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Absorption Spectra and Circular Dichroisms of Metal Complexes. I. Platinum(II)-, Palladium(II)- and Gold(III)-Complexes Containing Optically Active Diamines

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In order to study the nature of absorption bands in square-planar metal complexes of d^8 type, a number of platinum(II), palladium(II) and gold(III) complexes containing *l*-propylenediamine and *l*-cyclohexanediamine were prepared and their circular dichroism (CD) and rotatory dispersion (RD) as well as absorption spectra (AB) were measured. Three or four absorption bands corresponding to *d–d* transitions were observed for each platinum(II) and palladium(II) complex. All the complexes, except for $[\mathrm{Au}(l\text{-pn})_2]\mathrm{Cl}_3$, $[\mathrm{Au}(l\text{-chxn})_2]\mathrm{Cl}_3$ and $[\mathrm{PdCl}_2(l\text{-pn})]$, give two possitive CD bands in the wavelength region from visible to 210 mμ, which are assigned to the spin-forbidden and spin-allowed $\mathrm{A}_1 \to \mathrm{E}$ transition. Both $[\mathrm{Au}(l\text{-pn})_2]\mathrm{Cl}_3$ and $[\mathrm{Au}(l\text{-chxn})_2]\mathrm{Cl}_3$ exhibit only one strong positive CD band corresponding to the ligand field transition probably mixed with charge transfer transition. $[\mathrm{PdCl}_2(l\text{-pn})]$ gives a weak negative and a strong positive band corresponding to the transitions, $\mathrm{A}_1 \to \mathrm{A}_2$ and $\mathrm{A}_1 \to \mathrm{E}$, respectively. The CD strength of the bis-*l*-diamine complexes is almost twice those of the mono-*l*-diamine complexes. The vicinal effect of *l*-cyclohexanediamine was about twice as strong as that of *l*-propylenediamine. Absorption spectra of the $[\mathrm{MX}_4]^{n-}$ ($\mathrm{M}=\mathrm{Pt}^{2+}$, Pd^{2+} and Au^{3+}, $\mathrm{X}=\mathrm{Cl}^-$ and Br^-) show a shoulder and two bands in the ultraviolet region adjacent to the ligand field bands. The shoulder band was assigned to the symmetry forbidden, and the two strong bands to the symmetry allowed $p_\pi \to d_{x^2-y^2}$ and $p_\sigma \to d_{x^2-y^2}$ charge transfer transitions. In the $[\mathrm{MBr}_4]^{n-}$, the $p_\pi \to d_{x^2-y^2}$ band splits into two components, corresponding to $\mathrm{A}_{1g} \to \mathrm{A}_{1u}$ and the other $\mathrm{A}_{1g} \to \mathrm{E}_u$ transition.

The ordering of the metal *d* orbitals for a square-planar type complex is expected to change variously depending on the strength of tetragonal distortion of the complex or on the strength of the π-bonding between the metal ion and ligands. This makes the assignment of ligand field bands of square-planar complexes difficult. For $[\mathrm{PtCl}_4]^{2-}$, a typical complex ion of this type, a number of theoretical[1–5] and experimental[6–10] studies have been made for determining the relative ordering of the metal *d*-orbitals (Fig. 1). Of these, a recent magnetic circular dichroism study[9] gives a valuable information on this problem. In this paper we report the circular dichroism, the rotatory dispersion and the absorption spectra of a number of platinum(II), palladium(II) and gold(III) complexes containing optically active diamines, and compare the results with those obtained previously for $[\mathrm{PtCl}_4]^{2-}$.

Experimental

Ligands. The optically active ligands, *l*-propylenediamine[11][*1] and *l*-cyclohexandiamine[12][*1] were obtained by resolving their commercial racemates according to the methods described in the literature.

Preparations of the Complexes. Five new complexes were prepared by the following method.

Dichloro-l-cyclohexanediamineplatinum(II), $[\mathrm{PtCl}_2(l\text{-chxn})]$. To an aqueous solution of $\mathrm{K}_2[\mathrm{PtCl}_4]$, an equivalent amount of *l*-cyclohexanediamine in water was added at room temperature. In a few hours,

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[*1] The following abbreviations are used; *l*-pn= $(-)_\mathrm{D}$-propylenediamine, *l*-chxn $=(-)_\mathrm{D}$-cyclohexanediamine

TABLE 1. CHEMICAL ANALYSIS OF THE COMPLEXES

Complexes	C (%)		H (%)		N (%)		
	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Prep.
$[PtCl_2(l\text{-pn})]$	10.59	11.07	2.96	3.07	8.24	8.03	a
$[Pt(l\text{-pn})_2]Cl_2 \cdot H_2O$	16.67	16.22	5.13	5.35	12.96	12.66	b
$[Pt(en)(l\text{-pn})]Cl_2$	15.01	15.72	4.53	5.02	14.00	13.53	b
$[Pt(NH_3)_2(l\text{-pn})]Cl_2$	9.63	10.43	4.31	4.17	14.97	14.73	b
$[Pt(NH_3)_2(l\text{-chxn})]Cl_2$	17.40	17.41	4.87	5.05	13.52	13.31	c
$[Pt(l\text{-chxn})_2]Cl_2$	29.15	29.39	5.71	5.92	11.33	11.43	d
$[PdCl_2(l\text{-pn})]$	14.33	14.45	4.01	4.14	11.14	10.71	e
$[Pd(l\text{-pn})_2]Cl_2 \cdot H_2O$	20.98	21.30	6.45	6.41	16.31	16.04	b
$[Pd(l\text{-chxn})_2]Cl_2$	35.53	35.82	6.96	7.00	13.81	13.44	c
$[Au(l\text{-pn})_2]Cl_3$	15.96	15.43	4.46	4.46	12.41	12.04	c
$[Au(l\text{-chxn})_2]Cl_3$	27.11	25.88	5.31	5.66	10.53	9.60	c

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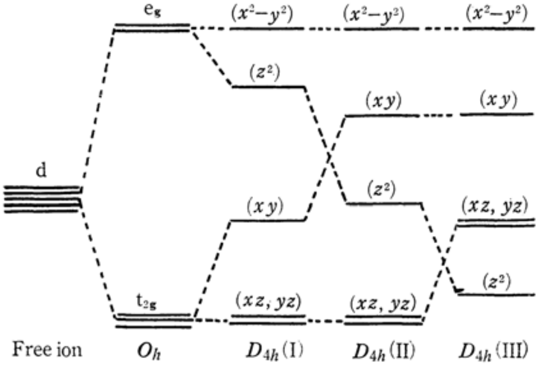

Fig. 1. Probable modes of orbital splitting in square-planar D_{4h} complexes.

yellow crystals began to appear and after 24 hr, the complex $[PtCl_2(l\text{-chxn})]$ precipitated almost quantitatively. This was filtered, and washed with water, ethanol and ether. This complex is almost insoluble in water and dilute hydrochloric acid.

Diammine-l-cyclohexanediamineplatinum(II) Chloride, $[Pt(NH_3)_2(l\text{-chxn})]Cl_2$, was obtained from $[PtCl_2(l\text{-chxn})]$ and aqueous ammonia by a similar method that for $[Pt(NH_3)_2(l\text{-pn})]Cl_2$.

Bis-l-cyclohexanediaminepalladium(II) Chloride, $[Pd(l\text{-chxn})_2]Cl_2$, was prepared by the same method as the bisethylenediamine complex using *l*-cyclohexanediamine.

White Crystals of Bis-l-propylenediaminegold(III) Chloride $[Au(l\text{-pn})_2]Cl_3$ *and Bis-l-cyclohexanediaminegold(III) Chloride* $[Au(l\text{-chxn})_2]Cl_3$ were prepared by the method described by Block and Bailar[13] for the $[Au(en)_2]Cl_3$.

Other complexes used in this work were prepared according to the methods described in the literatures given in Table 1.

The results of the chemical analysis of all the complexes prepared here are also given in Table 1.

Measurements. Visible and ultraviolet absorption spectra were obtained by using Hitachi recording spectrophotometer Model EPS-3. The diffuse reflectance spectrum of $[PdCl_2(l\text{-pn})]$ was measured by Hitachi EPU-2A spectrophotometer with a diffuse reflectance attachment. The RD and the CD curves were determined with a Model ORD/UV-5 spectrophotometer of Japan Spectroscopic Co.

To avoid the aquation of coordinated halide, the halogeno complexes were dissolved in an aqueous solution containing an excess of appropriate halide; $K_2[PtCl_4]$ and $[PtCl_2(l\text{-pn})]$ in 2.0 N hydrochloric acid, $K_2[PdCl_4]$ in 1.0 N hydrochloric acid solution, $[PdCl_2(l\text{-pn})]$ and $H[AuCl_4]$ in 0.2 M potassium chloride solution. Absorption spectra of $K_2[PtBr_4]$, $K_2[PdBr_4]$ and $K[AuBr_4]$ were measured in 0.2 M potassium bromide solutions. $[Au(l\text{-pn})_2]Cl_3$ and $[Au(l\text{-chxn})_2]Cl_3$ were dissolved in 10^{-4} M perchloric acid to prevent deprotonation of the amino groups in coordinated diamines. Other complexes were dissolved in water. All the measurements were made at room temperature, 15—20°C.

It has been reported[14] that the above mentioned complexes may form a hexa-coordinated, distorted octahedral complex taking two halide in a solution containing an excess of halide. In the present measurements, however, no such complexes seemed to be present, since the absorption spectrum of $[Pd(l\text{-pn})_2]Cl_2$ in a 0.2 M potassium chloride solution was identical with that in an aqueous solution. The absorption spectrum of $[PdCl_2(l\text{-pn})]$ in 0.2 M potassium chloride solution was also very similar to the reflectance spectrum (see Table 2).

Results and Discussion

Numerical data for the AB and the CD maxima of the complexes are summarized in Table 2,

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TABLE 2. NUMERICAL DATA OF ABSORPTION AND CIRCULAR DICHROISM

	Band 2				Band 3				Band 4			
	Absorption*		CD*		Absorption*		CD*		Absorption*		CD*	
	ν_{max}	log ε	ν_{max}	$\varepsilon_l-\varepsilon_r$	ν_{max}	log ε	ν_{max}	$\varepsilon_l-\varepsilon_r$	ν_{max}	log ε	ν_{max}	$\varepsilon_l-\varepsilon_r$
$K_2[PtCl_4]$†	21.0	1.18	—	—	25.7	1.78	—	—	30.5	1.80	—	—
$[PtCl_2(l\text{-pn})]$	27.3	1.56	27.0	+0.15	33.1	2.37			~37	~2.10	37.2	+0.38
$[Pt(l\text{-pn})_2]Cl_2$	35.7	1.65	35.7	+0.54	41.6	1.00*2			44.6	2.68	45.2	+1.03
$[Pt(en)(l\text{-pn})]Cl_2$	35.7	1.61	35.7	+0.29	~41.5sh				44.6	2.65	45.1	+0.54
$[Pt(NH_3)_2(l\text{-pn})Cl_2$	35.2	1.60	35.2	+0.22	~41.5sh				45.3	2.64	44.8	+0.51
$[Pt(l\text{-chxn})_2]Cl_2$	35.3	1.67	35.5	+0.94	~41.1sh				45.0	2.69	45.3	+2.02
$[Pt(NH_3)_2(l\text{-chxn})]Cl_2$	35.2	1.62	35.0	+0.40	~41.5sh				45.1	2.64	45.0	+0.86
$[Pt(NH_3)_4]Cl_2$	34.8	1.57	—	—	~41.5sh		—	—	~46sh		—	—
$K_2[PdCl_4]$	16.5	0.81*2	—	—	21.0	2.16*2	—	—	23.7	1.73*2	—	—
$[PdCl_2(l\text{-pn})]$	22.5	1.28			26.2	2.37*2	25.3	(−0.10)	28.7	2.26*2	28.7	+0.43
$[PdCl_2(l\text{-pn})]$*3					26.3							
$[Pd(l\text{-pn})_2]Cl_2$	~29		29.0	+0.06					34.8	2.50	35.5	+1.22
$[Pd(l\text{-chxn})_2]Cl_2$	~29		29.1	+0.13					34.8	2.59	35.3	+2.94
$[Au(l\text{-pn})_2]Cl_3$											~43.5	+2.8
$[Au(l\text{-chxn})_2]Cl_3$									45.5	4.26	~42.8	+6.3

* ν in 10^3 cm^{-1}, *2 Obtained from Gaussian analysis, *3 reflectance spectrum, † also gives band 1 at ν_{max} ~18 and log ε ~0.7, sh: shoulder

some of which were obtained by analizing an absorption curve into Gaussian components. Some representative curves for different types of the complexes are shown in Figs. 2—4.

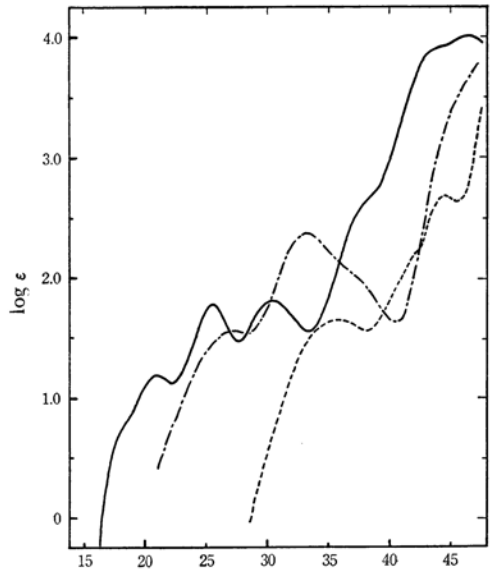

Fig. 2a

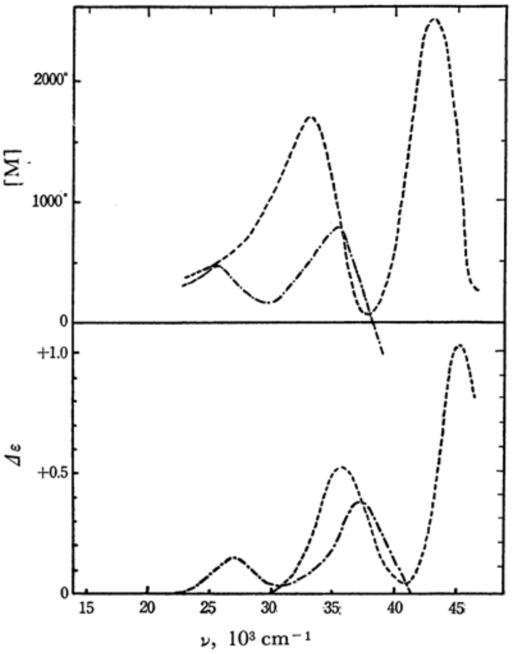

Fig. 2b

Fig. 2. Absorption spectra of $K_2[PtCl_4]$ (——), $[PtCl_2(l\text{-pn})]$ (·—·) in 2.0 N HCl and $[Pt(l\text{-pn})_2]Cl_2$ (----); 2b: Rotatory dispersion and circular dichroism of $[PtCl_2(l\text{-pn})]$ in 2.0 N HCl (·—·) and $[Pt(l\text{-pn})_2]Cl_2$ (----).

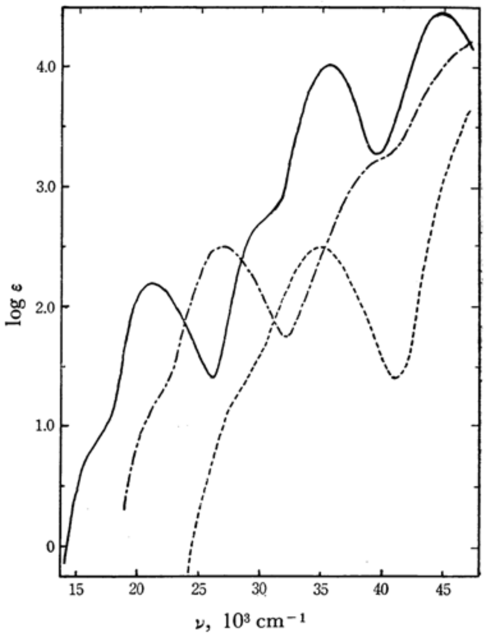

Fig. 3a

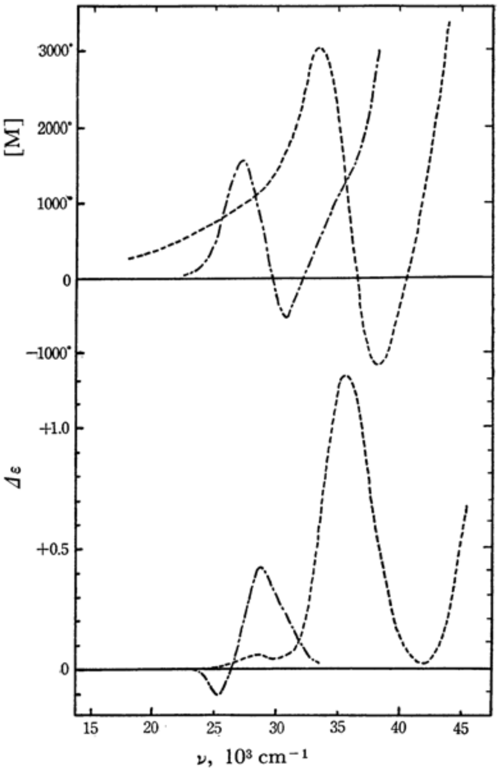

Fig. 3b

Fig. 3. Absorption spectra of $K_2[PdCl_4]$ in 1.0 N HCl (——), $[PdCl_2(l\text{-pn})]$ in 0.2 M KCl (·—·) and $[Pd(l\text{-pn})_2]Cl_2$ (----); 3b: Rotatory dispersion and circular dichroism of $[PdCl_2(l\text{-pn})]$ in 0.2 M KCl (·—·) and $[Pd(l\text{-pn})_2]Cl_2$ (----).

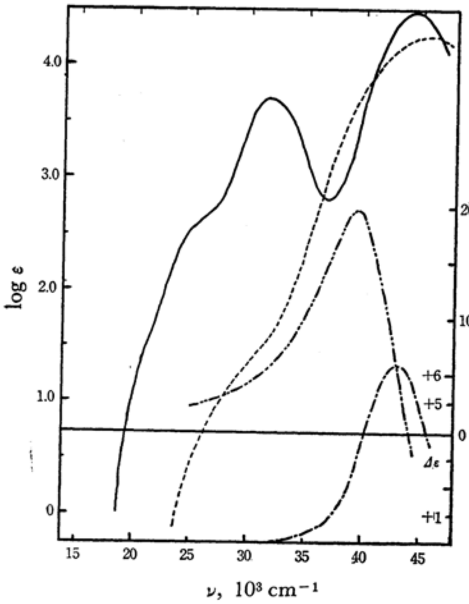

Fig. 4. Absorption spectrum of $H[AuCl_4]$ in 0.2 M KCl (——), and absorption spectrum (----), rotatory dispersion (—·—) and circular dichroism (—‥—) of $[Au(l\text{-chxn})_2]Cl_3$ in 10^{-4} M $HClO_4$.

***d-d* Transitions.** As is seen in Fig. 2, $K_2[PtCl_4]$ gives four medium intensity bands in range between 15000 and 35000 cm^{-1}. We denote them tentatively band 1, band 2, band 3 and band 4, from long to short wave length region. Since the ground state of this ion having D_{4h} symmetry is considered to be $^1A_{1g}$, three spin-allowed and three spin-forbidden *d-d* transitions $^1A_{1g}\rightarrow{}^1A_{2g}$, $^3A_{2g}$, $^1A_{1g}\rightarrow{}^1B_{2g}$, $^3B_{2g}$ and $^1A_{1g}\rightarrow{}^1E_g$, ^3E_g will be expected. The band 1 is reasonably assigned to the spin-forbidden transition, because of its low intensity.⁶⁾ The bands 3 and 4 have been assigned to the spin-allowed transitions, $d_{xy}\rightarrow d_{x^2-y^2}$ ($^1A_{2g}$) and d_{xz}, $d_{yz}\rightarrow d_{x^2-y^2}$ (^1E_g), respectively, from plane-polarized dichroism studies of a single crystal⁷,⁸,¹⁵⁾ and a magnetic circular dichroism study in a solution⁹⁾. Concerning the band 2, there are two possible assignments, the one being to a spin-forbidden (^3E_g or $^3A_{2g}$) and the other to a spin-allowed $d_{z^2}\rightarrow d_{x^2-y^2}$ ($^1B_{2g}$) transition. Although the intensity of a spin-forbidden band is usually much weaker than that of a spin-allowed, heavy metal complexes such as those of platinum(II) often give fairly strong spin-forbidden bands owing to a strong spin-orbit interaction. This makes the assignment of ligand field bands of platinum(II) complexes complicated. According to recent theoretical calculations,³⁻⁵⁾ the band 2 is assigned to a spin-forbidden transition.

Absorption spectra of the diamine complexes such as $[Pt(l\text{-pn})_2]^{2+}$ and $[Pt(en)(l\text{-pn})]^{2+}$ are very similar to that of $[Pt(NH_3)_4]^{2+}$, although the symmetries of the former are much lower than that of the latter (D_{4h}). This indicates that the perturbation to the D_{4h} field is not very significant in the diamine complexes, hence mixing between the *d*-orbitals is very small. From these experimental results, we use the same notations for *d* orbitals and electronic states of low symmetry complexes as those for $[PtCl_4]^{2-}$ described above, without subscripts g and u.

It can be seen from Table 3 that only the transitions $d_{xy}\rightarrow d_{x^2-y^2}$ and d_{xz}, $d_{yz}\rightarrow d_{x^2-y^2}$ have magnetic moment in D_{4h} field. For complexes with lower symmetry, the transition, $d_{z^2}\rightarrow d_{x^2-y^2}$, can also have a magnetic moment, theoretically. For the present diamine complexes which can be approximated as D_{4h}, however, the CD strength corresponding to this transition might be very weak, as in case of the II band of optically active $[Co(en)_3]^{3+}$.¹⁶⁾

TABLE 3. THE SYMMETRIES OF THE EXCITED STATES AND THE MAGNETIC MOMENTS IN D_{4h} SYMMETRY

	Excited configuration	Magnetic polarization
$d_{xy}\rightarrow d_{x^2-y^2}$	A_{2g}	μ_z
$d_{xz}, d_{yz}\rightarrow d_{x^2-y^2}$	E_g	μ_x, μ_y
$d_{z^2}\rightarrow d_{x^2-y^2}$	B_{1g}	—

As is seen in Figs. 2 and 3, the complexes of a type $[PtN_4]^{2+}$ or $[PdN_4]^{2+}$ exhibit two positive CD bands corresponding to bands 2 and 4. It is impossible at present to correlate the sign of CD band and the symmetry of transition. Band 4 with positive CD sign, however, can be reasonably assigned to $^1A_1\rightarrow{}^1E$ transition, from comparison with the CD data of tetragonal *trans*-$[CoCl_2\cdot(l\text{-pn})_2]^+$, which gives a strong positive and weak negative CD band corresponding to $^1A_1\rightarrow{}^1E$ and $^1A_1\rightarrow{}^1A_2$ transition, respectively. Band 2 may be assigned to the triplet transition, $^1A_1\rightarrow{}^3E$ rather than to the singlet $^1A_1\rightarrow{}^1A_2$, since its CD sign is the same as that of band 4.

$[PtCl_2(l\text{-pn})]$ gives also two positive CD signs in the bands 2 and 4 region. These bands would be of the same nature as those of $[Pt(l\text{-pn})_2]Cl_2$. The $[PdCl_2(l\text{-pn})]$, on the other hand, exhibits a weak negative and a strong positive CD peak in the region of bands 3 and 4, respectively. Its CD peak corresponding to band 2 was not detected, because of its low solubility. From a comparison of these results with that for *trans*-$[CoCl_2(l\text{-pn})_2]^+$ mentioned above, it is suggested that band 3 is assinged to the $^1A_1\rightarrow{}^1A_2$ transition. In platinum(II) complexes, this negative CD component would be hidden or compensated by the adjacent positive components.

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In Fig. 5 are plotted the absorption frequencies for bands 2, 3 and 4 of platinum(II) and palladium(II) complexes belonging to chloro-*l*-propylenediamine series. The relationship is similar between the platinum(II) and the palladium(II) complexes.

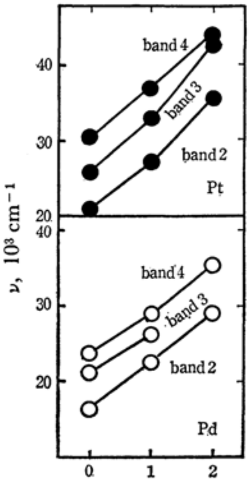

Fig. 5. Absorption frequencies for bands 2, 3 and 4 of Pt(II) and Pd(II) complexes belonging to chloro-*l*-propylenediamine series.

No indication of CD is seen in the region of band 1. It will be reasonable, however, to assign this band to the triplet transition $^1A_1 \rightarrow ^3A_2$ in relation to the assignment of the other bands described above.

All the above-mentioned facts lead to the conclusion that bands 1, 2, 3 and 4 are assigned to the transitions, $^1A_1 \rightarrow ^3A_2$, $^1A_1 \rightarrow ^3E$, $^1A_1 \rightarrow ^1A_2$ and $^1A_1 \rightarrow ^1E$, respectively, and that the ordering of *d* orbitals in the present platinum(II) and palladium(II) complexes will be $d_{x^2-y^2} \gg d_{xy} > d_{xz}, d_{yz} > d_{z^2}$ (Fig. 1. D_{4h}(III)).

The [Au(*l*-pn)$_2$]Cl$_3$ gives a monotonic absorption curve without maximum from visible to 210 mμ but its CD curve exhibits a positive peak at 224 mμ, while [Au(*l*-chxn)$_2$]Cl$_3$ shows an absorption peak and a positive CD peak at 220 mμ. These CD bands may correspond to band 4 of platinum(II) and palladium(II) complexes stated before. However, their big absorption coefficient and CD strength indicate that these bands are not due to simple *d–d* transition but to one probably coupled with some charge transfer transition. Such a mixing will be also seen in the platinum(II) complexes. As may be seen in Table 2, the absorption maxima of band 4 in platinum(II)-ammine-propylenediamine complexes are shifted to the shorter wave length in the order [Pt(*l*-pn)$_2$]$^{2+}$, [Pt(NH$_3$)$_2$(*l*-pn)]$^{2+}$ and [Pt(NH$_3$)$_4$]$^{2+}$, although the ammonia has a lower position on the spectrochemical series than the propylenediamine. This fact might be explained by the mixing of *d–d* band with some charge transfer transitions; the energy of charge transfer transition between the propylenediamine and the metal ion is in general lower than that between the ammonia and the metal ion. Therefore, band 4 in the propylenediamine complex couples more strongly with the charge transfer band and is shifted to the longer wavelength to a greater extent as compared with the band 4 in the ammine complex.

Vicinal Effects of *l*-Diamines. It is well known that both *l*-propylenediamine and *l*-cyclohexanediamine coordinate to the metal ion in a λ-gauche form and bring about a non-planar chelate ring. The CD data which have been reported so far show that the vicinal effect of diamine in a λ-form gives a positive CD sign for the band corresponding to a transition $^1A_1 \rightarrow ^1E$, irrespective of the kind of metal ion.[17–20] In the present complexes, the CD signs of *l*-cyclohexanediamine complexes are the same as those of *l*-propylenediamine complexes, but the strength of the formers is almost twice that of the latters, as is seen in Table 2. This result contrasts with the fact that the CD strength of *trans*-[CoCl$_2$(*l*-pn)$_2$]$^+$ has an almost equal magnitude to that of *trans*-[CoCl$_2$(*l*-chxn)$_2$]$^+$.[19,20] *l*-Propylenediamine has only one assymmetric carbon atom, while *l*-cyclohexanediamine has two such atoms. According to the Octant rule for metal complexes,[21] the 1 and 2 carbon atoms (attached to amino groups) of both chelated diamines in a λ-form lie in the Octant minus region which gives positive Cotton effect, but *l*-cyclohexanediamine has two more carbon atoms, 4 and 5, both of which also contribute to the vicinal effect with Octant minus sign (see Fig. 6). The 3 and 6 carbon atoms are located in an almost Octant zero region as the nitrogen atoms are. Although the vicinal effect due to the 4 and 5 carbon atoms may be weaker than that of the 1 and 2 carbon atoms because their locations are farther from the central metal ion, they would still contribute to the vicinal effect in the present platinum(II), palladium(II), and gold(III) complexes. In these complexes, the coordination bond is expected to have more covalent character as compared with that in the similar cobalt(III) complex. The *d* electrons in a covalent complex might be still affected appreciably by electrons on atoms or by a field produced by atoms apart from the central metal ion.

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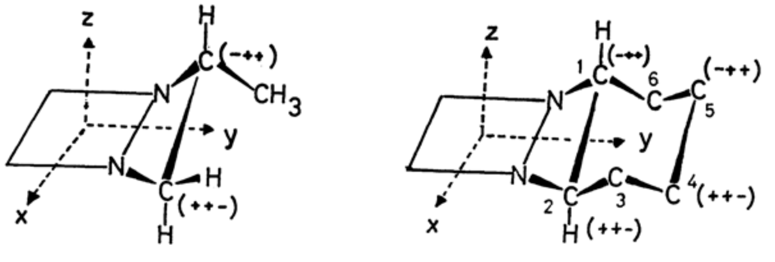

l-pn *l*-chxn

Fig. 6. Octant signs for coordinated *l*-propylenediamine and *l*-cyclohexanediamine

TABLE 4. ABSORPTION DATA OF CHARGE TRANSFER TRANSITIONS OF TETRAHALOGENO COMPLEXES

	Symmetry-forbidden band		$p_\pi \to d_{x^2-y^2}$				$p_\sigma \to d_{x^2-y^2}$	
			A_{1u}		$E_u^{(b)}$		$E_u^{(a)}$	
	ν (10^3 cm^{-1})	(log ε)	ν (10^3 cm^{-1})	(log ε)	ν (10^3 cm^{-1})	(log ε)	ν (10^3 cm^{-1})	(log ε)
$K_2[PtCl_4]^a$	~38.3^{sh}	(2.6)			~43.9^{sh}	(3.9)	46.5	(4.02)
$K_2[PdCl_4]^b$	~30.5^{sh}	(2.7)			35.7	(4.00)	45.1	(4.45)
$H[AuCl_4]^c$	~26.0^{sh}	(2.6)			32.0	(3.69)	44.3	(4.48)
$K_2[PtBr_4]^d$	~31.0^{sh}	(2.6)	~34.0^{sh}	(3.2)	38.1	(3.82)	~40.3^{sh}	(3.8)
$K_2[PdBr_4]^d$	~24.0^{sh}	(2.9)	~27.5^{sh}	(3.6)	30.3	(4.03)	40.5	(4.46)
$K[AuBr_4]^d$	~19.5^{sh}	(2.5)	~23.0^{sh}	(3.2)	26.3	(3.69)	39.4	(4.64)

sh, shoulder; a, in 2 N HCl solution; b, in 1 N HCl solution; c, in 0.2 M KCl solution; d, in 0.2 M KBr solution

Table 2 shows that the CD strengths of $[Pt(\textit{l}\text{-pn})_2]^{2+}$ and $[Pt(\textit{l}\text{-chxn})_2]^{2+}$ is almost twice those of $[Pt(en)(\textit{l}\text{-pn})]^{2+}$ or $[Pt(NH_3)_2(\textit{l}\text{-pn})]^{2+}$, and $[Pt(NH_3)_2(\textit{l}\text{-chxn})]^{2+}$, respectively. This indicates that the magnitude of the vicinal effect is proportional to the number of optically active ligands; there is no appreciable interaction between the ligands.

Charge Transfer Transitions in Halogeno Complexes. It is well known that the complex ions, $[MX_4]^{n-}$ ($M=Pt^{2+}$, Pd^{2+} and Au^{3+}, $X=Cl^-$ and Br^-) give two strong absorption bands in visible and ultraviolet region.[2,22] They have been assigned to the charge transfer bands from the halides to the central metal ion, the longer wavelength band involving $p_\pi \to d_{x^2-y^2}$, and the shorter wavelength, $p_\sigma \to d_{x^2-y^2}$, transition. Day, *et al.* found another shoulder band in an even longer wavelength region for $K_2[PtCl_4]$ and $K_2[PdCl_4]$ in a solid state spectrum, and assigned them tentatively to a orbitally-forbidden charge transfer band. Martin *et al.*,[3] Basch and Gray[4] and Cotton and Harris[5] assigned it to a $d_{z^2} \to d_{x^2-y^2}$ transition. All of the tetra-halogeno complexes studied show shoulder bands on the foot of the strong charge transfer band. If they were due to the $d_{z^2} \to d_{x^2-y^2}$ transition, the complexes $[PtCl_2(\textit{l}\text{-pn})]$, $[PdCl_2(\textit{l}\text{-pn})]$ and $[Pd(\textit{l}\text{-pn})_2]^{2+}$ should show some indication for this transition in their spectra at around 42000, 34000 and 42000 cm^{-1}, respectively, those frequency values being estimated from the linear relationship shown in Fig. 5. None of them, however, could be observed. Therefore, we conclude that the shoulder band in the

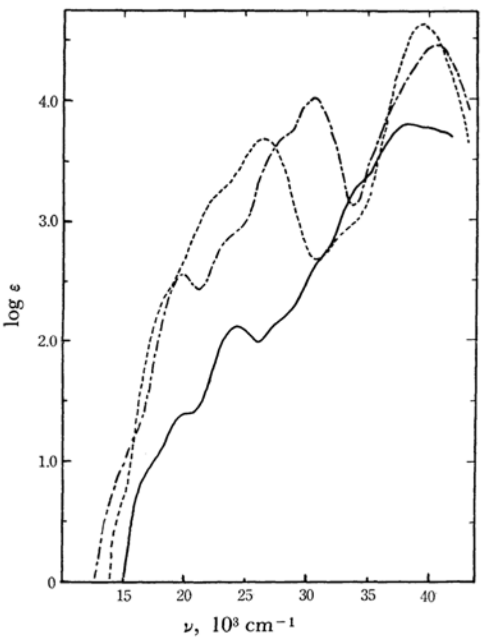

Fig. 7. Absorption spectra of $K_2[PtBr_4]$ (——), $K_2[PdBr_4]$ (·—·) and $K[AuBr_4]$ (----) in 0.2 M KBr.

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[22] A. K. Gangopadhayay and A. Chakravorty, *J. Chem. Phys.*, **35**, 2206 (1961).

tetra-halogeno complexes could be assigned to an orbitally-forbidden charge transfer band.

The symmetries of the excited states of orbitally-allowed charge transfer transitions will be $E_u^{(a)}$ for $p_\sigma \rightarrow d_{x^2-y^2}$, A_{1u} and $E_u^{(b)}$ for $p_\pi \rightarrow d_{x^2-y^2}$. Of the last two, the A_{1u} corresponds to the transition from the non-bonding p_π orbitals of halide and the $E_u^{(b)}$ to that from the bonding p_π orbitals. A band due to the latter transition would appear at a shorter wavelength and have higher intensity as compared with a band due to the former. As is shown in Fig. 7 and Table 4, the bands due to the $p_\pi \rightarrow d_{x^2-y^2}$ split into two components in the bromo-complexes. The longer wavelength shoulder could be assigned to the $^1A_{1g} \rightarrow {}^1A_{1u}$ transition and the shorter wave length peak to the $^1A_{1g} \rightarrow {}^1E_u^{(b)}$ transition for each complex.

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