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Absorption Spectra and Circular Dichroisms of Metal Complexes. III.[*1] *trans*-Dihalogeno-bis-*l*-propylenediamine Complexes of Cobalt(III), Rhodium(III), Palladium(IV) and Platinum(IV)

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Absorption (AB) and circular dichroism (CD) spectra of *trans*-$[\mathrm{MX}_2(l\text{-pn})_2]^{n+}$ (where M$=$Rh$^{\mathrm{III}}$, Pd$^{\mathrm{IV}}$- and Pt$^{\mathrm{IV}}$-, and X$=$Cl$^-$ and Br$^-$) have been discussed by comparing them with those of cobalt(III) complexes which had been studied extensively. A positive CD peak was observed at around the so called I$_a$ band region of all the complexes studied except for *trans*-$[\mathrm{PtBr}_2(l\text{-pn})_2]^{2+}$. A negative CD peak of this complex ion at 26000 cm^{-1} was assigned to be a split component of the I$_a$ band. The AB peaks at 38000, 28600 and 31100 cm^{-1} for *trans*-$[\mathrm{PtCl}_2(l\text{-pn})_2]^{2+}$, *trans*-$[\mathrm{PdCl}_2(l\text{-pn})_2]^{2+}$ and *trans*-$[\mathrm{PtBr}_2(l\text{-pn})_2]^{2+}$ respectively were assigned to $p_\pi \rightarrow d_{z^2}$ charge transfer transition. An ion association band was observed for *trans*-$[\mathrm{PtBr}_2(l\text{-pn})_2]\mathrm{Br}_2$ in 1N hydrobromic acid.

In the first paper of this series,[1] the absorption spectra of square planar platinum(II), palladium(II) and gold(III) complexes containing optically active diamines were interpreted on the basis of an analysis of their circular dichroism spectra. The present paper deals with the AB and CD spectra of octahedral platinum(IV) and palladium(IV) complexes of the type, *trans*-$[\mathrm{MX}_2(l\text{-pn})_2]^{2+}$ (X$=$Cl$^-$ and Br$^-$, *l*-pn$=(-)_\mathrm{D}$-propylenediamine).

Since both platinum(IV) and palladium(IV) ions have strong tendency to form diamagnetic d^6 complexes, their AB spectra are expected to resemble those of cobalt(III) and rhodium(III) complexes.

However, assignment of their absorption bands still remains uncertain, partly because both the *d–d* transition and the charge transfer band appear in overlapping regions. The trans complexes in this paper have no optical dissymmetry around the central metal ion, but give CD peaks due to the vicinal effect coming from asymmetric ligands. Usefulness of the examination of these peaks for the band assignment has been demonstrated with various cobalt(III),[2,3] platinum(II) and palladium(II) complexes.[1]

We have attempted, therefore, to assign tentatively the absorption bands of some platinum(IV) and palladium (IV) complexes by comparing their CD spectra with those of cobalt (III) complexes which had been studied extensively.

Experimental

Preparations of the Complexes. Six new complexes were prepared by the following methods.

trans-Dichloro-bis-l-propylenediamineplatinum(IV) Chloride monohydrate, *trans*-$[\mathrm{PtCl}_2(l\text{-pn})_2]\mathrm{Cl}_2\cdot\mathrm{H_2O}$, *trans-Dichloro-bis-l-cyclohexanediamineplatinum(IV) Chloride Monohydrate*, *trans*-$[\mathrm{PtCl}_2(l\text{-chxn})_2]\mathrm{Cl}_2\cdot\mathrm{H_2O}$ and *trans-Dibromo-bis-l-propylenediamineplatinum (IV) Bromide Monohydrate*, *trans*-$[\mathrm{PtBr}_2(l\text{-pn})_2]\mathrm{Br}_2\cdot\mathrm{H_2O}$ were prepared from $[\mathrm{Pt}(l\text{-pn})_2]\mathrm{Cl}_2$ and $[\mathrm{Pt}(l\text{-chxn})_2]\mathrm{Cl}_2$ and halogens by Basolo, Bailar and Tarr's method[4] for the corresponding ethylenediamine complexes. The dichloro complexes were recrystallized from an aqueous solution by adding ethanol. The dibromo complex was converted into bromide by dissolving it in 3N hydrobromic acid and evaporating on a water bath. *trans*-$[\mathrm{PtCl}_2(l\text{-pn})_2\mathrm{Cl}_2$ and *trans*-$[\mathrm{PtBr}_2(l\text{-pn})_2]\mathrm{Br}_2$ were converted into perchlorate by dissolving them in a small amount of water and adding concentrated perchloric acid. The crystals were filtered off, dried over potassium hydroxide *in vacuo*.

trans-Dichloro-bis-l-propylenediaminepalladium(IV) Nitrate, *trans*-$[\mathrm{PdCl}_2(l\text{-pn})_2](\mathrm{NO}_3)_2$ was prepared by a similar method to that for *trans*-$[\mathrm{PdCl}_2(\mathrm{en})_2](\mathrm{NO}_3)_2$[5] in bright yellow crystals.

trans-Dibromo-bis-l-propylenediaminerhodium(III) Perchlorate, *trans*-$[\mathrm{RhBr}_2(l\text{-pn})_2]\mathrm{ClO}_4$. Seven hundred milligrams of $\mathrm{RhBr}_3\cdot2\mathrm{H_2O}$, 1.13 g of *l*-pn·2HCl and 0.43 g of potassium hydroxide were dissolved in 50 m*l* of water, heated on a water bath with reflux, treated with a solution containing 0.43 g potassium hydroxide in 50 m*l* of

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[*1] Part II, K. Ohashi, J. Fujita, B. Shimoyama and K. Saito, This Bulletin, **41**, 2422 (1968).

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

2) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 202 (1965).

3) C. J. Hawkins, E. Larsen and I. Olsen, *Acta Chem. Scand.*, **19**, 1915 (1965).

4) F. Basolo, J. C. Bailar, Jr., and B. R. Tarr, *J. Am. Chem. Soc.*, **72**, 2433 (1950).

5) A. V. Babaeva and E. Ya. Khananova, *Russ. J. Inorg. Chem.*, **10**, 1441 (1965).

TABLE 1. CHEMICAL ANALYSIS OF THE COMPLEXES

Complexes	C (%)		H (%)		N (%)	
	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
$[PtCl_2(l\text{-pn})_2]Cl_2\cdot H_2O$	14.32	14.74	4.41	4.71	11.13	10.97
$[PtCl_2(l\text{-chxn})_2]Cl_2\cdot H_2O$	24.71	24.59	5.18	5.70	9.60	9.06
$[PtBr_2(l\text{-pn})_2]Cl_2\cdot H_2O$	12.18	12.12	3.75	4.00	9.46	8.98
$[PtCl_4(l\text{-pn})]$	8.77	9.60	2.45	2.27	6.82	6.63
$[PtBr_4(l\text{-pn})]$	6.12	6.80	1.70	2.14	4.76	4.50
$[PdCl_2(l\text{-pn})_2](NO_3)_2$	16.03	16.25	4.48	4.75	18.69	18.24
$[RhCl_2(l\text{-pn})_2]ClO_4$	17.10	17.28	4.78	4.87	13.29	12.51
$[RhBr_2(l\text{-pn})_2]ClO_4$	14.12	13.80	3.95	4.09	10.98	11.22
$[CoCl_2(l\text{-pn})_2]Cl\cdot 2H_2O$	20.62	20.97	6.92	6.88	16.03	16.27
$[CoBr_2(l\text{-pn})_2]Br_2\cdot 2H_2O$	17.23	17.70	5.79	5.34	13.40	12.54
$[PtCl_2(l\text{-pn})_2](ClO_4)_2$	11.75	11.68	3.29	3.36	9.14	8.87
$[PtBr_2(l\text{-pn})_2](ClO_4)_2$	10.27	10.34	2.87	3.20	7.98	7.78

water dropwise, heated for about 2 hr and filtered. The filtrate was passed through a column containing cation exchanger Dowex 50 W in H form. The column was washed with water and the adsorbed band eluted with 3% hydrobromic acid. The eluate was evaporated to dryness *in vacuo* at 60°C. The residue was extracted with methanol and treated with ether. The precipitate was dissolved in a small amount of water and concentrated perchloric acid was added. The product was recrystallized from methanol solution by adding ether.

Tetrabromo-l-propylenediamineplatinum(IV), $[PtBr_4(l\text{-pn})]$ was obtained by oxidizing $[PtBr_2(l\text{-pn})]$ in water with bromine. Orange crystals were precipitated by concentrating the solution on a water bath.

The other complexes were prepared by the method described in the literatures.[2,3,6,7]

The results of the chemical analysis are given in Table 1.

Measurements. Visible and ultraviolet absorption spectra were obtained by using 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.

To avoid the aquation of coordinated halides, cobalt and rhodium complexes, *trans*-$[PtCl_2(l\text{-pn})_2](ClO_4)_2$ and *trans*-$[PtBr_2(l\text{-pn})_2](ClO_4)_2$ were dissolved in methanol, and *trans*-$[PtCl_2(l\text{-pn})_2]Cl_2$, *trans*-$[PtCl_2(l\text{-chxn})_2]Cl_2$ and *trans*-$[PdCl_2(l\text{-pn})_2](NO_3)_2$ in 1.0N hydrochloric acid. All the measurements were made at room temperature.

Results and Discussion

The AB and CD spectra of the complexes measured are shown in Figs. 1—5. The CD spectra of *trans*-$[CoX_2(l\text{-pn})_2]^+$ ($X=Cl^-$ and Br^-)[2,3] and *trans*-$[RhCl_2(l\text{-pn})_2]^+$ [6] had been measured only in the region of $d\rightarrow d$ transitions of these complexes.

***d-d* Transition.** Since the complex ions, *trans*-$[MX_2(l\text{-pn})_2]^{n+}$ have a pseudo-tetragonal symmetry, the two spin-allowed $d\rightarrow d$ transitions expected for a d^6-diamagnetic system, ${}^1A_1\rightarrow{}^1T_1$ and ${}^1A_1\rightarrow{}^1T_2$, should split into two components, ${}^1A_1\rightarrow{}^1A_1+{}^1E^{(a)}$ and ${}^1A_1\rightarrow{}^1B_2+{}^1E^{(b)}$, respectively. Of these four transitions, only the ${}^1A_1\rightarrow{}^1B_2$ is magnetically forbidden.

Fairly strong positive CD peaks at 16600 and 15600 cm⁻¹ for dichloro- and dibromo-cobalt(III)

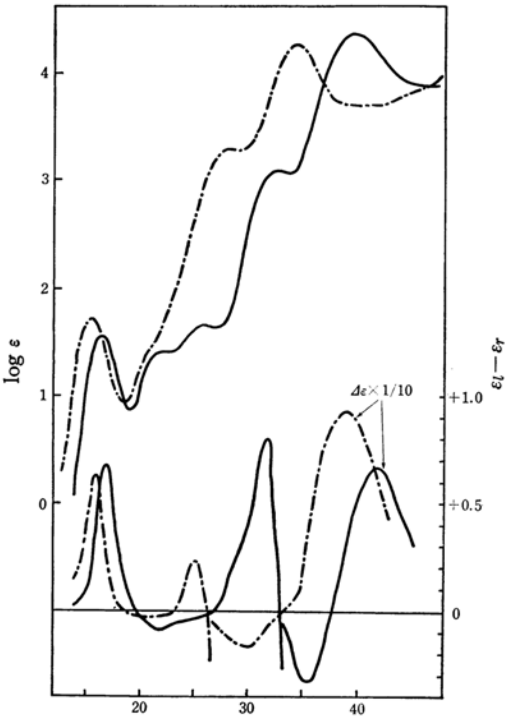

Fig. 1. AB and CD spectra of *trans*-$[CoCl_2(l\text{-pn})_2]$-Cl (——) and *trans*-$[CoBr_2(l\text{-pn})_2]$ Br (-·-·-) in methanol.

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[6] S. K. Hall and B. E. Douglas, *Inorg. Chem.*, **7**, 533 (1968); J. H. Dunlop and R. D. Gillard, *Mol. Phys.*, **7**, 494 (1964).

[7] F. P. Dwyer and A. M. Sargeson, *J. Am. Chem. Soc.*, **81**, 5272 (1959).

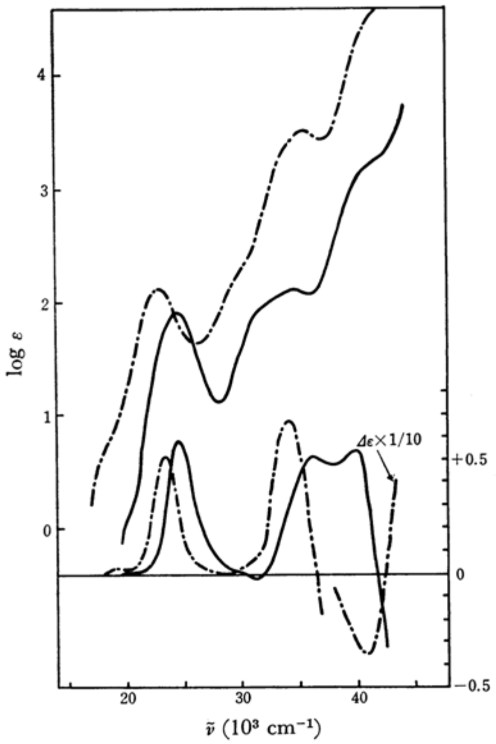

Fig. 2. AB and CD spectra of *trans*-$[RhCl_2$-(l-pn$)_2]$-ClO_4 (——) and *trans*-$[RhBr_2(l\text{-pn})_2]\ ClO_4$ (–·–·–) in methanol.

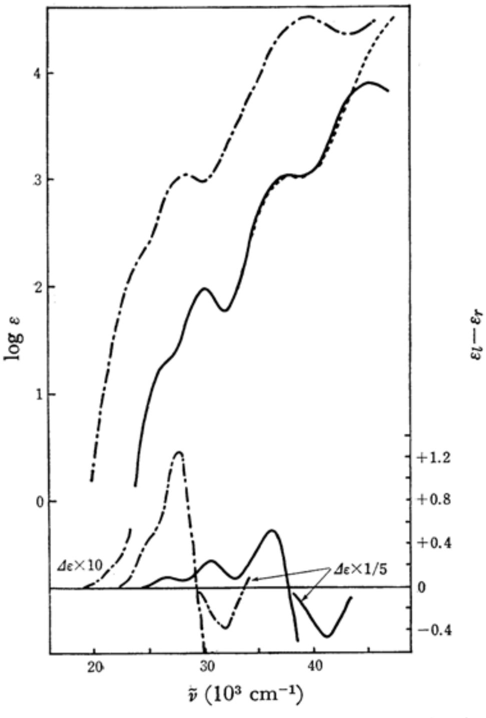

Fig. 3. AB and CD spectra of *trans*-$[PtCl_2(l\text{-pn})_2]$-Cl_2 (-----) and *trans*-$[PdCl_2\ (l\text{-pn})_2]\ (NO_3)_2$ (–·–·–) in 1N hydrochloric acid and those of *trans*-$[PtCl_2$-(l-pn)] $(ClO_4)_2$ in methanol (——).

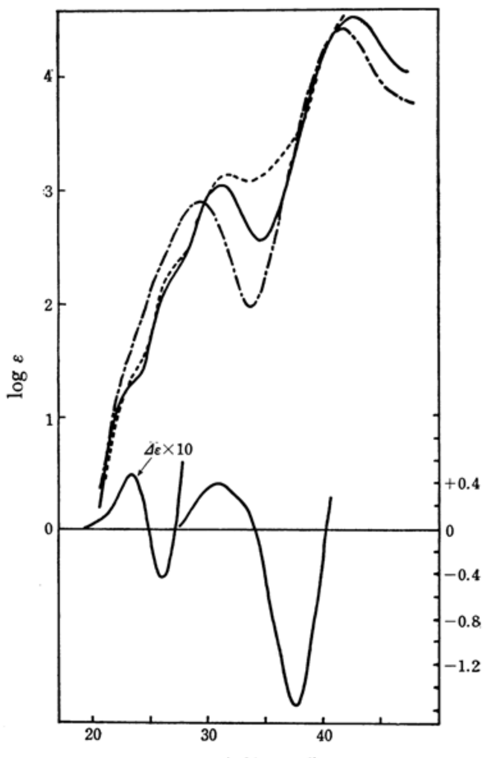

Fig. 4. AB and CD spectra of *trans*-$[PtBr_2(l\text{-pn})_2]$-$(ClO_4)_2$ in methanol (——) and AB spectrum of *trans*-$[PtBr_2(l\text{-pn})_2]Br_2$ in 1N hydrobromic acid (------) and that of *trans*-$K_2[PtBr_2(CN)_4]$ (–·–·–).

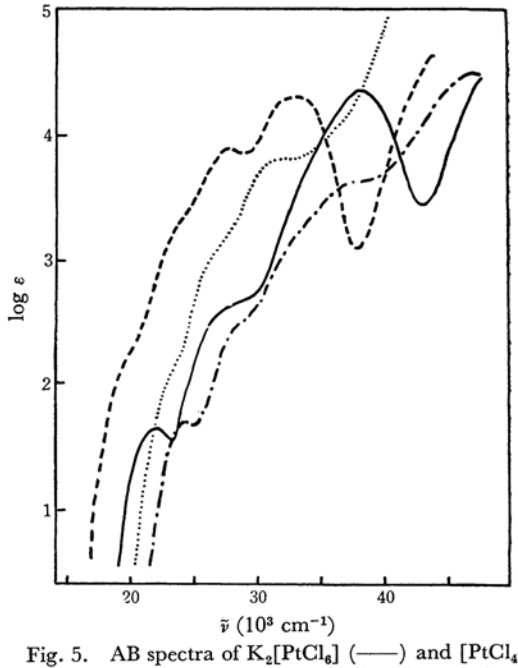

Fig. 5. AB spectra of $K_2[PtCl_6]$ (——) and $[PtCl_4$-(l-pn)] (–·–·–) in 1N hydrochloric acid and those of $K_2[PtBr_6]$ (------) and $[PtBr_4(l\text{-pn})]$ (······) in 1N hydrobromic acid.

complexes, respectively, have been assigned to the $^1\mathrm{A}_1 \rightarrow {}^1\mathrm{E}^{(a)}$ transition ($\mathrm{I_a}$ band), a split component of the so-called first band[2,3,8] (Fig. 1).

The CD and AB spectra of rhodium(III) complexes are very similar to those of cobalt(III) complexes, except that the transition energies are higher in the former complexes (Fig. 2). Therefore, the positive CD bands at 24600 cm^{-1} for dichloro- and at 23500 cm^{-1} for dibromo complexes of rhodium(III) can reasonably be assgined to $^1\mathrm{A}_1 \rightarrow {}^1\mathrm{E}^{(a)}$ transition ($\mathrm{I_a}$ band).

The AB spectrum of *trans*-$[\mathrm{PdCl_2}(l\text{-pn})_2]^{2+}$ exhibits no distinct ligand field bands because of the overlapping of strong charge transfer bands (Fig. 3). However, a positive CD shoulder appears at about 24500 cm^{-1} corresponding to a shoulder AB band in the same energy region. Since this frequency value is almost the same as that of $\mathrm{I_a}$ band of rhodium(III) complex with an isoelectronic structure, this shoulder band could be assigned to the $^1\mathrm{A}_1 \rightarrow {}^1\mathrm{E}^{(a)}$ transition ($\mathrm{I_a}$).

Both *trans*-$[\mathrm{PtCl_2}(l\text{-pn})_2]^{2+}$ and *trans*-$[\mathrm{PtCl_2}(l\text{-chxn})_2]^{2+}$ show two positive CD peaks in the ligand field band region (at around 26500 and 30500 cm^{-1}) (Fig. 3). The absorption intensities of these bands indicate that the positive CD peak at the longer wavelength could correspond to the spin-forbidden transition, and the other positive peak at the shorter wavelength to the spin-allowed $^1\mathrm{A}_1 \rightarrow {}^1\mathrm{E}^{(a)}$ transition, although the CD intensity is relatively weak. The rhodium(III) complexes and the palladium(IV) complex show also a trace of positive CD band in the region of their spin-forbidden $d \rightarrow d$ transition (see Figs. 2 and 3).

trans-$[\mathrm{PtBr_2}(l\text{-pn})_2]^{2+}$ gives no definite AB peak corresponding to the $d \rightarrow d$ transitions, but its CD spectrum exhibits a weak positive and a weak negative band at 23300 and 26000 cm^{-1} respectively (Fig. 4). Comparison with the data for the other complexes described above suggests that the positive CD component would be due to the spin-forbidden $d \rightarrow d$ transition.

The negative CD peak, however, should not be assigned to the $\mathrm{I_a}$ band, since the energy difference between this band and the $\mathrm{I_a}$ band of *trans*-$[\mathrm{PtCl_2}(l\text{-pn})_2]^{2+}$ amounts to about 4500 cm^{-1}, which is somewhat too large as compared with the difference between the $\mathrm{I_a}$ band of dichloro- and that of dibromo complex of cobalt(III) (1000 cm^{-1}) and rhodium(III) (1100 cm^{-1}). The actual symmetry of *trans*-$[\mathrm{MX_2}(l\text{-pn})_2]^{n+}$ ion should be lower than D_{4h}, and $^1\mathrm{A}_1 \rightarrow {}^1\mathrm{E}^{(a)}$ transition can split further into two components. Hawkins *et al.*[3] observed another weak negative CD band at longer wavelength side of the strong positive peak ($\mathrm{I_a}$) for *trans*-$[\mathrm{CoCl_2}(l\text{-pn})_2]^{+}$ ion and assigned both of them to the components resulting from the splitting of degenerate $^1\mathrm{A}_1 \rightarrow {}^1\mathrm{E}^{(a)}$ transition. We also observed a weak negative peak at 18600 cm^{-1} of *trans*-$[\mathrm{RhBr_2}(l\text{-pn})_2]^{+}$ ion in 3N hydrobromic acid solution. Thus, the weak negative CD band of *trans*-$[\mathrm{PtBr_2}(l\text{-pn})_2]^{+}$ at 26000 cm^{-1} may be considered to be a split component of this type. The positive CD component corresponding to $\mathrm{I_a}$ band might be hidden by the positive CD peak of charge transfer transition, which is discussed below.

The AB spectra of $[\mathrm{PtCl_4}(l\text{-pn})]$ and $[\mathrm{PtBr_4}(l\text{-pn})]$ are very similar to those of $\mathrm{K_2[PtCl_6]}$ and $\mathrm{K_2[PtBr_6]}$, respectively (Fig. 5). Thus, on the basis of the results of spectroscopic study reported by Jϕrgensen,[9] the positive CD peaks at 24100 cm^{-1} for tetrachloro and 21500 cm^{-1} for tetrabromo complex were assigned to spin-forbidden bands and those at 28700 cm^{-1} for tetrachloro and 26500 cm^{-1} for tetrabromo complexes were assgined to the $^1\mathrm{A}_1 \rightarrow {}^1\mathrm{E}^{(a)}$ transition (assumed as pseudo D_{4h} symmetry[6]).

Concerning the so-called second absorption bands, a weak negative and a positive CD were observed for *trans*-$[\mathrm{CoCl_2}(l\text{-chxn})_2]^{+}$, which were assigned to be $^1\mathrm{A}_1 \rightarrow {}^1\mathrm{B}_2$ and $^1\mathrm{A}_1 \rightarrow {}^1\mathrm{E}^{(b)}$ transition, respectively.[8] On the basis of these data, the positive CD peak at 36500 cm^{-1} of *trans*-$[\mathrm{RhCl_2}(l\text{-pn})_2]^{+}$ is considered to correspond to the $^1\mathrm{A}_1 \rightarrow {}^1\mathrm{E}^{(b)}$ transition, though its CD intensity is somewhat too large for the magnetically forbidden II band (in O_h symmetry).

Charge Transfer Transition. It is well known that complex ions, $[\mathrm{CoX(NH_3)_5}]^{2+}$ and $[\mathrm{CoX_2(NH_3)_4}]^{+}$, where X=Cl$^-$ and Br$^-$, have two intense bands in the ultraviolet region of their spectra. These are interpreted on the basis of LCAO-MO theory to be charge transfer bands from p orbitals of the halide ion to mainly $d_z{}^2$ orbital of the cobalt(III) ion,[10] the one at longer wavelength involving $p_\pi \rightarrow d_z{}^2$ and the other at shorter wavelength $p_\sigma \rightarrow d_z{}^2$ transition. Two intense bands were observed for all the complexes studied in this work except for *trans*-$[\mathrm{RhCl_2}(l\text{-pn})_2]^{+}$ in the ultraviolet region, which are expected to be of the same nature as those of cobalt(III) complexes. The energy of $p_\sigma \rightarrow d_z{}^2$ transition of *trans*-$[\mathrm{RhCl_2}(l\text{-pn})_2]^{+}$ is too high to be measured, and only the $p_\pi \rightarrow d_z{}^2$ band was observed.

In the CD spectra, three CD peaks appear in the charge transfer band region, a relatively weak positive, a strong negative and a strong positive peak from longer to shorter wavelength. According to Treptow,[8] *trans*-$[\mathrm{MX_2}(l\text{-chxn})_2]^{n+}$ ion (approximated as D_{4h} symmetry) can have three charge transfer transitions from halide ions to $d_z{}^2$ orbital; of these two are $p_\pi \rightarrow d_z{}^2$ and one is $p_\sigma \rightarrow d_z{}^2$.

As can be seen in Figs. 3 and 4, the CD behavior of the bands at 38000 cm^{-1} for *trans*-$[\mathrm{PtCl_2}(l\text{-}$

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[8] R. S. Treptow, *Inorg. Chem.*, **5**, 1593 (1966).

[9] C. K. Jϕrgensen, *Acta Chem. Scand.*, **10**, 518 (1956).

[10] H. Yamatera, *J. Inorg. Nucl. Chem.*, **15**, 50 (1960).

TABLE 2. NUMERICAL DATA OF ABSORPTION AND CIRCULAR DICHROISM ($\tilde{\nu}$ in $10^3\,cm^{-1}$)

	AB $\tilde{\nu}_{max}(\log \varepsilon)$	CD $\tilde{\nu}_{max}(\varepsilon_l - \varepsilon_r)$	Assignment
$[CoCl_2(l\text{-pn})_2]Cl\cdot 2H_2O^{a)}$	16.4(1.61)	16.6(+0.76)	$E^{(a)}$
	21.7(1.45)	21.6(−0.10)	A_2
	25.6(1.70)	~25 (−0.04)	B_2
	32.6(3.14)	31.3(+0.91) 35.2(−3.6)	$p_\pi \rightarrow d_{z^2}$
	39.7(4.42)	41.7(+7.6)	$p_\sigma \rightarrow d_{z^2}$
$[CoBr_2(l\text{-pn})_2]Br\cdot 2H_2O^{a)}$	~13 (0.4)		
	15.4(1.76)	15.6(+0.69)	$E^{(a)}$
	~20.5(1.3)	20.4(−0.02)	A_2
	~23 (1.9)	~22.5(−0.02)	B_2
	28.3(3.34)	25.1(+0.27) 31.1(−1.8)	$p_\pi \rightarrow d_{z^2}$
	34.3(4.30)	38.5(+10.3)	$p_\sigma \rightarrow d_{z^2}$
$[RhCl_2(l\text{-pn})_2]ClO_4^{a)}$	~20	~20 (+)	Triplet
	24.7(1.92)	24.6(+0.59)	$E^{(a)}$
	~31.5(1.9)	31.0(−0.03)	A_2
	34.8(2.12)	36.5(+0.51)	$E^{(b)}$
	~42(~3.1)	40.0(+0.55) >44(>−3.5)	$p_\pi \rightarrow d_{z^2}$
$[RhBr_2(l\text{-pn})_2]ClO_4^{a)}$		~16.5(+0.006)$^{b)}$	Triplet
	23.40(2.11)	18.6(−0.010)$^{b)}$ 23.5(+0.51)	$E^{(a)}$
		26.7(−0.051)	A_2
	30 (2.2)		B_2
	35.7(3.50)	34.1(+0.67) ~40 (−3.6)	$p_\pi \rightarrow d_{z^2}$
	42.4(4.57)	>43.5(>+4.2)	$p_\sigma \rightarrow d_{z^2}$
$[PdCl_2(l\text{-pn})_2](NO_3)_2^{a)}$	~24 (2.1)	~24.5(+0.4)	$E^{(a)}$
	28.6(3.03)	27.8(+1.3) 32.0(−1.8)	$p_\pi \rightarrow d_{z^2}$
	39.5(4.49)	(+)	
$[PtCl_2(l\text{-pn})_2](ClO_4)_2^{a)}$	~26.5(1.2)	26.6(+0.13)	Triplet
	30.2(1.99)	30.5(+0.27)	$E^{(a)}$
	38.0(3.0)	36.2(+0.76) 41.7(−1.8)	$p_\pi \rightarrow d_{z^2}$
	44.8(3.89)	>44.4(>+0.8)	$p_\pi \rightarrow d_{z^2}$
$[PtCl_2(l\text{-pn})_2]Cl_2\cdot H_2O^{c)}$	~26.5(1.2)	26.7(+0.11)	Triplet
	30.3(1.98)	30.6(+0.25)	$E^{(a)}$
	38.0(3.03)	36.4(+0.54) 41.2(−2.2)	$p_\pi \rightarrow d_{z^2}$
$[PtCl_2(l\text{-chxn})_2]Cl_2\cdot H_2O^{c)}$	~26.5(1.2)	26.5(+0.17)	Triplet
	30.1(2.03)	30.1(+0.35)	$E^{(a)}$
	38.0(3.18)	35.7(+0.62) 39.4(−1.36)	$p_\pi \rightarrow d_{z^2}$
$[PtBr_2(l\text{-pn})_2](ClO_4)_2^{a)}$	~23.5(1.3)	23.3(+0.05)	Triplet
	~26.5(2.2)	26.0(−0.04)	$E^{(a)}$
	31.1(3.05)	~30.5(+0.4) ~38 (−1.7)	$p_\pi \rightarrow d_{z^2}$
	42.6(4.51)	>43.5(>+5.5)	$p_\sigma \rightarrow d_{z^2}$
$[PtCl_4(l\text{-pn})]$	24.2(1.70)	24.1(+0.10)	Triplet
	~28.5(2.5)	28.7(+0.23)	
	~32.5(3.0)	~34.8(−0.2)	CT
	~37.6(3.6)	42.6(+2.34)	CT
$[PtBr_4(l\text{-pn})]$		21.5(+0.08)	Triplet
		26.5(+0.29)	
		~40.8(+3.5)	CT

a) in methanol, b) $[RhBr_2(l\text{-pn})_2]Br$ in 3N HBr, c) in 1N HCl, CT: charge transfer band.

$pn)_2]^{2+}$, 31100 cm^{-1} for *trans*-$[PtBr_2(l\text{-pn})_2]^{2+}$ and 28600 cm^{-1} for *trans*-$[PdCl_2(l\text{-pn})_2]^{2+}$ is quite similar to those assigned to $p_\pi \rightarrow d_{z^2}$ charge transfer for the cobalt(III) complexes. Therefore, those CD peaks could be assigned to charge transfer transitions.

The similarity of absorption spectra between $K_2[PtBr_2(CN)_4]$ and $[PtBr_2(l\text{-pn})_2](ClO_4)_2$ will support the above assignment. If the bands at 31100 cm^{-1} of the latter and 29200 cm^{-1} of the former were due to $d \rightarrow d$ transition, the order of the "spectrochemical series" of CN^- and *l*-pn should be reversed, to contradict with the usual observation. Since the d_{z^2} orbital might not be affected by coordinated ligands in the *xy* plane, the energy of charge transfer transition from *p* orbitals of halide ions to d_{z^2} orbital for *trans*-$[PtBr_2(CN)_4]^{2-}$ and *trans*-$[PtBr_2(l\text{-pn})_2]^{2+}$ should not differ largely.

Consequently, the energies of charge transfer band agree well with the general trend of ligand to metal charge transfer. That is, the energy of a charge transfer band is higher for the metal with larger atomic number, whenever the oxidation number of the central metals is the same (*e. g.* Co(III) and Rh(III) or Pd(IV) and Pt(IV)), and is also higher for the metal of smaller oxidation number with an isoelectronic structure (Rh(III) and Pd(IV)).

The AB and CD data are summarized in Table 2.

Ion Association Band. It is known that $[Pt(en)_3]^{4+}$ associates with Cl^- or $S_2O_3^{2-}$ to change

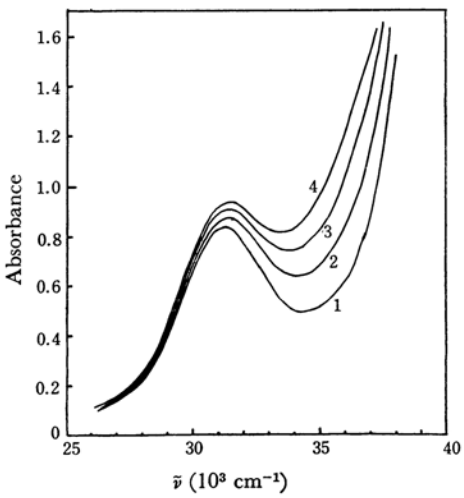

Fig. 6. AB spectra of *trans*-$[PtBr_2(l\text{-pn})_2]Br_2$ (0.664 $\times 10^{-3}$ mol/*l*) in 0.05N perchloric acid containing (1) 0.2M, (2) 0.4M, (3) 0.6M and (4) 0.8M sodium bromide.

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11) R. Larsson, *Acta Chem. Scand.*, **21**, 1081 (1967).
12) A. J. Poë, *J. Chem. Soc.*, **1963**, 183.

the absorption and circular dichroism spectra.[11] Though absorption spectra of *trans*-[$PtCl_2$(*l*-pn)$_2$]$^{2+}$ in methanol and in 1N hydrochloric acid are not very different (see Fig. 3), those of *trans*-[$PtBr_2$(*l*-pn)$_2$]$^{2+}$ in methanol and in 1N hydrobromic acid are significantly different, *i. e.* a new band appears at about 35000 cm^{-1} in 1N hydrobromic acid (Fig. 4). Poë[12] studied the absorption spectra of *trans*-[$PtBr_2$(en)$_2$]$^{2+}$ in detail and assigned this band to an ion association band. The absorption spectra of [$PtBr_2$(*l*-pn)$_2$]Br_2 in 0.05N perchloric acid (to prevent deprotonation of the coordinated amine) with varying bromide concentration are shown in Fig. 6. The intensity of this band increases with an increase in bromide concentration. The CD spectra of the solutions, however, are quite similar to one another, to indicate that the ion association is not stereoselective.

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