

# Tris-complexes of $(-)_D$ - and $(+)_D$ -[1-(2-Pyridyl)ethylamine] and Cobalt(III). Preparation and Partial Structural Assignment of Geometrical and Optical Isomers

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Tris-complexes of  $(-)_D$  and  $(+)_D$ -[1-(2-pyridyl)ethylamine] with cobalt(III) were prepared, and three different isomers and their enantiomers were isolated by column chromatography. The absorption spectra, circular dichroism spectra and  $^1\text{H}$  NMR spectra of the compounds suggest that they are:

A: *fac*- $\Delta(+)_D$ -[Co{(S)(-) $_D$ -C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>}\_3]Cl<sub>3</sub>, B: *fac*- $\Delta(-)_D$ -[Co{(S)(-) $_D$ -C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>}\_3]Cl<sub>3</sub>, C: *mer*- $\Delta(+)_D$ -[Co{(S)(-) $_D$ -C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>}\_3]Cl<sub>3</sub>, A': *fac*- $\Delta(-)_D$ -[Co{(R)(+) $_D$ -C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>}\_3]Cl<sub>3</sub>, B': *fac*- $\Delta(+)_D$ -[Co{(R)(+) $_D$ -C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>}\_3]Cl<sub>3</sub>, C': *mer*- $\Delta(-)_D$ -[Co{(R)(+) $_D$ -C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>}\_3]Cl<sub>3</sub>.

In a recent paper<sup>1</sup> tris-complexes of cobalt(III) with the bidentate ligand 2-picolyamine [(2-pyridyl)methylamine] (Fig. 1a) were described. In this work the corresponding complexes of cobalt(III) with the related ligand 1-(2-pyridyl)ethylamine (Fig. 1b) have been investigated. Resolution of the racemic form of this amine with tartaric acid gives the two optically active amines, the  $(-)_D$ -form of which is reported to have the *S*-configuration.<sup>2,3</sup> Theoretically each of the formulas [Co{(–) $_D$ -C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>}\_3]X<sub>3</sub> and [Co{(+)  $_D$ -C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>}\_3]X<sub>3</sub> represents several iso-

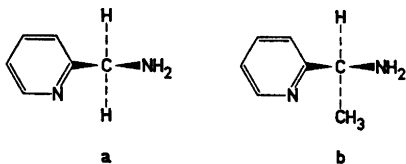


Fig. 1. a. (2-Pyridyl)methylamine (2-picolyamine). b. 1-(2-Pyridyl)ethylamine.

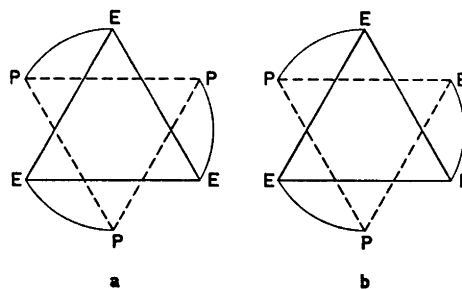


Fig. 2. Geometrical isomers of tris-complexes of 1-(2-pyridyl)ethylamine and cobalt(III). P symbolizes the "pyridine nitrogen", E the "ethylamine nitrogen". a. A *facial* isomer. b. A *meridional* isomer. Both isomers have the configuration  $\Delta$ .

mers. First, the ligand is unsymmetrical and consequently two geometrical forms of the tris-complexes may occur, namely *facial* and *meridional* forms (Fig. 2). Secondly, the ligands may adopt a  $\Delta$  or a  $\Lambda$  configuration around the central atom, and thirdly, their conformations may be  $\delta$  or  $\lambda$ .

We succeeded in isolating 3 different tris-complexes (A, B, and C) with  $(-)_D$ -1-(2-pyridyl)ethylamine and the corresponding 3 enantiomers (A', B', and C') with the  $(+)_D$ -amine.

*General remarks concerning the preparative methods.* Racemic 1-(2-pyridyl)ethylamine was prepared by way of a zinc-acetic acid reduction of 2-pyridylmethyl ketoxime,<sup>4</sup> and the yield was acceptable contrary to the experience of Kolloff *et al.*<sup>5</sup>

Recently the amine has been resolved independently at 3 different laboratories. The methods were in principle the same, tartaric acid being used as the resolving agent. Smith *et al.*<sup>2</sup> and Cervinka *et al.*<sup>3</sup> report to have prepared the (-)<sub>D</sub>-amine, the latter without giving any experimental details. We have isolated both the (-)<sub>D</sub>- and the (+)<sub>D</sub>-amine.

The cobalt complexes were prepared by two different methods. In method 1<sup>6</sup> *trans*-dichlorotetrakis(pyridine)cobalt(III) chloride reacted with the amine in a convenient medium, and in method 2 a solution of cobalt(II) chloride was oxidized by atmospheric oxygen in the presence of the amine. The crude products obtained from either method were separated in the different isomers on a column, and gave the same 3 tris-complexes, named A (A'), B (B') and C (C') in the order of their elution. If activated charcoal was added to the cobalt(II) chloride, A (A') and B (B') were formed as before, but the yield of C (C') was negligible.

## EXPERIMENTAL

**Reagents.** The initial material *trans*[Co py<sub>4</sub>Cl<sub>2</sub>].6H<sub>2</sub>O was prepared by a method developed by Glerup and Schäffer.<sup>7</sup> 2-Acetylpyridine was purchased from Fluka AG, Buchs, Switzerland, Norit SA 1 from Norit Sales Corp. Ltd., Amsterdam and SE-Sephadex C-25 from Pharmacia, Uppsala, Sweden. All other chemicals were of reagent grade and were used without further purification.

**Physical measurements.** Electronic absorption spectra were recorded on a Cary Model 14 spectrophotometer. The solvent was 0.1 M hydrochloric acid. The spectra are characterized by their maxima and minima ( $\epsilon$ ,  $\lambda$ ), where the molar extinction coefficient  $\epsilon$  is in units of l mol<sup>-1</sup> cm<sup>-1</sup>, and  $\lambda$  is in nm. Circular dichroism was measured on a Roussel-Jouan Dichrographe I. The solvent was 0.1 M hydrochloric acid. The maxima are given below as ( $\Delta\epsilon$ ,  $\lambda$ ) = ( $\epsilon_l - \epsilon_r$ ,  $\lambda$ ). Optical rotation was measured on a Perkin Elmer Model 141 polarimeter. The amine tartrates were dissolved in water, the cobalt complexes in 0.1 M hydrochloric acid. <sup>1</sup>H NMR spectra were obtained on a Varian Model A-60 spectrometer using sodium 3-trimethylsilyl-1-propane sulfonate (TPSNa) as an internal standard. The solvents were D<sub>2</sub>O and D<sub>2</sub>O + D<sub>2</sub>SO<sub>4</sub>.

**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. Thermogravimetric determinations of water

contents in the cobalt complexes were performed on a thermobalance previously described.<sup>8</sup>

## Preparation of the ligand

**2-Pyridylmethyl ketoxime.** A modification of Pinner's method<sup>9</sup> was used. 60 g of hydroxylamine hydrochloride (0.86 mol) was dissolved in 140 ml of water. 100 g of 2-acetylpyridine (0.90 mol) was added. After 1 h the oxime was set free by the addition of a saturated solution of potassium carbonate (~300 ml). After cooling on ice and stirring, white crystals separated. They were filtered, washed with water and recrystallized from ethanol. Yield: 91 g (78%), m.p. 115–118° (lit.<sup>9,10</sup> m.p. 120°, 121°).

**1-(2-Pyridyl)ethylamine.** In principle the method was the same as that used by La Forge<sup>4</sup> for the preparation of 1-(3-pyridyl)ethylamine. 50 g of 2-pyridyl ketoxime (0.37 mol) was dissolved in 700 ml of ethanol (95%). The solution was placed in a beaker (2 l) equipped with magnetic stirring. 400 g of zinc dust and 400 ml of glacial acetic acid were added alternately in small portions over a period of 7 h. The reaction mixture was left for further 17 h. Then the precipitate of undissolved zinc and zinc acetate was filtered off and carefully washed with ethanol (700 ml). The combined filtrates were evaporated on a vacuum rotatory evaporator, and the acetic acid was removed by repeated additions of water to the residue followed by evaporations. Finally, the amine was set free by the addition of a saturated solution of potassium hydroxide. The separated oil was extracted with ether, the ethereal solution was dried over sodium sulfate, filtered, dried over sodium, and the solvent was evaporated. Distillation of the residue gave an almost colourless oil, b.p.<sub>16</sub> 89° (lit.<sup>3</sup> b.p.<sub>24</sub> 96–97°). The yields varied in different experiments from 37 to 42 g (82–93%).

**(-)<sub>D</sub> and (+)<sub>D</sub>-1-(2-Pyridyl)ethylammonium (+)<sub>D</sub>-hydrogentartrate.** A solution of 75 g of tartaric acid (0.50 mol) in 50 ml of water (80°) was added to a solution of 100 ml of 1-(2-pyridyl)ethylamine (0.84 mol) in 50 ml of water (80°). The mixture was allowed to cool to room temperature, and the following day fraction 1, 40 g of white crystals,  $[\alpha]_D^{25} = 4.8^\circ$ , could be filtered and washed with ethanol. The mother liquor was heated to 80°, and 45 g of tartaric acid (0.30 mol) was added. When the solution was cooled on ice, fraction 2, 47 g,  $[\alpha]_D^{25} = 8.5^\circ$  separated. The filtrate was evaporated on a vacuum rotatory evaporator to give fraction 3, 38 g,  $[\alpha]_D^{25} = 24.1^\circ$ , fraction 4, 24 g,  $[\alpha]_D^{25} = 18.7^\circ$ , and several smaller fractions with  $[\alpha]_D^{25}$  ranging from 12° to 19°. Fraction 1 was recrystallized once and fraction 2 twice from water to give a total amount of 49 g of (-)<sub>D</sub>-1-(2-pyridyl)ethylammonium (+)<sub>D</sub>-hydrogentartrate monohydrate; 40% (Found: C 45.8; N 9.62; H 6.39. Calc. for C<sub>11</sub>N<sub>2</sub>H<sub>16</sub>O<sub>7</sub>: C 45.5; N 9.65; H 6.25).  $[\alpha]_D^{25} = +4.3^\circ$  ( $c = 0.01$  g/ml),  $[\alpha]_D^{25} = +4.8^\circ$  ( $c = 0.04$

g/ml). (Lit.<sup>3,2</sup>  $[\alpha]_D^{25} = +5.4^\circ$  ( $c=0.04$  g/ml) and  $[\alpha]_D^{25} = +5.1^\circ$  ( $c=0.04$  g/ml). Fraction 3 was recrystallized once and fraction 4 twice from water to give a total amount of 36 g of (+)<sub>D</sub>-1-(2-pyridyl)ethylammonium (+)<sub>D</sub>-hydrogentartrate monohydrate, 30%. (Found: C 45.3; N 9.65; H 6.21. Calc. for C<sub>11</sub>N<sub>2</sub>H<sub>18</sub>O<sub>7</sub>: C 45.5; N 9.65; H 6.25).  $[\alpha]_D^{25} = +24.8^\circ$  ( $c=0.01$  g/ml). This value for  $[\alpha]_D^{25}$  could not be improved by further recrystallizations, and the "symmetric" results for molar rotations and circular dichroism of the corresponding cobalt complexes with (-)<sub>D</sub>- and (+)<sub>D</sub>-1-(2-pyridyl)ethylamine, respectively, proved that the separation had been complete. The impure fractions mentioned above were recrystallized several times to give 5 to 10 g of each of the pure salts. The pure, optically active amines could be isolated as described above for the racemic amine, but it was not necessary for our special purpose.

#### Preparation of the cobalt complexes

*Tris-((-)<sub>D</sub>-1-(2-pyridyl)ethylamine)cobalt-(III) chloride*, [Co((-)<sub>D</sub>-C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)<sub>3</sub>]Cl<sub>3</sub>. Preparation of the crude product by means of method 1: 0.80 g of lithium hydroxide monohydrate (19 mmol) was dissolved in 8 ml of boiling water, and 3.00 g of (-)<sub>D</sub>-1-(2-pyridyl)ethylammonium (+)<sub>D</sub>-hydrogentartrate, monohydrate (10.3 mmol) was added. The solution was cooled on ice. The addition of 30 ml of pyridine and 20 ml of ethanol caused the lithium tartrate to precipitate. The filtrate, containing (-)<sub>D</sub>-1-(2-pyridyl)ethylamine, was added to a solution of 1.50 g [Copy<sub>4</sub>Cl<sub>2</sub>]Cl<sub>6</sub>H<sub>2</sub>O (2.54 mmol) in 30 ml of pyridine. An immediate colour-shift from green to red-brown took place. After 15 min the solution was cooled on ice, and a sticky, yellow-brown solid was precipitated by the addition of ethanol and ether. Washing with ether.

Separation of the isomers: The crude product, a mixture of bis- and tris-complexes, was dissolved in water. The solution was poured on a column of a SE-Sephadex C-25 cation exchanger (length 40 cm, vol. 400 ml), and the adsorbed bands were eluted with 0.1 M sodium sulfate solution. After the elution of 5 reddish bands (the bis-complexes), 2 yellow and one orange band (the tris-complexes) remained. These 3 bands were eluted, and each fraction was treated in the following way: The solution was acidified (pH ~ 4) and poured on a small Sephadex column (length 20 cm, vol. 100 ml). Sodium and sulfate ions were removed by a subsequent elution with 0.1 M hydrochloric acid. When the eluate showed negative sulfate reaction, the complex was eluted with 1 M hydrochloric acid. The concentrated solution was evaporated to dryness on a vacuum rotatory evaporator. The residue was dissolved in ethanol (99%), the solution was cooled on ice, and the complex was precipitated by the slow addition of ether. Washing with ether. Letters A, B, and

C were used to indicate the bands in the order of their first elution.

A = (+)<sub>D</sub>-[Co((-)<sub>D</sub>-C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)<sub>3</sub>]Cl<sub>3</sub>. Yield: 641 mg of yellow crystals (41%). (Found: C 9.65; C 41.2; N 13.7. Calc. for [Co(C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)<sub>3</sub>]Cl<sub>3</sub>·4.5H<sub>2</sub>O: Co 9.62; C 41.2; N 13.7). The water content was determined by thermogravimetry to be 4.5 mol per mol cobalt. In other experiments the complex crystallized with 5.5 mol of water.  $(\epsilon, \lambda)_{\max}$ : (149, 461), (156, 338).  $(\epsilon, \lambda)_{\min}$ : (15.0, 388), (138, 322.5).  $(\Delta\epsilon, \lambda)$ : (+2.22, 471.5), (-0.32, 343).  $[M]_D^{25} = +947^\circ$  ( $c=1.8$  mg/ml).

B = (-)<sub>D</sub>-[Co((-)<sub>D</sub>-C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)<sub>3</sub>]Cl<sub>3</sub>. Yield: 400 mg of lemon-yellow crystals (25%). (Found: Co 9.28; C 39.9; N 13.5. Calc. for [Co(C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)<sub>3</sub>]Cl<sub>3</sub>·5.5H<sub>2</sub>O: Co 9.34; C 40.0; N 13.3). The water content was determined by thermogravimetry to be 5.5 mol per mol cobalt.  $(\epsilon, \lambda)_{\max}$ : (155, 459), (128, 336).  $(\epsilon, \lambda)_{\min}$ : (15.2, 385), (124, 325).  $(\Delta\epsilon, \lambda)$ : (-2.50, 464), (+0.58, 344).  $[M]_D^{25} = -544^\circ$  ( $c=1.7$  mg/ml).

C = (+)<sub>D</sub>-[Co((-)<sub>D</sub>-C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)<sub>3</sub>]Cl<sub>3</sub>. Yield: 262 mg of orange-coloured crystals (18%). (Found: Co 10.31; C 44.6; N 15.0. Calc. for [Co(C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)<sub>3</sub>]Cl<sub>3</sub>·2H<sub>2</sub>O: Co 10.38; C 44.4; N 14.8). The water content was determined by thermogravimetry to be 2.1 mol per mol cobalt. In other experiments the complex crystallized with 3 mol of water.  $(\epsilon, \lambda)_{\max}$ : (194, 475), (209, 341).  $(\epsilon, \lambda)_{\min}$ : (19.9, 394), (186, 325).  $(\Delta\epsilon, \lambda)$ : (+5.33, 473), (-0.94, 342).  $[M]_D^{25} = +1622^\circ$  ( $c=1.2$  mg/ml).

*Tris-(+)<sub>D</sub>-1-(2-pyridyl)ethylamine)cobalt-(III) chloride*, [Co((+)<sub>D</sub>-C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)<sub>3</sub>]Cl<sub>3</sub>. The compounds were prepared from 1.50 g [Copy<sub>4</sub>Cl<sub>2</sub>]Cl<sub>6</sub>H<sub>2</sub>O and 3.00 g (+)<sub>D</sub>-1-(2-pyridyl)ethylammonium (+)<sub>D</sub>-hydrogentartrate monohydrate, exactly as described above in the case of the complexes with the (-)<sub>D</sub>-amine.

A' = (-)<sub>D</sub>-[Co((+)<sub>D</sub>-C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)<sub>3</sub>]Cl<sub>3</sub>. Yield: 680 mg of yellow crystals (43%). (Found: Co 9.46; C 40.4; N 13.5. Calc. for [Co(C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)<sub>3</sub>]Cl<sub>3</sub>·5H<sub>2</sub>O: Co 9.48; C 40.6; N 13.5). The water content was determined by thermogravimetry to be 4.9 mol per mol cobalt. In other experiments the complex crystallized with 5.5 mol of water.  $(\epsilon, \lambda)_{\max}$ : (148, 461), (154, 338).  $(\epsilon, \lambda)_{\min}$ : (15.7, 388), (136, 322).  $(\Delta\epsilon, \lambda)$ : (-2.21, 471.5), (+0.28, 343).  $[M]_D^{25} = -949^\circ$  ( $c=1.8$  mg/ml).

B' = (+)<sub>D</sub>-[Co((+)<sub>D</sub>-C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)<sub>3</sub>]Cl<sub>3</sub>. Yield: 330 mg of lemon-yellow crystals (21%). (Found: Co 9.28; C 39.7; N 13.4. Calc. for [Co(C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)<sub>3</sub>]Cl<sub>3</sub>·5.5H<sub>2</sub>O: Co 9.34; C 40.0; N 13.3). The water content was determined by thermogravimetry to be 5.5 mol per mol cobalt.  $(\epsilon, \lambda)_{\max}$ : (156, 459), (130, 336).  $(\epsilon, \lambda)_{\min}$ : (16.6, 386), (127, 326).  $(\Delta\epsilon, \lambda)$ : (+2.48, 464), (-0.57, 344).  $[M]_D^{25} = +554^\circ$  ( $c=1.7$  mg/ml).

C' = (-)<sub>D</sub>-[Co((+)<sub>D</sub>-C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)<sub>3</sub>]Cl<sub>3</sub>. Yield: 195 mg of orange-coloured crystals (14%). (Found: Co 10.34; C 44.1; N 14.9. Calc. for [Co(C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)<sub>3</sub>]Cl<sub>3</sub>·2H<sub>2</sub>O: Co 10.38; C 44.4; N 14.8). The water content was determined by thermogravimetry to be 1.9 mol per mol cobalt. In other experiments the complex crystallized with 3 mol of

water. ( $\epsilon, \lambda$ )<sub>max</sub>: (193, 475), (206, 341). ( $\epsilon, \lambda$ )<sub>min</sub>: (19.7, 394), (185, 325). ( $\Delta\epsilon, \lambda$ ): (-5.30, 473), (+0.95, 342).  $[\text{M}]_{\text{D}}^{25} = -1632^\circ$  ( $c = 1.2$  mg/ml).

*Tris-(+)-D-1-(2-pyridyl)ethylamine)cobalt(III) chloride*,  $[\text{Co}(+)\text{D}-\text{C}_7\text{H}_{10}\text{N}_2\text{O}_3]_3\text{Cl}_3$ . Preparation of the crude product by means of method 2: 0.80 g of lithium hydroxide monohydrate (19 mmol) was dissolved in 10 ml of hot water. 3.00 g of (+)-D-1-(2-pyridyl)ethylammonium (+)-D-hydrogentartrate (10.3 mmol) was added. The solution was cooled on ice, and 40 ml ethanol was added to precipitate lithium tartrate. 3 ml 1 M hydrochloric acid, 0.1 g activated charcoal Norite SA 1, and 0.600 g cobalt chloride hexahydrate (2.52 mmol) was added to the filtrate. The solution was then oxidized, air being drawn through it for 3 h. 2 ml 4 M hydrochloric acid was added, and the solution was filtered and cooled on ice. A sticky, crude product was precipitated with ethanol and ether and poured on a column and separated as described before.  $\text{A}' = (-)\text{D}-[\text{Co}(+)\text{D}-\text{C}_7\text{H}_{10}\text{N}_2\text{O}_3]_3\text{Cl}_3$ . Yield: 480 mg (30 %).

$\text{B}' = (+)\text{D}-[\text{Co}(+)\text{D}-\text{C}_7\text{H}_{10}\text{N}_2\text{O}_3]_3\text{Cl}_3$ . Yield: 490 mg (31 %).

## RESULTS AND DISCUSSION

*Characterization of the isomers.* The compounds A (A') and C (C') crystallize easily and well in contrast to the compound B (B'), which is inclined to deliquescence. The yellow com-

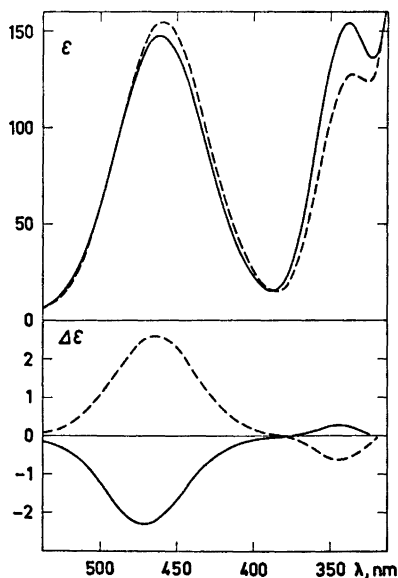


Fig. 3. The absorption spectra (top) and the circular dichroism spectra (bottom) of A' (—) and B' (---).

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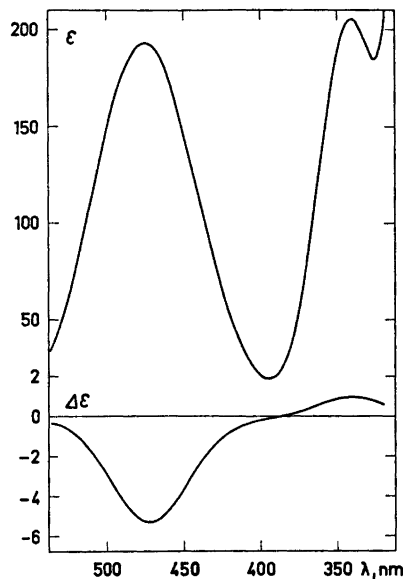


Fig. 4. The absorption spectrum (top) and the circular dichroism spectrum (bottom) of C'.

pounds A (A') and B (B') have nearly the same colour as the *facial* isomer of tris-(2-picolylamine)cobalt(III) bromide,<sup>1</sup> while the orange compound C (C') has the same colour as the *meridional* isomer. This suggests that A (A') and B (B') could be *facial* isomers, while C (C') is a *meridional* isomer.

*Electronic spectra* The electronic spectra in the visible region of A' (A), B' (B), and C' (C) are given in Figs. 3 and 4. A comparison of the long-wavelength bands shows a great similarity between A', B' and the *facial* tris-(2-picolylamine)cobalt(III) isomer<sup>1</sup> regarding intensity and position of the band, whereas C' and the *meridional* isomer of tris-(2-picolylamine)cobalt(III) bromide<sup>1</sup> are very much alike, both having a higher intensity and occurring at a lower energy than the former (Table 1). Furthermore, the C'-type complex is characterized by a band of greater half-width than the A' and B'-type bands. This would agree with the assumption that C' (C) is a *meridional* isomer, and consequently has a lower symmetry than A' (A) and B' (B), the *facial* isomers.

*Circular dichroism spectra.* The CD spectra of A', B', and C' are shown in Figs. 3 and 4. The C'-type spectrum differs from the other spectra

Table 1. The wavelengths  $\lambda_{\max}$ , the molar extinction coefficients  $\epsilon_{\max}$  and the corresponding half-widths  $\delta$  of the long-wavelength bands of 3 tris-((+)<sub>D</sub>-1-(2-pyridyl)ethylamine)cobalt(III) complexes, named A', B', and C', and of *fac*- and *mer*-tris(2-picolyamine)cobalt(III) bromide.<sup>1</sup>

Complex	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$	$\delta$ (cm <sup>-1</sup> )
A'. (-) <sub>D</sub> -[Co{(+) <sub>D</sub> -C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> ] <sub>3</sub> ]Cl <sub>3</sub> .aq.	461	148	3327
B'. (+) <sub>D</sub> -[Co{(+) <sub>D</sub> -C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> ] <sub>3</sub> ]Cl <sub>3</sub> .aq.	459	156	3301
<i>fac</i> -[Co(C <sub>8</sub> H <sub>8</sub> N <sub>2</sub> )] <sub>3</sub> Br <sub>3</sub> .aq.	462	130	3360
C'. (-) <sub>D</sub> -[Co{(+) <sub>D</sub> -C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> ] <sub>3</sub> ]Cl <sub>3</sub> .aq.	475	193	3526
<i>mer</i> -[Co(C <sub>8</sub> H <sub>8</sub> N <sub>2</sub> )] <sub>3</sub> Br <sub>3</sub> .aq.	471	155	3450

as regards the intensities of the bands, but apart from that, the spectra are all very much alike, showing only one CD band corresponding to the first absorption band. For many tris-(diamine)-cobalt(III) complexes it has been possible to establish a relationship between the CD spectrum and the absolute configuration, a positive dominating CD band in the region of the octahedral  $^1T_{1g} \leftarrow ^1A_{1g}$  absorption band generally being tantamount to a  $\Delta$  configuration.<sup>11</sup> If this method of assigning the isomers by means of the sign of the dominating CD band can be applied equally successfully to our compounds, the configurations of A' and C' should be  $\Delta$  and the configuration of B'  $\Lambda$ . Similarly, A and C should have the configurations  $\Delta$  and B  $\Delta$ .

**Nuclear magnetic resonance.** A *facial* isomer has three equivalent rings and a threefold axis of symmetry and should therefore show one doublet in the methyl region, while an unsymmetrical, *meridional* isomer is expected to show a more complicated spectrum with up to three doublets. Figs. 5, 6, and 7 and Table 2 show the

<sup>1</sup>H NMR resonances of NH<sub>2</sub>, CH and CH<sub>3</sub> protons in A'(A), B'(B), and C'(C) (solvent: D<sub>2</sub>O + D<sub>2</sub>SO<sub>4</sub>). In the case of A' and C', the signals arising from the NH<sub>2</sub> protons are partly overlapped by bands due to water protons (~5.7–5.8 ppm). Contrary to what should be expected, similar spectra were found for all the

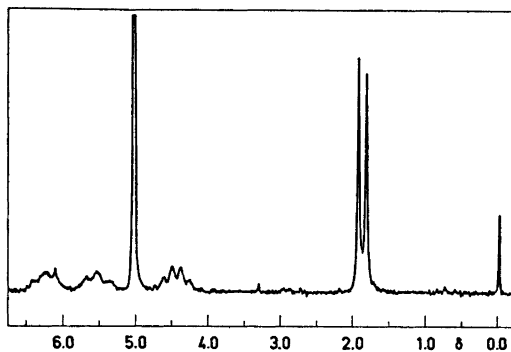


Fig. 6. <sup>1</sup>H NMR spectrum of the CH<sub>3</sub>, CH and NH<sub>2</sub> protons in B'.

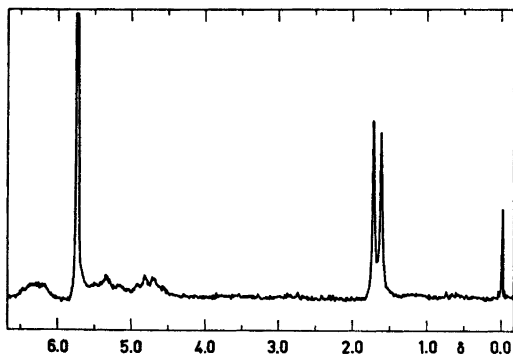


Fig. 5. <sup>1</sup>H NMR spectrum of the CH<sub>3</sub>, CH and NH<sub>2</sub> protons in A'.

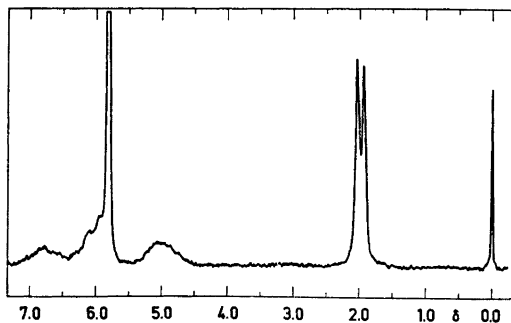


Fig. 7. <sup>1</sup>H NMR spectrum of the CH<sub>3</sub>, CH and NH<sub>2</sub> protons in C'.

Table 2. Proton chemical shifts ( $\delta$  ppm) in tris- $\{(+)_D$ -1-(2-pyridyl) ethylamine)cobalt(III) complexes.<sup>a</sup> The relative areas of the peaks are given in brackets.

Complex	(NH <sub>2</sub> )	(CH)	(CH <sub>3</sub> )
A'. $(-)_D$ -[Co $\{(+)_D$ -C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> \}_3]Cl <sub>3</sub> .aq.	6.28 (1) ~ 5.37 (1)	4.75 (1)	1.67 (3)
B'. $(+)_D$ -[Co $\{(+)_D$ -C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> \}_3]Cl <sub>3</sub> .aq.	6.20 (1) 5.52 (1)	4.42 (1)	1.87 (3)
C'. $(-)_D$ -[Co $\{(+)_D$ -C <sub>7</sub> H <sub>10</sub> N <sub>2</sub> \}_3]Cl <sub>3</sub> .aq.	6.72 (1) ~ 6.00 (1)	4.98 (1)	1.97 (3)

<sup>a</sup> Measured from TPSNa as an internal standard. All spectra were run in mixed D<sub>2</sub>O–D<sub>2</sub>SO<sub>4</sub> solutions.

isomers, one doublet being observed in the CH<sub>3</sub> region, one broad band in the CH region and two broad bands in the NH<sub>2</sub> region. When the compounds were measured in D<sub>2</sub>O, the two broad bands in the region 5.30–6.80 ppm disappeared owing to deuteration of the NH<sub>2</sub> groups. Fig. 8 shows the <sup>1</sup>H NMR resonances of the pyridine protons in A'(A), B'(B), and C'(C). It is noticeable that the C' spectrum is more complicated than the A' and B' spectra, which offer points of resemblance. This could be in agreement with the assumption that A'(A) and B'(B) are both *facial* isomers, while C'(C) is a *meridional* isomer.

**Conclusion.** Results from the physical meas-

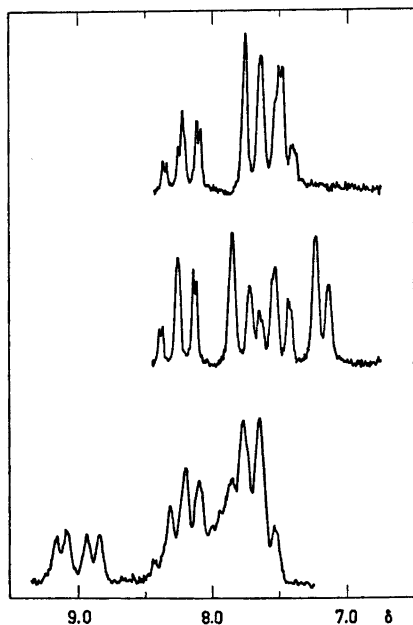


Fig. 8. <sup>1</sup>H NMR spectra of the pyridine protons in A' (top), B' (in the middle) and C' (bottom).

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urements thus indicate that A:  $(+)_D$ -[Co $\{(S)$ - $(-)_D$ -C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>\}\_3]Cl<sub>3</sub> is *fac-A*, B:  $(-)_D$ -[Co $\{(S)$ - $(-)_D$ -C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>\}\_3]Cl<sub>3</sub> is *fac-Δ*, C:  $(+)_D$ -[Co $\{(S)$ - $(-)_D$ -C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>\}\_3]Cl<sub>3</sub> is *mer-A*, and that A':  $(-)_D$ -[Co $\{(R)$  $(+)_D$ -C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>\}\_3]Cl<sub>3</sub> is *fac-Δ*, B':  $(+)_D$ -[Co $\{(R)$  $(+)_D$ -C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>\}\_3]Cl<sub>3</sub> is *fac-A*, C':  $(-)_D$ -[Co $\{(R)$  $(+)_D$ -C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>\}\_3]Cl<sub>3</sub> is *mer-Δ*. Two important questions remain, namely: Why did only 3 (+3) isomers occur in recognizable amounts? and what are the conformations of the ligands? If, however, as in the case of propylenediamine,<sup>12</sup> there is a preference for the conformation in which the methyl group is equatorial, (S)(-)<sub>D</sub>-1-(2-pyridyl)ethylamine will chelate with the conformation  $\delta$  and (R)(+)<sub>D</sub>-1-(2-pyridyl)ethylamine with the conformation  $\lambda$ . This hypothetical preference might explain why we obtained 2 (+2) *facial* isomers instead of the theoretical 4 (+4). In the case of the *meridional* isomers, models show that the steric interactions are much smaller for 1 (+1) isomer, namely a  $\Delta R\lambda$  ( $\Delta S\delta$ ), than for the others. This might explain the fact that we found only 1 (+1) *meridional* isomer, suggested above to be  $\Delta R$  ( $\Delta S$ ).

The structure and absolute configuration of the A-type will now be determined by X-ray analysis at this laboratory, and our work on complexes of cobalt(III) and 1-(2-pyridyl)ethylamine is being continued.

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