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Absorption Spectra and Circular Dichroisms of Metal Complexes. IV.*[1] Dichloro-diamine Type Complexes of Platinum(II) and Palladium(II)

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Absorption (AB) spectra of dichloro(*l*-tetrahydrogenpropylenediaminetetraacetato)platinum(II) and palladium(II) and dichloro(*d*-hydrogendiaminopropionato)platinum(II) and palladium(II) were interpreted on the basis of a comparison of their circular dichroism (CD) spectra with those of dichloro(*l*-propylenediamine)platinum(II) and palladium(II). The *d*-*d* bands of edtaH$_4$ and *l*-pdtaH$_4$ complexes shifted to longer wavelength as compared with those of *l*-pn complexes. The shift was discussed, based on the effects of the weaker ligand field strength and apical interaction of the acetato groups of these ligands.

In the first paper of this series,[1] we examined the absorption spectra of dichloro(*l*-propylenediamine)-platinum(II) and palladium(II)*[2] and found that the analysis of ciruclar dichroism spectra gave useful information about the assignment of the absorption bands of these metal complexes. Bailar and Busch[2] prepared dichloro(tetrahydrogenethylenediaminetetraacetato) platinum(II) and palladium(II) pentahydrate, [PtCl$_2$(edtaH$_4$)]·5H$_2$O and [PdCl$_2$(edtaH$_4$)]·5H$_2$O, and predicted that ethylenediaminetetraacetic acid coordinated to the metal ions as a bidentate ligand. The structure was recently confirmed by X-ray analysis for the palladium compound.[3] However, no spectroscopic study of such complexes has been reported. In this paper AB and CD spectra of [PtCl$_2$(*l*-pdtaH$_4$)]·5H$_2$O and [PdCl$_2$(edtaH$_4$)]·5H$_2$O are interpreted by comparing them with those of dichloro-diamine complexes of platinum(II) and palladium(II).

Experimental

Ligands. *l*-Propylenediamine was obtained by resolving its commercial racemate.[4] *l*-Propylenediaminetetraacetic acid and *d*-diaminopropionic acid were prepared according to Dwyer's[5] and Karrer's[6] method, respectively.

Preparations of the Complexes. *(1) Dichloro(l-tetrahydrogenpropylenediaminetetraacetato) platinum(II) pentahydrate,* [PtCl$_2$(*l*-pdtaH$_4$)]·5H$_2$O and *dichloro (l-tetrahydrogenpropylenediaminetetraacetato)palladium(II) pentahydrate,* [PdCl$_2$(*l*-pdtaH$_4$)]·5H$_2$O were prepared by Busch and Bailer's method[2] for the corresponding edtaH$_4$ complexes.

Found: C, 19.94; H, 4.69; N, 4.02%. Calcd for $C_{11}H_{28}N_2O_{13}Cl_2Pt$: C, 19.95; H, 4.26; N, 4.88%.

Found: C, 22.42; H, 5.32; N, 5,12%. Calcd for $C_{11}H_{28}N_2O_{13}Cl_2Pd$: C, 23.03; H, 4.92; N, 4.88%.

(2) Dibromo(l-tetrahydrogenpropylenediaminetetraacetato)platinum(II), [PtBr$_2$(*l*-pdtaH$_4$)], was obtained by recrystallizing [PtCl$_2$(*l*-pdtaH$_4$)] twice from hot 3 M hydrobromic acid.

Found: C, 19.86; H, 3.44; N, 3.95%. Calcd for $C_{11}H_{18}N_2O_8Br_2Pt$: C, 19.98; H, 2.74; N, 4.24%.

(3) Dichloro(d-hydrogendiaminopropionato)platinum(II) [PtCl$_2$(*d*-dampH)]. A mixture of 1 g of K$_2$[PtCl$_4$], 0.34 g of *d*-diaminopropionic acid monohydrochloride and 0.33 g of K$_2$CO$_3$ in 30 m*l* of water was heated on a water bath at 80°C for two hours and then cooled to room temperature. Purple crystals of Magnus type salt produced during the reaction were filtered off and the filtrate was evaporated to dryness on a water bath. The residue was dissolved in a minimum amount of hot water and filtered. To the filtrate were added a few drops of concentrated hydrochloric acid. Yellow crystals were formed on cooling. They were recrystallized from 2 M hydrochloric acid.

Found: C, 9.83; H, 2.52; N, 7.50%. Calcd for $C_3H_8N_2O_2Cl_2Pt$: C, 9.74; H, 2.18; N, 7.57%.

(4) Dichloro(d-hydrogendiaminopropionato)palladium(II), [PdCl$_2$(*d*-dampH)]. Five hundred milligrams of

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*[1] Part III, H. Ito, J. Fujita and K. Saito, This Bulletin, **42**, 1286 (1969).

*[2] Following abbreviations were used in this paper; *l*-pn=D-(−)$_D$-propylenediamine, *d*-dampH=L-(+)$_D$-diaminopropionic acid, *l*-pdtaH$_4$=D-(−)$_D$-propylenediaminetetraacetic acid, *l*-pdtaH$_3$=unianion of D-(−)$_D$-propylenediaminetetraacetic acid, eddaH$_2$=ethylenediamine-*N,N′*-diacetic acid, *NN′*-Meen=*N,N′*-dimethylethylenediamine, *NN′*-MeenH=unication of *N,N′*-dimethylethylenediamine, *NN*-Eten=*N,N*-diethylethylenediamine, Me$_4$en=*N,N,N′,N′*-tetramethylethylenediamine.

1) H. Ito, J. Fujita and K. Saito, This Bulletin, **40**, 2584 (1967).

2) D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **78**, 716 (1956).

3) D. J. Robinson, and C. H. Kennard, *Chem. Commun.*, **1967**, 1236.

4) F. P. Dwyer, F. L. Garvan and A. Shulman, *J. Am. Chem. Soc.*, **81**, 290 (1959).

5) F. P. Dwyer and F. L. Garvan, *ibid.*, **81**, 2955 (1959).

6) P. Karrer and A. Schlosser, *Helv. Chim. Acta*, **6**, 415 (1913).

$K_2[PdCl_4]$ was dissolved in a small amount of water, and then 0.25 g of *d*-diaminopropionic acid monohydrochloride in 5 m*l* of water was added dropwise with stirring. A gelatinous substance appeared, and crystallized gradually. The product was filtered off, washed with cold water, ethanol and ether.

Found: C, 13.25; H, 3.05; N, 9.68%. Calcd for $C_3H_8N_2O_2Cl_2Pd$: C, 12.80; H, 2.80; N, 9.95%.

(5) Dichloro (dihydrogenethylenediaminediacetato) palladium(II), $[PdCl_2(eddaH_2)]$. An aqueous solution containing 1 g of $K_2[PdCl_4]$ and 0.54 g of ethylenediaminediacetic acid was heated on a water bath (about 80°C) for half an hour and cooled. Orange yellow precipitate was filtered off, dissolved in hot water, cooled to room temperature rapidly, and treated with several drops of concentrated hydrochloric acid, the wall of the vessel being scratched to induce crystallization. The crystals were filtered off, and washed with cold water, ethanol and ether.

Found: C, 20.83; H, 3.49; N, 7.79%. Calcd for $C_6H_{12}N_2O_4$: C, 20.39; H, 3.42; N, 7.93%.

(6) Dichloro (N, N′-dimethylethylenediamine) palladium(II), $[PdCl_2(NN'\text{-Meen})]$. One gram of $[Pd(NN'\text{-Meen})_2]Cl_2$, which was obtained by a similar method to that described for $[Pd(en)_2]Cl_2$, was dissolved in 3 m*l* of water, and treated with 3 m*l* of concentrated hydrochloric acid under cooling in an ice bath. The solution was filtered to remove a small amount of unknown product, and then ethanol was added to the filtrate. Orange yellow precipitate was filtered off. Chemical analysis of the product shows the following compound, $[PdCl_2(NN'\text{-MeenH})_2]Cl_2$. Found: C, 22.59; H, 5.77; N, 13.22%. Calcd for $C_8H_{24}N_4Cl_4Pd$: C, 22.74; H, 5.25; N, 13.26%. This was dissolved in a small amount of hot water and cooled to room temperature, and treated with 6 M hydrochloric acid to produce 0.5 M hydrochloric acid solution. Orange yellow crystals precipitated on cooling. They were filtered off, and washed with water, ethanol and ether.

Found: C, 18.60; H, 4.39; N, 10.58%. Calcd for $C_4H_{12}N_2Cl_2Pd$: C, 18.24; H, 3.83; N, 10.63%.

Other complexes were prepared according to the methods described in literature.[1,7,8)]

Measurements. Visible and ultraviolet absorption spectra were obtained with a Hitachi 124 recording spectrophotometer. The CD curves were recorded with a Model ORD/UV-5 spectrophotometer of Japan Spectroscopic Co. with its CD attachment. The diffuse reflectance spectra were measured with a Hitachi EPU-2A spectrophotometer with appropriate attachment. All the measurements were made at room temperature.

To avoid the aquation of coordinated halides, dichlorodiamine platinum(II) complexes were dissolved in 2 M hydrochloric acid, $[PtBr_2(l\text{-pn})]$ in 2 M hydrobromic acid, $[PtBr_2(l\text{-pdtaH}_4)]$ in 3 M hydrobromic acid and dichloro-diamine palladium(II) complex in 0.2 M potassium chloride solution, unless otherwise stated.

Proton magnetic resonance (PMR) spectra were measured with a Varian A-60 spectrometer in deuterated methanol, with tetramethylsilane (TMS) as internal reference. For the PMR measurement, the complex $[PtCl_2(edtaH_4)]\cdot 5H_2O$ and $[PdCl_2(edtaH_4)]\cdot 5H_2O$ were dehydrated at 60°C *in vacuo.*

Results and Discussion

The AB and CD spectra of the complexes are shown in Figs. 1—6. Numerical data are summarized in Tables 1—3.

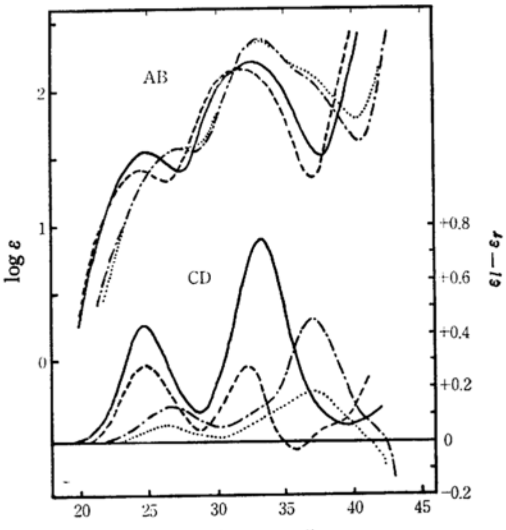

Fig. 1. AB and CD spectra of $[PtCl_2(l\text{-pn})]$ (—·—), $[PtCl_2(d\text{-dampH})]$ (······), in 2M hydrochloric acid, and $[PtCl_2(l\text{-pdtaH}_4)]\cdot 5H_2O$ in 6 M hydrochloric acid (——) and in ethanol (----).

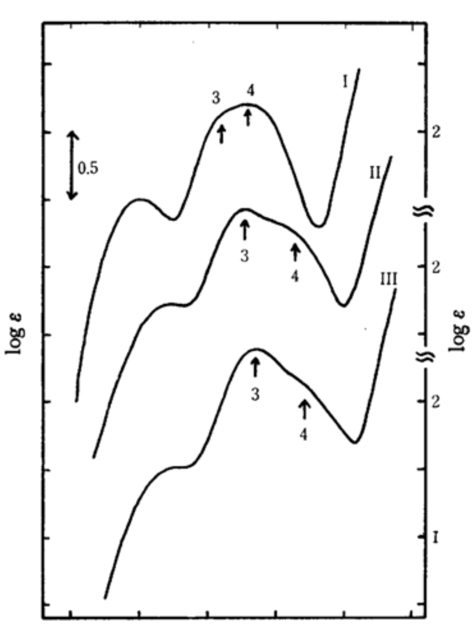

Fig. 2. AB spectra of $[PtCl_2(en)]$ (I), $[PtCl_2(eddaH_2)]$ (II), in 2M hydrochloric acid and $[PtCl_2(edtaH_4)]$(III), in 6 M hydrochloric acid.

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7) S. P. Tanner, F. Basolo and R. G. Pearson, *Inorg. Chem.*, **6**, 1089 (1967).

8) G. W. Watt and D. G. Upchurch, *J. Am. Chem. Soc.*, **89**, 177 (1967).

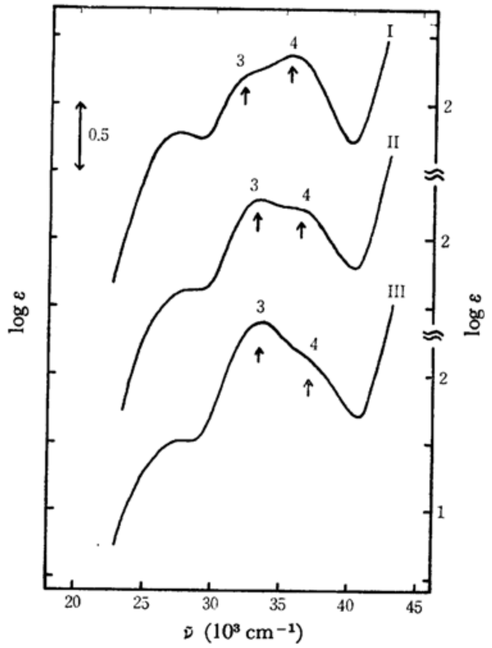

Fig. 3. AB spectra of $[PtCl_2(en)]$ (I), $[PtCl_2(NN'\text{-Meen})]$ (II) and $[PtCl_2(Me_4en)]$ (III) in 2 M hydrochloric acid.

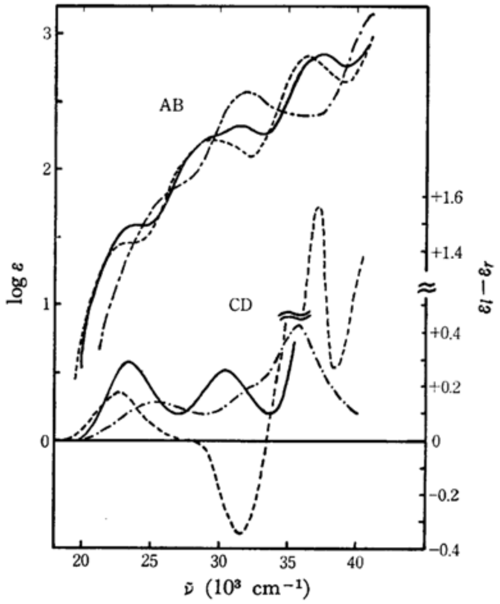

Fig. 5. AB and CD spectra of $[PtBr_2(l\text{-pn})]$ in 2 M hydrobromic acid (—·—), $[PtBr_2(l\text{-pdtaH}_4)]$ in 3 M hydrobromic acid (——) and in ethanol (----).

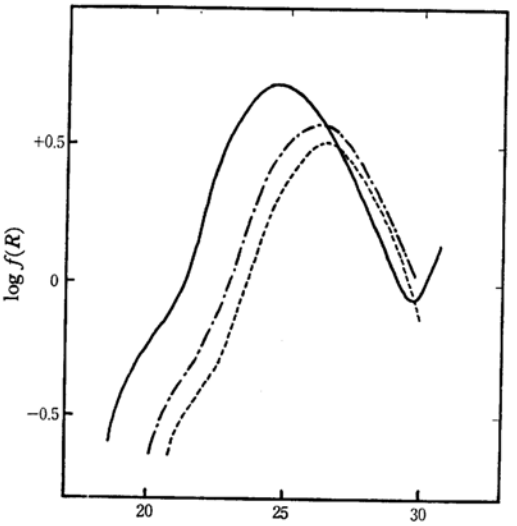

Fig. 4. Diffuse reflectance spectra of $[PdCl_2(l\text{-pdtaH}_4)]\cdot 5H_2O$ (——), $[PdCl_2(eddaH_2)]$ (—·—) and $[PdCl_2(l\text{-pn})]$ (----).

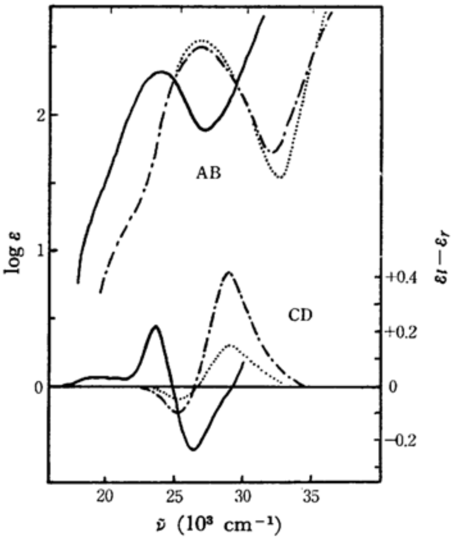

Fig. 6. AB and CD spectra of $[PdCl_2(l\text{-pdtaH}_4)]\cdot 5H_2O$ in ethanol - conc. hydrochloric acid (99:1) mixed solvent (——), $[PdCl_2(l\text{-pn})]$ (—·—) and $[PdCl_2(d\text{-dampH})]$ (······) in 0.2 M KCl soln.

Complexes Containing *d*-Diaminopropionic Acid. The infrared absorption spectra indicate that the *d*-diaminopropionic acid of $[PtCl_2(d\text{-dampH})]$ and $[PdCl_2(d\text{-dampH})]$ coordinates through two amino groups, though it is a potential terdentate ligand with two amino groups and a carboxyl group;[9] the band at 1754 cm⁻¹ must correspond to antisymmetric stretching frequency of uncoordinated carboxylic acid.

The absolute configuration of this ligand is compared with that of D-(−)$_D$-propylenediamine in Fig. 7. Recent conformational analysis on the

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[9] W. A. Freeman and C. F. Liu, *Inorg. Chem.*, **7**, 764 (1968).

Table 1. AB data of platinum(II) complexes, $\tilde{\nu}$ in 10^3 cm^{-1}

	Solvent	$\tilde{\nu}_{max}$ (log ε)	$\tilde{\nu}_{max}$ (log ε)	$\tilde{\nu}_{max}$ (log ε)
[PtCl$_2$(en)]	a	*ca.* 27.0 (1.4)	33.2 (2.40)	*ca.* 37 (2.1)
[PtCl$_2$(*l*-pn)]	a	*ca.* 27.3 (1.5)	33.1 (2.37)	*ca.* 37 (2.1)
[PtCl$_2$(*d*-dampH)]	a	*ca.* 27.0 (1.5)	33.0 (2.35)	*ca.* 37 (2.2)
[PtCl$_2$(*NN'*-Meen)]	a	*ca.* 27.5 (1.6)	33.2 (2.34)	*ca.* 36 (2.2)
[PtCl$_2$(Me$_4$en)]	a	27.0 (1.77)	*ca.* 32.3 (2.2)	35.5 (2.37)
[PtCl$_2$(*NN*-Eten)]	a	27.4 (1.62)	32.8 (2.39)	*ca.* 36 (2.2)
	b	26.7 (1.56)	32.3 (2.36)	*ca.* 35.7 (2.1)
[PtCl$_2$(eddaH$_2$)]	a	*ca.* 27.0 (1.7)	32.5 (2.43)	*ca.* 36 (2.3)
[PtCl$_2$(edtaH$_4$)]	c	25.0 (1.51)	*ca.* 31 (2.1)	32.8 (2.22)
[PtCl$_2$(*l*-pdtaH$_4$)]	c	24.8 (1.50)	*ca.* 31 (2.1)	32.7 (2.19)
	b	24.4 (1.40)	*ca.* 30 (2.0)	32.1 (2.15)
	d	24.4 (1.40)	*ca.* 30.2 (2.05)	32.0 (2.07)
[PtBr$_2$(*l*-pn)]†	e	*ca.* 26.5 (1.8)	31.8 (2.57)	*ca.* 36 (2.4)
[PtBr$_2$(*l*-pdtaH$_4$)]††	f	*ca.* 23.5 (1.6)	*ca.* 29 (2.25)	31.0 (2.33)
	b	*ca.* 23.0 (1.48)	*ca.* 28.5 (2.2)	29.7 (2.24)

† Another band appears at 37300 cm^{-1} (log ε=2.87), †† another band appears at 36400 cm^{-1} (log ε=2.86)
a, 2 M HCl; b, ethanol; c, 6 M HCl; d, tetrahydrofuran; e, 2 M HBr; f, 3 M HBr

Table 2. CD data of platinum(II) complexes, $\tilde{\nu}$ in 10^3 cm^{-1}

	Solvent	$\tilde{\nu}_{max}$ ($\varepsilon_l-\varepsilon_r$)	$\tilde{\nu}_{max}$ ($\varepsilon_l-\varepsilon_r$)	$\tilde{\nu}_{max}$ ($\varepsilon_l-\varepsilon_r$)	$\tilde{\nu}_{max}$ ($\varepsilon_l-\varepsilon_r$)
[PtCl$_2$(*l*-pn)]	a	26.3 (+0.13)		37.0 (+0.45)	
[PtCl$_2$(*d*-dampH)]	a	26.3 (+0.07)		37.0 (+0.19)	
[PtCl$_2$(*l*-pdtaH$_4$)]	c	24.7 (+0.43)		33.3 (+0.75)	
	b	24.3 (+0.29)		31.7 (+0.28)	35.2 (−0.02)
	d	24.0 (+0.31)		31.0 (+0.15)	34.2 (−0.16)
[PtBr$_2$(*l*-pn)]	e	25.3 (+0.14)	*ca.* 32 (*ca.* +0.15)	35.7 (+0.42)	
[PtBr$_2$(*l*-pdtaH$_4$)]	f	23.3 (+0.30)		30.3 (+0.27)	
	b†	22.8 (+0.18)			31.7 (−0.34)

† Another band was observed at 37100 cm^{-1} ($\varepsilon_l-\varepsilon_r$=+1.56).
a, 2 M HCl; b, ethanol; c, 6 M HCl; d, tetrahydrofuran; e, 2 M HBr; f, 3 M HBr

Table 3. AB and CD data of palladium(II) complexes, $\tilde{\nu}$ in 10^3 cm^{-1}

	AB	CD		Measurement
	$\tilde{\nu}_{max}$ (log ε)	$\tilde{\nu}_{max}$ ($\varepsilon_l-\varepsilon_r$)	$\tilde{\nu}_{max}$ ($\varepsilon_l-\varepsilon_r$)	
[PdCl$_2$(*l*-pn)]	27.0 (2.54)	25.3 (−0.10)	28.7 (+0.43)	a
	26.3			b
[PdCl$_2$(*d*-dampH)]	27.0 (2.56)	25.3 (−0.06)	29.2 (+0.25)	a
[PdCl$_2$(*NN'*-Meen)]	26.7 (2.57)			a
[PdCl$_2$(Me$_4$en)]	26.0 (2.51)			a
[PdCl$_2$(eddaH$_2$)]	26.3			b
[PdCl$_2$(*l*-pdtaH$_4$)]	24.1 (2.32)	23.5 (+0.19)	26.3 (−0.20)	c
	24.6			b

a, in 0.2M KCl solution; b, diffuse reflectance spectrum; c, in a mixed solution (ethanol: conc. HCl= 99 : 1 v/v)

basis of PMR study[10] has shown that in diamagnetic cobalt(III), palladium(II) and platinum(II) complexes, the *l*-propylenediamine coordinates to the metal ions to form a fixed λ-gauche chelate with the methyl group equatorial direction to the chelate ring even in an aqueous solution at room temperature. If the carboxyl group of *d*-diaminopropionic acid also required such an equatorial conformation, the gauche form of the chelate in its platinum(II) and palladium(II) complex should also be of λ-type. The CD spectra of these complexes shown in Figs. 1 and 6 are quite similar to those of *l*-pn complexes, though the intensities are smaller, to

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[10] S. Yano, H. Ito, Y. Koike, J. Fujita and K. Saito, *Chem. Commun.*, **1969**, 460.

indicate that the chelate ring of *d*-dampH is of λ-gauche form.

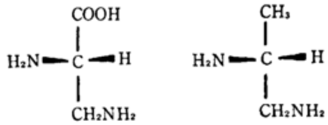

Fig. 7. Absolute configurations of D-(−)D-propylenediamine and L-(+)D-diaminopropionic acid.

Complexes Containing *l*-Propylenediaminetetraacetic Acid. Recent kinetic study7) has shown that acetato groups participate in the elimination reaction of the chloride ions from $[PtCl_2(eddaH_2)]$. Such participation of a neighboring group and anchimeric assistance is expected to be more remarkable in platinum(II) and palladium(II) complexes containing $edtaH_4$ and *l*-$pdtaH_4$. For example, the spectrum of $[PtCl_2(l\text{-}pdtaH_4)]$ in 0.1 M hydrochloric acid is subject to a rapid change to reach a constant curve after about 80 min at room temperature. During the reaction isosbestic points appear at 345, 320 and 250 mμ and the absorption peak shifts to 288 mμ, as shown in Fig. 8. The spectral change may correspond to the following equilibrium shift.

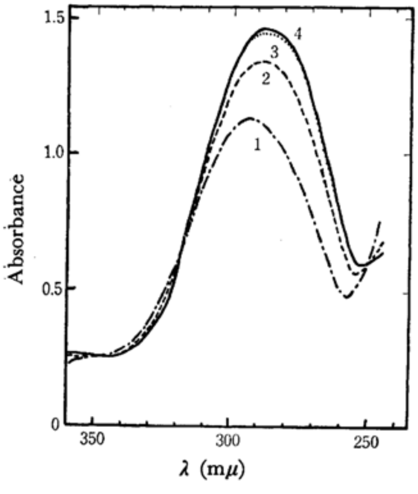

Fig. 8. Change in the spectrum of $[PtCl_2(l\text{-}pdtaH_4)]\cdot 5H_2O$ in 0.1 M hydrochloric acid with time. After (1), 10 min; (2), 20 min; (3), 30 min; (4), after equilibrium is reached.

$$[PtCl_2(l\text{-}pdtaH_4)] \rightarrow [PtCl(l\text{-}pdtaH_3)] + H^+ + Cl^-$$

Thus, the spectrum of $[PtCl_2(l\text{-}pdtaH_4)]$ was measured in 6 M hydrochloric acid.

The spectra of the complexes $[PtCl_{4-n}(NH_3)_n]^{(n-2)+}$ in the *d-d* band region consist of four bands, which are denoted as band 1, band 2, band 3 and band 4 from longer to shorter wavelength.11) They were assigned to triplets of $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$, and singlets of $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$, respectively.1,11) As in the case of *cis*-$[PtCl_2(NH_3)_2]$, $[PtCl_2(l\text{-}pn)]$ gives a peak at 33100 cm^{-1} (band 3) and a shoulder at about 37000 cm^{-1} (band 4), while $[PtCl_2(l\text{-}pdtaH_4)]$ gives a peak at 32700 cm^{-1} and presumably a shoulder band at the longer wavelength side (at about 31000 cm^{-1}). The energy difference of these two neighboring bands are 3900 and about 2000 cm^{-1} for $[PtCl_2(l\text{-}pn)]$ and $[PtCl_2(l\text{-}pdtaH_4)]$, respectively.

When the *l*-$pdtaH_4$ coordinates to the metal with the methyl group equatorial, the structure of chelate ring should be of λ -type, which is the same as that of the chelated *l*-pn. Therefore, the CD spectra of *l*-$pdtaH_4$ and *l*-pn complex should have the same sign in a corresponding transition band. Figure 1 suggests that the positive peak at 33300 cm^{-1} of $[PtCl_2(l\text{-}pdtaH_4)]$ corresponds to the positive peak of $[PtCl_2(l\text{-}pn)]$ at 37000 cm^{-1} (band 4).

In order to examine the large difference in the spectral shape and the transition energy of the band 4 between *l*-pn and *l*-$pdtaH_4$ complex, the absorption spectra of a series of $[PtCl_2(en)]$, $[PtCl_2(NN'\text{-}Meen)]$ and $[PtCl_2(Me_4en)]$ and a series of $[PtCl_2(en)]$, $[PtCl_2(eddaH_2)]$ and $[PtCl_2(edtaH_4)]$ are compared in Figs. 2 and 3. The trend of change in spectra is similar in the two series: (1) The intensity of band 4 relative to that of band 3 increases with increase in the number of the substituents on the nitrogen atoms.

(2) The absorption maxima of the bands 3 and 4 of *N,N,N′,N′*-tetrasubstituted ethylenediamines shift to a longer wavelength as compared with those of *N,N′*-disubstituted and non-substituted compounds. This phenomenon is also observed for palladium(II) complexes in 0.2 M potassium chloride solution (Table 3).

These results further support the fact that the positive CD peak at 33300 cm^{-1} of $[PtCl_2(l\text{-}pdtaH_4)]$ corresponds to band 4 and the absorption shoulder at about 31000 cm^{-1} to band 3. Such an assignment leads to the conclusion that the ligand field strength of $pdtaH_4$ and $edtaH_4$ is considerably weaker than that of the other diamines, because the energy of band 3 ($d_{xy} \rightarrow d_{x^2-y^2}$) corresponds approximately to the so-called 10 *Dq*. It is known that the treatment of $[PtCl_2(en)]$ and $[PtCl_2(eddaH_2)]$12) with aqueous ammonia produces $[Pt(NH_3)_2(en)]Cl_2$ and $[Pt(NH_3)_2(eddaH_2)]Cl_2$, respectively. For $[PtCl_2(l\text{-}pdtaH_4)]$, however, the same treatment gave $[Pt(NH_3)_4]^{2+}$. Such a difference in chemical reaction suggests a weaker bond between platinum(II) and nitrogens of $edtaH_4$ and *l*-$pdtaH_4$. In the diffuse reflectance spectra

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11) J. Chatt, G. A. Gamlen and L. E. Orgel, *J. Chem. Soc.*, **1958**, 486.

12) C. F. Liu, *Inorg. Chem.*, **3**, 680 (1964).

shown in Fig. 4, the absorption peak of [PdCl$_2$(*l*-pdtaH$_4$)]·5H$_2$O is also shifted to longer wavelength as compared with those of [PdCl$_2$(*l*-pn)] and [PdCl$_2$(eddaH$_2$)].

The shift of band 4 to longer wavelength in edtaH$_4$ and *l*-pdtaH$_4$ complexes seems to be abnormally large. According to the X-ray analysis of [PdCl$_2$(edtaH$_4$)]·5H$_2$O, two oxygen atoms of the acetato groups on each nitrogen atom are present above and below the palladium atom (distance 3.04 Å). Such a structure may also cause the spectra red shift. If two acetato groups were coordinated weakly to form a distorted octahedral complex, chemical environment of two acetato groups on one nitrogen atom would be non-equivalent and would give PMR spectrum with two different methylene signals. However, the PMR spectrum of [PdCl$_2$(edtaH$_4$)] in deuterated water reported by Aochi and Sawyer,[13] and that of [PtCl$_2$(edtaH$_4$)] in 6 M deuterium chloride solution reported by Erickson *et al.*[14] indicate no such difference. We also measured the spectra of these complexes in deuterated methanol as shown in Fig. 9. No difference between the four acetato groups were observed either; the singlets at 3.39 ppm of the palladium complex and 3.58 ppm of the platinum complex, and the qualtets centered at 4.31 ppm ($J=17.7$ Hz) of the palladium complex and 4.43 ppm ($J=17.3$ Hz) of the platinum complex were assigned to signals of the ethylene and the methylene protons, respectively. Such an equivalence for the four acetato groups may not necessarily reject the electrical perturbation from apical positions to cause spectral red shift. Whenever one acetato oxygen parts from palladium or platinum, oxygen of the other acetato group on the same nitrogen atom can occupy the site in its place. This may be reflected in the rapid elimination reaction of the chloride ions in the complex, [PtCl$_2$(*l*-pdtaH$_4$)], as stated before. The signals at about 3.8 ppm of the platinum complex may be due to the satellites corresponding to ^{195}Pt.

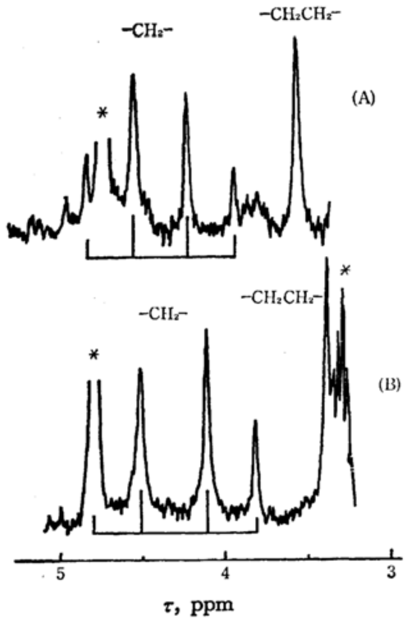

Fig. 9. PMR spectra of [PtCl$_2$(edtaH$_4$)] (A) and [PdCl$_2$(edtaH$_4$)] (B) in deuterated methanol, TMS as internal reference. (* indicates signals of solvent)

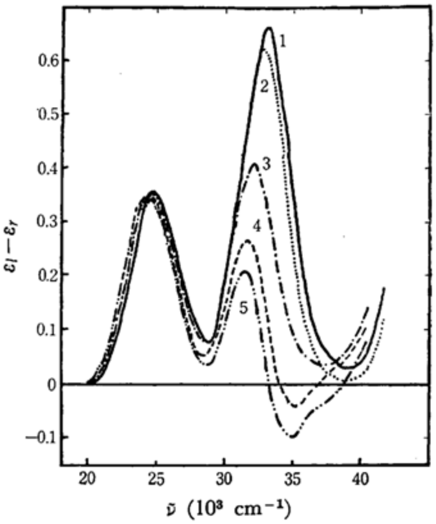

Fig. 10. CD spectra of [PtCl$_2$(*l*-pdtaH$_4$)]·5H$_2$O in mixtures of ethanol and water containing abont 2 mol/*l* of hydrogen chloride: (1), 10%; (2), 55%; (3), 82%; (4), 100% ethanol.

As mentioned before, bands 3 and 4 were assigned to $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$, respectively, therefore the spectral red shift is considered to be larger for band 4 than that for band 3, since the presence of very weakly attracted dipolar molecules in the apical positions destabilizes d_{z^2}, d_{xz} and d_{yz} orbitals to a greater extent than d_{xy} and $d_{x^2-y^2}$ orbitals. In fact the energy difference between bands 3 and 4 is smaller for [PtCl$_2$(*l*-pdtaH$_4$)] (about 2000 cm^{-1}) than that for [PtCl$_2$(*l*-pn)] (3900 cm^{-1}).

The absorption spectrum of [PtCl$_2$(*l*-pdtaH$_4$)] in ethanol solution shifts to longer wavelength as a whole as compared with that in hydrochloric acid (Fig. 1). Such a shift was also observed for [PtCl$_2$(*NN*-Eten)] in hydrochloric acid and ethanol (Table 1). On the other hand, the shape of the CD spectrum in ethanol is quite different from that in hydrochloric acid (Fig. 1). A negative CD peak (35200 cm^{-1}) appears at shorter wavelength side of a positive CD peak (31700 cm^{-1}) in ethanol, which corresponds to the positive one at 33300 cm^{-1}

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[13] Y. O. Aochi and D. T. Sawyer, *ibid.*, **5**, 2085 (1966).

[14] L. E. Erickson, J. W. McDonald, J. K. Howie and R. P. Clow, *J. Am. Chem. Soc.*, **90**, 6371 (1968).

in hydrochloric acid. The CD spectra in methanol, dioxane and tetrahydrofuran are quite similar to that in ethanol. Figure 10 shows the CD spectra in mixtures of water and ethanol containing about 2 M hydrogen chloride. With increase in the intensity of the negative CD component, the positive CD peak shifts to longer wavelength and its intensity decreases.

In Fig. 5 the AB and CD spectrum of [$PtBr_2$-(l-pn)] in 2 M hydrobromic acid, and those of [$PtBr_2$-(l-pdtaH_4)] in 3 M hydrobromic acid and in ethanol are shown. The spectrum of [$PtBr_2$(l-pn)] is quite similar to that of [$PtCl_2$(l-pn)] in acid solution except that the corresponding bands appear at longer wavelengths for the dibromo complex. In AB spectrum of [$PtBr_2$(l-pdtaH_4)] in hydrobromic acid, apparently four absorption bands are observed at about 23500, 29000, 31000 and 37300 cm^{-1}. The AB and CD spectra are compared to those of the corresponding dichloro complex, and the band at 23500 cm^{-1} can be assigned to the spin forbidden band (band 2) and the bands at 29000 and 31000 cm^{-1} to bands 3 and 4, respectively. The band at 37300 cm^{-1} may be due either to $d_{z^2} \rightarrow d_{z^2-y^2}$ transition or a charge transfer transition. A fairly strong positive CD appears in this region (in ethanol). Since $d_{z^2} \rightarrow d_{x^2-y^2}$ transition is magnetic dipole forbidden, the CD strength of the band corresponding to $d_{z^2} \rightarrow d_{x^2-y^2}$ transition should be weak. Therefore, this absorption peak can be assigned to a charge transfer band involving p orbitals of the bromide and $d_{x^2-y^2}$ orbital of the platinum(II).*[1,1)] The location of the band corresponding to $d_{z^2} \rightarrow d_{x^2-y^2}$ transition remains uncertain.

The difference of the CD spectra of [$PtBr_2$ (l-pdtaH_4)] in the band 4 region between hydrobromic acid and ethanol solution is striking; the signs of CD in the two solvents are different (Fig. 5). Considering that the AB and CD peaks of chloro- and bromo-platinum(II) complexes in ethanol appear at longer wavelengths than those in hydrochloric or hydrobromic acid, the negative CD band of the bromo-complex at 31700 cm^{-1} in ethanol seems to correspond to the negative CD band (35200 cm^{-1}) of [$PtCl_2$(l-pdtaH_4)] in ethanol. In the bromo-complex, the positive component around band 4 may be canceled by the adjacent strong negative component with unknown nature. Such a remarkable CD difference in the two solvents is not clear at present.

The AB and CD spectra of [$PdCl_2$(l-pdtaH_4)] in a mixed solution (ethanol : conc. HCl=99 : 1 v/v) are shown in Fig. 6. Corresponding to the absorption peak at 24100 cm^{-1}, a positive and a negative CD appear at 23700 and 26300 cm^{-1}. The positive CD component at longer wavelength can be assigned to spin forbidden transition. The CD spectrum seems to be similar to that of the corresponding platinum complex in ethanol. The complex decomposed rapidly in 1 M hydrochloric acid to give [$PdCl_4$]$^{2-}$. Beer's law did not hold even in dehydrated ethanol. The CD spectrum of a solution 4.07×10^{-3} mol/l in ethanol is quite similar to that in the mixed solvent. However, in a very dilute solution, the absorption peak corresponding to [$PdCl$(l-pdtaH_3)] was observed.

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