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Circular Dichroism of Some Optically Active Rhodium–Diamine Complexes[1]

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The circular dichroism (CD) and electronic absorption spectra are reported for some rhodium(III) complexes of optically active 1,2-propanediamine and 2,3-butanediamine. The absolute configurations of the tris(diamine) complexes were determined from the CD curves. For complexes of the general formulas *trans*-[Rh(am)$_2$Cl$_2$]$^+$ and [Rh(am)Cl$_4$]$^-$, optical activity arises from induced asymmetry at the site of the metal ion due to the conformational effect of the optically active ligand. Assignments of the CD bands were made according to the pseudo-tetragonal symmetry (D$_{4h}$ point group). The tetragonal splitting for the *trans*-bis(diamine) complexes is twice as large as for the mono(diamine) complexes.

The dissymmetry of complexes of bidentate ligands arises because of the helical distribution of their chelate rings about the central ion. In this paper, the configuration of a tris(diamine) complex with a right-handed spiral arrangement of ligands along the C_3 axis will be designated Δ, and that with a left-handed spiral arrangement will be designated Λ.

Conformational analysis of saturated five-membered chelate rings by Corey and Bailar[2] showed that for a complex such as the Λ-(+)D-[Co(en)$_3$]$^{3+}$ ion the most stable form has all of the ligand C–C bonds parallel to the C_3 axis of the ion. Thus the most stable form can be designated as Λ-$\delta\delta\delta$ of "*lel*" as confirmed by X-ray analysis.[3,4]

Circular dichroism studies by McCaffery, Mason, and Ballard[5] in the solid state of (−)D-[Rh(en)$_3$]Cl$_3\cdot$H$_2$O showed that the first ligand-field absorption band in [Rh(en)$_3$]$^{3+}$ (D$_3$ point group) derived from the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition in [Rh(NH$_3$)$_6$]$^{3+}$ (O$_h$ point group) is composed of two transitions, $^1A_1 \rightarrow {}^1E^a$ and $^1A_1 \rightarrow {}^1A_2$, with the former component at lower energy. A comparison of the crystal and the solution circular dichroism spectra of (+)D-[Co(en)$_3$]$^{3+}$ and (−)D-[Rh(en)$_3$]$^{3+}$ by these authors showed that these two ions probably have the same configurations. Mathieu[6] published ORD and CD data for *trans*-[Co((*R*)-pn)$_2$Cl$_2$]$^+$. Dunlop and Gillard[7] and Wentworth and Piper[8] made assignments for electronic transitions based on pseudo-tetragonal symmetry (D$_{4h}$ point group). Hawkins, Larsen, and Olsen[9] reported the circular dichroism spectra for a number of mono- and *trans*-bis((*R*)-propanediamine)cobalt(III) complexes and they made their assignments based on D$_2$ symmetry. For the *trans*-bis((*R*)-propanediamine) complex, the two methyl groups can be either *trans* or *cis*. An X-ray study of *trans*-[Co((*R*)-pn)$_2$Cl$_2$]Cl$\cdot$HCl$\cdot$2H$_2$O revealed that the two methyl groups are *trans* to each other,[10] although this is not necessarily true for the cobalt or rhodium complexes in solution. Two complexes of rhodium(III) are now reported for which the optical activity arises solely from the presence of the optically active ligands.

Experimental Section

Preparation of Sodium Tetrachloro-(*R*)-propanediaminerhodate(III) Monohydrate.—Rhodium trichloride trihydrate (1.4 g) was dissolved in 50 ml of water, and 0.4 g of (*R*)-(−)-propanediamine,[11] resolved by the method of Dwyer, Garvan, and Shulman,[12] was added. The mixture was refluxed for about 2 hr and the solution turned orange-yellow. The solution was first concentrated to about 10 ml and then passed through a cation-exchange column (150 × 13 mm) in the Na$^+$ form (Dowex 50W-X8) to remove the undesired bis- and tris-(*R*)-pn complexes. Fractional crystallization of the solution which passed through the column yielded four crops of orange-red precipitate. The third crop was found to have the highest optical activity. This was fractionally crystallized until a constant and highest rotation was obtained; $[\alpha]_D$ +188°. *Anal.* Calcd for C$_3$H$_{12}$Cl$_4$N$_2$NaORh: C, 10.01; H, 3.36; N, 7.78. Found: C, 10.06; H, 3.38; N, 7.68.

Preparation of *trans*-Dichlorobis((*R*)-propanediamine)rhodium(III) Chloride.—One gram of rhodium trichloride trihydrate was dissolved in 50 ml of water, and 0.56 g of (*R*)-propanediamine was added. The mixture was refluxed for about 2 hr during which time the color changed from red to pale yellow. The resulting solution was then concentrated under a stream of compressed air to about 5 ml and filtered into 3 ml of ice-cold concentrated nitric acid. On scratching the sides of the container, a yellow precipitate appeared. It was filtered, washed with several drops of dilute nitric acid, two drops of cold water, absolute ethanol, and finally with acetone and air dried. The nitrate form was converted to the chloride form by passing through an anion-exchange column (200 × 13 mm) in the chloride form (Dowex 1-X8) to facilitate elementary analysis so that N comes solely from the diamine. The compound was recrystallized from the minimum amount of warm water; $[\alpha]_D$ +158°. *Anal.* Calcd for C$_6$H$_{20}$Cl$_3$N$_4$Rh: C, 20.16; H, 5.65; N, 15.66. Found: C, 20.17; H, 5.70; N, 15.57.

Preparation and Resolution of Tris((*R*)-propanediamine)-

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[1] Taken from the Ph.D. Dissertation of S. K. Hall, The University of Pittsburgh, 1967. This work was supported by a research grant (GM10829-09) from the Division of General Medical Studies, U. S. Public Health Service.

[2] E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

[3] K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, **30**, 795 (1957).

[4] The chelate ring conformations are designated in accordance with a forthcoming recommendation of the IUPAC such that $\delta = k'$ and $\lambda = k$ with reference to usage of k and k' defined by Figure 2 of ref 2. The less stable "*ob*" form of the complex is Δ-$\lambda\lambda\lambda$.

[5] A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).

[6] J. P. Mathieu, *Ann. Phys.*, **19**, 335 (1944).

[7] J. H. Dunlop and R. D. Gillard, *Mol. Phys.*, **7**, 493 (1964).

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

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

[10] Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Japan*, **35**, 1131 (1962).

[11] (*R*) designates the absolute configuration of the 1,2-propanediamine in accordance with R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem. Intern. Ed. Engl.*, **5**, 385 (1966).

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

TABLE I

ELECTRONIC ABSORPTION AND CIRCULAR DICHROISM OF SOME RHODIUM–DIAMINE COMPLEXES

	Absorption		Circular dichroism		
Complex ion	$\bar{\nu}$, cm^{-1}	ϵ_{max}	$\bar{\nu}$, cm^{-1}	$\Delta\epsilon_{max}$	Assignment
$[Rh((R)\text{-pn})Cl_4]^-$ [a]	23,260	70 (70)	23,150	+0.44 (+0.46)	E^a (D_{4h})
			27,030	−0.07 (−0.08)	A_2
	28,570	80 (82)	31,250	+0.26 (+0.29)	E^b
trans-$[Rh((R)\text{-pn})_2Cl_2]^+$ [a]	24,690	75 (75)	24,690	+0.76 (+0.81)	$E_g{}^a$ (D_{4h})
			31,750	−0.11 (−0.12)	A_{2g}
	35,090	120 (120)	37,040	+0.57 (+0.57)	$E_g{}^b$
(+)D-$[Rh(en)_3]^{3+}$	33,330	250	31,250	−2.01	E^a (D_3)
			34,720	+0.09	A_2
(+)-$[Rh((R)\text{-pn})_3]^{3+}$ [a]	33,330	270 (270)	31,250	−2.12 (−2.31)	E^a (D_3)
			34,970	+0.61 (+0.61)	A_2

[a] The E_{max} and $\Delta\epsilon_{max}$ values for the corresponding *R*,*R*-butanediamine complex are given in parentheses. The positions of the peaks are the same as for the pn complex.

rhodium(III) Iodide Monohydrate.—This compound was prepared by modifying Schmidtke's method.[13] One gram of rhodium trichloride trihydrate was dissolved in about 2 ml of water and 2 ml of (*R*)-propanediamine was added. The mixture was heated on a steam bath for about 3 hr during which time the color changed to pale yellow. The compound was precipitated as the iodide by the addition of a concentrated solution of sodium iodide (2 g). It was resolved by fractional crystallization of the iodide salt. The least soluble fraction was recrystallized many times by dissolving in a minimum amount of warm water and precipitating by the careful addition of ethanol; $[\alpha]_D$ +162° (lit.[5] $[\alpha]$ +154°). *Anal.* Calcd for $C_9H_{32}I_3N_6ORh$: C, 14.93; H, 4.46; N, 11.60. Found: C, 15.02; H, 4.46; N, 11.50.

Preparation and Resolution of (*R*,*R*)-Butanediamine.—The amine was prepared, separated, and resolved after the procedure given by Dickey, Fickett, and Lucas[14] with slight modifications. To a solution of 116 g of dimethylglyoxime and 371 g of sodium hydroxide in 3 l. of water at 50° was added 248 g of Raney nickel catalyst powder (W. R. Grace; No. 2813) in 1–2-g portions at about 1-min intervals. The temperature was maintained between 50 and 55° and the mixture was vigorously stirred throughout the experiment. Three hours was required for the addition. The reaction mixture was left overnight and the residual nickel was removed by suction filtration. The red filtrate was distilled quickly. The distillate, 2 l., was adjusted to pH 3 with concentrated hydrochloric acid and evaporated to dryness. The dry salt was decomposed with an excess of sodium methylate in methanol and a mixture of racemic and *meso* diamine was recovered by fractional distillation. Only the fraction with a boiling range of 57–61° (60 mm) was collected. Addition of concentrated hydrochloric acid and subsequent evaporation yielded 55 g of the racemic salt, the *meso* being the less soluble. The racemic salt was decomposed with an excess of sodium methylate in methanol and the diamine was recovered by fractional distillation, bp 58° (60 mm).

The racemic butanediamine was resolved into its optical isomers using tartaric acid as resolving agent. A solution of 18 g of racemic diamine dissolved in 150 ml of absolute ethanol was added to a warm solution of 61 g of tartaric acid dissolved in 2 l. of an ethanol–water (2:1 by volume) mixture. After standing overnight, the white, less soluble diastereoisomer was filtered, washed with ethanol and acetone, and dried in a vacuum oven. The less soluble diastereoisomer (42 g) was recrystallized by dissolution in warm ethanol–water (2:1) followed by pouring the clear solution into a large vessel containing an additional part of ethanol so that the ratio of ethanol to water in the final mixture was 3:1 by volume. It was then left overnight to crystallize and was filtered. Recrystallization was repeated until a 5% aqueous solution of the less soluble diastereoisomer gave α_D +0.89°.

The optically active (*R*,*R*)-butanediamine dihydrochloride was recovered from the hydrogen tartrate diastereoisomer by the method of Bailar, Jonassen, and Gott.[15] Optically pure (*R*,*R*)-(−)-butanediamine was recovered by decomposing the dihydrochloride in methanol containing an excess of sodium methylate followed by fractional distillation, bp 58° (60 mm).

Preparation of Sodium Tetrachloro-(*R*,*R*)-butanediaminerhodate(III) Monohydrate.—Sodium hexachlororhodate(III) dodecahydrate (3 g) was dissolved in 25 ml of water and heated to boiling. The solution was boiled for 3 hr after the slow addition of 25 ml of water containing 0.45 g of (*R*,*R*)-butanediamine. The cooled solution was concentrated under a stream of compressed air at room temperature to about 10 ml. The resulting NaCl crystals were filtered and three drops of concentrated HCl were added to the filtrate. More NaCl crystals appeared on standing and they were filtered. On standing overnight in a refrigerator at 5° the filtrate yielded orange-red crystals of sodium tetrachloro-(*R*,*R*)-butanediaminerhodate(III) monohydrate. These were filtered, then washed with several drops of ice-cold water, ethanol, and finally acetone. Recrystallization was from a minimum amount of warm water; $[\alpha]_D$ +198°. *Anal.* Calcd for $C_4H_{14}Cl_4N_2NaORh$: C, 12.84; H, 3.77; N, 7.49. Found: C, 13.05; H, 3.88; N, 7.60.

Preparation of *trans*-Dichlorobis((*R*,*R*)-butanediamine)rhodium(III) Chloride.—This compound was prepared by a method similar to that described for the *trans*-(*R*)-propanediamine complex; $[\alpha]_D$ +170°. *Anal.* Calcd for $C_8H_{24}Cl_3N_4Rh$: C, 24.92; H, 6.28; N, 14.52. Found: C, 25.05; H, 6.30; N, 14.67.

Preparation and Resolution of Tris((*R*,*R*)-butanediamine)-rhodium(III) Iodide Monohydrate.—This compound was prepared by a method similar to that described for the tris-(*R*)-propanediamine complex and was also resolved as the iodide salt by fractional recrystallization from water; $[\alpha]_D$ +175°. *Anal.* Calcd for $C_{12}H_{38}I_3N_6ORh$: C, 18.81; H, 5.00; N, 10.97. Found: C, 18.98; H, 5.12; N, 11.08.

Measurements.—The CD spectra were taken in aqueous solutions in 1- or 2-cm cells. The concentrations of the solutions were 0.002–0.008 *M*. Measurements of optical rotations were made in aqueous solution in a 1-dm tube at the sodium D line, at room temperature. Absorption spectra were recorded on a Cary Model 14 spectrophotometer, using 1-cm cells. Results of measurements on the optically active rhodium–diamine complexes are summarized in Table I.

Discussion

The optically active diamines which have been used for this work are (*R*)-propanediamine [(−)-pn][10] and (*R*,*R*)-butanediamine [(−)-bn].[14] Corey and Bailar[2] predicted that the most stable conformations of such metal chelate rings have the methyl groups in equatorial positions. Therefore for coordinated (*R*)-

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(13) H. H. Schmidtke, *Z. Physik. Chem.* (Frankfurt), **38**, 170 (1963).

(14) F. H. Dickey, W. Fickett, and H. J. Lucas, *J. Am. Chem. Soc.*, **74**, 944 (1952).

(15) J. C. Bailar, Jr., H. B. Jonassen, and A. D. Gott, *ibid.*, **74**, 3131 (1952).

pn and (*R*,*R*)-bn, the chelate rings should adopt the stable λ conformation for which the more stable configuration of the complex is Δ.

The aqueous CD spectra of (+)D-[Rh((*R*)-pn)$_3$]$^{3+}$ (Figure 1) and (+)D-[Rh((*R*,*R*)-bn)$_3$]$^{3+}$ (Table I) show a dominant negative E^a component and a small positive A$_2$ component, which are similar to the mirror image of the aqueous CD spectrum[5] of (+)D-[Co((*S*)-pn)$_3$]$^{3+}$. The absolute configuration of (−)D-[Co((*R*)-pn)$_3$]Br$_3$ as determined by Iwasaki and Saito[16] possess the Δ-$\lambda\lambda\lambda$ configuration. It is assumed that two related dissymmetric molecules have the same configuration if they give the same Cotton effect in the absorption region. Since the aqueous CD spectra of (+)D-[Rh((*R*)-pn)$_3$]$^{3+}$ and (+)D-[Rh((*R*,*R*)-bn)$_3$]$^{3+}$ are similar to the CD spectrum of (−)D-[Co((*R*)-pn)$_3$]$^{3+}$ in their respective absorption regions, all of these ions probably have the same absolute configuration in agreement with previous results.[17]

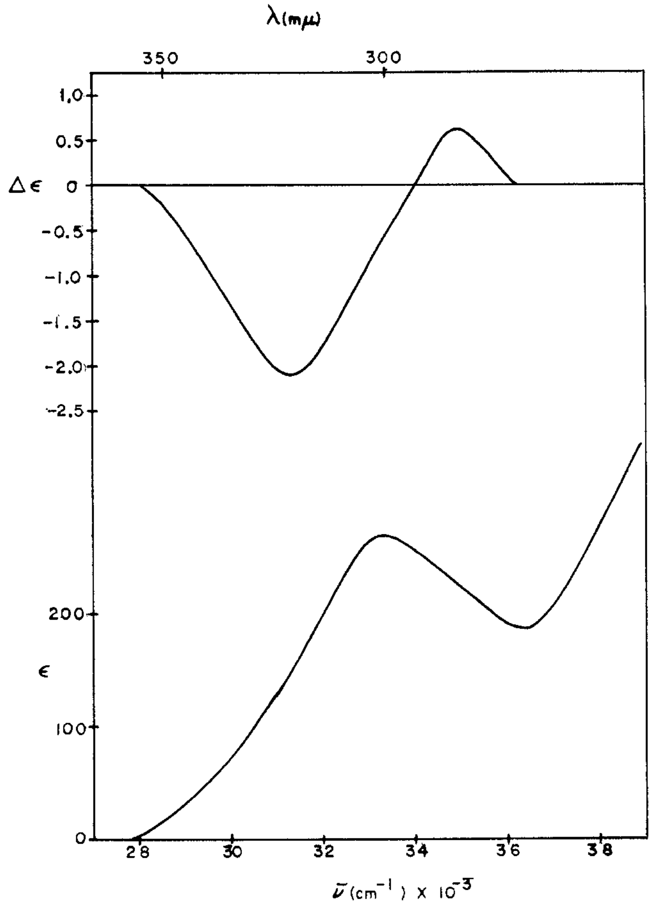

Figure 1.—Absorption and CD curves for (+)D-[Rh((*R*)-pn)$_3$]I$_3$ · H$_2$O.

The CD spectrum and specific rotation of (+)D-[Rh((*R*)-pn)$_3$]$^{3+}$ in the present work are different from the previously reported values.[5,17] Examination of the CD curves[5] of (+)D-[Co((*S*)-pn)$_3$]$^{3+}$ and (+)D-[Co(en)$_3$]$^{3+}$ showed that the intensities of the first two CD bands of the former are larger than those of the latter and that these two ions have the same absolute configurations. However, the previously reported value for the first CD band of (+)D-[Rh((*R*)-pn)$_3$]$^{3+}$ was smaller than that of (+)D-[Rh(en)$_3$]$^{3+}$ while the second CD band of the former was much larger than that of the latter. The present results indicate the intensities of both the first and the second CD bands of (+)D-[Rh((*R*)-pn)$_3$]$^{3+}$ are larger than those of (+)D-[Rh(en)$_3$]$^{3+}$. Considering the relative intensities for the first two CD bands of the cobalt analogs, it is believed that the present results are probably correct.

trans-Bis(diamine) complexes possess pseudo-tetragonal symmetry. The two ligand-field absorption bands in d^6 systems in an octahedral field are $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, in order of increasing energy. In a tetragonal field, the two transitions split into two components each, *i.e.*, $^1T_{1g} = {}^1A_{2g} + {}^1E_g{}^a$ and $^1T_{2g} = {}^1B_{2g} + {}^1E_g{}^b$. Ballhausen and Moffit[18] observed only three electronic bands in the crystal spectrum of *trans*-[Co(en)$_2$Cl$_2$]ClO$_4$. Their interpretation was that $^1T_{1g}$ probably split into its two components $^1A_{2g}$ and $^1E_g{}^a$ while the splitting of $^1T_{2g}$ would be small or obscured by the onset of charge transfer in the ultraviolet region. Furthermore, for monodentate ligands which are lower in the spectrochemical series than the bidentate ligands, $^1E_g{}^a$ should be lower in energy than $^1A_{2g}$.

The aqueous CD spectrum of *trans*-[Rh((*R*)-pn)$_2$Cl$_2$]$^+$ is given in Figure 2 and the parameters for the similar CD spectrum of *trans*-[Rh((*R*,*R*)-bn)$_2$Cl$_2$]$^+$ are given in Table I. Assuming pseudo-tetragonal symmetry (D$_{4h}$ point group) for these two *trans*-bis(diamine) complexes and since Cl$^-$ lies lower in the spectrochemical series than either pn or bn, the CD peak with the lowest energy (24,690 cm^{-1}) is assigned to the $^1A_{1g} \rightarrow {}^1E_g{}^a$ transition while the peak with the next higher energy (31,750 cm^{-1}) is assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition. This CD peak is outside of the first absorption band region, but both CD peaks are well below the T$_{1g}$ (O$_h$) band of [Rh(pn)$_3$]$^{3+}$ (Figure 1). The CD peak with highest energy (37,040 cm^{-1}) is assigned the $^1A_{1g} \rightarrow {}^1E_g{}^b$ transition. In the second ligand-field band, transition to the $^1B_{2g}$ component in D$_{4h}$ symmetry is magnetically forbidden while transition to the $^1E_g{}^b$ component is magnetically allowed. Dunlop and Gillard[7] reported the CD curve of *trans*-[Rh((*R*)-pn)$_2$Cl$_2$]$^+$. However, the intensities of the positive CD peaks in the present research are larger than those reported by these authors. In addition, a negative CD peak was observed in the present work.

Although Hawkins, Larsen, and Olsen[9] used D$_2$ symmetry to make transition assignments for *trans*-[Co((*R*)-pn)$_2$Cl$_2$]$^+$, Dingle[19] has shown that D$_{4h}$ is a reasonable approximation. The spectra of *trans*-[Rh((*R*)-pn)$_2$Cl$_2$]$^+$ and *trans*-[Rh((*R*,*R*)-bn)$_2$Cl$_2$]$^+$ have been interpreted here using D$_{4h}$ symmetry. When

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(16) H. Iwasaki and Y. Saito, *Bull. Chem. Soc. Japan*, **39**, 92 (1966).

(17) J. H. Dunlop, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, 3160 (1964).

(18) C. J. Ballhausen and W. Moffit, *J. Inorg. Nucl. Chem.*, **3**, 178 (1956).

(19) R. Dingle, *J. Chem. Phys.*, **46**, 1 (1967).

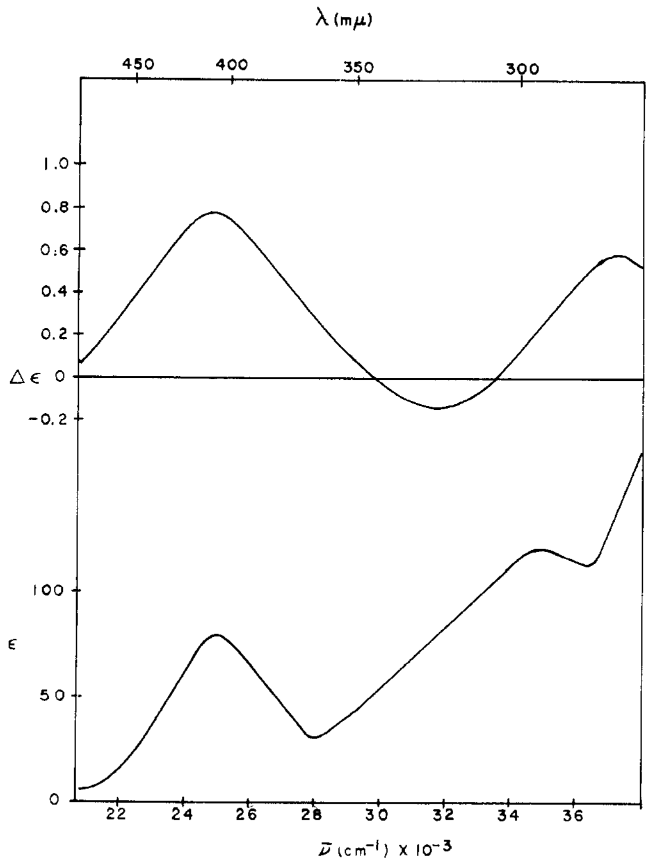

Figure 2.—Absorption and CD curves for *trans*-[Rh((*R*)-pn)$_2$Cl$_2$]-Cl.

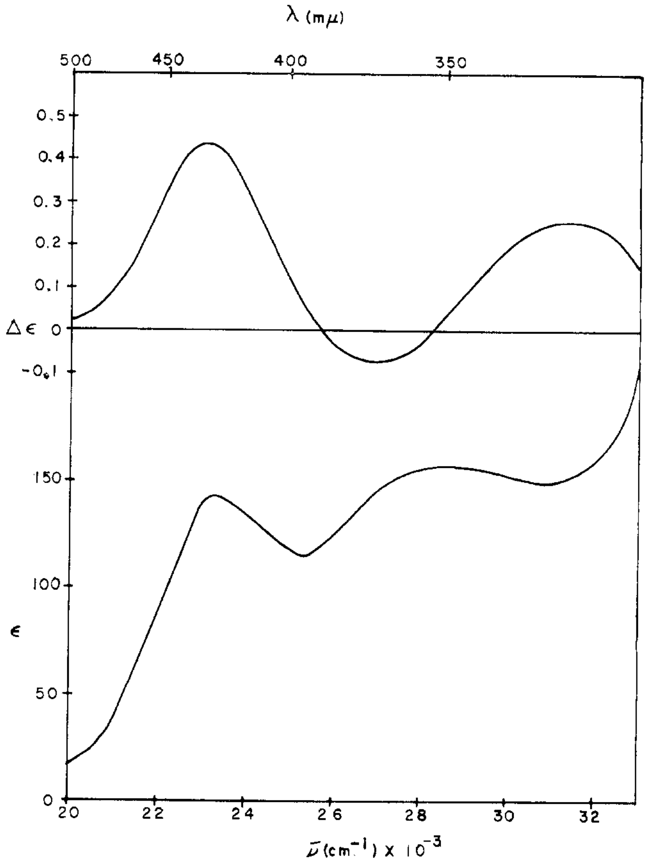

Figure 3.—Absorption and CD curves for Na[Rh((*R*)-pn)Cl$_4$] · H$_2$O.

one of the two bidentate diamine ligands is replaced by two chloro groups, the complex ion now possesses C_{2v} symmetry. However, owing to the fact that only the sum of the charges on each axis often determines the effective field symmetry of a given complex, the symmetry groups of *trans*-[MN$_4$Cl$_2$] and *cis*-[MN$_2$Cl$_4$] can both be considered to be D_{4h}, even if formally the symmetry group of the *cis* complex is C_{2v}. Furthermore, from the consideration of the tetragonality parameter, the *trans* complex is expected to exhibit a tetragonal splitting two times that of the *cis* complex.[20]

Examination of the aqueous CD spectrum of [Rh((*R*)-pn)Cl$_4$]$^-$ (Figure 3) and the parameters for the similar CD spectrum of [Rh((*R*,*R*)-bn)Cl$_4$]$^-$ (Table I) shows that these spectra are similar in shape to that of the *trans*-bis(diamine) complexes. The CD bands in order of increasing energy are +, −, +, the tetragonal splitting in the *trans*-bis(diamine) complexes is approximately two times larger than that of the mono(diamine) complexes, and the intensities of the bands in the former are larger than those in the latter.

The reduced splitting ($^1/_2$) indicated for the first two CD peaks of the mono(diamine) complexes compared to the bis(diamine) complexes and the identical sign patterns give confidence in the use of D_{4h} symmetry for both cases. Yamatera[20] indicated a reversal of the energies of the E^a and A_2 in going from *trans*-[Ma$_4$b$_2$] to *cis*-[Ma$_4$b$_2$]. No reversal is expected in the present case since the groups along *z* remain the same (2Cl$^-$), but the field in the tetragonal plane is lowered by the substitution of 2Cl$^-$ for one diamine, lowering the splitting by $^1/_2$. Assuming D_{4h} symmetry, the band with the lowest energy (23,150 cm^{-1}) is assigned to the $^1A_1 \rightarrow {}^1A_2$ transition. The band with highest energy (31,250 cm^{-1}) is assigned to the $^1A_1 \rightarrow {}^1E^b$ transition.

Most of the complexes investigated to date contain *cis*-bis(bidentate) ligands or tris(bidentate) ligands where the bidentate ligands may or may not be the same. In such complexes, optical activity arises from both the configuration of the complex ion and the conformation of the chelates. In the *trans*-bis(diamine) and mono(diamine) complexes investigated in the present work, optical activity arises only from induced asymmetry at the site of the metal ion due to the conformational effect of the optically active ligand. The intensities of the CD peaks are approximately the same for the corresponding pn and bn complexes, suggesting that the conformational contributions are nearly the same for the two ligands. The intensities are approximately twice as great for the bis(diamine) complexes as for the mono(diamine) complexes indicating that the contributions of the chelate rings are nearly additive. Some deviation from additivity is expected because of the differences in the extent of overlap of neighboring peaks.

(20) H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).