

## Tris(2-picolyamine) Complexes of Chromium(III) and Cobalt(III).

### Preparation and Structural Assignment of the Isomers

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The two geometrical isomers of tris(2-picolyamine)chromium(III) bromide and tris(2-picolyamine)cobalt(III) bromide have been prepared, and their absorption spectra measured. X-Ray powder photographs show isomorphism between the yellow chromium and cobalt complexes (called the  $\alpha$ -type) and between the orange chromium and cobalt complexes (called the  $\beta$ -type). The PMR spectra of the cobalt compounds suggest the yellow isomer to be the *facial* and the orange isomer to be the *meridional* form.

The investigations on methylamine and pyridine complexes of chromium(III) and cobalt(III) in this laboratory have encouraged an interest in similar complexes with the bidentate ligand 2-picolyamine (2-aminomethylpyridine). This ligand lacks a twofold axis of symmetry, and consequently two geometrical isomers of the tris complexes of chromium(III) and cobalt(III) may occur, namely a *facial* and a *meridional* form (Fig. 1). Previous work on this topic is very scarce. The interest in cobalt complexes with 2-picolyamine seems in the main to be concerning complexes with divalent cobalt. In 1962 Sutton<sup>1</sup> reported the preparation of tris(2-picolyamine)chromium(III) chloride and sulfate from anhydrous chromium(III) chloride and sulfate, respectively. The compounds were characterized by their analytical data and by the results from measurements of conductance and magnetic susceptibilities. It is therefore not immediately possible for us to tell by a comparison with our compounds, whether the complexes have been the *facial* or the *meridional* form. Unfortunately we did not succeed in reproducing the experiments. We always obtained red or brownish products from which we were unable to isolate a tris complex.

This work describes suitable synthetic methods for the preparation of *facial* as well as *meridional* tris(2-picolyamine) complexes of chromium(III)

and cobalt(III). The assignment of the isomers is established on the basis of PMR data and X-ray powder photography.

The chromium and cobalt complexes are prepared by methods that are in extensive use in this laboratory,<sup>2</sup> and whose main principles are much alike. In both cases the initial material is a *trans*-dichloro- or dibromotetrakis-(pyridine) complex of the metal in question. This is allowed to react with the amine in a convenient solvent. The fact that the halides of the isomers show different relative solubilities in different solvents, is utilized in their separation. Thus, one of the chromium isomers (the yellow  $\alpha$ -type) can be isolated by recrystallization of the product formed by the reaction of *trans*-dibromotetrakis(pyridine)chromium(III) iodide and 2-picolyamine in a 1:1 mixture of 2-methoxyethanol and ethanol, while the other isomer (the orange  $\beta$ -type) is obtained in appreciable amounts from the product formed when *trans*-dibromotetrakis(pyridine)chromium(III) chloride reacts with the amine in a 2:1 mixture of pyridine and ethanol. Analogously the yellow cobalt isomer (the  $\alpha$ -type) results as a main product when *trans*-dichlorotetrakis(pyridine)-cobalt(III) chloride, hexahydrate reacts with 2-picolyamine in ethanol, while the orange form (the  $\beta$ -type) can be obtained by fractionated crystallization from the crude product formed when the reaction takes place in pyridine.

In addition the yellow cobalt complex can be obtained by the reaction of the amine and the compound now alleged to be sodium tris(carbonato)cobaltate(III) trihydrate, an initial material that was first prepared, described and used in other preparations by Barbieri<sup>3</sup> and later by several other authors.<sup>4</sup>

## EXPERIMENTAL

*Reagents.* The initial materials *trans*-[Crpy<sub>4</sub>Br<sub>2</sub>]I, *trans*-[Crpy<sub>4</sub>Br<sub>2</sub>]Cl, and *trans*-[Crpy<sub>4</sub>Cl<sub>2</sub>]Cl·6H<sub>2</sub>O were all prepared by methods developed by Glerup and Schäffer.<sup>2</sup> Presumed Na<sub>3</sub>[Co(CO<sub>3</sub>)<sub>3</sub>]·3H<sub>2</sub>O was prepared according to a method described in the literature.<sup>5</sup> 2-Picolyamine was purchased from Aldrich Chemical Co., Inc. All other chemicals were reagent grade and were used without further purification.

## Preparations

1.  $\alpha$ -*Tris*(2-picolyamine)chromium(III) iodide,  $\alpha$ -[Cr(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>3</sub>]I<sub>3</sub>. 4 g *trans*-[Crpy<sub>4</sub>Br<sub>2</sub>]I (6.1 mmol) was suspended in a mixture of 10 ml 2-methoxyethanol and 10 ml ethanol (99 %). 4 ml 2-picolyamine (37 mmol) was added. After stirring for half an hour, the yellow precipitate (presumably [Cr(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>3</sub>]Br<sub>2</sub>I) was filtered off and washed with ethanol and ether. Yield: 3 g. The product was dissolved in 10 ml water (80°, slightly acid), and a saturated solution of 5 g sodium iodide (33 mmol) in water was added. After cooling in ice, the glistening yellow crystals were filtered and washed with ice-cold water, ethanol and ether. Yield: 2.7 g. The iodide was recrystallized by dissolving it in 20 ml water at 80°, adding a solution of 3 g sodium iodide and cooling. Washing as above. Yield: 2.5 g (53 %). (Found: Cr 6.71; C 27.8; N 11.4; I 49.1. Calc. for [Cr(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>3</sub>]I<sub>3</sub>·H<sub>2</sub>O: Cr 6.71; C 27.9; N 10.8; I 49.1). ( $\epsilon, \lambda$ )<sub>max</sub>: (90.6, 457). ( $\epsilon, \lambda$ )<sub>min</sub>: (22.5, 398). Half-width: 3410 cm<sup>-1</sup>. Medium: water. The hydrogen analyses for this and the following compounds failed to come out reproducibly.

2.  $\alpha$ -*Tris*(2-picolyamine)chromium(III) bromide,  $\alpha$ -[Cr(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>3</sub>]Br<sub>2</sub>. 3 g  $\alpha$ -[Cr(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>3</sub>]I<sub>3</sub>·H<sub>2</sub>O (3.9 mmol) was dissolved in 25 ml hot water (70°). The solution was added to silver chloride (prepared from 4 g silver acetate and 10 ml 4 M hydrochloric acid and washed by decantation). Stirring for 5 min was followed by filtering and addi-

tion of a solution of 5 g lithium bromide (58 mmol) in ethanol to the filtrate. After cooling in ice, 200 ml ethanol and 50 ml ether was added, and the bromide separated as shining yellow needle-shaped crystals, which were washed with ethanol and ether. Yield: 2 g. The product was recrystallized by dissolving it in 10 ml water at 90°, adding 5 ml conc. hydrobromic acid, cooling on ice and precipitation with 150 ml ethanol. Washing as above. Yield: 1.8 g (71 %). (Found: Cr 7.90; C 32.2; N 12.6; Br 36.6. Calc. for  $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Br}_3 \cdot 2.5\text{H}_2\text{O}$ : Cr 7.86; C 32.7; N 12.7; Br 36.3).  $(\epsilon, \lambda)_{\text{max}}$ : (89.2, 457).  $(\epsilon, \lambda)_{\text{min}}$ : (19.1, 398). Half-width: 3410  $\text{cm}^{-1}$ . Medium: water.

3.  $\alpha$ -*Tris(2-picolyamine)chromium(III) chloride*,  $\alpha$ - $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Cl}_3$ . The preparation was carried out in a way that was similar to that of the bromide. 3 g  $\alpha$ - $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{I}_3 \cdot \text{H}_2\text{O}$  (3.9 mmol) was treated with silver chloride as above. The chloride separated after cooling of the filtrate and addition of 200 ml ethanol and 100 ml ether. The recrystallization was performed by dissolving the product in 7 ml water (90°), cooling the solution and adding 3 ml conc. hydrochloric acid and 150 ml ethanol. Yield: 1.7 g (81 %). (Found: Cr 9.64; C 40.5; N 15.7; Cl 20.1. Calc. for  $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ : Cr 9.69; C 40.3; N 15.7; Cl 19.8).  $(\epsilon, \lambda)_{\text{max}}$ : (88.3, 457).  $(\epsilon, \lambda)_{\text{min}}$ : (18.9, 398). Half-width: 3410  $\text{cm}^{-1}$ . Medium: water.

4.  $\beta$ -*Tris(2-picolyamine)chromium(III) bromide*,  $\beta$ - $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Br}_3$ . 4 g *trans*- $[\text{Cry}_4\text{Br}_2]\text{Cl}$  (7.1 mmol) was dissolved in 20 ml pyridine. 10 ml ethanol (99 %) was added and then 4 ml 2-picolyamine (37 mmol) dissolved in 4–5 ml ethanol. After stirring for 15 min at room temperature, a brown-yellow compound separated. The crude product, presumably  $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Br}_2\text{Cl}$ , was filtered off and washed with ethanol and ether. Yield: 2.4 g. The compound was converted into the bromide by dissolving it in 5 ml hot water (90°) and adding a solution of 5 g lithium bromide (58 mmol) in 40 ml ethanol. Cooling on ice and further addition of 100 ml ethanol caused the precipitation of the orange bromide. Washing as above. 2.1 g. The product was recrystallized by dissolving it in 10 ml hot water (90°), adding a few ml conc. hydrobromic acid, cooling on ice and precipitation with 400 ml ethanol (99 %). Washing as before. Yield: 1.6 g (34 %). (Found: Cr 7.84; C 32.7; N 12.8; Br 36.5. Calc. for  $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Br}_3 \cdot 2.5\text{H}_2\text{O}$ : Cr 7.86; C 32.7; N 12.7; Br 36.3).  $(\epsilon, \lambda)_{\text{max}}$ : (103, 466.5).  $(\epsilon, \lambda)_{\text{min}}$ : (22.4, 402). Half-width: 3640  $\text{cm}^{-1}$ .

5.  $\beta$ -*Tris(2-picolyamine)chromium(III) iodide*,  $\beta$ - $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{I}_3$ . 1.0 g  $\beta$ - $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Br}_3 \cdot 2.5 \text{H}_2\text{O}$  (1.5 mmol) was dissolved in a few ml hot water (70°). The solution was poured into another solution consisting of 2.0 g lithium iodide (15 mmol) in 10 ml ethanol. After cooling on ice, further 100 ml ethanol and 100 ml ether was added. The yellow iodide that separated, was filtered off and washed with ethanol and ether. The recrystallization was performed by dissolving the product in 5 ml water (90°), adding a solution of 2 g sodium iodide in 2 ml hot water and cooling on ice. Washing as above. Yield: 0.9 g (74 %). (Found: Cr 6.41; C 26.9; N 10.4; I 46.9. Calc. for  $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{I}_3 \cdot 3\text{H}_2\text{O}$ : Cr 6.41; C 26.7; N 10.4; I 46.9).  $(\epsilon, \lambda)_{\text{max}}$ : (103, 466).  $(\epsilon, \lambda)_{\text{min}}$ : (26.3, 404). Half-width: 3630  $\text{cm}^{-1}$ . Medium: water.

6.  $\alpha$ -*Tris(2-picolyamine)cobalt(III) chloride*,  $\alpha$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Cl}_3$ . 16 g *trans*- $[\text{Cory}_4\text{Cl}_2]\text{Cl} \cdot 6\text{H}_2\text{O}$  (27 mmol) was dissolved in 100 ml ethanol. 8 ml 2-picolyamine (74 mmol) was added dropwise with stirring. The colour of the solution changed from green to red-brown and a silky yellow precipitate appeared. This was filtered off and washed with ethanol and ether. 12.5 g. The crude product was recrystallized by dissolving 1.5 g in 6 ml hot water (90°, slightly acid), adding 2 ml conc. hydrochloric acid and 50 ml ethanol and cooling on ice. The lemon-yellow crystals were filtered and washed as above. Yield: 1.3 g (74 %). (Found: Co 10.04; C 36.7; N 14.3; Cl 18.2. Calc. for  $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Cl}_3 \cdot 5.5\text{H}_2\text{O}$ : Co 10.04; C 36.7; N 14.3; Cl 18.1).  $(\epsilon, \lambda)_{\text{max}}$ : (131, 462), (136, 336.5).  $(\epsilon, \lambda)_{\text{min}}$ : (14.5, 388). Half-width: 3360  $\text{cm}^{-1}$ .

7.  $\alpha$ -*Tris(2-picolyamine)cobalt(III) bromide*,  $\alpha$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Br}_3$ . 2 g  $\alpha$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Cl}_3 \cdot 5.5\text{H}_2\text{O}$  (3.4 mmol) was dissolved in 10 ml water (90°). A solution of 4 g lithium bromide (46 mmol) in 50 ml ethanol was added. Cooling on ice resulted in the separation of yellow crystals. Washing with ethanol and ether. Yield: 2.2 g. The product was recrystallized by dissolving in 15 ml water (90°), adding 15 ml conc. hydrobromic acid and 120 ml ethanol and cooling on ice. The glistening, flaky crystals that appeared were filtered and washed as above. Yield: 1.8 g (79 %). (Found: Co 8.85; C 32.2; N 12.4; Br 35.2. Calc. for  $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Br}_3 \cdot 2.5\text{H}_2\text{O}$ : Co 8.82; C 32.4; N 12.6; Br 35.6).  $(\epsilon, \lambda)_{\text{max}}$ : (130, 462), (135, 336.5).  $(\epsilon, \lambda)_{\text{min}}$ : (14.4, 388). Half-width: 3360  $\text{cm}^{-1}$ . The same compound was prepared direct from the so-called  $^6 \text{Na}_3[\text{Co}(\text{CO}_3)_3] \cdot 3\text{H}_2\text{O}$ . 1.8 g of this

material (5 mmol) was added slowly and with stirring to an ice-cold mixture of 7 ml 4 M hydrobromic acid and 2 ml 2-picolyamine (19 mmol). The small amount of cobalt(II) carbonate that separated was filtered off. 2 ml 4 M hydrobromic acid was added to the solution, which was then gently heated until the effervescence ceased. During the following cooling on ice, a solution of 2 g LiBr (23 mmol) in 60 ml ethanol was added. The yellow crystals that appeared were filtered, washed and recrystallized as above. Yield: 2.4 g (71 %). (Found: Co 8.73; N 12.5; C 32.0; Br 36.2. Calc. for  $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Br}_3 \cdot 3\text{H}_2\text{O}$  Co 8.70; N 12.4; C 31.9; Br 35.4).  $(\epsilon, \lambda)_{\text{max}}$ : (129, 462), (134, 336.5).  $(\epsilon, \lambda)_{\text{min}}$ : (14.2, 387). Half-width:  $3360 \text{ cm}^{-1}$ . In other experiments the complex crystallized with 5 moles of crystal water.

8.  $\alpha$ -*Tris(2-picolyamine)cobalt(III) iodide*,  $\alpha$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{I}_3$ . 2 g  $\alpha$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Br}_3 \cdot 3\text{H}_2\text{O}$  (4.4 mmol) was dissolved in 8 ml hot water ( $90^\circ$ ). A saturated solution of 4 g sodium iodide (27 mmol) in water was slowly added. The brown-yellow crystals that separated on cooling were filtered and washed with ethanol and ether. 2.2 g. The recrystallization was performed by dissolving the product in 20 ml hot water ( $90^\circ$ ), adding a solution of 2 g sodium iodide in water and cooling on ice. Filtering and washing as above. Yield: 2.2 g (73 %). (Found: Co 7.61; C 27.8; N 10.7; I 48.9. Calc. for  $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{I}_3 \cdot \text{H}_2\text{O}$ : Co 7.54; C 27.6; N 10.8; I 48.7).  $(\epsilon, \lambda)_{\text{max}}$ : (130, 462), (183, 333).  $(\epsilon, \lambda)_{\text{min}}$ : (26.3, 392). Half-width:  $3410 \text{ cm}^{-1}$ . The second absorption band shows another position and intensity than observed for the corresponding bromide and chloride. This is due to the fact that the second band is overlapped, not only by a "normal" charge transfer band, but also by a band associated with the charge transfer that takes place from the iodide ion to the cation. The intensity of the latter charge transfer band depends on the concentration of the measured solutions (here  $\sim 2.5 \times 10^{-3} \text{ M}$ ). The same effect is observed in the case of  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{I}_3$  and in iodides of other cobalt(III) complexes.<sup>6</sup>

9.  $\beta$ -*Tris(2-picolyamine)cobalt(III) bromide*,  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Br}_3$ . 6 g *trans*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (10.2 mmol) was dissolved in 120 ml pyridine. 3.5 ml 2-picolyamine (32 mmol) diluted with 10 ml pyridine was added slowly with stirring. The yellow-brown precipitate that appeared was filtered and washed with acetone until the filtrate was colourless. The product was dissolved in 15 ml hot water ( $90^\circ$ , slightly acid), and the filtrate was poured into an ice-cold solution of 5 g lithium bromide (58 mmol) in 100 ml ethanol. A mixture of 150 ml ethanol and 2 ml conc. hydrobromic acid was added, and  $\alpha$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Br}_3 \cdot n\text{H}_2\text{O}$  precipitated on cooling. Ether was added to the filtrate until an oily precipitate separated. The liquid was decanted from this product, which was then treated with methanol until it appeared as orange crystals. Filtering and washing with small portions of boiling ethanol, methanol and ether left 1.5 g  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Br}_3 \cdot n\text{H}_2\text{O}$ . The product was recrystallized by dissolving in 4 ml hot water and precipitating with a solution of 2 g lithium bromide in 100 ml ethanol. The sticky precipitate was treated with methanol and washed as above. Yield: 1.4 g (21 %). (Found: Co 8.82; C 32.5; N 12.5; Br 36.0. Calc. for  $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Br}_3 \cdot 2.5\text{H}_2\text{O}$ : Co 8.82; C 32.4; N 12.6; Br 35.6).  $(\epsilon, \lambda)_{\text{max}}$ : (155, 471), (170, 339).  $(\epsilon, \lambda)_{\text{min}}$ : (17.5, 393). Half-width:  $3450 \text{ cm}^{-1}$ . In other experiments the complex crystallized with 1 and 1.5 moles of water, respectively.

10.  $\beta$ -*Tris(2-picolyamine)cobalt(III) iodide*,  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{I}_3$ . 2 g  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Br}_3 \cdot \text{H}_2\text{O}$  (3.1 mmol) was dissolved in 10 ml hot water ( $90^\circ$ ). The addition of a conc. solution of 4 g sodium iodide (27 mmol) in water and cooling on ice, resulted in the precipitation of the iodide, which was filtered and washed with ethanol and ether. Yield: 2.3 g. The product was recrystallized by dissolving in 15 ml water ( $90^\circ$ ), adding a conc. solution of 2 g sodium iodide and cooling on ice. Washing as above. Yield: 2 g (80 %). (Found: Co 7.26; C 26.7; N 10.3; I 47.1. Calc. for  $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{I}_3 \cdot 2.5\text{H}_2\text{O}$ : Co 7.28; C 26.7; N 10.4; I 47.1).  $(\epsilon, \lambda)_{\text{max}}$ : (155, 471), (221, 339).  $(\epsilon, \lambda)_{\text{min}}$ : (63.7, 398). Half-width:  $3520 \text{ cm}^{-1}$ .

*Physical measurements.* Electronic absorption spectra were recorded on a Cary Model 14 spectrophotometer. The measurements were made on water solutions at room temperature. PMR spectra were obtained on a Varian Model A-60 spectrometer using sodium 3-trimethyl-silyl-1-propane sulfonate (TPSNa) as an internal standard. In  $\text{D}_2\text{O}$  the signals arising from the methylene protons were overlapped by a band due to water protons (from water of crystallization and formed by the fast exchange of protons on the nitrogen atoms). This difficulty was overcome by the following addition of  $\text{CF}_3\text{COOH}$ ,

whereby the water band was moved, while the methylene signals remained intact. The X-ray powder photographs were obtained on a camera of the Guinier type with  $\text{CuK}\alpha$  radiation. Silicon was used as a standard.

RESULTS AND DISCUSSION

*Characterization of the isomers.* Assuming on the basis of the evidence given below that the complexes of the  $\alpha$ -type have *facial* and the complexes of the  $\beta$ -type *meridional* geometry, both of the *facial* isomers are characterized by their yellow colour and both of the *meridional* isomers by their orange

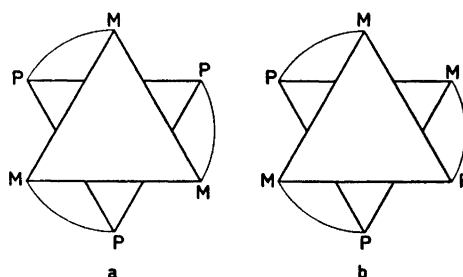


Fig. 1. The geometrical isomers of the tris(2-picolyamine)chromium(III) or cobalt(III) ion. P symbolizes the "pyridine nitrogen", M, the "methylamine nitrogen". a. The *facial* isomer. b. The *meridional* isomer.

colour. Furthermore, the solubilities of the isomers in water as well as in ethanol differ markedly. In general the *facial* isomers are much less soluble than the *meridional* isomers.

*Electronic spectra.* The electronic spectra in the visible region of  $\alpha$ - and  $\beta$ -tris(2-picolyamine)chromium(III) bromide and of  $\alpha$ - and  $\beta$ -tris(2-picolyamine)cobalt(III) bromide are given in Figs. 2 and 3. A comparison of the

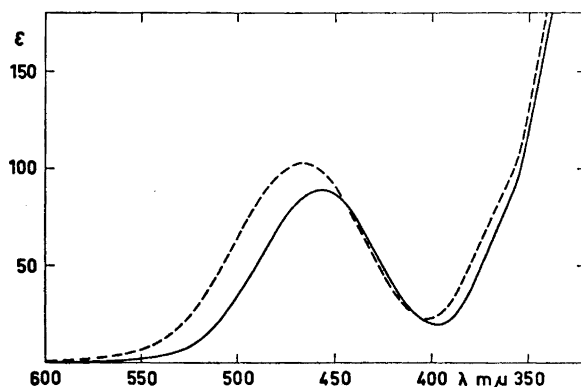


Fig. 2. The absorption spectrum of  $\alpha$ - $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Br}_3 \cdot 2.5\text{H}_2\text{O}$  (—) and of  $\beta$ - $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_3]\text{Br}_3 \cdot 2.5\text{H}_2\text{O}$  (---). Visible region.

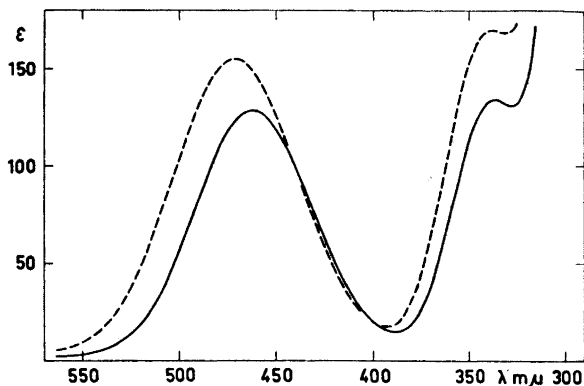


Fig. 3. The absorption spectrum of  $\alpha$ -[Cr(C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>)<sub>3</sub>]Br<sub>3</sub>·2.5H<sub>2</sub>O (—) and of  $\beta$ -[Co(C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>)<sub>3</sub>]Br<sub>3</sub>·2.5H<sub>2</sub>O (---). Visible region.

Table 1. The wavelength  $\lambda_{\max}$ , the molar extinction coefficients  $\epsilon_{\max}$  and the corresponding half-widths  $\delta$  of the long-wavelength bands of  $\alpha$ - and  $\beta$ -[Cr(C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>)<sub>3</sub>]Br<sub>3</sub> and of  $\alpha$ - and  $\beta$ -[Co(C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>)<sub>3</sub>]Br<sub>3</sub>.

| Complex   | $\lambda_{\max}$ (m $\mu$ ) | $\epsilon_{\max}$ | $\delta$ (cm <sup>-1</sup> ) |
|---|-----------------------------|-------------------|------------------------------|
| $\alpha$ -[Cr(C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> ) <sub>3</sub> ]Br <sub>3</sub> ·2.5H <sub>2</sub> O | 457                         | 89                | 3410                         |
| $\beta$ -[Cr(C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> ) <sub>3</sub> ]Br <sub>3</sub> ·2.5H <sub>2</sub> O  | 466.5                       | 103               | 3640                         |
| $\alpha$ -[Co(C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> ) <sub>3</sub> ]Br <sub>3</sub> ·2.5H <sub>2</sub> O | 462                         | 130               | 3360                         |
| $\beta$ -[Co(C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> ) <sub>3</sub> ]Br <sub>3</sub> ·2.5H <sub>2</sub> O  | 471                         | 155               | 3450                         |

long-wavelength bands shows that the  $\beta$ -type complexes are characterized by bands of a greater half-width and a slightly less symmetrical shape than the  $\alpha$ -type bands (Table 1). This is in agreement with the assumption that the  $\beta$ -type complexes are the *meridional* isomers and consequently possess a lower symmetry than the  $\alpha$ -type complexes, the *facial* isomers. Further, the intensities of the  $\beta$ -type bands are higher than the intensities of the  $\alpha$ -type bands, which on the other hand occur at higher energies, and in the chromium case moreover at nearly the same energy as the band of the corresponding ethylenediamine complex. This last fact is noteworthy. The second absorption band is in all four cases more or less veiled by a charge transfer band.

*Nuclear magnetic resonance.* Figs. 4 and 5 and Table 2 show the PMR resonances of the methylene protons in  $\alpha$ - and  $\beta$ -tris(2-picolylamine)cobalt(III) bromide. The simple spectrum of the  $\alpha$ -compound compared to the more complicated spectrum of the  $\beta$ -compound immediately causes one to assign the *facial* configuration to the  $\alpha$ -complex, the *meridional* configuration to the  $\beta$ -complex. A *facial* isomer possesses a C<sub>3</sub> axis, and the corresponding atoms on the different ligands are consequently related by symmetry. Thus only

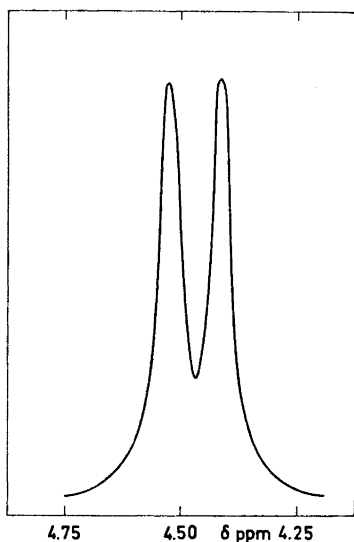


Fig. 4. The methylene proton resonance spectrum of  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>3</sub>]Br<sub>3</sub>·2.5H<sub>2</sub>O.

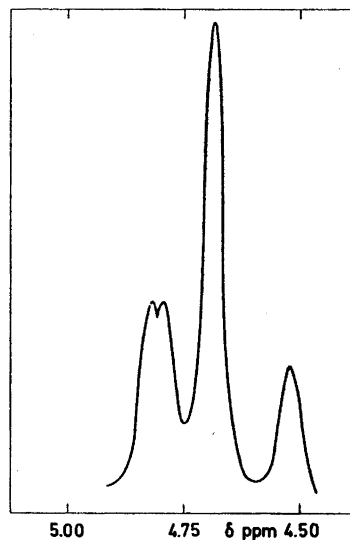


Fig. 5. The methylene proton resonance spectrum of  $\beta$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>3</sub>]Br<sub>3</sub>·2.5H<sub>2</sub>O.

Table 2. Methylene proton chemical shifts.<sup>a</sup>

| Complex   | Chemical shift $\delta$ (ppm) | Relative areas of peaks |
|---|-------------------------------|-------------------------|
| $\alpha$ -[Co(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>3</sub> ]Br <sub>3</sub> ·2.5H <sub>2</sub> O | 4.42, 4.53                    | 1:1                     |
| $\beta$ -[Co(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>3</sub> ]Br <sub>3</sub> ·2.5H <sub>2</sub> O  | 4.52, 4.68, 4.78, 4.82        | 1:3:1:1                 |

<sup>a</sup> Measured from TPSNa as an internal standard. All spectra were run in D<sub>2</sub>O. CF<sub>3</sub>COOH was added.

one resonance signal is expected for each kind of protons on the ligand. In this case we have two different methylene protons (we do not consider the pyridine protons), and therefore expect to observe two singlets. The  $\alpha$ -compound just shows a spectrum consisting of two bands (areas in the ratio 1:1) with  $\delta$  values of 4.53 and 4.42 ppm. A *meridional* isomer is asymmetric, and three resonance signals are expected for each kind of methylene protons on the ligand. We have a total of six different protons and should expect six singlets. We observe in the  $\beta$ -case four bands (areas in the ratio 1:1:3:1) with  $\delta$  values ranging from 4.82 to 4.52 ppm. This is in agreement with the expected lack of symmetry for a *meridional* isomer. Perhaps the greater similarity between the two ligands with respect to a pseudo-threefold axis contributes to the fact that four of the expected six bands seem to appear pairwise (4.82–4.78),

Table 3. Data from X-ray powder photographs.

| Complex   | <i>d</i> -Spacings (Å)   |  |  |  |  |  |  |  |
|---|--|--|--|--|--|--|--|--|
| $\alpha$ -[Co(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>3</sub> ]Br <sub>3</sub> ·2.5H <sub>2</sub> O | 15.2 s,<br>7.02 s,<br>5.29 w,<br>4.29 m,<br>3.73 s,<br>3.40 m, | 12.7 m,<br>6.37 s,<br>5.12 w,<br>4.25 w,<br>3.69 s,<br>3.38 m, | 10.3 s,<br>6.20 s,<br>5.04 w,<br>4.16 s,<br>3.65 s,<br>3.35 m, | 8.90 m,<br>5.77 w,<br>4.81 w,<br>4.10 m,<br>3.56 w,<br>3.33 w, | 8.17 m,<br>5.72 w,<br>4.51 m,<br>4.08 m,<br>3.50 m,<br>3.31 s, | 7.30 s,<br>5.43 w,<br>4.47 w,<br>3.98 w,<br>3.45 m,<br>3.29 m, | 7.16 w,<br>5.39 w,<br>4.33 m,<br>3.90 s,<br>3.42 m,<br>3.19 w. |  |
| $\alpha$ -[Cr(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>3</sub> ]Br <sub>3</sub> ·2.5H <sub>2</sub> O | 15.1 s,<br>7.11 s,<br>5.14 w,<br>4.30 w,<br>3.69 m,<br>3.32 s, | 12.8 m,<br>6.43 m,<br>5.04 w,<br>4.20 s,<br>3.60 w,<br>3.23 m. | 10.3 m,<br>6.25 m,<br>4.82 w,<br>4.13 s,<br>3.53 w,            | 8.99 m,<br>5.84 w,<br>4.55 w,<br>4.04 w,<br>3.49 w,            | 8.19 m,<br>5.75 w,<br>4.51 w,<br>3.91 s,<br>3.43 w,            | 7.33 s,<br>5.43 w,<br>4.37 w,<br>3.73 m,<br>3.39 w,            | 7.21 w,<br>5.33 w,<br>4.34 w,<br>3.72 m,<br>3.35 w,            |  |
| $\beta$ -[Co(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>3</sub> ]Br <sub>3</sub> ·2.5H <sub>2</sub> O  | 14.4 m,<br>6.70 w,<br>4.82 w,<br>3.70 s,<br>3.30 m,            | 10.5 s,<br>6.25 w,<br>4.54 s,<br>3.66 s,<br>3.27 m,            | 8.90 m,<br>5.94 w,<br>4.12 s,<br>3.58 m,                       | 8.03 s,<br>5.67 w,<br>3.87 s,<br>3.54 w,                       | 7.74 m,<br>5.33 s,<br>3.82 m,<br>3.49 w,                       | 7.65 w,<br>5.19 s,<br>3.77 s,<br>3.46 w,                       | 7.20 s,<br>4.89 s,<br>3.73 m,<br>3.40 w,<br>3.21 m.            |  |
| $\beta$ -[Cr(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>3</sub> ]Br <sub>3</sub> ·2.5H <sub>2</sub> O  | 14.7 w,<br>4.88 w,<br>3.62 m,                                  | 10.6 s,<br>4.58 m,<br>3.53 m.                                  | 9.14 m,<br>4.04 w,   | 8.13 m,<br>3.90 w,   | 7.30 m,<br>3.81 m,   | 5.40 m,<br>3.75 m,   | 5.21 m,<br>3.70 m,   |  |

(2 ~4.68), while the last two show a greater difference in chemical shift (~4.68–4.52).

*X-Ray powder photographs.* Table 3 gives the *d*-spacings (calculated from the  $\theta$  values) for the bromides of the four different complexes. The chromium compounds tend to give more diffuse lines than the cobalt compounds. That is why some chromium lines appear with weaker intensity than the corresponding cobalt lines, and why weak cobalt lines sometimes even are unrecognizable in the chromium case. Nevertheless the photographs clearly show isomorphism between the  $\alpha$ -type complexes of chromium and cobalt and between the  $\beta$ -type complexes of the same two metals.

Consequently the yellow chromium compound (the  $\alpha$ -type) is bound to be the *facial* isomer, while the orange chromium compound is the *meridional* isomer. This is in agreement with the earlier assumptions based on the absorption spectra.

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