

Correlation of the Absolute Configurations of Tris-(diamine)complexes by Means of X-ray Powder Photographs of Active Racemates

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Racemates and active compounds of $[\text{Men}_3]\text{Cl}_3 \cdot \text{aq}$ and $[\text{Mpn}_3]\text{Br}_3$ and the active racemates $\{[\text{M}'\text{en}_3][\text{M}''\text{en}_3]\text{Cl}_3 \cdot \text{aq}$ and $\{[\text{M}'\text{pn}_3][\text{M}''\text{pn}_3]\text{Br}_3$ have been prepared, where M is one of the metals Cr, Co, and Rh, M' and M'' two different ones of these metals, en=ethylenediamine, and pn=propylenediamine. By the investigation of X-ray powder photographs of these compounds it has been possible to conclude that $(+)_589[\text{Cren}_3]^{3+}$, $(+)_589[\text{Coen}_3]^{3+}$, and $(-)_589[\text{Rhen}_3]^{3+}$ have the same absolute configuration, and that the same is true of $(+)_589[\text{Cr}(+)\text{pn}_3]^{3+}$, $(+)_589[\text{Co}(+)\text{pn}_3]^{3+}$, and $(-)_589(-)_{277}[\text{Rh}(+)\text{pn}_3]^{3+}$. This conclusion is in agreement with that of earlier work. All of the complexes mentioned have the absolute configuration *A* (IUPAC 1968), and the ring conformation δ (IUPAC 1968). This has the consequence that the C-C direction within each chelate ring is nearly parallel to the three-fold axis of the complex ions.

X-Ray powder photographs provide a simple method of correlating crystal structures. The factors which determine the diffraction pattern of such photographs, *i.e.* the position of the diffraction lines and their intensity distribution, are mainly: unit cell dimensions, the mutual position of the different atoms in the unit cell, and the scattering power of these atoms. Thus, if powder photographs of different crystals show a resemblance to each other, it is reasonable to conclude that there is some relationship between the structures.

When comparing complex molecules in this way one must realize that the diffraction pattern usually is dominated by the heaviest atoms in the structure. Thus, crystals containing completely different molecules may show similarities in their powder photographs if the structures are dominated by heavy atoms or groups of atoms packed in the same way in the different crystals. In connection with the present work it is worth mentioning that examples are known where the powder photograph of crystals containing

only one of the antipodes of an optically active molecule¹ to some extent resembles that of the corresponding racemic crystals.² Generally a resemblance would not be expected in such cases as the packing of the molecules would be quite different. Nevertheless it is possible, in many cases, to correlate the structures of molecules which form part of crystal structures by comparing the respective powder photographs. Providing the differences between the molecules being compared are small enough, the powder photographs may be almost identical. Such small differences are obtained, *e.g.* when one transition metal is substituted for another.

Thus, if two powder photographs (of related compounds) with a reasonable number of diffraction lines (compounds crystallizing in the cubic system will usually be unsuited for such investigations) are almost identical, then there can only be minor differences in the two structures.

The absolute configurations of tris(diamine) cobalt(III) complexes are known from several X-ray investigations by Saito *et al.*,³ the diamines being ethylenediamine (en), propylenediamine (pn), or trimethylenediamine. Werner⁴ introduced a criterion of least soluble diastereoisomers which correlates the absolute configurations of optically active complexes with the solubility of their diastereoisomers with the same optically active agent. Delépine^{5,6} prepared the active racemates $\{(-)_{589}[\text{Coen}_3](-)_{589}[\text{Rhen}_3]\}\text{X}_6 \cdot aq$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), and this in connection with their properties (among these the X-ray powder photographs) led to a correlation of the absolute configurations in question. In the later years conformational analysis of tris-complexes of optically active diamine ligands^{7,8} together with comparison of Cotton effects for related electronic transitions⁹⁻¹³ has been an important tool for the determination of absolute configurations.

In the present work some systems have been investigated for which there is full agreement on the absolute configuration in the literature. The method used is based upon a comparison of X-ray powder photographs of optically active compounds and of the corresponding racemates and active racemates. The active racemates have been prepared according to the absolute configurations which have been proposed in the literature, and this investigation fully confirms and supports the statements of the literature on this point. The purpose of this investigation has been to put forward a strong piece of evidence and at the same time to demonstrate the applicability to different systems of the method used here.

NOMENCLATURE AND ISOMERISM

Basic principle. Recently IUPAC has published a tentative nomenclature proposal¹⁴ (1) for the designation of configurational chirality caused by chelation in six-coordinated complexes based on the octahedron and (2) for the designation of conformational chirality of chelate rings which owe their chirality to their non-planarity.

This proposal is based upon the principle that two skew lines which are non-orthogonal define a helix. One line is the axis of the helix and the other is the tangent of the helix at the common normal for the skew lines. If this helix is right-handed, the Greek letter delta is used, if it is left-handed, the

Greek letter lambda is used. Upper case letters are used for configuration, lower case letters for conformation.

Absolute configuration. The two ligating atoms of a chelate ring define a line. Two such lines for a pair of chelate rings define the skew lines on whose chirality the nomenclature is based. For tris-bidentate complexes the three pairs of chelate rings have the same chirality, *i.e.* any one of the three pairs may be chosen to designate the configuration. Fig. 1 illustrates a representation of the absolute configuration Λ of $(+)\text{}_{589}[\text{Coen}_3]^{3+}$ as determined by Nakatsu *et al.*^{15,28} by X-ray single crystal methods.

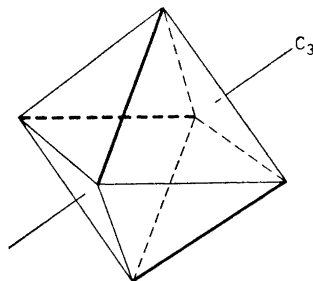
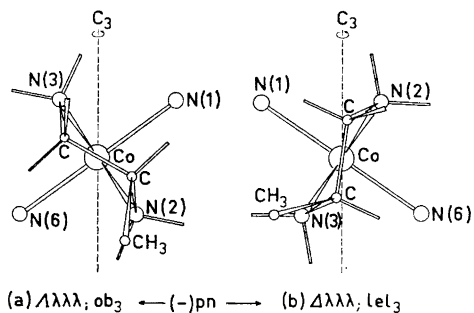


Fig. 1. The absolute configuration Λ of $(+)\text{}_{589}[\text{Coen}_3]^{3+}$ as determined by Nakatsu *et al.*^{15,28} The three edges spanned by the chelate rings have been drawn in heavy line, and the figure has been drawn in such a way that the helicity of one of the three pairs of skew lines may be easily visualized.

Conformation. The line joining the two ligating atoms and the line joining the two atoms of the chelate ring adjacent to each of the ligating atoms define the skew lines, on whose chirality the nomenclature is based. Fig. 2 illustrates the conformation λ of the $(-)$ propylenediamine chelate ring in its stable conformer with the methyl group equatorial.

Fig. 2. The conformation λ of the $(-)$ propylenediamine chelate ring in its stable conformer with the methyl group equatorial. (a) the Λ configuration, where the C—C bond of the propylenediamine ring is oblique to the three-fold axis of $(+)\text{}_{589}[\text{Co}(-)\text{pn}_3]^{3+}$ and (b) the Δ configuration, where the C—C bond direction is nearly parallel to the three-fold axis of $(-)\text{}_{589}[\text{Co}(-)\text{pn}_3]^{3+}$.

In the figure two of the octahedral positions, N(4) and N(5) are covered by N(3) and N(2), respectively, and for clearness only one of the chelate rings, N(2)—N(3), has been drawn, the two others being N(1)—N(5) and N(4)—N(6) in molecule (a), and N(1)—N(4) and N(5)—N(6) in molecule (b). The C_3 -axis and the atoms N(1), Co, and N(6) are in the plane of the paper.



Isomerism. The formula $[\text{Co}(\pm)\text{pn}_3]^{3+}$ represents several isomers caused by (1) the relative positions of the methyl groups, (2) the conformations of the chelate rings, and (3) the absolute configuration of the complex. The

whole problem of isomerism has been discussed by Sargeson.⁸ Here the discussion will mainly be limited to the isomers which arise when only one of the enantiomers of propylenediamine is bound to the central atom, *e.g.* the isomers of $[\text{Co}(-)\text{pn}_3]^{3+}$.

The isomers caused by the configurational position of the methyl groups can be illustrated by noting that because of the methyl group, propylenediamine is different in its two ends so that one may get the configurational isomers of a molecule of the type $\text{Co}(\text{A}-\text{B})_3$ where $\text{A}-\text{B}$ represents a bidentate ligand different in the two ends. The isomers may accordingly be characterized as facial (or *cis*) and meridional (or *trans*) referring to the methyl groups. Saito¹⁶ has found one of the conformational isomers, $(-)\text{}_{589}[\text{Co}(-)\text{pn}_3]\text{Br}_3$, to be facial. In the following discussion we will assume that this is so in all of the lel_3 -isomers (*vide infra*) considered below. The conformation of the propylenediamine chelate ring has been ignored so far. There is evidence that the preferred conformation is the one which places the methyl group equatorially. An energy difference of about 2 kcal/mol between this conformation and that in which the methyl group is axial has been estimated.⁷ The methyl group therefore is considered to be equatorial with the consequence that $(-)\text{pn}$ has a λ and $(+)\text{pn}$ a δ conformation. The two diastereoisomers of $[\text{Co}(-)\text{pn}_3]^{3+}$ thus have the C—C bond of the propylenediamine ring nearly parallel to the three-fold axis in the Δ configuration and oblique to it in the Λ configuration as illustrated in Fig. 2. These were denoted lel and ob , respectively, by Corey and Bailar.⁷ Here these isomers will be denoted by lel_3 and ob_3 , which is an obvious extension of the original proposal. Tris(propylenediamine) complexes containing both $(-)\text{pn}$ and $(+)\text{pn}$ would in this extended notation be of the types lel_2ob and lelob_2 , but these will not be discussed here.

SYSTEMS INVESTIGATED

We have prepared the active racemates $\{\Delta[\text{M}'\text{en}_3; \text{lel}_3] \Lambda[\text{M}''\text{en}_3; \text{lel}_3]\}\text{Cl}_6 \cdot \text{aq}$ and $\{\Delta[\text{M}'\text{pn}_3; \text{lel}_3] \Lambda[\text{M}''\text{pn}_3; \text{lel}_3]\}\text{Br}_6$ (M' and M'' being two of the metals Cr, Co, and Rh), and compared their X-ray powder photographs with those of the corresponding ordinary racemates, $[\text{Men}_3; \text{lel}_3]\text{Cl}_3 \cdot \text{aq}$ and $[\text{Mpn}_3; \text{lel}_3]\text{Br}_3$, and active forms, $\text{act}[\text{Men}_3]\text{Cl}_3 \cdot \text{aq}$ and $\text{act}[\text{Mpn}_3; \text{lel}_3]\text{Br}_3$ (M being one of the metals Cr, Co, and Rh). In this way it has been possible to correlate the absolute configurations of the ions $\text{act}[\text{Men}_3]^{3+}$ and of $\text{act}[\text{Mpn}_3; \text{lel}_3]^{3+}$.

EXPERIMENTAL

X-Ray powder photographs were all taken with $\text{CuK}\alpha$ radiation using a focussing camera of the Guinier type calibrated with silicon at 25°C. The photographs are reproduced in Fig. 3. All racemates, active racemates, and $\text{act}[\text{Mpn}_3]\text{Br}_3$ have been indexed as hexagonal. The unit cell dimensions are given in Table I.

Chromium complexes. 200 g of *trans* $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ were dissolved in 400 ml of DMSO (DMSO = dimethylsulfoxide), concentrated to a boiling point of 189°C (1 atm), and cooled slowly to room temperature. The green hygroscopic product was ground in a mortar. Yield: 380 g. The compound contained approx. 6 moles of DMSO. This is a modification of the method of Woldbye¹⁷ and Pedersen.¹⁸

2.5 g of DMSO-complex and 2.5 g of dry pn were mixed, heated to reaction (green → yellow) while stirred, and cooled. 5 ml of 4 M HCl were added, and the solution was dissolved in a mixture of water-saturated 1-butanol (approx. 1.5 l) and dry 1-butanol (approx. 0.3 l). This solution was run through a Whatman CF 11 cellulose powder column, and the complex eluted as described by Dwyer *et al.*¹⁹ It was necessary to protect the column against light and increase the elution rate by using a slight nitrogen pressure. The complex was extracted from the eluate with water, and the aqueous solution evaporated to dryness in a rotating vacuum evaporator (bath temperature 35°C). During the synthesis with (-)pn, two bands were observed on the column. The first to be eluted was the lel_3 -isomer, $(-)_589[Cr(-)pn_3]Cl_3$, and the second the ob_3 -isomer, $(+)_589[Cr(-)pn_3]Cl_3$. As it was difficult to obtain the isomer $(-)_589[Cr(-)pn_3]Br_3$ in a crystalline form, we adopted the following procedure: 20 g of $(-)_589[Cr(-)pn_3]Cl_3 \cdot aq$ were dissolved in 30 ml of water and then precipitated with 23 ml of 47% HBr. After two reprecipitations from water a slightly supersaturated solution was seeded with a tiny crystal of $(+)_589(+)_277[Rh(-)pn_3]Br_3$. Yield 46 mg of crystalline $(-)_589[Cr(-)pn_3]Br_3$. The fact that it was only possible to obtain 46 mg of crystalline isomer from a solution containing about 20 g of complex may indicate that the other methyl group isomer was also present. This problem, however, was not investigated further.

Three bands were eluted from the column when racemic pn was used in the synthesis. The fastest moving band was the racemic lel_3 -isomer $[Cr(\pm)pn_3]Cl_3$, *i.e.* $\{(-)_589[Cr(-)pn_3]-(+)_589[Cr(+)pn_3]\}Cl_3$. The bromide, recrystallized three times from water, was used for the powder photograph.

$[Cren_3]Cl_3 \cdot aq$ was prepared by the method of Rollinson and Bailar²⁰ and resolved as described elsewhere.²¹

Cobalt complexes. The optically active lel_3 -isomers, $(+)_589[Co(+)pn_3]Br_3$ and $(-)_589[Co(-)pn_3]Br_3$, were prepared by chromatography as chlorides as described by Dwyer *et al.*¹⁹ After metathesis, the bromides were recrystallized three times from water. They gave identical powder photographs.

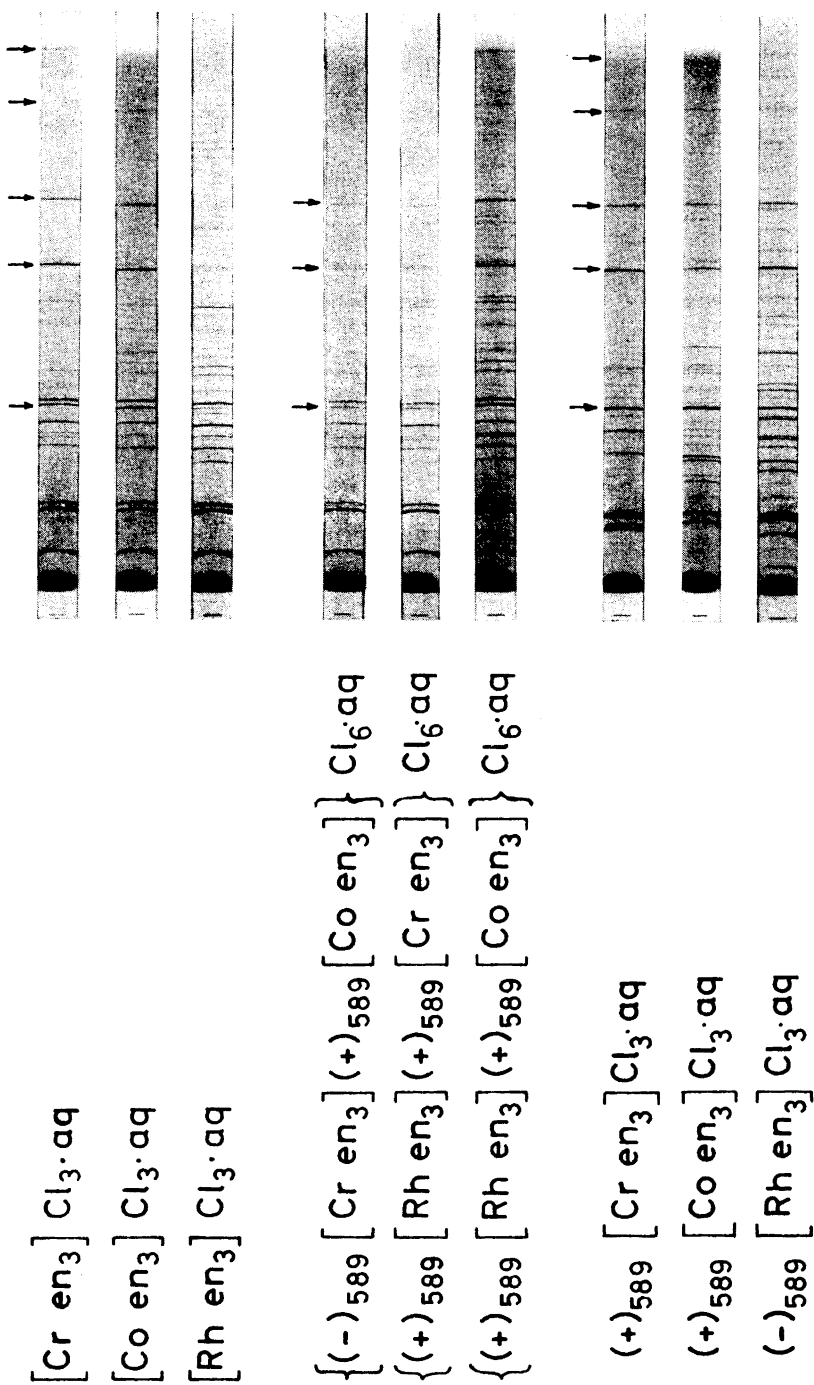
The racemic lel_3 -isomer, $[Co(\pm)pn_3]Br_3$, was prepared from the fastest moving band on the column as described by Dwyer *et al.*²² and above for the chromium complexes. This complex was also obtained by mixing almost saturated aqueous solutions of equimolar amounts of $(-)_589[Co(-)pn_3]Br_3$ and $(+)_589[Co(+)pn_3]Br_3$. The precipitate, recrystallized twice, gave a powder photograph identical to that of the racemic complex previously described.

$[Coen_3]Cl_3 \cdot aq$ was prepared by the method of Work.²³ $(+)_589[Coen_3]Cl_3 \cdot aq$ was prepared²⁴ from $(+)_589[Coen_3]Cl(+)tartrate \cdot 5H_2O$ which was prepared by the partially asymmetric synthesis of Broomhead *et al.*²⁵

Rhodium complexes. The optically active lel_3 -isomers, $(+)_277[Rh(-)pn_3]Br_3$ and $(-)_277[Rh(+)pn_3]Br_3$,* were separated from the ob_3 -isomers by fractional crystallization. The isomers of $[Rh(-)pn_3]Cl_3$ were prepared from 5.26 g of $RhCl_3 \cdot 3H_2O$, a mixture of 6 ml of (-)pn and 8 ml of water, and 3 ml of ethanol analogous to the corresponding en complex.²¹ The reaction mixture was filtered and the filtrate evaporated to dryness in a rotating vacuum evaporator (bath temperature 90°C). The crystalline residue was dissolved in 10 ml of water and precipitated with 14 ml of 47% HBr. Crystalline ob_3 -isomer, $(-)_277[Rh(-)pn_3]Br_3$, was obtained from the mother liquor,** and crystalline lel_3 -isomer, $(+)_277[Rh(-)pn_3]Br_3$, from the precipitate after three recrystallizations from water. The lel_3 -isomer $(-)_277[Rh(+)pn_3]Br_3$ was prepared in the same way from 10.52 g of $RhCl_3 \cdot 3H_2O$, 130 ml of 1.08 M (+)pn, and 10 ml of ethanol. The purity of the complexes was tested by descending paper chromatography on Whatman paper 3MM with a mixture of 100 ml of water-saturated 1-butanol and 8 ml of 12 M HCl as eluent. The spots were detected by UV light.

* The lel_3 -isomer, $\Delta(+)_589(+)_277[Rh\{(R)(-)pn\}_3\lambda\lambda\lambda]^{3+}$, shows positive rotation in the region 790–190 nm while the ob_3 -isomer, $\Delta(+)_589(-)_277[Rh\{(R)(-)pn\}_3\lambda\lambda\lambda]^{3+}$, shows positive rotation in the same region except from 298 to 242 nm and from 199 to 190 nm where it shows negative rotation with an extremum at 277 nm.

** In a forthcoming paper, C. E. Schäffer and S. E. Harnung are going to characterize the $[Mpn_3; ob_3]Cl_3$ complexes with $M=Cr, Co, \text{ and } Rh$.



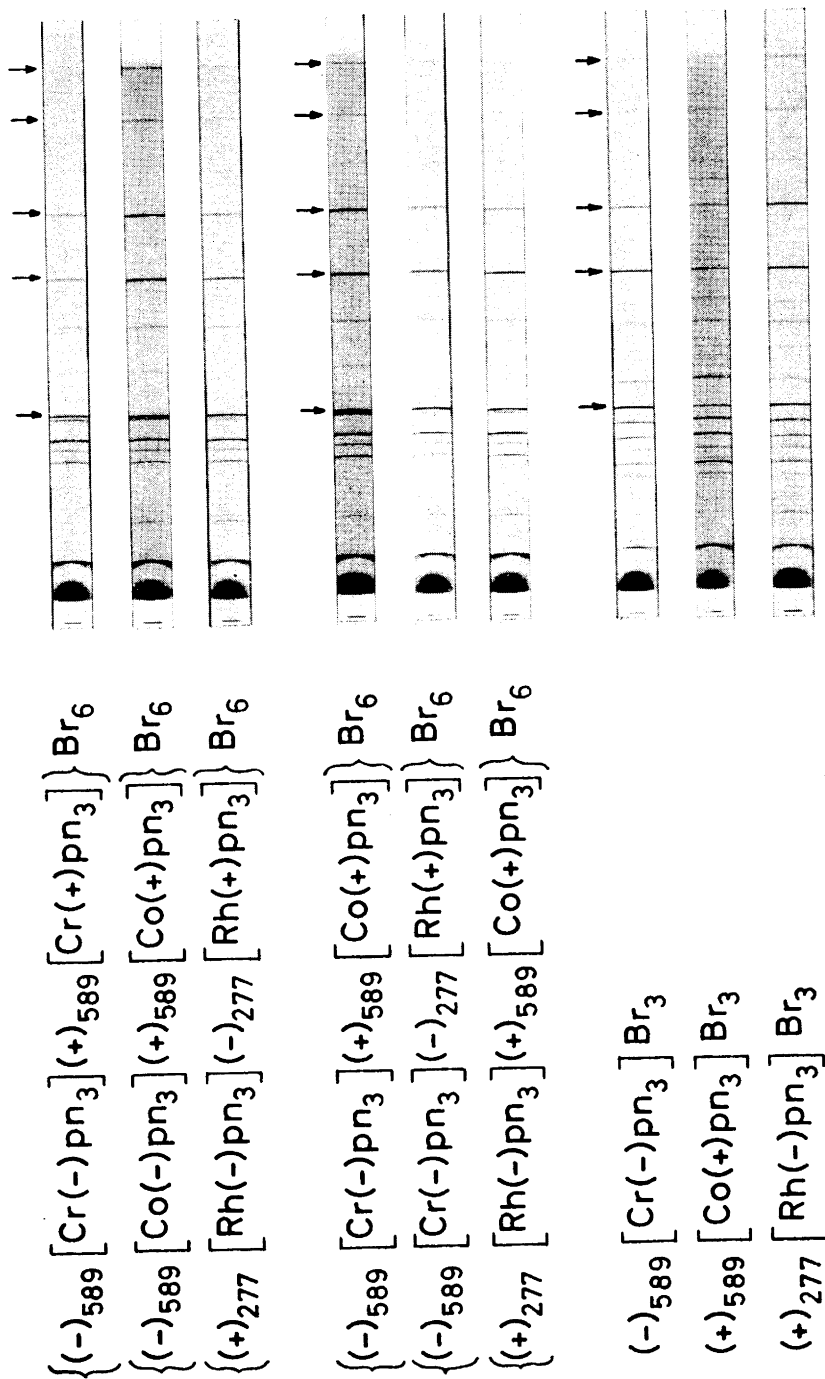


Fig. 3. X-Ray powder photographs (Guinier, $CuK\alpha$) of the investigated compounds. Silicon has been added as a reference and its diffraction lines are marked by arrows. As to the quality of the $[Coen_3]Cl_3$ -diagram, see note to Table I.

The racemic le_3 -isomer, $[Rh(\pm)pn_3]Br_3$, was prepared by mixing almost saturated solutions of equimolar amounts of the active forms as described for the racemic cobalt complex.

$[Rhen_3]Cl_3 \cdot aq$ was prepared and resolved by published methods.²¹

Active racemates. $\{(-)_{589}[Cr(-)pn_3](+)_{589}[Co(+)pn_3]\}Br_6$ was prepared by mixing solutions of 1.0 g of $(-)_{589}[Cr(-)pn_3]Br_3$ in 5.0 ml of water and 1.0 g of $(+)_{589}[Co(+)pn_3]Br_3$ in 5.0 ml of water. After cooling in ice the crystals were filtered and dried in air. Yield 0.34 g. The crystalline product was recrystallized from water without change in the circular dichroism spectrum.

$\{(-)_{589}[Cr(-)pn_3](-)_{277}[Rh(+)pn_3]\}Br_6$ (yield 0.21 g) and $\{(+)_{277}[Rh(-)pn_3](+)_{589}[Co(+)pn_3]\}Br_6$ (yield 0.08 g) were prepared in the same fashion from 0.74 g of $(-)_{589}[Cr(-)pn_3]Br_3$ in 4.0 ml of water and 0.90 g of $(-)_{277}[Rh(+)pn_3]Br_3$ in 3.0 ml of water and from 0.11 g of $(+)_{277}[Rh(-)pn_3]Br_3$ in 0.7 ml of water and 0.10 g of $(+)_{589}[Co(+)pn_3]Br_3$ in 0.7 ml of water, respectively, but were cooled in ice-NaCl before filtration.

$\{(-)_{589}[Cren_3](+)_{589}[Coen_3]\}Cl_6 \cdot aq$ was prepared by mixing solutions of 3.67 g of $(-)_{589}[Cren_3]Cl_3 \cdot 1.6H_2O$ in 4.5 ml of water and 3.64 g of $(+)_{589}[Coen_3]Cl_3 \cdot H_2O$ in 3.5 ml of water. After cooling in ice the crystals were filtered, washed with 40 % ethanol, and dried in air. Yield 3.83 g.

$\{(+)_{589}[Rhen_3](+)_{589}[Cren_3]\}Cl_6 \cdot aq$ (yield 1.08 g) and $\{(+)_{589}[Rhen_3](+)_{589}[Coen_3]\}Cl_6 \cdot aq$ (yield 1.09 g) were prepared in the same way from 1.08 g of $(+)_{589}[Rhen_3]Cl_3 \cdot 2.3H_2O$ in 1.5 ml of water and 0.919 g of $(+)_{589}[Cren_3]Cl_3 \cdot 1.6H_2O$ in 1 ml of water, and from 1.08 g of $(+)_{589}[Rhen_3]Cl_3 \cdot 2.3H_2O$ in 1.5 ml of water and 0.909 g of $(+)_{589}[Coen_3]Cl_3 \cdot H_2O$ in 1 ml of water, respectively.

(-) and (+)propylenediamine were prepared by the method of Dwyer *et al.*²⁶ using (+) and (-)tartaric acid, respectively. The free amine was obtained from the hydrogen tartrate by means of saturated KOH-solution, dried over KOH and distilled from Na (120–121°C, 1 atm).

Identification of the compounds. The different compounds were identified by a combination of electronic and CD-spectra, rotatory power, X-ray powder photographs, chemical and thermogravimetric analysis, and the method of preparation. The chlorides of the en complexes had a water of crystallization content which could vary between 0 and 3.5 molecules *per* metal atom depending upon their history. As to the racemates this is connected with the zeolitic inclusion of the water molecules in channels parallel to the *c*-axis of the hexagonal crystals, and it has been shown that the unit cell dimensions do not vary with the water content.^{2,27} For this reason the water content of the chlorides is not specified. The bromides of the pn complexes showed little or no water content.

CONCLUSION

It is seen from Fig. 3 that the racemates and the corresponding active racemates have almost identical powder photographs, different from those of the active compounds. Considering this and the other experimental data we find it safe to conclude that $(+)_{589}[Cren_3]^{3+}$, $(+)_{589}[Coen_3]^{3+}$, and $(-)_{589}[Rhen_3]^{3+}$ all have the same chirality. This is also true of $(+)_{589}[Cr(+)pn_3]^{3+}$, $(+)_{589}[Co(+)pn_3]^{3+}$, and $(-)_{589}(-)_{277}[Rh(+)pn_3]^{3+}$. Now the absolute configuration of $[Coen_3; le_3]^{3+}$ in $(+)_{589}$ and $(-)_{589}[Coen_3; le_3]Cl_3 \cdot \frac{1}{2}NaCl \cdot 3H_2O$ ²⁸ and in $(+)_{589}[Coen_3; le_3]Br_3 \cdot H_2O$,¹⁵ and of $[Copen_3; le_3]^{3+}$ in $(-)_{589}[Co(-)pn_3; le_3]Br_3$ ¹⁶ have all been determined by X-ray single crystal methods. On this basis the three tris(ethylenediamine)- and the three tris((+)propylenediamine)complexes mentioned must all be of the $A\delta\delta\delta$ (*A*; le_3) type.

The cobalt complex $(-)_{589}[Co(-)pn_3]Br_3$ has been shown to be *fac A* le_3 ,¹⁶ and the establishment of the crystal series V of Table 1 indicates that the

Table 1. Unit cell dimensions from X-ray powder photographs (Guinier, CuK α), 25°C. All crystals are indexed as belonging to the hexagonal crystal system.

All the complexes in the table are of the 1el $_3$ -type. The three act[Men $_3$ Cl $_3$ ·aq (see Fig. 3) show mutually different powder photographs, different also from the crystal series I-V, and they have not been included in the table.

A complete X-ray structure analysis exists for [Coen $_3$ Cl $_3$ ·3H $_2$ O ($a=11.50$ Å, $c=15.52$ Å)² and for (-)₅₈₉[Co(-)pn $_3$]Br $_3$ ($a=11.08$ Å, $c=8.59$ Å).¹⁶

Photographs of several different preparations of [Coen $_3$ Cl $_3$ ·aq were measured as the diffraction lines were all slightly diffuse. Unit cell dimensions were found to vary from sample to sample by about 0.02 Å.

Crystal series	Phenomenological characterization	Full characterization ¹⁴	a (Å)	c (Å)
I	[Cr en $_3$]Cl $_3$ ·aq [Co en $_3$]Cl $_3$ ·aq [Rh en $_3$]Cl $_3$ ·aq	{ Δ (-) ₅₈₉ [Cr en $_3$]Cl $_3$ ·aq { Δ (-) ₅₈₉ [Co en $_3$]Cl $_3$ ·aq { Δ (+) ₅₈₉ [Rh en $_3$]Cl $_3$ ·aq	11.60 ₆ 11.44 ₃ 11.59 ₉	15.45 ₈ 15.48 ₃ 15.48 ₃
II	{(-) ₅₈₉ [Cr en $_3$]Cl $_3$ ·aq {(+) ₅₈₉ [Rh en $_3$]Cl $_3$ ·aq {(+) ₅₈₉ [Rh en $_3$]Cl $_3$ ·aq	{ Δ (-) ₅₈₉ [Cr en $_3$]Cl $_3$ ·aq { Δ (+) ₅₈₉ [Rh en $_3$]Cl $_3$ ·aq { Δ (+) ₅₈₉ [Rh en $_3$]Cl $_3$ ·aq	11.53 ₉ 11.57 ₅ 11.53 ₈	15.51 ₁ 15.51 ₁ 15.49 ₆
III	{(-) ₅₈₉ [Cr(-)pn $_3$]Br $_3$ {(-) ₅₈₉ [Co(-)pn $_3$]Br $_3$ {(+) ₂₇₇ [Rh(-)pn $_3$]Br $_3$	{ Δ (-) ₅₈₉ [Cr(-)pn $_3$]Br $_3$ { Δ (-) ₅₈₉ [Co(-)pn $_3$]Br $_3$ { Δ (+) ₂₇₇ [Rh(-)pn $_3$]Br $_3$	12.06 ₃ 11.99 ₂ 12.10 ₂	8.05 ₁ 8.02 ₃ 8.05 ₂
IV	{(-) ₅₈₉ [Cr(-)pn $_3$]Br $_3$ {(-) ₅₈₉ [Cr(-)pn $_3$]Br $_3$ {(+) ₂₇₇ [Rh(-)pn $_3$]Br $_3$	{ Δ (-) ₅₈₉ [Cr(-)pn $_3$]Br $_3$ { Δ (-) ₅₈₉ [Cr(-)pn $_3$]Br $_3$ { Δ (+) ₂₇₇ [Rh(-)pn $_3$]Br $_3$	12.01 ₉ 12.08 ₆ 12.04 ₇	8.01 ₉ 8.04 ₆ 8.03 ₇
V	{(-) ₅₈₉ [Cr(-)pn $_3$]Br $_3$ {(+) ₅₈₉ [Co(+)pn $_3$]Br $_3$ {(+) ₂₇₇ [Rh(-)pn $_3$]Br $_3$	Δ (-) ₅₈₉ [Cr(-)pn $_3$]Br $_3$ Δ (+) ₅₈₉ [Co(+)pn $_3$]Br $_3$ Δ (+) ₂₇₇ [Rh(-)pn $_3$]Br $_3$	11.21 ₇ 11.05 ₀ 11.22 ₂	8.62 ₆ 8.56 ₂ 8.59 ₈

corresponding chromium and rhodium compounds are also *fac* lel_3 . This leads to the same correlation of the pn complexes as does the active racemate method, because when they are all of the *fac* lel_3 -type, the chirality of the complexes is determined solely by the absolute configuration of the active propylenediamine.^{7,8}

The results obtained here agree with those obtained from conformational analysis of tris complexes of optically active diamine ligands^{7,8} together with comparison of Cotton effects for related electronic transitions,⁹⁻¹³ and are in full agreement with Werner's criterion of least soluble diastereoisomers.⁴

All of the racemates and active racemates have been indexed as hexagonal. Any symmetry element in the racemates, connecting the active antipodes, must be absent in the active racemates because of the different metal atoms. Nevertheless, the racemates and the active racemates treated here all belong to the same crystal system — the hexagonal — and inspection of Table 1 shows that the chromium and rhodium compounds have unit cells of very nearly the same size, larger than those of the corresponding cobalt compounds, presumably due to a somewhat smaller metal-ligand distance in the cobalt complexes.

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