

Electronic Absorption, Magnetic Circular Dichroism, and Circular Dichroism Spectra of *cis*- and *trans*-[Pd(Cl)₂(N)₂]-type Complexes and Their Electronic Structures

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The electronic absorption and MCD spectra of [PdCl₂L] (L=ethylenediamine(en), 1,3-propanediamine, *N,N*-dimethylethylenediamine, *N,N'*-dimethylethylenediamine, *N,N*-diethylethylenediamine, and *N,N*-dimethyl-1,3-propanediamine) and *trans*-[PdCl₂(L)₂] (L=EtNH₂, Me₂NH, Me₃N, *n*-BuNH₂, *i*-BuNH₂, *s*-BuNH₂, *t*-BuNH₂, and *rac*-pea (pea=1-phenylethylamine)), and CD spectra of [PdCl₂L] (L=(*S*)-1,2-propanediamine-(*S*-pn) and (2*S*)-*N*¹,*N*¹-diethyl-1,2-propanediamine) and *trans*-[PdCl₂(*S*-pea)₂] have been measured over the visible-near UV region, together with the corresponding spectra of [PtCl₂L] (L=en and *S*-pn). The examination of the three kinds of spectra as well as their Gaussian analyses indicates that the splitting pattern of metal d orbitals for the *cis* type complexes is similar to that for [PdCl₄]²⁻, and that as to the *trans* complexes the d_{x²-y²}←d_{xz} and d_{yz} transitions split largely to give apparent two spin-allowed d-d bands characteristic of the *trans* complexes. The average energy of the d_{x²-y²}←d_{xz} and d_{yz} transitions for the *trans* complexes is approximately equal to the energy of the d_{x²-y²}←d_{xz,yz} (D_{4h}) ones for the *cis* complexes. The transition energies of d_{x²-y²}←d_{xy} and d_z do not differ largely between both types of complexes. The assignments of high-intensity bands have also been made tentatively.

Palladium(II) complexes generally exhibit a less informative d-d absorption spectrum than the platinum analogs because of a small splitting of the metal d orbitals. Although three spin-allowed d-d bands are expected in a D_{4h} symmetry (or four in D_{2h}), most of palladium(II) complexes exhibit only a single unsymmetrical band. This situation makes assignment difficult for the d-d spectra of palladium(II) complexes. In the case of [PdCl₄]²⁻,¹⁾ the difficulty could be overcome by a concurrent examination of the MCD and absorption spectra and by a comparison with the corresponding spectra of [PtCl₄]²⁻.

There have been known a few rare examples exhibiting a distinct splitting of spin-allowed d-d bands.^{2,3)} The typical examples are *trans*-[Pd(Cl)₂(N)₂]-type complexes,²⁾ but there has been no detailed investigation of them. Although the electronic and CD spectra of some complexes of *cis*-[M(Cl)₂(N)₂]-type (M=Pt and Pd) were reported by Ito *et al.*,⁴⁾ the discussion of electronic structure was almost limited to the platinum complexes. The concurrent study of *cis*- and *trans*-[Pd(Cl)₂(N)₂]-type complexes is desirable to understand systematically the electronic structure of square-planar palladium(II) complexes.

This paper presents new spectral assignment for *cis*- and *trans*-[Pd(Cl)₂(N)₂]-type complexes on the basis of the absorption, MCD, and CD spectra and their Gaussian analysis. These spectral and analytical data have been compared with those of [PdCl₄]²⁻¹⁾ and [PtCl₂(en)]; a similarity of spectra and electronic structure such as noted between [PtCl₄]²⁻ and [PdCl₄]²⁻¹⁾ is also found between [PtCl₂(en)] and [PdCl₂(en)]. Although every *cis*-[Pd(Cl)₂(N)₂]-type complex gives MCD with a nearly ideal A-term pattern in the spin-allowed d-d region, the MCD is based not only on a transition to a degenerate excited state but on all the spin-allowed d-d transitions. Each of four transitions of the *trans* complexes proves to exhibit either CD or MCD selectively. In addition, the

relationship between the electronic structures of the *cis* and the *trans* complexes has been discussed in detail.

Experimental

trans-[PdCl₂(L)₂] Complexes. 1) L=MeNH₂: Palladium chloride (350 mg) was mixed with an aqueous solution of methylamine (20%, 10 cm³). The mixture was heated at ca. 50 °C with stirring to give an almost colorless solution. After filtration the filtrate cooled was treated with concentrated hydrochloric acid (430 mg), giving yellow needles, which were collected, washed with water, ethanol, and ether; and dried *in vacuo*. Yield: 415 mg. Found: C, 10.13; H, 4.20; N, 11.71%. Calcd for *trans*-[PdCl₂(MeNH₂)₂]=C₂H₁₀N₂Cl₂Pd: C, 10.03; H, 4.21; N, 11.70%.

2) L=Me₂NH, EtNH₂, *n*-PrNH₂, and *n*-BuNH₂: Each of these complexes was obtained in good yield by a method similar to that in 1). Found: C, 18.05; H, 5.27; N, 10.55%. Calcd for *trans*-[PdCl₂(Me₂NH)₂]=C₄H₁₄N₂Cl₂Pd: C, 17.96; H, 5.28; N, 10.47%. Found: C, 17.99; H, 5.25; N, 10.52%. Calcd for *trans*-[PdCl₂(EtNH₂)₂]=C₄H₁₄N₂Cl₂Pd: C, 17.96; H, 5.28; N, 10.47%. Found: C, 24.51; H, 6.10; N, 9.50%. Calcd for *trans*-[PdCl₂(*n*-PrNH₂)₂]=C₆H₁₈N₂Cl₂Pd: C, 24.38; H, 6.14; N, 9.48%. Found: C, 29.58; H, 6.82; N, 8.64%. Calcd for *trans*-[PdCl₂(*n*-BuNH₂)₂]=C₈H₂₂N₂Cl₂Pd: C, 29.69; H, 6.85; N, 8.66%.

3) L=Me₃N: After bis(benzonitrile)dichloropalladium(II)⁵⁾ (400 mg) had been dissolved in 2 cm³ of acetone at 50 °C, a small amount of undissolved solid was filtered off and washed with a minimum volume of acetone. An aqueous solution of trimethylamine (30%, 450 mg) was added dropwise to the combined filtrate and washings, with stirring at room temperature. Continuous stirring and cooling gave orange-brown crystals, which were collected, washed with cold acetone, and dried *in vacuo*. Yield: 150 mg. Found: C, 24.50; H, 6.10; N, 9.41%. Calcd for *trans*-[PdCl₂(Me₃N)₂]=C₆H₁₈N₂Cl₂Pd: C, 24.38; H, 6.14; N, 9.48%.

4) L=Et₂NH: Diethylamine (99%, 160 mg) diluted with acetone (1 cm³) was added dropwise to a solution (filtered if necessary) of bis(benzonitrile)dichloropalladium(II) (400 mg) in acetone (8 cm³), with stirring at room temperature. After 1.5 hours of stirring, the desired orange-yellow product was filtered off, washed with water, ethanol, and ether;

and dried *in vacuo*. Yield: 220 mg. Found: C, 29.99; H, 6.87; N, 8.56%. Calcd for *trans*-[PdCl₂(Et₂NH)₂]=C₈H₂₂N₂Cl₂Pd: C, 29.69; H, 6.85; N, 8.66%.

5) *L*=*i*-PrNH₂: This was prepared by a method similar to that in 4). The crude product was recrystallized from *N,N*-dimethylformamide at ca. 80 °C. Found: C, 24.56; H, 6.19; N, 9.51%. Calcd for *trans*-[PdCl₂(*i*-PrNH₂)₂]=C₆H₁₈N₂Cl₂Pd: C, 24.38; H, 6.14; N, 9.48%.

6) *L*=*s*-BuNH₂: An acetone solution (1 cm³) of *s*-butylamine (153 mg) was added dropwise with stirring to a solution of bis(benzonitrile)dichloropalladium(II) (400 mg) in acetone (4.5 cm³). The mixture was stirred for half an hour and then concentrated to about one-fourth of its original volume. Yellow crystals were obtained from the concentrate by addition of ether followed by stirring for 2 h in an ice-bath. Yield: 230 mg. Found: C, 29.83; H, 6.89; N, 8.67%. Calcd for *trans*-[PdCl₂(*s*-BuNH₂)₂]=C₈H₂₂N₂Cl₂Pd: C, 29.69; H, 6.85; N, 8.66%.

7) *L*=*i*-BuNH₂ and *rac*-pea: These were prepared in the same way as in 6). In the case of the *rac*-pea complex, the crude product was recrystallized from carbon tetrachloride at ca. 70 °C. Found: C, 29.78; H, 6.81; N, 8.71%. Calcd for *trans*-[PdCl₂(*i*-BuNH₂)₂]=C₈H₂₂N₂Cl₂Pd: C, 29.69; H, 6.85; N, 8.66%. Found: C, 35.65; H, 3.87; N, 4.84%. Calcd for *trans*-[PdCl₂(*rac*-pea)₂].CCl₄=C₁₇H₂₂N₂Cl₆Pd: C, 35.60; H, 3.87; N, 4.88%.

8) *L*=*t*-BuNH₂: This was prepared in the same manner as in 4), but a twofold concentration was adopted for the reaction mixture. The crude product was recrystallized from *N,N*-dimethylformamide at 70–75 °C. Found: C, 29.86; H, 6.85; N, 8.67%. Calcd for *trans*-[PdCl₂(*t*-BuNH₂)₂]=C₈H₂₂N₂Cl₂Pd: C, 29.69; H, 6.85; N, 8.66%.

9) *L*=*S*-pea: This complex was obtained by a method similar to that of Bosnich.² Found: C, 40.89; H, 4.61; N, 5.77%. Calcd for *trans*-[PdCl₂(*S*-pea)₂].0.4CCl₄=C₁₆.4H₂₂N₂Cl_{3.6}Pd: C, 40.93; H, 4.61; N, 5.82%.

[PdCl₂L] Complexes. *L*=*en*, *S*-*pn*, *tn*, *N,N*-Me₂en, *N,N'*-Me₂en, *N,N*-Et₂en, *N*¹,*N*¹-Et₂(*S*)-*pn*, and *N,N*-Me₂tn: These complexes were prepared according to the methods described in the literature⁶ or ones similar to them.

[PtCl₂L] Complexes. *L*=*en* and *S*-*pn*: These were obtained by a method similar to that reported⁷ (K₂PtCl₄: ligand=1:1).

Measurements. Electronic absorption, MCD, and CD spectra were recorded with the same apparatus and in the same manner as described elsewhere.^{1,6} Spectral measurements of *trans*-[Pd(Cl)₂(N)₂]-type complexes were made in DCE (1,2-dichloroethane) and in methanol, and *cis*-[Pd-(Cl)₂(N)₂]- and *cis*-[Pt(Cl)₂(N)₂]-type ones in 0.20 M KCl and 0.50 M HCl aqueous solutions, respectively, all at room temperature (1 M=1 mol dm⁻³). No spectra of *trans*-[PdCl₂L₂] (*L*=MeNH₂, Et₂NH, *n*-PrNH₂, and *i*-PrNH₂) could be obtained because of their virtual insolubility in both DCE and methanol, and the spectrum of *trans*-[PdCl₂(Me₃N)₂] in methanol could not be obtained because of its decomposition in the solvent.

Gaussian Analyses. Gaussian analyses of absorption, MCD, and CD spectra were carried out in the same way as described previously.¹ Standard deviations given in Tables 2, 6, 7, 12, and 13 are from the observed values of ϵ , $\Delta\epsilon$, or $\Delta\epsilon_M$ for the corresponding calculated values.

Results and Discussion

Ligand-field Absorption Bands. The typical electronic absorption spectra of *cis*- and *trans*-[Pd-(Cl)₂(N)₂]-type complexes⁸ are shown in Fig. 1. The absorption curves of the *cis* complexes are composed

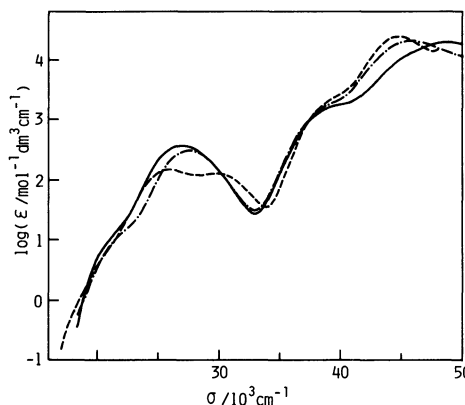


Fig. 1. A comparison of the absorption spectra of typical *cis*- and *trans*-[Pd(Cl)₂(N)₂]-type complexes. —: [PdCl₂(*en*)] in 0.20 M KCl. ---: [PdCl₂(*tn*)] in 0.20 M KCl. - · - ·: *trans*-[PdCl₂(EtNH₂)₂] in DCE.

of an unsymmetrical main band (spin-allowed d-d band) and a lower-lying shoulder (spin-forbidden d-d band) in the ligand field transition region, being similar to that of [PdCl₄]²⁻.¹¹ On the other hand, the spin-allowed d-d band of the *trans* complex, spreads toward both high and low energies as compared with those of the *cis* complexes to split into two bands (Fig. 1). Although such a distinct splitting has not been found in the ligand field absorption spectra of *trans*-[Pd(*S*-ala)₂]⁹ and *trans*-[Pd(*N*-Megly)₂]¹⁰ one shoulder and one peak have been observed corresponding to the split bands. Therefore, it is reasonable to consider that the difference in ligand-field strength between two kinds of ligating atoms mainly determines the magnitude of the splitting.

For simplicity, we discuss the electronic structure of *cis*- and *trans*-[Pd(Cl)₂(N)₂]-type complexes under holohedrized symmetries.¹¹ Namely, the *cis* and *trans* complexes are approximately described by D_{4h} and D_{2h} symmetries, respectively. Then, the *cis* complexes should give rise to three spin-allowed d-d transitions (¹A_{2g}, ¹B_{1g}, and ¹E_g←¹A_{1g}) similarly to [PdCl₄]²⁻; and the *trans* complexes four (¹A_g, ¹B_{1g}, ¹B_{2g}, and ¹B_{3g}←¹A_g).

In the preceding paper,¹¹ we demonstrated that the absorption and MCD spectra of [PdCl₄]²⁻ can be easily correlated with those of the platinum analog, [PtCl₄]²⁻, by taking into account two points: firstly the energy separation of the Γ₂(¹A_{2g}) and Γ₅(¹E_g) excited states is considerably large in the latter complex in comparison with the former; and secondly, in [PtCl₄]²⁻ singlet-triplet transitions remarkably increase in absorption and MCD intensities and give more complicated spectra. Such a spectral resemblance between palladium and platinum complexes has been also found in [MCl_n(OH₂)_{4-n}]²⁻ⁿ (M=Pd and Pt; *n*=0–4).¹² Thus, it is helpful to examine first the spectra of [PtCl₂(*en* or *S*-*pn*)], which is expected to exhibit larger energy separations between d-d excited states than the palladium analog.

1) [PtCl₂(*en* or *S*-*pn*)] Complex: The absorption, MCD, and CD spectra are shown in Fig. 2 together

TABLE 1. SPECTRAL DATA OF $[\text{PtCl}_2\text{L}]$ COMPLEXES

L=en				L=S-pn	
Absorption		MCD		CD	
$\sigma_{\max}$ 10^3 cm^{-1}	ϵ $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	σ_{ext} 10^3 cm^{-1}	$\Delta\epsilon_M$ $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1} \text{ T}^{-1}$	σ_{ext} 10^3 cm^{-1}	$\Delta\epsilon$ $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$
27.8 sh ^{a)}	35	24.0	+0.0015		
		27.2	−0.0035	26.6	−0.13
		30.6	+0.0077		
33.28	240	34.4	+0.0089	33 sh	−0.1
37.5 sh	117	38.1	−0.018	36.7	−0.46
48.76	6500	45.4	−1.1	45.2	+1.2

a) sh: shoulder (ϵ or $\Delta\epsilon$ is for the value of σ given).

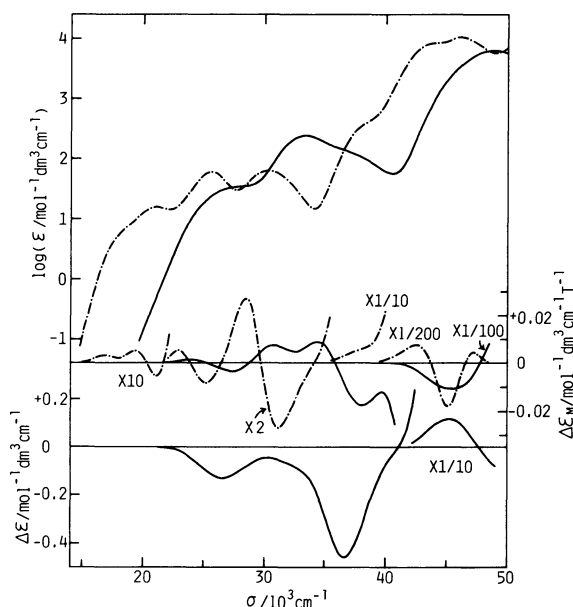


Fig. 2. Absorption and MCD spectra of $[\text{PtCl}_2(\text{en})]$ (—) and $\text{K}_2[\text{PtCl}_4]$ (---); and CD spectrum of $[\text{PtCl}_2(\text{S-pn})]$ (—), all in 0.50 M HCl.

with the absorption and MCD spectra of $[\text{PtCl}_4]^{2-}$, and the numerical data in Table 1. Although the splitting of the d-d absorption band of $[\text{PtCl}_2(\text{en})]$ is not so pronounced as observed for $[\text{PtCl}_4]^{2-}$, these two spectra can be easily correlated to each other. Such a correlation is also observed between their MCD spectra, except that the band corresponding to a negative band at $25.2 \times 10^3 \text{ cm}^{-1}$ of $[\text{PtCl}_4]^{2-}$ disappears in $[\text{PtCl}_2(\text{en})]$ (Fig. 2). The dispersion of MCD at $ca. 36 \times 10^3 \text{ cm}^{-1}$ is considered to be primarily composed of a negative A term, and assigned to the $\Gamma_5(^1E_g) \leftarrow \Gamma_1(^1A_{1g})$ transition. The dispersion changes sign around the middle of the whole spin-allowed d-d absorption band. From this fact and the similarities to $[\text{PtCl}_4]^{2-}$ as described above, the $\Gamma_2(^1A_{2g})$ and $\Gamma_3(^1B_{1g}) \leftarrow \Gamma_1(^1A_{1g})$ transition components are reasonably considered to lie in the lower and higher energy side of the $\Gamma_5(^1E_g) \leftarrow \Gamma_1(^1A_{1g})$ transition, respectively. The results of Gaussian analysis on the basis of this deduction are tabulated in Table 2, together with

TABLE 2. GAUSSIAN-ANALYSIS DATA FOR THE ABSORPTION CURVE OF $[\text{PtCl}_2(\text{en})]$

$\sigma_{\max}$ 10^3 cm^{-1}	ϵ $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	$\Delta\sigma_{1/2}$ 10^3 cm^{-1}	$S^a)$	Assignment ^{b)} $\leftarrow \Gamma_1(^1A_{1g})$
27.3 f ^{c)}	32 f	4.94	168	d)
30.96	12.6	3.89	52.2	$\Gamma_5(^3B_{1g})$
33.04	210	3.57	798	$\Gamma_2(^1A_{2g})$
36.10	111	3.97	471	$\Gamma_5(^1E_g)$
38.89	53.3	3.60	205	$\Gamma_3(^1B_{1g})$
SD ^{e)} = 0.43				

a) $S(\text{band area}) = 1.0645 \times (\epsilon_{\max}/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}) \times (\Delta\sigma_{1/2}/10^3 \text{ cm}^{-1})$. b) On the basis of holohedrized symmetry. c) f: fixed value. d) Spin-forbidden d-d transitions. e) Standard deviation (See Experimental).

the assignment. The three spin-allowed d-d transitions are blue-shifted by $6.8 \times 10^3 \text{ cm}^{-1}$ on the average from $[\text{PtCl}_4]^{2-}$.¹⁾ The blue shift of the $\Gamma_2 \leftarrow \Gamma_1$ transition is larger than the average shift by $0.6 \times 10^3 \text{ cm}^{-1}$, and on the contrary that of the $\Gamma_5 \leftarrow \Gamma_1$ transition is smaller by the same amount; thus the proximity of the Γ_2 and Γ_5 excited states relative to the case of $[\text{PtCl}_4]^{2-}$ makes the splitting of the spin-allowed d-d band less distinct.

The dispersion of MCD at $ca. 36 \times 10^3 \text{ cm}^{-1}$ deviates from an ideal A-term pattern even by assuming such a positive B term as in $[\text{PtCl}_4]^{2-}$ for the $\Gamma_3(^1B_{1g}) \leftarrow \Gamma_1(^1A_{1g})$ transition, which may be due to the reduction of symmetry from D_{4h} . The deformed dispersion pattern further suggests that the $\Gamma_5(^1E_g) \leftarrow \Gamma_1(^1A_{1g})$ transition exhibits a positive B term in addition to a negative A term because the zero point of the dispersion lies at lower energy than the corresponding absorption component obtained by Gaussian analysis. The positive band at $30.6 \times 10^3 \text{ cm}^{-1}$ can be assigned to a positive lobe of the negative A term based on the $\Gamma_5(^3B_{1g}) \leftarrow \Gamma_1(^1A_{1g})$ transition by analogy with $[\text{PtCl}_4]^{2-}$.¹⁾ Then a negative B term is required for the $\Gamma_2(^1A_{2g}) \leftarrow \Gamma_1(^1A_{1g})$ transition in order to reproduce the observed curve because the negative lobe of the negative A term for $\Gamma_5(^3B_{1g}) \leftarrow \Gamma_1(^1A_{1g})$ is expected to be overlapping the band based on $\Gamma_2(^1A_{2g}) \leftarrow \Gamma_1(^1A_{1g})$.

As for the CD spectrum of $[\text{PtCl}_2(\text{S-pn})]$, the shoul-

TABLE 3. ABSORPTION DATA OF [PdCl₂L] COMPLEXES

L=en	<i>N,N</i> -Me ₂ en	<i>N,N'</i> -Me ₂ en $\sigma_{\max}/10^3 \text{ cm}^{-1}$	<i>N,N</i> -Et ₂ en ($\epsilon/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$)	tn	<i>N,N</i> -Me ₂ tn
22.0 sh ^a (17)	22.0 sh (38)	22.1 sh (36)	21.8 sh (35)	22.5 sh (15)	21.7 sh (33)
26.93 (360)	26.31 (425)	26.52 (408)	26.18 (443)	27.59 (300)	26.38 (430)
39.5 sh (1670)	38.0 sh (2030)	38.3 sh (2080)	38.1 sh (2900)	39.3 sh (1860)	36.9 sh (1650)
45.3 sh (11400)	42.6 sh (13200)				
48.97 (19400)	45.34 (20900)	45.50 (21100)	44.80 (18100)	45.81 (20200)	43.40 (20900)

a) sh: shoulder (ϵ is for the value of σ given).TABLE 4. MCD DATA OF [PdCl₂L] COMPLEXES

L=en	<i>N,N</i> -Me ₂ en	<i>N,N'</i> -Me ₂ en $\sigma_{\text{ext}}/10^3 \text{ cm}^{-1}$	<i>N,N</i> -Et ₂ en ($\Delta\epsilon_M/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1} \text{ T}^{-1}$)	tn	<i>N,N</i> -Me ₂ tn
25.8 (+0.022)	25.3 (+0.018)	25.4 (+0.019)	25.1 (+0.016)	26.1 (+0.027)	25.1 (+0.027)
29.1 (−0.023)	28.7 (−0.020)	28.9 (−0.023)	28.3 (−0.021)	29.4 (−0.020)	28.3 (−0.020)
39.3 (+0.36)	37.8 (+0.44)	38.0 (+0.45)	37.6 (+0.45)	39 sh ^a (+0.4)	36.9 (+0.40)
				43.2 (+1.7)	40.7 (+0.88)
47.2 (−0.67)	44.5 (−0.57)	44.5 (−0.59)	44.2 (−0.55)	47.6 (−2.4)	45.0 (−1.5)

a) sh: shoulder.

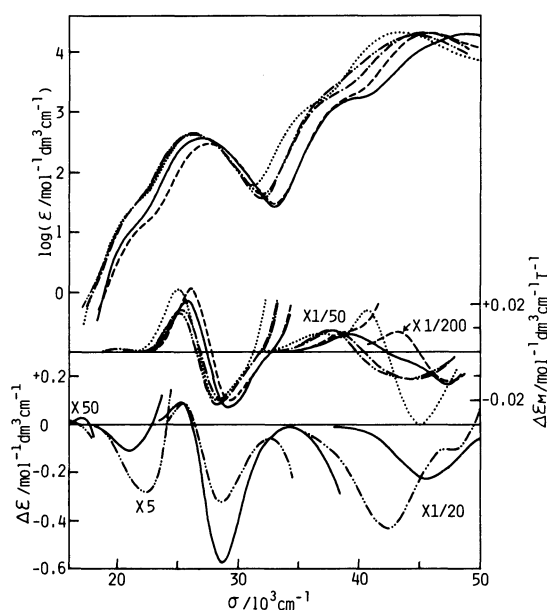


Fig. 3. Absorption, MCD, and CD spectra of [PdCl₂L] in 0.20 M KCl. For absorption and MCD spectra, —: L=en, ----: L=tn, -.-.: L=*N,N*-Me₂en, ---.: L=*N,N*-Et₂en, and: L=*N,N*-Me₂tn; and for CD spectra, —: L=*S*-pn and -.-.: L=*N*¹,*N*¹-Et₂-(*S*)-pn.

der around $33 \times 10^3 \text{ cm}^{-1}$ and the main band at $36.7 \times 10^3 \text{ cm}^{-1}$ were assigned to $\Gamma_2(1A_{2g})$ and $\Gamma_5(1E_g) \leftarrow \Gamma_1(1A_{1g})$, respectively, by Ito *et al.*¹³ However, the latter band lies in somewhat higher energy than the $\Gamma_5(1E_g) \leftarrow \Gamma_1(1A_{1g})$ component obtained by the Gaussian analysis of the absorption spectrum. This fact can be rationalized by considering that the $\Gamma_3(1B_{1g}) \leftarrow \Gamma_1(1A_{1g})$ ($d_{x^2-y^2} \leftarrow d_{z^2}$) transition at $38.9 \times 10^3 \text{ cm}^{-1}$ is exhibiting a weak negative CD band,¹⁴ which is due to the magnetic moment acquired through the reduction

TABLE 5. CD DATA OF [PdCl₂L] COMPLEXES

L= <i>S</i> -pn		L= <i>N</i> ¹ , <i>N</i> ¹ -Et ₂ -(<i>S</i>)-pn	
σ_{ext} 10^3 cm^{-1}	$\Delta\epsilon$ $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	σ_{ext} 10^3 cm^{-1}	$\Delta\epsilon$ $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$
17.2	+0.0006		
21.2	−0.022	22.4	−0.056
25.4	+0.093	25.4	+0.091
28.8	−0.58	28.6	−0.32
45.7	−4.5	42.3	−8.6
		47.6	−2.1

of symmetry (C_{2v} from D_{4h}). This will be demonstrated in the case of [PdCl₂(*S*-pn)] (*vide infra*).

2) [PdCl₂(*en* or *S*-pn)] Complex: The absorption, MCD, and CD data are given in Fig. 3 and Tables 3–5 together with those of the related complexes, and discussed on the basis of the results for [PtCl₂(*en* or *S*-pn)] described above. The spin-allowed d-d band exhibits a swelling in the higher energy side, which corresponds to the shoulder observed at *ca.* $37.5 \times 10^3 \text{ cm}^{-1}$ in [PtCl₂(*en*)]. The relative position of the zero point of the apparent A term (*ca.* $27.4 \times 10^3 \text{ cm}^{-1}$) to the main CD band is also the same as that in [PtCl₂(*en*)]. On the basis of this resemblance, the Gaussian analysis of the absorption spectrum of [PdCl₂(*en*)] was carried out (Table 6). Three spin-allowed d-d components are assigned to $1A_{2g}$, $1E_g$, and $1B_{1g} \leftarrow 1A_{1g}$ from lower energy, which for convenience we denote bands I, II, and III, respectively (Table 6).

Although the MCD spectrum shows a nearly ideal A-term pattern, or dispersion, in the spin-allowed d-d region, the dispersion band is difficult to attribute only to the $1E_g \leftarrow 1A_{1g}$ transition. A positive B term based on the $1B_{1g} \leftarrow 1A_{1g}$ transition is expected to be included in the negative lobe of the dis-

TABLE 6. GAUSSIAN-ANALYSIS DATA FOR THE ABSORPTION CURVES OF $[\text{PdCl}_2\text{L}]$ COMPLEXES

No. ^{a)}	$\frac{\sigma_{\max}}{10^3 \text{ cm}^{-1}}$	$\frac{\epsilon}{\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}}$	$\frac{\Delta\sigma_{1/2}}{10^3 \text{ cm}^{-1}}$	S ^{b)}	$\frac{\sigma_{\max}}{10^3 \text{ cm}^{-1}}$	$\frac{\epsilon}{\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}}$	$\frac{\Delta\sigma_{1/2}}{10^3 \text{ cm}^{-1}}$	S
L=en					L=tn			
	22.0 f ^{c)}	14 f	3.48	51.9	22.5 f	13.5 f	3.50	50.3
I	26.16	270	3.35	963	26.71	195	3.26	676
II	28.07	179	3.07	584	28.32	156	3.02	500
III	30.08	72.8	3.13	243	30.27	69.5	3.13	232
	39.5 f	1600 f	4.70 f		39.3 f	1700 f	4.40 f	
SD ^{d)} =0.46					SD=0.31			
L=N,N-Me ₂ en					L=N,N-Me ₂ tn			
	22.0 f	27.5 f	3.27	95.3	21.7 f	28.5 f	3.32	101
I	25.55	298	3.23	1023	25.51	268	3.18	908
II	27.30	215	3.10	711	27.05	228	2.99	725
III	29.32	85.4	3.16	288	28.98	98.0	3.08	321
	38.0 f	1900 f	4.30 f		36.9 f	1500 f	4.40 f	
SD=0.65					SD=0.64			

a) Band number. b) $S(\text{band area}) = 1.0645 \times (\epsilon_{\text{max}}/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}) \times (\Delta\sigma_{1/2}/10^3 \text{ cm}^{-1})$. c) f: fixed value. d) Standard deviation (See Experimental).

TABLE 7. GAUSSIAN-ANALYSIS DATA FOR THE CD CURVE OF $[\text{PdCl}_2(\text{S-pn})]$

No. ^{b)}	3 components ^{a)}			2 components ^{a)}		
	σ_{ext} 10^3 cm^{-1}	$\Delta\epsilon$ $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	$\Delta\sigma_{1/2}$ 10^3 cm^{-1}	σ_{ext} 10^3 cm^{-1}	$\Delta\epsilon$ $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	$\Delta\sigma_{1/2}$ 10^3 cm^{-1}
	21.2 f ^{c)}	-0.023 f	2.99	21.2 f	-0.023 f	3.00 f
I	25.98	+0.153	2.72	26.05	+0.205	2.66
II	28.42	-0.488	3.17	28.72	-0.583	3.89
III	30.18	-0.183	3.29			
	SD ^{d)} = 2.3×10^{-3}			SD= 4.1×10^{-3}		

a) See text. b) Band number. c) f: fixed value. d) Standard deviation.

persion by analogy with $[\text{PtCl}_4]^{2-}$ and $[\text{PdCl}_4]^{2-}$.¹⁾ Moreover, a positive B term in addition to a negative A term is assigned to ${}^1\text{E}_g \leftarrow {}^1\text{A}_{1g}$ because the dispersion changes sign at lower energy than the corresponding absorption component (band II) obtained by Gaussian analysis; the situation resembles that in $[\text{PtCl}_2(\text{en})]$. A negative B term is consequently predicted for band I in order to reproduce the observed MCD curve. The prediction is parallel with that made on a different basis in the case of $[\text{PtCl}_2(\text{en})]$. As the MCD spectra of *cis*- $[\text{M}(\text{Cl})_2(\text{N})_2]$ -type complexes (M=Pt and Pd) are of a poor precision because of low solubility of the complexes, their Gaussian analyses were not performed. However, it was found that the MCD as well as the absorption spectra of $[\text{PtCl}_2(\text{en})]$ and $[\text{PdCl}_2(\text{en})]$ nicely corresponded to each other.

The CD spectrum of $[\text{PdCl}_2(\text{S-pn})]$ was analyzed by assuming two or three components in the spin-allowed d-d region (Table 7.) The component corresponding to the ${}^1\text{B}_{1g} \leftarrow {}^1\text{A}_{1g}$ transition (which is magnetic dipole forbidden in a D_{4h} symmetry) is neglected in the former case, where the half-value width of the negative band became rather wide relative to that of the positive band. The two-component case is fur-

TABLE 8. BAND SHAPE PARAMETERS FOR THE SPIN-ALLOWED d-d BAND OF $[\text{PdCl}_2\text{L}]$ COMPLEXES

L	$\Delta\sigma^{-\text{a})}$ 10^3 cm^{-1}	$\Delta\sigma^{+\text{a})}$ 10^3 cm^{-1}	$\Delta\sigma_{1/2}^{\text{a})}$ 10^3 cm^{-1}	Unsymmetry parameter ^{b)}
en	2.14	2.61	4.75	9.9
N,N-Me ₂ en	2.04	2.46	4.51	9.3
N,N'-Me ₂ en	2.11	2.56	4.67	9.6
N,N-Et ₂ en	2.07	2.47	4.54	8.8
tn	2.07	2.36	4.43	6.5
N,N-Me ₂ tn	2.01	2.28	4.30	6.3
cf. K ₂ [PdCl ₄]	1.68	2.44	4.12	18.4

a) See text; these parameters are obtained from the observed intact absorption curve, not by Gaussian analysis.¹⁵⁾ b) See text.

ther inferior to the three-component one with respect to coincidence between the positions of the CD and absorption components for band II and to standard deviation. Thus, it seems reasonable to assign a weak negative CD band to the ${}^1\text{B}_{1g} \leftarrow {}^1\text{A}_{1g}$ transition, as expected in the case of $[\text{PtCl}_2(\text{S-pn})]$.

3) Other *cis*- $[\text{Pd}(\text{Cl})_2(\text{N})_2]$ -type Complexes: It is concluded that these complexes possess the same elec-

tronic structure with regard to metal d orbitals as [PdCl₂(en)] from the similarity of their absorption, MCD, and CD spectra. The spin-allowed d-d absorption bands are similarly unsymmetrical. We characterize the band shape by half-value width parameters¹⁵⁾ $\Delta\sigma^-$, $\Delta\sigma^+$, and $\Delta\sigma_{1/2}$ ($\epsilon=\epsilon_{\max}/2$ at $\sigma=\sigma_{\max}-\Delta\sigma^-$ and $\sigma_{\max}+\Delta\sigma^+$; and $\Delta\sigma_{1/2}=\Delta\sigma^-+\Delta\sigma^+$) and unsymmetry parameter, $(\Delta\sigma^+-\Delta\sigma^-/\Delta\sigma_{1/2})\times 100$. The parameters for the *cis*-[Pd(Cl)₂(N)₂]-type complexes are given in Table 8, which leads to the following findings. (1) $\Delta\sigma^+$ is larger than $\Delta\sigma^-$ for all the complexes. The bands of the complexes with a five-membered chelate ring are (2) more highly unsymmetrical and (3) wider than those of the complexes with a six-membered chelate ring. (4) An introduction of alkyl groups on amine nitrogen atom(s) makes the band widths smaller; this is more pronounced with tertiary amine than with secondary amine. It is interesting to interpret the findings in terms of the results of Gaussian analysis for the absorption spectra. Findings (1) and (2) can be explained primarily by the relative position of band II. The band II's of the en, *N,N*-Me₂en, tn, and *N,N*-Me₂tn complexes lie at energies higher than the observed absorption peaks by 1.14, 0.99, 0.77, and 0.67 $\times 10^3$ cm⁻¹, respectively. The unsymmetry parameters decrease in this order. Findings (3) and (4) are attributable to a variation in the energy difference between the three bands, particularly between bands I and II. Accordingly, the transition energy of band I (¹A_{2g}←¹A_{1g}) is affected by the variation of ligands in a different fashion from those of the other two bands (*i.e.* ¹E_g and ¹B_{1g}←¹A_{1g}). This result is compatible with the assignment of band I to an electronic transition in the coordination plane.

The MCD spectra in the d-d transition region are

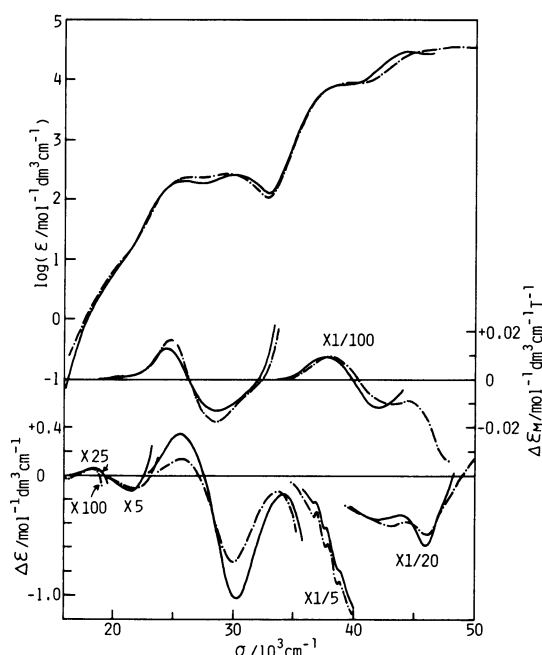


Fig. 4. Absorption and MCD spectra of *trans*-[PdCl₂(*rac*-pea)₂], and CD spectra of *trans*-[PdCl₂(*S*-pea)₂]. —: in DCE and - - -: in methanol.

similar to one another and shifted together with the absorption spectra by the variation of ligands, which suggests that all the complexes possess a common electronic structure. A detailed examination of the MCD spectra shows that the intensity ratio of the positive to the negative lobe of the dispersion gives its larger absolute value for the complexes with a six-membered chelate ring than for those with a five-membered one.

The CD pattern of [PdCl₂(*N*¹,*N*¹-Et₂(*S*)-pn)] is similar to that of [PdCl₂(*S*-pn)] (Fig. 3). The negative band in the spin-forbidden d-d region becomes intense as compared with [PdCl₂(*S*-pn)], whereas the main negative band in the spin-allowed d-d

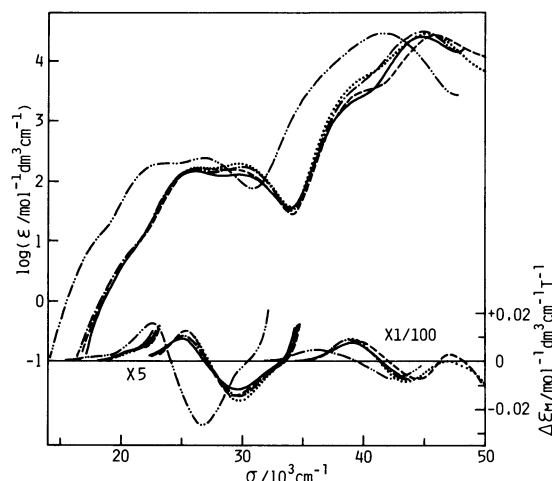


Fig. 5. Absorption and MCD spectra of *trans*-[PdCl₂L₂]. —: L=EtNH₂ in DCE, - - -: L=EtNH₂ in methanol, — · —: L=Me₂NH in DCE, · · · ·: L=Me₂NH in methanol, and - - - -: L=Me₃N in DCE.

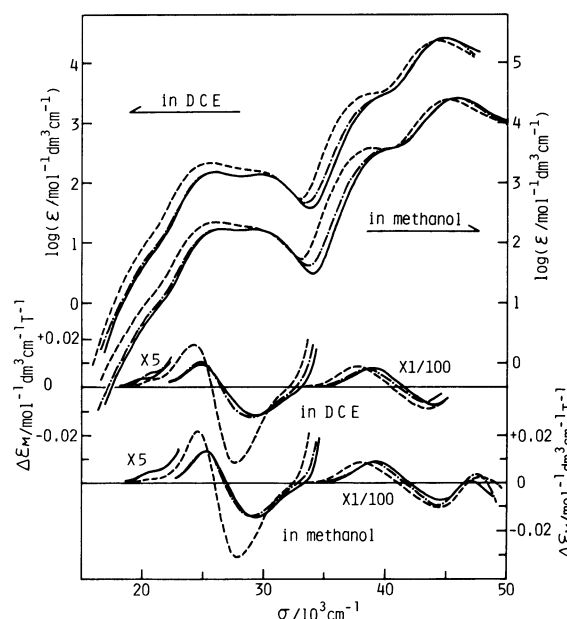


Fig. 6. Absorption and MCD spectra of *trans*-[PdCl₂L₂] in DCE and methanol. —: L=*n*-BuNH₂, — · —: L=*s*-BuNH₂, and - - -: L=*t*-BuNH₂.

TABLE 9. ABSORPTION, MCD, AND CD DATA OF *trans*-[PdCl₂(pea)₂]^a

Absorption			MCD		CD		Absorption			MCD		CD	
$\sigma_{\max}$ 10^3 cm^{-1}	ϵ $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	σ_{ext} 10^3 cm^{-1}	$\Delta\epsilon_{\text{M}}$ $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1} \text{ T}^{-1}$	σ_{ext} 10^3 cm^{-1}	$\Delta\epsilon$ $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$		$\sigma_{\max}$ 10^3 cm^{-1}	ϵ $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	σ_{ext} 10^3 cm^{-1}	$\Delta\epsilon_{\text{M}}$ $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1} \text{ T}^{-1}$	σ_{ext} 10^3 cm^{-1}	$\Delta\epsilon$ $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	
in DCE													
21.3 sh ^{b)}	13	21.5 sh 24.5	+0.0020 +0.013	18.5 21.6	+0.0026 -0.025		21.2 sh	13	21 sh 24.8	+0.0017 +0.017	16.4 18.4 21.9	-0.0004 +0.0005 -0.023	
25.81	200	28.6	-0.013	25.7	+0.34		26.53	236	28.6	-0.018	25.8	+0.14	
30.08	255			30.3 36.6 37.5	-1.02 -1.1 -2.2		29.44	264			30.1 36.7 37.7	-0.72 -1.7 -3.0	
39 sh	8200	37.6	+1.0	38.7 sh 39.5 sh 42.0	-3.9 -5.0 -7.3				38.0	+1.0	38.6 39.6 sh 43.0	-4.5 -5.5 -8.4	
44.35	28200	42.0	-1.2	45.8	-11.7		45.2 sh 48.26	29000 35700			46.0	-9.9	

a) Absorption and MCD data are for *rac*-pea complex, and CD ones for *S*-pea complex. b) sh: shoulder (ϵ , $\Delta\epsilon_M$, or $\Delta\epsilon$ is for the value of σ given).TABLE 10. ABSORPTION DATA OF *trans*-[PdCl₂L₂] COMPLEXES

L = EtNH ₂	Me ₂ NH	Me ₃ N $\sigma_{\max}/10^3 \text{ cm}^{-1}$	<i>n</i> -BuNH ₂ ($\epsilon/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$)	<i>i</i> -BuNH ₂	<i>s</i> -BuNH ₂	<i>t</i> -BuNH ₂	
			in DCE				
21.5 sh ^a	(9.6)	19.0 sh	(18)	21.5 sh	(10)	21.1 sh	(17)
25.90	(147)	23.72	(202)	25.97	(152)	25.53	(215)
29.74	(128)	26.82	(240)	29.85	(138)	29.6 sh	(156)
39.8 sh	(2500)	36.7 sh	(6300)	39.8 sh	(2900)	38.6 sh	(3000)
44.80	(24300)	41.67	(28000)	44.86	(25800)	44.33	(23000)
			in methanol				
21.5 sh	(9.2)	21.3 sh	(9.0)	21.5 sh	(9.5)	21.1 sh	(16)
26.56	(163)	26.49	(171)	26.67	(173)	26.04	(225)
29.2	(158)	29.63	(196)	28.99	(168)	29.4 sh	(177)
40.1 sh	(3200)	39.7 sh	(5100)	40.1 sh	(3600)	38.94	(3680)
45.85	(26200)	45.27	(28300)	45.79	(26400)	45.21	(24300)

a) sh: shoulder (ϵ is for the value of σ given). b) Decomposition.

TABLE 11. MCD DATA OF *trans*-[PdCl₂L₂] COMPLEXES

L = EtNH ₂	Me ₂ NH	Me ₃ N	$\sigma_{\text{ext}}/10^3 \text{ cm}^{-1}$	<i>n</i> -BuNH ₂ ($\Delta\epsilon_M/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1} \text{ T}^{-1}$)	<i>i</i> -BuNH ₂	<i>s</i> -BuNH ₂	<i>t</i> -BuNH ₂
				in DCE			
21 sh ^a (+0.001)	21 sh (+0.001)	18 sh (+0.002)	20.5 sh (+0.0007)	21 sh (+0.0012)	21 sh (+0.0013)	21 sh (+0.0031)	
25.1 (+0.0094)	25.2 (+0.011)	22.5 (+0.016)	24.9 (+0.0095)	24.8 (+0.010)	24.9 (+0.011)	24.2 (+0.018)	
29.7 (-0.012)	29.7 (-0.014)	26.7 (-0.027)	29.4 (-0.012)	29.3 (-0.011)	29.0 (-0.012)	27.7 (-0.032)	
39.1 (+0.08)	38.8 (+0.9)	36.0 (+0.5)	39.0 (+0.8)	38.9 (+0.8)	38.5 (+0.8)	37.7 (+0.9)	
		42.3 (-0.7)	43.9 (-0.7)		43.3 (-0.6)	43.6 (-0.9)	
			in methanol				
21.5 sh (+0.001)	21 sh (+0.001)		21 sh (+0.001)	21 sh (+0.0010)	21 sh (+0.0010)	21 sh (+0.0019)	
25.4 (+0.013)	25.4 (+0.013)		25.3 (+0.013)	25.2 (+0.013)	25.2 (+0.013)	24.5 (+0.022)	
29.4 (-0.014)	29.8 (-0.016)	b)	29.4 (-0.014)	29.1 (-0.014)	28.9 (-0.014)	27.8 (-0.031)	
39.4 (+0.8)	39.0 (+1.0)		39.3 (+0.9)	39.3 (+0.9)	39.0 (+0.9)	38.0 (+0.9)	
44.6 (-0.7)	43.4 (-0.9)		44.5 (-0.7)	44.1 (-0.9)	44.2 (-0.9)	44.4 (-1.0)	
47.0 (+0.3)					47.4 (+0.4)	47.7 (+0.2)	

a) sh: shoulder ($\Delta\epsilon_M$ is for the value of σ given). b) Decomposition.TABLE 12. GAUSSIAN-ANALYSIS DATA FOR THE SPECTRA OF *trans*-[PdCl₂(pea)₂]

No. a)	Absorption			MCD			CD		
	$\sigma_{\text{max}}/10^3 \text{ cm}^{-1}$	ϵ $\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$	$\Delta\sigma_{1/2}/10^3 \text{ cm}^{-1}$	$S^{b)}$	$\sigma_{\text{ext}}/10^3 \text{ cm}^{-1}$	$\Delta\epsilon_M/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1} \text{ T}^{-1}$	$\Delta\sigma_{1/2}/10^3 \text{ cm}^{-1}$	$\sigma_{\text{ext}}/10^3 \text{ cm}^{-1}$	$\Delta\epsilon/\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$
1	21.3 f ^{c)}	10 f	3.16	33.6	21.5 f	+0.0017 f	2.38	21.8 f	-0.028 f
	24.70	101	3.08	331	24.69	+0.0145	2.89	24.74	+0.145
2	26.53	142	3.49	526	26.44	-0.0024	3.15	26.18	+0.280
3	29.21	110	3.11	363	28.56	-0.0115	3.62	29.67	-0.170
4	30.95	187	3.55	706	30.68	-0.0029	3.26	30.55	-0.896
	38.3 f	7600 f	4.00 f		37.6 f	+0.97 f	4.00 f		
		SD ^{d)} = 0.54				SD = 0.00011			SD = 0.0036

a—d) As in Table 6.

region weak. This observation can be explained by considering that the spin-forbidden transition takes its intensity from the spin-allowed transition through an increased spin-orbit coupling and that substantial cancellation occurs between bands I and II which have a CD sign opposite to each other.

4) *trans*-[Pd(Cl)₂(N)₂]-type Complexes: The absorption, MCD, and CD data are given in Figs. 4–6 and Tables 9–11. Since absorption spectra in DCE show a more distinct splitting in the d-d transition region than those in methanol, the data in DCE will be primarily used in the following discussion on the d-d transitions. At first, we will examine *trans*-[PdCl₂(*rac*- or *S*-pea)₂] complex, for which all the

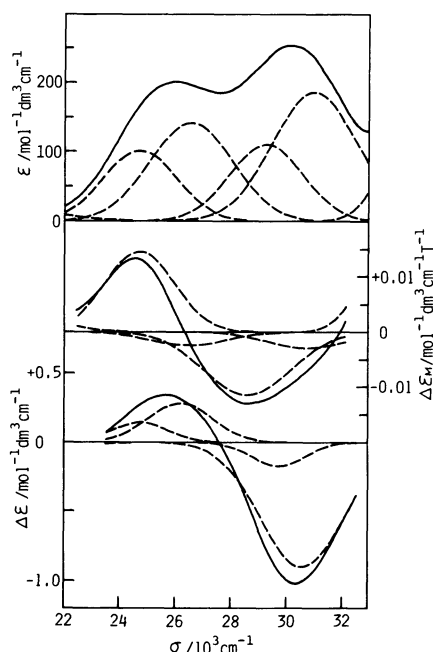


Fig. 7. Gaussian analysis curves for three spectra of *trans*-[PdCl₂(pea)₂] in DCE. ----: Gaussian components and —: sum of them.

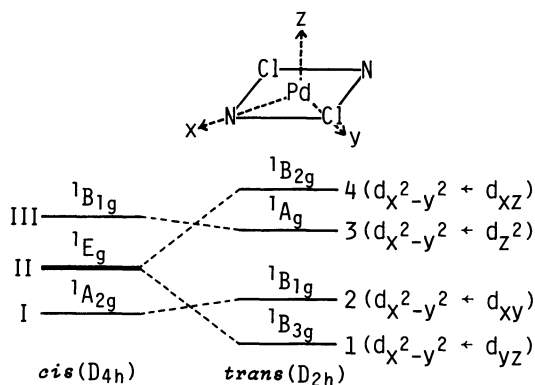


Fig. 8. The orderings of the singlet excited states arising from d-d transitions for *cis*- and *trans*-[Pd(Cl)₂(N)₂]-type complexes (on the basis of holohedrized symmetry) and the relation between them. I—III and 1—4 represent component band numbers of the *cis* and *trans* complexes, respectively (See also Tables 6, 12, and 13).

three kinds of spectra are available. The MCD and the CD spectrum each exhibit a positive and a negative band in the spin-allowed d-d region, and the positions of these four (two MCD and two CD) bands are different from one another. It is sufficient to take into account only B terms for an interpretation of the MCD because the complex has no degenerate excited state. Therefore, it is reasonable to consider that the four bands approximately correspond one by one to the four spin-allowed d-d transitions. On the basis of this consideration, the Gaussian analyses of the three spectra were carried out (Fig. 7 and Table 12). We denote the four components bands 1, 2, 3, and 4 from lower energy (Table 12). The assignment of the bands will be made in the following paragraph.

The Gaussian analyses of absorption spectra for the other *trans* complexes were performed by analogy with the case of the pea complex (Table 13). In assigning the spectra of the *trans* complexes, it is helpful to compare them with those of the *cis* analogs. It is *trans*-[PdCl₂(EtNH₂)₂] that is most suited for a comparison with [PdCl₂(en or tn)]. The transition energies for bands 2 and 3 of *trans*-[PdCl₂(EtNH₂)₂] are close to those for bands I and III of [PdCl₂(en or tn)], respectively, and the average energy of bands 1 and 4 of the *trans* complex to the energy of band II of the *cis* complex (Tables 6 and 13). From these facts, bands 1, 2, 3, and 4 can be assigned to ¹B_{3g}, ¹B_{1g}, ¹A_g, and ¹B_{2g} ← ¹A_g transitions (d_{x²-y²} ← d_{yz}, d_{xy}, d_{z²}, and d_{xz}), respectively. The assignment is summarized in Fig. 8, together with that for the corresponding *cis* complex; the Cartesian coordinate axes are also shown. Figures 7 and 8 visualize how the four spin-allowed d-d bands overlap to look like two bands in *trans*-[Pd(Cl)₂(N)₂]-type complexes.

The band area (or oscillator strength) of bands 3 and 4 increased with an introduction of alkyl groups on the nitrogen atoms (Fig. 5 and Table 13). The pronounced effect was found with the band 4 of *trans*-[PdCl₂(*rac*-pea)₂] complex, which exhibited a strong absorption based on pea ligands in the near-UV region (Table 12). On the other hand, the area of band 1 is hardly affected by the variation of ligands (Table 13). These results support the above assignment where bands 4 and 1 are attributed to transitions from the d_{xz} and d_{yz} orbitals, respectively, which lie in the planes containing only N-ligands and only chloro ligands, respectively. In the *S*-pea complex, the CD for band 4 is intense, whereas for bands 1 and 3 weak (Fig. 7). That is to say, high CD intensity is observed for the transition from the d_{xz} orbital lying in the plane containing only optically active ligands, and low for the transition from the d_{yz} orbital lying in the plane containing only optically inactive ligands (Cl) as well as for the transition magnetic dipole-forbidden. This description suggests a certain relation connecting vicinal CD and its intensity with electronic structure.

The replacement of EtNH₂ ligand by *n*-BuNH₂ caused scarcely any change in the position and intensity of every absorption component. On the other hand, the replacement by *t*-BuNH₂ caused shifts

a--d) As in Table 6. e) In methanol.

11). On the contrary, the CD spectrum of the S-pea complex is less intense in methanol. The Gaussian-analysis result of absorption spectra for the *n*-BuNH₂ complex indicates that the energy separations between four d-d components are reduced in methanol in comparison with those in DCE (Table 13). Therefore, the CD spectrum in methanol is partly explained by a cancellation between the positive and the negative band; whereas the MCD spectrum by a larger mixing between the d-d vibronic excited states in which ¹B_{3g} and ¹A_g are involved, because the magnitude of a contribution to a B term is inversely proportional to the energy difference between the states which are mixed. The overlapping B terms may be considered to form a pseudo A term.¹⁸⁾ The separation of bands 1 and 4 for the *n*-BuNH₂ complex is smaller by 0.5×10³ cm⁻¹ in methanol than in DCE, indicating that the difference between the ligand-field strengths of chloro and amine ligands decreases in methanol. This is conceivably ascribed to the relative weakening of the ligand-field strength of the amine ligand by hydrogen bondings with methanol, which is more polar than DCE.

High-intensity Bands. The high-intensity bands observed above 35×10³ cm⁻¹ of *cis*- and *trans*-[Pd(Cl)₂(N)₂]-type complexes are attributable to dipole allowed charge transfer transitions from their intensities, and moreover to ones with ligand-to-metal nature (LMCT) because the bands of the *trans* complexes are blue-shifted with replacing DCE solvent by methanol. There are three kinds of LMCT to be considered here: Pd(σ*)←Cl(π), Cl(σ), and N(σ).

The shoulder located in (35–40)×10³ cm⁻¹ for the *cis* complexes is assigned to Pd(σ*)←Cl(π) transition, to which a negative B term corresponds. In [PdCl₂(en)], another shoulder is observed at ca. 45.3×10³ as well as the peak at 49.0×10³ cm⁻¹ (Fig. 3). The corresponding shoulder is barely appreciable in the *N,N*-Me₂en complex, but undetectable in the *N,N'*-Me₂en and *N,N*Et₂en complexes owing to the overlapping of the neighboring intense band. Their MCD spectra show a broad negative band above 40×10³ cm⁻¹, supporting the presence of more than one component. Although the CD spectrum of the S-pn complex exhibits only a negative CD band corresponding to the absorption shoulder, that of the *N*¹,*N*¹-

Et₂-(S)-pn complex shows an additional minor negative band in the higher energy side of the main band. Figure 9 shows the absorption spectra of [PdCl₂(*N,N'*-Me₂en)] in 0.20 M KCl and in an aqueous solution. In the latter solution, the d-d absorption band is blue-shifted and the shoulder at ca. 38×10³ cm⁻¹ remarkably reduced. The observations are attributed to a significant degree of aquation of the complex, being consistent with the assignment of the shoulder to Pd(σ*)←Cl(π). Since the band centered at 45.5×10³ cm⁻¹ still retains a considerable intensity (ε_{max}=15000), it seems to contain a Pd(σ*)←N(σ) as well as a Pd(σ*)←Cl(σ) transition. Then, the lower and the higher absorption (or CD) component in the en (or *N*¹,*N*¹-Et₂-(S)-pn) complex are assigned to Pd(σ*)←N(σ) and Cl(σ) transitions, respectively. This assignment is based on the expectation that the CT transition from the nitrogen atoms will exhibit more intense vicinal CD than that from the chlorine atoms since the nitrogen atoms lie more close to the asymmetric carbon atom of an *N*¹,*N*¹-Et₂-(S)-pn or S-pn ligand than the chlorine atoms. The assignment then suggests that the molecular orbitals comprising mainly Cl(σ) orbitals lie below those comprising mainly N(σ) ones. The situation is the reverse of that having been accepted generally. In any case no definitive experimental evidence seems available for the point.

The spectra of the complexes with a six-membered chelate ring are likewise assigned. The MCD of the tn and the *N,N*-Me₂tn complex show a negative A-term pattern around the absorption bands occurring at 45.8 and 43.4×10³ cm⁻¹, respectively. The sign of the "A" terms is the same as for a Pd(σ*)←N(σ) transition in [Pd(N)₄]-type complexes with one or two tn ligands¹⁶⁾ but the reverse of the sign of the A term for a Pd(σ*)←Cl(σ) transition in [PdCl₄]²⁻.¹⁾ Thus, it is likely that the MCD of the tn or *N,N*-Me₂tn complex is contributed mainly from the former kind of transition.

The absorption bands above 35×10³ cm⁻¹ of the *trans* type complexes are assigned in comparison with those of the *cis* type complexes discussed above. The shoulder around (39–40)×10³ cm⁻¹, which shows a negative B term, is assigned to a Pd(σ*)←Cl(π) transition; and the band centered at ca. 45×10³ cm⁻¹, which shows a positive and a negative B term in methanol, is to a composite of Pd(σ*)←Cl(σ) and N(σ).

The absorption, MCD, and CD spectra above 40×10³ cm⁻¹ in [PtCl₂(en or S-pn)] are quite different from those of [PdCl₂(en or S-pn)] in the corresponding region (Figs. 2 and 3). Thus, it is irrational to assign the absorption band at ca. 48.8×10³ cm⁻¹ to the same set of transitions as in [PdCl₂(en)]. As the band exhibits a positive A-term pattern in the MCD spectrum it may be attributed to a d-p transition (p_z←d_{xz,yz}), because the corresponding transition in [PtCl₄]²⁻ gives an A term with the same sign.¹⁾ More data need to be accumulated on complexes with different chromophores containing nitrogen and/or chlorine for a more detailed assignment of all the above high-intensity bands.

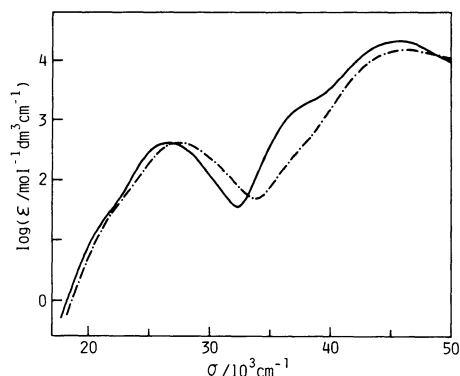


Fig. 9. Absorption spectra of [PdCl₂(*N,N'*-Me₂en)] in 0.20 M KCl (—) and in H₂O (---).

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