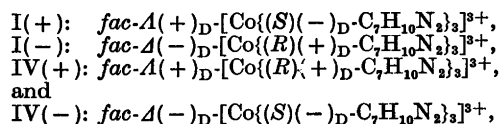# Tris-[(±)_D-1-(2-pyridyl)ethylamine]cobalt(III) Complexes. Preparation and Partial Structural Assignment of Geometrical and Optical Isomers*

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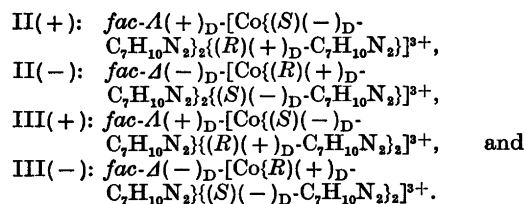
Tris-[(±)_D-1-(2-pyridyl)ethylamine]cobalt(III) chloride has been prepared and separated into five distinct, racemic fractions by column chromatography. Four of the racemates were separated into their catoptric forms by column chromatography using an optically active eluent.

X-Ray powder photographs, absorption spectra and CD spectra identified four of these new isomers as:

I(+): fac-Λ(+)_D-[Co{(S)(−)_D-C_7H_10N_2}_3]^{3+},
I(−): fac-Δ(−)_D-[Co{(R)(+)_D-C_7H_10N_2}_3]^{3+},
IV(+): fac-Λ(+)_D-[Co{(R)(+)_D-C_7H_10N_2}_3]^{3+}, and
IV(−): fac-Δ(−)_D-[Co{(S)(−)_D-C_7H_10N_2}_3]^{3+},

compounds that have been prepared recently using optically active amines as initial materials.

The physical measurements suggest the remaining four isomers to be:

II(+): fac-Λ(+)_D-[Co{(S)(−)_D-C_7H_10N_2}_2{(R)(+)_D-C_7H_10N_2}]^{3+},
II(−): fac-Δ(−)_D-[Co{(R)(+)_D-C_7H_10N_2}_2{(S)(−)_D-C_7H_10N_2}]^{3+},
III(+): fac-Λ(+)_D-[Co{(S)(−)_D-C_7H_10N_2}{(R)(+)_D-C_7H_10N_2}_2]^{3+}, and
III(−): fac-Δ(−)_D-[Co{R)(+)_D-C_7H_10N_2}{(S)(−)_D-C_7H_10N_2}_2]^{3+}.

Recently tris-diamine complexes of cobalt(III) and chromium(III) have been given considerable attention by this laboratory.[2-5]The present work represents an extension of this attention by including tris-complexes of cobalt(III) and the hitherto rather unknown bidentate ligand 1-(2-pyridyl)-ethylamine (Fig. 1b).
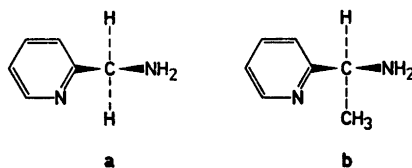
* See Ref. 1.

Fig. 1. a. (2-Pyridyl)methylamine (2-picolylamine). b. 1-(2-Pyridyl)ethylamine.

In a previous paper[1] tris-complexes of cobalt and the optically active ligands (−)_D- and (+)_D-1-(2-pyridyl)ethylamine were described. Because of geometrical and configurational isomerism, four isomers of each of the formulas [Co{(−)_D-C_7H_10N_2}_3]X_3 and [Co{(+)_D-C_7H_10N_2}_3]X_3 should be expected. We succeeded in isolating and assigning three different complexes with (−)_D-1-(2-pyridyl)ethylamine, namely two facial and one meridional isomer and the corresponding three enantiomers with the (+)_D-amine.

In this work concerning the tris-[(±)_D-1-(2-pyridyl)ethylamine]cobalt(III) system, we succeeded in isolating and identifying eight facial isomers. Analogously with the corresponding propylenediamine system[5] the racemic amine should, at least theoretically, give rise to eight facial isomers.

THE PREPARATIVE METHODS AND THE ASSIGNMENT OF THE ISOMERS

The racemic mixture of [Co{(±)_D-C_7H_10N_2}_3]Cl_3 was prepared from an ethanolic

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solution of *trans*-dichlorotetrakis(pyridine)-cobalt(III) chloride and racemic amine.[3,6] The crude product was separated by column chromatography into four *facial* (I, II, III, IV) and one *meridional* fraction (V). The *facial* compounds were further resolved into their enantiomers on a column with a tartrate eluent. From fraction V it was possible to isolate one *meridional* compound, while another, the racemate of *mer*-$\Lambda(+)_D$-[Co{(S)(−)$_D$-$C_7H_{10}N_2$}$_3$]$^{3+}$ (abbrev. *mer*-ΛS_3) and *mer*-$\Delta(−)_D$-[Co{(R)(+)$_D$-$C_7H_{10}N_2$}$_3$]$^{3+}$ (abbrev, *mer*-ΔR_3), which was expected to be present in a very small amount, disappeared. As the yield of the remaining compound was small, and the first attempts at resolution were unsuccessful, further investigations of the *meridional* compounds were postponed.

As in the previous work [1] it is assumed to be correct that the (−)$_D$-form of the amine has the configuration S,[7,8] the (+)$_D$-form consequently the configuration R. It is also assumed that there is a relationship between the total (net) $d−d$ rotatory strength (or the sign of the algebraic sum of the $d−d$ CD band areas) and the absolute configuration of the complexes, the strength being positive for the Λ isomers.[9] The nomenclature is that proposed by IUPAC.[10]

EXPERIMENTAL

Reagents. The initial material *trans*-[Copy$_4$Cl$_2$]Cl.6H$_2$O was prepared by a method developed by Glerup and Schäffer.[11] Racemic 1-(2-pyridyl)ethylamine was prepared as described before.[1] SP-Sephadex C-25 was purchased from Pharmacia, Uppsala, Sweden. All other chemicals were of reagent grade and were used without further purification.

Analyses. The cobalt analyses were performed on a Perkin Elmer 403 Atomic Absorption Spectrophotometer. The microanalytical laboratory of this institute carried out the carbon and the nitrogen analyses by standard methods.

Physical measurements. Absorption spectra were recorded on a Cary Model 14 spectrophotometer. The spectra are characterized by their maxima and minima (ε, λ), where the molar extinction coefficient ε is in units of $l\ mol^{-1}\ cm^{-1}$ and λ is in nm. Circular dichroism was measured on a Roussel-Jouan Dichrographe I. The maxima are given below as $(\Delta\varepsilon, \lambda) = [(\varepsilon_1 - \varepsilon_r), \lambda]$. Optical rotation was measured on a Perkin Elmer Model 141 polarimeter. In all cases the solvent was 0.1 M hydrochloric acid. The X-ray powder photographs were

obtained on a camera of the Guinier type with CuKα radiation. Silicium was used as standard.

Preparation of the cobalt complexes. 2.00 g of [Copy$_4$Cl$_2$]Cl.6H$_2$O (3.39 mmol) was dissolved in 50 ml of ethanol (99 %). 1.25 ml of racemic amine (∼ 10.2 mmol) was added. An immediate colour-shift from green to yellow-brown took place. After 10 min a yellow-brown solid was precipitated by addition of ether. Washing with ether.

Ion exchange separations. The crude product was dissolved in 0.1 M hydrochloric acid. The solution was poured on a column (length 60 cm, diameter 5 cm) of an SP-Sephadex C-25 cation exchanger (Sephadex was introduced for similar purposes by Yoshikawa and Yamasaki [12]), and the adsorbed bands were eluted with a solution that was 0.2 M in sodium dihydrogenorthophosphate and 0.02 M in disodium hydrogenorthophosphate (acid solutions were necessary in order to avoid destruction of the compounds). Four yellow and one orange band resulted. They were named I, II, III, IV, and V, following the order of their elution.

I: The first yellow fraction was a very small one. The eluate was diluted with an equal amount of water and poured on a small Sephadex column (length 20 cm, diameter 1.25 cm). Sodium and phosphate ions were removed by a subsequent elution with 0.1 M hydrochloric acid. When the eluate showed negative phosphate reaction, the complex was eluted with 0.5 M sulfuric acid. The concentrated solution weas evaporated to nearly dryness on a vacuum rotatory evaporator. The residue was dissolved in ethanol (99 %), the solution was cooled on ice, and the complex was precipitated with ether. The compound was redissolved in 2 M sulfuric acid and reprecipitated with ethanol and ether after filtering. Yield: 195 mg (8.0 %). (Found: Co 8.38; N 11.7. Calc. for [Co(C$_7$H$_{10}$N$_2$)$_3$](HSO$_4$): Co 8.22; N 11.7). In another experiment the yield was 8.1 %. When sodium perchlorate was added to a concentrated solution of the complex, compact bright yellow crystals precipitated. They were filtered and washed with ice-cold water. (Found: Co 7.79; C 33.2; N 11.2; Cl 14.1. Calc. for [Co(C$_7$H$_{10}$N$_2$)$_3$](ClO$_4$)$_3$.2H$_2$O Co 7.76; C 33.2; N 11.1; Cl 14.0). $(\varepsilon, \lambda)_{max}$: (149,461), (160,338). $(\varepsilon, \lambda)_{min}$: (15,388), (143,322). The X-ray powder photograph of this compound was identical with that of the perchlorate prepared in a similar manner from a solution of an equimolar mixture of the previously described compounds [1] assumed to be *fac*-ΛS_3 and *fac*-ΔR_3. (About the abbreviations: see Table 1).

II: The second yellow fraction was a large one. It was treated like fraction I with the exception that it was finally eluted with 1 M hydrochloric acid instead of sulfuric acid. The solution was evaporated on a vacuum rotatory evaporator, and the complex was precipitated by means of ethanol and ether. Yield:

Table 1. The *facial* isomers of $[Co\{(\pm)_D\text{-}C_7H_{10}N_2\}_3]^{3+}$.

Symbol	Formula	Abbrev.
I(+)	$fac\text{-}\Lambda(+)_D\text{-}[Co\{(S)(-)_D\text{-}C_7H_{10}N_2\}_3]^{3+}$	$fac\text{-}\Lambda S_3$
II(+)	$fac\text{-}\Lambda(+)_D\text{-}[Co\{(S)(-)_D\text{-}C_7H_{10}N_2\}_2\{(R)(+)_D\text{-}C_7H_{10}N_2\}]^{3+}$	$fac\text{-}\Lambda S_2R$
III(+)	$fac\text{-}\Lambda(+)_D\text{-}[Co\{(S)(-)_D\text{-}C_7H_{10}N_2\}\{(R)(+)_D\text{-}C_7H_{10}N_2\}_2]^{3+}$	$fac\text{-}\Lambda SR_2$
IV(+)	$fac\text{-}\Lambda(+)_D\text{-}[Co\{(R)(+)_D\text{-}C_7H_{10}N_2\}_3]^{3+}$	$fac\text{-}\Lambda R_3$
I(−)	$fac\text{-}\Delta(-)_D\text{-}[Co\{(R)(+)_D\text{-}C_7H_{10}N_2\}_3]^{3+}$	$fac\text{-}\Delta R_3$
II(−)	$fac\text{-}\Delta(-)_D\text{-}[Co\{(R)(+)_D\text{-}C_7H_{10}N_2\}_2\{(S)(-)_D\text{-}C_7H_{10}N_2\}]^{3+}$	$fac\text{-}\Delta R_2S$
III(−)	$fac\text{-}\Delta(-)_D\text{-}[Co\{(R)(+)_D\text{-}C_7H_{10}N_2\}\{(D)(-)_D\text{-}C_7H_{10}N_2\}_2]^{3+}$	$fac\text{-}\Delta RS_2$
IV(−)	$fac\text{-}\Delta(-)_D\text{-}[Co\{(S)(-)_D\text{-}C_7H_{10}N_2\}_3]^{3+}$	$fac\text{-}\Delta S_3$

757 mg (35 %). (Found: Co 9.19. Calc. for $[Co(C_7H_{10}N_2)_3]Cl_3.6H_2O$: Co 9.20). In another experiment the yield was 31 %. As the chloride inclined to deliquescence, it was converted into the perchlorate as described above. (Found: Co 8.13; C 34.8; N 11.7; Cl 14.9. Calc. for $[Co(C_7H_{10}N_2)_3](ClO_4)_3$: Co 8.14; C 34.9; N 11.6; Cl 14.7). $(\varepsilon,\lambda)_{max}$: (149,459.5), (155,336). $(\varepsilon,\lambda)_{min}$: (17,386), (146,324).

III: This relatively large, yellow fraction was isolated exactly like II. Yield: 525 mg (26 %). (Found: Co 9.83. Calc. for $[Co(C_7H_{10}N_2)_3]Cl_3.4H_2O$: Co 9.76). In another experiment the yield was 29 %. The perchlorate was prepared, as it was easier to handle in humid air. (Found: Co 7.84; C 33.3; N 11.2; Cl 14.4. Calc. for $[Co(C_7H_{10}N_2)_3]$-$(ClO_4)_3.1\frac{1}{2}H_2O$: Co 7.85; C 33.6; N 11.2; Cl 14.2). $(\varepsilon,\lambda)_{max}$: (150,459), (160,330). $(\varepsilon,\lambda)_{min}$: (17,386).

IV: The fourth yellow fraction was very small. It was isolated as a chloride and identified (see later) as a racemic mixture of the previously described compounds [1] assumed to be $fac\text{-}\Delta S_3$ and $fac\text{-}\Delta R_3$. Based on a comparison with their absorption spectra the yield was estimated to be 3.4 % (74 mg of $[Co(C_7H_{10}N_2)_3]Cl_3.6\frac{1}{2}H_2O$). In another experiment it was 3.8 %.

V: The fifth band was orange, indistinct, and probably consisted of two compounds, one of which was present only in a very small amount. From the eluate the most abundant compound was isolated and purified by recrystallization as described for fraction I. Yield: 183 mg of orange crystals (7.0 %). (Found: Co 7.67; C 32.8; N 10.9. Calc. for $[Co(C_7H_{10}N_2)_3](HSO_4)_3.3H_2O$: Co 7.65; C 32.3; N 10.9). $(\varepsilon,\lambda)_{max}$: (190,474), (221,337). $(\varepsilon,\lambda)_{min}$: (20,393), (218,329). In another experiment the yield was 5.3 %. "The impurity" that vanished during the recrystallization was presumably a racemic mixture of the two earlier desribed compounds [1] $mer\text{-}\Lambda S_3$ and $mer\text{-}\Delta R_3$, as one should expect this racemic mixture to be formed, although in a small amount.

Resolution into enantiomers. Each of the four racemates was resolved on columns (length 60 cm, diameter 2.5 cm) of SP-Sephadex

C-25. The compounds (in amounts ranging from 0.1 to 0.5 mmol) were absorbed to the columns from water solutions, and the bands were eluted with a solution that was 0.09 M in sodium $(+)_D$-tartrate and 0.04 M in sodium $(+)_D$-hydrogentartrate. The resolution was complete in the case of the compounds II, III, and IV, but only partial for I. In all cases the Λ-fraction was eluted first. The single fractions were treated in nearly the same way. They were absorbed on smaller columns. Sodium and tartrate ions were removed by a subsequent elution with 0.1 M hydrochloric acid, and finally the complexes were eluted with 1 M hydrochloric acid or 0.5 M sulfuric acid. Isolation of the solid chlorides or hydrogensulfates was performed as described above (see I and II).

I(+) and (−): In this case only, the separation was not complete, but the first fraction consisted mainly of the Λ-form, the last one of the Δ-form. As the racemate was identified by other means as an equimolar mixture of the earlier described [1] compounds $fac\text{-}\Lambda S_3$ and $fac\text{-}\Delta R_3$, an attempt to accomplish the separation on a longer column was not considered worthwhile.

II(+) and (−): The column had exactly the right dimensions to give a complete separation. The enantiomers II(+) and II(−) were both isolated as chlorides. II(+): (Found: Co 9.36. Calc. for $[Co(C_7H_{10}N_2)_3]Cl_3.5\frac{1}{2}H_2O$: Co 9.34). $(\varepsilon,\lambda)_{max}$: (149,459.5), (146,337). $(\varepsilon,\lambda)_{min}$: (16,386), (130,322). $(\Delta\varepsilon,\lambda)_{max}$: (+2.16,470), (−0.46,340). $[M]_D^{25} = +653°$ $(c=1.7$ mg/ml). II(−): (Found: Co 9.34. Calc. for $[Co(C_7H_{10}N_2)_3]$-$Cl_3.5\frac{1}{2}H_2O$: Co 9.34). $(\varepsilon,\lambda)_{max}$: (150,459.5), (150,337). $(\varepsilon,\lambda)_{min}$: (17,386), (137,322). $(\Delta\varepsilon,\lambda)_{max}$: (−2.15,470), (+0.47,344). $[M]_D^{25} = -651°$ $(c=1.7$ mg/ml).

III(+) and (−): A smaller column (45 cm instead of 60 cm) would have sufficed to complete the separation. The enantiomers III(+) and III(−) were both isolated as the hydrogensulfates. III(+): (Found: Co 7.43. Calc. for $[Co(C_7H_{10}N_2)_3](HSO_4)_3.4H_2O$: Co 7.47). $(\varepsilon,\lambda)_{max}$: (150,459), (135,336.5). $(\varepsilon,\lambda)_{min}$: (17,385.5), (125,323). $(\Delta\varepsilon,\lambda)_{max}$: (+2.23,464),

Table 2. Electronic spectral parameters for $[Co\{C_7H_{10}N_2\}_3]^{3+}$. VI(+) is *mer*-$\Lambda$(+)$_D$-[Co{(S)(−)$_D$-C_7H_{10}N_2}_3]Cl_3$.[1] δ is the half-width of the long-wavelength band.

Symbol	$\lambda_{max}(1)$ (nm)	$\varepsilon_{max}1)$	$\delta(1)$ cm^{-1}	$\lambda_{max}(2)$ (nm)	$\varepsilon_{max}(2)$
I(+)[a]	460.5	149	3327	338	156
I(+)	459.5	149	3335	337	146
III(+)	459	150	3363	336.5	135
IV(+)	459	156	3301	336	131
V	474	190	3575	337	221
VI(+)[a]	475	193	3526	341	209

[a] The measurements were carried out on previously prepared and described compounds.

(−0.61,343). $[M]_D^{25} = +542°$ (1.9 mg/ml). III(−): (Found: Co 7.20. Calc. for $[Co_7H_{10}N_2)_3]$ (HSO_4)_3.5H_2O$: 7.31). $(\varepsilon,\lambda)_{max}$: (151,459), (137,336.5). $(\varepsilon,\lambda)_{min}$: (17,385.5), (128,323). $(\Delta\varepsilon,\lambda)_{max}$: (−2.22,464), (+0.63,344). $[M]_D^{25} = -543°$ (1.9 mg/ml).

IV(+) and (−): A column of only 30 cm would have been sufficiently large to ensure a complete separation. Both isomers were isolated as the hydrogensulfates. IV(+): (Found: Co 7.07. Calc. for $[Co(C_7H_{10}N_2)_3]$ (HSO_4)_3.6H_2O$: Co 7.15). $(\varepsilon,\lambda)_{max}$: (156,459), (131,336). $(\varepsilon,\lambda)_{min}$: (20,385), (127,326). $(\Delta\varepsilon,\lambda)_{max}$: (+2.39,464), (−0.57,344). IV(−): (Found: Co 7.35. Calc. for $[Co(C_7H_{10}N_2)_3]$ (HSO_4)_3.5H_2O$: Co 7.31). $(\varepsilon,\lambda)_{max}$: (154,459), (136,333). $(\varepsilon,\lambda)_{min}$: (17,385), (135,326). $(\Delta\varepsilon,\lambda)_{max}$: (−2.40,464), (+0.57,343). X-Ray powder photographs, absorption spectra and CD-spectra showed that IV(+) and IV(−) were identical with the hydrogensulfates of the earlier investigated compounds,[1] *fac*-ΛR_3 and *fac*-ΔS_3.

RESULTS AND DISCUSSION

Characterization and identification of the isomers. $[Co\{(\pm)_D\text{-}C_7H_{10}N_2\}_3]Cl_3$ was separated into five distinct fractions on a Sephadex column with a phosphate eluent. The fractions I−IV had the same yellow colour as the *facial* isomer of tris-[2-picolylamine]cobalt(III) bromide[3] [2-picolylamine = (2-pyridyl)methylamine], see Fig. 1a), while the orange fraction (V) had the same colour as the meridional isomer. This immediately suggests that I, II, III, and IV are *facial* isomers, while V is a *meridional* isomer. The assumption is supported by the data from the electronic absorption spectra (see later). Fraction I was partially and fractions II, III and IV were completely resolved into their enantiomers on a Sephadex column with

a tartrate eluent. In all cases the Λ-form was eluted as the first one.

I: The X-ray powder photograph of the perchlorate of this compound was identical with that of the perchlorate prepared from an equimolar mixture of the previously described compounds[1] assumed to be *fac*-ΛS_3 and *fac*-ΔR_3 (as to the abbrev. see Table 1). I, therefore, can
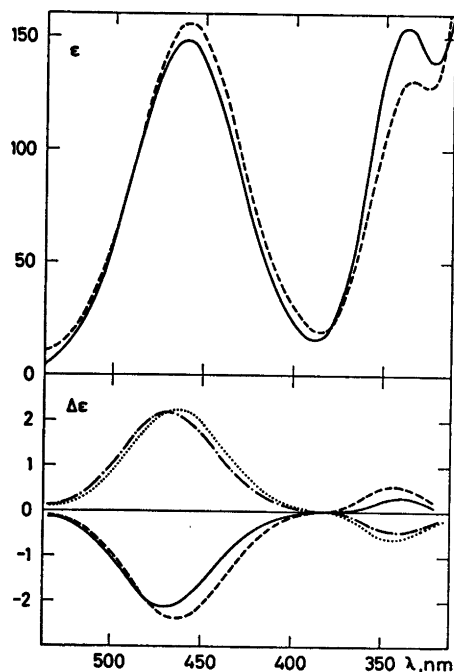

Fig. 2. The absorption spectra (top) of I [I(+), I(−)] (———) and IV [IV(+), IV(−)] (- - -) and the circular dichroism spectra (bottom) of I(−) (———), II(+) (− · −), III(+) (· · ·) and IV(−) (- - -).

Table 3. Circular dichroim data for *fac-Λ*(+)$_D$-[Co{C$_7$H$_{10}$N$_2$}$_3$]$^{3+}$. In the same table the molar optical rotations at the Na$_D$-line are given as [M]$_D$[25].

Symbol	λ_{max}(1) (nm)	$\Delta\varepsilon_{max}$(1)	λ_{max}(2) (nm)	$\Delta\varepsilon_{max}$	[M]$_D$[25] (°)
I(+)[a]	470	+2.14	340	−0.36	+947
II(+)	470	+2.16	340	−0.46	+653
III(+)	464	+2.23	343	−0.61	+542
IV(+)	464	+2.39	344	−0.57	+566

[a] The measurements was carried out on a previously prepared and described compound.

be characterized as the racemate *fac-(ΛS$_3$, ΔR$_3$)*.

IV: X-Ray powder photographs, absorption spectra and CD spectra proved that IV(+) and IV(−) were identical with the hydrogensulfates of the earlier investigated compounds *fac-ΛR$_3$* and *fac-ΔS$_3$*.[1] IV, therefore, is characterized as the racemate *fac-(ΔR$_3$,ΛS$_3$)*.

II and III: It is an obvious thought that the variation in the elution rate of the compounds I−IV is connected with a systematic variation in the structure of the compounds. This coherence is observed in the tris-[(±)$_D$-1,2-propanediamine]cobalt(III) system[5] and would imply that II is the racemate *fac-(ΛS$_2$R,ΔR$_2$S)* and III the racemate *fac-(ΛSR$_2$,ΔRS$_2$)*. These suppositions are supported by the data from the absorption and CD spectra.

Electronic spectra. The electronic spectra of I [I(+), I(−)] and IV [IV(+), IV(−)] in the visible region are given in Fig. 1. The spectra of II [II(+), II(−)] and III [III(+), III(−)] are so similar to the former that they are situated between them. The resemblance between these four spectra (see Table 2) and that belonging to *fac*-tris-[2-picolylamine]cobalt(III) bromide,[3] ((ε,λ)$_{max}$: (130,462), (135,336.5). δ = 3360 cm^{-1}) supports the supposition that I−IV have *facial* structures. A comparison of the absorption spectra of V, of the previously described *mer-Λ*(+)$_D$-[Co{(S)(−)$_D$-C$_7$H$_{10}$N$_2$}$_3$]Cl$_3$ and of *mer*-tris-[2-picolylamine]cobalt(III) bromide,[3] ((ε,λ)$_{max}$: (155,471), (170,339). δ = 3450 cm^{-1}), shows that V is likely to be a *meridional* compound. Furthermore, the half-width of the long-wavelength band is greater for V than for the compounds of a higher symmetry I−IV. The variation, if any, in the λ and ε values, is systematic, going from I to IV (see Table 2).

Circular dichroism spectra. The CD spectra of II(+), III(+) and (to avoid coincidence) (I−)

and IV(−) are shown in Fig. 2. The spectra are all very alike showing one CD band only corresponding to the first absorption band. As mentioned before, we use the sign of the algebraic sum of the *d−d* CD band areas to assign the configuration *Λ* to the four compounds I(+)−IV(+), and the configuration *Δ* to the compounds I(−)−IV(−).[5]

As is appears from Table 3, the variation, if any, in the CD data is nearly systematic going from I(+) to IV(+). It is also noticeable that there is a strong mutual resemblance between the spectra of I(+) and II(+) and between III(+) and IV(+), respectively. This might be due to greater similarities in the composition of the compounds in question providing a further support to our suppositions about the systematic variation of the structure when going from I to IV.

Conclusion. The assignments of the eight obtainable *facial* isomers are summarized in Table 1, while the problems concerning the *meridional* isomers require further investigations. Another important question is so far unanswered: What are the conformations of the ligands? Are they fixed in preferred conformations, or are they flexible, the methyl-groups flapping between an equatorial and an axial position? The determination of the structure and absolute configuration of I(+) by X-ray analysis, presently being carried out at this laboratory, may perhaps throw some light upon this problem.

REFERENCES

1. This work represents a continuation of the earlier publication: Michelsen, K. *Acta Chem. Scand. A 28* (1974) 428.
2. Andersen, P., Galsbøl, F. and Harnung, S. E. *Acta Chem. Scand.* 23 (1969) 3027.

3. Michelsen, K. *Acta Chem. Scand.* *24* (1970) 2003.
4. Toftlund, H. and Pedersen, E. *Acta Chem. Scand.* *26* (1972) 4019.
5. Harnung, S. E., Kallesøe, S., Sargeson, A. M. and Schäffer, C. E. *Acta Chem. Scand.* *A 28* (1974) 385.
6. Smirnoff, A. P. *Helv. Chim. Acta 3* (1920) 181.
7. Smith, H. E., Schaad, L. J., Banks, R. B., Wiant, C. J. and Jordan, C. F. *J. Amer. Chem. Soc. 95* (1973) 811.
8. Cervinka, O., Belovsky, O. and Rejmanova, P. *Z. Chem. 10* (1970) 69.
9. Schäffer, C. E. *Proc. Roy. Soc. London A 297* (1967) 96.
10. IUPAC *Inorg. Chem. 9* (1970) 1.
11. Glerup, J. and Schäffer, C. E. *Acta Chem. Scand. To be published.*
12. Yoshikawa, J. and Yamasaki, K. *Inorg. Nucl. Chem. Lett. 6* (1970) 523.