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Absolute Configurations of Octahedral Metal Complexes

II. Mono- and *Trans*-bis(*l*-propylenediamine)cobalt(III) Complexes

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Circular dichroism and absorption spectra are reported for a number of mono- and *trans*-bis(*l*-propylenediamine)cobalt(III) complexes and also for the *trans*-dichlorobis(*l*-*trans*-1,2-cyclohexanediamine)cobalt(III) complex. A symmetry lower than D_{4h} is necessary to explain the observed splitting of the doubly degenerate level $^1E_g(D_{4h})$ for these complexes. It is suggested that the sign of the Cotton effect for the $^1A \rightarrow {}^1B_1(D_2)$ transition be used as a guide to the absolute configuration of the above types of complexes.

A large number of papers have been published concerning the circular dichroism (CD) spectra of cobalt(III) complexes whose dissymmetry arises because of the helical distribution of their chelate rings about the central ion, for example, tris(oxalato)cobaltate(III).[1] However, complexes deriving their dissymmetry directly from the conformations of the chelate rings themselves have been relatively little studied. Mathieu,*,[2] Dunlop and Gillard,[3] and recently Wentworth and Piper [4] have published data for *trans*-$[Co(l\text{-pn})_2Cl_2]^+$ while Wentworth and Piper also studied the corresponding dinitro complex. The CD spectra of $[Co(NH_3)_4$tartrate$]^+$ and $[Co(NH_3)_4$am$]^{2+}$ (where am = anion of an α-amino acid) [5,6] are the only other spectra published for this category. In the present paper, the absorption and CD spectra are given for a number of mono- and *trans*-bis(*l*-propylenediamine)cobalt(III) complexes and also for the *trans*-dichloro-bis(*l*-*trans*-1,2-cyclohexanediamine)cobalt(III) complex.

On the basis of their CD spectrum of $[Co(l\text{-pn})_2Cl_2]^+$, Dunlop and Gillard [3] proposed an energy level scheme for this complex and its equivalent ethylenediamine complex different to that which had been previously reported for the ethylenediamine complex by Ballhausen and Moffitt [7] from polarised crystal spectra investigations. The CD spectrum of Dunlop and Gillard could not be

* Mathieu studied the *d*-pn isomer.

reproduced by Wentworth and Piper nor by the present authors; the CD spectra of these latter groups are basically in agreement with the Ballhausen and Moffitt assignment, for which the "effective" symmetry was taken to be D_{4h}. Wentworth and Piper interpreted their CD spectra on the basis of a "pseudo-tetragonal" symmetry but a lower symmetry (D_2) has been invoked by the present authors because a splitting of the doubly degenerate $^1E_g(D_{4h})$ level was observed.

EXPERIMENTAL

l-Propylenediamine (*l*-pn) was prepared by resolution of AnalaR grade *dl*-propylenediamine (Fluka) with tartaric acid. The tartrate was repeatedly recrystallised using a basket centrifuge to effect very efficient filtration. The free amine was obtained by neutralisation with saturated alkali solution. The amine was separated, dried with sodium hydroxide and distilled under vacuum.

l-Trans-1,2-cyclohexanediamine (*l*-chxn) was obtained from the racemic by the method of Jaeger and Bijkerk.[8]

Ammonium *cis*-bis(sulphito)*trans*-diamminemono(*l*-propylenediamine)cobaltate(III) was prepared from *cis*-$NH_4[Co(NH_3)_4(SO_3)_2]$ (prepared according to Bailar and Peppard [9]) by reaction in a minimum of water at room temperature with an equivalent amount of *l*-propylenediamine. The solution was stirred for 30 min and then filtered. The yellow product was precipitated from the filtrate by the addition of alcohol. Following filtration, it was washed with methanol and dried over calcium chloride. (Yield 70 %). Found: C 10.46; H 5.80; Co 17.12. Calc. for $CoC_3H_{20}N_5S_2O_6$: C 10.44; H 5.84; Co 17.07).

Trans-dibromodiamminemono(*l*-propylenediamine)cobalt(III) bromide. 40 % Hydrobromic acid (14 ml) was heated to 80° in a water bath. Powdered $NH_4[Co(l\text{-pn})(NH_3)_2(SO_3)_2]$ (2 g) was added with stirring and the heating was continued for 2 min. The green solution was cooled in an ice-salt mixture and concentrated perchloric acid was added dropwise to precipitate as much of the product as possible. The green perchlorate (1.35 g) was washed twice by suspension in a minimum of ice-cold water, then twice with absolute alcohol and dried in the air. As the perchlorate was contaminated with a colourless salt (probably ammonium perchlorate), which proved difficult to remove by recrystallisation, the perchlorate was converted to the bromide by dissolving it in a minimum of cold methanol, cooling the solution in an ice-salt mixture, and adding 63 % hydrobromic acid dropwise to precipitate green crystals of the bromide. These were filtered and washed with ice-cold methanol and dried in the air. (Overall yield 20 %). For analysis the bromide was recrystallised from methanol. (Found: C 8.95; H 3.94; Co 14.37. Calc. for $CoC_3H_{16}N_4Br_2$: C 8.86; H 3.96; Co 14.48).

Trans-dichlorodiamminemono(*l*-propylenediamine)cobalt(III) hydrogen sulphate was synthesised *via* the dibromo and carbonato complexes. *Trans**-$[Co(l\text{-pn})(NH_3)_2Br_2*]ClO_4$ (4 g) was ground with dry silver carbonate (4.2 g). The mortar was cooled in ice and water (2.5 ml) was added. The grinding was continued for half an hour, after which the solid was filtered and washed with cold water. The combined filtrate and washings were evaporated *in vacuo* to give carbonatodiamminemono(*l*-propylenediamine)cobalt(III) carbonate (2 g). The carbonato complex (0.5 g) was treated with concentrated hydrochloric acid (3 ml) at 0°. After the reaction had ceased, ice-cold concentrated sulphuric acid (3 ml) was added dropwise to the violet solution. The mixture was allowed to stand in a tightly closed flask in a refrigerator for 3 days by which time the solution had turned green. Absolute ethanol was added to precipitate the complex which was filtered and washed with ice-cold ethanol. (Yield 0.25 g). The complex, *trans*-dichlorodiamminemono(*l*-propylenediamine)cobalt(III) hydrogen sulphate, was recrystallised from methanol containing a few drops of concentrated sulphuric acid, washed with ice-cold methanol and dried *in vacuo*. (Found: C 10.77; H 4.95; N 16.85; Co 17.76. Calc. for $CoC_3H_{17}N_4Cl_2SO_4$: C 10.75; H 5.11; N 16.72; Co 17.59). Preparation of the dichloro complex was also attempted by a method similar to that used for the dibromo complex but crystals could not be isolated.

Tetramminemono(*l*-propylenediamine)cobalt(III) chloride was prepared by pouring liquid ammonia onto *trans**-$[Co(l\text{-pn})(NH_3)_2Br_2*]Br$. Reaction was instantaneous forming

an orange solution of the tetrammine. The orange oil which remained after the ammonia had evaporated was solidified by adding ethanol. The solid was dissolved in 4 M hydrochloric acid with heating and ethanol added to precipitate orange plates of the chloride (yield 90 %). These were recrystallised from 80 % aqueous ethanol and dried over calcium chloride *in vacuo*. (Found: C 11.56; H 7.15; N 27.20 Calc. for $CoC_3H_{22}N_6Cl_3$: C 11.71; H 7.21; N 27.33). The compound was also prepared by a method analogous to that of Shimura [10] for the equivalent ethylenediamine complex but the yield was much lower than that of the previous method.

Trans-dichlorobis(*l*-propylenediamine)cobalt(III) chloride was prepared according to Werner and Frohlich [11] (Found: Cl 17.82; Co 31.80. Calc. for $CoC_6H_{20}N_4Cl_3.H_2O$: Cl 17.78; Co 32.08).

Trans-diamminebis(*l*-propylenediamine)cobalt(III) chloride was prepared by the method of O'Brien and coworkers [12] by treating *trans*-$[Co(l\text{-pn})_2Cl_2]Cl.H_2O$ with liquid ammonia. (Found: Cl 27.75; Co 15.55. Calc. for $CoC_6H_{26}N_6Cl_3.2H_2O$: Cl 27.73; Co 15.36).

Trans-dibromobis(*l*-propylenediamine)cobalt(III) bromide was prepared according to Werner.[13] (Found: Br 51.71; Co 12.74. Calc. for $CoC_6H_{20}N_4Br_3.H_2O$: Br 51.57; Co 12.68).

Trans-dithiocyanatobis(*l*-propylenediamine)cobalt(III) thiocyanate was synthesised according to Werner and Dawe.[14] (Found: C 28.20; H 5.31; N 25.60; S 24.85; Co 15.57. Calc. for $CoC_9H_{20}N_7S_3$: C 28.34; H 5.28; N 25.71; S 25.22; Co 15.45).

Trans-dichlorobis(*l-trans*-1,2-cyclohexanediamine)cobalt(III) chloride was synthetised by a method analogous to that for the corresponding *l*-propylenediamine complex.[11]

Table 1. Absorption and circular dichroism spectral data for some mono- and *trans*-bis(diamine)cobalt(III) complexes.

Complex	Absorption λ^{-1}(kK)	Absorption ε_{max}	Circular dichroism λ^{-1}(kK)	Circular dichroism $\Delta\varepsilon_{max}$	Assignment [g]
$[Co(l\text{-pn})_2(NH_3)_2]Cl_3$ [a]			19.30	−0.125	B_3 or B_2
	21.50	65.2	21.58	+0.500	B_2 or $B_3(B_1)$ [h]
	29.77	57.2	27.95	−0.050	T_2 [i]
$[Co(l\text{-pn})_2Cl_2]Cl$ [b]	16.45	38.7	16.57	+0.815	B_2 or $B_3(B_3$ or $B_2)$ [h]
	22.00	27.5	21.50	−0.115	B_1
	25.75	49.0			T_2 [i]
$[Co(l\text{-pn})_2Cl_2]Cl$ [c]			14.00	−0.012	B_3 or B_2
	16.20	38.1	16.45	+0.770	B_2 or B_3
	22.3 [e]	31.5	21.8	−0.126	B_1
	25.2 [e]	43			T_2 [i]
$[Co(l\text{-pn})_2Br_2]Br$ [b]	15.37	55.0	15.50	+0.810	B_2 or $B_3(B_3$ or $B_2)$ [h]
	21.5 [f]	34.5	22.10	−0.037	B_1
$[Co(l\text{-pn})_2(NCS)_2]CNS$ [a]	19.61	264	19.95	+0.592	B_2 or $B_3(B_3$ or $B_2)$ [h]
			23.15	−0.310	B_1
$[Co(l\text{-pn})(NH_3)_4]Cl_3$ [a]			19.34	−0.063	B_3 or B_2
	21.19	63.9	21.69	+0.339	B_2 or B_3 (B_1) [h]
	29.50	54.45	28.01	−0.014	T_2 [i]
$[Co(l\text{-pn})(NH_3)_2Br_2$ [d]$]Br$ [b]	15.25	52.2	15.32	+0.306	B_2 or B_3 or $B_2)$ [h]
	20.5 [f]	41			B_1 [h]
$[Co(l\text{-pn})(NH_3)_2Cl_2$ [d]$]HSO_4$ [b]	16.16	40.3	16.26	+0.349	B_2 or $B_3(B_3$ or $B_2)$ [h]
	21.37	30.5	21.28	−0.071	B_1
	25.32	48.0	24.35	+0.054	T_2 [i]
$NH_4[Co(l\text{-pn})(NH_3)_2$ [d]$(SO_3)_2]$ [a]	22.37	243	21.37	+0.677	?
$[Co(l\text{-chxn})_2Cl_2]Cl$ [b]	16.30	40.0	16.31	+0.786	B_2 or $B_3(B_3$ or $B_2)$ [h]
	21.85	31.5	21.25	−0.074	B_1
	25.52	53.7			T_2 [i]

a — in water; *b* — in methanol; *c* — in 4 M HCl; *d* — *trans*; *e* — shoulder; *f* — point of inflection for ill-defined shoulder; *g* — D_2 representations used to characterise transitions; *h* — CD band hidden by more dominant band; *i* — the components of the T_{2g} cubic band are not identified.

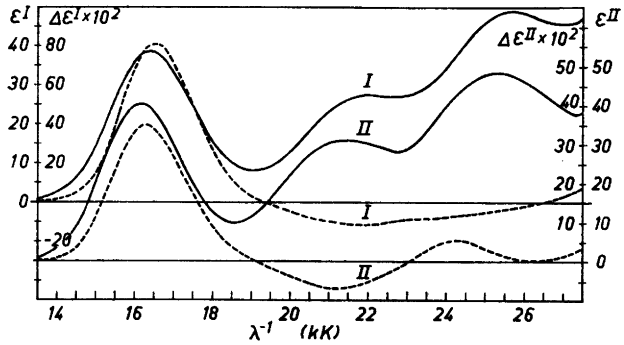


Fig. 1. Absorption (—) and circular dichroism (- -) spectra for *trans*-[Co(*l*-pn)$_2$Cl$_2$]Cl (I) and *trans**-[Co(*l*-pn)(NH$_3$)$_2$Cl$_2$*]HSO$_4$ (II) in methanol.

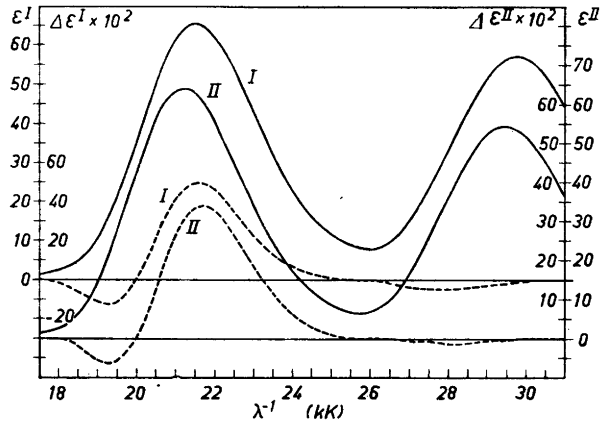


Fig. 2. Absorption (—) and circular dichroism (- -) spectra for *trans*-[Co(*l*-pn)$_2$(NH$_3$)$_2$]Cl$_3$ (I) and [Co(*l*-pn)(NH$_3$)$_4$]Cl$_3$ (II) in water.

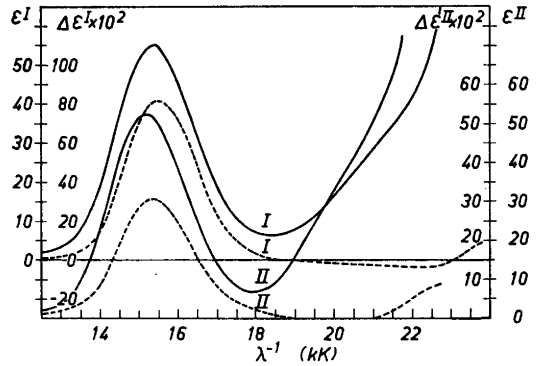


Fig. 3. Absorption (—) and circular dichroism (- -) spectra for *trans*-[Co(*l*-pn)$_2$Br$_2$]Br (I) and *trans**-[Co(*l*-pn)(NH$_3$)$_2$Br$_2$*]Br (II) in methanol.

The green crystals were recrystallised from methanol. (Found: Cl 25.70; Co 14.42. Calc. for $CoC_{12}H_{28}N_4Cl_3.H_2O$: Cl 25.84; Co 14.31).

The above compounds were checked for isomeric impurities after recrystallisation by chromatography on a cellulose powder column with a solution of water saturated 1-butanol mixed with 12 M hydrochloric acid in the ratio 50:1 as eluent, except for the *cis*-bis(sulphito)diamminemono(*l*-propylenediamine) complex, which was checked by paper chromatography.

The CD and absorption spectra were measured with a Roussel-Jouan dichrograph (with an extended wavelength scale, 800—200 nm) and a Cary model 14 spectrophotometer, respectively. The spectra for the above compounds are given in Figs. 1 to 6 and the details are summarised in Table 1.

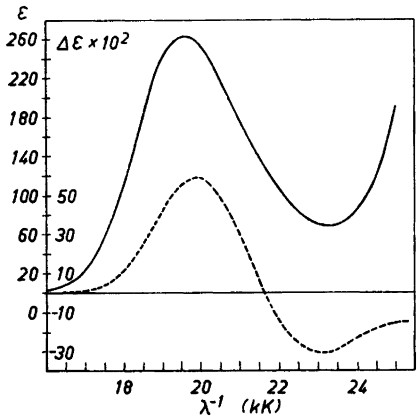


Fig. 4. Absorption (—) and circular dichroism (– –) spectra for *trans*-[Co(*l*-pn)$_2$(NCS)$_2$]CNS in water.

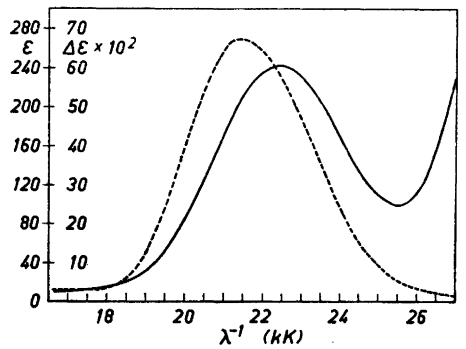


Fig. 5. Absorption (—) and circular dichroism (– –) spectra for *trans**-NH_4[Co(*l*-pn)$(NH_3)_2$*$(SO_3)_2$] in water.

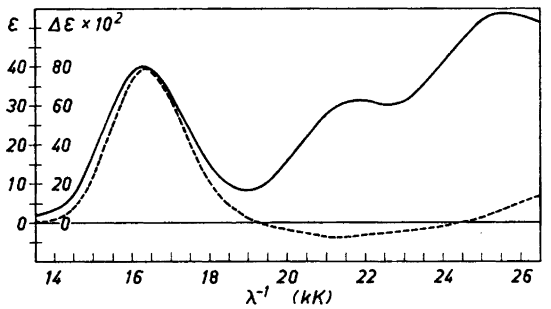
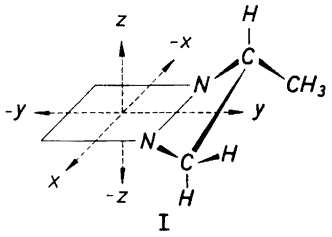


Fig. 6. Absorption (—) and circular dichroism (– –) spectra for *trans*-[Co(*l*-chxn)$_2$Cl$_2$]Cl in methanol.

DISCUSSION

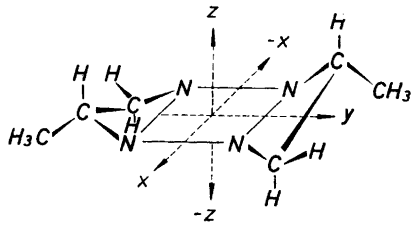
The most stable conformation of a *l*-propylenediamine metal chelate ring has the methyl group in an equatorial position.[15] Thus the absolute configuration of the most stable isomer of the mono(*l*-propylenediamine) complexes

is that given by structure I. For the *trans*-bis complexes in which the two unidentate ligands are identical, there are two possible isomers in which both methyl groups are equatorial, the compound described by structure II and the complex in which the two methyl groups are *cis* to one another. The chromatography of the dichloro compound on a cellulose powder column



I

showed two green bands, one very much weaker than the other. These have been attributed to the two isomers mentioned above, the major band corresponding to compound II. This choice was based on the fact that *trans*-[Co(*l*-pn)$_2$Cl$_2$]Cl.HCl.2H$_2$O has been found by X-ray analysis [16] to have the structure II. As structures I and II are thought to be markedly predominant for the respective complexes, the observed CD spectra are basically those for the absolute configurations I and II, which are denoted as *L* because they have a negative octant sign.[17] The problem of not knowing the equilibrium ratio



II

between the two possible conformations of the chelate rings is absent for the corresponding *l-trans*-1,2-cyclohexanediamine complexes. This ligand is stereospecific and forms chelate rings with the same conformation as that shown in structures I and II for the *l*-propylenediamine complexes.

The energy levels in tetragonal chromophores have been discussed by a number of authors using both the electrostatic model and approximated LCAO-MO models.[18] For *trans*-[Co(NH$_3$)$_4$X$_2$]$^{n+}$ complexes, which possess D_{4h} symmetry, the energy difference between the ^1E_g and $^1A_{2g}$ components from the $^1T_{1g}$ cubic level has been expressed as $(\Delta_{NH_3}-\Delta_x)/2$. Thus this theory would predict the same order of the components for *trans*-[Co(en)$_2$Cl$_2$]$^+$ as that given by Ballhausen and Moffitt's interpretation [7] of crystal spectra measurements. The CD spectrum of the related *trans*-[Co(*l*-pn)$_2$Cl$_2$]$^+$ complex provides no evidence to contradict this, contrary to the statements of Dunlop and Gillard.[3] The order of the two split components would be expected to

remain the same for all *trans*-bis(*l*-propylenediamine) complexes reported here. However, for the dinitro complex, for which Δ_{NO_2} is thought to be greater than $\Delta_{l\text{-pn}}$, the $^1A_{2g}$ level would be expected to lie at the lower energy.

From the CD spectrum of *trans*-$[Co(l\text{-pn})_2Cl_2]^+$ in methanol, the $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions (D_{4h}) are seen in Fig. 1 to have a positive and a negative Cotton effect, respectively. The absolute configurations of all the *trans* complexes considered are the same and the signs of the Cotton effects are expected to remain independent of X. Therefore, the observation of a negative band at lowest energy in the CD spectrum for the *trans*-diamine, when a positive $^1A_{1g} \rightarrow {}^1E_g$ transition was expected to lie lowest in energy, suggests that a symmetry lower than D_{4h} must be invoked because the doubly degenerate level must have been split to give a low energy component with a negative Cotton effect. Alternatively, this band could be due to a spin-forbidden band. However, the two low energy spin-forbidden bands for the hexammines have much lower energies than the observed band.[19] Therefore the possibility of the observed negative band being a spin-forbidden band has been discounted.

Moffitt and Moscowitz [20] have proposed that for an electronically-forbidden transition the absorption maximum should lie at higher energy than its corresponding CD maximum. However, for all the *trans*-bis complexes studied, the positive dichroism peaks lie at higher frequencies than the corresponding absorption peaks. This suggests that a band of opposite sign lies at a lower energy cancelling out part of the positive band and moving its maximum to higher frequencies. This negative band was observed for the dichloro complex in 4 M hydrochloric acid as well as for the diammine complex. The small negative band at 14 kK for the dichloro compound was completely reproducible and was not associated with any hydrolysis in the aqueous medium because hydrolysis was seen to proceed only slowly and the small negative band gradually disappeared as the dichloro was hydrolysed. Similar enhancements of minor residual bands on varying solvent or ionic media have been observed previously.[21]

Further support for the splitting of the ^1E_g (D_{4h}) level is obtained by comparing the intensities of the positive and negative CD bands in the dichloro and the dinitro complexes. The negative band in the latter lies at lower energy than the positive band and has a larger intensity than this;[4] the reverse is true for the former complex. This suggests that the order of levels in the dichloro could well be −, +, −, as observed in 4 M hydrochloric acid, and in the dinitro −, −, +, in agreement with the above conclusions.

The observation of the splitting of the ^1E_g (D_{4h}) level means that a symmetry lower than tetragonal must be used to explain the CD spectra. If the methyl groups are ignored, the *trans*-bis(*l*-propylenediamine) complexes have a D_2 symmetry. The representations for this symmetry group have been used to characterise the various transitions. Complexes with D_2 symmetry have three transitions of B type symmetry associated with the low energy T_{1g} cubic band. The B_1 level which transforms as the z-coordinate has A_{2g} tetragonal parentage. The other two levels come from the E_g tetragonal level, the B_2 transforming as the x-coordinate and the B_3 as the y-coordinate. From the above discussion and the results in Table 1, it is seen that the transition with

B_1 symmetry has a negative Cotton effect. Although it is known that the other two transitions have opposite signs, it is impossible at present to give a sign to the CD of these transitions.

The CD spectra of the diamminemono(*l*-propylenediamine) complexes are very similar to those for the comparable bis complexes. The mono complexes can be looked upon as being formed by lowering the symmetry of the bis complexes from D_2 to C_2. For this low symmetry the following transformations occur if the 2-fold axis of the mono complex is positioned to correspond with the y-coordinate of the *trans*-bis complex: A and B_3 go to A; B_1 and B_2 go to B. From the CD spectrum of *trans**-$[Co(l\text{-pn})(NH_3)_2Cl_2{*}]^+$ it is seen that the $^1A \rightarrow {}^1B[B_1(D_2)]$ transition has a negative Cotton effect as was found for the corresponding $^1A \rightarrow {}^1B_1$ (D_2) transition in *trans*-$[Co(l\text{-pn})_2Cl_2]^+$. This transition was not observed in the CD spectrum of *trans**-$[Co(l\text{-pn})(NH_3)_2Br_2{*}]^+$. This is not surprising because the observed optical rotatory power of the transitions for the mono-(*l*-propylenediamine) complexes is much less than that for the corresponding bis(*l*-propylenediamine) complexes and $\Delta\varepsilon$ for the $^1A \rightarrow {}^1B_1$ (D_2) transition in *trans*-$[Co(l\text{-pn})_2Br_2]^+$ is only -0.037.

Mason and his coworkers [22] have recently proposed that the sign of the Cotton effect for the charge-transfer band lying at 40—50 kK for complexes of the type $[Co(diamine)_3]^{3+}$ and $[Co(diamine)_2X_2]^{n+}$ is indicative of the puckering of the chelate rings. They found that complexes in which the chelate rings have a positive octant sign [17] (which is equivalent to a k conformation [15]) have a negative charge-transfer band. The CD spectra of $[Co(l\text{-pn})(NH_3)_4]^{3+}$ and *trans*-$[Co(l\text{-pn})_2(NH_3)_2]^{3+}$ were measured in the charge-transfer region and found to have a positive band. This is in agreement with Mason's proposal as the chelates in these complexes have negative octant signs.

Much of the above discussion is based on the assumption that the signs of the Cotton effects of the d—d transitions for the mono and *trans*-bis complexes are dependent directly or indirectly on the conformations of the chelate rings and independent of the unidentate ligands. This assumed dependence of the CD on the conformation of the chelate rings is supported by the close similarity of the CD spectra for the *trans*-dichlorobis(*l*-*trans*-1,2-cyclohexanediamine)cobalt(III) complex and the corresponding *l*-propylenediamine complex because the chelate ring conformations are the same in the two complexes. All the other experimental results are also consistent with this assumption. If this assumption is correct, then all mono- and *trans*-bis(diamine)-cobalt(III) complexes with chelate ring conformations corresponding to those in structures I and II will have a transition with $B_1(D_2)$ symmetry (or its C_2 equivalent) with a negative Cotton effect.

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