9) |

a) As in Table 4. b) $\Delta\varepsilon$ is based on palladium.

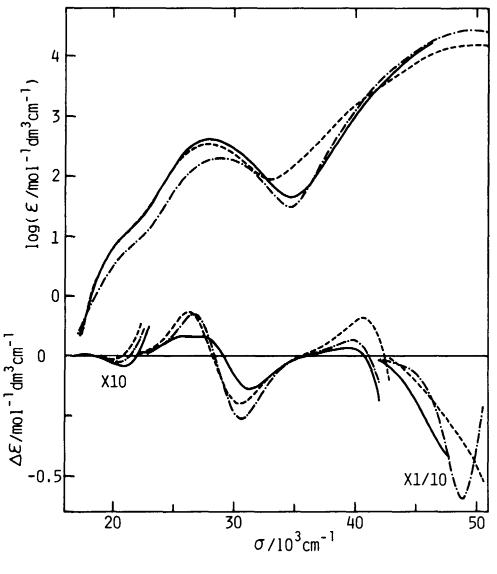


Fig. 13. Absorption and CD spectra of K[PdL(*S*-ala)]. L=(CH$_3$CO$_2$)$_2$ in 0.50 M CH$_3$CO$_2$Na (——) and in H$_2$O (----); and L=mal in H$_2$O (—·—).

in Tables 8 and 9. The K[Pd(CH$_3$CO$_2$)$_2$(*S*-ala)] complex aquates in water free from acetate ions similarly to [Pd(CH$_3$CO$_2$)$_2$(*S*-pn)]; the band ascribed to the di-$\mu$-hydroxo complex was obviously observed as a shoulder around 40×10$^3$ cm$^{-1}$. Both the absorption and CD spectra of the acetato complex were essentially the same in 0.50 and 1.0 M CH$_3$CO$_2$Na. The CD spectrum showed a pattern of +, +, and − from lower energy in the spin-allowed d-d region; the lowest-lying positive band is assigned to the $^1A_{2g}\leftarrow{}^1A_{1g}$ transition and the following dispersion is to the $^1E_g\leftarrow{}^1A_{1g}$ one ($D_{4h}$). Apparently, only one positive band is observed in the other alaninato complexes including the [Pd(*S*-ala)(N)$_2$]-type ones, which is ascribed to the overlapping of the two positive bands. This explanation implies a relatively large separation between the $^1A_{2g}$ and $^1E_g\leftarrow{}^1A_{1g}$ transitions in [Pd(CH$_3$CO$_2$)$_2$(*S*-ala)]$^-$, being compatible with the large value of unsymmetry parameter (Table 5). Consequently, the vicinal CD caused by *S*-ala ligand is considered to exhibit the definite pattern over the d-d and CT transition region, irrespective of the other ligand coordinated together. Similar CD spectra have been also observed in [Pd(*S*-ala)$_2$] and [PdCl$_2$(*S*-ala)]$^-$.[19)]

## References

1) K. Nakayama, T. Komorita, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **57**, 972 (1984).

2) K. Nakayama, T. Komorita, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, in press.

3) H. D. K. Drew, F. W. Pinkard, G. H. Preston, and W. Wardlaw, *J. Chem. Soc.*, **1932**, 1895.

4) M. C. Lim, *J. Chem. Soc., Dalton Trans.*, **1977**, 1398; **1978**, 726; *Inorg. Chem.*, **20**, 1377 (1981).

5) F. G. Mann, D. Crowfoot, D. C. Gattiker, and N. Wooster, *J. Chem. Soc.*, **1935**, 1642.

6) T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, **1965**, 3632.

7) For example, F. W. Pinkard, E. Sharratt, W. Wardlaw, and E. G. Cox, *J. Chem. Soc.*, **1934**, 1012; E. W. Wilson, Jr., and R. B. Martin, *Inorg. Chem.*, **9**, 528 (1970); O. Vicol, S. Repede, and V. Lascar, *Bull. Inst. Politeh. Iasi, Sect. 2*, **25**, 17 (1980); O. Yamauchi and A. Odani, *J. Am. Chem. Soc.*, **103**, 391 (1981).

8) E. A. Sullivan, *Can. J. Chem.*, **57**, 62 (1979).

9) H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **40**, 2584 (1967).

10) M. Suzuki and Y. Nishida, *Inorg. Chim. Acta*, **34**, 61 (1979).

11) K. Nakayama, T. Komorita, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, **54**, 1056 (1981).

12) M. C. Lim and R. B. Martin, *J. Inorg. Nucl. Chem.*, **38**, 1911 (1976).

13) L. E. Erickson, J. E. Sarneski, and C. N. Reilley, *Inorg. Chem.*, **14**, 3007 (1975); S. Yano, T. Tukuda, M. Saburi, and S. Yoshikawa, *ibid.*, **17**, 2520 (1978); T. Ama and T. Yasui, *Bull. Chem. Soc. Jpn.*, **52**, 79 (1979).

14) INEPT=Insensitive Nuclei Enhanced by Polarization Transfer; G. A. Morris and R. Freeman, *J. Am. Chem. Soc.*, **101**, 760 (1979).

15) It was confirmed by $^{13}$C NMR spectra that the crystals formed in the aged solution comprised only one isomer; therefore, the distribution of the isomers in solid state seems to depend on the synthetic method adopted.

16) K. M. Wellman and B. -K. Wong, *J. Chem. Soc., Chem. Commun.*, **1969**, 1213.

17) B. Bosnich and E. A. Sullivan, *Inorg. Chem.*, **14**, 2768 (1975).

18) Y. Nakayama, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **52**, 1377 (1979).

19) K. Nakayama, T. Komorita, and Y. Shimura, unpublished work.